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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/513,914	03/23/2017	1726	1620	19920NP	20	1

CONFIRMATION NO. 3998

UPDATED FILING RECEIPT

OC000000099870850

293
DOWELL & DOWELL, P.C.
2560 HUNTINGTON AVE, SUITE 203
ALEXANDRIA, VA 22303

Date Mailed: 05/31/2018

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Brian D. ADAMS, Mitchell, CANADA;
Dipan KUNDU, Kitchener, CANADA;
Linda F. NAZAR, Waterloo, CANADA;

Applicant(s)

UNIVERSITY OF WATERLOO, Waterloo, ON, CANADA

Power of Attorney: The patent practitioners associated with Customer Number 293

Domestic Priority data as claimed by applicant

This application is a 371 of PCT/CA2016/050613 05/31/2016
which claims benefit of 62/230,502 06/08/2015

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 05/24/2017

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/513,914**

Projected Publication Date: Not Applicable

Non-Publication Request: No

Early Publication Request: No
Title

Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom

Preliminary Class

429

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 15/513,914

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
FOR	NUMBER FILED	NUMBER EXTRA	RATE($)	FEE($)		RATE($)	FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	520
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	20 minus 20 =	*			OR	x 100 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	1 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1580

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
AMENDMENT A		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1)		(Column 2)	(Column 3)					
AMENDMENT B		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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United States Patent and Trademark Office
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Alexandria, Virginia 22313-1450
www.uspto.gov

U.S. APPLICATION NUMBER NO.	FIRST NAMED INVENTOR	ATTY. DOCKET NO.
15/513,914	Brian D. ADAMS	19920NP

293
DOWELL & DOWELL, P.C.
2560 HUNTINGTON AVE, SUITE 203
ALEXANDRIA, VA 22303

INTERNATIONAL APPLICATION NO.	
PCT/CA2016/050613	
I.A. FILING DATE	PRIORITY DATE
05/31/2016	06/08/2015

CONFIRMATION NO. 3998
371 ACCEPTANCE LETTER

OC000000099870851

Date Mailed: 05/31/2018

NOTICE OF ACCEPTANCE OF APPLICATION UNDER 35 U.S.C 371 AND 37 CFR 1.495

The applicant is hereby advised that the United States Patent and Trademark Office, in its capacity as a Designated / Elected Office (37 CFR 1.495), has ACCEPTED the above identified international application for national patentability examination in the United States Patent and Trademark Office.

The United States Application Number assigned to the application is shown above. A Filing Receipt will be issued for the present application in due course. **THE DATE APPEARING ON THE FILING RECEIPT AS THE "FILING DATE or 371(c) DATE" IS THE DATE ON WHICH THE LAST OF THE 35 U.S.C. 371 (c)(1) and (c)(2) REQUIREMENTS HAS BEEN RECEIVED IN THE OFFICE. THIS DATE IS SHOWN BELOW.** The filing date of the above identified application is the international filing date of the international application (Article 11(3) and 35 U.S.C. 363)

03/23/2017
DATE OF RECEIPT OF 35 U.S.C.
371(c)(1) and (c)(2) REQUIREMENTS

The following items have been received:

- Copy of the International Application filed on 03/23/2017
- Copy of the International Search Report filed on 03/23/2017
- Preliminary Amendments filed on 08/29/2017
- Information Disclosure Statements filed on 08/30/2017
- Inventor's Oath or Declaration filed on 12/06/2017
- U.S. Basic National Fees filed on 03/23/2017
- Authorize Access to Search Results filed on 03/23/2017
- Priority Documents filed on 03/23/2017
- Power of Attorney filed on 12/06/2017
- Authorization to Permit Access filed on 03/23/2017
- Application Data Sheet (37 CFR 1.76) filed on 03/23/2017

FORM PCT/DO/EO/903 (371 Acceptance Notice)

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

INDIA L EVANS

Telephone: (571) 272-9085

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
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POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date
15/513,914	

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☐ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above:

OR

☑ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☐ The address associated with the above-mentioned Customer Number

OR

☑ The address associated with Customer Number: 293

OR

Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

University of Waterloo

☐ Inventor or Joint Inventor (title not required below)
☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)
☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)
☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature	x	Date (Optional)	May 18/17
Name	x Michael Szarka		
Title	x Director, Research Partnerships		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ Total of forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/82C (07-13)
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POWER OF ATTORNEY BY APPLICANT

No more than ten (10) patent practitioners total may be appointed as set forth below by name and registration number. This page need not be submitted if appointing the Patent Practitioner(s) associated with a Customer Number (see form PTO/AIA/82B):

Name	Registration Number
RALPH A. DOWELL	26686
LYNN C. SCHUMACHER	36413
STEPHEN LEONARD	66584
WENDY M. SLADE	53604
ARLEN WESLEY FERREBEE	51312

Electronic Acknowledgement Receipt

EFS ID:	31146056
Application Number:	15513914
International Application Number:	
Confirmation Number:	3998
Title of Invention:	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom
First Named Inventor/Applicant Name:	Brian D. ADAMS
Customer Number:	293
Filer:	Ralph A. Dowell/WENDY SLADE
Filer Authorized By:	Ralph A. Dowell
Attorney Docket Number:	19920NP
Receipt Date:	06-DEC-2017
Filing Date:	23-MAR-2017
Time Stamp:	14:50:47
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Oath or Declaration filed	19920decs_substat.pdf	3179159 a959a82e4d619ada1e2c3c0a1e958637594f4335	no	5

Warnings:

Information:					
2	Transmittal Letter	19920poa_dec_trans.pdf	35301 31827f569155cdbda0b394dc798670286e70ba80	no	2
Warnings:					
Information:					
3	Power of Attorney	19920poa.pdf	751975 fc315946761135008d3bf3b70fc549f5165e2653	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	3966435	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/AIA/01 (06-12)
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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 15/513,914 filed on March 23, 2017.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Linda F. NAZAR
Date (Optional) : May 18, 2017
Signature: x LF Nazar

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 15/513,914
filed on March 23, 2017.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Dipan KUNDU Date (Optional) : 11/05/2017

Signature: Dipan Kundu

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc code: Oath
Document Description: Oath or declaration filed

PTO/AIA/02 (07-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

SUBSTITUTE STATEMENT IN LIEU OF AN OATH OR DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (35 U.S.C. 115(d) AND 37 CFR 1.64)

Title of Invention	ELECTRODE MATERIAL FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM

This statement is directed to:

☐ The attached application,

OR

☒ United States application or PCT international application number 15/513,914 filed on 2017-03-23

LEGAL NAME of inventor to whom this substitute statement applies:

(*E.g.*, Given Name (first and middle (if any)) and Family Name or Surname)

Brian D. ADAMS

Residence (except for a deceased or legally incapacitated inventor):

City Mitchell State ON Country CA

Mailing Address (except for a deceased or legally incapacitated inventor):

228 Morenz Drive

City Mitchell State ON Zip N0K 1N0 Country CA

I believe the above-named inventor or joint inventor to be the original inventor or an original joint inventor of a claimed invention in the application.

The above-identified application was made or authorized to be made by me.

I hereby acknowledge that any willful false statement made in this statement is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

Relationship to the inventor to whom this substitute statement applies:

- ☐ Legal Representative (for deceased or legally incapacitated inventor only),
- ☒ Assignee,
- ☐ Person to whom the inventor is under an obligation to assign,
- ☐ Person who otherwise shows a sufficient proprietary interest in the matter (petition under 37 CFR 1.46 is required), or
- ☐ Joint Inventor.

PTO/SB/AIA02 (07-13)
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Circumstances permitting execution of this substitute statement:

☐ Inventor is deceased,

☐ Inventor is under legal incapacity,

☐ Inventor cannot be found or reached after diligent effort, or

☒ Inventor has refused to execute the oath or declaration under 37 CFR 1.63.

If there are joint inventors, please check the appropriate box below:

☒ An application data sheet under 37 CFR 1.76 (PTO/AIA/14 or equivalent) naming the entire inventive entity has been or is currently submitted.

OR

☐ An application data sheet under 37 CFR 1.76 (PTO/AIA/14 or equivalent) has not been submitted. Thus, a Substitute Statement Supplemental Sheet (PTO/AIA/11 or equivalent) naming the entire inventive entity and providing inventor information is attached. See 37 CFR 1.64(b).

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Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

PERSON EXECUTING THIS SUBSTITUTE STATEMENT:

Name: Michael Szarka
Date (Optional):

Signature:

APPLICANT NAME AND TITLE OF PERSON EXECUTING THIS SUBSTITUTE STATEMENT:

If the applicant is a juristic entity, list the applicant name and the title of the signer:

Applicant Name: University of Waterloo

Title of Person Executing This Substitute Statement: Director, Research Partnerships

The signer, whose title is supplied above, is authorized to act on behalf of the applicant.

Residence of the signer (unless provided in an application data sheet, PTO/AIA/14 or equivalent):

City Waterloo
State Ontario
Country Canada

Mailing Address of the signer (unless provided in an application data sheet, PTO/AIA/14 or equivalent)

200 University Ave W.

City Waterloo
State Ontario
Zip N2L 3G1
Country Canada

Note: Use an additional PTO/AIA/02 form for each inventor who is deceased, legally incapacitated, cannot be found or reached after diligent effort, or has refused to execute the oath or declaration under 37 CFR 1.63.

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor	:	ADAMS et al
Appl. No.	:	15/513,914
Filed	:	March 23, 2017
Title	:	ELECTRODE MATERIAL FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM
Grp./A.U.	:	N/A
Examiner	:	
Docket No.	:	19920NP

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Commissioner:

LATE SUBMISSION OF DECLARATIONS AND POWER OF ATTORNEY

Counsel hereby submits a signed declarations for the above-referenced application. Inventor Adams has refused to signed. A substitute statement from the applicant and assignee is included along with their signed power of attorney.

Should the Office have any questions regarding this submission, Counsel invites the Office to contact the undersigned agent of record at the telephone number provided below.

Respectfully submitted,

DOWELL & DOWELL, P. C.

/WENDY M. SLADE/
WENDY M. SLADE
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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/513,914	03/23/2017	Brian D. ADAMS	19920NP

CONFIRMATION NO. 3998

PUBLICATION NOTICE

OC000000093802951

293
DOWELL & DOWELL, P.C.
2560 HUNTINGTON AVE, SUITE 203
ALEXANDRIA, VA 22303

Title: Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom

Publication No.US-2017-0250449-A1
Publication Date:08/31/2017

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

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PTO/SB/08a (03-15)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**	Application Number	15513914
	Filing Date	2017-03-23
	First Named Inventor	ADAMS et al.
	Art Unit	1726
	Examiner Name	n/a
	Attorney Docket Number	19920NP

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code1	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	5336572		1994-08-09	KOKSBANG	
	2	8663844		2014-03-04	KANG ET AL.	

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Examiner Initial*	Cite No	Publication Number	Kind Code1	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20130157138		2013-06-20	METTAN ET AL.	

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	1	102110858	CN		2011-06-29			☒
	2	2013112660	WO		2013-08-01	EOS ENERGY STORAGE, LLC		☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	15513914
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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T5
	1	LE et al., "Intercalation of Polyvalent Cations into V205 Aerogels", Chemistry of Materials, Volume 10 (3) (1998), Pages 682-684.	
	2	JIAHONG et al., "AC Impedance Study of the Aqueous Zn/V205 Secondary Battery", ACTA PHYSICOCHIMICA SINICA, Volume 16, No. 5 (2000), Pages 454-458 (abstract; and Figure 1).	☒
	3	GIORGETTI et al., "Identification of an unconventional zinc coordination site in anhydrous Zn,V205 aerogels from x-ray absorption", Chemistry of Materials, Volume 11(8) (1999), Pages 2257-2264.	☐
	4	ZHANG et al., "Hydrothermal synthesis and characterization of a series of novel zinc vanadium oxides as cathode materials", Materials Research Society Symposium ¬Proceedings, Materials for Electrochemical Energy Storage and Conversion II - Batteries, Capacitors and Fuel Cells, 496 (1998), Pages 367-372) .	☐
	5	XU, C., LI, B., DU, H., KANG, F., "Energetic Zinc Ion Chemistry: The Rechargeable Zinc Ion Battery." Angew. Chem. Int. Ed. 2012, 51, 933.	☐
	6	ZHANG, L.; CHEN, L.; ZHOU, X.; LIU, Z., "Towards High-Voltage Aqueous Metal-Ion Batteries Beyond 1.5V: The Zinc/Zinc Hexacyanoferrate System." Adv. Energy Mater. 2015, 5, 1400930.	☐
	7	PAN, Huilin, et al. Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. Published April 18, 2016 Article number: 16039 DOI: 10.1038 Nature Energy 2016.39; Pages 1-7	☐
	8	International Search Report (PCT/CA2016/050613) dated September 21, 2016.	☐
	9	Written Opinion (PCT/CA2016/050613) dated September 21, 2016	☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT **(Not for submission under 37 CFR 1.99)**		
	Application Number	15513914
	Filing Date	2017-03-23
	First Named Inventor	ADAMS et al.
	Art Unit	1726
	Examiner Name	n/a
	Attorney Docket Number	19920NP

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(**Not for submission under 37 CFR 1.99)**

Application Number	15513914
Filing Date	2017-03-23
First Named Inventor	ADAMS et al.
Art Unit	1726
Examiner Name	n/a
Attorney Docket Number	19920NP

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

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See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/RALPH A. DOWELL/	Date (YYYY-MM-DD)	2017-08-30
Name/Print	RALPH A. DOWELL	Registration Number	26868

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Show original
Fulltext

Chargeable zinc ion battery by taking oxide of vanadium as cathode

List of publications

	Publication number	Publ. date	Appl. Number	Appl. Date	Document type
▨	CN102110858	2011-06-29	2009CN-0238912	2009-12-29	A -

OTI	Vanadium oxide as the positive electrode of a rechargeable zinc battery

FROM
The invention discloses a chargeable zinc ion battery. A cathode is made from an oxide material of vanadium; an anode is made from a material which mainly comprises zinc elements; electrolyte is liquid or gel which takes the so
or removal of zinc ions in a cathode material lattice, and the energy storage mechanism that an anode material which mainly comprises the zinc elements is oxidized or the zinc ions are reduced on the surface of the anode, the ba

OAB
One kind of zinc ion rechargeable battery, the use of vanadium oxide cathode material, negative electrode element for the zinc-based material, electrolyte zinc soluble salt of the solute, and water as a solvent having ion condu
positive electrode material lattice, while the main elements of the zinc anode material is oxidized or zinc ions in the negative electrode surface of the reduced energy storage mechanism, the battery has a high capacity and recharg

APL	CHINESE (CHI)
IN	Feiyu KANG XU Chengjun LI Baohua DU HONGDA
FOOT	Kang Yu Fei Xu Cheng Jun Li Baohua Du Hongda
PA	GRADUATE SCHOOL AT SHENZHEN TSINGHUA UNIVERSITY
OPA	Tsinghua University, Shenzhen Graduate School
RP	WANG SUOLIN; LI BAOMING; WANG SUOLIN; LI BAOMING
ORP	Wang Lin lock, Shenzhen City, Stratton Patent and Trademark Agency Ltd. 44257; Li Bao-ming: Shenzhen City, Stratton Patent and Trademark Agency Ltd. 44257
You	CN200910238912 2009-12-29 [2009CN-0238912]
PR	CN200910238912 2009-12-29 [2009CN-0238912]
TECD	Electrical machinery, apparatus, energy
IC	H01M-010/38* H01M-004/42 H01M-004/48
NO	Number of Claims: 10
CT	Search Report [Examiner] -CN1109841 (A) [CN1109841]; -US5342712 (A) [US5342712]; -CN1238569 (A) [CN1238569], -CN1357934 (A) [CN1357934];

MCLM
1. A rechargeable zinc battery, a positive electrode, negative electrode, and between the two of the isolation film and having ion conductivity of the electrolyte composition containing the anion and cation, characterized in: A zinc
ion-occluding and releasing are hydrates thereof, The electrolyte solute of the soluble salts of zinc is in, water as a solvent and having ion conductivity of the liquid or gel material.
2. Group consisting of zinc ion rechargeable battery according to claim 1, characterized in: a vanadium oxide is vanadium pentaoxide, thirteen six vanadium oxide, vanadium dioxide, vanadium oxide or fourteen six vanadium theni
3. A rechargeable zinc-ion battery according to claim 2, characterized in: a positive electrode including a collector and a positive-electrode current collector is attached to the film, and includes a positive active material of the positi
4. A rechargeable zinc-ion battery according to claim 1, characterized in: an alloy of zinc or a zinc negative electrode is a pure metal.
5. A rechargeable zinc-ion battery according to claim 1, characterized in: including a collector and a negative electrode current collector is attached to a negative electrode film, the negative electrode of zinc powder and a binder to
6. Group consisting of zinc ion rechargeable battery according to claim 1, characterized in. a negative electrode including a collector and an anode current collector attached to the membrane, the anode film is made of zinc powde
7. Group consisting of zinc ion rechargeable battery according to claim 1, characterized in a negative electrode including a collector and an anode current collector attached to the membrane, the anode film is made of zinc powde
8. A rechargeable zinc battery according to claim 1, characterized in: a negative electrode including a collector and an anode current collector attached to the membrane, the anode film is made of zinc powder, a binder, and an ele
50% of the film quality electronic or less, not more than 1% of the corrosion inhibitor in an amount of the negative electrode film quality.
9. According to claim 1-8 group consisting of zinc ion rechargeable battery according to any one of, characterized in: the positive electrode active material mass is calculated to, the cathode active material is not less than the capa
10. According to claim 1-8 group consisting of zinc ion rechargeable battery according to any one of, characterized in: soluble salts of zinc nitrate, zinc or zinc chloride.

OCLM
A zinc ion rechargeable battery, a positive electrode, a negative electrode, the insulating film interposed therebetween and having an ion-containing anions and cations and conductivity an electrolyte, and is characterized in that:
referred to as soluble salts occlusion and release of zinc ions of vanadium oxide or its hydrates, said electrolyte solute is zinc, water and a solvent having ion conductivity liquid or gel state material.
The 1 of said zinc ion rechargeable battery as claimed in claim wherein: said vanadium oxide is vanadium pentoxide, thirteen six vanadium oxide, vanadium dioxide, vanadium oxide or fourteen seven six vanadium oxide.
3. 2 of said zinc ion rechargeable battery as claimed in claim wherein: said positive electrode comprises a current collector attached to the body and film on the positive electrode current collecting body, and the positive electrode i
4. 1 of said zinc ion rechargeable battery as claimed in claim wherein: said negative electrode is a pure metal or zinc alloys.
According to claim 1 said zinc ion rechargeable battery, wherein: said negative electrode includes a current collector attached to the body and the negative electrode current collector film body, the negative film is made of zinc pow
1 according to the said zinc ion rechargeable battery as claimed in claim wherein: said negative electrode comprises a current collector attached to the body and the negative electrode current collector film body, the negative film i
According to claim 1 said zinc ion rechargeable battery, wherein: said negative electrode includes a current collector attached to the body and the negative electrode current collector film body, the negative film is made of zinc pow
According to claim 1 said zinc ion rechargeable battery, wherein: said negative electrode includes a current collector attached to the body and negative electrode current collector film on the body, the negative film is made of zinc,
amount of 50% or less of the amount of the negative film quality, amount of corrosion inhibitor for the negative buffer membranous amount of 1% or less.
According to any of claims 1-8 one of said zinc ion rechargeable battery, comprising: a positive electrode active material mass in the calculation, said positive electrode active material of zinc ion storage capacity of not less than 1(
Said soluble salt of Zinc: according to any of claims 1-8 one of said zinc ion rechargeable battery, comprising zinc nitrate, zinc sulfate or zinc chloride.

DESC
Chargeable zinc ion battery by taking oxide of vanadium as cathode
Technical Field
The present invention belongs to the technical field of batteries, particularly relates to a zinc ion in the positive electrode active material reduction or oxidation of the negative electrode and the deinterca rechargeable zinc ion batter
Background Art
With the development of economical, necessarily cause a lack of oil resources and environmental contamination, the novel combination of green energy highly efficiently has become extremely essential problem of the develop
multiple times, the raw material can be fully utilized, so that it is more economical and practical.
The Chinese patent application CN 101540417A to manganese dioxide as the positive electrode is disclosed for the first time, to zinc as a negative electrode, a rechargeable zinc ion-containing solution is a liquid electrolyte
electrode through electrolyte solution was then, the process is reversed by the time of discharge
Such zinc ion battery of the electronic storage mechanism is as follows:
Positive electrode:
Negative electrode:
To take advantage of the zinc ion in the positive electrode material due to the reversible off block behavior, thus a battery having a high capacity rechargeable zinc ions may be such, the advantages of longer cycle life. Such zinc
telephone, BP machine, electronic toys, game machines, portable data terminals, personal audio-video equipment, the experimental setup, the field of palmtop computers etc.
Such rechargeable zinc ion battery properties of the positive electrode material may be a performance impact, and in order to further improve the performance of the rechargeable zinc ion battery, a positive electrode material havi
Summary
An object of the present invention is to provide a novel secondary battery.
Vanadium have multiple valences, have a variety of oxides, vanadium oxides have a variety of crystal forms, recently, the inventors have discovered a divalent zinc ion (Zn2+) in an aqueous solution of the oxide material in van
high-capacity of a zinc ion having such embedded behavior, degree of reversible good characteristics. On the other hand, the zinc can be carried out in an aqueous solution of the reversible electrochemical deposition and disso
electrode active material, zinc as a negative electrode active material, containing Zn2+aqueous solution as an electrolyte, the positive electrode active material vanadium oxides of zinc ions deintercalate during charging the
discharging the negative electrode material vanadium oxides of zinc ions through the tunnel of the positive electrode is embedded into.
Embodiments of the present invention proposes a secondary battery as follows:
A rechargeable zinc ion battery, the positive electrode, negative electrode, and an isolation film between the two and having ion conductivity of an electrolyte composition containing both anions and cations, characterized in: neg
and releasing of vanadium oxide or its hydrate zinc ions, a soluble salt as solute is zinc electrolyte, water as a solvent and has ion conductivity of the liquid or gel material
Vanadium oxides of vanadium pentaoxide may be (V2O5), dodecylenes six vanadium oxide (V6O13), a vanadium dioxide (VO2), vanadium oxide seven (V3O7), or fourteen six vanadium oxide (V6O14) and the like.
The negative electrode may be a pure metallic zinc or zinc alloy. The anode also can adopt the following scheme: a negative electrode including a collector and a negative electrode film adhered to the current collector, the nega
inhibitor and/or electron conductive agent to be added thereto. Wherein, the binder may select polyethtrafluoroethylene, water-soluble rubber, tetrafluoroethylene or cellulose polymeta; corrosion inhibitor is added by 1% or less a
reaction zinc element, preferred indium oxide, indium hydroxide or metal copper; electronic conductive agent in an amount of 50% or less of the mass of the negative electrode film, preferably graphite, carbon black, acetylene blac
A positive electrode including a collector and a positive electrode film adhered to the current collector. the positive electrode active material of the positive electrode film (that vanadium oxide or the oxide hydrate), an electronic cc
carbon fibers or carbon nano-wall nanotubes, the added amount is 50% or less of the positive electrode film quality, binder selected from polytetrafluoroethylene, water-soluble rubber, tetrafluoroethylene or cellulose polymeta, q
zinc ions may be reversibly inserting and extracting, to the positive electrode active material is calculated by mass, the positive electrode active material storage capacity of the zinc ion is not less than 100 mAh/g.
The soluble zinc salt preferably zinc nitrate, zinc sulfate or zinc chloride or the like inorganic salts of zinc. May by adding an acid, base or to adjust the pH value in the buffer solution and the like of the electrolyte 3-7.
The present invention a rechargeable zinc ion battery can be made in a coin shape, a cylinder or the square configuration
The present invention battery using a zinc ion (Zn2+) of the vanadium oxide lattice or released from a reversible insertion, while a negative electrode material is oxidized to zinc or a zinc ion as a main (Zn2+) the surface o
rechargeable. is proved by experiments, the present invention a rechargeable zinc ion batteries having excellent rate properties, reversibility can and cycle characteristics. It is contemplated that such a zinc ion battery can b
machine, electronic toys, game machines, portable data terminals, personal audio-video equipment, the experimental setup, the field of palmtop computers etc.
Description of Drawings
FIG. 1 is a vanadium oxide electrode is made of embodiment 1 1mol L-1ZnSO4electrolyte in the scan rate was 1mV s-1cyclic voltammograms of a single electrode at the time
FIG. 2 is a rechargeable zinc ion battery prepared in the embodiment 1 of the scan rate was 1mV s-1cyclic voltammograms of the time.
FIG. 3 a rechargeable zinc ion battery prepared in the embodiment 1 to 250 mA g-1(to the positive active material mass calculation) the initial discharge and charge curves.
FIG. 4 is a rechargeable zinc ion battery of the embodiment 2 was prepared in a 300 mA g-1(to the positive active material mass calculation) the initial discharge and charge curves.
Embodiment

Embodiment 1
To vanadium pentaoxide, the conductive agent is acetylene black and a binder in a mass ratio of 7: 2:1 polytetrafluoroethylene coated on a stainless steel foil was evenly mixed, cut to size, pentylphosphonic pentoxid dried in vacu
as working electrode, to metal platinum electrode is a counter electrode, with a Hg/Hg2SO4(in saturated K2SO4) as reference electrode is detected. Vanadium pentoxid at electrodes 1mol L-1ZnSO4the cyclic voltammograms sh
two reduction peaks appear, corresponding to the elution of vanadium oxide and embed in the zinc ions within the crystal lattice.
To the positive electrode sheet is vanadium pentaoxide, zinc foil having a thickness of 0.1 mm is the cathode to, electrolytic solution was 1mol L-1ZnSO4aqueous rechargeable zinc ion battery is assembled. This battery at 1mV
test. This battery at 250 mA g-1a constant current flow as shown in FIG. 3 plural times of charge and discharge cycle curve, it is seen that this battery is a rechargeable battery can be repeatedly charged and discharged, in this c
nearly 100%. The results indicate that such as a vanadium oxide-zinc ion battery includes a positive electrode active material on a chargeable characteristics of high capacity, its capacity is disclosed in Chinese patent applicatior
of the battery's capacity.
Embodiment 2:
Zinc powder, acetylene black and a binder in a mass ratio of the conductive agent is mixed at a ratio of the polytetrafluoroethylene after 40: 50:10, laminated onto a stainless steel mesh, cut to size, drying in vacuo to produce pov
to a zinc powder as a negative electrode, ten times by mass zinc powder mass of vanadium pentaoxide, negalyte is 0.1mol L-1ZnSO4aqueous rechargeable zinc ion battery assembled into a coin shape. Zinc ion battery obtai
current charge-discharge cycle curve shown in Figure 4, the battery capacity was 268 mAh g-1, the coulombic efficiency 90% or more
Embodiment 3:
Vanadium oxide sulfate heptahydrate, the conductive agent is acetylene black and a binder in a mass ratio of 7: 2:1 and uniformly mixed with polytetrafluoroethylene coated on a stainless steel foil, cut to size, vanadium oxide elec
In seven oxide vanadium piece is a positive electrode, to 0.1 mm thick zinc foil as a negative electrode, electrolyte is 1mol L-1ZnSO4aqueous rechargeable zinc ion battery is assembled. Wil have been tested, this battery at 20(
the coulombic efficiency 90% or more.

ODES

Vanadium oxide as the positive electrode of a rechargeable zinc battery
TECHNICAL FIELD
The present invention belongs to the field of battery technology, in particular to a zinc ion in the positive electrode active material in the negative electrode and deintercalation reduction or oxidation may zinc ion rechargeable batter
BACKGROUND
With the continuous economic development, inevitably lead to the pollution of scarce oil resources and the environment, so comprehensive and efficient development and use of new green energy it has become the essential issu
full use of raw materials, so it is more economical and practical.
CN 101540417A Chinese invention patent application for the first time discloses a manganese dioxide as cathode, zinc as a negative electrode, a solution containing zinc ions as electrolyte rechargeable zinc battery, a recharge
and then, discharge the above process is just the opposite.
This mechanism of zinc ion batteries to store electrons as follows
positive electrode:
negative electrode:
Due to the use of zinc ions in the reversible deintercalation behavior cathode material, so this zinc ion rechargeable battery with high capacity, cycle long life and other characteristics. This zinc ion batteries can be widely used i
games, portable data terminals, personal audio-video equipment, laboratory equipment, handheld computers and other fields.
This rechargeable zinc-ion battery performance is affected by the performance of the cathode material, and for the further improvement of the zinc ion rechargeable battery performance, looking for new cathode material with excel
SUMMARY
The object of the present invention is to provide a novel secondary battery.
Vanadium has a variety of valence, with a variety of oxides, vanadium oxides having various crystal form, most recently, the inventors have first discovered the divalent zinc ion (Zn2 +) reversible quick embedding and extraction
behavior is embedded zinc ions with high capacity and good reversibility characteristics. On the other hand, zinc can be reversible electrochemical deposition and dissolution in an aqueous solution. This finding basis, we invente
material, an aqueous solution containing Zn2 + as electrolyte, when charging a zinc ion extrusion vanadium oxide cathode active material through the electrolyte and deposited on the negative electrode, a negative electrode du
vanadium oxide tunnel
Specific programs of the secondary battery of the present invention provides the following:
One kind of zinc ion rechargeable battery, a positive electrode, a negative electrode, the insulating film interposed therebetween and containing ions and having an ionic conductivity electrolyte composition, characterized in thai
capable of occluding and and the release of zinc ions of vanadium oxide or its hydrates, said electrolyte is a soluble salt of zinc as solute and water as solvent and having ion conductivity liquid or gel state material.
Said vanadium oxide may be vanadium pentoxide (V2O5), thirteen six vanadium oxide (V6O13), vanadium dioxide (VO2), seven tetroxide vanadium (V3O7), or fourteen six vanadium oxide (V6O14) and the like
He said negative electrode may be a pure metal zinc or zinc alloy. He said negative electrode can also use the program as follows: The negative electrode comprises a negative electrode current collector membrane attached to tł
be added to further slow corrosion inhibitor and / or an electronic conductive agent in the negative film. Wherein, optionally PTFE binder, a water-soluble rubber, polytetrafluoroethylene or polyvinylidene cellulose; slow addi
suppressing or eliminating zinc elemental hydrogen evolution reaction, preferably indium oxide, indium hydroxide a metal oxide or copper; addition amount of the electroconductive agent is 50% or less of the amount of the negativ
Said positive electrode comprises a current collector body and attached to the positive electrode current collector film body, the positive electrode film made of the positive electrode active material of said (ie, vanadium oxide or
agent is graphite, carbon black, acetylene black, carbon fiber, or carbon nanotube, the addition amount of 50% or less of the amount of the positive electrode film quality; PTFE binder, a water-soluble rubber, polyvinylidene poly
quality. Zinc ions may be conducted in the lattice of the positive electrode active material reversibly embedded and extraction, to calculate the positive electrode active material mass, the positive electrode active materials zinc ion
Said zinc salt is preferably soluble zinc nitrate, zinc sulfate, zinc chloride or zinc salts. It can be used to adjust the pH of the electrolyte by adding an acid, alkaline or buffer solution and the like at 3-7.
The present invention is a zinc ion rechargeable battery can be made buckle style, round or rectangular column structure.
Battery of the present invention uses zinc ions (Zn2 +) reversible insert or prolapse in the vanadium oxide lattice, while the main elements of zinc the negative electrode material oxide or zinc ions (Zn2 +) in the energy storag
Features . The experiment proved that the present invention is a rechargeable zinc-ion battery has excellent rate performance, reversible performance and cycle performance. It is foreseeable that the zinc ion batteries can be
electric toys, games, portable data terminal, personal audio-video equipment, laboratory equipment, handheld computers and other fields.
BRIEF DESCRIPTION
Figure 1 is an embodiment of an electrode made of vanadium pentoxide obtained in Example 1mol L-1 ZnSO4 electrolyte when the sweep rate of 1mV s-1 single electrode cyclic voltammetry FIG.
Figure 2 is obtained in the Example 1 embodiment the zinc ion rechargeable battery in the scan rate of 1mV s-1 when a cyclic voltammogram.
Figure 3 is obtained in a case of a rechargeable battery of the zinc ion (in the positive electrode active material calculated mass) in the first discharge 250mA g-1 and charging curve.
Figure 4 is obtained in Example 2 of a rechargeable battery of the zinc ion (in the positive electrode active material calculated mass) in the first discharge 300mA g-1 and charging curve.
DETAILED DESCRIPTION
Example 1:
Vanadium pentoxide, a conductive agent, acetylene black and polytetrafluoroethylene 7:2:1 binder mass ratio of mixed uniformly coated on a stainless steel foil, cut to a certain size, and drying in vacuo to obtain an electrode she
a platinum electrode for the metal electrodes. Hg / Hg2SO4 (in saturated K2SO4) as a reference electrodes for testing. Vanadium pentoxide electrodes in 1mol L-1 ZnSO4 aqueous solution of the cyclic voltammograms sho
corresponding to zinc ions in the crystal lattice of vanadium pentoxide prolapse and embedding.
In pentoxide electrode sheet as a positive electrode to 0.1mm thick zinc foil as the anode, the electrolyte is an aqueous solution of 1mol L-1 ZnSO4 assembled into Rechargeable zinc ion batteries. This battery cyclic voltammetry a
battery 250mA g-1 under a constant current charge-discharge cycle curve shown in Figure 3, it can be seen that the battery can be repeated discharge of the rechargeable battery, this current capacity of 300mAh g-1 (positi
vanadium oxide cathode active material, zinc ion rechargeable battery having a high capacity, the capacity is higher than CN Chinese invention patent applications disclosed 101540417A manganese dioxide for the positive electro
Example 2:
After the zinc powder, a conductive agent, acetylene black and polytetrafluoroethylene binder mixing ratio by mass ratio of 40 50:10, the pressure on stainless steel net, cut into a certain size, in a vacuum drying to obtain zinc elec
electrode with the zinc powder, zinc powder quality the quality of the vanadium pentoxide times, the electrolyte is an aqueous solution of 0.1mol L-1 ZnSO4 assembled snap-in rechargeable zinc-ion battery. 2 prepared in Exampl
discharge cycle curve shown in Figure 4, the battery capacity of 268 mAh g-1, more than 90% coulombic efficiency
Example 3:
After seven vanadium oxide, a conductive agent, acetylene black and polytetrafluoroethylene binder in a mass ratio of mixed 7:2:1 coated on a stainless steel foil, cut into a certain size, drying to obtain seven vanadium oxide elect
With seven of vanadium oxide for the positive electrode sheet to 0.1mm thick zinc foil as the anode, the electrolyte is an aqueous solution of 1mol L-1ZnSO4 assembled so as to be zinc ion rechargeable batteries. After testing, the
calculation), Coulomb efficiency 90% or more.

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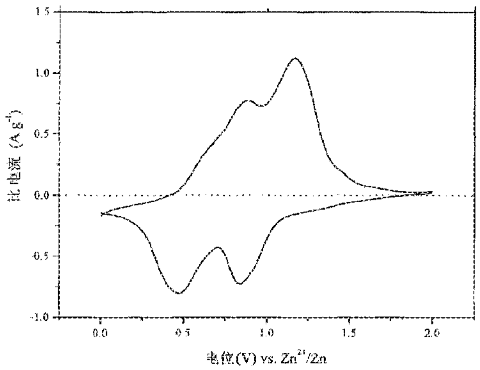
权利要求书 1 页　说明书 3 页　附图 2 页

(54) 发明名称

以钒的氧化物为正极的可充电锌离子电池

(57) 摘要

一种可充电锌离子电池，正极采用钒的氧化物材料，负极为以锌元素为主的材料，电解质为锌的可溶性盐为溶质、水为溶剂并具有离子导电性的液态或凝胶态电解质。本发明利用锌离子在正极材料晶格中的可逆插入或脱出，同时以锌元素为主的负极材料进行氧化或锌离子在负极表面还原的储能机理，该电池具有容量高和可充电的特点。



1. 一种可充电锌离子电池，由正极、负极、介于两者之间的隔离膜以及含有阴阳离子并具有离子导电性的电解质组成，其特征在于：

所述负极的活性材料以锌元素为主，

所述正极的活性材料为可吸藏和释放锌离子的钒的氧化物或其水化物，

所述电解质是以锌的可溶性盐为溶质、水为溶剂并具有离子导电性的液态或凝胶态材料。

2. 根据权利要求 1 所述的可充电锌离子电池，其特征在于：所述钒的氧化物为五氧化二钒、十三氧化六钒、二氧化钒、七氧化三钒或十四氧化六钒。

3. 根据权利要求 2 所述的可充电锌离子电池，其特征在于：所述正极包括集流体和附着于集流体上的正极膜，该正极膜由正极的所述活性材料、电子导电剂和粘结剂制成。

4. 根据权利要求 1 所述的可充电锌离子电池，其特征在于：所述负极是纯金属锌或锌的合金。

5. 根据权利要求 1 所述的可充电锌离子电池，其特征在于：所述负极包括集流体和附着于集流体上的负极膜，该负极膜由锌粉和粘结剂制成。

6. 根据权利要求 1 所述的可充电锌离子电池，其特征在于：所述负极包括集流体和附着于集流体上的负极膜，该负极膜由锌粉、粘结剂和缓蚀剂制成。

7. 根据权利要求 1 所述的可充电锌离子电池，其特征在于：所述负极包括集流体和附着于集流体上的负极膜，该负极膜由锌粉、粘结剂和电子导电剂制成。

8. 根据权利要求 1 所述的可充电锌离子电池，其特征在于：所述负极包括集流体和附着于集流体上的负极膜，该负极膜由锌粉、粘结剂、缓蚀剂和电子导电剂制成，电子导电剂的添加量为负极膜质量的 50％以下，缓蚀剂的添加量为负极膜质量的 1％以下。

9. 根据权利要求 1-8 任一项所述的可充电锌离子电池，其特征在于：以正极活性材料质量计算，所述正极活性材料储存锌离子的容量不小于 100mAh/g。

10. 根据权利要求 1-8 任一项所述的可充电锌离子电池，其特征在于：所述锌的可溶性盐为硝酸锌、硫酸锌或氯化锌。

以钒的氧化物为正极的可充电锌离子电池

技术领域

[0001]　本发明属电池技术领域，具体涉及一种锌离子在正极活性材料脱嵌和在负极还原或氧化的可充电的锌离子电池。

背景技术

[0002]　随着经济的不断发展，必然引起石油资源的匮乏和环境的污染，因此新型绿色能源的综合高效的开发和利用已成为十分必要的课题。相比较一次电池，二次电池能重复多次进行充放电循环，能充分利用原材料，故其更经济实用。

[0003]　CN 101540417A 中国发明专利申请首次公开了一种以二氧化锰为正极，以锌为负极，以含锌离子的溶液为电解液的可充电锌离子电池，在充电时锌离子脱出二氧化锰经过电解液然后在负极沉积，放电时上述过程刚好相反。

[0004]　这种锌离子电池储存电子的机理如下：

[0005]　正极：$xZn^{2+} + 2xe^- + MnO_2 \Leftrightarrow Zn_xMnO_2$　（1）

[0006]　负极：$Zn \Leftrightarrow Zn^{2+} + 2e^-$　（2）

[0007]　由于利用到锌离子在正极材料的可逆脱嵌行为，因此这种可充锌离子的电池具有容量高，循环寿命长等特点。这种锌离子电池可广泛应用于个人数字记事本、Electronic Organizers、移动电话、无绳电话、BP 机、电动玩具、游戏机、便携式数据终端、个人音频视频装置、实验装置、掌上计算机等领域。

[0008]　这种可充锌离子电池的性能受正极材料的性能影响，而为了进一步改善可充电锌离子电池的性能，寻找新的性能优良的正极材料不实为一种好的方法。

发明内容

[0009]　本发明的目的是提供一种新的二次电池。

[0010]　钒具有多种价态，具有多种氧化物，钒的氧化物具有多种晶型，最近，发明人首次发现了二价锌离子（Zn^{2+}）于水溶液中在钒的氧化物材料 V_2O_5、V_6O_{13}、VO_2、V_3O_7、V_6O_{14} 等中可逆快速的嵌入和脱出的行为，这种锌离子的嵌入行为具有容量高、可逆程度好等特点。另一方面，锌可以于水溶液中进行可逆的电化学沉积和溶解。在此发现基础之上，我们发明了一种可充电的锌离子电池，其以钒的氧化物为正极活性材料，锌为负极活性材料，含 Zn^{2+} 水溶液为电解液，在充电时锌离子脱出正极活性材料钒的氧化物经过电解液然后在负极沉积，放电时负极锌溶解为锌离子经过电解液嵌入到正极材料钒的氧化物的隧道中。

[0011]　本发明提出的二次电池的具体方案如下：

[0012]　一种可充电锌离子电池，由正极、负极、介于两者之间的隔离膜以及含有阴阳离子并具有离子导电性的电解质组成，其特征在于：所述负极的活性材料以锌元素为主，所述正极的活性材料为可吸藏和释放锌离子的钒的氧化物或其水化物，所述电解质是以锌的可溶性盐为溶质、水为溶剂并具有离子导电性的液态或凝胶态材料。

[0013]　所述钒的氧化物可以是五氧化二钒（V_2O_5）、十三氧化六钒（V_6O_{13}）、二氧化钒（VO_2）、

七氧化三钒 (V_3O_7)、或十四氧化六钒 (V_6O_{14}) 等。

[0014] 所述负极可以是纯金属锌或锌的合金。所述负极也可以采用如下方案:负极包括集流体和附着于集流体上的负极膜,该负极膜可以由锌粉和粘结剂制成,也可进一步在负极膜中添加缓蚀剂和/或电子导电剂。其中,粘结剂可选择聚四氟乙烯、水溶性橡胶、聚偏四氟乙烯或纤维素;缓蚀剂的添加量为负极膜质量的1%以下,缓蚀剂用于抑止或消除锌元素析氢反应,优选铟的氧化物、铟的氢氧化物或金属铜;电子导电剂的添加量为负极膜质量的50%以下,优选石墨、碳黑、乙炔黑、炭纤维或炭纳米管。

[0015] 所述正极包括集流体和附着于集流体上的正极膜,该正极膜由正极的所述活性材料(即钒的氧化物或该氧化物的水化物)、电子导电剂和粘结剂制成。其中,电子导电剂为石墨、碳黑、乙炔黑、炭纤维或炭纳米管,添加量为正极膜质量的50%以下;粘结剂为聚四氟乙烯、水溶性橡胶、聚偏四氟乙烯或纤维素,添加量为正极膜质量的20%以下。锌离子可在正极活性材料的晶格内进行可逆的嵌入和脱出,以正极活性材料质量计算,所述正极活性材料储存锌离子的容量不小于100mAh/g。

[0016] 所述锌的可溶性盐优选硝酸锌、硫酸锌或氯化锌等锌的无机盐。可通过添加酸、碱或缓冲溶液等来调节电解质的pH值在3～7。

[0017] 本发明可充电锌离子电池可以做成扣式、圆柱式或方型结构。

[0018] 本发明电池利用锌离子 (Zn^{2+}) 在钒的氧化物晶格中的可逆插入或脱出,同时以锌元素为主的负极材料进行氧化或锌离子 (Zn^{2+}) 在负极表面还原的储能机理,该电池具有容量高和可充电的特点。经实验证明,本发明可充电锌离子电池具有优良的倍率性能、可逆性能和循环性能。可以预见这种锌离子电池可广泛应用于个人数字记事本、Electronic Organizers、移动电话、无绳电话、BP机、电动玩具、游戏机、便携式数据终端、个人音频视频装置、实验装置、掌上计算机等领域。

附图说明

[0019] 图1为实施例1制得的五氧化二钒电极在1mol L^{-1} $ZnSO_4$电解液中扫描速率为1mV s^{-1}时的单电极循环伏安图。

[0020] 图2为实施例1制得的可充电锌离子电池在扫描速率为1mV s^{-1}时的循环伏安图。

[0021] 图3为实施例1制得的可充电锌离子电池在250mA g^{-1}(以正极活性材料质量计算)首次放电和充电曲线。

[0022] 图4为实施例2制得的可充电锌离子电池在300mA g^{-1}(以正极活性材料质量计算)首次放电和充电曲线。

具体实施方式

[0023] 实施例1:

[0024] 将五氧化二钒、导电剂乙炔黑和粘结剂聚四氟乙烯以7:2:1的质量比混合均匀后涂覆于不锈钢箔上,剪裁成一定大小,于真空中烘干制得五氧化二钒电极片。单电极测试采用五氧化二钒电极片为工作电极,以金属铂电极为对电极,以Hg/Hg_2SO_4(in saturated K_2SO_4) 为参比电极进行检测。五氧化二钒电极在1mol L^{-1} $ZnSO_4$水溶液中的循环伏安图如图1,扫描速率为1mV s^{-1},可以看出有两个氧化峰和两个还原峰出现,对应于锌离子在五氧

化二钒晶格内的脱出和嵌入。

[0025]　以五氧化二钒电极片为正极，以 0.1mm 厚的锌箔为负极，电解液为 1mol L^{-1} $ZnSO_4$ 水溶液组装成可充电锌离子电池。这种电池在 1mV s^{-1} 扫描速率下的循环伏安曲线如图 2，结果与单电极测试结果一致。这种电池在 250mA g^{-1} 恒电流下的多次充放电循环曲线如图 3 所示，可以看出这种电池可以重复充放电为可充电电池，在此电流下的容量为 300mAh g^{1}（以正极活性材料质量计算），库仑效率接近 100％。结果表明这种以钒的氧化物为正极活性材料的可充锌离子电池具有容量高的特点，其容量高于 CN101540417A 中国发明专利申请中公开的以二氧化锰为正极的可充电锌离子电池的容量。

[0026]　实施例 2：

[0027]　将锌粉、导电剂乙炔黑和粘结剂聚四氟乙烯按质量比为 40 ∶ 50 ∶ 10 的比例混合后，压于不锈钢网上，剪裁成一定大小，于真空中烘干制得锌粉电极。以实施例 1 制备的五氧化二钒电极为正极，以该锌粉电极为负极，锌粉质量为五氧化二钒质量的十倍，电解液为 0.1mol L^{-1} $ZnSO_4$ 水溶液组装成扣式可充电锌离子电池。实施例 2 所制得锌离子电池在 300mA g^{-1}（以正极活性材料质量计算）恒电流下充放电循环曲线见图4，电池容量为 268mAh g^{-1}，库仑效率在 90％以上。

[0028]　实施例 3：

[0029]　将七氧化三钒、导电剂乙炔黑和粘结剂聚四氟乙烯以 7 ∶ 2 ∶ 1 的质量比混合均匀后涂覆于不锈钢箔上，剪裁成一定大小，于真空中烘干制得七氧化三钒电极片。

[0030]　以七氧化三钒片为正极，以 0.1mm 厚的锌箔为负极，电解液为 1mol $L^{-1}$$ZnSO_4$ 水溶液组装成可充电锌离子电池。经测试，这种电池在 200mA g^{-1} 恒电流下的容量为 280mAh g^{-1}（以正极活性材料质量计算），库仑效率在 90％以上。

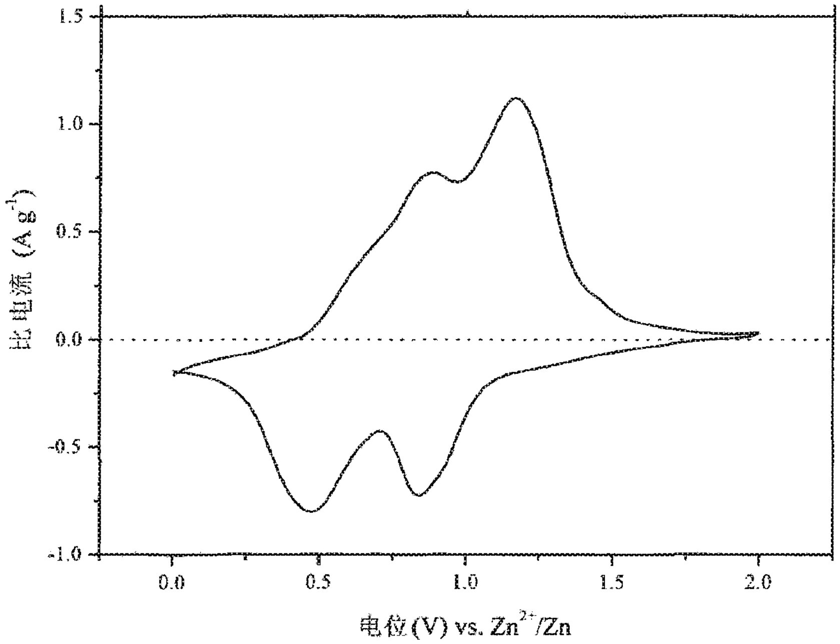

1.5
1.0
0.5
0.0
-0.5
-1.0
比电流 (A g^{-1})
0.0
0.5
1.0
1.5
2.0
电位(V) vs. Zn^{2+}/Zn

图 1

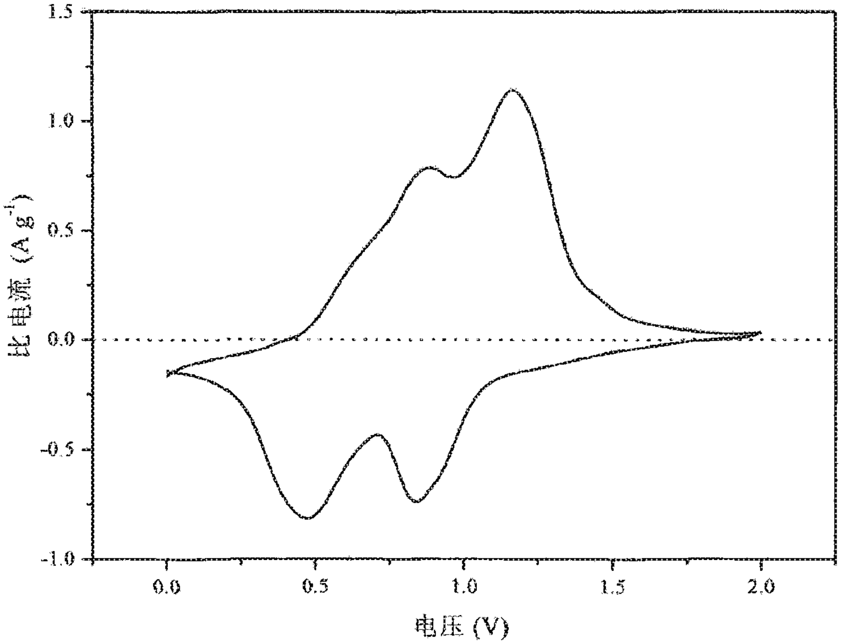

1.5
1.0
0.5
0.0
-0.5
-1.0
比电流 (A g^{-1})
0.0
0.5
1.0
1.5
2.0
电压 (V)

图 2

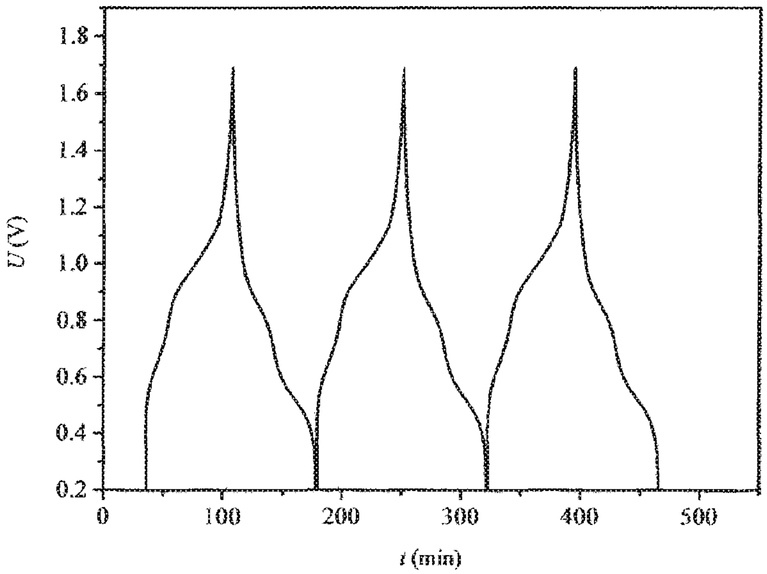

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
U (V)
0
100
200
300
400
500
t (min)

图 3

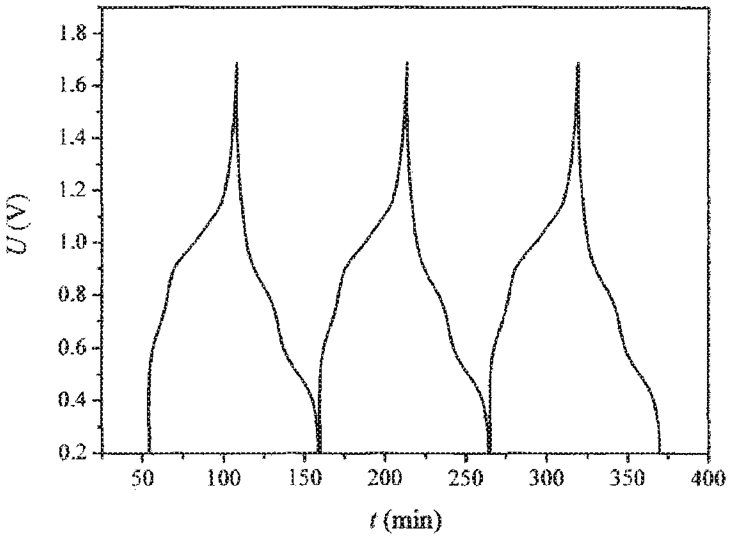

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
U (V)
50
100
150
200
250
300
350
400
t (min)

图 4

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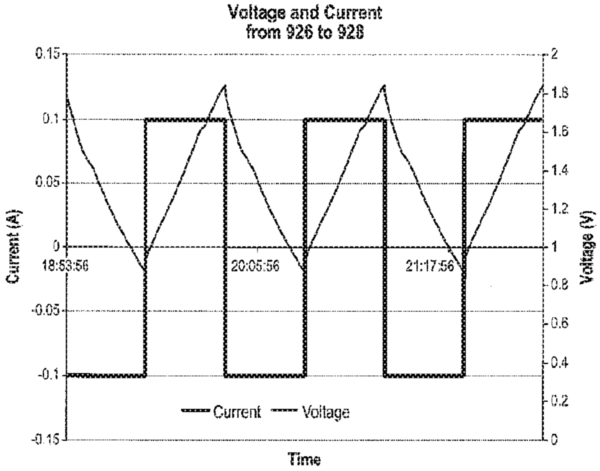

FIG. 1

(57) **Abstract**: The present invention provides a novel electrochemical cell that comprises a cathode, an anode, and an electrolyte, where an ion species present in the electrolyte intercalates into the cathode upon discharge of the electrochemical cell.

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ELECTROCHEMICAL CELL WITH DIVALENT CATION ELECTROLYTE AND AT LEAST ONE INTERCALATION ELECTRODE

CROSS REFERENCE TO RELATED APPLICATION

[0001] This PCT patent application claims the benefit of U.S. provisional application serial no. 61/591,526, filed on January 27, 2012. The entire contents of this application are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention is concerned with secondary electrochemical cells and batteries. In particular, this invention concerns electrolytes and electrodes for secondary electrochemical cells and methods of making the same.

BACKGROUND

[0003] An electrical storage battery comprises one electrochemical cell or a plurality of electrochemical cells of the same type, the latter typically being connected in series to provide a higher voltage or in parallel to provide a higher charge capacity than provided by a single cell. An electrochemical cell comprises an electrolyte interposed between and in contact with an anode and a cathode. During battery discharge, the anode active material is oxidized and the cathode active material is reduced so that electrons flow from the anode through an external load to the cathode and ions flow through the electrolyte between the electrodes.

[0004] Electrical storage batteries are classified as either "primary" or "secondary" batteries. Primary batteries involve at least one irreversible electrode reaction and cannot be recharged with useful charge efficiency by applying a reverse voltage. Secondary batteries involve relatively reversible electrode reactions and can be recharged with acceptable loss of charge capacity over numerous charge-discharge cycles.

[0005] Traditional secondary batteries, such as lithium ion batteries, are presently used to power electronic devices such as electric vehicles, portable computers, and other hand held electronic devices (e.g., cellular telephones, music players, or global positioning navigation systems). However, traditional secondary batteries are generally constructed from high cost materials, heavy metals, caustic electrolytes, and other materials that are harmful to the environment. Furthermore, traditional secondary batteries suffer from performance degradation over numerous charge and discharge cycles. For example, traditional secondary batteries lose charge capacity over several charge cycles, they are Coulombically inefficient, or they possess an elevated impedance or internal resistance that negatively effects battery discharge.

SUMMARY OF THE INVENTION

[0006] The electrochemical cells of the present invention provide environmentally safe energy storage systems that use low cost materials, reactants, and cell designs that are readily adaptable to accommodate a wide range of energy storage and power delivery applications. Moreover, the electrochemical cells of the present invention deliver superior battery performance including high energy density, high discharge/charge efficiency, and fast battery recharging.

[0007] In one aspect, the present invention provides a novel electrochemical cell that comprises a cathode, an anode, and an electrolyte, where an ion species present in the electrolyte intercalates into the cathode upon discharge of the electrochemical cell.

[0008] Another aspect of the present invention provides an electrochemical cell comprising an aqueous electrolyte comprising a divalent cation; a cathode comprising a layered material; and an anode comprising a metal, wherein the divalent cation intercalates into the layered material when the cell discharges; and the divalent cation de-intercalates from the cathode material and deposits onto the anode as a neutral metal when the cell charges.

[0009] In some embodiments, the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof. For example, the divalent cation is Zn^{2+}. In some examples, the Zn^{2+} divalent cation is generated upon the dissolution of $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water. In such instances, the aqueous electrolyte further comprises a counter ion selected from SO_4^{2-}, CHO^-, NO_3^-, $CO_2CH_3^-$, Cl^-, Br^-, ClO_4^-, or any combination thereof.

[0010] In some embodiments, the aqueous electrolyte has a pH that is approximately neutral. For example, the electrolyte has a pH of from about 6 to about 8.

[0011] In some embodiments, the aqueous electrolyte has a pH that is slightly acidic. For example, the electrolyte has a pH of from about 3 to about 6.

[0012] In some embodiments, the layered material comprises a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof. For example, the layered material comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof. In other examples, the layered material comprises a manganese oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0013] In some embodiments, the cathode comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2.

[0014] In some embodiments, the layered material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1.

[0015] In some embodiments, the layered material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7{\bullet}3H_2O$, $Mn_7O_{14}{\bullet}3H_2O$, $Mn_4O_9{\bullet}3H_2O$, Mn_2O_4, $Mn_4O_{18}{\bullet}H_2O$, or any combination thereof. For example, the layered material comprises Mn_5O_8 that comprises a power having a mean particle diameter of about 50 μm or less.

[0016] In some embodiments, the cathode is doped with Al, B, or any combination thereof.

[0017] In some embodiments, the cathode further comprises a carbon powder. For example, the cathode further comprises about 15 wt% or less of the carbon powder by weight of the cathode material. In other examples, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0018] In some embodiments, the cathode further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. For example, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other examples, the additive is present at a concentration of about 20 wt% or less by weight of the cathode.

[0019] In some embodiments, the anode comprises a metal, and a portion of the metal transforms into a divalent cation when the cell is discharged. For example, the metal material comprises zinc (Zn) or magnesium (Mg).

[0020] In some embodiments, the cathode material, the anode material, or both further comprises a binder. In some examples, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other examples, the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the cathode material.

[0021] In some embodiments, the anode, the cathode, or both further comprises a current collector. In some examples, the current collector comprises one or more electrically conductive metals or an electrically conductive polymer material. For example, the current collector comprises a woven material, a non-woven material, or a combination thereof. In other examples, the current collector comprises a sheet of non-woven material that optionally comprises perforations.

[0022] Another aspect of the present invention provides an electrochemical cell comprising an aqueous electrolyte comprising a divalent cation comprising Zn^{2+}, Mg^{2+}, or a combination thereof; a cathode comprising metal oxide (e.g., manganese oxide or manganese vanadium oxide); and an anode comprising zinc metal, magnesium metal, or a combination thereof, wherein the aqueous electrolyte has a nearly neutral pH, the divalent cation intercalates into the cathode when the cell discharges; and the divalent cation deposits onto the anode material as a neutral metal when the cell charges.

[0023] In some embodiments, the divalent cation is Zn^{2+}.

[0024] In some embodiments, the Zn^{2+} is generated upon the dissolution of $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water. In such instances, the aqueous electrolyte further comprises a counter ion selected from SO_4^{2-}, CHO^-, NO_3^-, $CO_2CH_3^-$, Cl^-, Br^-, ClO_4^-, or any combination thereof.

[0025] In some embodiments, the cathode comprises manganese oxide, and the manganese oxide is not substantially soluble in the electrolyte. For example, the manganese oxide has a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2. In some embodiments, the cathode comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1. In other examples, the cathode material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \bullet 3H_2O$, $Mn_7O_{14} \bullet 3H_2O$, $Mn_4O_9 \bullet 3H_2O$, Mn_2O_4, $Mn_4O_{18} \bullet H_2O$, or any combination thereof. And, in some embodiments, the cathode comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0026] In some embodiments, the manganese oxide has a chemical formula of Mn_5O_8, and the manganese oxide comprises a power having a mean particle diameter of about 50 μm or less.

[0027] In some embodiments, the cathode further comprises a carbon powder. For example, the cathode further comprises about 15 wt% or less of the carbon powder by weight of the cathode. In some instances, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0028] In some embodiments, the cathode further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. For example, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other examples, the additive is present at a concentration of about 20 wt% or less by weight of the cathode.

[0029] In some embodiments, the cathode is doped with Al, B, or any combination thereof.

[0030] In some embodiments, the anode comprises zinc metal.

[0031] In some embodiments, the anode comprises zinc metal and the divalent cation is Zn^{2+}.

[0032] In some embodiments, the anode material, the cathode material, or both further comprises a binder, such as any of the binders described above.

[0033] In some embodiments, the anode, the cathode, or both further comprises a current collector, such as any of the current collectors described above.

[0034] Another aspect of the present invention provides a method of manufacturing an electrochemical cell comprising providing a cathode comprising a layered material; providing an anode comprising a metal; and providing an aqueous electrolyte comprising a divalent cation, wherein the divalent cation intercalates into the layered material when the cell discharges; and the divalent cation de-intercalates from the cathode material and deposits onto the anode material as a neutral metal when the cell charges.

[0035] In some implementations, the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof.

[0036] In some implementations, the divalent cation is Zn^{2+}.

[0037] Some implementations further comprise dissolving $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water to generate the Zn^{2+} divalent cation.

[0038] In some implementations, the cathode material comprises a layered material comprising a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof.

[0039] In some implementations, the cathode material comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof.

[0040] In some implementations, the cathode material comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0041] In some implementations, the cathode comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2.

[0042] In some implementations, the cathode comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1.

[0043] In some implementations, the cathode comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \cdot 3H_2O$, $Mn_7O_{14} \cdot 3H_2O$, $Mn_4O_9 \cdot 3H_2O$, Mn_2O_4,

$Mn_4O_{18} \cdot H_2O$, or any combination thereof. In other embodiment, the cathode comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0044] In some implementations, the cathode comprises Mn_5O_8, and the Mn_5O_8 comprises a powder having a mean particle diameter of about 50 µm or less.

[0045] In some implementations, the cathode further comprises carbon powder.

[0046] In some implementations, the cathode further comprises about 15 wt% or less of the carbon powder by weight of the electrode material.

[0047] In some implementations, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0048] In some implementations, the cathode further comprises an additive that stabilizes the crystal lattice structure of manganese oxide.

[0049] In some implementations, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof.

[0050] In some implementations, the additive is present at a concentration of about 20 wt% or less by weight of the electrode material.

[0051] In some implementations, the anode material comprises a metal that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0052] In some implementations, the anode comprises zinc metal or magnesium metal.

[0053] In some implementations, the divalent cation is Zn^{2+}, and the anode comprises zinc metal.

[0054] In some implementations, the anode material, the cathode material, or both further comprises a binder.

[0055] In some implementations, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof.

[0056] In some implementations, the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the electrode material.

[0057] Some implementations further comprise providing a cathode current collector, an anode current collector, or both.

[0058] In some implementations, the cathode current collector, the anode current collector, or both comprises one or more electrically conductive metals or an electrically conductive polymer material.

[0059] In some implementations, the cathode current collector, the anode current collector, or both comprises a woven material, a non-woven material, or a combination thereof.

[0060] In some implementations, the cathode current collector, the anode current collector, or both comprises a sheet of non-woven material that optionally comprises perforations.

[0061] In some implementations, the cathode is doped with Al, B, or any combination thereof.

[0062] Another aspect of the present invention provides an electrochemical cell comprising an aqueous electrolyte comprising a divalent cation; a cathode comprising a cathode material; and an anode comprising an anode material, wherein the divalent cation intercalates into the cathode material and de-intercalates from the anode material when the cell discharges; and the divalent cation de-intercalates from the cathode material and intercalates into the anode material when the cell charges.

[0063] In some embodiments, the electrolyte comprises a nearly neutral pH. For example, the electrolyte has a pH from about 6 to about 8 (e.g., from about 6.5 to about 7.5).

[0064] In some embodiments, the aqueous electrolyte has a pH that is slightly acidic. For example, the electrolyte has a pH of from about 3 to about 6.

[0065] In other embodiments, the aqueous divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof. For instance, the aqueous divalent cation is Zn^{2+}. In some electrolytes, the Zn^{2+} divalent cation is generated upon the dissolution of $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water.

[0066] In other embodiments, the anode material, the cathode material, or both comprises a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof. For example, the anode material, the cathode material, or both comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof. In other examples, the cathode material comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell. And, in some examples, the anode material comprises a metal oxide that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0067] In some embodiments, the cathode material comprises a manganese oxide, wherein the manganese oxide is not substantially soluble in the electrolyte. For example, the cathode material comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2.

[0068] In some embodiments, the cathode material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1.

[0069] In other examples, the cathode material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \bullet 3H_2O$, $Mn_7O_{14} \bullet 3H_2O$, $Mn_4O_9 \bullet 3H_2O$, Mn_2O_4, $Mn_4O_{18} \bullet H_2O$, or any combination thereof. And, in some embodiments, the cathode material comprises manganese oxide having a predominant crystal structure of α–MnO_2, β--MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0070] In some embodiments, the anode material comprises manganese oxide, wherein the manganese oxide is not substantially soluble in the electrolyte. For example, the anode material comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2. In some embodiments, the anode material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1. In other examples, the anode material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \bullet 3H_2O$, $Mn_7O_{14} \bullet 3H_2O$, $Mn_4O_9 \bullet 3H_2O$, Mn_2O_4, $Mn_4O_{18} \bullet H_2O$, or any combination thereof. And, in some embodiments, the anode comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0071] In other embodiments, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is greater than the oxidation state of the manganese in the anode material when the cell has an SOC of at least about 90%. For example, the cathode material comprises manganese oxide having an oxidation state of about 4 when the cell has an SOC of at least about 90%. In other examples, the anode material comprises manganese oxide having an oxidation state of about 2 when the cell has an SOC of at least about 90%.

[0072] And, in some embodiments, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is approximately equal to the oxidation state of the manganese in the anode material when the cell has an SOC of less than about 10%. For example, the cathode material comprises manganese oxide and the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material and the manganese in the anode material is about 3 when the cell has an SOC of less than about 10%.

[0073] In other embodiments, the anode material, the cathode material, or both further comprises a carbon powder. For example, the anode material, the cathode material, or both further comprises about 15 wt% or less of the carbon powder by weight of the electrode material. In some instances, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0074] In alternative embodiments, the anode material, the cathode material, or both further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. In some examples, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other examples, the additive is present at a concentration of about 20 wt% or less by weight of the electrode material.

[0075] And, in some embodiments, the anode material, the cathode material, or both further comprises a binder. In some instances, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other instances, the binder is present at a concentration of from about 3 wt% to about 15 wt% (e.g., from about 4 wt% to about 12 wt% or from about 5 wt% to about 10 wt%) by weight of the electrode material (i.e., the cathode material and/or the anode material).

[0076] In some embodiments, the anode material, the cathode material, or both is doped with Al, B, or any combination thereof.

[0077] In other embodiments, the anode, the cathode, or both further comprises a current collector. In some instances, the current collector comprises one or more electrically conductive metals or an electrically conductive polymer material. In other instances, the current collector comprises a woven material, a non-woven material, or a combination thereof. For example, the current collector comprises a sheet of non-woven material that optionally comprises perforations.

[0078] Another aspect of the present invention provides an electrochemical cell comprising an aqueous electrolyte comprising Zn^{2+}; a cathode comprising manganese oxide; and an anode comprising manganese oxide, wherein the Zn^{2+} intercalates into the cathode and de-intercalates from the anode when the cell discharges; and the Zn^{2+} de-intercalates from the cathode and intercalates into the anode when the cell charges.

[0079] In some embodiments, the Zn^{2+} is generated upon the dissolution of $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water.

[0080] In some embodiments, the cathode material comprises a manganese oxide, wherein the manganese oxide is not substantially soluble in the electrolyte. For example, the cathode material comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2. In other examples, the cathode material comprises manganese oxide having a chemical formula of $Mn_3O_7 \cdot 3H_2O$, $Mn_7O_{14} \cdot 3H_2O$, $Mn_4O_9 \cdot 3H_2O$, Mn_2O_4, $Mn_4O_{18} \cdot H_2O$, or any combination thereof. And, in some embodiments, the cathode comprises manganese oxide having a predominant crystal structure of α--MnO_2, β--MnO_2, γ--MnO_2, δ--MnO_2, layered, or any combination thereof.

[0081] In other embodiments, the anode material comprises manganese oxide, wherein the manganese oxide is not substantially soluble in the electrolyte. In some examples, the anode material comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2. In other examples, the anode material comprises manganese oxide having a chemical formula of $Mn_3O_7 \cdot 3H_2O$, $Mn_7O_{14} \cdot 3H_2O$, $Mn_4O_9 \cdot 3H_2O$, Mn_2O_4, $Mn_4O_{18} \cdot H_20$, or any combination thereof. And, in some embodiments, the anode material comprises manganese oxide having a predominant crystal structure of α--MnO_2, β--MnO_2, γ--MnO_2, δ--MnO_2, layered, or any combination thereof.

[0082] In alternative embodiments, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is greater than the oxidation state of the manganese in the anode material when the cell has an SOC of at least about 90%. For example, the cathode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is about 4, when the cell has an SOC of at least about 90%. In other examples, the anode material comprises manganese oxide, and the oxidation state of the manganese in the anode material is about 2, when the cell has an SOC of at least about 90%.

[0083] In some embodiments, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is approximately equal to the oxidation state of the manganese in the anode material when the cell has an SOC of less than about 10%. For example, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material and the manganese in the anode material is about 3 when the cell has an SOC of less than about 10%.

[0084] In some embodiments, the anode material, the cathode material, or both further comprises a carbon powder. For example, the anode material, the cathode material, or both further comprises about 15 wt% or less of the carbon powder by weight of the electrode material. In some instances, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0085] In other embodiments, the anode material, the cathode material, or both further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. In some instances, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other instances, the additive is present at a concentration of about 20 wt% or less by weight of the electrode material.

[0086] Another aspect of the present invention provides a method of manufacturing an electrochemical cell comprising providing a cathode comprising a layered material; providing an anode comprising a metal; and providing an aqueous electrolyte comprising a divalent cation, wherein the divalent cation intercalates into the layered material when the cell discharges; and the divalent cation de-intercalates from the cathode material and deposits onto the anode material as a neutral metal when the cell charges.

[0087] In some implementations, the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof. For example, the divalent cation is Zn^{2+}.

[0088] Some implementations further comprise dissolving $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water to generate the Zn^{2+} divalent cation.

[0089] In some implementations, the cathode comprises a layered material comprising a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof. For example, the cathode material comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof. In other examples, the cathode comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell. And, in some instances, the cathode comprises manganese oxide having a chemical formula of Mn_xO_y, and x is greater than or equal to 1, and y is greater than or equal to 2. In some instances, the cathode comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1. In other instances, the cathode comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7{\bullet}3H_2O$, $Mn_7O_{14}{\bullet}3H_2O$, $Mn_4O_9{\bullet}3H_2O$, Mn_2O_4, $Mn_4O_{18}{\bullet}H_2O$, or any combination thereof. And, in some embodiments, the cathode comprises manganese oxide having a predominant crystal structure of α--MnO_2, β--MnO_2, γ--MnO_2, δ--MnO_2, layered, or any combination thereof. For example, the cathode comprises Mn_5O_8, and the Mn_5O_8 comprises a powder having a mean particle diameter of about 50 μm or less.

[0090] In some implementations, cathode further comprises carbon powder. For example, the cathode further comprises about 15 wt% or less of the carbon powder by weight of the electrode material. In other examples, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0091] In some implementations, the cathode further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. In some instances, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other instances, the additive is present at a concentration of about 20 wt% or less by weight of the electrode material.

[0092] In some implementations, the anode material comprises a metal that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell. For example, the anode comprises zinc metal or magnesium metal.

[0093] In some implementations, the divalent cation is Zn^{2+}, and the anode comprises zinc metal.

[0094] In some implementations, the cathode material, the anode material, or both is doped with Al, B, or any combination thereof.

[0095] In some implementations, the anode material, the cathode material, or both further comprises a binder. In some instances, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other instances, the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the electrode material.

[0096] Some implementations further comprise providing a cathode current collector, an anode current collector, or both. In some instances, the cathode current collector, the anode current collector, or both comprises one or more electrically conductive metals or an electrically conductive polymer material. In other instances, the cathode current collector, the anode current collector, or both comprises a woven material, a non-woven material, or a combination thereof. And, in some instances, the cathode current collector, the anode current collector, or both comprises a sheet of non-woven material that optionally comprises perforations.

[0097] Another aspect of the present invention provides a method of manufacturing an electrochemical cell comprising providing a cathode comprising a cathode material; providing an anode comprising an anode material; and providing an aqueous electrolyte comprising a divalent cation, wherein the cathode material and the anode material are not substantially soluble in the electrolyte, and the divalent cation intercalates into the cathode and the divalent cation de-intercalates from the anode when the cell discharges; and the divalent cation de-intercalates from the cathode and intercalates into the anode when the cell charges.

[0098] In some implementations, the electrolyte comprises a nearly neutral pH. For example, the electrolyte has a pH from about 6 to about 8 (e.g., from about 6.5 to about 7.5).

[0099] In other implementations, the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof. For example, the divalent cation is Zn^{2+}.

[0100] Some implementations further comprise dissolving $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water to generate the Zn^{2+} divalent cation.

[0101] In other implementations, the anode material, the cathode material, or both comprises a metal oxide, a mixed metal oxide, a metal sulfide, a layered compound, a zinc metal phosphate, a zinc metal oxide, or any combination thereof. For example, the anode material, the cathode material, or both comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof.

[0102] In some implementations, the cathode material comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0103] In other implementations, the anode material comprises a metal oxide that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0104] In some implementations, the cathode material, the anode material, or both comprises manganese oxide having a chemical formula of Mn_xO_y, and x is greater than or equal to 1, and y is greater than or equal to 2. In other implementations, the anode material, the cathode material, or both comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, and y is greater than or equal to 2, and z is greater than or equal to 1.

[0105] In alternative implementations, the cathode material, the anode material, or both comprises manganese oxide having a chemical formula of $Mn_3O_7{\bullet}3H_2O$, $Mn_7O_{14}{\bullet}3H_2O$, $Mn_4O_9{\bullet}3H_2O$, Mn_2O_4, $Mn_4O_{18}{\bullet}H_2O$, or any combination thereof. And, in some embodiments, the cathode material, the anode material, or both comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0106] In some implementations, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is greater than the oxidation state of the manganese in the anode material, when the cell has an SOC of at least about 90%. For example, the cathode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is about 4, when the cell has an SOC of at least about 90%.

[0107] In other implementations, the anode material comprises manganese oxide, and the oxidation state of the manganese in the anode material is about 2, when the cell has an SOC of at least about 90%.

[0108] In some implementations, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is approximately equal to the oxidation state of the manganese in the anode material when the cell has an SOC of less than about 10%. For example, the cathode material comprises manganese oxide and the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material and the anode material is about 3 when the cell has an SOC of less than about 10%.

[0109] In other implementations, the anode material, the cathode material, or both further comprises a carbon powder. In some instances, the anode material, the cathode material, or both further comprises about 15 wt% or less of the carbon powder by weight of the electrode material. In other instances, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0110] In some implementations, the anode material, the cathode material, or both further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. In some instances, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other instances, the additive is present at a concentration of about 20 wt% or less by weight of the electrode material.

[0111] In other implementations, the anode material, the cathode material, or both further comprises a binder. In some instances, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other instances, the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the electrode material.

[0112] And, some implementations further comprise providing a cathode current collector, an anode current collector, or both. In some instances, the cathode current collector, the anode current collector, or both comprises one or more electrically conductive metals or an electrically conductive polymer material. In some instances, the cathode current collector, the anode current collector, or both comprises a woven material, a non-woven material, or a combination thereof. And, in other instances, the cathode current collector, the anode current collector, or both comprises a sheet of non-woven material that optionally comprises perforations.

BRIEF DESCRIPTION OF THE DRAWINGS

[0113] Figures 1 and 2 graphically depict a charge profile for an exemplary electrochemical cell of the present invention.

[0114] Figures 3-5 are plots of current (Amps) vs. Potential (Volts) for several manganese oxide test cells of the present invention.

[0115] These figures are provided by way of example and are not intended to limit the scope of the invention.

DETAILED DESCRIPTION

[0116] The present invention provides an electrochemical cell comprising an aqueous electrolyte formulated with a divalent cation that intercalates into a cathode upon discharge of the cell.

[0117] I. DEFINITIONS

[0118] As used herein, the term "battery" encompasses electrical storage devices comprising one electrochemical cell (e.g., a button cell, a coin cell, or the like) or a plurality of electrochemical cells. A "secondary battery" is rechargeable, whereas a "primary battery" is not rechargeable. For secondary batteries of the present invention, a battery cathode is designated as the positive electrode during battery discharge and the negative electrode during battery charging. Accordingly, the anode is designated as the negative electrode during discharge, and as the positive electrode during charge.

[0119] As used herein, the terms "electrochemical cell" and "cell" are used interchangeably.

[0120] As used herein, the term "metal oxide" includes compounds that include at least one metal atom and at least one oxygen atom. 'Metal oxides' include "mixed metal oxides", wherein the metal oxide comprises at least two metal atoms of different elements and at least one oxygen atom.

[0121] As used herein, the term "manganese oxide" refers to any manganese compound that includes one or more oxygen atoms in its coordination sphere. Examples of manganese oxide include MnO, MnO_2, Mn_2O_3, Mn_3O_4, $Mn(OH)_2$, $Mn(OH)_4$, $MnO_2(OH)_2$, $Mn(OH)_3$, $MnOOH$, $Mn(ONa)_2$, $Mn(OK)_2$, $Mn(OLi)_2$, $Mn(ORb)_2$, $MnOONa$, $MnOOK$, $MnOOLi$, $MnOORb$, $ZnFeMnO_2$, $(MnFe)_2O_3$, $NiMnO_4$, any hydrate thereof, or any combination thereof. In other examples, manganese oxide has the chemical formula Mn_xO_y, wherein x is greater than or equal to 1, and y is greater than or equal to 2. Some examples of manganese oxide have the chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \bullet 3H_2O$, $Mn_7O_{14} \bullet 3H_2O$, $Mn_4O_9 \bullet 3H_2O$, Mn_2O_4, $Mn_4O_{18} \bullet H_2O$, or any combination thereof. In other examples, the manganese oxide has a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof. Note that 'hydrates' of manganese include hydroxides of manganese. The term 'manganese oxide' also includes any of the abovementioned species that are doped and/or coated with dopants and/or coatings that enhance one or more properties of the manganese.

[0122] As used herein, "vanadium oxide" refers to any vanadium compound having at least one oxygen atom in its coordination sphere. 'Vanadium oxide' includes oxides or hydroxide of vanadium, e.g., VO, VO_2, V_2O_3, V_2O_5, V_3O_7, V_4O_9, V_6O_{13}, V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13}, V_8O_{15}, or any combination thereof.

[0123] As used herein, an "electrolyte" refers to a substance that behaves as an electrically conductive medium. For example, the electrolyte facilitates the mobilization of electrons and cations (e.g., divalent cations) in the cell. Electrolytes include aqueous electrolytes that are formulated with mixtures of materials such as aqueous solutions of metal salts (e.g., $ZnSO_4$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof). Some electrolytes also comprise additives such as buffers. For example, an electrolyte comprises a buffer comprising a borate or a phosphate.

[0124] A "cycle" or "charge cycle" refers to a consecutive charge and discharge of a cell or a consecutive discharge and charge of a cell, either of which includes the duration between the consecutive charge and discharge or the duration between the consecutive discharge and charge. For example, a cell undergoes one cycle when, freshly prepared, it is discharged to about 100% of its DOD and re-charged to about 100% of its state of charge (SOC). In another example, a freshly prepared cell undergoes 2 cycles when the cell is: Cycle 1: discharged to about 100% of its DOD and re-charged to about 100% SOC; followed by Cycle 2: a second discharge to about 100% of its DOD and re-charged to about 100% SOC.

[0125] It is noted that this process may be repeated to subject a cell to as many cycles as is desired or practical.

[0126] For convenience, the polymer name "polyacrylonitrile" and its corresponding initials "PA" are used interchangeably as adjectives to distinguish polymers, solutions for preparing polymers, and polymer coatings. Use of these names and initials in no way implies the absence of other constituents. These adjectives also encompass substituted and co-polymerized polymers. A substituted polymer denotes one for which a substituent group, a methyl group, for example, replaces a hydrogen on the polymer backbone.

[0127] For convenience, the polymer name "polyvinyl alcohol" and its corresponding initials "PVA" are used interchangeably as adjectives to distinguish polymers, solutions for preparing polymers, and polymer coatings. Use of these names and initials in no way implies the absence of other constituents. These adjectives also encompass substituted and co-polymerized polymers.

[0128] For convenience, the polymer name "polyvinyl chloride" and its corresponding initials "PVC" are used interchangeably as adjectives to distinguish polymers, solutions for preparing polymers, and polymer coatings. Use of these names and initials in no way implies the absence of other constituents. These adjectives also encompass substituted and co-polymerized polymers.

[0129] For convenience, the polymer name "polyethylene oxide" and its corresponding initials "PEO" are used interchangeably as adjectives to distinguish polymers, solutions for preparing polymers, and polymer coatings. Use of these names and initials in no way implies the absence of other constituents. These adjectives also encompass substituted and co-polymerized polymers.

[0130] For convenience, the polymer name "polytetrafluoroethylene" and its corresponding initials "PTFE" are used interchangeably as adjectives to distinguish polymers, solutions for preparing polymers, and polymer coatings. Use of these names and initials in no way implies the absence of other constituents. These adjectives also encompass substituted and co-polymerized polymers. A substituted polymer denotes one for which a substituent group, a methyl group, for example, replaces a hydrogen on the polymer backbone.

[0131] For convenience, the polymer name "polyvinylidene difluoride" and its corresponding initials "PVD" are used interchangeably as adjectives to distinguish polymers, solutions for preparing polymers, and polymer coatings. Use of these names and initials in no way implies the absence of other constituents. These adjectives also encompass substituted and co-polymerized polymers.

[0132] For convenience, the polymer name "polymethylmethacrylate" and its corresponding initials "PMMA" are used interchangeably as adjectives to distinguish polymers, solutions for preparing polymers, and polymer coatings. Use of these names and initials in no way implies the absence of other constituents. These adjectives also encompass substituted and co-polymerized polymers.

[0133] As used herein, "Ah" refers to Ampere (Amp) Hour and is a scientific unit for the capacity of a battery or electrochemical cell. A derivative unit, "mAh" represents a milliamp hour and is 1/1000 of an Ah.

[0134] As used herein, an "anode" is an electrode through which (positive) electric current flows into a polarized electrical device. In a battery or galvanic cell, the anode is the negative electrode from which electrons flow during the discharging phase in the battery. The anode is also the electrode that undergoes chemical oxidation during the discharging phase. However, in secondary, or rechargeable, cells, the anode is the electrode that undergoes chemical reduction during the cell's charging phase. Anodes are formed from electrically conductive or semiconductive materials, e.g., metal oxides, metal sulfides, layered compounds, zinc-metal phosphates, zinc-metal oxides, or any combination thereof.

[0135] Anodes may have many configurations. For example, an anode may be configured from a conductive mesh or grid that is coated with one or more anode materials. In another example, an anode may be a solid sheet or bar of anode material.

[0136] As used herein, a "cathode" is an electrode from which (positive) electric current flows out of a polarized electrical device. In a battery or galvanic cell, the cathode is the positive electrode into which electrons flow during the discharging phase in the battery. The cathode is also the electrode that undergoes chemical reduction during the discharging phase. However, in secondary or rechargeable cells, the cathode is the electrode that undergoes chemical oxidation during the cell's charging phase. Cathodes are formed from electrically conductive or semiconductive materials, e.g., metal oxides, metal sulfides, layered compounds, zinc-metal phosphates, zinc-metal oxides, or any combination thereof.

[0137] Cathodes may also have many configurations. For example, a cathode may be configured from a conductive mesh that is coated with one or more cathode materials. In another example, a cathode may be a solid sheet or bar of cathode material.

[0138] As used herein, the term "Coulombic efficacy" refers to the number of Coulombs removed from a battery cell on discharge divided by the number of Coulombs that are added into the cell on charge.

[0139] As used herein, the term "electronic device" is any device that is powered by electricity. For example, and electronic device can include a portable computer, a portable music player, a cellular phone, a portable video player, global positioning satellite ("GPS") navigation devices, or any device that combines the operational features thereof.

[0140] As used herein, the term "cycle life" is the maximum number of times a secondary battery can be cycled while retaining a capacity useful for the battery's intended use (e.g., the number of times a cell may be cycled until the cell's 100% SOC, i.e., its actual capacity, is less than 90% of its rated capacity (e.g., less than 85% of its rated capacity, about 90% of its rated capacity, or about 80% of its rated capacity). In some instances, 'cycle life' is the number of times a secondary battery or cell can be cycled until the cell's 100% SOC is at least about 60 percent of its rated capacity (e.g., at least about 70 percent of its rated capacity, at least about 80 percent of its rated capacity, at least 90 percent of its rated capacity, at least 95 percent of its rated capacity, about 90% of its rated capacity, or about 80% of its rated capacity).

[0141] As used herein, the symbol "$\underline{M}$" denotes molar concentration.

[0142] As used herein, the term "oxide" applied to secondary batteries and secondary battery electrodes encompasses corresponding "hydroxide" species, which are typically present, at least under some conditions.

[0143] As used herein, the term, "powder" refers to a dry, bulk solid composed of a plurality of fine particles that may flow freely when shaken or tilted.

[0144] As used herein, the term, "mean diameter" or "mean particle diameter" refers to the diameter of a sphere that has the same volume/surface area ratio as a particle of interest.

[0145] As used herein, the terms "substantially stable" or "substantially inert" refer to a compound or component that remains substantially chemically unchanged in the presence of an aqueous electrolyte (e.g., aqueous divalent cations).

[0146] As used herein, "charge profile" refers to a graph of an electrochemical cell's voltage or capacity with time. A charge profile can be superimposed on other graphs such as those including data points such as charge cycles or the like.

[0147] As used herein, "resistivity" or "impedance" refers to the internal resistance of a cathode in an electrochemical cell. This property is typically expressed in units of Ohms or micro-Ohms.

[0148] As used herein, the terms "first" and/or "second" do not refer to order or denote relative positions in space or time, but these terms are used to distinguish between two different elements or components. For example, a first component does not necessarily proceed a second component in time or space; however, the first component is not the second component and vice versa. Although it is possible for a first component to precede a second component in space or time, it is equally possible that a second component precedes a first component in space or time.

[0149] As used herein, the term "nanometer" and "nm" are used interchangeably and refer to a unit of measure equaling 1×10^{-9} meters.

[0150] As used herein, the terms "analogous cathode" refer to a cathode of a pair of cathodes wherein the cathodes of the pair are substantially identical to each other (e.g., use substantially the same amount of cathode materials (e.g., manganese, binder, dopants, coatings, or any combination thereof); and/or using substantially the same methods of manufacturing) whose most significant difference is that one cathode of the pair is substantially free of stabilizing agent.

[0151] As used herein, the terms "battery capacity" or "capacity" refer to the mathematical product of a battery's discharge current and the time (in hours) during which the current is discharged.

[0152] As used herein, the terms "aggregate capacity" or "aggregate battery capacity" refers to the sum of a battery's capacities, i.e., the sum of the individual products of discharge current and the time during which the current is discharged after being discharged to about 100 percent depth of discharge (e.g., more than 97.5 % depth of discharge, or more than 99 % depth of discharge) over a course of one or more charge cycles.

[0153] As used herein, "depth of discharge" and "DOD" are used interchangeably to refer to the measure of how much energy has been withdrawn from a battery or cell, often expressed as a percentage of capacity, e.g., rated capacity. For example, a 100 Ah battery from which 30 Ah has been withdrawn has undergone a 30% depth of discharge (DOD).

[0154] As used herein, "state of charge" and "SOC" and used interchangeably to refer to the available capacity remaining in a battery, expressed as a percentage of the cell or battery's rated capacity.

[0155] The term "divalent cation" refers to an ion that lacks two electrons when compared to its neutral counterpart. Examples of divalent cations include Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof.

[0156] The term "intercalate" refers to a reversible insertion of a chemical species (e.g., a compound or ion (e.g., cation or anion)) between two other molecules.

[0157] The term "de-intercalate" refers to the expulsion of a chemical species from its location between two other molecules.

[0158] The term "layered material" refers to a material that possesses permanent or transient porosity within its crystalline or semi-crystalline structure. Examples of layered materials include some forms of metal oxides (e.g., manganese oxide or vanadium oxide) or metal sulfides (e.g., TiS_2).

[0159] II. ELECTROCHEMICAL CELLS

[0160] Electrochemical cells of the present invention comprise a cathode, an anode, and an aqueous electrolyte that comprises a divalent cation, wherein the divalent cation intercalates into the cathode when the cell is discharged.

[0161] While not being limited by theory, it is theorized that the electrochemical cells of the present invention employ a divalent cation intercalation mechanism, where divalent cations intercalate into the cathode from the aqueous electrolyte and the anode when the cell discharges. During cell charging or re-charging, the process is reversed and the cations deposit on the anode in as neutral species. Thus, the cathode material and the anode material reversibly, and with little or no physical change in their matrix structures, alternate between different oxidation states while divalent cations reversibly insert (intercalate) or deposit into the cathode or onto the anode.

[0162] A. Cathodes

[0163] Cathodes that are useful in electrochemical cells of the present invention are substantially insoluble in the electrolyte and are intercalatable with respect to cations in an aqueous environment.

[0164] In some embodiments, the cathode comprises a layered material that comprises a metal oxide, mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof. For example, the layered material comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof. In some examples, the layered material comprises a manganese oxide, wherein the manganese undergoes a reduction in its oxidation state of 1 or more when the cell is discharged. In other examples, the layered material comprises a manganese oxide, wherein the manganese undergoes an increase in its oxidation state of 1 or more when the cell is charged.

[0165] In some embodiments, the cathode comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2.

[0166] In some embodiments, the layered material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7{\bullet}3H_2O$, $Mn_7O_{14}{\bullet}3H_2O$, $Mn_4O_9{\bullet}3H_2O$, Mn_2O_4, $Mn_4O_{18}{\bullet}H_2O$, or any combination thereof. In other embodiments, the cathode comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0167] In some embodiments, the layered material comprises vanadium oxide having a chemical formula of VO, VO_2, V_2O_3, V_2O_5, V_3O_7, V_4O_9, V_6O_{13}, V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13}, V_8O_{15}, or any combination thereof.

[0168] In some embodiments, the layered material comprises a combination of manganese and vanadium oxide (e.g., manganese vanadium oxide). For instance, the layered material comprises a material having a chemical formula of $Mn_xV_zO_y$, wherein z is 1 or more, and x and y are as defined above.

[0169] In other embodiments, the layered material is doped with Al, B, or any combination thereof. For example, the layered material comprises a manganese oxide or manganese vanadium oxide that is doped with Al, B, or any combination thereof. In some instances, the layered material comprises manganese oxide, and the manganese oxide is doped with Al, B, or any combination thereof. In another example, the cathode comprises manganese vanadium oxide that is doped with Al, B, or any combination thereof.

[0170] In some embodiments, the layered material of the cathode comprises a bulk material. In other embodiments, the layered material of the cathode comprises a powder. For example, the layered material comprises Mn_5O_8 that comprises a power having a mean particle diameter of about 50 µm or less (e.g., about 10 µm or less, about 5 µm or less, about 1 µm or less, about 0.5 µm or less, or 0.1 µm or less).

[0171] Cathodes of the present invention may optionally comprise additives such as dopants, coatings (e.g., a hydrophobic coatings (e.g., a polymer coating)), conductivity enhancers, stabilizers, binders, or any combination thereof.

[0172] *1. Conductivity Enhancers*

[0173] In one embodiment, the cathode comprises a conductivity enhancer that improves the electrical conductivity of the layered material. In some examples, the cathode further comprises a carbon powder. For instance, cathode comprises about 20 wt% or less (e.g., about 15 wt% or less, about 10 wt% or less, about 5 wt% or less, or about 1 wt% or less) of the carbon powder by weight of the cathode. In other examples, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0174] *2. Stabilizers*

[0175] In another embodiment, the cathode further comprises a stabilizer that stabilizes the crystal lattice structure of the layered material. For example, the stabilizer stabilizes the crystal structure of manganese oxide. In some instances, the stabilizer comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other instances, the cathode comprises about 20 wt% or less (e.g., about 15 wt% or less, about 10 wt% or less, about 5 wt% or less, or about 1 wt% or less) of stabilizer by weight of the cathode.

[0176] 3. *Binders*

[0177] In some embodiments, the cathode further comprises a binder. For example, the cathode comprises a binder comprising polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other examples, the cathode comprises from about 1 wt% to about 20 wt% of binder (e.g., from about 3 wt% to about 15 wt%) by weight of the cathode.

[0178] 4. *Current Collectors and Supports*

[0179] Cathodes of the present invention can optionally include additional structures or supports such as current collectors. In some embodiments, the cathode comprises a current collector. In some instances, the current collector comprises one or more electrically conductive metals (e.g., Ti, Cu, Fe, or a combination thereof) or an electrically conductive polymer material (e.g., polyacetylene, polyphenylene vinylene, polypyrrole, polythiophene, polyaniline, polyphenylene sulfide, or any combination thereof). In other instances, the current collector comprises a woven material, a non-woven material (e.g., a screen, grid, or fabric material), or a combination thereof. And, in some instances, the current collector comprises a sheet of non-woven material that optionally comprises perforations.

[0180] B. Electrolytes

[0181] Electrolytes useful in electrochemical cells of the present invention readily dissolve some metal salts to generate divalent cations in solution (e.g., an aqueous solution).

[0182] In some embodiments, the electrolyte is substantially free of alkaline earth metal hydroxides (e.g., NaOH, KOH, or the like). In these embodiments, the electrolyte comprises less than 0.1 wt% of an alkaline earth metal hydroxide by weight of electrolyte.

[0183] In some embodiments, the electrolyte comprises a divalent cation (e.g., a divalent metal cation). In some examples, the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof. For instance, the divalent cation is Zn^{2+}. In some electrolytes, the Zn^{2+} divalent cation is generated upon the dissolution of $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water. In some embodiments, the electrolyte further comprises the salt counter ion to Zn^{2+}.

[0184] In some embodiments, the electrolyte comprises a nearly neutral pH. For example, the electrolyte has a pH from about 6 to about 8 (e.g., from about 6.5 to about 7.5 or from about 6.7 to about 7.3).

[0185] In some embodiments, the aqueous electrolyte has a pH that is slightly acidic. For example, the electrolyte has a pH of from about 3 to about 6.

[0186] In some embodiments, the electrolyte comprises one or more metal salts (e.g., zinc metal salts) with a concentration below saturation. For example, the concentration of the metal salt may be between about 1 mole per kilogram of solution and 2 moles per kilogram of solution.

[0187] Electrolytes of the present invention may optionally contain additives such as buffers, surfactants, polymers, or the like.

[0188] C. <u>Exemplary Electrochemical Cell No. 1.</u>

[0189] One aspect of the present invention provides an electrochemical cell comprising an aqueous electrolyte comprising a divalent cation; a cathode comprising a layered material; and an anode comprising a metal, wherein the divalent cation intercalates into the layered material when the cell discharges; and the divalent cation de-intercalates from the cathode material and deposits onto the anode as a neutral metal when the cell charges.

[0190] *1. Cathodes*

[0191] Cathodes useful in exemplary electrochemical cell no. 1 are as described above.

[0192] *2. Electrolytes*

[0193] Electrolytes useful in exemplary electrochemical cell no. 1 are as described above.

[0194] *3. Anodes*

[0195] Anodes useful in exemplary electrochemical cell no. 1 comprise a metal. In some embodiments, the anode comprises zinc, magnesium, or a combination thereof. For example, the anode comprises zinc.

[0196] In some embodiments, the metal comprises a bulk material. In other embodiments, the metal comprises a powder. For example, the anode comprises zinc powder having a mean particle diameter of about 50 μm or less (e.g., about 10 μm or less, about 5 μm or less, about 1 μm or less, about 0.5 μm or less, or 0.1 μm or less).

[0197] In other embodiments, the anode comprises a metal, and a portion of the metal transforms into a divalent cation when the cell is discharged.

[0198] In some embodiments, the anode metal is a neutral form of the divalent cation. For example, the anode comprises zinc metal, and the divalent cation is Zn^{2+}. In other embodiments, the anode metal is exclusive of the neutral form of the divalent cation. For example, the anode comprises zinc metal, and the divalent cation is Mg^{2+}.

[0199] Anodes useful in this exemplary cell may optionally comprise a binder. For example, the anode further comprises a binder, and the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other examples, the anode comprises from about 1 wt% to about 20 wt% (e.g., from about 3 wt% to about 15 wt%) of binder by weight of the anode.

[0200] In some embodiments, the anode comprises a current collector. Current collectors that are useful for combination with these anodes are as described above.

[0201] One exemplary electrochemical cell of the present invention comprises an aqueous electrolyte comprising a divalent cation comprising Zn^{2+}, Mg^{2+}, or a combination thereof; a cathode comprising manganese oxide; and an anode comprising zinc metal, magnesium metal, or a combination thereof, wherein the aqueous electrolyte has a nearly neutral pH, the divalent cation intercalates into the cathode when the cell discharges; and the divalent cation deposits onto the anode as a neutral metal when the cell charges.

[0202] D. Exemplary Electrochemical Cell No. 2.

[0203] Another aspect of the present invention provides an electrochemical cell comprising an aqueous electrolyte comprising a divalent cation; a cathode comprising a cathode material; and an anode comprising an anode material, wherein the divalent cation intercalates into the cathode material and de-intercalates from the anode material upon discharge of the electrochemical cell; and the divalent cation de-intercalates from the cathode material and intercalates into the anode material when the cell is charged or recharged.

[0204] *1. Electrolytes*

[0205] Electrolytes useful in exemplary electrochemical cell no. 2 are as described above.

[0206] *2. Electrodes (Anodes and Cathodes)*

[0207] Electrodes useful in these exemplary electrochemical cells are not substantially soluble in the aqueous electrolyte. Furthermore, these electrodes are susceptible to reversible intercalation by a divalent cation in an aqueous environment.

[0208] In some embodiments, the anode material, the cathode material, or both comprises a layered material. For example, the anode material, the cathode material, or both comprises metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof. In some instances, the anode material, the cathode material, or both comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof. In other examples, the cathode material comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell. And, in some examples, the anode material comprises a metal oxide that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0209] In some embodiments, the cathode material comprises a manganese oxide, wherein the manganese oxide is not substantially soluble in the electrolyte. For example, the cathode material comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2. In other examples, the cathode material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \cdot 3H_2O$, $Mn_7O_{14} \cdot 3H_2O$, $Mn_4O_9 \cdot 3H_2O$, Mn_2O_4, $Mn_4O_{18} \cdot H_2O$, or any combination thereof. And, in some embodiments, the cathode material comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0210] In some embodiments, the cathode material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, and y is greater than or equal to 2, and z is greater than or equal to 1.

[0211] In some embodiments, the anode material comprises a manganese oxide, wherein the manganese oxide is not substantially soluble in the electrolyte. For example, the anode material comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2. In some embodiments, the anode material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, and y is greater than or equal to 2, and z is greater than or equal to 1. In other examples, the anode material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \cdot 3H_2O$, $Mn_7O_{14} \cdot 3H_2O$, $Mn_4O_9 \cdot 3H_2O$, Mn_2O_4, $Mn_4O_{18} \cdot H_2O$, or any combination thereof. And, in some embodiments, the anode material comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0212] In other embodiments, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is greater than the oxidation state of the manganese in the anode material when the cell has an SOC of at least about 90% (e.g., at least about 95% or at least about 99%). For example, the cathode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is about 4, when the cell has an SOC of at least about 90% (e.g., at least about 95% or at least about 99%). In other examples, the anode material comprises manganese oxide, and the oxidation state of the manganese in the anode material is about 2, when the cell has an SOC of at least about 90% (e.g., at least about 95% or at least about 99%).

[0213] In some embodiments, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is approximately equal to the oxidation state of the manganese in the anode material when the cell has an SOC of less than about 10% (e.g., less than about 7.5%, less than about 5%, or less than about 7.5%). For example, the cathode material comprises manganese oxide and the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material and the manganese in the anode material is about 3 when the cell has an SOC of less than about 10% (e.g., less than about 7.5%, less than about 5%, or less than about 7.5%).

[0214] Electrodes (e.g., cathodes and/or anodes) useful in this exemplary electrochemical cell may optionally comprise additives such as surfactants, binders, stabilizers, conductivity enhancers (e.g., carbon powder), or other optional additives. For example, the anode material, the cathode material, or both further comprises a carbon powder. For example, the anode material, the cathode material, or both further comprises about 15 wt% or less (e.g., about 12 wt% or less, about 10 wt% or less, or about 5 wt% or less) of the carbon powder by weight of the electrode material. In some instances, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0215] In alternative embodiments, the anode material, the cathode material, or both further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. In some examples, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other examples, the additive is present at a concentration of about 20 wt% or less (e.g., about 15 wt% or less, about 15 wt% or less, or about 10 wt% or less) by weight of the electrode material.

[0216] And, in some embodiments, the anode material, the cathode material, or both further comprises a binder. In some instances, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other instances, the binder is present at a concentration of from about 3 wt% to about 15 wt% (e.g., from about 4 wt% to about 12 wt% or from about 5 wt% to about 10 wt%) by weight of the electrode material (i.e., the cathode material and/or the anode material).

[0217] In other embodiments, the anode, the cathode, or both further comprises a current collector. In some instances, the current collector comprises one or more electrically conductive metals (e.g., Ti, Cu, Fe, or a combination thereof) or an electrically conductive polymer material (e.g., polyacetylene, polyphenylene vinylene, polypyrrole, polythiophene, polyaniline, polyphenylene sulfide, or any combination thereof). In other instances, the current collector comprises a woven material, a non-woven material, or a combination thereof. For example, the current collector comprises a sheet or film of non-woven material that optionally comprises perforations.

[0218] In some embodiments, the anode material, the cathode material, or both are doped with Al, B, or any combination thereof.

[0219] Another aspect of the present invention provides an electrochemical cell comprising an aqueous electrolyte comprising Zn^{2+}; a cathode comprising manganese oxide; and an anode comprising manganese oxide, wherein the Zn^{2+} intercalates into the cathode and de-intercalates from the anode upon discharge of the electrochemical cell; and the Zn^{2+} de-intercalates into the cathode and intercalates into the anode when the cell is charged.

[0220] III. METHODS OF MANUFACTURING AN ELECTROCHEMICAL CELL

[0221] A. Methods of Manufacturing Exemplary Electrochemical Cell No. 1.

[0222] Another aspect of the present invention provides a method of manufacturing an electrochemical cell comprising providing a cathode comprising a layered material; providing an anode comprising a metal; and providing an aqueous electrolyte comprising a divalent cation, wherein the divalent cation intercalates into the layered material when the cell discharges; and the divalent cation de-intercalates from the cathode material and deposits onto the anode material as a neutral metal when the cell charges.

[0223] In some implementations, the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof.

[0224] In some implementations, the divalent cation is Zn^{2+}.

[0225] Some implementations further comprise dissolving $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water to generate the Zn^{2+} divalent cation.

[0226] In some implementations, the electrolyte comprises a nearly neutral pH. For example, the electrolyte has a pH from about 6 to about 8 (e.g., from about 6.5 to about 7.5).

[0227] In some implementations, the cathode material comprises a layered material comprising a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof.

[0228] In some implementations, the cathode material comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof.

[0229] In some implementations, the cathode material comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0230] In some implementations, the cathode comprises manganese oxide having a chemical formula of Mn_xO_y, and x is greater than or equal to 1, and y is greater than or equal to 2.

[0231] In some implementations, the cathode comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, and y is greater than or equal to 2, and z is greater than or equal to 1.

[0232] In some implementations, the cathode comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \bullet 3H_2O$, $Mn_7O_{14} \bullet 3H_2O$, $Mn_4O_9 \bullet 3H_2O$, Mn_2O_4, $Mn_4O_{18} \bullet H_2O$, or any combination thereof. And, in some implementations, the cathode comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0233] In some implementations, the cathode comprises Mn_5O_8, and the Mn_5O_8 comprises a powder having a mean particle diameter of about 50 μm or less (e.g., about 10 μm or less, about 5 μm or less, about 1 μm or less, about 0.5 μm or less, or 0.1 μm or less).

[0234] In some implementations, the cathode is doped with Al, B, or any combination thereof.

[0235] In some implementations, the cathode further comprises carbon powder.

[0236] In some implementations, the cathode further comprises about 15 wt% or less of the carbon powder by weight of the electrode material.

[0237] In some implementations, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0238] In some implementations, the cathode further comprises a stabilizer that stabilizes the crystal lattice structure of manganese oxide.

[0239] In some implementations, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof.

[0240] In some implementations, the additive is present at a concentration of about 20 wt% or less (e.g., about 15 wt% or less, about 10 wt% or less, about 5 wt% or less, or about 1 wt% or less) of stabilizer by weight of the cathode.

[0241] In some implementations, the anode material comprises a metal that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0242] In some implementations, the anode comprises zinc metal or magnesium metal.

[0243] In some implementations, the divalent cation is Zn^{2+}, and the anode comprises zinc metal.

[0244] In some implementations, the divalent cation is Mg^{2+}, and the anode comprises magnesium metal.

[0245] In some implementations, the anode, the cathode, or both further comprises a binder.

[0246] In some implementations, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof.

[0247] In some implementations, the binder is present at a concentration of from about 1 wt% to about 20 wt% of binder (e.g., from about 3 wt% to about 15 wt%) by weight of the electrode.

[0248] Some implementations further comprise providing a cathode current collector, an anode current collector, or both.

[0249] In some embodiments, the cathode current collector, the anode current collector, or both comprises one or more electrically conductive metals or an electrically conductive polymer material, as described above.

[0250] In some embodiments, the cathode current collector, the anode current collector, or both comprises a woven material, a non-woven material, or a combination thereof.

[0251] In some embodiments, the cathode current collector, the anode current collector, or both comprises a sheet of non-woven material that optionally comprises perforations.

[0252] B. Methods of Manufacturing Exemplary Electrochemical Cell No. 2.

[0253] Another aspect of the present invention provides a method of manufacturing an electrochemical cell comprising providing a cathode comprising a cathode material; providing an anode comprising an anode material; and providing an aqueous electrolyte comprising a divalent cation, wherein the cathode material and the anode material are not substantially soluble in the electrolyte; the divalent cation intercalates into the cathode and de-intercalates from the anode when the cell discharges; and the divalent cation de-intercalates from the cathode and intercalates into the anode when the cell charges.

[0254] In some implementations, the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof. For example, the divalent cation is Zn^{2+}.

[0255] Some implementations further comprise dissolving $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water to generate the Zn^{2+} divalent cation.

[0256] In other implementations, the anode material, the cathode material, or both comprises a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof. For example, the anode material, the cathode material, or both comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof.

[0257] In some implementations, the cathode material comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0258] In other implementations, the anode material comprises a metal oxide that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell.

[0259] In some implementations, the cathode material, the anode material, or both comprises manganese oxide having a chemical formula of Mn_xO_y, and x is greater than or equal to 1, and y is greater than or equal to 2. In some implementations, the layered material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, and y is greater than or equal to 2, and z is greater than or equal to 1.

[0260] In alternative implementations, the cathode material, the anode material, or both comprises manganese oxide having a chemical formula of $Mn_3O_7{\bullet}3H_2O$, $Mn_7O_{14}{\bullet}3H_2O$, $Mn_4O_9{\bullet}3H_2O$, Mn_2O_4, $Mn_4O_{18}{\bullet}H_2O$, or any combination thereof. And, in some implementations, the anode material, the cathode material, or both comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

[0261] In some implementations, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is greater than the oxidation state of the manganese in the anode material when the cell has an SOC of at least about 90%. For example, the cathode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is about 4, when the cell has an SOC of at least about 90%. In other implementations, the anode material comprises manganese oxide, and the oxidation state of the manganese in the anode material is about 2, when the cell has an SOC of at least about 90%.

[0262] In some implementations, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material is approximately equal to the oxidation state of the manganese in the anode material when the cell has an SOC of less than about 10%. For example, the cathode material comprises manganese oxide, the anode material comprises manganese oxide, and the oxidation state of the manganese in the cathode material and the anode material is about 3 when the cell has an SOC of less than about 10%.

[0263] In other implementations, the anode material, the cathode material, or both further comprises a carbon powder. In some instances, the anode material, the cathode material, or both further comprises about 15 wt% or less of the carbon powder by weight of the electrode material. In other instances, the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

[0264] In some implementations, the anode material, the cathode material, or both further comprises an additive that stabilizes the crystal lattice structure of manganese oxide. In some instances, the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof. In other instances, the additive is present at a concentration of about 20 wt% or less by weight of the electrode material.

[0265] In some implementations, the anode material, the cathode material, or both is doped with Al, B, or any combination thereof.

[0266] In other implementations, the anode material, the cathode material, or both further comprises a binder. In some instances, the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof. In other instances, the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the electrode material.

[0267] And, some implementations further comprise providing a cathode current collector, an anode current collector, or both. In some instances, the cathode current collector, the anode current collector, or both comprises one or more electrically conductive metals or an electrically conductive polymer material. In some instances, the cathode current collector, the anode current collector, or both comprises a woven material, a non-woven material, or a combination thereof. And, in other instances, the cathode current collector, the anode current collector, or both comprises a sheet of non-woven material that optionally comprises perforations.

[0268] IV. EXAMPLES

[0269] Referring to Figures 1-5, test cells were prepared and cycled as described below. The manganese oxide test cells were effectively charged and discharged over 1000 times with high Coulombic efficiency and with little loss in ampere-hour cell capacity.

[0270] The ~100 cm^2 test cells included an anode formed from zinc metal. The ~3" x 6" zinc anodes were generally prepared by electrochemically plating zinc metal on thin Ti sheets using aqueous solutions of $ZnCl_2$ and NH_4Cl.

[0271] The cathodes of the test cell were formed from manganese oxide and carbon black (Black Pearls 2000, commercially available from the Cabot Corp.). The cathode of test cell 1 was formed with MnO_2 and carbon black; the cathode of test cell 2 was formed with Mn_5O_8 and carbon black; the cathode of test cell 3 was formed with Mn_2O_3 and carbon black; the cathode of test cell 4 was formed with carbon black; and the cathode of test cell 5 was formed with Mn_3O_4 and carbon black. Cathodes were typically fabricated by blending 30% manganese oxide (e.g., MnO, Mn_2O_3, Mn_3O_4, or Mn_5O_8), 50% Black Pearls 2000 carbon black (a high surface area carbon black), and 20% PTFE (as a binder) and pressing this mixture onto a titanium metal screen current collector. Test cell 4 included 80% Black Pearls 2000 and 20% PTFE. The manganese oxide was prepared using standard procedures. For example, Mn_5O_8, was prepared by mixing an aqueous solution of manganese nitrate (16.7g in 150ml of H_2O) and an aqueous solution of NaOH (4.8g NaOH in 50 ml of H_2O) and adding this to an aqueous solution of cetyl-trimethylammonium bromide (67g in 150 ml of H_2O). The resulting mixture was heated to 75 °C and stirred for 1 hr. The obtained gel was transferred to an oven and heated for 12 h at 75 °C. The solid reside was filtered, washed with di water, and calcined at 500 °C for 6 hours.

[0272] The electrolyte used in the test cells was generally formulated as an aqueous solution of 20% NH_4Cl, 10% $ZnCl_2$, and 5% LiCl.

[0273] Figure 1 shows room temperature, galvanostatic voltage-time profiles for the 926th, 927th, and 928th cycles of a 100 cm^2 Zn(s) /Mn_5O_8(s) test cell, i.e., test cell 2. The constant current load (shown as square waves with their axis on the left side of this figure) was 0.1A during both cell discharge and cell charge. Cell voltage profiles (with their axis shown on the right side of this figure) ranged from 1.85V down to a cutoff of 0.9V during the 0.6 hour discharge and charge. Since a cell discharge rate of nC corresponds to a full cell discharge in 1/n hours, this cell discharge/charge rate corresponds to 1.66C. At the illustrated 926th cycle, this cell delivered 104mAh/g Mn_5O_8 at a current density of 208mA/g Mn_5O_8. As shown below in Figure 2, cell capacities for this cell, i.e., test cell 2, remained substantially unchanged for ~1200 cycles.

[0274] Figure 2 above shows Coulombic efficiencies (upper curve) and energy efficiencies (lower curve) for test cell 2 as a function of cycle number for the first 1200 discharge charge cycles. Coulombic efficiencies approached 100% while energy efficiencies, which initially were ~80%, slowly rose to >90%. Electrochemical activity of this cell demonstrates the adequate charge discharge cyclic performance of this zinc aqueous reversible system.

OTHER EMBODIMENTS

[0275] All publications and patents referred to in this disclosure are incorporated herein by reference to the same extent as if each individual publication or patent application were specifically and individually indicated to be incorporated by reference. Should the meaning of the terms in any of the patents or publications incorporated by reference conflict with the meaning of the terms used in this disclosure, the meaning of the terms in this disclosure are intended to be controlling. Furthermore, the foregoing discussion discloses and describes merely example embodiments of the present invention. One skilled in the art will readily recognize from such discussion and from the accompanying drawings and claims, that various changes, modifications and variations can be made therein without departing from the spirit and scope of the invention as defined in the following claims.

WHAT IS CLAIMED IS:

1. An electrochemical cell comprising:

an aqueous electrolyte comprising a divalent cation;

a cathode comprising a layered material; and

an anode comprising a metal,

wherein the divalent cation intercalates into the layered material when the cell discharges; and the divalent cation de-intercalates from the cathode material and deposits onto the anode material as a neutral metal when the cell charges.

2. The electrochemical cell of claim 1, wherein the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof.

3. The electrochemical cell of either of claims 1 or 2, wherein the divalent cation is Zn^{2+}.

4. The electrochemical cell of claim 3, wherein the aqueous electrolyte further comprises SO_4^{2-}, CHO^-, NO_3^-, $CO_2CH_3^-$, Cl^-, Br^-, ClO_4^-, or any combination thereof.

5. The electrochemical cell of any one of claims 1-4, wherein the electrolyte has a pH that is approximately neutral.

6. The electrochemical cell of any one of claims 1-5, wherein the electrolyte has a pH of from about 6 to about 8.

7. The electrochemical cell of any one of claims 1-4, wherein the electrolyte has a pH of from about 3 to about 6.

8. The electrochemical cell of any one of claims 1-7, wherein the layered material comprises a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof.

9. The electrochemical cell of claim 8, wherein the layered material comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof.

10. The electrochemical cell of any one of claims 1-9, wherein the layered material comprises manganese oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell.

11. The electrochemical cell of claim 10, wherein the cathode material comprises manganese oxide having a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2.

12. The electrochemical cell of claim 9, wherein the cathode material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1.

13. The electrochemical cell of claim 9, wherein the layered material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7{\bullet}3H_2O$, $Mn_7O_{14}{\bullet}3H_2O$, $Mn_4O_9{\bullet}3H_2O$, Mn_2O_4, $Mn_4O_{18}{\bullet}H_2O$, or any combination thereof.

14. The electrochemical cell of claim 9, wherein the layered material comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

15. The electrochemical cell of claim 13, wherein the layered material comprises Mn_5O_8 that comprises a power having a mean particle diameter of about 50 μm or less.

16. The electrochemical cell of any one of claims 1-15, wherein the cathode further comprises a carbon powder.

17. The electrochemical cell of claim 16, wherein the cathode further comprises about 15 wt% or less of the carbon powder by weight of the cathode.

18. The electrochemical cell of either of claims 16 or 17, wherein the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

19. The electrochemical cell of any one of claims 9-18, wherein the cathode further comprises an additive that stabilizes the crystal lattice structure of manganese oxide.

20. The electrochemical cell of claim 19, wherein the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof.

21. The electrochemical cell of either of claims 19 or 20, wherein the additive is present at a concentration of about 20 wt% or less by weight of the cathode.

22. The electrochemical cell of any one of claims 1-21, wherein the cathode is doped with Al, B, or any combination thereof.

23. The electrochemical cell of any one of claims 1-22, wherein the anode comprises a metal, and a portion of the metal transforms into a divalent cation when the cell is discharged.

24. The electrochemical cell of claim 23, wherein the metal comprises zinc, magnesium, or a combination thereof.

25. The electrochemical cell of any one of claims 1-24, wherein the cathode, the anode, or both further comprises a binder.

26. The electrochemical cell of claim 25, wherein the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof.

27. The electrochemical cell of either of claims 25 or 26, wherein the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the cathode or anode.

28. The electrochemical cell of any one of claims 1-27, wherein the anode, the cathode, or both further comprises a current collector.

29. The electrochemical cell of claim 28, wherein the current collector comprises one or more electrically conductive metals or an electrically conductive polymer material.

30. The electrochemical cell of either of claims 28 or 29, wherein the current collector comprises a woven material, a non-woven material, or a combination thereof.

31. The electrochemical cell of claim 30, wherein the current collector comprises a sheet of non-woven material that optionally comprises one or more perforations.

32. An electrochemical cell comprising:

an aqueous electrolyte comprising a divalent cation that comprises Zn^{2+}, Mg^{2+}, or a combination thereof;

a cathode comprising a metal oxide; and

an anode comprising zinc metal, magnesium metal, or a combination thereof,

wherein the aqueous electrolyte has a nearly neutral pH, the divalent cation intercalates into the cathode when the cell discharges; and the divalent cation deposits onto the anode as a neutral metal when the cell charges.

33. The electrochemical cell of claim 32, wherein the divalent cation is Zn^{2+}.

34. The electrochemical cell of claim 33, wherein the aqueous electrolyte further comprises SO_4^{2-}, CHO^-, NO_3^-, $CO_2CH_3^-$, Cl^-, Br^-, ClO_4^-, or any combination thereof.

35. The electrochemical cell of claim 34, wherein the cathode comprises manganese oxide, and the manganese oxide is not substantially soluble in the aqueous electrolyte.

36. The electrochemical cell of claim 35, wherein the manganese oxide has a chemical formula of Mn_xO_y, where x is greater than or equal to 1, and y is greater than or equal to 2.

37. The electrochemical cell of claim 34, wherein the cathode material comprises manganese vanadium oxide having a chemical formula of $Mn_xV_zO_y$, where x is greater than or equal to 1, y is greater than or equal to 2, and z is greater than or equal to 1.

38. The electrochemical cell of claim 34, wherein the cathode material comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \cdot 3H_2O$, $Mn_7O_{14} \cdot 3H_2O$, $Mn_4O_9 \cdot 3H_2O$, Mn_2O_4, $Mn_4O_{18} \cdot H_2O$, or any combination thereof.

39. The electrochemical cell of claim 34, wherein the layered material comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

40. The electrochemical cell of claim 38, wherein the manganese oxide has a chemical formula of Mn_5O_8, and the manganese oxide comprises a power having a mean particle diameter of about 50 μm or less.

41. The electrochemical cell of any one of claims 32-40, wherein the cathode further comprises a carbon powder.

42. The electrochemical cell of claim 41, wherein the cathode further comprises about 15 wt% or less of the carbon powder by weight of the cathode.

43. The electrochemical cell of claim 42, wherein the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

44. The electrochemical cell of any one of claims 35-43, wherein the cathode further comprises an additive that stabilizes the crystal lattice structure of manganese oxide.

45. The electrochemical cell of claim 44, wherein the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof.

46. The electrochemical cell of claim 45, wherein the additive is present at a concentration of about 20 wt% or less by weight of the cathode.

47. The electrochemical cell of any one of claims 32-46, wherein the anode comprises zinc metal.

48. The electrochemical cell of any one of claims 32-47, wherein the anode comprises zinc metal and the divalent cation is Zn^{2+}.

49. The electrochemical cell of any one of claims 32-48, wherein the anode material, the cathode material, or both further comprises a binder.

50. The electrochemical cell of claim 49, wherein the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof.

51. The electrochemical cell of either of claims 49 or 50, wherein the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the cathode or anode.

52. The electrochemical cell of any one of claims 32-51, wherein the anode, the cathode, or both further comprises a current collector.

53. The electrochemical cell of claim 52, wherein the current collector comprises one or more electrically conductive metals or an electrically conductive polymer material.

54. The electrochemical cell of either of claims 52 or 53, wherein the current collector comprises a woven material, a non-woven material, or a combination thereof.

55. The electrochemical cell of claim 54, wherein the current collector comprises a sheet of non-woven material that optionally comprises perforations.

56. The electrochemical cell of any one of claims 32-55, wherein the cathode is doped with Al, B, or any combination thereof.

57. A method of manufacturing an electrochemical cell comprising:

providing a cathode comprising a layered material;
providing an anode comprising a metal; and
providing an aqueous electrolyte comprising a divalent cation,

wherein the divalent cation intercalates into the layered material when the cell discharges; and the divalent cation de-intercalates from the cathode material and deposits onto the anode material as a neutral metal when the cell charges.

58. The method of claim 57, wherein the divalent cation is selected from Zn^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, or any combination thereof.

59. The method of claim 58, wherein the divalent cation is Zn^{2+}.

60. The method of claim 59, further comprising dissolving $ZnSO_4$, $Zn(CHO_2)_2$, $Zn(NO_3)_2$, $Zn(CO_2CH_3)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(ClO_4)_2$, or any combination thereof in water to generate the Zn^{2+} divalent cation.

61. The method of any one of claims 57-60, wherein the cathode comprises a layered material comprising a metal oxide, a mixed metal oxide, a metal sulfide, a zinc metal phosphate, a zinc metal oxide, or any combination thereof.

62. The method of claim 61, wherein the cathode comprises manganese oxide, vanadium oxide, manganese vanadium oxide, TiS_2, WO_2Cl_2, or any combination thereof.

63. The method of either of claims 61 or 62, wherein the cathode comprises a metal oxide that undergoes a reduction in its oxidation state of 1 or more during the discharge of the electrochemical cell.

64. The method of claim 63, wherein the cathode comprises manganese oxide having a chemical formula of Mn_xO_y, and x is greater than or equal to 1, and y is greater than or equal to 2.

65. The method of claim 64, wherein the cathode comprises manganese oxide having a chemical formula of MnO_2, Mn_5O_8, $Mn_3O_7 \cdot 3H_2O$, $Mn_7O_{14} \cdot 3H_2O$, $Mn_4O_9 \cdot 3H_2O$, Mn_2O_4, $Mn_4O_{18} \cdot H_2O$, or any combination thereof.

66. The method of claim 64, wherein the cathode comprises manganese oxide having a predominant crystal structure of α–MnO_2, β–MnO_2, γ–MnO_2, δ–MnO_2, layered, or any combination thereof.

67. The method of claim 65, wherein the cathode comprises Mn_5O_8, and the Mn_5O_8 comprises a powder having a mean particle diameter of about 50 μm or less.

68. The method of any one of claims 57-67, wherein the cathode further comprises carbon powder.

69. The method of claim 68, wherein the cathode further comprises about 15 wt% or less of the carbon powder by weight of the cathode.

70. The method of claim 69, wherein the carbon powder comprises acetylene black, furnace black, channel black, graphite, activated carbon, graphene, or any combination thereof.

71. The method of any one of claims 62-70, wherein the cathode further comprises an additive that stabilizes the crystal lattice structure of manganese oxide.

72. The method of claim 71, wherein the additive comprises TiS_2, TiB_2, Bi_2O_3, or any combination thereof.

73. The method of claim 72, wherein the additive is present at a concentration of about 20 wt% or less by weight of the cathode.

74. The method of any one of claims 57-73, wherein the cathode is doped with Al, B, or any combination thereof.

75. The method of any one of claims 57-74, wherein the anode material comprises a metal that undergoes an increase in its oxidation state of 1 or more during the discharge of the electrochemical cell.

76. The method of any one of claims 57-75, wherein the anode comprises zinc metal, magnesium metal, or a combination thereof.

77. The method of any one of claims 57-76, wherein the divalent cation is Zn^{2+}, and the anode comprises zinc metal.

78. The method of any one of claims 57-77, wherein the anode material, the cathode material, or both further comprises a binder.

79. The method of claim 78, wherein the binder comprises polyacrylonitrile, polyvinyl alcohol, polyvinyl chloride, polyethylene oxide, polytetrafluoroethylene, polyvinylidene difluoride, polymethylmethacrylate, or any combination thereof.

80. The method of either of claims 78 or 79, wherein the binder is present at a concentration of from about 3 wt% to about 15 wt% by weight of the cathode or anode.

81. The method of any one of claims 57-80, further comprising providing a cathode current collector, an anode current collector, or both.

82. The method of claim 81, wherein the cathode current collector, the anode current collector, or both comprises one or more electrically conductive metals or an electrically conductive polymer material.

83. The method of either of claims 81 or 82, wherein the cathode current collector, the anode current collector, or both comprises a woven material, a non-woven material, or a combination thereof.

84. The method of claim 83, wherein the cathode current collector, the anode current collector, or both comprises a sheet of non-woven material that optionally comprises perforations.

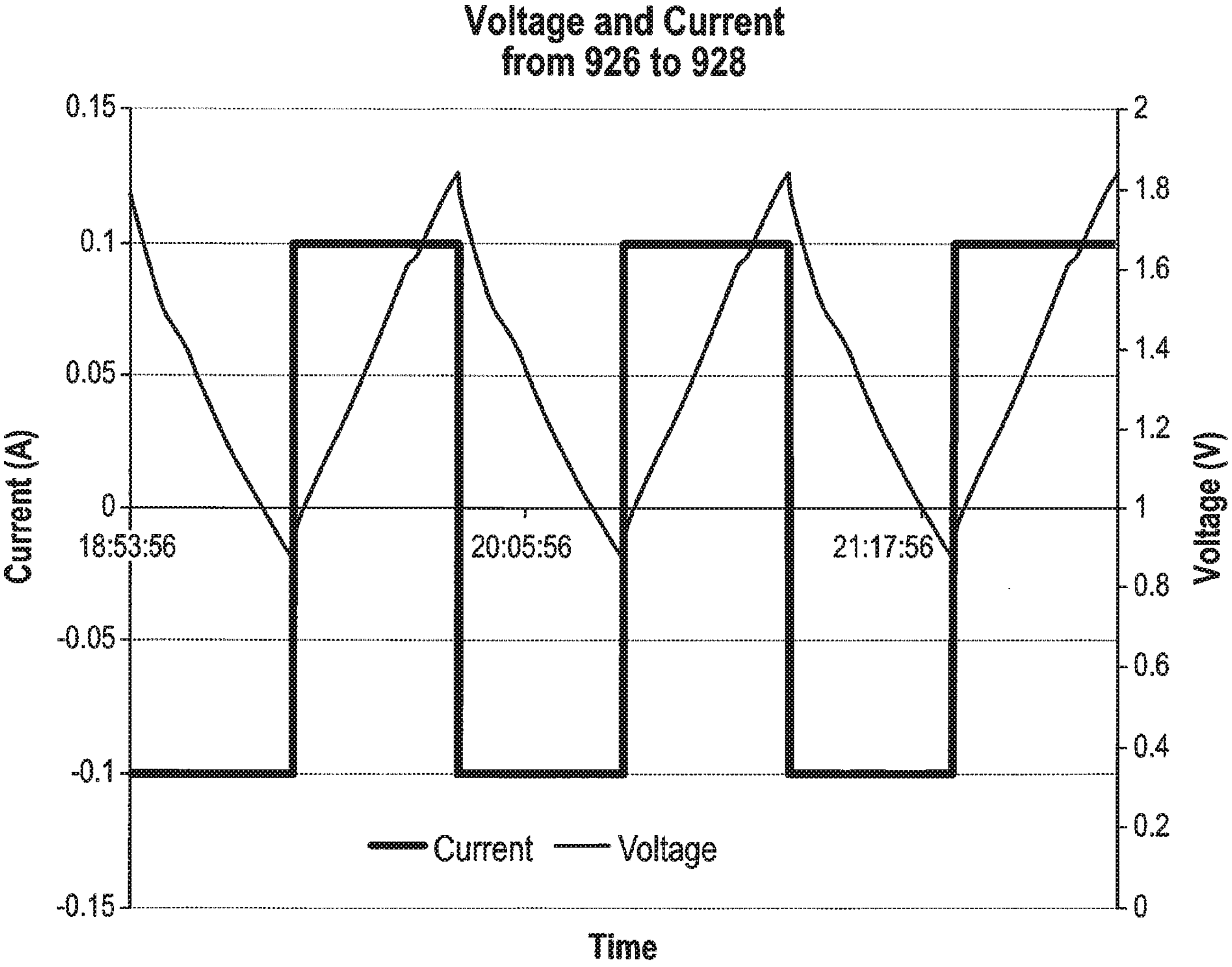
Voltage and Current
from 926 to 928
Current (A)
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
Voltage (V)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
18:53:56
20:05:56
21:17:56
Current
Voltage
Time

FIG. 1

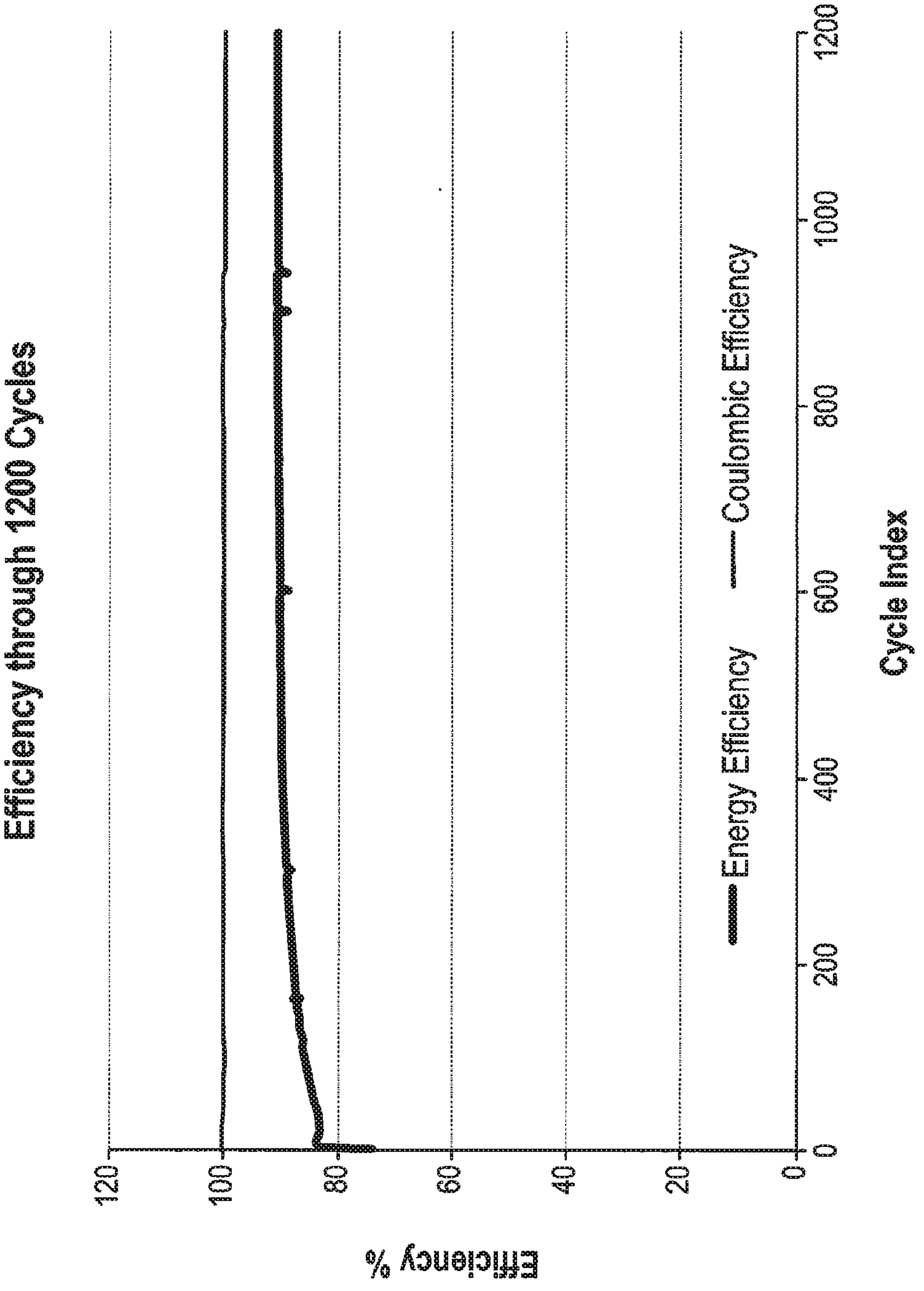
Efficiency through 1200 Cycles
Efficiency %
120
100
80
60
40
20
0
0
200
400
600
800
1000
1200
Cycle Index
Energy Efficiency
Coulombic Efficiency

FIG. 2

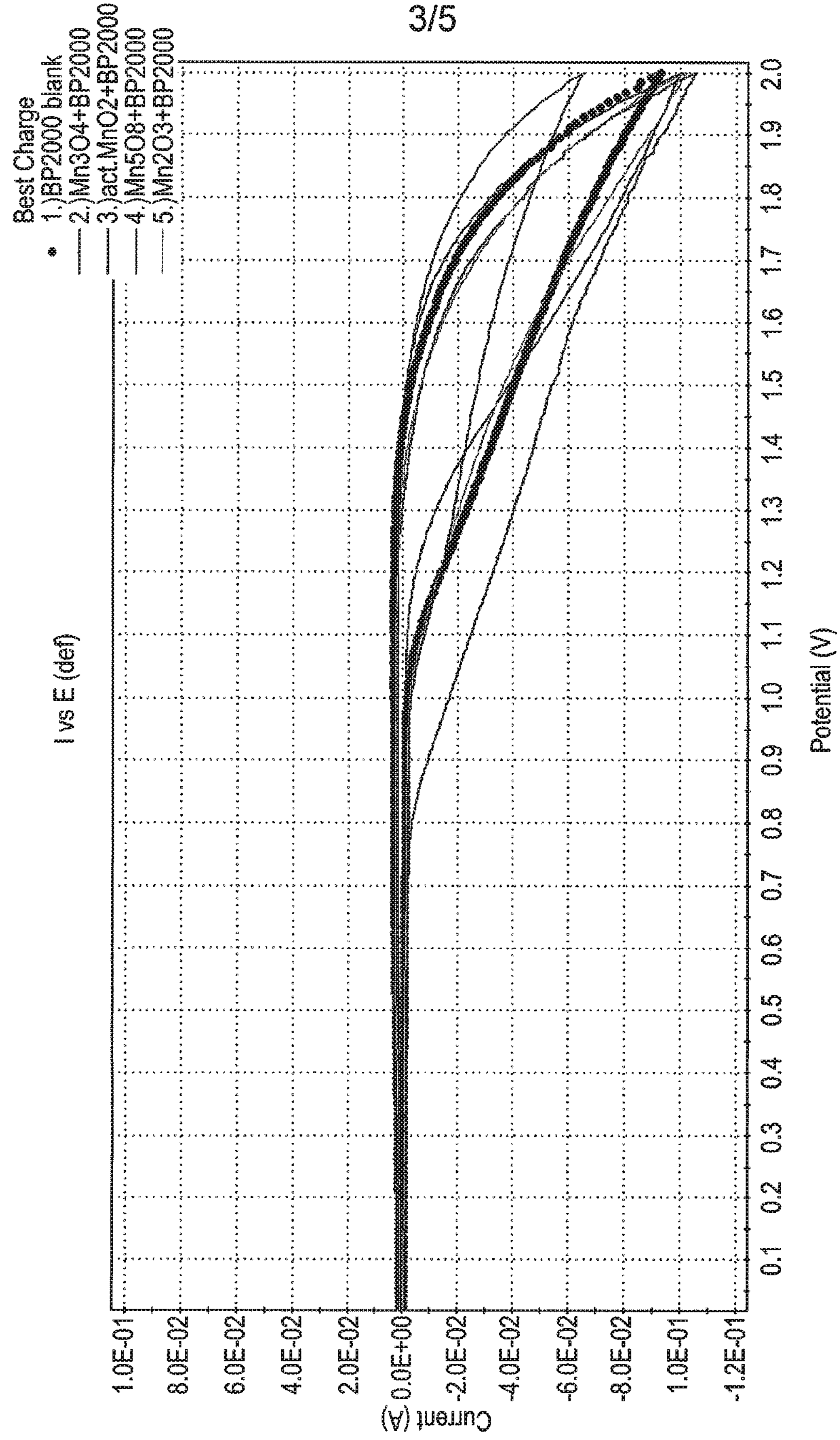
I vs E (def)
Best Charge
● 1.)BP2000 blank
2.)Mn3O4+BP2000
3.)act.MnO2+BP2000
4.)Mn5O8+BP2000
5.)Mn2O3+BP2000
Current (A)
1.0E-01
8.0E-02
6.0E-02
4.0E-02
2.0E-02
0.0E+00
-2.0E-02
-4.0E-02
-6.0E-02
-8.0E-02
-1.0E-01
-1.2E-01
Potential (V)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0

FIG. 3

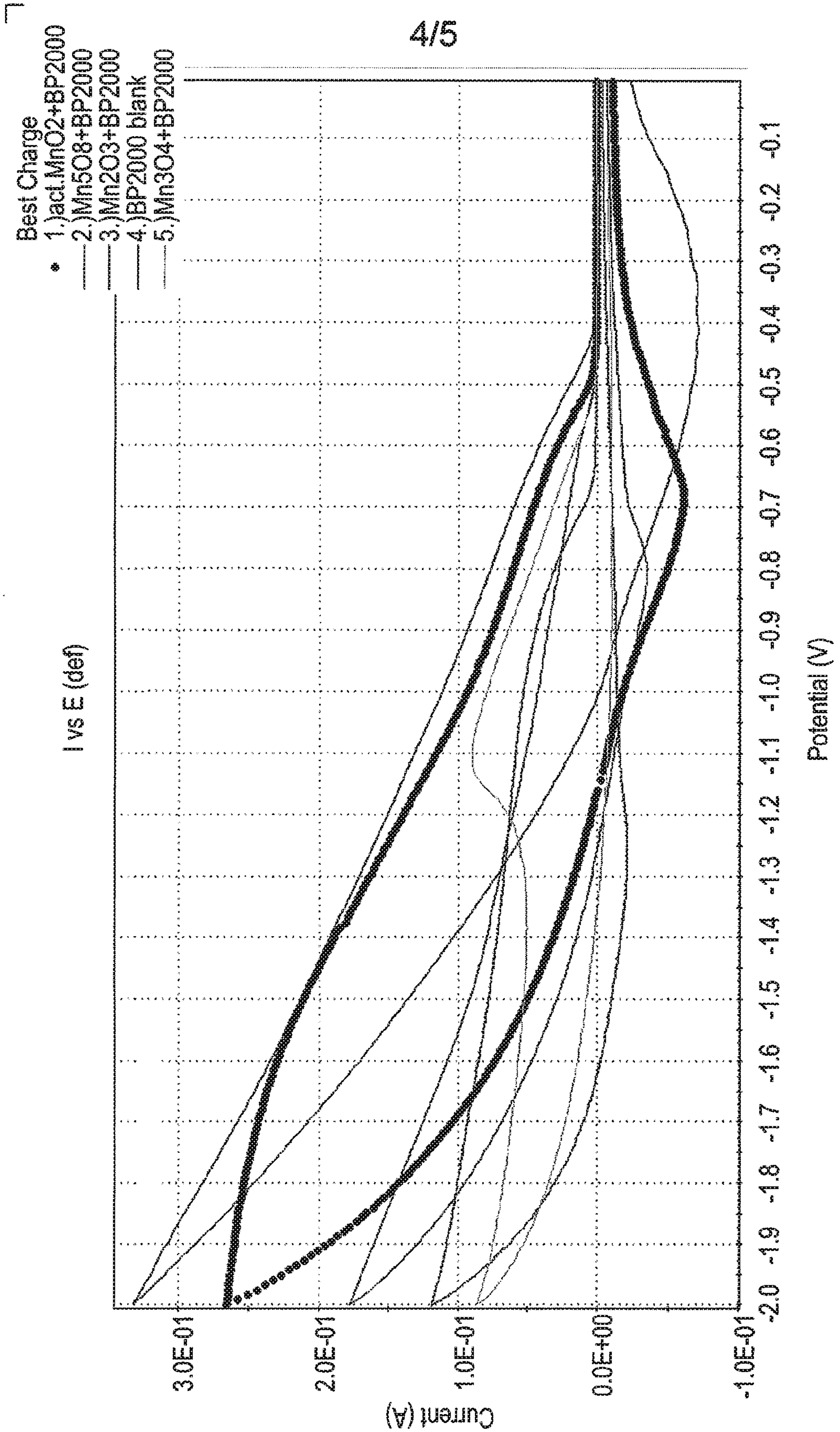
I vs E (def)
Best Charge
● 1.)act.MnO2+BP2000
2.)Mn5O8+BP2000
3.)Mn2O3+BP2000
4.)BP2000 blank
5.)Mn3O4+BP2000
Current (A)
3.0E-01
2.0E-01
1.0E-01
0.0E+00
-1.0E-01
Potential (V)
-2.0
-1.9
-1.8
-1.7
-1.6
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1

FIG. 4

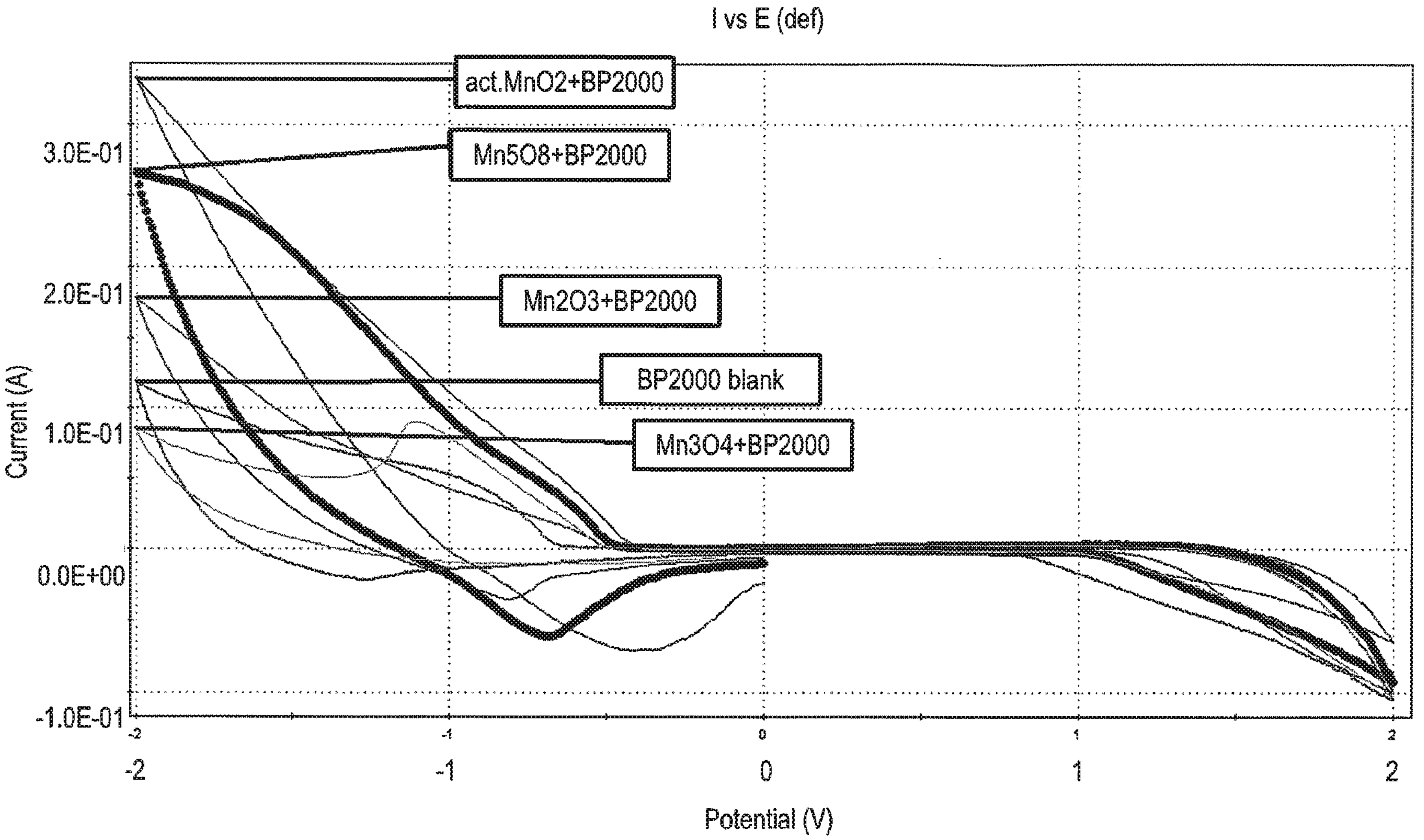
I vs E (def)
act.MnO2+BP2000
Mn5O8+BP2000
Mn2O3+BP2000
BP2000 blank
Mn3O4+BP2000
Current (A)
3.0E-01
2.0E-01
1.0E-01
0.0E+00
-1.0E-01
-2
-1
0
1
2
Potential (V)

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/022852

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M10/054 H01M4/24 H01M4/36

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/118586 A1 (UNIV TSINGHUA GRADUATE SCHOOL [CN]; KANG FEIYU [CN]; XU CHENGJUN [CN];) 21 October 2010 (2010-10-21)	1-11,13, 14,16, 18, 23-30, 32-36, 38-43, 47-54, 57-61, 63-70, 75-84
Y	the whole document	12,15, 17, 19-22, 31,37, 44-46, 55,56, 62,71-74
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 16 May 2013	Date of mailing of the international search report 29/05/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Wiedemann, Eric

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& US 2012/034515 A1 (KANG FEIYU [CN] ET AL) 9 February 2012 (2012-02-09) the whole document -----	
X	US 3 849 868 A (JOST E) 26 November 1974 (1974-11-26) column 1, line 61 - column 2, line 60; claim 1 -----	1,32,57
Y	US 2008/182176 A1 (AURBACH DORON [IL] ET AL) 31 July 2008 (2008-07-31) paragraph [0024] - paragraph [0076]; claims 1-83 -----	1,8,12, 15,17, 19-22, 31,32, 37, 44-46, 55-57, 62,71-74
Y	US 2007/196260 A1 (KIKKAWA SHINICHI [JP] ET AL) 23 August 2007 (2007-08-23) paragraph [0012] - paragraph [0018] -----	1,8,32, 57

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/022852

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010118586 A1	21-10-2010	CN 101540417 A	23-09-2009
		JP 2012524363 A	11-10-2012
		US 2012034515 A1	09-02-2012
		WO 2010118586 A1	21-10-2010
US 3849868 A	26-11-1974	NONE	
US 2008182176 A1	31-07-2008	NONE	
US 2007196260 A1	23-08-2007	US 2007196260 A1	23-08-2007
		WO 2006006531 A1	19-01-2006

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 672-001-P	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below
International application No. **PCT/CA2016/050613**	International filing date *(day/month/year)* 31 May 2016 (31-05-2016)	(Earliest)Priority date *(day/month/year)* 08 June 2015 (08-06-2015)
Applicant ADAMS, BRIAN D. ET AL		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 6 sheets.

☑ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   - a. With regard to the **language**, the international search was carried out on the basis of:
     - ☑ the international application in the language in which it was filed.
     - ☐ a translation of the international application into which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).
   - b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   - c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.
2. ☐ **Certain claims were found unsearchable** (see Box No. II).
3. ☑ **Unity of invention is lacking** (see Box No. III).
4. With regard to the **title**,
   - ☑ the text is approved as submitted by the applicant.
   - ☐ the text has been established by this Authority to read as follows:
5. With regard to the **abstract**,
   - ☑ the text is approved as submitted by the applicant.
   - ☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. With regard to the **drawings**,
   - a. the figure of the **drawings** to be published with the abstract is Figure No. 1A
     - ☑ as suggested by the applicant.
     - ☐ as selected by this Authority, because the applicant failed to suggest a figure.
     - ☐ as selected by this Authority, because this figure better characterizes the invention.
   - b. ☐ none of the figures is to be published with the abstract.

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Group A: Claims 1-25
Group B: Claims 26-48
Group C: Claims 49-73
Continued on extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

1-25

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2016/050613

A. CLASSIFICATION OF SUBJECT MATTER
IPC: *H01M 10/36* (2010.01) , *H01M 4/42* (2006.01) , *H01M 4/485* (2010.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
PC (2010.01): H01M 10/36, H01M 4/485; IPC (2006.01): H01M 4/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Databases: QUESTEL, Canadian Patent Database, CIPO Library Discovery Tool
Keywords: battery, cell, electrochemical, zinc, vanadium, vanadium oxide, vanadium pentoxide, znxv2o5 or znv2o5 or mxv2o5, cathode, positive, aqueous, water, alkaline

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/112660 A1 (ADAMSON et al.) 1 August 2013 (01-08-2013) *whole document*	1-25
A	US 5,336,572 (KOKSBANG) 9 August 1994 (09-08-1994) *whole document*	1-25
A	US 2013/0157138 A1 (METTAN et al.) 20 June 2013 (20-06-2013) *whole document*	1-25
A	CN 102110858 (WANG et al.) 29 June 2011 (29-06-2011), abstract and machine English translation of description.	1-25
A	LE et al., "Intercalation of Polyvalent Cations into V_2O_5 Aerogels", *Chemistry of Materials*, Volume 10 (3) (1998), Pages 682-684.	1-25

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 12 September 2016 (12-09-2016)	Date of mailing of the international search report 21 September 2016 (21-09-2016)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Philip Gbor (819) 639-8475

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JIAHONG et al., "AC Impedance Study of the Aqueous Zn/V_2O_5 Secondary Battery", *ACTA PHYSICOCHIMICA SINICA*, Volume 16, No. 5 (2000), Pages 454-458 (abstract; and Figure 1).	1-25
A	GIORGETTI et al., "Identification of an unconventional zinc coordination site in anhydrous $Zn_xV_2O_5$ aerogels from x-ray absorption", *Chemistry of Materials*, Volume 11(8) (1999), Pages 2257-2264.	1-25
A	ZHANG et al., "Hydrothermal synthesis and characterization of a series of novel zinc vanadium oxides as cathode materials", *Materials Research Society Symposium - Proceedings, Materials for Electrochemical Energy Storage and Conversion II - Batteries, Capacitors and Fuel Cells*, 496 (1998), Pages 367-372) .	1-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/CA2016/050613

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2013112660A1	01 August 2013 (01-08-2013)	WO2013112660A1	01 August 2013 (01-08-2013)
		US2015244031A1	27 August 2015 (27-08-2015)
US5336572A	09 August 1994 (09-08-1994)	US5336572A	09 August 1994 (09-08-1994)
		AU7104594A	03 January 1995 (03-01-1995)
		WO9429913A1	22 December 1994 (22-12-1994)
US2013157138A1	20 June 2013 (20-06-2013)	US2013157138A1	20 June 2013 (20-06-2013)
		US9023527B2	05 May 2015 (05-05-2015)
		EP2607319A1	26 June 2013 (26-06-2013)
		EP2607319B1	25 February 2015 (25-02-2015)
CN102110858A	29 June 2011 (29-06-2011)	CN102110858A	29 June 2011 (29-06-2011)
		CN102110858B	17 April 2013 (17-04-2013)

Continuation of Box No. III

The International Searching Authority found multiple (groups of) inventions in this international application, as follows:

Group A:
Claims 1-25 are directed to a zinc ion battery, comprising: a positive electrode compartment having enclosed therein the electrode material $M_xV_2O_5.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

Group B:
Claims 26-48 are directed to a zinc ion battery, comprising: a positive electrode compartment having enclosed therein the positive electrode material $M_xV_3O_7.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

Group C:
Claims 49-73 are directed to a zinc ion battery; comprising: a positive electrode compartment having enclosed therein the positive electrode material $M_xMoO_y.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
BILL & SCHUMACHER
264 Avenue Road
TORONTO, Ontario
Canada, M4V 2G7

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	21 September 2016 (21-09-2016)
Applicant's or agent's file reference 672-001-P	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/CA2016/050613	31 May 2016 (31-05-2016)	08 June 2015 (08-06-2015)

International Patent Classification (IPC) or both national classification and IPC
IPC: ***H01M 10/36*** (2010.01) , ***H01M 4/42*** (2006.01) , ***H01M 4/485*** (2010.01)

Applicant
ADAMS, BRIAN D. ET AL

1. This opinion contains indications relating to the following items:

- ☑ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☑ Box No. IV Lack of unity of invention
- ☑ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/CA	Date of completion of this opinion	Authorized officer
Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	14 September 2016 (14-09-2016)	Philip Ghor (819) 639-8475

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/CA2016/050613

Box No. I	**Basis of this opinion**

1. With regard to the **language**, this opinion has been established on the basis of:

☑ the international application in the language in which it was filed.

☐ a translation of the international application into which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

a. ☐ forming part of the international application as filed:

☐ in the form of an Annex C/ST.25 text file.

☐ on paper or in the form of an image file.

b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/CA2016/050613

Box No. IV **Lack of unity of invention**

1. ☑ In response to the invitation (Form PCT/ISA/206) to pay additional fees the applicant has, within the applicable time limit:

   ☐ paid additional fees

   ☐ paid additional fees under protest and, where applicable, the protest fee

   ☐ paid additional fees under protest but the applicable protest fee was not paid

   ☑ not paid additional fees

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

   ☐ complied with.

   ☑ not complied with for the following reasons:

The International Searching Authority found multiple (groups of) inventions in this international application, as follows:

Group A:
Claims 1-25 are directed to a zinc ion battery, comprising: a positive electrode compartment having enclosed therein the electrode material $M_xV_2O_5.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

Group B:
Claims 26-48 are directed to a zinc ion battery, comprising: a positive electrode compartment having enclosed therein the positive electrode material $M_xV_3O_7.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

Group C:
Claims 49-73 are directed to a zinc ion battery; comprising: a positive electrode compartment having enclosed therein the positive electrode material $M_xMoO_y.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, a negative electrode compartment having enclosed therein a negative electrode for storing zinc, a separator; and an electrolyte.

4. Consequently, this opinion has been established in respect of the following parts of the international application:

   ☐ all parts.

   ☑ the parts relating to claim Nos. 1-25

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	2-3, 10-11	YES
	Claims	1, 4-9, 12-25	NO
Inventive step (IS)	Claims	NONE	YES
	Claims	1-25	NO
Industrial applicability (IA)	Claims	1-25	YES
	Claims	NONE	NO

2. Citations and explanations:

1. Reference Cited

D1: WO 2013/112660 A1 (ADAMSON at al.) 1 August 2013 (01-08-2013)

D1 discloses a zinc ion battery comprising a cathode (positive electrode), anode (negative electrode), a separator and an electrolyte. The cathode comprises a layered material comprising zinc metal oxide or a mixed metal oxide, for example, MnV_yO_z (where z greater than or equal to 1 and y is greater than or equal to 2). Some of the oxides have water of hydration. The cathode further comprises carbon and binder. The cathode material is present in powdered form. The anode comprises a material for storing zinc, for example, zinc or magnesium or a combination and the zinc can be in the form of a powder. The cathode and anode materials are coated on a current collector comprising conductive metals. The electrolyte comprises a salt of zinc in water solution (paragraphs 0007-0196).

The inventive concept appears to be a zinc-ion battery, comprising a positive electrode compartment having enclosed therein an intercalation layered positive electrode material $M_xV_2O_5.nH_2O$, where x is from 0.05 to 1 and n is from 0 to 2 a negative electrode compartment having enclosed therein a negative electode for storing zinc; a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and an electrolyte comprising water and having a salt of zinc dissolved therein.

2. Novelty – PCT Article 33(2).

Claims 1, 4-9 and 12-25 lack novelty in view of D1 pursuant to PCT Article 33(2).
D1 discloses a zinc-ion battery comprising:
a positive electrode compartment having enclosed therein an intercalation layered positive electrode material, for example, MnV_2O_5 (paragraphs 0012-0014), which is equivalent to $M_xV_2O_5.nH_2O$ where M is Mn which is a d-block metal and has valence which includes +2 and +4, x is 1 and n is 0 (since D1 teaches a layered compound, the V_2O_5 will inherently be layered and Mn will be present between the layers);
a negative electrode compartment having enclosed therein a negative electrode for storing zinc (D1 teaches negative electrode materials that store zinc, for example, zinc metal or magnesium metal (paragraphs 0019 and 0022));
a separator (the battery inherently contains a separator for separating the positive electrode and negative electrode); and
an electrolyte comprising water and a salt of zinc, for example, zinc sulfate (0063-0065).
D1 further teaches that the positive electrode further comprises carbon and binder which includes polytetrafluoroethylene (paragraphs 0017-0020), thus the positive electrode material will be embedded in an electrically conducting matrix. The positive electrode material is present in powdered form and disclosed sizes of some of the powders include less than 100 nm (paragraph 0170). The negative electrode can also comprise a material containing a combination of zinc and magnesium. The zinc can be in the form of a powder (paragraphs 0019, 0022, 0135 and 0196). The positive and negative electrode materials are coated on a current collector comprising conductive metals, for example, copper (paragraph 0179). Disclosed concentration of the metal salt in the electrolyte includes 1 mole to 2 moles per kilogram of solution. Disclosed pH of the electrolyte solution includes 3-8 (paragraphs 0181-0186).

Claims 2-3 and 10-11 are novel and thus comply with PCT Article 33(2).

Continued in Supplemental Box.

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/CA2016/050613

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of: Box. No. V

3. Inventive Step – PCT Article 33(3)

As claims 1, 4-9 and 12-25 are not novel in view of D1, they cannot be considered to involve an inventive step and thus do not comply with PCT Article 33(3).

Claims 2-3 and 10-11 do not comply with PCT Article 33(3) having regard to D1 in view of common knowledge in the art. The subject matter of claims 1, 4-9 and 12-25 is disclosed in D1. The additional features specified in claims 2-3 (that is, the presence of water of hydration in the oxide) cannot be considered to involve an inventive step since D1 further teaches that some oxides have water of hydration present, and also the use of metal oxides with water of hydration present in electrode materials is an option that is within the purview of a person skilled in the art. Furthermore, coating the particles with electrically conducting material as specified in claims 10-11 is also a design option that is within the purview of a person skilled in the art, since coating electrode materials with carbon is commonly practiced in the art, thus, the subject matter of claims 10-11 cannot be considered to involve an inventive step.

4. Industrial Applicability – PCT Article 33(4)

The subject matter of claims 1-25 is considered to be industrially applicable and thus complies with the requirements of PCT Article 33(4).

Electronic Acknowledgement Receipt

EFS ID:	30224968
Application Number:	15513914
International Application Number:	
Confirmation Number:	3998
Title of Invention:	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom
First Named Inventor/Applicant Name:	Brian D. ADAMS
Customer Number:	293
Filer:	Ralph A. Dowell
Filer Authorized By:	
Attorney Docket Number:	19920NP
Receipt Date:	30-AUG-2017
Filing Date:	23-MAR-2017
Time Stamp:	16:30:35
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	19220idstransISR.pdf	45234 6ee673f8425a9a674d059480d5b73310db29c227	no	2

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	19220idsform08a.pdf	1051355 23d1ccecde721d5b92a8595752add386362c7032	no	5
Warnings:					
Information:					
3	Foreign Reference	CN102110858Acombo.pdf	1005470 c2fcb93aa36aa1dff34e7d3b6c81af2819ee91b4	no	9
Warnings:					
Information:					
4	Foreign Reference	WO2013112660A1.pdf	7457836 927dfd9f8cda9ecc725c745a2cbb81dc199e3f15	no	52
Warnings:					
Information:					
5	Non Patent Literature	ZhangTowards.pdf	2626878 7c600cd31dc75719899e9351a58f31abf5f44862	no	5
Warnings:					
Information:					
6	Non Patent Literature	ZhangHydrothermal.pdf	12360375 2d1f842b26e5324d7f5117990829e8f1855e40f8	no	7
Warnings:					
Information:					
7	Non Patent Literature	Xu.pdf	956978 d6bb8bd70eb993df6dc3df86df70d329449892c5	no	3
Warnings:					
Information:					
8	Non Patent Literature	Pan.pdf	1297362 421a7a13cab01874eed35c9f8eeebf62737db3be	no	7
Warnings:					
Information:					

9	Non Patent Literature	Le.pdf	3929483 15c197bb07fde56ad2e971a1f38db581d7be486b	no	3
Warnings:					
Information:					
10	Non Patent Literature	JiahongCOMBO.pdf	2486251 8fab98b07a6b6707876b00ab533b000980d24874	no	5
Warnings:					
Information:					
11	Non Patent Literature	Giorgetti.pdf	2645955 67b68dc387ef46f07c0c0aaa2c82289af219833b	no	8
Warnings:					
Information:					
12	Non Patent Literature	19220ISR.pdf	2344492 fe98b24b9bb12e04e37bac4fbc7f9d51009f4f48	no	6
Warnings:					
Information:					
13	Non Patent Literature	19220WO.pdf	2148608 b02b9376076cc9ff89c9d82533b346738074fbb3	no	5
Warnings:					
Information:					
		Total Files Size (in bytes):	40356277		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s)	:	Brian D. ADAMS et al.
Applicant	:	University of Waterloo
Appl. No.	:	15/513,914
Filed	:	March 23, 2017
Title	:	ELECTRODE MATERIAL FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM
Confirm. No.	:	3998
Grp./A.U.	:	1726
Examiner	:	N/A
Docket No.	:	19220NP

Honorable Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

Commissioner:

In accordance with 37 C.F.R. §§ 1.97-1.99, the Applicant, through and by counsel, submits the following information which may be of interest to the Examiner in charge of the above-referenced application for patent. Copies of the foreign and non-patent documents are attached.

The references were cited in an International Search Report and Written Opinion from the parent PCT application PCT/CA2016/050613 dated September 21, 2016. The Applicant respectfully asserts that no fees are required for this Information Disclosure Statement, however the Applicant authorizes the Office to charge any fees required *for this submission only* to deposit account no. 04-1577 to Dowell & Dowell, P.C.

In light of the above, the Applicant respectfully requests that the Examiner consider the references listed on the attached form PTO/SB/08a. Should the Examiner have any questions regarding this Information Disclosure Statement or the references cited herein, the Applicant invites the Examiner to contact the undersigned agent of record at the telephone number provided below.

Respectfully submitted,

DOWELL & DOWELL, P. C.

/Ralph A. Dowell/
Ralph A. Dowell
Reg. No.: 26868
Date: August 30, 2017

DOWELL & DOWELL, P.C.
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Alexandria, VA 22303
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Email: dowell@dowellpc.com
Customer Number: 00293

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	**UNIVERSITY OF WATERLOO**
First named Inventor:	**Brian D. ADAMS**
Appln. No.:	**15/513,914**
U.S. Filing Date:	**March 23, 2017**
International Applicant No:	**PCT/CA2016/050613**
International Filing Date:	**May 31, 2016**
Title:	**ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM**
Confirmation No.	**3998**
Grp./A.U.:	**Not Known**
Examiner:	**Not Known**
Docket No.:	**19920NP**

Honorable Commissioner for Patents
Alexandria, VA 22313-1450

Dear Sir:

PRELIMINARY AMENDMENT BEFORE EXAMINATION

Prior to examination, please amend the above-identified National Phase Patent Application as follows:

Amendments to Claims are reflected in the listing of claims which begins on page 2 of this paper.

Remarks/Arguments begin on page 7 of this paper.

Amendments to the Claims

This listing of claims will replace all prior versions, listings, of claims in the application:

Listing of Claims:

1. (Currently amended) A zinc ion battery, comprising:

a positive electrode compartment having enclosed therein an intercalation layered positive electrode material ~~$M_xV_2O_5$.**n**H_2O, wherein x is in a range from 0.05 to 1, **n** is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_2O_5 is~~ comprising a layered crystal structure having water **n**H_2O of hydration and/or [[the]] metal ions M pillared between the layers of the crystal structure, [[and]] where the waters of hydration is coordinated to the metal ions M;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

2. (Currently amended) The zinc ion battery according to claim 1 wherein **n** is ~~greater than 0 and less than 1~~ in a range from 0 to 2.

3. (Currently amended) The zinc ion battery according to ~~claims 1 or~~ claim 2 wherein ~~some of the waters of hydration are hydrogen bonded to the layers~~ the layered crystal structure comprises any one of V_2O_5, V_3O_7 and MoO_y, and the metal ions are any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, and the metal M ion is in a +2 to +4 valence state.

4. (Currently amended) The zinc ion battery according to ~~claims 1, 2 or~~ claim 3 wherein ~~the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery~~ the intercalated layered positive electrode material is $M_xV_2O_5.\mathbf{n}H_2O$ wherein x is in a range from 0.05 to less than 1.

5. (Currently amended) The zinc ion battery according to ~~claims 1, 2, 3 or 4~~ claim 1 wherein the electrolyte has a pH in a range from about 1 to about 8.

6. (Cancelled)

7. (Currently amended) The zinc ion battery according to ~~any one of claims 1 to 6~~ claim 1 wherein the intercalation layered cathode material has a nanostructured morphology which is defined by an average particle size of less than or equal to 1000 nm in at least one particle dimension.

8. (Cancelled)

9. (Cancelled)

10. (Currently amended) The zinc ion battery according to claim [[9]] 7 wherein the particles are coated with electrically conducting material.

11. (Currently amended) The zinc ion battery according to claim 10 wherein the electrically conducting material is any one or combination of carbon ~~powder~~ and conducting polymer.

12 – 14. (Cancelled)

15. (Currently amended) The zinc ion battery according to ~~any one of claims 1 to 14~~ claim 1 wherein the negative electrode comprises zinc metal or zinc alloy.

16. (Original) The zinc ion battery according to claim 15 wherein the negative electrode is a zinc metal electrode.

17. (Original) The zinc ion battery according to claim 15 wherein the negative electrode is a zinc alloy.

18. (Currently amended) The zinc ion battery according to ~~any one of claims 1 to 14~~ claim 1 wherein the negative electrode comprises a current collector, and a surface of the current collector facing into the negative electrode compartment having a layer of zinc or zinc alloy bound thereto.

19. (Currently amended) The zinc ion battery according to claim 18 wherein the layer of zinc comprises any one of powdered zinc metal or a sheet of zinc metal

20. (Cancelled)

21. (Currently amended) The zinc ion battery according to claim 18, ~~19 or 20~~ wherein the current collector is comprised [[on]] of any one or combination of carbon, boron, lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal.

22. (Currently amended) The zinc ion battery according to ~~any one of claims 1 to 14~~ claim 1 wherein the negative electrode comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage.

23. (Currently amended) The zinc ion battery according to ~~any one of claims 1 to 22~~ claim 1 wherein the electrolyte further comprises water dissolved zinc salt present in a range from about 0.01 to about 10 molar.

24 – 25. (Cancelled)

26. (Currently amended) [[A]] The zinc ion battery~~, comprising:~~ ~~a positive electrode compartment having enclosed therein and~~ according to claim 3, wherein the intercalated layered positive electrode material is $M_{\mathbf{x}}V_3O_7.\mathbf{n}H_2O$, wherein **x** is in a range from 0.05 to less than 1~~, **n** is greater than 0 and less than 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_3O_7 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M and/or hydrogen bonded to the layers;~~

~~a negative electrode compartment having enclosed therein a negative electrode for storing zinc;~~

~~a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and~~

~~an electrolyte comprising water and having a salt of zinc dissolved therein~~.

27. (Cancelled)

28. (Currently amended) The zinc ion battery according to claims ~~26 or 27~~ claim 1 wherein the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery.

29 – 48 (Cancelled)

49. (Currently amended) [[A]] The zinc ion battery~~; comprising:~~

~~a positive electrode compartment having enclosed therein an~~ according to claim 3 wherein the intercalated layered positive electrode material is $M_xMoO_y.nH_2O$, wherein x is in a range from 0 to 1, y is in a range from 2 to 3~~, n is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said MoO_y has a layer or tunnel crystal structure, and the metal ions M, if~~

~~present, pillared between the layers, and waters of hydration coordinated to the metal ions M pillared between the layers;~~

~~a negative electrode compartment having enclosed therein a negative electrode for storing zinc;~~

~~a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and~~

~~an electrolyte comprising water and having a salt of zinc dissolved therein~~.

50 - 73. (Cancelled)

74. (New) The zinc ion battery according to claim 3 wherein **n** is greater than 0 and less than 1.

REMARKS

Applicants hereby make amendments to (i) bring the total number of claims to 20 (with one independent claim), and (ii) remove multiple dependencies.

It is respectfully submitted that these amendments are for the purpose of reducing claims fees, without prejudice.

The independent claim 1 has been amended to more succinctly and appropriately recite the scope of protection to which the Applicants are entitled to. Further amendments have been made throughout the claims, in order to reflect the amendments to claim 1.

Applicants respectfully submit that all the amendments made herein are clearly and sufficiently supported by the application as originally filed, and no new matter has been added.

Respectfully Submitted,
Dowell & Dowell, P.C.

By: /Ralph A. Dowell/
Ralph A. Dowell, Registration No. 26868

Date: August 29, 2017

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Fax: 703-739-9889
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Electronic Patent Application Fee Transmittal

Application Number:	15513914
Filing Date:	23-Mar-2017
Title of Invention:	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom
First Named Inventor/Applicant Name:	Brian D. ADAMS
Filer:	Ralph A. Dowell
Attorney Docket Number:	19920NP

Filed as Large Entity

Filing Fees for **U.S. National Stage under 35 USC 371**

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
NATL STAGE SEARCH FEE - REPORT PROVIDED	1642	1	480	480
NATIONAL STAGE EXAM - ALL OTHER CASES	1633	1	720	720
Pages:				
Claims:				
Miscellaneous-Filing:				
OATH/DECL > 30 MOS FROM 371 COMMENCEMENT	1617	1	140	140
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Extension - 2 months with $0 paid	1252	1	600	600
Miscellaneous:				
		Total in USD ($)		**1940**

Electronic Acknowledgement Receipt

EFS ID:	30216553
Application Number:	15513914
International Application Number:	
Confirmation Number:	3998
Title of Invention:	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom
First Named Inventor/Applicant Name:	Brian D. ADAMS
Customer Number:	293
Filer:	Ralph A. Dowell
Filer Authorized By:	
Attorney Docket Number:	19920NP
Receipt Date:	29-AUG-2017
Filing Date:	23-MAR-2017
Time Stamp:	16:57:27
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1940
RAM confirmation Number	083017INTEFSW16585900
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Applicant Response to Pre-Exam Formalities Notice	19920rmp.pdf	112916 6ec679fb2bb67c01da95b5bb3d0c774addf28002	no	4
Warnings:					
Information:					
2	Extension of Time	19920ret0817.pdf	161965 19d1dfc5477f4dd95afbd534782a2fa1bf3597f4	no	2
Warnings:					
Information:					
3	Preliminary Amendment	19920prelamend0817.pdf	37454 483fb2e7274b7ae4f48b7dc2afc8bafb0ec1cc0a	no	7
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	37894 02860a4c2ce7e64dd5a46ec5af71f98f8458bcfe	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	350229		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: **UNIVERSITY OF WATERLOO**
First named Inventor: **Brian D. ADAMS**
Appln. No.: **15/513,914**
U.S. Filing Date: **March 23, 2017**
International Applicant No: **PCT/CA2016/050613**
International Filing Date: **May 31, 2016**
Title: **ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM**
Confirmation No. **3998**
Grp./A.U.: **Not Known**
Examiner: **Not Known**
Docket No.: **19920NP**

Honorable Commissioner for Patents
Alexandria, VA 22313-1450

Dear Sir:

RESPONSE TO NOTICE TO FILE MISSING PARTS

In response to the notice to file missing parts mailed May 26, 2017, submitted here with is a Preliminary Amendment in which the number of claims has been reduced to twenty total claims with one independent claim for purposes of calculating the filing fees. Further there are no longer any multiple dependent claims.

The filing, search, examination and surcharge fees of $1,340.00 being paid by credit card. Any deficiency in the fees may be charged to Deposit Account 041577 to Dowell & Dowell, PC.

A copy of the Notice is attached. A two month extension of time is also being filed concurrently and the fees paid be credit card.

Respectfully submitted,

DOWELL & DOWELL, P. C.

/Ralph A. Dowell/
Ralph A. Dowell, Reg. No.: 26,868
Date: August 29, 2017

DOWELL & DOWELL, P. C.
Suite 203, 2560 Huntington Ave.
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Telephone: (703) 739-9888
Customer Number: 293

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

U.S. APPLICATION NUMBER NO.	FIRST NAMED INVENTOR	ATTY. DOCKET NO.
15/513,914	Brian D. ADAMS	19920NP

293
DOWELL & DOWELL, P.C.
2560 HUNTINGTON AVE, SUITE 203
ALEXANDRIA, VA 22303

INTERNATIONAL APPLICATION NO.	
PCT/CA2016/050613	
I.A. FILING DATE	PRIORITY DATE
05/31/2016	06/08/2015

CONFIRMATION NO. 3998
371 FORMALITIES LETTER

OC000000091615296

Date Mailed: 05/26/2017

Notification of Insufficiency Under 37 CFR 1.492 and/or 1.495 (DO/EO/US)

The following items have been submitted by the applicant or the International Bureau to the United States Patent and Trademark Office as a Designated / Elected Office (37 CFR 1.495).

- Priority Document
- Copy of the International Application filed on 03/23/2017
- Copy of the International Search Report filed on 03/23/2017
- U.S. Basic National Fees filed on 03/23/2017
- Authorize Access to Search Results filed on 03/23/2017
- Priority Documents filed on 03/23/2017
- Authorization to Permit Access filed on 03/23/2017
- Application Data Sheet (37 CFR 1.76) filed on 03/23/2017

The following items **MUST** be furnished within the period set forth below:

- Additional claim fees of **$5260** as a undiscounted entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due.
- To avoid abandonment, a surcharge (for late submission of search fee, examination fee or inventor's oath or declaration) as set forth in 37 CFR 1.492(h) of $140 for an undiscounted entity , must be submitted with the missing items identified in this letter.

SUMMARY OF FEES DUE:

Total additional fees required for this application is **$6600** for an Undiscounted Entity:

- **$140** Surcharge.

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.495(c).

- Properly executed inventor's oath or declaration for the following inventor(s) has not been submitted: **Brian D. ADAMS**, **Dipan KUNDU**, and **Linda F. NAZAR**

- The application search fee has not been paid. Applicant must submit **$480** to complete the search fee. Note a surcharge will be required if submitted later than commencement of the national stage (37 CFR 1.492(h)).

- The application examination fee has not been paid. Applicant must submit **$720** to complete the examination fee for an undiscounted entity. Note a surcharge will be required if submitted later than commencement of the national stage (37 CFR 1.492(h)) and the basic national fee was not paid before July 1, 2005.

Total additional claim fee(s) for this application is $**5260**

- **$4480** for **56** total claims over 20.
- **$780** for multiple dependent claim surcharge.

ALL OF THE ITEMS SET FORTH ABOVE MUST BE SUBMITTED WITHIN TWO (2) MONTHS FROM THE DATE OF THIS NOTICE. FAILURE TO PROPERLY RESPOND WILL RESULT IN ABANDONMENT.

The time period set above may be extended by filing a petition and fee for extension of time under the provisions of 37 CFR 1.136(a).

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

Registered users of EFS-Web may alternatively submit their reply to this notice via EFS-Web.
https://sportal.uspto.gov/authenticate/AuthenticateUserLocalEPF.html

For more information about EFS-Web please call the USPTO Electronic Business Center at **1-866-217-9197** or visit our website at http://www.uspto.gov/ebc.

If you are not using EFS-Web to submit your reply, you must include a copy of this notice.

INDIA L EVANS

Telephone: (571) 272-9085

PTO/AIA/22 (03-13)
Approved for use through 7/31/2016. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PETITION FOR EXTENSION OF TIME UNDER 37 CFR 1.136(a)

Docket Number (Optional) 19920NP

Application Number 15/513,914

Filed 03/23/2017

For Electrode Materials for Rechargeable Zinc Cells and Batteries Produced Therefrom

Art Unit

Examiner

This is a request under the provisions of 37 CFR 1.136(a) to extend the period for filing a reply in the above-identified application.

The requested extension and fee are as follows (check time period desired and enter the appropriate fee below):

	Fee	Small Entity Fee	Micro Entity Fee	
☐ One month (37 CFR 1.17(a)(1))	$200	$100	$50	$
☑ Two months (37 CFR 1.17(a)(2))	$600	$300	$150	$ 600.00
☐ Three months (37 CFR 1.17(a)(3))	$1,400	$700	$350	$
☐ Four months (37 CFR 1.17(a)(4))	$2,200	$1,100	$550	$
☐ Five months (37 CFR 1.17(a)(5))	$3,000	$1,500	$750	$

☐ Applicant asserts small entity status. See 37 CFR 1.27.

☐ Applicant certifies micro entity status. See 37 CFR 1.29.
Form PTO/SB/15A or B or equivalent must either be enclosed or have been submitted previously.

☐ A check in the amount of the fee is enclosed.

☐ Payment by credit card. Form PTO-2038 is attached.

☐ The Director has already been authorized to charge fees in this application to a Deposit Account.

☐ The Director is hereby authorized to charge any fees which may be required, or credit any overpayment, to Deposit Account Number ____________.

☑ Payment made via EFS-Web.

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

I am the

☐ applicant.

☑ attorney or agent of record. Registration number 26868.

☐ attorney or agent acting under 37 CFR 1.34. Registration number ____________.

/Ralph A. Dowell/	August 29, 2017
Signature	Date
Ralph A. Dowell	703-739-9888
Typed or printed name	Telephone Number

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. Submit multiple forms if more than one signature is required, see below*.

☐ * Total of ________ forms are submitted.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/513,914	03/23/2017		280	19920NP	73	3

CONFIRMATION NO. 3998

FILING RECEIPT

OC000000091613295

293
DOWELL & DOWELL, P.C.
2560 HUNTINGTON AVE, SUITE 203
ALEXANDRIA, VA 22303

Date Mailed: 05/26/2017

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Brian D. ADAMS, Mitchell, CANADA;
Dipan KUNDU, Kitchener, CANADA;
Linda F. NAZAR, Waterloo, CANADA;

Applicant(s)

UNIVERSITY OF WATERLOO, Waterloo, ON, CANADA

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a 371 of PCT/CA2016/050613 05/31/2016
which claims benefit of 62/230,502 06/08/2015

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 05/24/2017

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/513,914**

Projected Publication Date: 08/31/2017

Non-Publication Request: No

Early Publication Request: No
Title

Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom

Preliminary Class

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

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This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number
15/513,914

APPLICATION AS FILED - PART I

FOR	NUMBER FILED (Column 1)	NUMBER EXTRA (Column 2)	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	280
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	480
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	720
TOTAL CLAIMS (37 CFR 1.16(i))	76 minus 20 =	* 56			OR	x 80 =	4480
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*				x 420 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							780
			TOTAL			TOTAL	6740

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED - PART II

AMENDMENT A

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

AMENDMENT B

	CLAIMS REMAINING AFTER AMENDMENT (Column 1)		HIGHEST NUMBER PREVIOUSLY PAID FOR (Column 2)	PRESENT EXTRA (Column 3)	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
Application Size Fee (37 CFR 1.16(s))									
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

U.S. APPLICATION NUMBER NO.	FIRST NAMED INVENTOR	ATTY. DOCKET NO.
15/513,914	Brian D. ADAMS	19920NP

293
DOWELL & DOWELL, P.C.
2560 HUNTINGTON AVE, SUITE 203
ALEXANDRIA, VA 22303

INTERNATIONAL APPLICATION NO.	
PCT/CA2016/050613	
I.A. FILING DATE	PRIORITY DATE
05/31/2016	06/08/2015

CONFIRMATION NO. 3998
371 FORMALITIES LETTER

OC000000091615296

Date Mailed: 05/26/2017

Notification of Insufficiency Under 37 CFR 1.492 and/or 1.495 (DO/EO/US)

The following items have been submitted by the applicant or the International Bureau to the United States Patent and Trademark Office as a Designated / Elected Office (37 CFR 1.495).

- Priority Document
- Copy of the International Application filed on 03/23/2017
- Copy of the International Search Report filed on 03/23/2017
- U.S. Basic National Fees filed on 03/23/2017
- Authorize Access to Search Results filed on 03/23/2017
- Priority Documents filed on 03/23/2017
- Authorization to Permit Access filed on 03/23/2017
- Application Data Sheet (37 CFR 1.76) filed on 03/23/2017

The following items **MUST** be furnished within the period set forth below:

- Additional claim fees of $**5260** as a undiscounted entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due.
- To avoid abandonment, a surcharge (for late submission of search fee, examination fee or inventor's oath or declaration) as set forth in 37 CFR 1.492(h) of $140 for an undiscounted entity , must be submitted with the missing items identified in this letter.

SUMMARY OF FEES DUE:

Total additional fees required for this application is $**6600** for an Undiscounted Entity:

- $**140** Surcharge.

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.495(c).

- Properly executed inventor's oath or declaration for the following inventor(s) has not been submitted: **Brian D. ADAMS**, **Dipan KUNDU**, and **Linda F. NAZAR**

- The application search fee has not been paid. Applicant must submit $**480** to complete the search fee. Note a surcharge will be required if submitted later than commencement of the national stage (37 CFR 1.492(h)).

- The application examination fee has not been paid. Applicant must submit $**720** to complete the examination fee for an undiscounted entity. Note a surcharge will be required if submitted later than commencement of the national stage (37 CFR 1.492(h)) and the basic national fee was not paid before July 1, 2005.

Total additional claim fee(s) for this application is $**5260**
- $**4480** for **56** total claims over 20.
- $**780** for multiple dependent claim surcharge.

ALL OF THE ITEMS SET FORTH ABOVE MUST BE SUBMITTED WITHIN TWO (2) MONTHS FROM THE DATE OF THIS NOTICE. FAILURE TO PROPERLY RESPOND WILL RESULT IN ABANDONMENT.

The time period set above may be extended by filing a petition and fee for extension of time under the provisions of 37 CFR 1.136(a).

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

Registered users of EFS-Web may alternatively submit their reply to this notice via EFS-Web.
https://sportal.uspto.gov/authenticate/AuthenticateUserLocalEPF.html

For more information about EFS-Web please call the USPTO Electronic Business Center at **1-866-217-9197** or visit our website at http://www.uspto.gov/ebc.

If you are not using EFS-Web to submit your reply, you must include a copy of this notice.

INDIA L EVANS

Telephone: (571) 272-9085

FORM PCT/DO/EO/923 (371 Formalities Notice)

MULTIPLE DEPENDENT CLAIM FEE CALCULATION SHEET

Substitute for Form PTO-1360
(For use with Form PTO/SB/06)

Application Number
15513914

Filing Date

Applicant(s) Brian ADAMS

* May be used for additional claims or amendments

CLAIMS	AS FILED		AFTER FIRST AMENDMENT		AFTER SECOND AMENDMENT	
	Indep	Depend	Indep	Depend	Indep	Depend
1	1					
2		1				
3		2				
4		(1)				
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6		(1)				
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26	1					
27		1				
28		2				
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47		(1)				
48	1					
49		1				
50		2				
Total Indep	3		0		0	
Total Depend	73	↵	0	↵	0	↵
Total Claims	76	▨	0	▨	0	▨

	*		*		*	
	Indep	Depend	Indep	Depend	Indep	Depend
51		(1)				
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove
Legal Name

Prefix	**Given Name**	**Middle Name**	**Family Name**	**Suffix**
	Brian	D.	ADAMS	

Residence Information (Select One) ○ US Residency ● Non US Residency ○ Active US Military Service

City	Mitchell	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	228 Morenz Drive		
Address 2			
City	Mitchell	**State/Province**	ON
Postal Code	~~N0K 2N0~~ N0K 1N0	**Country** i	CA

Inventor 2 Remove
Legal Name

Prefix	**Given Name**	**Middle Name**	**Family Name**	**Suffix**
	Dipan		KUNDU	

Residence Information (Select One) ○ US Residency ● Non US Residency ○ Active US Military Service

City	Kitchener	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	11 Overlea Drive		
Address 2			
City	Kitchener	**State/Province**	ON
Postal Code	N2M 5C8	**Country** i	CA

Inventor 3 Remove
Legal Name

CORRECTED ADS 15/513,914

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Prefix	**Given Name**	**Middle Name**	**Family Name**	**Suffix**
	Linda	F.	NAZAR	

Residence Information (Select One) ○ US Residency ● Non US Residency ○ Active US Military Service

City	Waterloo	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	504 Fox Cove Place		
Address 2			
City	Waterloo	**State/Province**	ON
Postal Code	N2K 4A7	**Country** i	CA

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below. For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	293	
Email Address	dowell@dowellpc.com	Add Email Remove Email

Application Information:

Title of the Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom		
Attorney Docket Number	19920NP	**Small Entity Status Claimed** ☐	
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	14	**Suggested Figure for Publication (if any)**	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country i

PTO/AIA/14 (11-15)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One: ○ Customer Number ● US Patent Practitioner ○ Limited Recognition (37 CFR 11.9)

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	
	Ralph	A.	Dowell		Remove
Registration Number	26868				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	
	Lynn	C.	Schumacher		Remove
Registration Number	36413				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	
	Stephen	W.	Leonard		Remove
Registration Number	53604				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	
	Wendy	M.	Slade		Remove
Registration Number	53604				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	
	Arlen	Wesley	Ferrebee		Remove
Registration Number	51312				

Additional Representative Information blocks may be generated within this form by selecting the **Add** button.

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	a 371 of international	PCT/CA2016/050613	2016-05-31
Prior Application Status			Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
PCT/CA2016/050613	Claims benefit of provisional	62230502	2015-06-08

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button.

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

			Remove
Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

CORRECTED ADS 15/513,914

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

○ Assignee ○ Legal Representative under 35 U.S.C. 117 ○ Joint Inventor

● Person to whom the inventor is obligated to assign. ○ Person who shows sufficient proprietary interest

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	UNIVERSITY OF WATERLOO		
Mailing Address Information For Applicant:			
Address 1	200 University Avenue West		
Address 2			
City	Waterloo	**State/Province**	ON
Country	CA	Postal Code	N2L 3G1
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button.

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button.

Signature:

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	~~/Ralph A. Dowell/~~ /WENDY M. SLADE/			Date (YYYY-MM-DD)	~~2017-03-23~~ 2017-04-25
First Name	~~Ralph~~ WENDY	Last Name	~~Dowell~~ SLADE	Registration Number	~~26868~~ 53604

Additional Signature may be generated within this form by selecting the Add button.

CORRECTED ADS 15/513,914

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1 The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3 A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent CooperationTreaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	29022298
Application Number:	15513914
International Application Number:	
Confirmation Number:	3998
Title of Invention:	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom
First Named Inventor/Applicant Name:	Brian D. ADAMS
Customer Number:	293
Filer:	Ralph A. Dowell/WENDY SLADE
Filer Authorized By:	Ralph A. Dowell
Attorney Docket Number:	19920NP
Receipt Date:	25-APR-2017
Filing Date:	
Time Stamp:	15:07:11
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Application Data Sheet	19920ads_CORR.pdf	121169 788faaf9221f2b4d57feef9de72341b058d8200b	no	9

Warnings:

Information:	
This is not an USPTO supplied ADS fillable form	
Total Files Size (in bytes):	121169

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO-1390 (01-17)
Approved for use through 8/31/2019. OMB 0651-0021
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371

		Attorney Docket No. 19920NP
		U.S. Application No. (if known, see 37 CFR 1.5)
International Application No. PCT/CA2016/050613	International Filing Date 31 May 2016	Priority Date Claimed 08 June 2015

Title of Invention
Electrode Materials for Rechargeable Zinc Cells and Batteries Produced Therefrom

First Named Inventor
Brian D. ADAMS

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). NOTE: The express request under 35 U.S.C. 371(f) will not be effective unless the requirements under 35 U.S.C. 371(c)(1), (2), and (4) for payment of the basic national fee, copy of the International Application and English translation thereof (if required), and the oath or declaration of the inventor(s) have been received.
2. ☐ A copy of the International Application (35 U.S.C. 371(c)(2)) is attached hereto (not required if the International Application was previously communicated by the International Bureau or was filed in the United States Receiving Office (RO/US)).
3. An English language translation of the International Application (35 U.S.C. 371(c)(2))
   a. ☐ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
4. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4))
   a. ☐ is attached.
   b. ☐ was previously filed in the international phase under PCT Rule 4.17(iv).

Items 5 to 8 below concern amendments made in the international phase.

PCT Article 19 and 34 amendments

5. ☐ Amendments to the claims under PCT Article 19 are attached (not required if communicated by the International Bureau) (35 U.S.C. 371(c)(3)).
6. ☐ English translation of the PCT Article 19 amendment is attached (35 U.S.C. 371(c)(3)).
7. ☐ English translation of annexes (Article 19 and/or 34 amendments only) of the International Preliminary Examination Report is attached (35 U.S.C. 371(c)(5)).

Cancellation of amendments made in the international phase

8a. ☐ Do not enter the amendment made in the international phase under PCT Article 19.

8b. ☐ Do not enter the amendment made in the international phase under PCT Article 34.

NOTE: A proper amendment made in English under Article 19 or 34 will be entered in the U.S. national phase application absent a clear instruction from applicant not to enter the amendment(s).

The following items 9 to 17 concern a document(s) or information included.

9. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
10. ☐ A preliminary amendment.
11. ☑ An Application Data Sheet under 37 CFR 1.76.
12. ☐ A substitute specification. NOTE: A substitute specification cannot include claims. See 37 CFR 1.125(b).
13. ☐ A power of attorney and/or change of address letter.
14. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13*ter*.3 and 37 CFR 1.821-1.825.
15. ☐ Assignment papers *(cover sheet and document(s))*. Name of Assignee: ____________________
16. ☐ 37 CFR 3.73(c) Statement *(when there is an Assignee)*.

PTO-1390 (01-17)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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U.S. APPLN. No. (if known – see 37 CFR 1.5)	INTERNATIONAL APPLICATION No.	ATTORNEY DOCKET No.
	PCT/CA2016/050613	19920NP

17. ☐ Other items or information:

Copy of WO 2016/197236 A1 with the International Search Report

The following fees have been submitted.	CALCULATIONS	PTO USE ONLY
18. ☑ Basic national fee (37 CFR 1.492(a)) **$280**	$ 280	
19. ☐ Examination fee (37 CFR 1.492(c)) If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4) .... **$0** All other situations **$720**	$	
20. ☐ Search fee (37 CFR 1.492(b)) If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4) .... **$0** Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority ....**$120** International Search Report prepared by an ISA other than the US and provided to the Office or previously communicated to the US by the IB ....**$480** All other situations **$600**	$	
TOTAL OF 18, 19, and 20 =	$	
☐ Additional fee for specification and drawings filed in paper over 100 sheets (excluding sequence listing in compliance with 37 CFR 1.821(c) or (e) in an electronic medium or computer program listing in an electronic medium) (37 CFR 1.492(j)). Fee for each additional 50 sheets of paper or fraction thereof **$400**		

Total Sheets	Extra Sheets	Number of each addition 50 or fraction thereof (round **up** to a whole number)	RATE	CALCULATIONS	PTO USE ONLY
- 100 =	/ 50 =		x **$400**	$	

Surcharge of **$140.00** for furnishing any of the search fee, examination fee, or the oath or declaration after the date of commencement of the national stage (37 CFR 1.492(h)).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	CALCULATIONS	PTO USE ONLY
Total claims	- 20 =		x **$80**	$	
Independent claims	- 3 =		x **$420**	$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			**+ $780**	$	

Processing fee of **$140.00** for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i)). +	$	
TOTAL OF ABOVE CALCULATIONS =	$ 280	
☐ **Applicant asserts small entity status.** See 37 CFR 1.27. Fees above are reduced by ½.		
☐ **Applicant certifies micro entity status.** See 37 CFR 1.29. Fees above are reduced by ¾. Applicant must attach form PTO/SB/15A or B or equivalent.		
TOTAL NATIONAL FEE =	$ 280	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property. +	$	
TOTAL FEES ENCLOSED =	$ 280	
	Amount to be refunded:	$
	Amount to be charged:	$

PTO-1390 (01-17)
Approved for use through 8/31/2019. OMB 0651-0021
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

a. ☐ A check in the amount of $____________________ to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. __________________ in the amount of $___________________ to cover the above fees.

c. ☐ The Director is hereby authorized to charge additional fees which may be required, or credit any overpayment, to Deposit Account No. __________________ as follows:

- i. ☐ any required fee.
- ii. ☐ any required fee except for excess claims fees required under 37 CFR 1.492(d) and (e) and multiple dependent claim fee required under 37 CFR 1.492(f).

d. ☑ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. The PTO-2038 should only be mailed or faxed to the USPTO. However, when paying the basic national fee, the PTO-2038 may NOT be faxed to the USPTO.

ADVISORY: If filing by EFS-Web, do **NOT** attach the PTO-2038 form as a PDF along with your EFS-Web submission. Please be advised that this is **not** recommended and by doing so your **credit card information may be displayed via PAIR**. To protect your information, it is recommended to pay fees online by using the electronic payment method.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the International Application to pending status.

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File)Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013, and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.

NOTE 1: By providing this statement under 37 CFR 1.55 or 1.78, **this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA**.

NOTE 2: A U.S. national stage application may not claim priority to the international application of which it is the national phase. The filing date of a U.S. national stage application is the international filing date. See 35 U.S.C. 363.

Correspondence Address

☑ The address associated with Customer Number: 293 **OR** ☐ Correspondence address below

Name					
Address					
City		State		Zip Code	
Country		Telephone			
Email					

Signature	/Ralph A. Dowell/	Date	March 23, 2017
Name (Print/Type)	Ralph A. Dowell	Registration No. (Attorney/Agent)	26868

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	**Given Name**	**Middle Name**	**Family Name**	**Suffix**
	Brian	D.	ADAMS	

Residence Information (Select One) US Residency ● Non US Residency Active US Military Service

City	Mitchell	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	228 Morenz Drive		
Address 2			
City	Mitchell	**State/Province**	ON
Postal Code	N0K 2N0	**Country** i	CA

Inventor 2 Remove

Legal Name

Prefix	**Given Name**	**Middle Name**	**Family Name**	**Suffix**
	Dipan		KUNDU	

Residence Information (Select One) US Residency ● Non US Residency Active US Military Service

City	Kitchener	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	11 Overlea Drive		
Address 2			
City	Kitchener	**State/Province**	ON
Postal Code	N2M 5C8	**Country** i	CA

Inventor 3 Remove

Legal Name

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Prefix	Given Name	Middle Name	Family Name	Suffix
	Linda	F.	NAZAR	

Residence Information (Select One) US Residency ● Non US Residency Active US Military Service

City	Waterloo	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	504 Fox Cove Place		
Address 2			
City	Waterloo	**State/Province**	ON
Postal Code	N2K 4A7	**Country** i	CA

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below. For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	293
Email Address	dowell@dowellpc.com Add Email Remove Email

Application Information:

Title of the Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom		
Attorney Docket Number	19920NP	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	14	**Suggested Figure for Publication (if any)**	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country i

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	Customer Number	● US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)		
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	Remove
	Ralph	A.	Dowell		
Registration Number	26868				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	Remove
	Lynn	C.	Schumacher		
Registration Number	36413				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	Remove
	Stephen	W.	Leonard		
Registration Number	53604				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	Remove
	Wendy	M.	Slade		
Registration Number	53604				
Prefix	**Given Name**	Middle Name	**Family Name**	Suffix	Remove
	Arlen	Wesley	Ferrebee		
Registration Number	51312				

Additional Representative Information blocks may be generated within this form by selecting the **Add** button. Add

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	19920NP
		Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom		

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	a 371 of international	PCT/CA2016/050613	2016-05-31
Prior Application Status			Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
PCT/CA2016/050613	Claims benefit of provisional	62230502	2015-06-08
Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button.			Add

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)i the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

			Remove
Application Number	Countryi	Filing Date (YYYY-MM-DD)	Access Codei (if applicable)
Additional Foreign Priority Data may be generated within this form by selecting the **Add** button.			Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	19920NP
	Application Number	
Title of Invention	Electrode Materials For Rechargeable Zinc Cells and Batteries Produced Therefrom	

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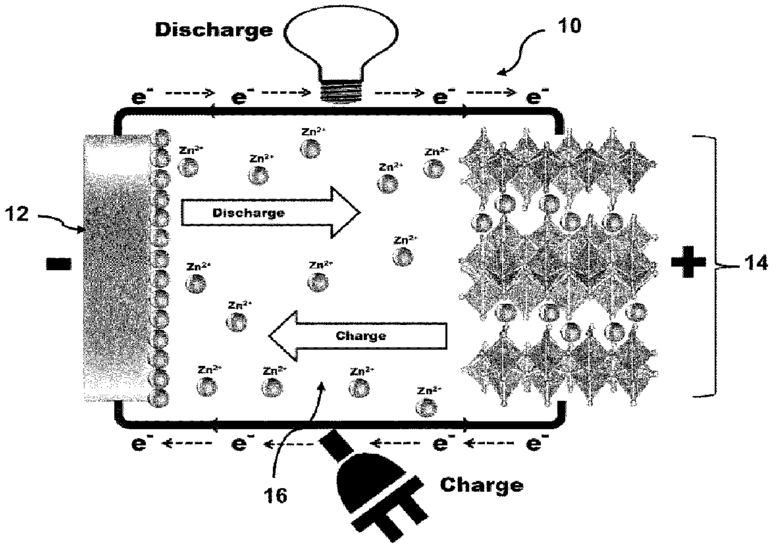

Figure 1A

(57) **Abstract**: The present disclosure discloses a rechargeable Zn battery based on layered/tunnelled structure vanadium/molybdenum oxides, with/without the presence of neutral/cationic/anionic species and/or water molecules inserted into the interlayers/tunnels, of nano/micro-particle morphology as robust materials for high rate and long term reversible Zn^{2+} ion intercalation storage at the positive electrode, that are coupled with a metallic Zn negative electrode, and an aqueous electrolyte. The positive electrode may include electronically conducting additives and one or more binders along with the Zn^{2+} intercalation material; the negative electrode is Zn metal in any form; the aqueous electrolyte is of pH 1 to 9 and contains a soluble zinc salt in a concentration range from 0.01 to 10 molar.

ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM

FIELD

This disclosure relates generally to batteries, and, more specifically to zinc ion batteries involving zinc intercalation positive electrode materials, zinc metal based negative electrodes in any form, and an aqueous electrolyte containing zinc salt and batteries using these positive electrode materials.

BACKGROUND

Given the looming concerns of climate change, sustainable energy resources such as solar and wind have entered the global spotlight, triggering the search for reliable, low cost electrochemical energy storage. Among the various options, lithium ion batteries are currently the most attractive candidates due to their high energy density, and foothold in the marketplace. However, many factors (cost, safety, and lifetime) will likely limit their large scale applications, and dictate against their use in stationary grid storage where low cost and durability are more of a concern than weight. What is needed is a high energy density battery that is rechargeable, cheap, safe, and easy to manufacture and dispose of or recycle. Aqueous batteries (water based electrolytes) are therefore attracting tremendous attention. Their high conductivity (up to 1 Siemens (S) cm^{-1}) compared to the non-aqueous electrolytes (0.001 to 0.01 S cm^{-1}) also favour high rate capabilities suitable for emerging applications.

The use of metallic negative electrodes is a means to achieve high energy density and ease of battery assembly (hence lower cost). There is a trade-off between the reduction potential of a metal, E°, (low values give higher cell voltages) and safety. Metals with low reduction potentials (e.g., lithium, potassium, calcium, sodium, and magnesium) react with water to produce hydrogen. However, zinc is stable in water and for that reason it has been used as the negative electrode in primary aqueous battery systems. Moreover, zinc has (a) high abundance and large production which makes it inexpensive; (b) non-toxicity; (c) low redox potential (-0.76 V vs. standard hydrogen electrode (SHE)) compared to other negative electrode materials used in aqueous batteries; and (d) stability in water due to a high overpotential for hydrogen evolution. The latter renders a large voltage window (~2 V) for aqueous zinc-ion batteries (AZIBs) employing a metallic Zn negative electrode.

Vanadium and molybdenum are low cost metals possessing a range of oxidation states (V: +2 to +5; Mo: +2 to +6), which allows for multiple redox and hence large specific capacities for vanadium or molybdenum based electrode materials. Layered V_nO_m (vanadium oxides: V_2O_5, V_3O_8, V_4O_{11}) and MoO_y (molybdenum oxides) that are made of two dimensional sheet structures were the subject of much past investigation for non-aqueous and aqueous alkali (Li and Na) ion batteries. The additional presence of interlayer neutral molecules, ions, metal ions and/or water of hydration in such layered oxides act as pillars, providing structural stability during long term charge discharge cycling.

SUMMARY

The present disclosure discloses a rechargeable Zn battery based on layered/tunnelled structure vanadium/molybdenum oxides, with/without the presence of neutral/cationic/anionic species and/or water molecules inserted into the interlayers/tunnels, of nano/microparticle morphology as robust materials for high rate and long term reversible Zn^{2+} ion intercalation storage at the positive electrode, that are coupled with a metallic Zn negative electrode, and an aqueous electrolyte. The positive electrode may include electronically conducting additives and one or more binders along with the Zn^{2+} intercalation material; the negative electrode is Zn metal in any form; the aqueous electrolyte is may have a pH in a range of 1 to 9 and contains a soluble zinc salt which may be in a concentration range from 0.01 to 10 molar.

Thus, disclosed herein is a zinc ion battery, comprising:

a positive electrode compartment having enclosed therein an intercalation layered positive electrode material $M_{\mathbf{x}}V_2O_5.\mathbf{n}H_2O$, wherein x is in a range from 0.05 to 1, **n** is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_2O_5 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

There is also disclosed herein a zinc ion battery, comprising:

a positive electrode compartment having enclosed therein and intercalated layered positive electrode material $M_{\mathbf{x}}V_3O_7.\mathbf{n}H_2O$, wherein **x** is in a range from 0.05 to 1, **n** is greater than 0 and less than 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_3O_7 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M and/or hydrogen bonded to the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

There is also disclosed a zinc ion battery; comprising:

a positive electrode compartment having enclosed therein an intercalated layered positive electrode material $M_xMoO_y.nH_2O$, wherein x is in a range from 0 to 1, y is in a range from 2 to 3, n is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said MoO_y has a layer or tunnel crystal structure, and the metal ions M, if present, pillared between the layers, and waters of hydration coordinated to the metal ions M pillared between the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and an electrolyte comprising water and having a salt of zinc dissolved therein.

A further understanding of the functional and advantageous aspects of the disclosure can be realized by reference to the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the disclosure will now be described, by way of example only, with reference to the drawings, in which:

Figure 1A shows a **c**onceptual scheme of a zinc-ion battery constructed in accordance with the present disclosure.

Figure 1B is a cross section of a zinc-ion battery.

Figure 2 shows linear sweep voltammograms at 1 mV/s on Pt, Ti, and Zn in 1 M Na_2SO_4 showing the onset of the hydrogen evolution reaction.

Figure 3 shows linear sweep voltammograms at 1 mV/s in 1 M Na_2SO_4 showing the hydrogen evolution reaction. The dotted voltammogram in (a) shows zinc deposition on a zinc disk electrode in 1 M $ZnSO_4$ for comparison.

Figure 4A shows cyclic voltammograms at 5 mV/s on a Ti disk electrode.

Figure 4B shows cyclic voltammograms at 5 mV/s on stainless steel rod in 1 M $ZnSO_4$.

Figure 5 shows linear sweep voltammograms on a zinc disk electrode (cathodic sweep) and a stainless steel disk electrode (anodic sweep) at 1 mV/s in 1 M $ZnSO_4$. The cathodic sweep on zinc shows zinc deposition and the anodic sweep on the stainless steel shows the oxygen evolution reaction.

These two electrochemical reactions dictate the potential operating window for aqueous zinc-ion batteries using this electrolyte.

Figure 6A shows Rietveld refinement of $H_2V_3O_8$. Data points (circles); calculated profile (line); difference profile (dotted line); Bragg positions (vertical lines) are as indicated. Refined lattice parameters are a = 16.87 Å, b = 9.332 (3) Å, c = 3.63 Å, and $\alpha = \beta = \gamma = 90°$. Inset shows the layered structure projected in the *ac* plane. VOx polyhedra are shown in black.

Figure 6B shows the Rietveld refinement of $Zn_{0.25}V_2O_5.nH_2O$. Data points (circles); calculated profile (black line); difference profile (blue line) are as indicated. Refined parameters are *a* = 10.75 Å, *b* = 7.77 Å, *c* = 10.42 Å, α = 91.26°, β = 90.31°, and γ = 88.66°. The VO_x and ZnO_x polyhedra are shown in black and grey, respectively.

Figures 7A, 7B, 7C and 7D show a typical SEM image of the $H_2V_3O_8$ (**7A** and **7B**) and $Zn_{0.25}V_2O_5.nH_2O$ (**7C** and **7D**) nanofibers.

Figures 8A and **8B** show galvanostatic polarization curves for the (**8A**) $H_2V_3O_8$ and (**8B**) $Zn_{0.25}V_2O_5.nH_2O$ electrodes at various current rates. Here, 1C is defined as 350 mA g^{-1} for $H_2V_3O_8$ and 300 mA g^{-1} for $Zn_{0.25}V_2O_5.nH_2O$.

Figures 9A. 9B, 9C and 9D show specific capacity and coulombic efficiency of the $H_2V_3O_8$ (**9A** and **9B**) and $Zn_{0.25}V_2O_5.nH_2O$ (**9C** and **9D**) as a function of cycling at 4C (**9A** and **9C**) and 8C (**9B** and **9D**) current rates.

Figures 10A and **10B** show rate capability of the (**9A**) $H_2V_3O_8$ and (**9B**) $Zn_{0.25}V_2O_5.nH_2O$ cells studied under variable current loading as a function of cycling. The corresponding coulombic efficiencies are also shown.

Figure 11 shows the tradeoff between energy and power density (Ragone plot) for reversible Zn^{2+} storage in $Zn_{0.25}V_2O_5.nH_2O$, $H_2V_3O_8$, MnO_2, and $Zn_3[Fe(CN)_6]_2$.

DETAILED DESCRIPTION

Various embodiments and aspects of the disclosure will be described with reference to details discussed below. The following description and drawings are illustrative of the disclosure and are not to be construed as limiting the disclosure. Numerous specific details are described to provide a thorough understanding of various embodiments of the present disclosure. However, in certain instances, well-known or conventional details are not described in order to provide a concise discussion of embodiments of the present disclosure.

The Figures are not to scale and some features may be exaggerated or minimized to show details of particular elements while related elements may have been eliminated to prevent obscuring novel aspects. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present disclosure.

As used herein, the term “about”, when used in conjunction with ranges of dimensions, temperatures, concentrations or other physical properties or characteristics is meant to cover slight variations that may exist in the upper and lower limits of the ranges of dimensions so as to not exclude embodiments where on average most of the dimensions are satisfied but where statistically dimensions may exist outside this region.

As used herein, the phrase "a negative electrode for storing zinc" means that the negative electrode can incorporate and release zinc reversibly by electrodeposition/dissolution (plating/stripping) of elemental zinc from/to the electrolyte, by alloying/dealloying reaction, or the negative electrode comprises a material that can store zinc by any one or combination of intercalation, conversion, and capacitive storage (adsorption/deadsorption of Zn^{2+} ions).

Figure 1A shows a **c**onceptual scheme of a zinc-ion battery shown generally at **10**, which includes an anode **12**, and an intercalated layered positive electrode material **14** separated by an electrolyte **16**, with **Figure 1A** showing diagrammatically the operation of the battery **10**, namely during the charging cycle Zn ions are attracted to the negative electrode **12**, and during the discharge cycle Zn ions are attracted to the intercalated positive electrode material **14** into which they intercalate. Electrons flow through the external circuit connecting the negative and positive electrodes which are used to do work.

Figure 1B is a cross section of an actual zinc-ion battery showing the positive electrode **14** contained in a positive electrode compartment **20**, the negative electrode **12** contained in a negative electrode compartment **22**, and the electrolyte **16** contained in an electrolyte compartment **24** in which a separator **28** which is electrically insulating and permeable to zinc ions separating the positive and negative compartments is located. Non-limiting examples of separator **28** include organic polymers (polyethylene (PE), polypropylene (PP), poly(tetrafluoroethylene) (PTFE), poly(vinyl chloride) (PVC)), polyvinylidene fluoride (PVDF), nylon, organic polymer-inorganic oxide, silica glass fiber, porous silica or alumina ceramic membranes, cellulose, cellulose-ceramic oxide, wood, or any combination of these.

The present disclosure provides several embodiments of the intercalated layered positive electrode material **14**. In an embodiment the intercalation layered positive electrode material **14** may be $M_xV_2O_5.\mathbf{n}H_2O$, where x is in a range from 0.05 to 1, **n** is in a range from 0 to 2, and M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion with the metal M ion being in a +2 to +4 valence state. The V_2O_5 has a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M. The number of waters of hydration **n** in some embodiments may be greater than 0 and less than 1. Some of the waters of hydration may be hydrogen bonded to the layers.

In a preferred embodiment x = 0.25, and n = 1.

In another embodiment, the intercalated layered positive electrode material **14** may be $M_xV_3O_7.\mathbf{n}H_2O$, wherein **x** is in a range from 0.05 to 1, **n** is greater than 0 and less than 2. M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, with the metal M ion being in a +2 to +4 valence state. The V_3O_7 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M and/or hydrogen bonded to the layers. In an embodiment **n** is greater than 0 and less than 1.

In a preferred embodiment x = 0.05, and n = 1.

In another embodiment, the intercalated layered positive electrode material **14** may be $M_xMoO_y.nH_2O$, in which **x** is in a range from 0 to 1, **y** is in a range from 2 to 3, and **n** is in a range from 0 to 2. M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, with the metal M ion being in a +2 to +4 valence state. The MoO_y has a layer or tunnel crystal structure, and the metal ions M, if present, are pillared between the layers, and waters of hydration are coordinated to the metal ions M pillared between the layers.

In some embodiments n is greater than 0 and less than 2. In some embodiments the waters of hydration are hydrogen bonded to the layers.

In a preferred embodiment $x = 0.25$, $y = 3$ and $n = 0$.

The electrolyte **16** is an aqueous based electrolyte and contains a salt of zinc dissolved therein. Non-limiting examples of the zinc salt comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide to mention a few.

The dissolved zinc is present in an amount in the liquid in a range from about 0.01 to about 10 molar (M), and preferably is present in a range from about 0.1 to about 4 M.

The electrolyte may have a pH in a range between 1 and about 8 but preferably between 4 and about 8 and more preferably 4 to 7. The electrolyte is an aqueous based electrolyte and may be just water containing the dissolved salt of zinc, or additional solvents may be included, for example alcohols, nitriles, carbonates, ethers, sulfoxides, glycols, esters, and amines. Typically, the zinc salt may comprise anyone or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide in 0.1 to 4 M concentration of Zn^{2+} with or without the nonaqueous component and with or without additional ionically-conductive salts such as quaternary ammonium salts or alkali metal salts.

The negative electrode may be made of a solid sheet, mesh, or rod of zinc, or it may be comprised of a zinc layer formed on a current collector. When the battery is assembled with metallic zinc contained in the negative electrode, the battery is typically referred to as a zinc battery. This is opposed to a zinc ion battery in which the negative electrode in its initial state does not contain any zinc. The zinc layer may be a thin sheet of zinc or an alloy, or powder zinc bonded adhered to the surface of the negative electrode facing into the negative electrode compartment. The zinc may be a constituent of a formulation which is adhered to the surface of the current collector. Non-limiting examples of zinc alloys that may be used include alloys of zinc with lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, and titanium.

The negative current collector is an electrically conductive support for active zinc which may be comprised of any one or combination of carbon, boron, lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal. A feature of the negative electrode is that it comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage. In a conversion process, the electrochemical reaction of the negative electrode material with zinc leads to its decomposition into two or more products. In capacitive storage the Zn^{2+} ions are stored at the surface of the negative electrode material by a non-faradic process.

The intercalated layered positive electrode material may have different morphologies. The intercalation layered positive electrode material **14** has a nanostructured morphology. Preferably the average particle size is less than 1000 nm in a direction of Zn ion transport through the particle, and more preferably less than 500 nm in a direction of Zn ion transport through the particle. Non-limiting morphologies include nanowires, fibers, wires, cubes, platelets, spheres, and uneven morphology. They may be simple particles. The particles may have a mean size in a range from about 5 nm to about 50 µm.

The particles may be coated with electrically conducting material, in which

the electrically conducting material is any one or combination of carbon powder and conducting polymer. The particles may be embedded in an electrically conducting matrix and the electrically conducting matrix may comprise any one or combination of carbon and conducting polymer, and including a binder. The binder may be any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

The zinc ion battery materials disclosed herein will now be illustrated by the following non-limiting examples.

Examples

Two vanadium oxide based compounds with layered crystal structures and in ultralong one-dimensional morphology exhibiting as robust host materials for high rate and long term reversible Zn^{2+} ion storage in aqueous electrolyte were produced. Vanadium is a cheap and environmentally benign metal possessing a range of oxidation states (+2 to +5), which allows for multiple redox and hence large specific capacities for vanadium based electrode materials. Particularly, oxides of vanadium e.g., V_2O_5 which is non-toxic and produced in large quantities, displays numerous crystal and compositional chemistries for reversible metal ion storage. Layered $M_xV_nO_m$ oxides (M = metal ion) of compositions such as V_2O_5, V_3O_8, V_4O_{11} that are made of two dimensional sheet structures have been the subject of intense investigation for both non-aqueous and aqueous alkali (Li and Na) ion batteries. The presence of interlayer metal ions and/or water of hydration act as pillars, providing structural stability during long term charge discharge cycling.

Embodying such qualities are $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$, which we have synthesized in nanofiber morphology by a simple and rapid microwave hydrothermal treatment of V_2O_5, without using any toxic or corrosive chemicals, and converted to freestanding film electrodes by adopting a cheaper and greener water based electrode fabrication process. Nanomorphology and compact film structure allows for facile release of strain resulting upon Zn^{2+} cycling, shorter ion diffusion paths, better interaction of carbon additives with the active material and robust conductive wiring - facilitating high specific capacities of ~300 mAh g^{-1} and long term cyclabilities up to 1000 cycles at high coulombic efficiency using fast current rates.

Experimental Methods

Synthesis of $H_2V_3O_8$ and $Zn_xV_2O_5$

Microwave solvothermal method developed over last two decades are now often used to prepare positive electrode materials for lithium ion batteries. In this work, we have modified a time consuming and energy expensive hydrothermal approach used in the synthesis of single crystalline $H_2V_3O_8$ nanobelt to a rapid and scalable microwave hydrothermal method for the synthesis of highly homogeneous $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$ nanofibers. In a typical procedure, 3 to 4 millimoles (mmol) V_2O_5 was dispersed in 15:1 water/ethanol (v) mixture with or without stoichiometric amount of zinc acetate (for $Zn_xV_2O_5.nH_2O$) and transferred to a sealed Teflon^{TM} vessel. The vessels were fitted to a rotor equipped with temperature and pressure sensors. The rotor containing the vessels was then placed in a rotating platform for uniform heating in an Anton Parr microwave synthesis system (Synthos 3000). The system temperature was raised to 180℃ in 10 minutes and maintained for 60 to 90 minutes. The preset temperature was maintained automatically by continuous adjustment of the applied power (limited to 800 Watts). The as-synthesized product was thoroughly washed with distilled water followed by a small amount of iso-propanol and dried at 60℃ for 24 h.

Characterization Methods

Powder X-ray diffraction was performed on a Bruker D8-Advance powder diffractometer equipped with Vantec-1 detector, using Cu-Kα radiation (λ= 1.5405Å) in the range from 5° to 80° (2θ) at a step size of 0.025° using Bragg-Brentano geometry. X-ray data refinement was carried out by conventional Rietveld refinement method using the Bruker-AXS TOPAS 4.2 software (Bruker-AXS, 2008). The background, scale factor, zero point, lattice parameters, atomic positions and coefficients for the peak shape function were iteratively refined until convergence was achieved. The morphologies of the samples were examined by field-emission scanning electron microscopy (FE-SEM, LEO 1530) equipped with an energy dispersive X-ray spectroscopy (EDX) attachment.

Battery Cycling

For electrochemical performance evaluation, a freestanding film type electrode was fabricated by a facile green approach. In a typical process, nanofibers were mixed with conducting nanocarbon Super P® and water based composite binder carboxymethylcellulose (CMC) and styrene-butadiene rubber(SBR) (CMC/SBR= 2:1) in 70:27:3 weight ratio. The mixture was dispersed in small amount of water by using an ultrasonic mixer to obtain a stable homogeneous ink which was filtered through Durapore® DVPP 0.65 µm filtration membrane. The water soluble CMC facilitates the dispersion of hydrophobic carbon particles into water and enables its intimate mixing with the nanofibers. Whereas SBR with high binding abilities for a small amount provides adhesion and electrode flexibility. The binder molecules not involved in this anchoring and adhesion get washed away during filtration and that way electrode films with very small binder content is achieved. After drying at 60℃ the composite film automatically came off which was then punched into 1 cm^2 electrode coins. The electrodes were further dried at 180℃ for 1 h ($H_2V_3O_8$) or 60°C for 12 h (for $Zn_xV_2O_5.nH_2O$). The electrochemical properties were investigated in PFA based Swagelok® type cell using 1 M $ZnSO_4$ in water as the electrolyte and titanium or stainless steel rods as the current collector. The $H_2V_3O_8$ or $Zn_xV_2O_5.nH_2O$ and zinc foil served as the positive and negative electrodes, respectively. Galvanostatic cycling studies were performed using multichannel biologic VMP3 potentiostat/galvanostat.

Three-Electrode Electrochemical Measurements

The voltammetric electrochemical experiments were performed with a three-electrode cell consisting of the working electrode, Pt mesh (1 cm^2) as the counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. The working electrodes examined were a Zn disk (φ = 2 mm), a Ti disk (φ = 2 mm), a stainless steel rod (316 grade, φ = 12 mm), and the $H_2V_3O_8$ composite electrode. Cyclic voltammetry was performed at a scan rate of 5 mV/s and linear sweep voltammograms were acquired at 1 mV/s. These techniques were controlled with a CHI700E potentiostat (CH Instruments, Inc.). The electrolytes used were 1 M Na_2SO_4 for the hydrogen evolution reaction and 1 M $ZnSO_4$ for zinc plating/stripping and the oxygen evolution reaction. All experiments were performed at room temperature (23 ± 2°C).

Results and Discussion

The operating voltage of all secondary aqueous batteries is limited by the potentials for hydrogen evolution and oxygen evolution from water electrolysis. Since both the hydrogen and oxygen evolution reactions (HER and OER, respectively) are pH dependent (see reactions 2 to 5) and catalytic in nature, the precise potential at which they occur is sensitive to the electrolyte composition and electrode material. HER and OER occur during charge at the negative and positive electrodes, respectively, and are displayed below in reactions 2 to 5, while the zinc deposition reaction is shown in reaction 1:

Cathodic Reactions:

Zinc Deposition:

(1) $Zn^{2+} + 2e^- \rightarrow Zn$ E°= -0.76 V vs. SHE

Hydrogen Evolution Reaction (HER):

(2) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ E°= -0.83 V vs. SHE

(3) $2H^+ + 2e^- \rightarrow H_2$ E°= 0.00 V vs. SHE

Anodic Reactions:

Oxygen Evolution Reaction (OER):

(4) $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ E°= 0.40 V vs. SHE

(5) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ E°= 1.23 V vs. SHE

To examine the suitability of a metallic zinc negative electrode for secondary zinc-ion batteries, linear sweep voltammetry was used to probe the HER. In **Figure 2**, a zinc-ion-free (1 M Na_2SO_4) electrolyte was used which contained the same concentration of the sulfate anion and similar pH value (4-5) as the 1 M $ZnSO_4$ electrolyte used for all other studies. Here, it can be seen that the hydrogen evolution reaction has an overpotential of ~0.4 V with respect to Pt on both zinc metal and titanium metal. Titanium was found to be an excellent current collector for the negative, comparable to Zn itself, as evident from **Figure 3A**, which also shows that zinc deposition on a zinc electrode in 1 M $ZnSO_4$ occurs at a higher potential than the HER. Stainless steel was deemed to be unsuitable as a current collector for the negative electrode as it catalyzes the HER and competes with zinc electrodeposition (**Figure 3B**).

On the other hand, zinc deposition and stripping was completely reversible on titanium as displayed in **Figure 4A**. The coulombic efficiency (Q_{ox}/Q_{red}) was 100 % over 100 cycles on titanium with no loss in the electrical charge (Q) for deposition or stripping. Stainless steel suffered from a decay in both Q_{red} and Q_{ox}, even for the first 10 cycles (**Figure 4B**). On stainless steel the coulombic efficiency was only 87 % for the first cycle and 74 % for the tenth cycle. This shows that the excess charge during reduction (Q_{red}) goes towards the HER.

Since the OER dictates the maximum potential for the positive electrode, this was first examined on stainless steel, a practical current collector material. Titanium also has a high overpotential for OER, however, we suspect that OER on many Zn^{2+}-intercalation materials will have activity similar to stainless steel which is why we show the result for OER on stainless steel rather than titanium.

Figure 5 displays the linear voltammograms for Zn electrodeposition onto a Zn disk and OER on a stainless steel rod in 1 M $ZnSO_4$ at 1 mV/s. This plot provides the maximum possible operating voltage window of a secondary Zn-ion battery using 1 M $ZnSO_4$ which is ~2.4 V. Obviously, the positive electrode of choice must be tested, particularly if a high-voltage material is to be used. In our case, the upper voltage cut-off for batteries with $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$ are 1.1 V and 1.4 V respectively, which is well below the limit at which OER will occur at these materials.

The hydrothermal method has evolved into an important wet chemistry method for the synthesis of nanostructured vanadium oxide materials. However, such process could though be time consuming, as in the synthesis of $H_2V_3O_8$ nanobelts which requires hydrothermal treatment of V_2O_5 in water for 2-3 days at 210°C. By introducing the microwave heat treatment, we have developed a versatile and scalable synthetic approach for the rapid synthesis of ultralong $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$ nanofibers. Water is known to strongly interact with the microwave radiation via a dipolar-microwave interaction, leading to rapidly superheated local regions in the reaction media. In contrast to typical hydrothermal methods where slow heating mainly occurs via thermal conduction mechanism, heating of the entire reaction media through penetration of microwaves triggers rapid intercalation-exfoliation and cleavage of V_2O_5 into nanosheets and finally into $H_2V_3O_8$ or $Zn_xV_2O_5.nH_2O$ nanofibers.

Phase purity of the as-synthesized materials was confirmed by Rietveld refinement of the powder diffraction pattern as shown in **Figure 6A** for $H_2V_3O_8$ and **Figure 6B** for $Zn_xV_2O_5.nH_2O$. The XRD pattern in **Figure 6A** could be refined to an orthorhombic Pnam $V_3O_7.H_2O$ ($H_2V_3O_8$) with the lattice parameters of a = 16.87 Å, b = 9.33 Å, c = 3.63 Å, and α = β = γ = 90°. Here V_3O_8 layers, which are constructed of VO_6 octahedra and VO5 trigonal bipyramids, are held by strong hydrogen bonding together with van der walls interaction. The H_2O molecule bound to the vanadium atom in place of one oxygen in VO_6 octahedra creates hydrogen bond with the octahedra in the next layer, forming a layered 3D structure. The hydrogen bonded layered structure is found to be very stable up to a temperature of ~300℃ when the structure dehydrates.

The pattern in **Figure 6B** was refined to a composition of $Zn_{0.25}V_2O_5.H_2O$ crystallizing in P-1 triclinic system with lattice parameters of a = 10.75 Å, b = 7.77 Å, c = 10.42 Å, α = 91.26°, β = 90.31°, and γ = 88.66°, which closely resemble the $Zn_{0.25}V_2O_5.H_2O$ phase for which the structure was solved by single crystal diffraction. Here the structure consists of V_2O_5 layer, built up of VO_6 octahedra, VO_5 trigonal bypyramids, and VO_4 tetrahedra, stacked along ***c*** axis with the interlayer Zn atom coordinating to the oxygen apices on opposite sides and the oxygen atoms of the in plane water molecules.

SEM investigation as presented in **Figures 7A, 7B, 7C** and **7C** reveals highly uniform and ultralong one dimensional morphology for both the materials. At a closer look, $H_2V_3O_8$ (**Figure 7A and 7B**) appears to have a ribbon like morphology and $Zn_{0.25}V_2O_5.H_2O$ (**Figure 7C and 7D**) seems to adopt a feather like structure. Both the fibers have a diameter of about 100 nm. To the inventors' knowledge, this is first time $Zn_{0.25}V_2O_5.H_2O$ has been synthesized in such nanomorphology.

Unlike conventional NMP (N-methyl-2-pyrrolidone) based Li-ion battery electrode slurry fabrication, which is expensive and time consuming due to the use of NMP, we have developed a novel and versatile electrode fabrication approach in this work. A water based ink was prepared for both the material by ultrasonic dispersion with conductive carbon and minimum (3%) amount of aqueous based binder CMC and SBR. The ink was passed through a PVDF based membrane filter resulting in a compact film, which upon drying (at 60℃) spontaneously comes off the hydrophobic membrane due to the hydrophilic nature of the oxide based electrode film. The wool like textile morphology of the used materials facilitate dense mat type film electrode formation. Notably, the thickness and the loading of the film can be easily varied by adjusting the amount of ink and the PVDF membrane filter can be reused multiple times. The use of water as the solvent and water based cheap binders along with the recurring use of the PVDF filter membrane makes the process very cost effective and environmentally green. The use of freestanding film electrode also allow us to avoid possible corrosion issues of metal foil, which is otherwise used to deposit an electrode film, and focus on electrochemical zinc storage properties of the active materials only.

The reversible electrochemical Zn^{2+} storage capabilities of $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ were explored in full cells by applying galvanostatic techniques. The electrodes were studied in different voltage windows to elucidate the optimal voltage range for highly reversible electrochemical cycling. Based on this study, voltage windows of 0.4 V – 1.1 V and 0.5 – 1.4 V vs. Zn were determined for the $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ electrodes, respectively, which clearly fall within the safe operational window in aqueous electrolyte (1 M $ZnSO_4$ in H_2O) using Zn anode and Ti rod as the current collector (see discussion above). Cycling in larger voltage window results in higher specific capacities, but structural stress generated from the insertion of large amount of zinc results in pulverization of the electrode and rapid capacity fading and therefore was avoided. Moreover, a practical voltage window not only enable better cyclability, but also ensure lesser voltage polarization and an adequate operating voltage suitable for practical application.

Figures 8A and **8B** show the voltage polarization curves for the two electrodes at different current rates. A rate of 1C (the C-rate is a measure of rate at which the cell is discharged or charged relative to its maximum capacity; a 1C rate means that the discharge/charge current will discharge/charge the cell in 1 h) was defined as 350 mA g^{-1} and 300 mA g^{-1} for $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ respectively, based on the highest capacity achieved at a moderate current density. **Figure 8A** demonstrates the variation of cell voltage for $H_2V_3O_8$ electrode as a function of obtainable specific capacity. The voltage profile shows a small plateau delivering ~100 mAh g^{-1} of capacity at around 0.8 V, following which it varies in slope registering high specific capacity of 325 mAh g^{-1} and 270 mAh g^{-1} at high rates of 4C (1400 mA g^{-1}) and 8C (2800 mA g^{-}

^{1}), respectively. Depending on the applied current rates close to 1.5 to 2, Zn^{2+} ions are electrochemically intercalated during discharge. An average operating voltage of ~0.64 V is obtained for this electrode irrespective of the rate. On the contrary $Zn_{0.25}V_2O_5.H_2O$ electrode demonstrates a higher average operating voltage of ~0.8 V at all current densities (**Figure 8B**). This is most likely the consequence of higher average oxidation state of V in $Zn_{0.25}V_2O_5.H_2O$ ($V^{4.8+}$) compared to that in $H_2V_3O_8$ ($V^{4.66+}$) including the effect from structural energetics.

For $Zn_{0.25}V_2O_5.H_2O$, typical discharge-charge polarization curves display sloping behavior with some small plateau like feature, suggesting a dominant solid-solution type process associated with electrochemical zinc (de)insertion. Interestingly, at higher current rates, discharge-charge capacities increased with cycling, reaching highest value after some cycling. This is most likely related to the kinetic limitation of Zn^{2+} diffusion into the layered structure of the electrode, requiring multiple discharge-charge cycles to open up accessible intercalation sites, before optimal capacity could be achieved. The $Zn_{0.25}V_2O_5.H_2O$ electrodes registered a specific capacity of ~300 mAh g^{-1} (at C/6: 50 mA g^{-1}), which is slightly lower than the $H_2V_3O_8$ electrode. Typically, about 1.2 Zn^{2+} ions are intercalated per mole of $Zn_{0.25}V_2O_5.H_2O$ during the electrochemical discharge process. The high specific capacities obtained for both materials can be ascribed to the large specific surface area and short diffusion distances provided by the nanofiber morphology. It is also important to note that for both the electrodes the voltage polarization curves recorded in the subsequent cycles exhibit identical feature as the first cycle, indicating that the initial structure is recovered at the end of each charge cycle.

As a result of nanostructural morphology, flexible film like electrode architecture, and structural reversibility upon Zn^{2+} de(intercalation) both the electrodes demonstrate superior cyclability at high current rates. **Figures 9A** to **9D** show specific capacity and coulombic efficiency of the $H_2V_3O_8$ (**Figure 9A** and **Figure 9B**) and $Zn_{0.25}V_2O_5.H_2O$ (**Figure 9C** and **Figure 9D**) as a function of cycling at **4C** (**Figure 9A** and **Figure 9C**) and 8C (**Figure 9B** and **Figure 9D**) current rates (For the definition of C rate for $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ see above). As evident, the $Zn_{0.25}V_2O_5.H_2O$ based cell registered excellent cyclability at 8C rate, retaining 80% of the initial specific capacity after 1000 cycles. At 4C, a similar cell delivered 500 cycles with only 20% drop in the initial capacity. Whereas, identical $H_2V_3O_8$ cells demonstrated slightly inferior capacity retention delivering about 40% and 30% of the initial reversible capacity at the end of 300 and 500 cycles, when operated at current rate of 4C and 8C, respectively.

It is important to note that the $H_2V_3O_8$ cell showed distinctively better cycling behavior at higher current rate (8C). This can be linked to the comparatively lower amount Zn^{2+} intercalation per mole of $H_2V_3O_8$, leading to lesser structural strain, which ensures better cyclability. However this feature is not very prominent for the $Zn_{0.25}V_2O_5.H_2O$ based electrode, which suggests higher structural flexibility of $Zn_{0.25}V_2O_5.H_2O$ towards Zn^{2+} (de)intercalation. Higher structural flexibility granted by the presence of interlayer Zn^{2+} ions also ensures excellent electrochemical cyclability of the $Zn_{0.25}V_2O_5.H_2O$ cells. On the contrary, hydrogen bonded VO_x interlayer in $H_2V_3O_8$ lack structural rigidity and flexibility of $Zn_{0.25}V_2O_5.H_2O$, resulting in slightly poor capacity retention. For all the studies nearly 100% coulombic efficiency was registered as a function of cycling, which further confirms the high degree of reversibility of electrochemical Zn^{2+} (de)intercalation into the layered structure of presented vanadium oxide materials.

By virtue of 1D nanomorphology and film like compact yet flexible electrode architecture both the materials delivered splendid rate performance under variable current loading as a function of cycling. **Figure 10A** shows rate capability of $H_2V_3O_8$ and **Figure 10B** shows rate capability of $Zn_{0.25}V_2O_5.H_2O$ cell studied under variable current loading as a function of cycling. The corresponding coulombic efficiencies are also shown. The results are shown in **Figures 10A** and **10B** together with the corresponding coulombic efficiencies registered at variable rates. As expected, $Zn_{0.25}V_2O_5.H_2O$ electrode demonstrates better rate capability; starting with an initial capacity of 285 mAh g^{-1} at 1C rate, the cell delivers 260 mAh g^{-1} of durable capacity at 8C, which reverts back to 285 mAh g^{-1} of capacity at 1C rate, nearly identical to the initial 1C capacity. Whereas $H_2V_3O_8$, starting with a slightly higher initial 1C capacity of 335 mAh g^{-1} falls to 222 mAh g^{-1} of capacity at 8C rate, which doesn't completely recover at 1C at the end of variable current load test. Similar to electrochemical cyclability, better rate performance of $Zn_{0.25}V_2O_5.H_2O$ compared to the $H_2V_3O_8$ electrode is attributed to its more robust and flexible layered structure which is efficiently pillared by immobile Zn^{2+} ions. In both cases, coulombic efficiency increases with current load, which is expected as the unwanted side reactions are suppressed at higher current rates.

Based on the galvanostatic cycling and rate performance results, energy and power densities could be calculated and are presented in the Ragone plot shown in **Figure 11.** The specific energy density is the total energy that can be derived per unit mass of the active electrode material at the cathode. It is the product of specific discharge capacity (Q in mAh g^{-1}) based on the total mass of the active electrode material and the operating voltage in one full discharge. The power density is obtained from the product of current density and average operating voltage.

As evident, beside good cyclability and excellent rate capability, both the $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ based cells delivers good energy density at high power density in comparison to α-MnO_2 (see reference 1) and $Zn_3[Fe(CN)_6]_2$, see reference 2. $Zn_{0.25}V_2O_5.H_2O$ exhibits the highest energy density of the three positive electrodes at high power and delivers a steady and high energy density over a wide range of power.

Conclusions

In summary, we have developed two novel layered vanadium oxide nanomaterials for highly reversible Zn^{2+} storage at high current rates and long term cyclability. Besides, a simple scalable microwave synthesis of vanadium oxide nanomaterials and a versatile water based environmentally green electrode fabrication process is presented. As has been found, presence of stable interlayer species, e.g., H_2O in $H_2V_3O_8$ and Zn^{2+} and/or H_2O in $Zn_{0.25}V_2O_5.H_2O$, plays pivotal role in stabilizing the layered structure against repeated Zn^{2+} de(intercalation), and thereby enables long term cyclability with high specific capacities. Although the average operating cell voltages (0.64 V for $H_2V_3O_8$ and 0.81 V for $Zn_{0.25}V_2O_5.H_2O$) are rather modest, high specific capacities of ~300 mAh g^{-1} ensure high energy density (230-280 Wh kg^{-1}), highest on record among the known aqueous Zn-ion batteries (see **Table 1** below). Good energy density, impressive rate performance and cyclability, cost effective scalable processing of raw materials and electrodes, and not the least high abundance and production of zinc metal make these aqueous zinc ion secondary cells viable candidates for large scale application like grid storage.

Positive/Negative Electrodes	Average Operating Voltage (V)	Energy Density (Wh kg^{-1})	Capacity Retention (Rate)	Reference
α-MnO_2/Zn	1.3 V	225	75% After 100 cycles (6C rate)	**1**
Zinc-hexacyanoferrate/Zn	1.7 V	100	75% After 100 cycles (1C rate)	**2**
$H_2V_3O_8$/Zn	0.64 V	230	70% after 500 cycles (8C rate)	Present Work
$Zn_{0.25}V_2O_5.H_2O$/Zn	0.81 V	280	80% after 1000 cycles (8C rate)	Present Work

Table 1. Operating voltage, energy density, and cycling performance of different rechargeable aqueous Zn-ion batteries.

The foregoing description of the preferred embodiments of the present disclosure has been presented to illustrate the principles of the invention and not to limit the disclosure to the particular embodiments illustrated and described. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.

References

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THEREFORE WHAT IS CLAIMED IS:

1. A zinc ion battery, comprising:

a positive electrode compartment having enclosed therein an intercalation layered positive electrode material $M_xV_2O_5.\mathbf{n}H_2O$, wherein x is in a range from 0.05 to 1, **n** is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_2O_5 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

2. The zinc ion battery according to claim 1 wherein **n** is greater than 0 and less than 1.

3. The zinc ion battery according to claims 1 or 2 wherein some of the waters of hydration are hydrogen bonded to the layers.

4. The zinc ion battery according to claims 1, 2 or 3 wherein the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery.

5. The zinc ion battery according to claims 1, 2, 3 or 4 wherein the electrolyte has a pH in a range from about 1 to about 8.

6. The zinc ion battery according to any one of claims 1 to 5 wherein the electrolyte has a pH in a range from about 4 to about 8.

7. The zinc ion battery according to any one of claims 1 to 6 wherein the intercalation layered cathode material has a nanostructured morphology which is defined by an average particle size of less than or equal to 1000 nm in at least one particle dimension.

8. The zinc ion battery according to claim 7 wherein the average particle size is less than 500 nm in a direction of Zn ion transport through the particle.

9. The zinc ion battery according to any one of claims 1 to 8 wherein the intercalation layered positive electrode material has a particulate morphology being particles having a mean size in a range from about 5 nm to about 50 μm.

10. The zinc ion battery according to claim 9 wherein the particles are coated with electrically conducting material.

11. The zinc ion battery according to claim 10 wherein the electrically conducting material is any one or combination of carbon powder and conducting polymer.

12. The zinc ion battery according to claim 9 wherein the particles are embedded in an electrically conducting matrix.

13. The zinc ion battery according to claim 12 wherein the electrically conducting matrix comprises any one or combination of carbon and conducting polymer, and including a binder.

14. The zinc ion battery according to claim 13 wherein the binder is any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

15. The zinc ion battery according to any one of claims 1 to 14 wherein the negative electrode comprises zinc metal.

16. The zinc ion battery according to claim 15 wherein the negative electrode is a zinc metal electrode.

17. The zinc ion battery according to claim 15 wherein the negative electrode is a zinc alloy.

18. The zinc ion battery according to any one of claims 1 to 14 wherein the negative electrode comprises a current collector, and a surface of the current collector facing into the negative electrode compartment having a layer of zinc bound thereto.

19. The zinc ion battery according to claim 18 wherein the layer of zinc comprises powdered zinc metal.

20. The zinc ion battery according to claim 18 wherein the layer of zinc comprises a sheet of zinc metal.

21. The zinc ion battery according to claim 18, 19 or 20 wherein the current collector is comprised on any one or combination of carbon, boron, lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal.

22. The zinc ion battery according to any one of claims 1 to 14 wherein the negative electrode comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage.

23. The zinc ion battery according to any one of claims 1 to 22 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.01 to about 10 molar.

24. The zinc ion battery according to any one of claims 1 to 23 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.1 to about 4 M.

25. The zinc ion battery according to claim 23 wherein the salt of zinc comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide.

26. A zinc ion battery, comprising:

a positive electrode compartment having enclosed therein and intercalated layered positive electrode material $M_{\mathbf{x}}V_3O_7.\mathbf{n}H_2O$, wherein **x** is in a range from 0.05 to 1, **n** is greater than 0 and less than 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_3O_7 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M and/or hydrogen bonded to the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

27. The material according to claim 26 wherein **n** is greater than 0 and less than 1.

28. The zinc ion battery according to claims 26 or 27 wherein the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery.

29. The zinc ion battery according to claims 26, 27, or 28 wherein the electrolyte has a pH in a range from about 1 to about 8.

30. The zinc ion battery according to any one of claims 26 to 29 wherein the intercalation layered positive electrode material has nanostructured morphology which is defined by an particle size of less than or equal to 1000 nm in at least one particle dimension.

31. The zinc ion battery according to claim 30 wherein the average particle size is less than 500 nm in a direction of Zn ion transport through the particle.

32. The zinc ion battery according to any one of claims 26 to 30 wherein the

intercalation layered positive electrode material has a particulate morphology being particles having a mean size in a range from about 5 nm to about 50 μm.

33. The zinc ion battery according to claim 32 wherein the particles are coated with an electrically conducting material.

34. The zinc ion battery according to claim 33 wherein the electrically conducting material is any one or combination of carbon powder and conducting polymer.

35. The zinc ion battery according to claim 32 wherein the particles are embedded in an electrically conducting matrix.

36. The zinc ion battery according to claim 35 wherein the electrically conducting matrix comprises any one or combination of carbon and conducting polymer, and including a binder.

37. The zinc ion battery according to claim 36 wherein the binder is any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

38. The zinc ion battery according to any one of claims 26 to 37 wherein the negative electrode comprises zinc metal.

39. The zinc ion battery according to claim 38 wherein the negative electrode is a zinc metal electrode.

40. The zinc ion battery according to claim 38 wherein the negative electrode is a zinc alloy.

41. The zinc ion battery according to any one of claims 26 to 37 wherein the negative electrode comprises a current collector, and a surface of the current collector facing into the negative electrode compartment having a layer of zinc bound thereto.

42. The zinc ion battery according to claim 41 wherein the layer of zinc comprises powdered zinc metal.

43. The zinc ion battery according to claim 41 wherein the layer of zinc comprises a sheet of zinc metal.

44. The zinc ion battery according to claim 41, 42 or 43 wherein the current collector is comprised of any one or combination of carbon, boron, lead, vanadium,

chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal.

45. The zinc ion battery according to any one of claims 26 to 37 wherein the negative electrode comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage.

46. The zinc ion battery according to any one of claims 26 to 45 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.01 to about 10 Molar.

47. The zinc ion battery according to any one of claims 26 to 46 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.1 to about 4 M.

48. The zinc ion battery according to any one of claims 26 to 47 wherein the salt of zinc comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide.

49. A zinc ion battery; comprising:

a positive electrode compartment having enclosed therein an intercalated layered positive electrode material $M_xMoO_y.nH_2O$, wherein x is in a range from 0 to

1, y is in a range from 2 to 3, n is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said MoO_y has a layer or tunnel crystal structure, and the metal ions M, if present, pillared between the layers, and waters of hydration coordinated to the metal ions M pillared between the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

50. The zinc ion battery according to claim 49 wherein the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery.

51. The zinc ion battery according to claims 49 or 50 wherein the electrolyte has a pH in a range from about 1 to about 8.

52. The zinc ion battery according to any one of claims 49 to 51 wherein the electrolyte has a pH in a range from about 4 to about 8.

53. The zinc ion battery according to any one of claims 49 to 52 wherein the intercalation layered positive electrode material has nanostructured morphology

which is defined by a particle size of less than or equal to 1000 nm in at least one particle dimension.

54. The zinc ion battery according to claim 53 wherein the average particle size is less than 500 nm in a direction of Zn ion transport through the particle.

55. The zinc ion battery according to any one of claims 49 to 54 wherein the intercalation layered positive electrode material has a particulate morphology being particles having a mean size in a range from about 5 nm to about 50 μm.

56. The zinc ion battery according to claim 55 wherein the particles are coated with electrically conducting material.

57. The zinc ion battery according to claim 56 wherein the electrically conducting material is any one or combination of carbon powder and conducting polymer.

58. The zinc ion battery according to claim 55 wherein the particles are embedded in an electrically conducting matrix.

59. The zinc ion battery according to claim 58 wherein the electrically conducting matrix comprises any one or combination of carbon and conducting polymer, and including a binder.

60. The zinc ion battery according to claim 59 wherein the binder is any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

61. The zinc ion battery according to any one of claims 49 to 60 wherein the negative electrode comprises zinc metal.

62. The zinc ion battery according to claim 61 wherein the negative electrode is a zinc metal electrode.

63. The zinc ion battery according to claim 61 wherein the negative electrode is a zinc alloy.

64. The zinc ion battery according to any one of claims 49 to 60 wherein the negative electrode comprises a current collector, and a surface of the current collector facing into the negative electrode compartment having a layer of zinc bound thereto.

65. The zinc ion battery according to claim 64 wherein the layer of zinc comprises powdered zinc metal.

66. The zinc ion battery according to claim 64 wherein the layer of zinc comprises a sheet of zinc metal.

67. The zinc ion battery according to claim 64, 65 or 66 wherein the current collector is comprised on any one or combination of carbon, boron, lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal.

68. The zinc ion battery according to any one of claims 49 to 67 wherein the negative electrode comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage.

69. The zinc ion battery according to any one of claims 49 to 68 wherein the electrolyte further comprises water said dissolved zinc present in a range from about 0.01 to about 10 molar.

70. The zinc ion battery according to any one of claims 49 to 69 wherein the electrolyte further comprises water said dissolved zinc present in a range from about 0.1 to about 4 M.

71. The zinc ion battery according to any one of claims 49 to 70 wherein the salt of zinc comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate,

zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide.

72. The zinc ion battery according to any one of claims 49 to 71 wherein n is greater than 0 and less than 2.

73. The zinc ion battery according to any one of claims 49 to 72 wherein some of the waters of hydration are hydrogen bonded to the layers.

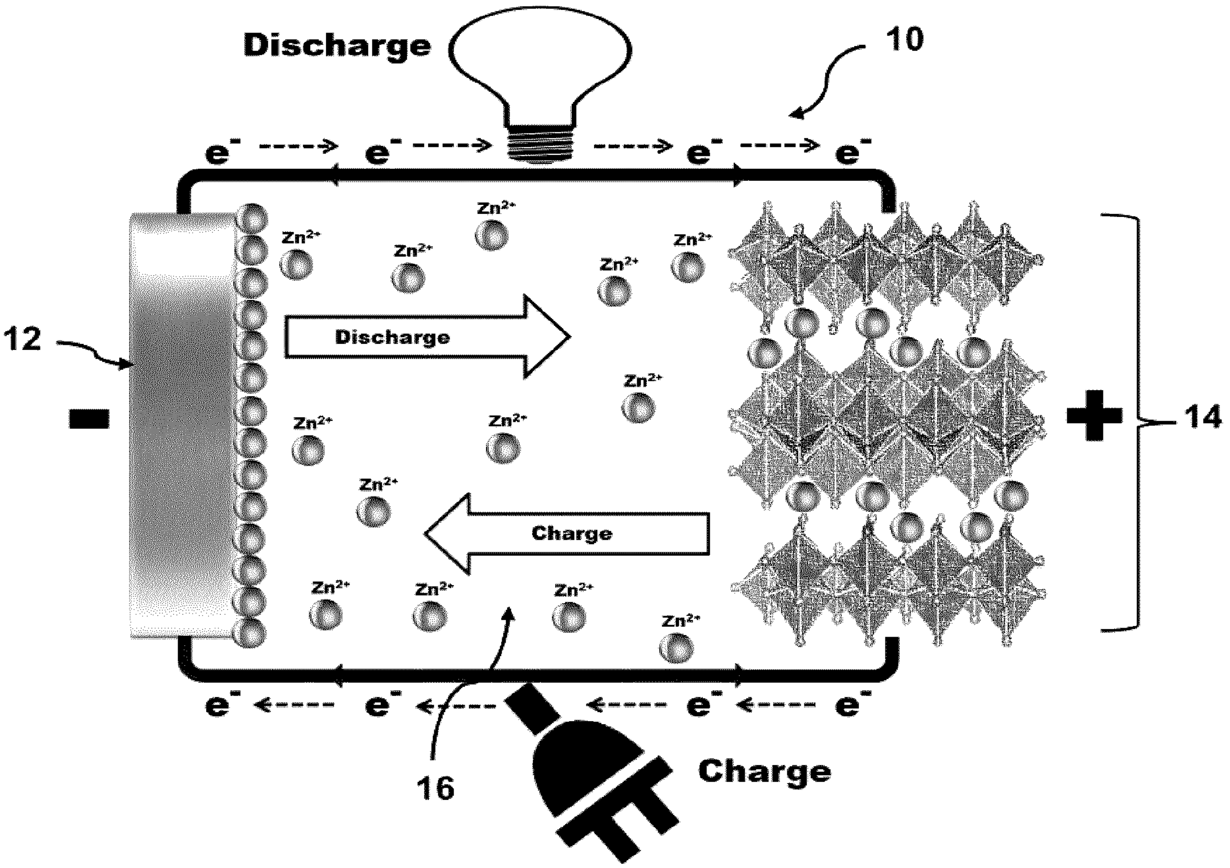


Figure 1A

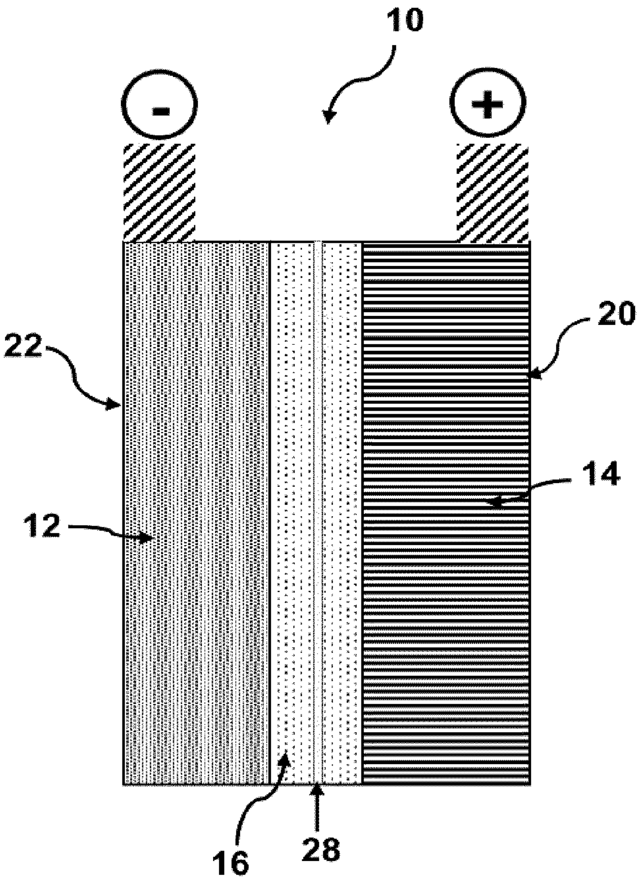
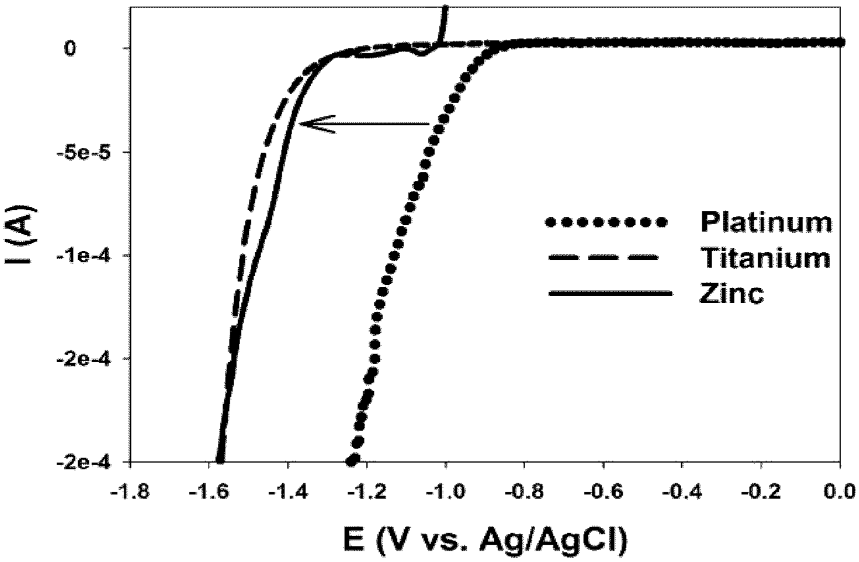


Figure 1B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-2e-4
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-1.4
-1.2
-1.0
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0.0
E (V vs. Ag/AgCl)
Platinum
Titanium
Zinc

Figure 2

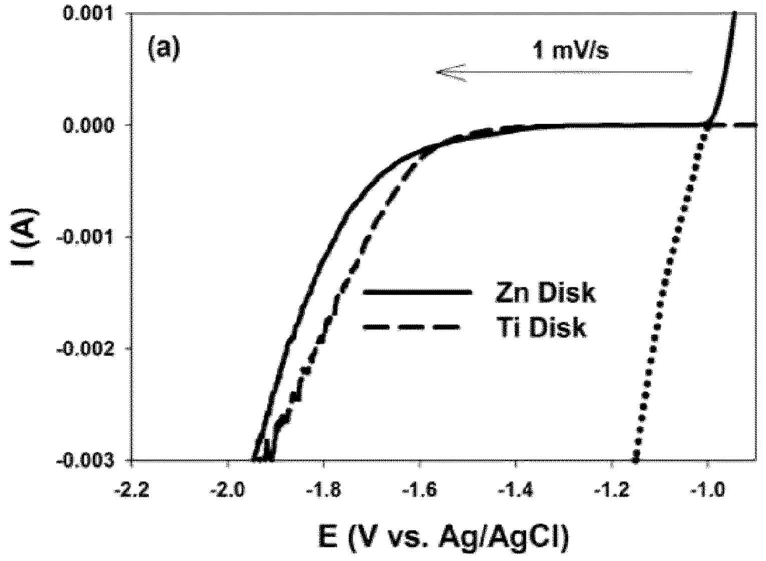


Figure 3A

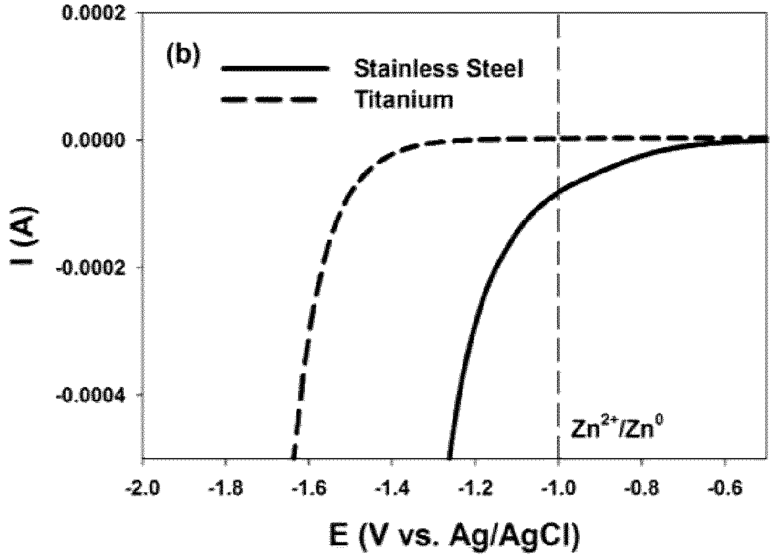


Figure 3B

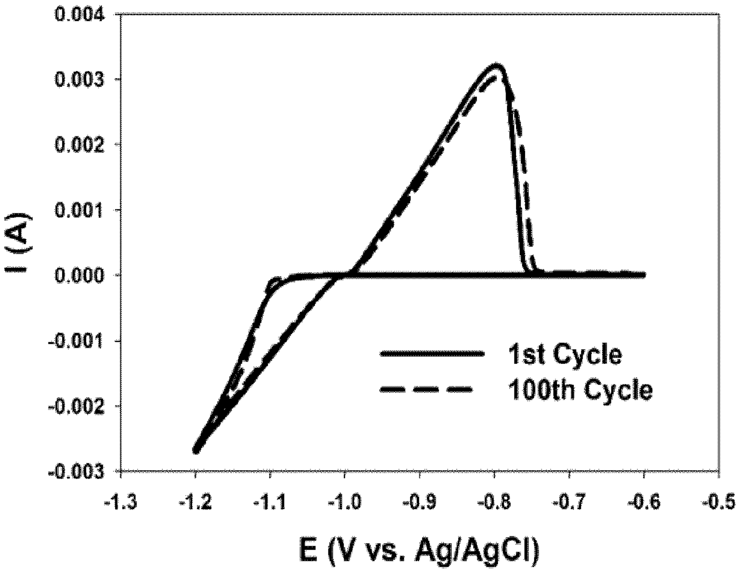


Figure 4A

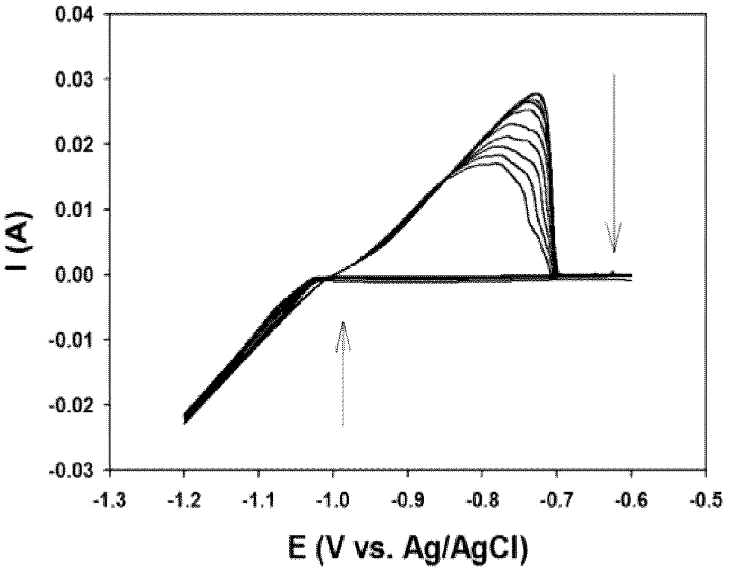
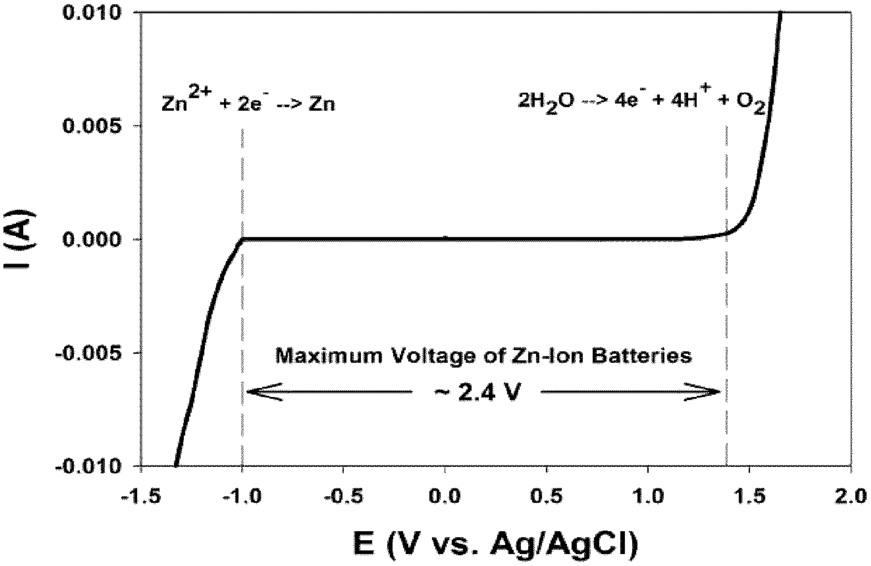


Figure 4B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0.000
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-0.010
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-0.5
0.0
0.5
1.0
1.5
2.0
E (V vs. Ag/AgCl)
$Zn^{2+} + 2e^- \rightarrow Zn$
$2H_2O \rightarrow 4e^- + 4H^+ + O_2$
Maximum Voltage of Zn-Ion Batteries
~ 2.4 V

Figure 5

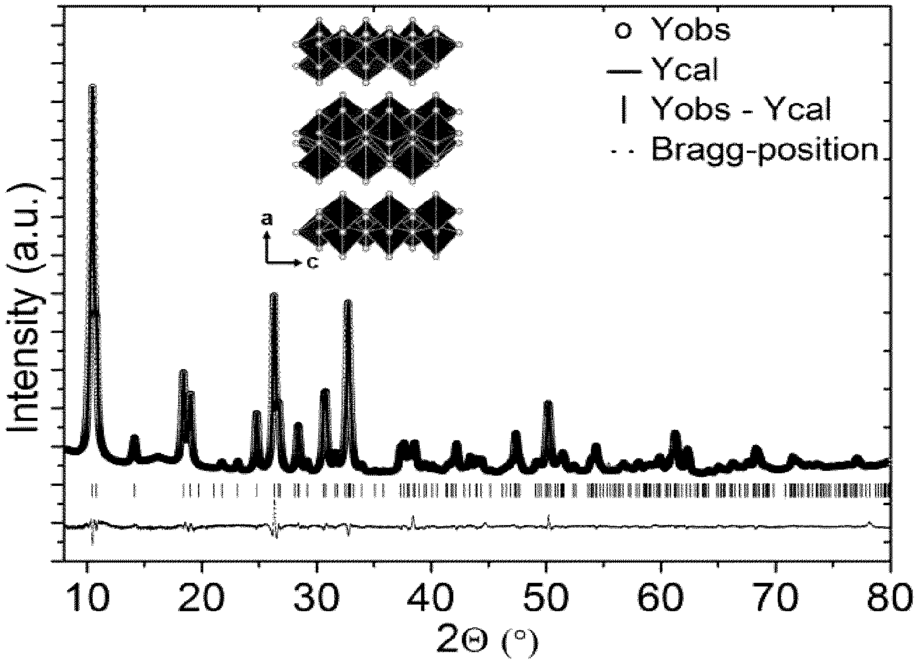

Figure 6A

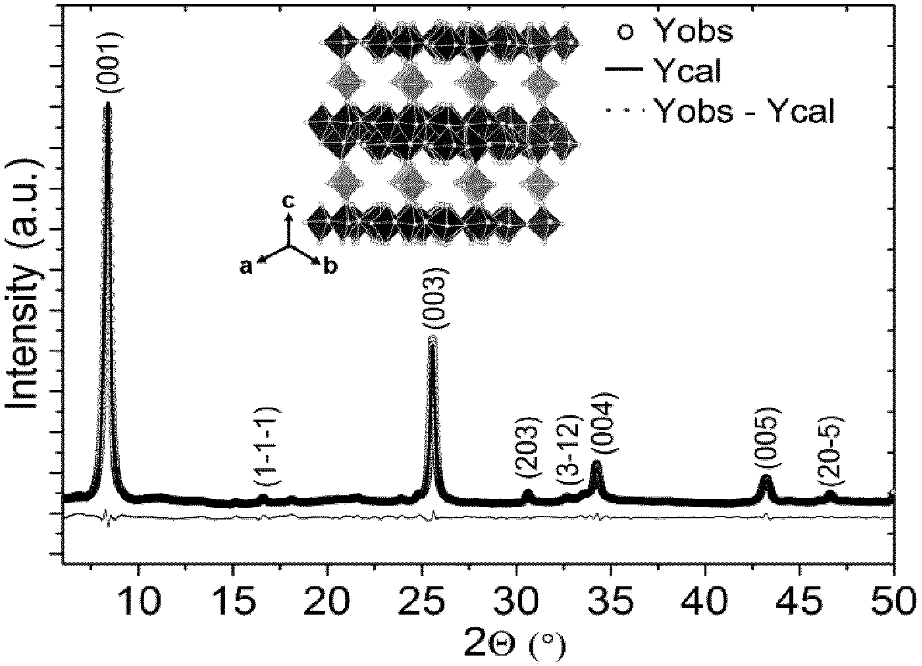

Figure 6B

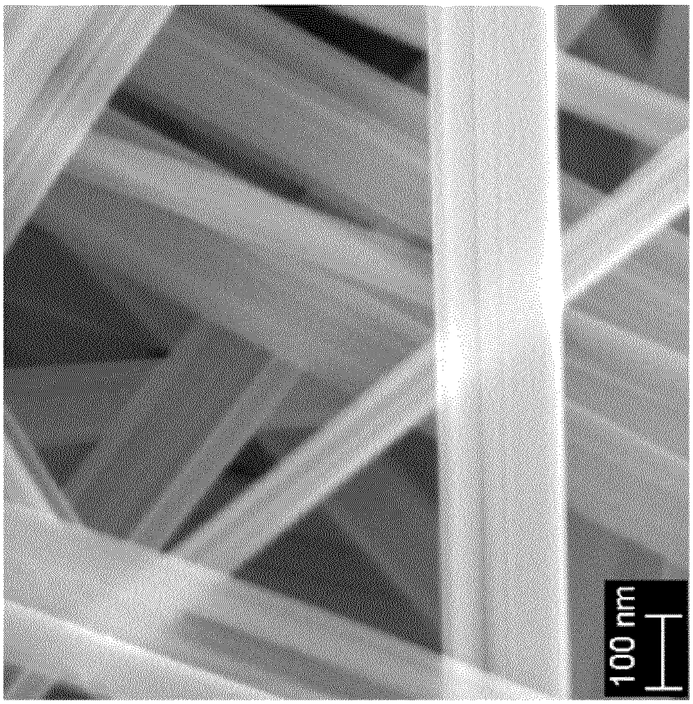

Figure 7B

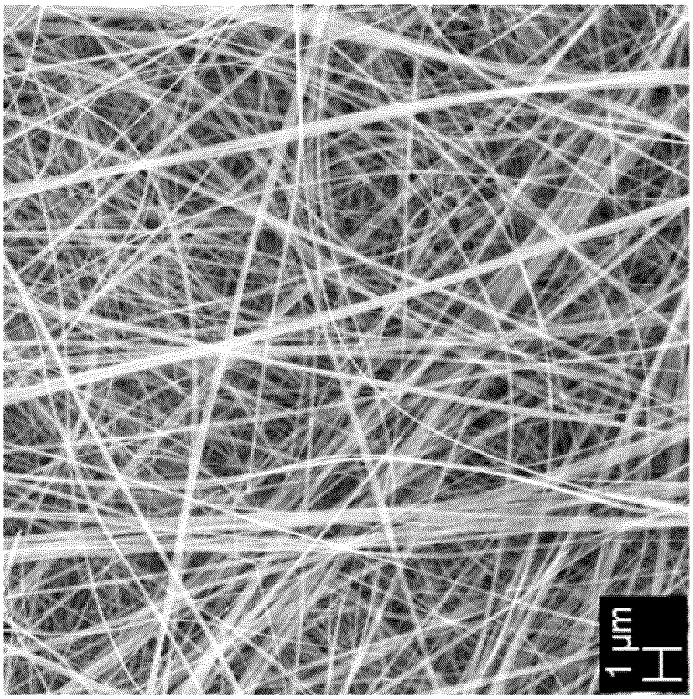

Figure 7A

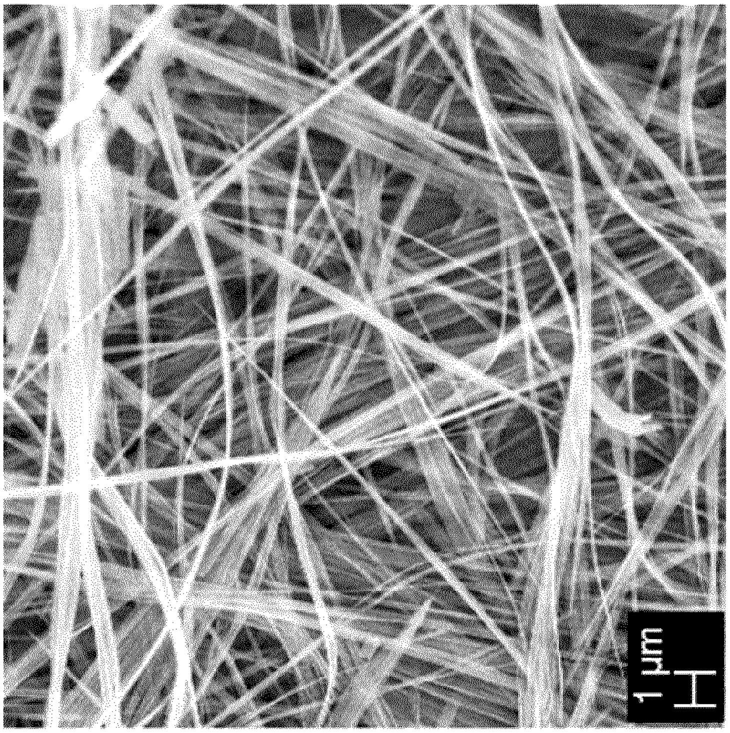

Figure 7C

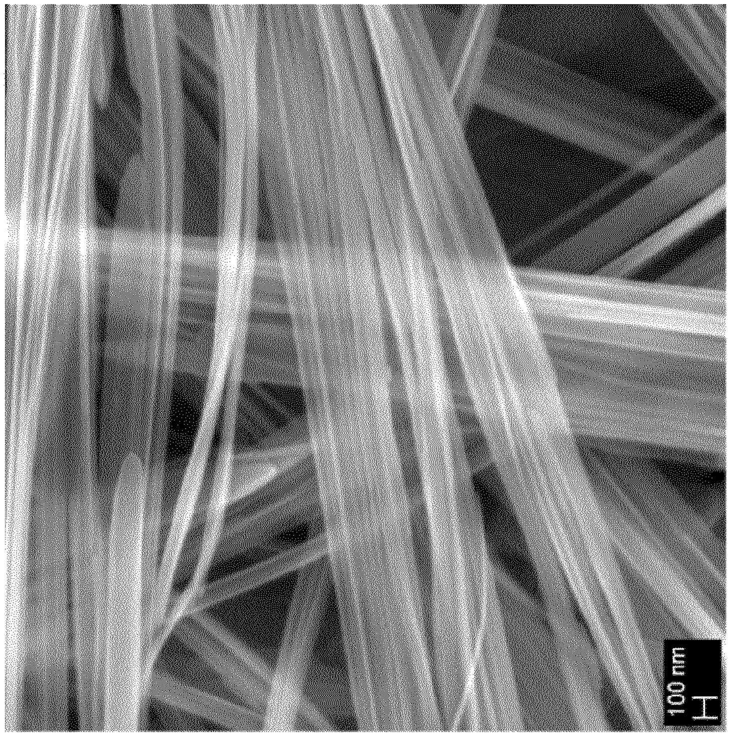

Figure 7D

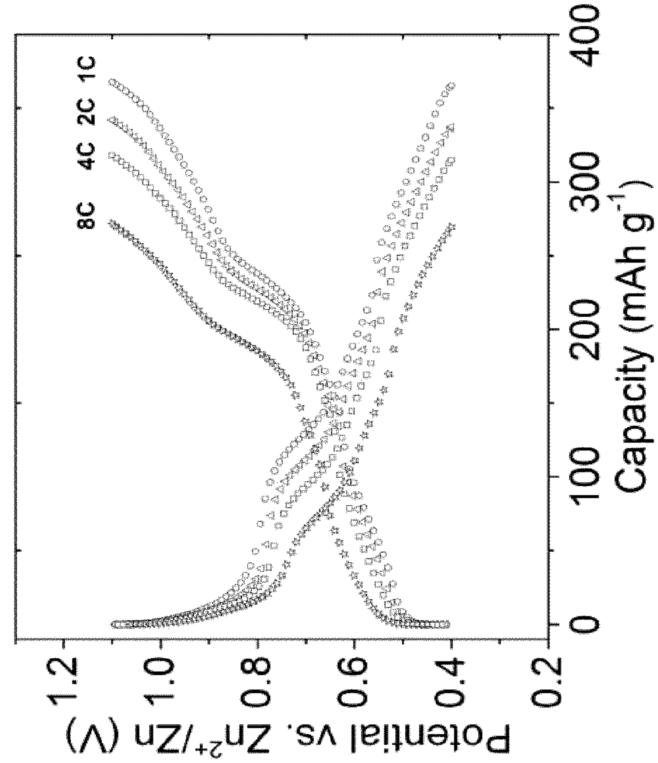

Figure 8A

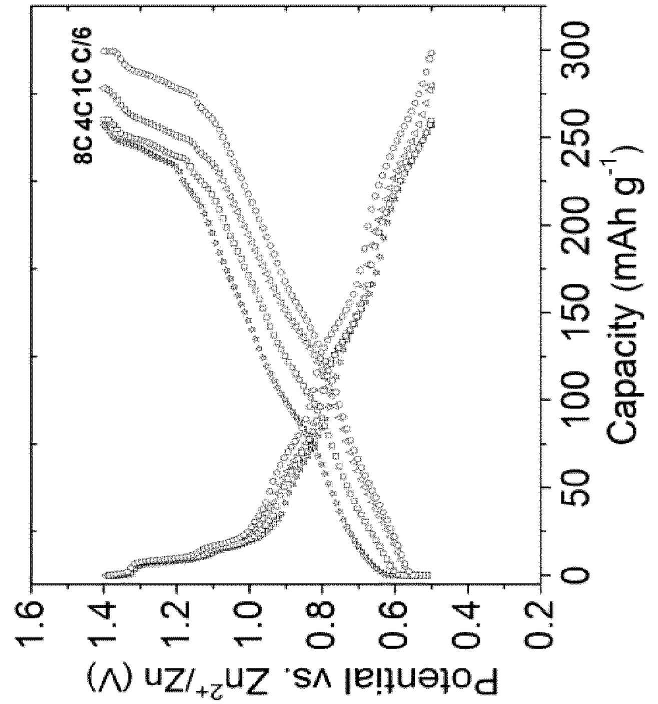

Figure 8B

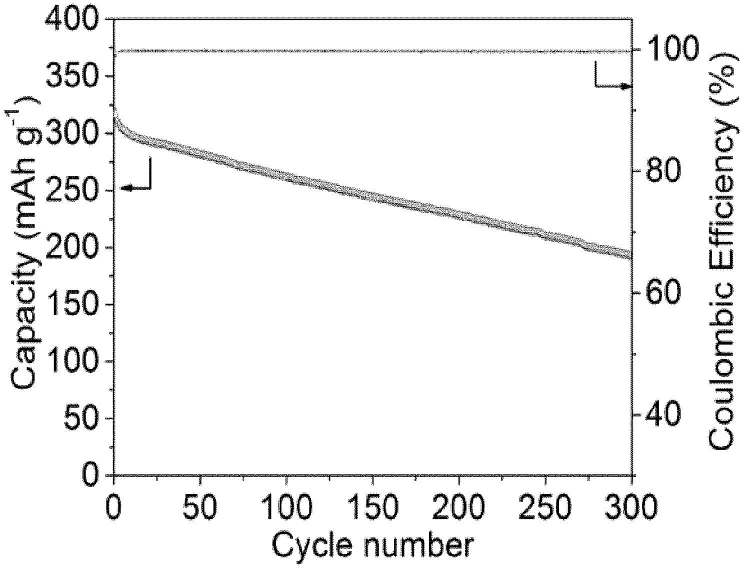

Figure 9A

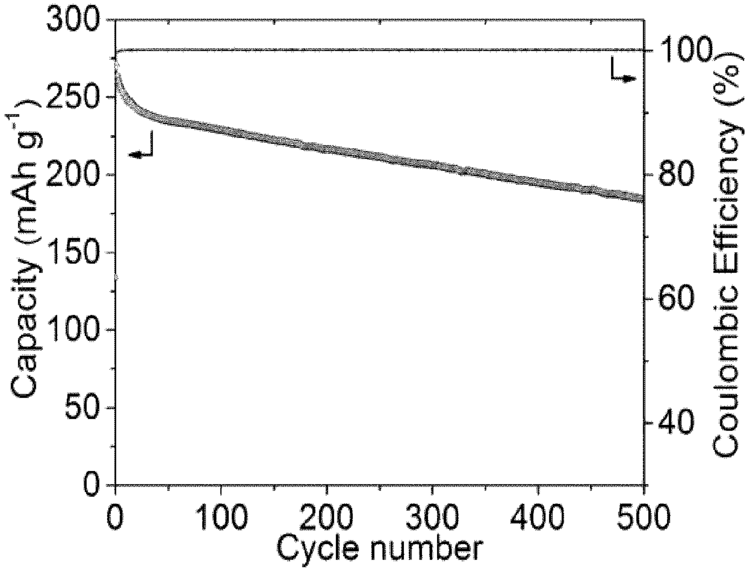

Figure 9B

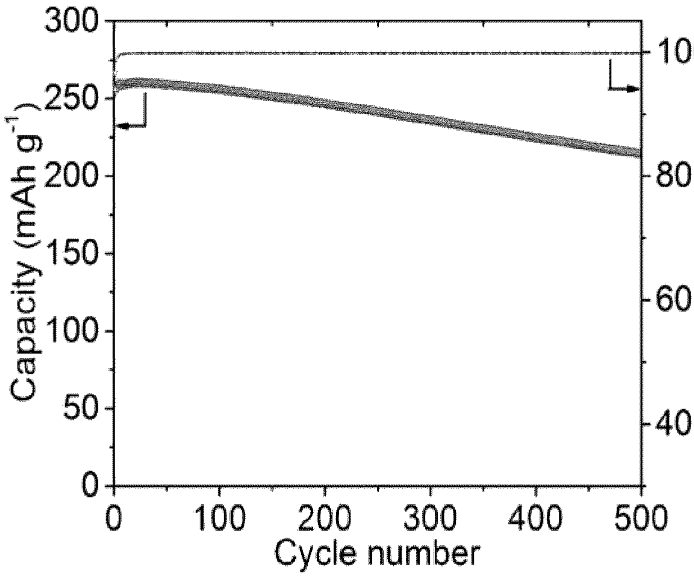

Figure 9C

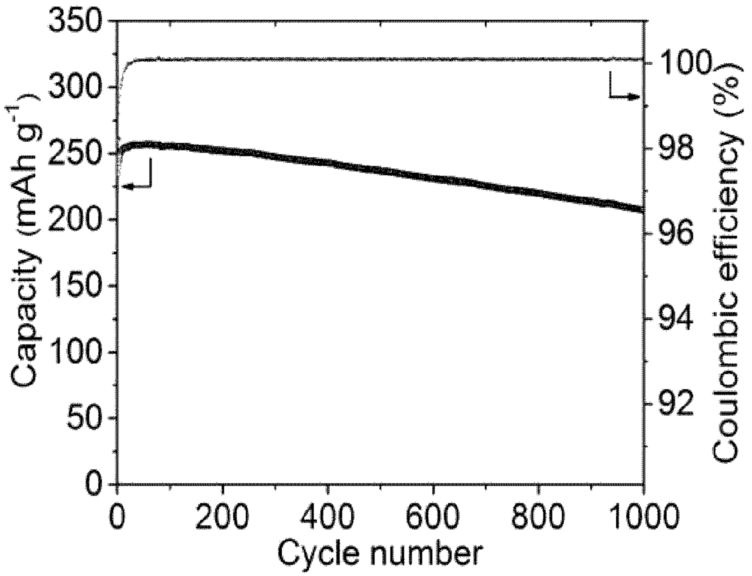

Figure 9D

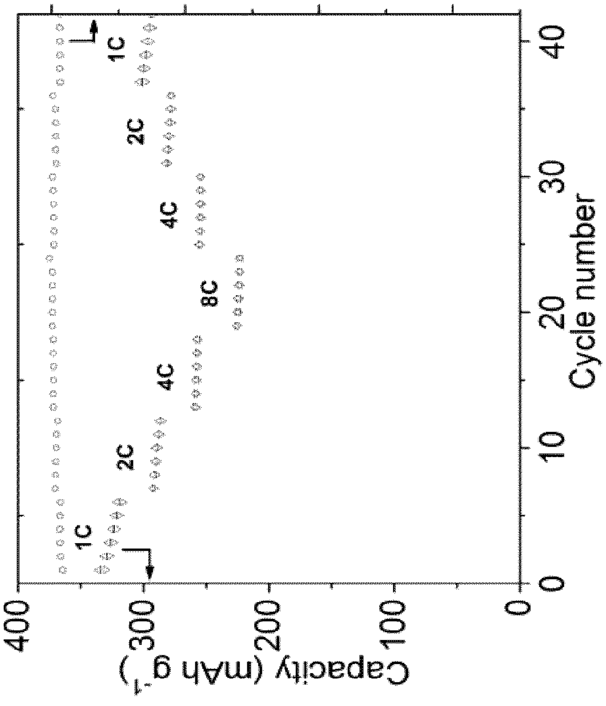

Figure 10A

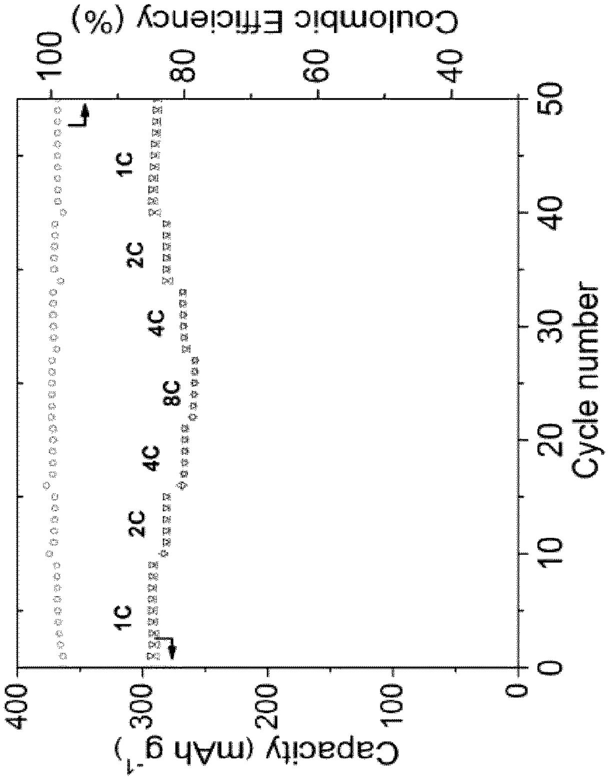

Figure 10B

14/14

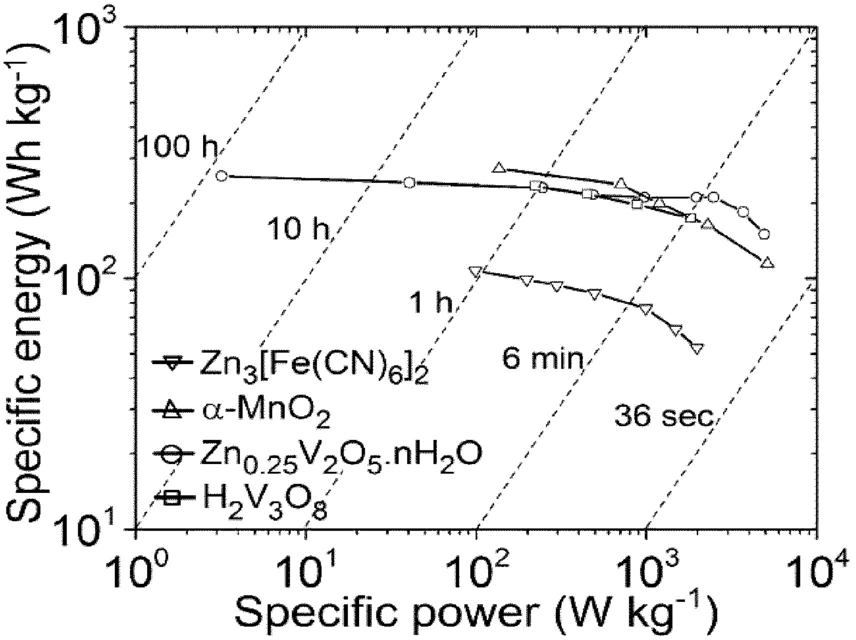

Figure 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2016/050613

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***H01M 10/36*** (2010.01) , ***H01M 4/42*** (2006.01) , ***H01M 4/485*** (2010.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
PC (2010.01): H01M 10/36, H01M 4/485; IPC (2006.01): H01M 4/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Databases: QUESTEL, Canadian Patent Database, CIPO Library Discovery Tool
Keywords: battery, cell, electrochemical, zinc, vanadium, vanadium oxide, vanadium pentoxide, znxv2o5 or znv2o5 or mxv2o5, cathode, positive, aqueous, water, alkaline

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/112660 A1 (ADAMSON at al.) 1 August 2013 (01-08-2013) *whole document*	1-25
A	US 5,336,572 (KOKSBANG) 9 August 1994 (09-08-1994) *whole document*	1-25
A	US 2013/0157138 A1 (METTAN et al.) 20 June 2013 (20-06-2013) *whole document*	1-25
A	CN 102110858 (WANG et al.) 29 June 2011 (29-06-2011), abstract and machine English translation of description.	1-25
A	LE et al., "Intercalation of Polyvalent Cations into V_2O_5 Aerogels", *Chemistry of Materials*, Volume 10 (3) (1998), Pages 682–684.	1-25

☑ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
12 September 2016 (12-09-2016)

Date of mailing of the international search report
21 September 2016 (21-09-2016)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 819-953-2476

Authorized officer

Philip Gbor (819) 639-8475

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JIAHONG et al., "AC Impedance Study of the Aqueous Zn/V_2O_5 Secondary Battery", *ACTA PHYSICOCHIMICA SINICA*, Volume 16, No. 5 (2000), Pages 454-458 (abstract; and Figure 1).	1-25
A	GIORGETTI et al., "Identification of an unconventional zinc coordination site in anhydrous $Zn_xV_2O_5$ aerogels from x-ray absorption", *Chemistry of Materials*, Volume 11(8) (1999), Pages 2257-2264.	1-25
A	ZHANG et al., "Hydrothermal synthesis and characterization of a series of novel zinc vanadium oxides as cathode materials", *Materials Research Society Symposium - Proceedings, Materials for Electrochemical Energy Storage and Conversion II - Batteries, Capacitors and Fuel Cells*, 496 (1998), Pages 367-372) .	1-25

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Group A: Claims 1-25
Group B: Claims 26-48
Group C: Claims 49-73
Continued on extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

1-25

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2013112660A1	01 August 2013 (01-08-2013)	WO2013112660A1 US2015244031A1	01 August 2013 (01-08-2013) 27 August 2015 (27-08-2015)
US5336572A	09 August 1994 (09-08-1994)	US5336572A AU7104594A WO9429913A1	09 August 1994 (09-08-1994) 03 January 1995 (03-01-1995) 22 December 1994 (22-12-1994)
US2013157138A1	20 June 2013 (20-06-2013)	US2013157138A1 US9023527B2 EP2607319A1 EP2607319B1	20 June 2013 (20-06-2013) 05 May 2015 (05-05-2015) 26 June 2013 (26-06-2013) 25 February 2015 (25-02-2015)
CN102110858A	29 June 2011 (29-06-2011)	CN102110858A CN102110858B	29 June 2011 (29-06-2011) 17 April 2013 (17-04-2013)

Continuation of Box No. III

The International Searching Authority found multiple (groups of) inventions in this international application, as follows:

Group A:
Claims 1-25 are directed to a zinc ion battery, comprising: a positive electrode compartment having enclosed therein the electrode material $M_xV_2O_5.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

Group B:
Claims 26-48 are directed to a zinc ion battery, comprising: a positive electrode compartment having enclosed therein the positive electrode material $M_xV_3O_7.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

Group C:
Claims 49-73 are directed to a zinc ion battery; comprising: a positive electrode compartment having enclosed therein the positive electrode material $M_xMoO_Y.nH_2O$, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state; a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator; and an electrolyte.

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM
First Named Inventor/Applicant Name:	Brian D. ADAMS
Filer:	Ralph A. Dowell
Attorney Docket Number:	19920NP

Filed as Large Entity

Filing Fees for **U.S. National Stage under 35 USC 371**

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
NATIONAL STAGE FEE	1631	1	280	280
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		280

Electronic Acknowledgement Receipt

EFS ID:	28723630
Application Number:	15513914
International Application Number:	PCT/CA2016/050613
Confirmation Number:	3998
Title of Invention:	ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM
First Named Inventor/Applicant Name:	Brian D. ADAMS
Customer Number:	293
Filer:	Ralph A. Dowell
Filer Authorized By:	
Attorney Docket Number:	19920NP
Receipt Date:	23-MAR-2017
Filing Date:	
Time Stamp:	18:15:41
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$280
RAM confirmation Number	032417INTEFSW18171100
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

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<tr><td rowspan="2">3</td><td rowspan="2"></td><td rowspan="2">19920WOapp.pdf</td><td>3678733</td><td rowspan="2">yes</td><td rowspan="2">61</td></tr>
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<tr><td rowspan="7"></td><td colspan="5">Multipart Description/PDF files in .zip description</td></tr>
<tr><td colspan="3">Document Description</td><td>Start</td><td>End</td></tr>
<tr><td colspan="3">Abstract</td><td>1</td><td>1</td></tr>
<tr><td colspan="3">Specification</td><td>2</td><td>28</td></tr>
<tr><td colspan="3">Claims</td><td>29</td><td>42</td></tr>
<tr><td colspan="3">Drawings-only black and white line drawings</td><td>43</td><td>56</td></tr>
<tr><td colspan="3">Documents submitted with 371 Applications</td><td>57</td><td>61</td></tr>
<tr><td colspan="6">Warnings:</td></tr>
<tr><td colspan="6">Information:</td></tr>
<tr><td rowspan="2">4</td><td rowspan="2">Fee Worksheet (SB06)</td><td rowspan="2">fee-info.pdf</td><td>30191</td><td rowspan="2">no</td><td rowspan="2">2</td></tr>
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<tr><td colspan="6">Warnings:</td></tr>
<tr><td colspan="6">Information:</td></tr>
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Total Files Size (in bytes):	5866477

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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Application number: 62230502

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THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

July 13, 2016

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: *62/230,502*
FILING DATE: *June 08, 2015*

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US62/230,502*

Certified by

Michelle K. Lee

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

02215 U.S.PTO
060815

U.S. PTO
62/230502
06/08/2015

Doc Code: **TR.PROV**
Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 05/31/2015. OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
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Provisional Application for Patent Cover Sheet

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

Inventor(s)

Inventor 1 Remove

Given Name	Middle Name	Family Name	City	State	Country i
Linda	Faye	Nazar	Waterloo	ON	CA

Inventor 2 Remove

Given Name	Middle Name	Family Name	City	State	Country i
Dipan		Kundu	Kitchener	ON	CA

Inventor 3 Remove

Given Name	Middle Name	Family Name	City	State	Country i
Brian		Adams	Mitchell	ON	CA

All Inventors Must Be Listed – Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Title of Invention	Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes
Attorney Docket Number (if applicable)	

Correspondence Address

Direct all correspondence to (select one):

○ The address corresponding to Customer Number ● Firm or Individual Name

Firm or Individual Name 1	University of Waterloo
Firm or Individual Name 2	Waterloo Commercialization Office

Mailing Address of Applicant:

Address 1	Office of Research		
Address 2	200 University Avenue West		
City	Waterloo	State/Province	ON
Postal Code	N2L 3G1	Country i	CA
Phone	519-888-4567 ext. 33300		

Doc Code: **TR.PROV**
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.
● No.
○ Yes, the invention was made by an agency of the United States Government. The U.S. Government agency name is:
○ Yes, the invention was under a contract with an agency of the United States Government. The name of the U.S. Government agency and Government contract number are:

Doc Code: **TR.PROV**
Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
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Entity Status
Applicant asserts small entity status under 37 CFR 1.27 or applicant certifies micro entity status under 37 CFR 1.29

● Applicant asserts small entity status under 37 CFR 1.27

○ Applicant certifies micro entity status under 37 CFR 1.29. Applicant must attach form PTO/SB/15A or B or equivalent.

○ No

Warning

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

Signature

Please see 37 CFR 1.4(d) for the form of the signature.

Signature				Date (YYYY-MM-DD)	2013-06-08
First Name	Linda	Last Name	Nazar	Registration Number (If appropriate)	

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.**

Doc Code: **TR.PROV**
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● Applicant asserts small entity status under 37 CFR 1.27

○ Applicant certifies micro entity status under 37 CFR 1.29. Applicant must attach form PTO/SB/15A or B or equivalent.

○ No

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Signature

Please see 37 CFR 1.4(d) for the form of the signature.

Signature	L.Y. Naz			Date (YYYY-MM-DD)	2013-06-08
First Name	Linda	Last Name	Nazar	Registration Number (If appropriate)	

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.**

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or paten. Accordingly, pursuant to the requirements of the Act, please be advised that : (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

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1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to an other federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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FEE TRANSMITTAL

☒ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 130

Complete if known

Application Number	
Filing Date	
First Named Inventor	Linda Nazar
Examiner Name	
Art Unit	
Practitioner Docket No.	

METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): ____________

☒ Deposit Account Deposit Account Number: 501411 Deposit Account Name: Fikre Tekeste, Questel

For the above-identified deposit account, the Director is hereby authorized to (check all that apply):

☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, **except for the filing fee**

☐ Charge any additional fee(s) or underpayment of fee(s) under 37 CFR 1.16 and 1.17 ☐ Credit any overpayment of fee(s)

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FEE CALCULATION

1. BASIC FILING, SEARCH, AND EXAMINATION FEES

	FILING FEES		SEARCH FEES		EXAMINATION FEES		
Application Type	Fee ($)	Small Entity Fee ($)	Fee ($)	Small Entity Fee ($)	Fee ($)	Small Entity Fee ($)	Fees Paid ($)
Utility	390	195	620	310	250	125	
Design	250	125	120	60	160	80	
Plant	250	125	380	190	200	100	
Reissue	390	195	620	310	760	380	
Provisional	250	125	0	0	0	0	130

2. EXCESS CLAIM FEES

Fee Description	Fee ($)	Small Entity Fee ($)
Each claim over 20 (including Reissues)	62	31
Each independent claim over 3 (including Reissues)	250	125
Multiple dependent claims	460	230

Total Claims ______ -20 or HP = Extra Claims ______ x Fee ($) ______ = Fee Paid ($) ______

HP = highest number of total claims paid for, if greater than 20.

Indep. Claims ______ -3 or HP = Extra Claims ______ x Fee ($) ______ = Fee Paid ($) ______

HP = highest number of independent claims paid for, if greater than 3.

Multiple Dependent Claims Fee ($) ______ Fee Paid ($) ______

3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is $320 ($160 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets ______ - 100 = Extra Sheets ______ / 50 = Number of each additional 50 or fraction thereof ______ (round up to a whole number) x Fee ($) ______ = Fee Paid ($) ______

4. OTHER FEE(S)

Fees Paid ($)

Non-English specification, $130 fee (no small entity discount) ______

Non-electronic filing fee under 37 CFR 1.16(t) for a utility application, $400 fee ($200 small entity) ______

Other (e.g., late filing surcharge): ______

SUBMITTED BY

Signature		Registration No. (Attorney/Agent)	Telephone 703-519-5744
Name (Print/Type)	Fikre Tekeste		Date 06/08/2015

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	
	Application Number	
Title of Invention	Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	**Given Name**	**Middle Name**	**Family Name**	**Suffix**
Dr.	Linda	Faye	Nazar	

Residence Information (Select One) ○ US Residency ● Non US Residency ○ Active US Military Service

City	Waterloo	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	45-225 Benjamin Road		
Address 2			
City	Waterloo	**State/Province**	ON
Postal Code	N2V 1Z3	**Country i**	CA

Inventor 2 Remove

Legal Name

Prefix	**Given Name**	**Middle Name**	**Family Name**	**Suffix**
Dr.	Dipan		Kundu	

Residence Information (Select One) ○ US Residency ● Non US Residency ○ Active US Military Service

City	Kitchener	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	1012 - 11 Overlea Drive		
Address 2			
City	Kitchener	**State/Province**	ON
Postal Code	N2M 5C8	**Country i**	CA

Inventor 3 Remove

Legal Name

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	
	Application Number	
Title of Invention	Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes	

Prefix	Given Name	Middle Name	Family Name	Suffix
Mr.	Brian		Adams	

Residence Information (Select One) ○ US Residency ● Non US Residency ○ Active US Military Service

City	Mitchell	Country of Residence i	CA

Mailing Address of Inventor:

Address 1	228 Morenz Drive		
Address 2			
City	Mitchell	**State/Province**	ON
Postal Code	N0K 1N0	**Country i**	CA

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☒ **An Address is being provided for the correspondence Information of this application.**

Name 1	WatCo, Office of Research	**Name 2**	University of Waterloo
Address 1	200 University Avenue West		
Address 2			
City	Waterloo	**State/Province**	ON
Country i	CA	**Postal Code**	N2L 3G1
Phone Number	519-888-4567 ext. 33300	**Fax Number**	
Email Address	zadilsky@uwaterloo.ca	Add Email	Remove Email
Email Address	sbagheri@uwaterloo.ca	Add Email	Remove Email

Application Information:

Title of the Invention	Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes		
Attorney Docket Number		**Small Entity Status Claimed**	☒
Application Type	Provisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)		**Suggested Figure for Publication (if any)**	

Filing By Reference :

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	
	Application Number	
Title of Invention	Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes	

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	
	Application Number	

Title of Invention	Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes

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Title of Invention	Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes	

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First Name	Linda	Last Name	Nazar	Registration Number	

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Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes

Inventors:

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The United States Government has rights in this invention pursuant to DOE-FOA-0000559, Energy Innovation Hub — Batteries and Energy Storage, and [ANL Subcontract No. 3F-32281], issued under DOE Prime Contract No. DE-AC02-06CH11357 between the United States Government and UChicago Argonne, LLC representing Argonne National Laboratory.

What is claimed here are material composition and method of synthesis for Aqueous Zn-Ion Batteries Using a Metallic Zinc Negative Electrode and Vanadate Positive Electrodes, related to the field of rechargeable Zinc-Ion batteries and their applications in power storage, as generally and as specifically described herein;

Abstract

The present invention pertains to claims related to a low cost rechargeable Zn battery based on a cathode comprised of nanostructured hydrated vanadium oxides as robust materials for high rate and long term reversible Zn^{2+} ion intercalation storage at the cathode, that are coupled with a metallic Zn anode, and an aqueous electrolyte. Vanadium possesses a range of oxidation states (+2 to +5), which allows for multiple redox and hence large specific capacities. Layered $M_xV_nO_m$ oxides (M = metal ion) of compositions such as V_2O_5, V_3O_8, V_4O_{11} - that are made of two dimensional sheet structures - have been the subject of intense investigation for both non-aqueous and aqueous alkali (Li and Na) ion batteries. The additional presence of interlayer metal ions and/or water of hydration in such layered oxides act as pillars, providing structural stability during long term charge discharge cycling. Two vanadates that embody such qualities are $H_2V_3O_8$ and $Zn_xV_2O_5$, which we have synthesized in nanofiber morphology by a simple and rapid microwave hydrothermal method, without using any toxic or corrosive chemical. These are converted to freestanding film electrodes by adopting a low-cost and green, water based electrode fabrication process. The nanomorphology of the product and compact film structure allows for facile release of strain resulting upon Zn^{2+} cycling, short ion diffusion paths, good interaction with carbon additives with the active material and robust conductive wiring at the cathode. An additional contribution to the technology is the use of a titanium or titanium coated

current collector for Zn deposition at the negative electrode. This material has a substantial overpotential for hydrogen evolution, which is comparable to Zn itself. This combination facilitates high specific capacities of up to 350 mAh g^{-1} and long term cyclabilities up to 1000 cycles at 100% coulombic efficiency using fast current rates. It thus gives rise to predicted gravimetric energy densities up to 280 Wh/kg for the cathode alone, and between 200 – 250 Wh/kg including the mass of the zinc anode.

Introduction

The energy driven technological revolution of the past century has made our lives easy in many ways. However, in doing so, we have relied solely on the combustion of fossil fuels that has led to severe environmental damage and now we are on the verge of a global climate change. This has raised the call for an environmentally responsible energy economy relying on cheap and sustainable energy generation and storage. In this backdrop, renewable energy resources (solar, wind, etc.) along with electrochemical energy storage devices based on batteries have gained prominence as a result of considerable breakthroughs in the last two decades. Primary batteries have been replaced with rechargeable (secondary) types for all uses, with the exception of small consumer portable electronics. Four main types of secondary batteries currently dominate the commercial market: lead-acid, nickel-cadmium, nickel metal-hydride, and lithium-ion. Lead-acid batteries have remained as the leader (for the past century) for certain applications where their low gravimetric energy density is not a major concern; specifically automotive starter sources and backup power supplies. Nickel-cadmium cells made their way into markets of portable power tools in the 1980s and 1990s, but have been since replaced by nickel metal-hydride cells due to the toxicity of cadmium. Nickel metal-hydride are still used today for certain applications, but are being replaced by lithium ion batteries (LIBs) which have become the frontrunner by revolutionizing the portable electronics market and raising the stake of electrified transportation. Unfortunately, despite the high energy and high power of some LIBs, concerns over the future cost of lithium and the sustainability of the resources, and safety hazards of using highly flammable and toxic organic electrolyte limit their application to some extent. In this context, rechargeable aqueous batteries which utilize cheap and safe water based electrolytes, and do not involve the dry atmospheric assembly conditions of non-aqueous batteries, are attracting tremendous attention. In addition, the high ionic conductivities of aqueous electrolytes (1 S cm^{-1}) compared to non-aqueous electrolytes (1-10 mS cm^{-1}) favor high rate capabilities suitable for emerging applications.

The use of metallic negative electrodes in either primary or secondary type batteries is also quite attractive as a means to achieve high energy densities and for ease of battery assembly (and ultimately lowering costs). In general, the most reducing metals (**Table 1**) happen to be the lightest weight, and thus, have the highest theoretical gravimetric capacities. On the other hand, the heavier metals have greater densities, which in turn lead to higher volumetric capacities. There is a trade-off between the reduction potential of a metal – low values giving higher cell voltages – and safety concerns. Since all metals listed in **Table 1** have E° values below 0 V vs. SHE (defined by $2H^+ + 2e^- \rightarrow H_2$), they all have the potential to react with water to evolve hydrogen. Particularly, the lightweight metals (lithium, potassium, calcium, sodium, and magnesium) spontaneously react with even trace amounts of water from the atmosphere.

Of all the metals, zinc is the most reducing candidate which is stable in water. For this reason, zinc has been utilized as the negative electrode in primary aqueous battery systems including Leclanché cells (i.e., modern zinc-carbon cells), zinc-chloride cells, alkaline cells, zinc-air cells, and mercury oxide cells. In most of these battery types, an alkaline electrolyte is used, where zinc metal is oxidized to form the soluble zincate ion (eq. 1) or further can be irreversibly oxidized to ZnO precipitates (eq. 2,3):

(1) $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$

(2) $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

(3) $Zn(OH)_2 \rightarrow ZnO + H_2O$

Table 1. Comparison of various metals for use as battery anodes (negative electrodes).

Metal	**E° (V vs. SHE)**	**Theoretical Gravimetric Capacity (mAh g^{-1})**	**Theoretical Volumetric Capacity (mAh cm^{-3})**	**Commercial Battery Types***	**Issues with Metal Anodes in Commercial Battery Systems**
Lithium $Li^+ + e^- \rightarrow Li(s)$	-3.04	3861	2061	$Li\text{-}SO_2$ (P), $Li\text{-}SOCl_2$ (P), $Li\text{-}FeS_2$ (P), $Li\text{-}I_2$ (P), $Li\text{-}MnO_2$ (P), $Li\text{-}(CF)_n$ (P)	Reactive with atmosphere.
Potassium $K^+ + e^- \rightarrow K(s)$	-2.92	686	590	None	Extremely reactive.
Calcium $Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.76	1337	2060	None	Reactive with atmosphere.
Sodium $Na^+ + e^- \rightarrow Na(s)$	-2.71	1166	1131	Sodium-Sulfur (S)	Reactive with atmosphere.
Magnesium $Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.38	2205	3837	Mg-CuCl (P)	High self discharge rate of Mg-CuCl cells requires them to be made "dry charged" and add water when energy is required. Mg plating/stripping is difficult in non-aqueous electrolytes inhibiting development of secondary cells.
Aluminum $Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66	2980	8046	Aluminum-Air (P)	Primary or mechanically rechargeable only.
Zinc $Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76	820	5845	Leclanché (P), Alkaline (P), Zinc-Air (P), Zinc-Chloride (P), Mecury Oxide (P)	Dissolution of Zn at high pH.
Iron $Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.41	960	7554	Iron Nickel (S), Iron-Air (S), Iron Silver (S)	Self-discharge of iron electrode due to H_2 evolution ($Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$).
Cadmium $Cd^{2+} + 2e^- \rightarrow Cd(s)$	-0.40	477	4149	Mercury Oxide (P), Nickel Cadmium (S)	Toxic element.
Nickel $Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.23	913	8138	None	Batteries based off of nickel typically utilize NiOOH as the cathode in an alkaline electrolyte. Ni is a good catalyst for H2 evolution, inhibiting its use as a negative electrode.
Lead $Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13	259	8934	Lead-Acid (S)	Heavy element, low gravimetric capacity.

* P=primary, S=secondary

Additionally, irreversibility in these systems can arise at the cathode. For example, in the case of modern zinc-chloride and alkaline batteries where MnO_2 is the active cathode material, the following chemistry occurs:

(4) $MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$

(5) $MnOOH + H_2O + e^- \rightarrow Mn(OH)_2 + OH^-$

Rechargeable aqueous batteries are extremely appealing for emerging energy storage markets as discussed above. In particular, Li^+-based shuttle systems have been extensively researched. However, in attempts to move beyond lithium, naturally abundant Na^+ and K^+ systems, and very recently, the intercalation chemistry of divalent cations are being explored. Zn^{2+} based systems are promising for multiple reasons: (a) the high abundance and large production of zinc which makes it very low-cost; (b) the high corrosion resistance of zinc in atmospheric and other environments; (c) the non-toxicity of zinc; (d) the low redox potential of the Zn anode (-0.76 V vs. SHE) compared to the redox potential of host materials used in other aqueous batteries; (e) the high potential volumetric energy density of the zinc negative electrode, owing to its density (7.14 g cm^{-3}); and lastly, the extremely small exchange current for hydrogen evolution on zinc from solutions with Zn^{2+} concentrations higher than 10^{-4} M, which renders Zn deposition the major electrochemical reaction at low cathodic potential. The last feature facilitates a much larger kinetic voltage window (~2.5 V) for Zn^{2+} based rechargeable batteries containing aqueous electrolytes, a Zn^{2+} host, and a Zn anode, compared to the small thermodynamic window of 1.23 V of aqueous electrolytes. This concept of a zinc-ion battery is depicted in **Figure 1**. Nonetheless, the inventory of host materials capable of reversible Zn^{2+} storage is currently sparse and only a few materials, namely MnO_2 (α, β, γ, λ, and todorokite), zinc hexacyanoferrate, and copper hexacyanoferrate have been explored. Among the different polymorphs of MnO_2, the alpha version delivers a large initial specific capacity of ~210 mAh g^{-1} at a discharge potential of 1.3 V. Poor rate performance and sharp initial capacity fading due to manganese dissolution in the electrolyte bar its practical application, however.$^{\text{Error! Bookmark not defined.}}$ Even though open framework metal hexacyanaoferrates offer possibilities of a range of multivalent cation insertion and a rather high operational voltage (~1.7 V for Zn/Zn-hexacyanoferrate) for zinc insertion, a very low specific capacity (65 mAh g^{-1} at 1C) dampens their contention. Therefore, new host materials and chemistries are required favoring multiple redox per molecular unit for high specific capacities, and stable architectures with facile zinc ion pathways that enable fast and reversible cycling.

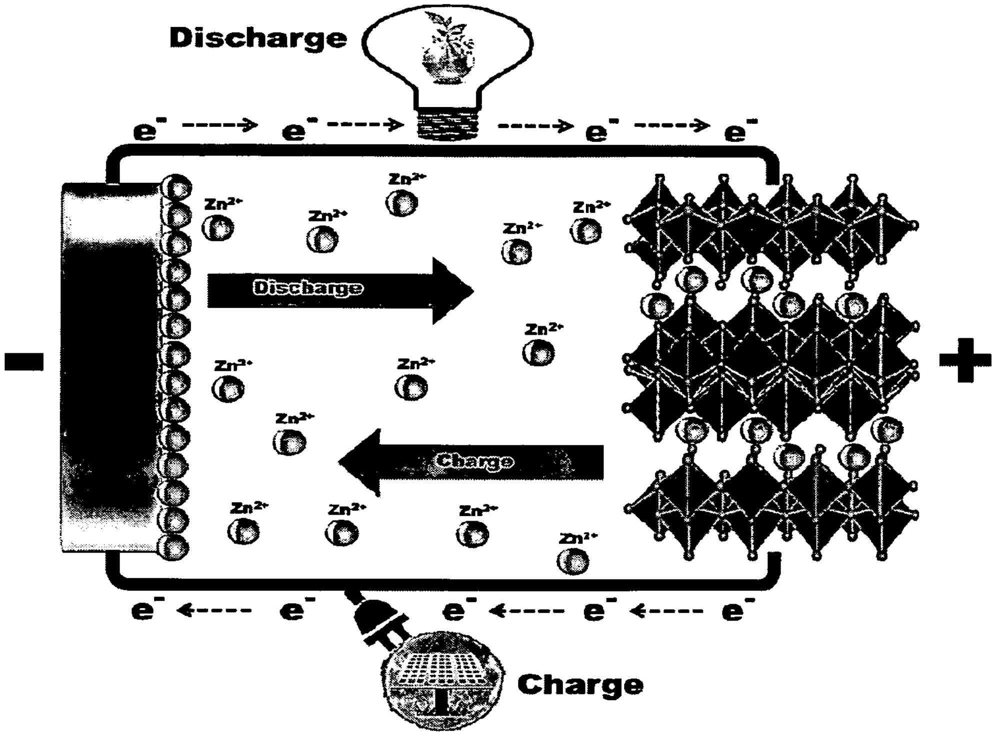


Figure 1. Conceptual scheme of a zinc-ion battery.

Herein, we introduce two vanadium oxide based compounds with layered crystal structures containing crystalline water and a nanostructured morphology as robust host materials for high rate and long term reversible Zn^{2+} ion storage in aqueous electrolyte. Vanadium is a low-cost metal possessing a range of oxidation states (+2 to +5), which allows for multiple redox and hence large specific capacities for vanadium based electrode materials. Particularly, oxides of vanadium e.g., V_2O_5 which is produced in large quantities, display numerous crystal and compositional chemistries for reversible metal ion storage. Layered $M_xV_nO_m$ oxides (M = metal ion) with pure oxide compositions such as V_2O_5, V_3O_8, V_4O_{11} have been the subject of intense investigation for both non-aqueous and aqueous alkali (Li and Na) ion batteries. However, as we demonstrate here, interlayer metal ions and/or water of hydration in these layered oxides can act as pillars, providing structural stability during long term cycling and facilitating the mobility of divalent cations such as Zn^{2+} and Mg^{2+}. Hydrated vanadium oxides that possess such qualities are $H_2V_3O_8$ and $Zn_xV_2O_5$, which we have synthesized in nanofiber morphology by a simple and rapid microwave hydrothermal treatment of V_2O_5, without using any toxic or corrosive chemicals. Their nanomorphology and compact film structure allows for facile release of strain resulting upon Zn^{2+} cycling, short ion diffusion paths, good interaction of carbon additives and robust conductive wiring. They were converted to freestanding film electrodes by adopting a "green", low cost water based electrode fabrication process. This facilitates high specific capacities of ~350 mAh g^{-1} and long term cyclabilities up to 1000 cycles at high coulombic efficiency using fast current rates. Predicted gravimetric energy densities are up to 280 Wh/kg for the cathode alone, and between 200 – 250 Wh/kg including the mass of the zinc anode.

Experimental Methods

Synthesis of $H_2V_3O_8$ and $Zn_xV_2O_5$: Microwave solvothermal methods developed over the last two decades are now often used to prepare cathode materials for lithium ion batteries. In our study we have modified a time consuming and energy expensive hydrothermal approach used in the synthesis of single crystalline $H_2V_3O_8$ nanobelts to a rapid and scalable microwave hydrothermal method for the synthesis of highly homogeneous $H_2V_3O_8$ and $Zn_xV_2O_5$ nanofibers. In a typical procedure, 3-4 mmol V_2O_5 was dispersed in 15:1 water/acetone (v) mixture with or without a stoichiometric amount of zinc chloride (for $Zn_xV_2O_5$) and transferred to a sealed Teflon™ vessel. The vessels were fitted to a rotor equipped with temperature and pressure sensors and placed in an Anton Parr microwave synthesis system (Synthos 3000). The system temperature was raised to 180°C in 10 minutes and maintained for 60 to 90 minutes. The as-synthesized product was thoroughly washed with distilled water followed by a small amount of isopropanol and dried at 60°C for 24 h.

Characterization Methods: Powder X-ray diffraction was performed on a Bruker D8-Advance powder diffractometer equipped with Vantec-1 detector, using Cu-Kα radiation (λ= 1.5405Å) in the range from 5° to 80° (2θ) at a step size of 0.025° using Bragg-Brentano geometry. X-ray data refinement was carried out by conventional Rietveld refinement method using the Bruker-AXS TOPAS 4.2 software (Bruker-AXS, 2008). The background, scale factor, zero point, lattice parameters, atomic positions and coefficients for the peak shape function were iteratively refined until convergence was achieved. The morphologies of the samples were examined by field-emission scanning electron microscopy (FE-SEM, LEO 1530) equipped with an energy dispersive X-ray spectroscopy (EDX) attachment. For high resolution transmission electron microscopy (HRTEM), samples were dispersed in iso-propanol by ultrasonication and loaded onto a carbon coated copper grid for imaging on a FEI Titan 80-300.

Battery Cycling: For electrochemical performance evaluation, a freestanding film type electrode was fabricated by a facile green approach. In a typical process, nanofibers were mixed with conducting nanocarbon Super P® and a water based composite binder carboxymethylcellulose (CMC) and styrene-butadiene rubber(SBR) (CMC/SBR= 2:1) in 70:27:3 weight ratio. The mixture was dispersed in small amount of water using an ultrasonic mixer to obtain a stable homogeneous ink which was filtered through a Durapore® DVPP 0.65 μm filtration membrane.

After drying at 60°C the composite film was then punched into 1 cm^2 electrode coins and further dried at 180°C for 1 h. The electrochemical properties were investigated in PFA based Swagelok® type cells using 1 M $ZnSO_4$ in water as the electrolyte and titanium or stainless steel rods as the current collector. Galvanostatic cycling studies were performed using a multichannel Biologic VMP3 potentiostat/galvanostat.

Three-Electrode Electrochemical Measurements: The voltammetric electrochemical experiments were performed with a three-electrode cell consisting of the working electrode, Pt mesh (1 cm^2) as the counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. The working electrodes were a Zn disk ($\varphi = 2$ mm), a Ti disk ($\varphi = 2$ mm), a stainless steel rod (316 grade, $\varphi = 12$ mm), and the $H_2V_3O_8$ composite electrode. Cyclic voltammetry was performed at a scan rate of 5 mV/s and linear sweep voltammograms were acquired at 1 mV/s. These techniques were controlled with a CHI700E potentiostat (CH Instruments, Inc.). The electrolytes used were 1 M Na_2SO_4 for the hydrogen evolution reaction and 1 M $ZnSO_4$ for zinc plating/stripping and the oxygen evolution reaction. All experiments were performed at room temperature (23 ± 2 °C).

Results and Discussion

Electrochemistry.

The operating voltage of all secondary aqueous batteries is limited by the potentials for hydrogen evolution and oxygen evolution from water electrolysis. Since both the hydrogen and oxygen evolution reactions (HER and OER, respectively) are pH dependent (see equations 7-10) and catalytic in nature, the precise potential at which they occur is sensitive to the electrolyte composition and electrode material. HER and OER occur during charge at the negative and positive electrodes, respectively, and are displayed below:

Cathodic Reactions:

Zinc Deposition:

(6) $Zn^{2+} + 2e^- \rightarrow Zn$ $E^\circ = -0.76$ V vs. SHE

Hydrogen Evolution:

(7) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^\circ = -0.83$ V vs. SHE

(8) $2H^+ + 2e^- \rightarrow H_2$ $E^\circ = 0.00$ V vs. SHE

Anodic Reactions:

Oxygen Evolution:

(9) $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ $E^\circ = 0.40$ V vs. SHE

(10) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^\circ = 1.23$ V vs. SHE

To examine the suitability of a metallic zinc negative electrode for secondary zinc-ion batteries, linear sweep voltammetry was used to probe the HER. In **Figure 1**, a zinc-ion-free (1 M Na_2SO_4) electrolyte was used which contained the same concentration of the sulfate anion and similar pH value (4-5) as the 1 M $ZnSO_4$ electrolyte used for all other studies. It can be seen that the hydrogen evolution reaction has an overpotential of ~0.4 V with respect to Pt on both zinc metal and titanium metal.

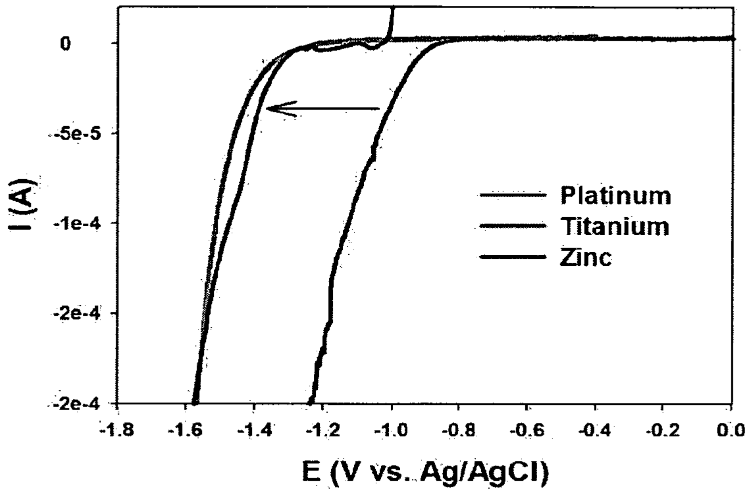


Figure 1. Linear sweep voltammograms at 1 mV/s on Pt, Ti, and Zn in 1 M Na_2SO_4 showing the onset of the hydrogen evolution reaction.

Stainless steel was deemed to be unsuitable as a current collector for the negative electrode as it catalyzes the HER and competes with zinc electrodeposition, but titanium was found to be an excellent current collector for the negative, comparable to Zn itself (**Figure 2a,b**).

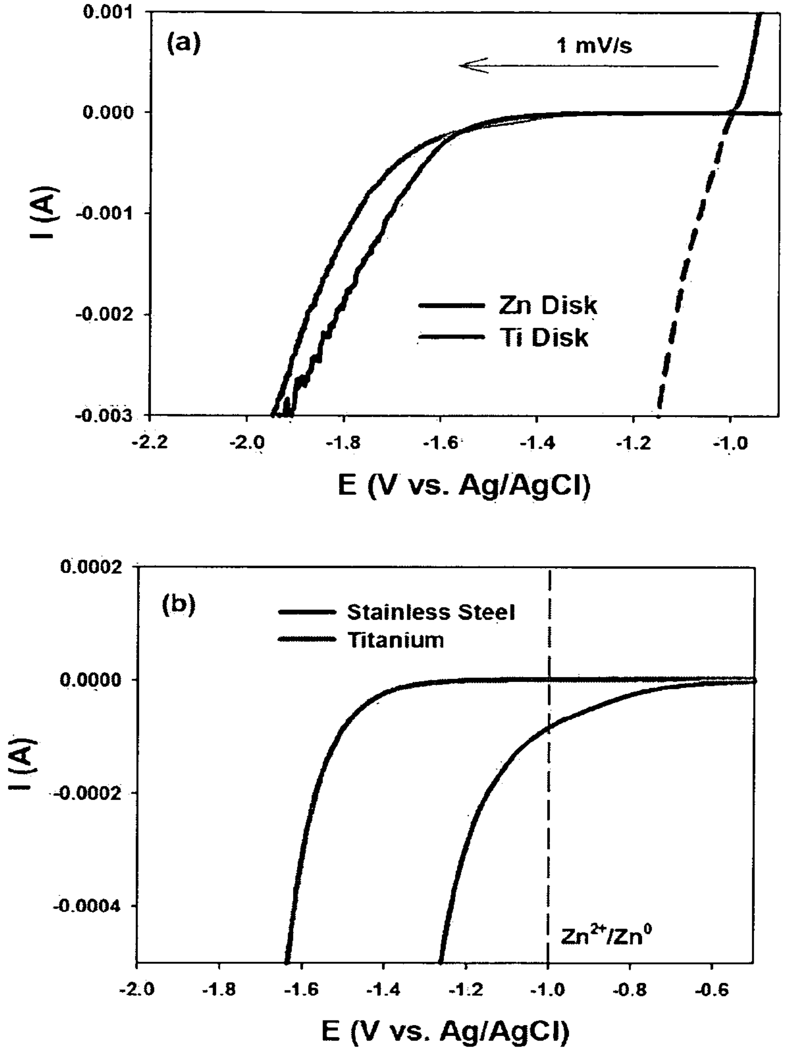


Figure 2. Linear sweep voltammograms at 1 mV/s in 1 M Na_2SO_4 showing the hydrogen evolution reaction. The dashed red voltammogram in (a) shows zinc deposition on a zinc disk electrode in 1 M $ZnSO_4$ for comparison.

Furthermore, zinc deposition and stripping was completely reversible on titanium as displayed in **Figure 3a**. The Coulombic efficiency (Q_{ox}/Q_{red}) was 100 % over 100 cycles on titanium with no loss in the electrical charge (Q) for deposition or stripping. Stainless steel suffered from a decay in both Q_{red} and Q_{ox}, even for the first 10 cycles (**Figure 3b**). On stainless steel the Coulombic efficiency was only 87 % for the first cycle and 74 % for the tenth cycle. This shows that the excess charge during reduction (Q_{red}) goes towards the HER.

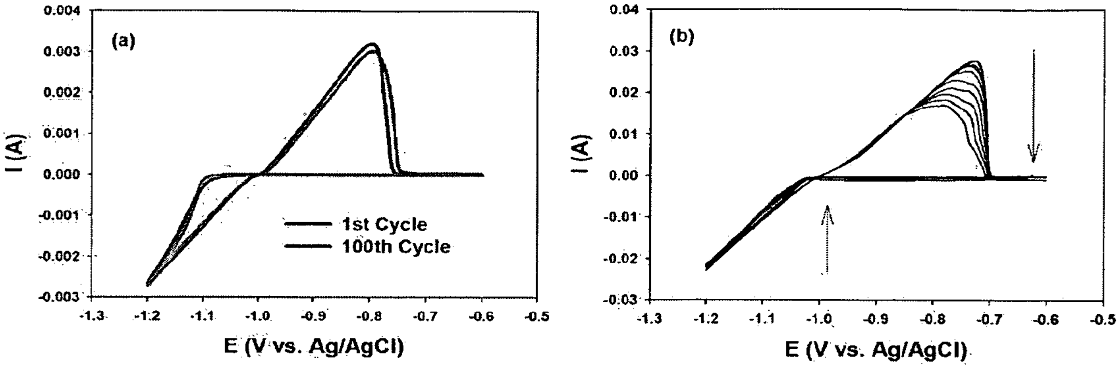


Figure 3. Cyclic voltammograms at 5 mV/s on (a) a Ti disk electrode and (b) stainless steel rod in 1 M $ZnSO_4$.

Since the OER dictates the maximum potential for the positive electrode, this was first examined on stainless steel, a practical current collector material. Titanium also has a high overpotential for OER, however, we suspect that OER on many Zn^{2+}-intercalation materials will have activity similar to stainless steel which is why we show the result for OER on stainless steel rather than titanium. **Figure 4** displays the linear voltammograms for Zn electrodeposition onto a Zn disk and OER on a stainless steel rod in 1 M $ZnSO_4$ at 1 mV/s. This plot shows the maximum possible operating voltage window of a secondary Zn-ion battery using 1 M $ZnSO_4$, which is ~2.4 V. Obviously, the positive electrode of choice must be within this window, particularly if a high-voltage material is to be used. In our case, the upper voltage cut-off for batteries with $H_2V_3O_8$ and $Zn_xV_2O_5$ are 1.1 V, which is well below the limit at which OER will occur at these materials.

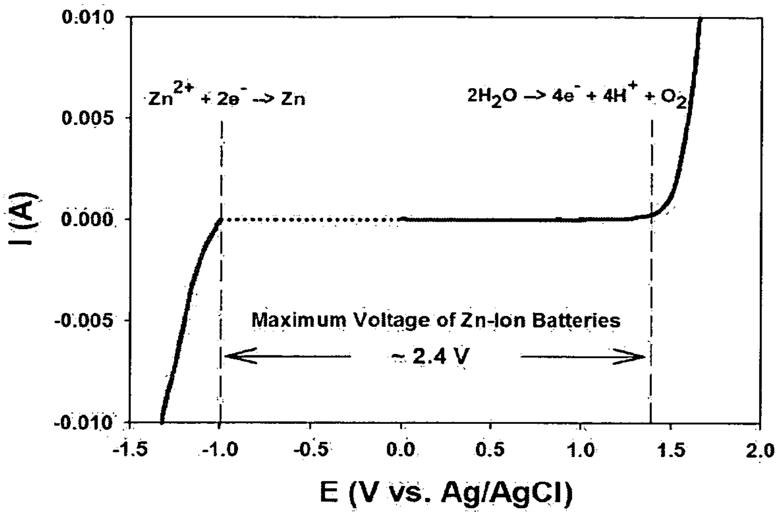


Figure 4. Linear sweep voltammograms on a zinc disk electrode (red) and a stainless steel disk electrode (blue) at 1 mV/s in 1 M $ZnSO_4$. The cathodic sweep on zinc shows zinc deposition and the anodic sweep on the stainless steel shows the oxygen evolution reaction. These two electrochemical reactions dictate the potential operating window for aqueous zinc-ion batteries using this electrolyte.

Figure 5 displays the chronopotentiometric curves for charging α-MnO_2 (which has been explored as a Zn-ion intercalation host previously) and $H_2V_3O_8$ electrodes without prior discharge. This gives an indication of the possible upper voltage cut-off which can be used for a given material. Clearly, the $H_2V_3O_8$ material undergoes structural transitions between 1.5 V and 2.4 V, at which point OER occurs. In contrast, with α-MnO_2, the voltage quickly rises to 2.4 V where a flat OER plateau arises. Thus, upper voltages of 1.1 V for $H_2V_3O_8$ and 1.8 V for α-MnO_2 were used in all subsequent battery cycling protocols.

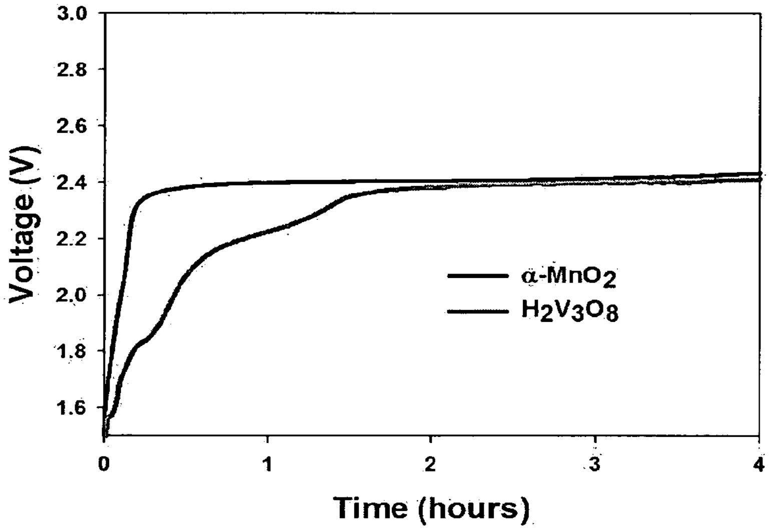


Figure 5. Galvanostatic charging of $H_2V_3O_8$ (red) and α-MnO_2 (black) electrodes at 0.5 mA/cm^2 in 1 M $ZnSO_4$ with metallic zinc negative electrodes.

Cathode Materials: Synthesis and Characterization. The hydrothermal method has evolved into an important wet chemistry method for the synthesis of nanostructured vanadium oxide materials. However, such process can be time consuming, as in the synthesis of $H_2V_3O_8$ nanobelts which requires hydrothermal treatment of V_2O_5 in water for 2-3 days at 210°C. By introducing a microwave heat treatment, we have developed a versatile and scalable synthetic approach for the rapid synthesis of ultralong $H_2V_3O_8$ and $Zn_xV_2O_5$ nanofibers. Water is known to strongly interact with the microwave radiation via a dipolar-microwave interaction, leading to rapidly superheated local regions in the reaction media. In contrast to typical hydrothermal methods where slow heating mainly occurs via thermal conduction mechanism, heating of the entire reaction media through penetration of microwaves triggers rapid intercalation-exfoliation and cleavage of V_2O_5 into nanosheets and finally into $H_2V_3O_8$ or $Zn_xV_2O_5$ nanofibers. The phase purity of the as-synthesized materials was confirmed by Rietveld refinement of the powder diffraction pattern as shown in **Figure 6a** for $H_2V_3O_8$ and **Figure 6b** for $Zn_xV_2O_5$. The XRD pattern in **Figure 6a** could be refined to an orthorhombic Pnam $V_3O_7.H_2O$ ($H_2V_3O_8$) with the lattice parameters of a = 16.871 Å, b = 9.332 Å, c = 3.634 Å, and $\alpha = \beta = \gamma = 90°$. Here V_3O_8 layers, which are constructed of VO_6 octahedra and VO_5 trigonal

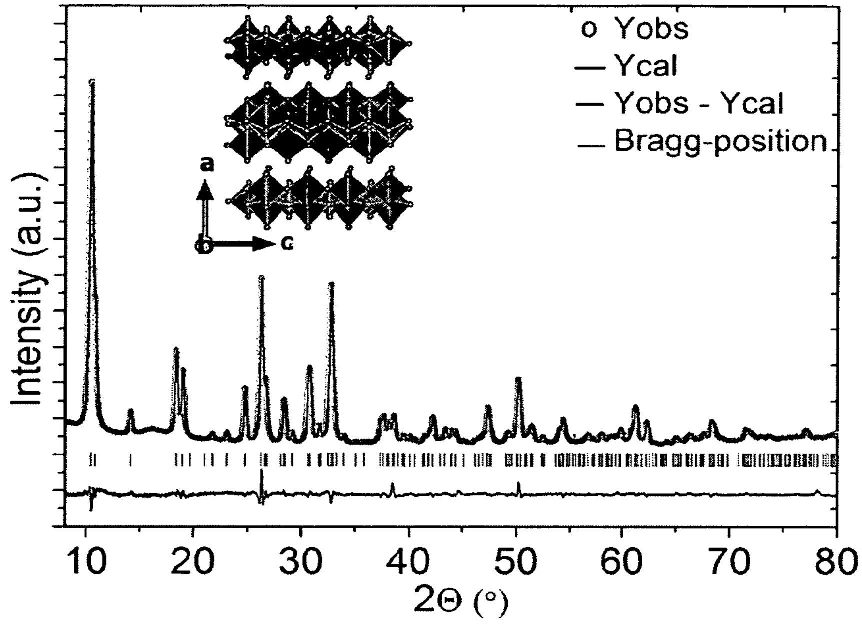


Figure 6a. Rietveld refinement of $H_2V_3O_8$ with $R_{exp} = 0.97$, $R_{wp} = 2.47$, and Gof = 2.55. Data points (red circles); calculated profile (black line); difference profile (blue line); Bragg positions (magenta lines). Inset shows the layered structure projected in the *ac* plane. VOx polyhedras are shown in brick red color.

bipyramids, are held by strong hydrogen bonding. The H_2O molecule bound to the vanadium atom in place of one oxygen in the VO_6 octahedra creates a hydrogen bond with the octahedra in the next layer. The hydrogen bonded layered structure is very stable up to ~300°C, where the structure dehydrates.

The pattern in **Figure 6b** was refined to a composition of $Zn_{0.2}V_2O_5$. H_2O that crystallizes in P-1 triclinic system with lattice parameters of a = 10.874 (5), b = 7.901 (2), c = 10.474 (2), α = 90.65, β = 91.14, and γ = 90.09, which closely resemble the $Zn_{0.25}V_2O_5.H_2O$ phase for which the structure was solved by single crystal diffraction. The interlayer spacing shrinks from 10.76 Å to 10.47 Å as a result of the slightly lesser amount of zinc in the interlayer space. Here the structure consists of V_2O_5 layer, built up of VO_6 octahedra, VO_5 trigonal bypyramids and VO_4 tetrahedra. These are stacked along *c* axis with the interlayer Zn atom coordinating to the oxygen apices on opposite sides and the oxygen atoms of the in-plane water molecules.

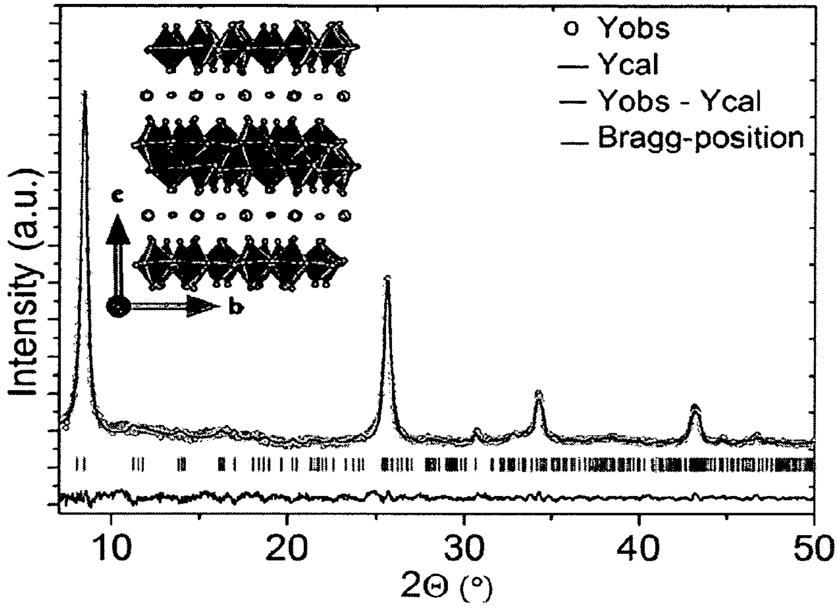


Figure 6b. Rietveld refinement of $Zn_{0.2}V_2O_5.H_2O$ with $R_{exp} = 1.52$, $R_{wp} = 2.38$, and Gof = 1.572. Data points (red circles); calculated profile (black line); difference profile (blue line); Bragg positions (magenta lines). Inset shows the layered structure projected in the *bc* plane. The VOx polyhedras are shown in brick red. The Zn and O atoms are depicted as silver and red spheres, respectively.

SEM images (**Figure 7**) reveal a highly uniform fiber-like morphology for both materials, $H_2V_3O_8$ and $Zn_{0.2}V_2O_5$. Both the fibers have a diameter of about 100 nm. To our knowledge, this is first time $Zn_{0.2}V_2O_5$ has been synthesized in this nanomorphology.

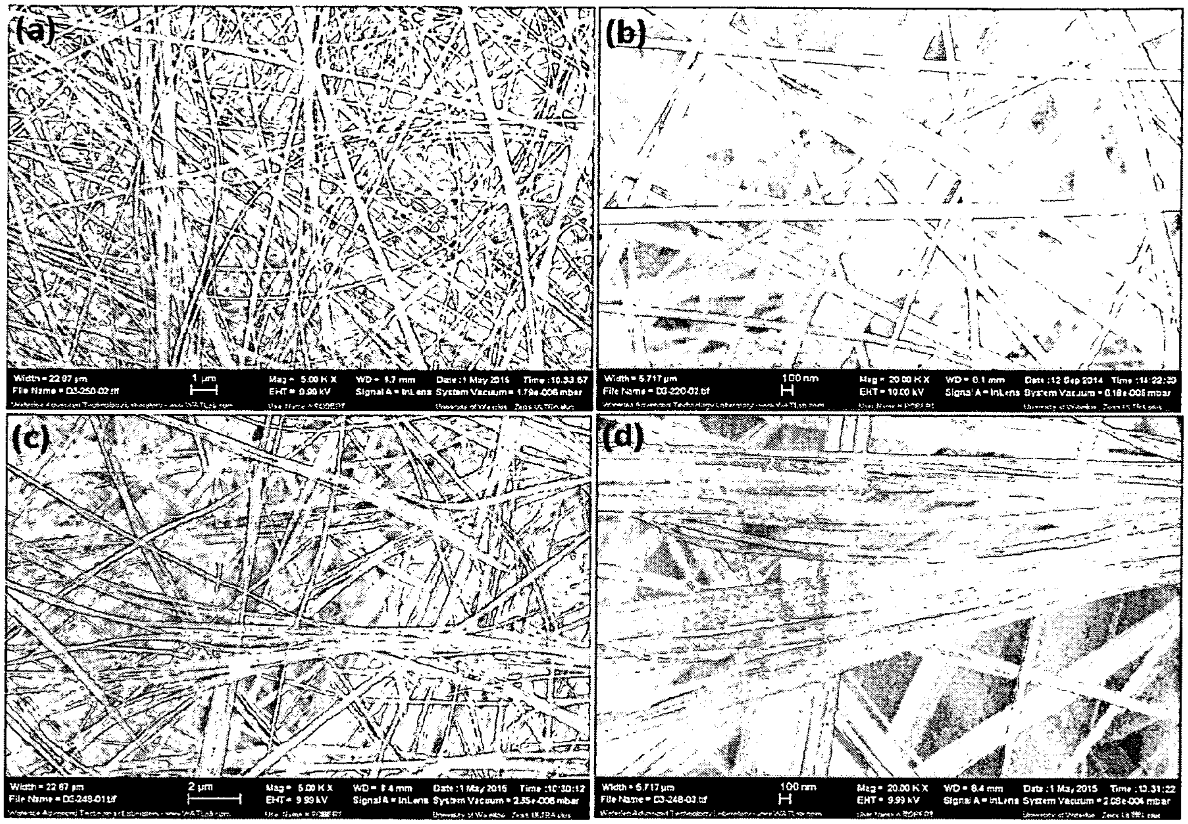
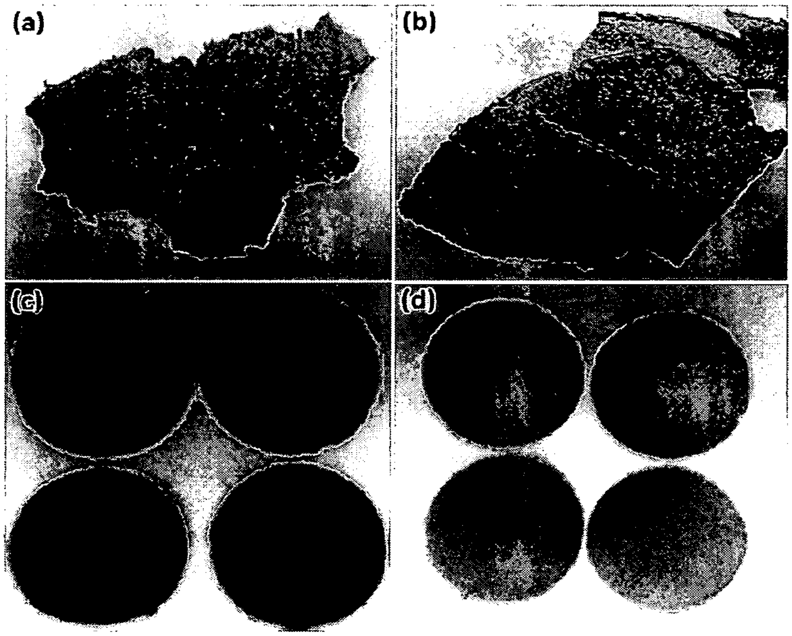


Figure 7. Typical SEM image of the $H_2V_3O_8$ (a & b) and $Zn_{0.2}V_2O_5$ (c & d) nanofibers.

Electrochemical Cells. Prior to electrode fabrication, the as-synthesized materials were dried at 200°C for 5 h to remove any loosely bound water of hydration from between the vanadium oxide layers. After heat treatment, the $H_2V_3O_8$ diffraction pattern remains unchanged, as expected. The peak positions for the $Zn_{0.2}V_2O_5.H_2O$ phase shifted slightly together with the appearance of few small peaks as a result of heat treatment. A small contraction in the interlayer spacing was detected as a result of the dehydration but the presence of Zn^{2+} ions in the interlayer ensures structural stabilization.

Unlike conventional NMP (N-methyl-2-pyrrolidone) based Li-ion battery electrode slurry fabrication, which is expensive and time consuming due to the use of NMP, we developed a novel and versatile electrode fabrication approach in this work. A water based ink was prepared for both materials by ultrasonic dispersion with conductive carbon using a minimum (3%) amount of aqueous based binder CMC and SBR. The ink was passed through a PVDF based membrane filter resulting in a compact film, which upon drying (at 60°C) spontaneously peels off the hydrophobic membrane due to the hydrophilic nature of the oxide based electrode film. The fiber morphology of the materials (**Figure 8a and 8b**) enables formation of dense mat-like film electrodes. The thickness and the loading of the film can be easily varied by adjusting the amount of ink. The use of water as the solvent and water based low-cost binders makes the process very cost effective and environmentally green. The use of freestanding film electrode also allows us to avoid possible corrosion issues of metal foil, which is typically used to deposit an electrode film. The fabricated film electrodes are shown in **Figure 8c and 8d**.

Figure 8. Photographs of the as-synthesized (a) $H_2V_3O_8$ and (b) $Zn_{0.2}V_2O_5$. (c) and (d) are the photographs of the corresponding film electrodes.



The reversible electrochemical Zn^{2+} storage capabilities of $H_2V_3O_8$ and $Zn_{0.2}V_2O_5$ were explored in full cells by applying galvanostatic techniques. The electrodes were studied in different voltage windows to determine the optimal voltage range for highly reversible electrochemical cycling. Based on this study, voltage windows of 0.4 V – 1.1 V and 0.5 – 1.4 V vs. Zn were determined for the $H_2V_3O_8$ and $Zn_{0.2}V_2O_5$ electrodes, respectively, which clearly fall within the safe operational window in the aqueous electrolyte (1 M $ZnSO_4$ in H_2O) using Zn anode and Ti rod as the current collector (see discussion above). Cycling in wider voltage window results in higher specific capacities, but structural stress generated from the insertion of a large amount of zinc results in pulverization of the electrode and rapid capacity fading. Moreover, a practical voltage window not only enable better cyclability, but also ensures lower voltage polarization.

Figure 9 shows the voltage polarization curves for the two electrodes at different current rates. At a current density of 350 mA g^{-1} both the electrodes deliver initial discharge capacities in the range of 325-350 mAh^{-1}. Based on this observation, 1C rate was defined to be about 350 mA g^{-1}. **Figure 9a** demonstrates the variation of cell voltage for $H_2V_3O_8$ electrode as a function of obtainable specific capacity. The voltage profile shows a small plateau delivering ~100 mAh g^{-1} of capacity at around 0.8 V, followed by a sloping region, giving a high specific capacity of 325 mAh g^{-1} and 270 mAh g^{-1} at high rates of 4C (1400 mA g^{-1}) and 8C (2800 mA g^{-1}), respectively.

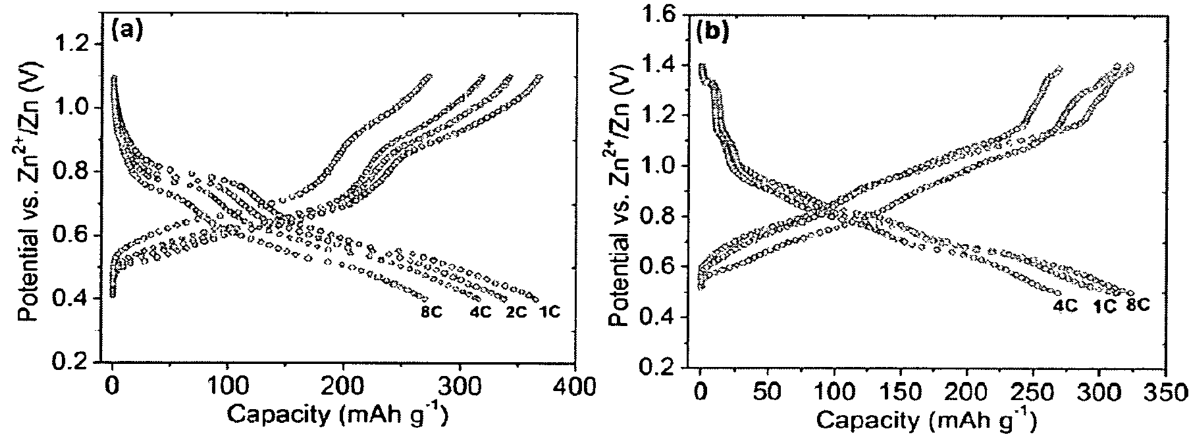


Figure 9. Galvanostatic polarization curves for the (a) $H_2V_3O_8$ and (b) $Zn_{0.2}V_2O_5$ electrodes at various current rates. Here, 1C is define as 350 mA g^{-1} for $H_2V_3O_8$ electrodes and 325 mA g^{-1} for $Zn_{0.2}V_2O_5$ electrode.

Depending on the applied current rates, close to 1.5 to 2 Zn^{2+} ions are electrochemically intercalated during discharge. An average operating voltage of ~0.64 V is obtained for this electrode irrespective of the rate. The $Zn_{0.2}V_2O_5$ electrode demonstrates a higher average operating voltage of ~0.82 V at all current densities (**Figure 9b**). This is most likely the consequence of a higher average vanadium oxidation state in $Zn_{0.2}V_2O_5$ ($V^{4.8+}$) compared to that in $H_2V_3O_8$ ($V^{4.66+}$). Typical discharge-charge polarization curves for $Zn_{0.2}V_2O_5$ display a sloping behavior, suggesting a dominant solid-solution type process associated with electrochemical zinc (de)insertion. Interestingly, at higher current rates, discharge-charge capacities increased with cycling, reaching their highest value after cycling. This is most likely related to the kinetic limitation of Zn^{2+} diffusion into the layered structure of the electrode, requiring multiple discharge-charge cycles to open up accessible intercalation sites, before optimal capacity can be achieved. The $Zn_{0.2}V_2O_5$ electrodes delivered a specific capacity of ~300 mAh g^{-1}, which is slightly lower than the $H_2V_3O_8$ electrode. Typically, about 1.5 Zn^{2+} ions are intercalated per mole of $Zn_{0.2}V_2O_5$ during the electrochemical discharge process. The high specific capacities obtained for both materials can be ascribed to the large specific surface area and short diffusion distances provided by the nanofiber morphology. It is also important to note that for both the electrodes, the voltage polarization curves recorded in the subsequent cycles exhibit identical feature as the first cycle, indicating that the initial structure is recovered at the end of each charge cycle.

As a result of nanostructural morphology, flexible film like electrode architecture, and structural reversibility upon Zn^{2+} de(intercalation) both the electrodes demonstrate superior cyclability at high current rates. **Figure 10** shows the variation of specific capacity and the corresponding coulombic efficiency as a function of cycling at 4C and 8C rates. The plots show that the $Zn_{0.2}V_2O_5$ based cell exhibits excellent cyclability at an 8C rate, retaining 70% of the initial specific capacity after 1000 cycles. At half the current density (4C), the cells exhibited only a 20% drop in the initial capacity over 400 cycles. Identical $H_2V_3O_8$ cells demonstrated

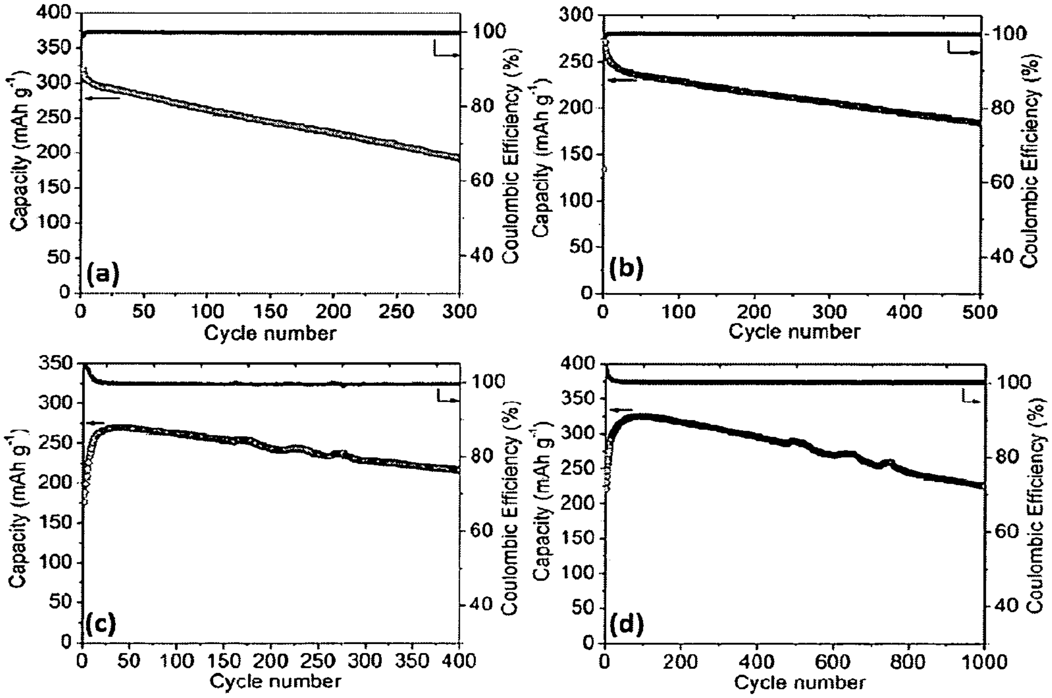


Figure 10. Specific capacity and coulombic efficiency of the $H_2V_3O_8$ (a & b) and $Zn_{0.2}V_2O_5$ (c & d) as a function of cycling at 4C (a & c) and 8C (b & d) current rates.

slightly inferior capacity retention, delivering about 40% and 30% of the initial reversible capacity at the end of 300 and 500 cycles when operated at current rate of 4C and 8C, respectively. Interestingly, the $H_2V_3O_8$ cell showed distinctly better cycling behavior at higher current rates (8C). This can be linked to the comparatively lower amount of Zn^{2+} intercalation per mole of $H_2V_3O_8$, leading to lesser structural strain, which ensures better cyclability. However this feature is not very prominent for the $Zn_{0.2}V_2O_5$ based electrode, which suggests higher structural flexibility of $Zn_{0.2}V_2O_5$ towards Zn^{2+} (de)intercalation. Higher structural flexibility granted by the presence of interlayer Zn^{2+} ions also ensures excellent electrochemical cyclability of the $Zn_{0.2}V_2O_5$ cells. In contrast, the hydrogen bonded VO_x interlayer in $H_2V_3O_8$ lacks the structural rigidity and flexibility of $Zn_{0.2}V_2O_5$, resulting in slightly poorer capacity retention. For all the studies nearly 100% Coulombic efficiency was registered even over long cycling, which further confirms the high degree of reversibility of electrochemical Zn^{2+} (de)intercalation into the layered structure of the vanadium oxide materials.

By virtue of 1D nanomorphology and film like compact yet flexible electrode architecture, both the materials delivered excellent rate performance under variable current loading as a function of cycling. The results are shown in **Figure 11** together with the corresponding Coulombic efficiencies registered at variable rates. As expected, the $Zn_{0.2}V_2O_5$ electrode demonstrates better rate capability; starting with an initial capacity of 323 mAh g^{-1} at 1C rate, the cell delivers 270 mAh g^{-1} of durable capacity at 8C, which reverts back to 315 mAh g^{-1} of capacity at 1C rate, nearly identical to the initial 1C capacity. A slightly higher initial 1C capacity is observed for $H_2V_3O_8$ of 335 mAh g^{-1}, which falls to 222 mAh g^{-1} at an 8C rate, but is not completely recovered

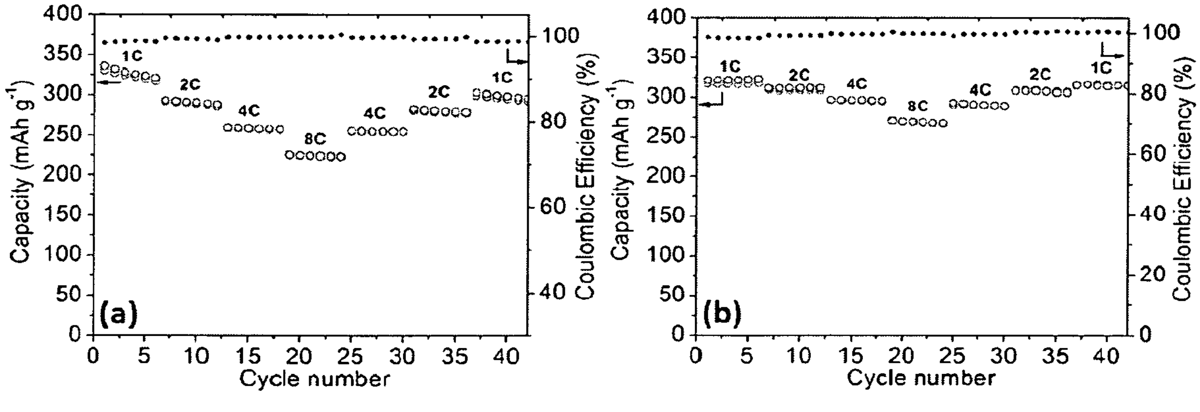


Figure 11. Rate capability of the (a) $H_2V_3O_8$ and (b) $Zn_{0.2}V_2O_5$ cell studied under variable current loading as a function of cycling. The corresponding coulombic efficiencies are plotted in blue.

when the current density is returned to 1C at the end of variable current load test. Similar to the electrochemical cyclability, the better rate performance of $Zn_{0.2}V_2O_5$ compared to the $H_2V_3O_8$ electrode is attributed to its more robust and flexible layered structure which is efficiently pillared by immobile Zn^{2+} ions. In both cases, the Coulombic efficiency increases with current load, which is expected as side reactions are suppressed at higher current rates.

Based on the galvanostatic cycling and rate performance results, energy and power densities were calculated and are presented in the Ragone plot shown in **Figure 12.** Along with good cyclability and excellent rate capability, both the $H_2V_3O_8$ and $Zn_{0.2}V_2O_5$ based cells deliver good energy density at high power density. At a power density of ~270 W kg^{-1} the $Zn_{0.2}V_2O_5$ cell exhibits a high specific energy density of about 280 Wh kg^{-1}, calculated based on the weight of the active electrode material. This is maintained even at very high power densities: 240 and 220 Wh kg^{-1} at power density of 1100 and 2300 W kg^{-1} are achieved, in complete accord with the superior rate performance observed for this material. The $H_2V_3O_8$ cell delivers slightly lower energy and power densities due to its lower average operating voltage (0.64 V vs Zn).

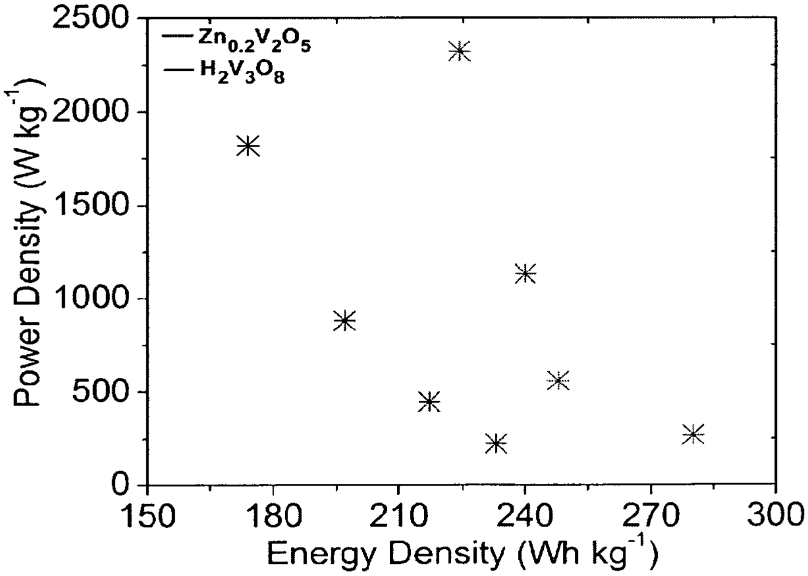


Figure 12. Ragone plot for the $Zn_{0.2}V_2O_5$|1M $ZnSO_4$-H_2O|Zn, and $H_2V_3O_8$|1M $ZnSO_4$-H_2O|Zn cells. The energy and power densities were calculated based on the total weight of the active electrode materials.

Conclusions

In summary, we have developed two novel layered vanadium oxide nanomaterials for highly reversible Zn^{2+} storage at high current rates and long term cyclability. A simple scalable microwave synthesis of vanadium oxide nanomaterials and a versatile water based environmentally green electrode fabrication process is also presented. The presence of stable interlayer species, e.g., H_2O in $H_2V_3O_8$ and Zn^{2+} and/or H_2O in $Zn_{0.2}V_2O_5$, plays a pivotal role in stabilizing the layered structure against repeated Zn^{2+} de(intercalation), and thereby enables long term cyclability with high specific capacities. Although the average operating cell voltages (0.64 V for $H_2V_3O_8$ and 0.82 V for $Zn_{0.2}V_2O_5$) are rather modest, high specific capacities of ~300 mAh g^{-1} ensure high energy density (230-280 Wh kg^{-1}), which is the highest reported amongst the known aqueous Zn-ion batteries (see **Table 2** below). Good energy density, impressive rate performance and cyclability, cost effective scalable processing of raw materials and electrodes, and not the least high abundance and production of zinc metal make these aqueous zinc ion secondary cells viable candidates for large scale applications such as grid storage.

Table 2. Operating voltage, energy density, and cycling performance of different rechargeable aqueous Zn-ion batteries.

Cathode/Anode Couple	Average Operating Voltage (V)	Energy Density (Wh kg^{-1})	Capacity Retention (Rate)	Reference
α-MnO_2/Zn	1.3 V	225	75% After 100 cycles (6C rate)	**Error! Bookmark not defined.**
Zinc-hexacyanoferrate/Zn	1.7 V	100	75% After 100 cycles (1C rate)	**Error! Bookmark not defined.**
$H_2V_3O_8$/Zn	0.64 V	230	70% after 500 cycles (8C rate)	Present Work
$Zn_{0.2}V_2O_5$	0.82 V	280	70% after 1000 cycles (8C rate)	Present Work

What is claimed is:

1. A rechargeable zinc ion battery, comprising:

A cathode composed of a mixture of nanofibers of layered vanadium oxide containing intercrystalline or interlayer water and/or metal ions, which can store and release zinc ions (Zn^{2+} ions), electrical conductive particles and one or more binders; a zinc anode; a separator for separating said cathode from said anode; and an aqueous electrolyte containing zinc ions, in which the pH value is between 3 to 7. The water or metal ion stabilized layered vanadium oxide nanofibers of the cathode hosts and releases zinc in/from its structural lattice via intercalation/deintercalation during discharge and charge.

1. The rechargeable cell as in claim 1, wherein said zinc anode is in any shapes or pure zinc or zinc alloys
2. The rechargeable cell as in claim 1, wherein if the anode is not as in claim 2, then the electrical contacts in the anode are titanium coated
3. The rechargeable cell as in claim 1, wherein said zinc anode is composed of a compressed mixture of pure zinc and/or zinc alloy particles, electrically conductive particles and a binder.
4. The rechargeable cell as in claim 1, wherein said one or more binders is selected from the group consisting of natural and synthetic rubbers, polysulfone, acrylic polymers, epoxy resins, polystyrene and polytetafluoroethylene
5. The rechargeable cell as in claim 1, wherein said one or more binders where the binder content can be practically zero.

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0-4	**Form PCT/RO/101 PCT Request**	
0-4-1	Prepared Using	ePCT-Filing Version 3.3.000 MT/FOP 20151028/0.20.5.24
0-5	**Petition** The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	**Receiving Office (specified by the applicant)**	Canadian Intellectual Property Office (RO/CA)
0-7	**Applicant's or agent's file reference**	672-001-P
I	**Title of Invention**	ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM
II	**Applicant**	
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III-1-7	State of residence	CA

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V	**DESIGNATIONS**	
V-1	**The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.**	
VI-1	**Priority claim of earlier national application**	
VI-1-1	Filing date	08 June 2015 (08.06.2015)
VI-1-2	Number	62/230,502
VI-1-3	Country or Member of WTO	US
VI-2	**Priority document request** The International Bureau is requested to obtain from a digital library a certified copy of the earlier application(s) identified above as item(s), using, where applicable, the access code(s) indicated:	VI-1 Access code: 8739

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VI-3	**Incorporation by reference :** where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.		
VII-1	**International Searching Authority Chosen**	Canadian Intellectual Property Office (ISA/CA)	
VIII	**Declarations**	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	**Check list**	Number of sheets	Electronic file(s) attached
IX-1	Request (including declaration sheets)	4	✓
IX-2	Description	27	✓
IX-3	Claims	14	✓
IX-4	Abstract	1	✓
IX-5	Drawings	14	✓
IX-7	TOTAL	60	
	Accompanying Items	Paper document(s) attached	Electronic file(s) attached
IX-8	Fee calculation sheet	-	✓
IX-20	**Figure of the drawings which should accompany the abstract**	1A	
IX-21	**Language of filing of the international application**	English	

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X-1	**Signature of applicant, agent or common representative**	/Lynn C. Schumacher/
X-1-1	Name	HILL & SCHUMACHER
X-1-2	Name of signatory	Lynn C. Schumacher
X-1-3	Capacity (if such capacity is not obvious from reading the request)	Agent

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10-1	**Date of actual receipt of the purported international application**	31 May 2016 (31.05.2016)
10-2	**Drawings:**	
10-2-1	Received	
10-2-2	Not received	
10-3	**Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application**	
10-4	**Date of timely receipt of the required corrections under PCT Article 11(2)**	
10-5	**International Searching Authority**	ISA/CA
10-6	**Transmittal of search copy delayed until search fee is paid**	

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11-1	**Date of receipt of the record copy by the International Bureau**	

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and
Administrative Instructions, Section 422)

To:

HILL & SCHUMACHER
264 Avenue Road
Toronto, Ontario M4V 2G7
CANADA

Date of mailing *(day/month/year)*
27 March 2017 (27.03.2017)

Applicant's or agent's file reference
672-001-P

IMPORTANT NOTIFICATION

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31 May 2016 (31.05.2016)

1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

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2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

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☐ Notifications by e-mail authorized

3. Further observations, if necessary:
The person identified in Box 2 has been added as applicant for all designated States. The persons identified in Box 1 are now inventors only.

4. A copy of this notification has been sent to:
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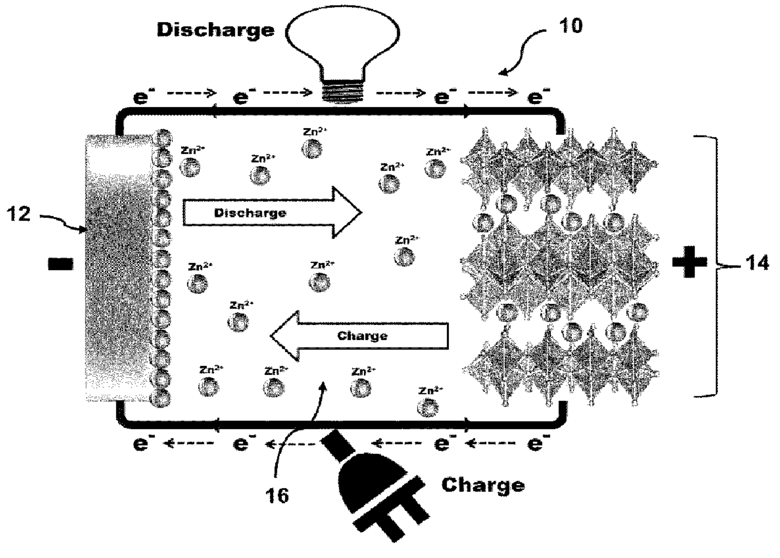

Figure 1A

(57) **Abstract**: The present disclosure discloses a rechargeable Zn battery based on layered/tunnelled structure vanadium/molybdenum oxides, with/without the presence of neutral/cationic/anionic species and/or water molecules inserted into the interlayers/tunnels, of nano/microparticle morphology as robust materials for high rate and long term reversible Zn^{2+} ion intercalation storage at the positive electrode, that are coupled with a metallic Zn negative electrode, and an aqueous electrolyte. The positive electrode may include electronically conducting additives and one or more binders along with the Zn^{2+} intercalation material; the negative electrode is Zn metal in any form; the aqueous electrolyte is of pH 1 to 9 and contains a soluble zinc salt in a concentration range from 0.01 to 10 molar.

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ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM

FIELD

This disclosure relates generally to batteries, and, more specifically to zinc ion batteries involving zinc intercalation positive electrode materials, zinc metal based negative electrodes in any form, and an aqueous electrolyte containing zinc salt and batteries using these positive electrode materials.

BACKGROUND

Given the looming concerns of climate change, sustainable energy resources such as solar and wind have entered the global spotlight, triggering the search for reliable, low cost electrochemical energy storage. Among the various options, lithium ion batteries are currently the most attractive candidates due to their high energy density, and foothold in the marketplace. However, many factors (cost, safety, and lifetime) will likely limit their large scale applications, and dictate against their use in stationary grid storage where low cost and durability are more of a concern than weight. What is needed is a high energy density battery that is rechargeable, cheap, safe, and easy to manufacture and dispose of or recycle. Aqueous batteries (water based electrolytes) are therefore attracting tremendous attention. Their high conductivity (up to 1 Siemens (S) cm^{-1}) compared to the non-aqueous electrolytes (0.001 to 0.01 S cm^{-1}) also favour high rate capabilities suitable for emerging applications.

The use of metallic negative electrodes is a means to achieve high energy density and ease of battery assembly (hence lower cost). There is a trade-off between the reduction potential of a metal, E°, (low values give higher cell voltages) and safety. Metals with low reduction potentials (e.g., lithium, potassium, calcium, sodium, and magnesium) react with water to produce hydrogen. However, zinc is stable in water and for that reason it has been used as the negative electrode in primary aqueous battery systems. Moreover, zinc has (a) high abundance and large production which makes it inexpensive; (b) non-toxicity; (c) low redox potential (-0.76 V vs. standard hydrogen electrode (SHE)) compared to other negative electrode materials used in aqueous batteries; and (d) stability in water due to a high overpotential for hydrogen evolution. The latter renders a large voltage window (~2 V) for aqueous zinc-ion batteries (AZIBs) employing a metallic Zn negative electrode.

Vanadium and molybdenum are low cost metals possessing a range of oxidation states (V: +2 to +5; Mo: +2 to +6), which allows for multiple redox and hence large specific capacities for vanadium or molybdenum based electrode materials. Layered V_nO_m (vanadium oxides: V_2O_5, V_3O_8, V_4O_{11}) and MoO_y (molybdenum oxides) that are made of two dimensional sheet structures were the subject of much past investigation for non-aqueous and aqueous alkali (Li and Na) ion batteries. The additional presence of interlayer neutral molecules, ions, metal ions and/or water of hydration in such layered oxides act as pillars, providing structural stability during long term charge discharge cycling.

SUMMARY

The present disclosure discloses a rechargeable Zn battery based on layered/tunnelled structure vanadium/molybdenum oxides, with/without the presence of neutral/cationic/anionic species and/or water molecules inserted into the interlayers/tunnels, of nano/microparticle morphology as robust materials for high rate and long term reversible Zn^{2+} ion intercalation storage at the positive electrode, that are coupled with a metallic Zn negative electrode, and an aqueous electrolyte. The positive electrode may include electronically conducting additives and one or more binders along with the Zn^{2+} intercalation material; the negative electrode is Zn metal in any form; the aqueous electrolyte is may have a pH in a range of 1 to 9 and contains a soluble zinc salt which may be in a concentration range from 0.01 to 10 molar.

Thus, disclosed herein is a zinc ion battery, comprising:

a positive electrode compartment having enclosed therein an intercalation layered positive electrode material $M_{\mathbf{x}}V_2O_5.\mathbf{n}H_2O$, wherein x is in a range from 0.05 to 1, **n** is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_2O_5 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

There is also disclosed herein a zinc ion battery, comprising:

a positive electrode compartment having enclosed therein and intercalated layered positive electrode material $M_{\mathbf{x}}V_3O_7.\mathbf{n}H_2O$, wherein **x** is in a range from 0.05 to 1, **n** is greater than 0 and less than 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_3O_7 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M and/or hydrogen bonded to the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

There is also disclosed a zinc ion battery; comprising:

a positive electrode compartment having enclosed therein an intercalated layered positive electrode material $M_xMoO_y.nH_2O$, wherein x is in a range from 0 to 1, y is in a range from 2 to 3, n is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said MoO_y has a layer or tunnel crystal structure, and the metal ions M, if present, pillared between the layers, and waters of hydration coordinated to the metal ions M pillared between the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and an electrolyte comprising water and having a salt of zinc dissolved therein.

A further understanding of the functional and advantageous aspects of the disclosure can be realized by reference to the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the disclosure will now be described, by way of example only, with reference to the drawings, in which:

Figure 1A shows a **c**onceptual scheme of a zinc-ion battery constructed in accordance with the present disclosure.

Figure 1B is a cross section of a zinc-ion battery.

Figure 2 shows linear sweep voltammograms at 1 mV/s on Pt, Ti, and Zn in 1 M Na_2SO_4 showing the onset of the hydrogen evolution reaction.

Figure 3 shows linear sweep voltammograms at 1 mV/s in 1 M Na_2SO_4 showing the hydrogen evolution reaction. The dotted voltammogram in (a) shows zinc deposition on a zinc disk electrode in 1 M $ZnSO_4$ for comparison.

Figure 4A shows cyclic voltammograms at 5 mV/s on a Ti disk electrode.

Figure 4B shows cyclic voltammograms at 5 mV/s on stainless steel rod in 1 M $ZnSO_4$.

Figure 5 shows linear sweep voltammograms on a zinc disk electrode (cathodic sweep) and a stainless steel disk electrode (anodic sweep) at 1 mV/s in 1 M $ZnSO_4$. The cathodic sweep on zinc shows zinc deposition and the anodic sweep on the stainless steel shows the oxygen evolution reaction.

These two electrochemical reactions dictate the potential operating window for aqueous zinc-ion batteries using this electrolyte.

Figure 6A shows Rietveld refinement of $H_2V_3O_8$. Data points (circles); calculated profile (line); difference profile (dotted line); Bragg positions (vertical lines) are as indicated. Refined lattice parameters are a = 16.87 Å, b = 9.332 (3) Å, c = 3.63 Å, and $\alpha = \beta = \gamma = 90°$. Inset shows the layered structure projected in the *ac* plane. VOx polyhedra are shown in black.

Figure 6B shows the Rietveld refinement of $Zn_{0.25}V_2O_5.nH_2O$. Data points (circles); calculated profile (black line); difference profile (blue line) are as indicated. Refined parameters are *a* = 10.75 Å, *b* = 7.77 Å, *c* = 10.42 Å, α = 91.26°, β = 90.31°, and γ = 88.66°. The VO_x and ZnO_x polyhedra are shown in black and grey, respectively.

Figures 7A, 7B, 7C and 7D show a typical SEM image of the $H_2V_3O_8$ (**7A** and **7B**) and $Zn_{0.25}V_2O_5.nH_2O$ (**7C** and **7D**) nanofibers.

Figures 8A and **8B** show galvanostatic polarization curves for the (**8A**) $H_2V_3O_8$ and (**8B**) $Zn_{0.25}V_2O_5.nH_2O$ electrodes at various current rates. Here, 1C is defined as 350 mA g^{-1} for $H_2V_3O_8$ and 300 mA g^{-1} for $Zn_{0.25}V_2O_5.nH_2O$.

Figures 9A. 9B, 9C and 9D show specific capacity and coulombic efficiency of the $H_2V_3O_8$ (**9A** and **9B**) and $Zn_{0.25}V_2O_5.nH_2O$ (**9C** and **9D**) as a function of cycling at 4C (**9A** and **9C**) and 8C (**9B** and **9D**) current rates.

Figures 10A and **10B** show rate capability of the (**9A**) $H_2V_3O_8$ and (**9B**) $Zn_{0.25}V_2O_5.nH_2O$ cells studied under variable current loading as a function of cycling. The corresponding coulombic efficiencies are also shown.

Figure 11 shows the tradeoff between energy and power density (Ragone plot) for reversible Zn^{2+} storage in $Zn_{0.25}V_2O_5.nH_2O$, $H_2V_3O_8$, MnO_2, and $Zn_3[Fe(CN)_6]_2$.

DETAILED DESCRIPTION

Various embodiments and aspects of the disclosure will be described with reference to details discussed below. The following description and drawings are illustrative of the disclosure and are not to be construed as limiting the disclosure. Numerous specific details are described to provide a thorough understanding of various embodiments of the present disclosure. However, in certain instances, well-known or conventional details are not described in order to provide a concise discussion of embodiments of the present disclosure.

The Figures are not to scale and some features may be exaggerated or minimized to show details of particular elements while related elements may have been eliminated to prevent obscuring novel aspects. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present disclosure.

As used herein, the term “about”, when used in conjunction with ranges of dimensions, temperatures, concentrations or other physical properties or characteristics is meant to cover slight variations that may exist in the upper and lower limits of the ranges of dimensions so as to not exclude embodiments where on average most of the dimensions are satisfied but where statistically dimensions may exist outside this region.

As used herein, the phrase “a negative electrode for storing zinc” means that the negative electrode can incorporate and release zinc reversibly by electrodeposition/dissolution (plating/stripping) of elemental zinc from/to the electrolyte, by alloying/dealloying reaction, or the negative electrode comprises a material that can store zinc by any one or combination of intercalation, conversion, and capacitive storage (adsorption/deadsorption of Zn^{2+} ions).

Figure 1A shows a **c**onceptual scheme of a zinc-ion battery shown generally at **10**, which includes an anode **12**, and an intercalated layered positive electrode material **14** separated by an electrolyte **16**, with **Figure 1A** showing diagrammatically the operation of the battery **10**, namely during the charging cycle Zn ions are attracted to the negative electrode **12**, and during the discharge cycle Zn ions are attracted to the intercalated positive electrode material **14** into which they intercalate. Electrons flow through the external circuit connecting the negative and positive electrodes which are used to do work.

Figure 1B is a cross section of an actual zinc-ion battery showing the positive electrode **14** contained in a positive electrode compartment **20**, the negative electrode **12** contained in a negative electrode compartment **22**, and the electrolyte **16** contained in an electrolyte compartment **24** in which a separator **28** which is electrically insulating and permeable to zinc ions separating the positive and negative compartments is located. Non-limiting examples of separator **28** include organic polymers (polyethylene (PE), polypropylene (PP), poly(tetrafluoroethylene) (PTFE), poly(vinyl chloride) (PVC)), polyvinylidene fluoride (PVDF), nylon, organic polymer-inorganic oxide, silica glass fiber, porous silica or alumina ceramic membranes, cellulose, cellulose-ceramic oxide, wood, or any combination of these.

The present disclosure provides several embodiments of the intercalated layered positive electrode material **14**. In an embodiment the intercalation layered positive electrode material **14** may be $M_xV_2O_5.\mathbf{n}H_2O$, where x is in a range from 0.05 to 1, **n** is in a range from 0 to 2, and M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion with the metal M ion being in a +2 to +4 valence state. The V_2O_5 has a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M. The number of waters of hydration **n** in some embodiments may be greater than 0 and less than 1. Some of the waters of hydration may be hydrogen bonded to the layers.

In a preferred embodiment $x = 0.25$, and $n = 1$.

In another embodiment, the intercalated layered positive electrode material **14** may be $M_xV_3O_7.\mathbf{n}H_2O$, wherein **x** is in a range from 0.05 to 1, **n** is greater than 0 and less than 2. M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, with the metal M ion being in a +2 to +4 valence state. The V_3O_7 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M and/or hydrogen bonded to the layers. In an embodiment **n** is greater than 0 and less than 1.

In a preferred embodiment $x = 0.05$, and $n = 1$.

In another embodiment, the intercalated layered positive electrode material **14** may be $M_xMoO_y.nH_2O$, in which **x** is in a range from 0 to 1, **y** is in a range from 2 to 3, and **n** is in a range from 0 to 2. M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, with the metal M ion being in a +2 to +4 valence state. The MoO_y has a layer or tunnel crystal structure, and the metal ions M, if present, are pillared between the layers, and waters of hydration are coordinated to the metal ions M pillared between the layers.

In some embodiments n is greater than 0 and less than 2. In some embodiments the waters of hydration are hydrogen bonded to the layers.

In a preferred embodiment $x = 0.25$, $y = 3$ and $n = 0$.

The electrolyte **16** is an aqueous based electrolyte and contains a salt of zinc dissolved therein. Non-limiting examples of the zinc salt comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide to mention a few.

The dissolved zinc is present in an amount in the liquid in a range from about 0.01 to about 10 molar (M), and preferably is present in a range from about 0.1 to about 4 M.

The electrolyte may have a pH in a range between 1 and about 8 but preferably between 4 and about 8 and more preferably 4 to 7. The electrolyte is an aqueous based electrolyte and may be just water containing the dissolved salt of zinc, or additional solvents may be included, for example alcohols, nitriles, carbonates, ethers, sulfoxides, glycols, esters, and amines. Typically, the zinc salt may comprise anyone or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide in 0.1 to 4 M concentration of Zn^{2+} with or without the nonaqueous component and with or without additional ionically-conductive salts such as quaternary ammonium salts or alkali metal salts.

The negative electrode may be made of a solid sheet, mesh, or rod of zinc, or it may be comprised of a zinc layer formed on a current collector. When the battery is assembled with metallic zinc contained in the negative electrode, the battery is typically referred to as a zinc battery. This is opposed to a zinc ion battery in which the negative electrode in its initial state does not contain any zinc. The zinc layer may be a thin sheet of zinc or an alloy, or powder zinc bonded adhered to the surface of the negative electrode facing into the negative electrode compartment. The zinc may be a constituent of a formulation which is adhered to the surface of the current collector. Non-limiting examples of zinc alloys that may be used include alloys of zinc with lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, and titanium.

The negative current collector is an electrically conductive support for active zinc which may be comprised of any one or combination of carbon, boron, lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal. A feature of the negative electrode is that it comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage. In a conversion process, the electrochemical reaction of the negative electrode material with zinc leads to its decomposition into two or more products. In capacitive storage the Zn^{2+} ions are stored at the surface of the negative electrode material by a non-faradic process.

The intercalated layered positive electrode material may have different morphologies. The intercalation layered positive electrode material **14** has a nanostructured morphology. Preferably the average particle size is less than 1000 nm in a direction of Zn ion transport through the particle, and more preferably less than 500 nm in a direction of Zn ion transport through the particle. Non-limiting morphologies include nanowires, fibers, wires, cubes, platelets, spheres, and uneven morphology. They may be simple particles. The particles may have a mean size in a range from about 5 nm to about 50 µm.

The particles may be coated with electrically conducting material, in which

the electrically conducting material is any one or combination of carbon powder and conducting polymer. The particles may be embedded in an electrically conducting matrix and the electrically conducting matrix may comprise any one or combination of carbon and conducting polymer, and including a binder. The binder may be any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

The zinc ion battery materials disclosed herein will now be illustrated by the following non-limiting examples.

Examples

Two vanadium oxide based compounds with layered crystal structures and in ultralong one-dimensional morphology exhibiting as robust host materials for high rate and long term reversible Zn^{2+} ion storage in aqueous electrolyte were produced. Vanadium is a cheap and environmentally benign metal possessing a range of oxidation states (+2 to +5), which allows for multiple redox and hence large specific capacities for vanadium based electrode materials. Particularly, oxides of vanadium e.g., V_2O_5 which is non-toxic and produced in large quantities, displays numerous crystal and compositional chemistries for reversible metal ion storage. Layered $M_xV_nO_m$ oxides (M = metal ion) of compositions such as V_2O_5, V_3O_8, V_4O_{11} that are made of two dimensional sheet structures have been the subject of intense investigation for both non-aqueous and aqueous alkali (Li and Na) ion batteries. The presence of interlayer metal ions and/or water of hydration act as pillars, providing structural stability during long term charge discharge cycling.

Embodying such qualities are $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$, which we have synthesized in nanofiber morphology by a simple and rapid microwave hydrothermal treatment of V_2O_5, without using any toxic or corrosive chemicals, and converted to freestanding film electrodes by adopting a cheaper and greener water based electrode fabrication process. Nanomorphology and compact film structure allows for facile release of strain resulting upon Zn^{2+} cycling, shorter ion diffusion paths, better interaction of carbon additives with the active material and robust conductive wiring - facilitating high specific capacities of ~300 mAh g^{-1} and long term cyclabilities up to 1000 cycles at high coulombic efficiency using fast current rates.

Experimental Methods

Synthesis of $H_2V_3O_8$ and $Zn_xV_2O_5$

Microwave solvothermal method developed over last two decades are now often used to prepare positive electrode materials for lithium ion batteries. In this work, we have modified a time consuming and energy expensive hydrothermal approach used in the synthesis of single crystalline $H_2V_3O_8$ nanobelt to a rapid and scalable microwave hydrothermal method for the synthesis of highly homogeneous $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$ nanofibers. In a typical procedure, 3 to 4 millimoles (mmol) V_2O_5 was dispersed in 15:1 water/ethanol (v) mixture with or without stoichiometric amount of zinc acetate (for $Zn_xV_2O_5.nH_2O$) and transferred to a sealed Teflon^{TM} vessel. The vessels were fitted to a rotor equipped with temperature and pressure sensors. The rotor containing the vessels was then placed in a rotating platform for uniform heating in an Anton Parr microwave synthesis system (Synthos 3000). The system temperature was raised to 180℃ in 10 minutes and maintained for 60 to 90 minutes. The preset temperature was maintained automatically by continuous adjustment of the applied power (limited to 800 Watts). The as-synthesized product was thoroughly washed with distilled water followed by a small amount of iso-propanol and dried at 60℃ for 24 h.

Characterization Methods

Powder X-ray diffraction was performed on a Bruker D8-Advance powder diffractometer equipped with Vantec-1 detector, using Cu-Kα radiation (λ= 1.5405Å) in the range from 5° to 80° (2θ) at a step size of 0.025° using Bragg-Brentano geometry. X-ray data refinement was carried out by conventional Rietveld refinement method using the Bruker-AXS TOPAS 4.2 software (Bruker-AXS, 2008). The background, scale factor, zero point, lattice parameters, atomic positions and coefficients for the peak shape function were iteratively refined until convergence was achieved. The morphologies of the samples were examined by field-emission scanning electron microscopy (FE-SEM, LEO 1530) equipped with an energy dispersive X-ray spectroscopy (EDX) attachment.

Battery Cycling

For electrochemical performance evaluation, a freestanding film type electrode was fabricated by a facile green approach. In a typical process, nanofibers were mixed with conducting nanocarbon Super P® and water based composite binder carboxymethylcellulose (CMC) and styrene-butadiene rubber(SBR) (CMC/SBR= 2:1) in 70:27:3 weight ratio. The mixture was dispersed in small amount of water by using an ultrasonic mixer to obtain a stable homogeneous ink which was filtered through Durapore® DVPP 0.65 μm filtration membrane. The water soluble CMC facilitates the dispersion of hydrophobic carbon particles into water and enables its intimate mixing with the nanofibers. Whereas SBR with high binding abilities for a small amount provides adhesion and electrode flexibility. The binder molecules not involved in this anchoring and adhesion get washed away during filtration and that way electrode films with very small binder content is achieved. After drying at 60℃ the composite film automatically came off which was then punched into 1 cm^2 electrode coins. The electrodes were further dried at 180℃ for 1 h ($H_2V_3O_8$) or 60°C for 12 h (for $Zn_xV_2O_5.nH_2O$). The electrochemical properties were investigated in PFA based Swagelok® type cell using 1 M $ZnSO_4$ in water as the electrolyte and titanium or stainless steel rods as the current collector. The $H_2V_3O_8$ or $Zn_xV_2O_5.nH_2O$ and zinc foil served as the positive and negative electrodes, respectively. Galvanostatic cycling studies were performed using multichannel biologic VMP3 potentiostat/galvanostat.

Three-Electrode Electrochemical Measurements

The voltammetric electrochemical experiments were performed with a three-electrode cell consisting of the working electrode, Pt mesh (1 cm^2) as the counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. The working electrodes examined were a Zn disk (φ = 2 mm), a Ti disk (φ = 2 mm), a stainless steel rod (316 grade, φ = 12 mm), and the $H_2V_3O_8$ composite electrode. Cyclic voltammetry was performed at a scan rate of 5 mV/s and linear sweep voltammograms were acquired at 1 mV/s. These techniques were controlled with a CHI700E potentiostat (CH Instruments, Inc.). The electrolytes used were 1 M Na_2SO_4 for the hydrogen evolution reaction and 1 M $ZnSO_4$ for zinc plating/stripping and the oxygen evolution reaction. All experiments were performed at room temperature (23 ± 2°C).

Results and Discussion

The operating voltage of all secondary aqueous batteries is limited by the potentials for hydrogen evolution and oxygen evolution from water electrolysis. Since both the hydrogen and oxygen evolution reactions (HER and OER, respectively) are pH dependent (see reactions 2 to 5) and catalytic in nature, the precise potential at which they occur is sensitive to the electrolyte composition and electrode material. HER and OER occur during charge at the negative and positive electrodes, respectively, and are displayed below in reactions 2 to 5, while the zinc deposition reaction is shown in reaction 1:

Cathodic Reactions:

Zinc Deposition:

(1) $Zn^{2+} + 2e^- \rightarrow Zn$ $E° = -0.76$ V vs. SHE

Hydrogen Evolution Reaction (HER):

(2) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E° = -0.83$ V vs. SHE

(3) $2H^+ + 2e^- \rightarrow H_2$ $E° = 0.00$ V vs. SHE

Anodic Reactions:

Oxygen Evolution Reaction (OER):

(4) $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ $E° = 0.40$ V vs. SHE

(5) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E° = 1.23$ V vs. SHE

To examine the suitability of a metallic zinc negative electrode for secondary zinc-ion batteries, linear sweep voltammetry was used to probe the HER. In **Figure 2**, a zinc-ion-free (1 M Na_2SO_4) electrolyte was used which contained the same concentration of the sulfate anion and similar pH value (4-5) as the 1 M $ZnSO_4$ electrolyte used for all other studies. Here, it can be seen that the hydrogen evolution reaction has an overpotential of ~0.4 V with respect to Pt on both zinc metal and titanium metal. Titanium was found to be an excellent current collector for the negative, comparable to Zn itself, as evident from **Figure 3A**, which also shows that zinc deposition on a zinc electrode in 1 M $ZnSO_4$ occurs at a higher potential than the HER. Stainless steel was deemed to be unsuitable as a current collector for the negative electrode as it catalyzes the HER and competes with zinc electrodeposition (**Figure 3B**).

On the other hand, zinc deposition and stripping was completely reversible on titanium as displayed in **Figure 4A**. The coulombic efficiency (Q_{ox}/Q_{red}) was 100 % over 100 cycles on titanium with no loss in the electrical charge (Q) for deposition or stripping. Stainless steel suffered from a decay in both Q_{red} and Q_{ox}, even for the first 10 cycles (**Figure 4B**). On stainless steel the coulombic efficiency was only 87 % for the first cycle and 74 % for the tenth cycle. This shows that the excess charge during reduction (Q_{red}) goes towards the HER.

Since the OER dictates the maximum potential for the positive electrode, this was first examined on stainless steel, a practical current collector material. Titanium also has a high overpotential for OER, however, we suspect that OER on many Zn^{2+}-intercalation materials will have activity similar to stainless steel which is why we show the result for OER on stainless steel rather than titanium.

Figure 5 displays the linear voltammograms for Zn electrodeposition onto a Zn disk and OER on a stainless steel rod in 1 M $ZnSO_4$ at 1 mV/s. This plot provides the maximum possible operating voltage window of a secondary Zn-ion battery using 1 M $ZnSO_4$ which is ~2.4 V. Obviously, the positive electrode of choice must be tested, particularly if a high-voltage material is to be used. In our case, the upper voltage cut-off for batteries with $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$ are 1.1 V and 1.4 V respectively, which is well below the limit at which OER will occur at these materials.

The hydrothermal method has evolved into an important wet chemistry method for the synthesis of nanostructured vanadium oxide materials. However, such process could though be time consuming, as in the synthesis of $H_2V_3O_8$ nanobelts which requires hydrothermal treatment of V_2O_5 in water for 2-3 days at 210°C. By introducing the microwave heat treatment, we have developed a versatile and scalable synthetic approach for the rapid synthesis of ultralong $H_2V_3O_8$ and $Zn_xV_2O_5.nH_2O$ nanofibers. Water is known to strongly interact with the microwave radiation via a dipolar-microwave interaction, leading to rapidly superheated local regions in the reaction media. In contrast to typical hydrothermal methods where slow heating mainly occurs via thermal conduction mechanism, heating of the entire reaction media through penetration of microwaves triggers rapid intercalation-exfoliation and cleavage of V_2O_5 into nanosheets and finally into $H_2V_3O_8$ or $Zn_xV_2O_5.nH_2O$ nanofibers.

Phase purity of the as-synthesized materials was confirmed by Rietveld refinement of the powder diffraction pattern as shown in **Figure 6A** for $H_2V_3O_8$ and **Figure 6B** for $Zn_xV_2O_5.nH_2O$. The XRD pattern in **Figure 6A** could be refined to an orthorhombic Pnam $V_3O_7.H_2O$ ($H_2V_3O_8$) with the lattice parameters of a = 16.87 Å, b = 9.33 Å, c = 3.63 Å, and $\alpha = \beta = \gamma = 90°$. Here V_3O_8 layers, which are constructed of VO_6 octahedra and VO5 trigonal bipyramids, are held by strong hydrogen bonding together with van der walls interaction. The H_2O molecule bound to the vanadium atom in place of one oxygen in VO_6 octahedra creates hydrogen bond with the octahedra in the next layer, forming a layered 3D structure. The hydrogen bonded layered structure is found to be very stable up to a temperature of ~300℃ when the structure dehydrates.

The pattern in **Figure 6B** was refined to a composition of $Zn_{0.25}V_2O_5.H_2O$ crystallizing in P-1 triclinic system with lattice parameters of a = 10.75 Å, b = 7.77 Å, c = 10.42 Å, α = 91.26°, β = 90.31°, and γ = 88.66°, which closely resemble the $Zn_{0.25}V_2O_5.H_2O$ phase for which the structure was solved by single crystal diffraction. Here the structure consists of V_2O_5 layer, built up of VO_6 octahedra, VO_5 trigonal bypyramids, and VO_4 tetrahedra, stacked along ***c*** axis with the interlayer Zn atom coordinating to the oxygen apices on opposite sides and the oxygen atoms of the in plane water molecules.

SEM investigation as presented in **Figures 7A, 7B, 7C** and **7C** reveals highly uniform and ultralong one dimensional morphology for both the materials. At a closer look, $H_2V_3O_8$ (**Figure 7A and 7B**) appears to have a ribbon like morphology and $Zn_{0.25}V_2O_5.H_2O$ (**Figure 7C and 7D**) seems to adopt a feather like structure. Both the fibers have a diameter of about 100 nm. To the inventors' knowledge, this is first time $Zn_{0.25}V_2O_5.H_2O$ has been synthesized in such nanomorphology.

Unlike conventional NMP (N-methyl-2-pyrrolidone) based Li-ion battery electrode slurry fabrication, which is expensive and time consuming due to the use of NMP, we have developed a novel and versatile electrode fabrication approach in this work. A water based ink was prepared for both the material by ultrasonic dispersion with conductive carbon and minimum (3%) amount of aqueous based binder CMC and SBR. The ink was passed through a PVDF based membrane filter resulting in a compact film, which upon drying (at 60℃) spontaneously comes off the hydrophobic membrane due to the hydrophilic nature of the oxide based electrode film. The wool like textile morphology of the used materials facilitate dense mat type film electrode formation. Notably, the thickness and the loading of the film can be easily varied by adjusting the amount of ink and the PVDF membrane filter can be reused multiple times. The use of water as the solvent and water based cheap binders along with the recurring use of the PVDF filter membrane makes the process very cost effective and environmentally green. The use of freestanding film electrode also allow us to avoid possible corrosion issues of metal foil, which is otherwise used to deposit an electrode film, and focus on electrochemical zinc storage properties of the active materials only.

The reversible electrochemical Zn^{2+} storage capabilities of $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ were explored in full cells by applying galvanostatic techniques. The electrodes were studied in different voltage windows to elucidate the optimal voltage range for highly reversible electrochemical cycling. Based on this study, voltage windows of 0.4 V – 1.1 V and 0.5 – 1.4 V vs. Zn were determined for the $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ electrodes, respectively, which clearly fall within the safe operational window in aqueous electrolyte (1 M $ZnSO_4$ in H_2O) using Zn anode and Ti rod as the current collector (see discussion above). Cycling in larger voltage window results in higher specific capacities, but structural stress generated from the insertion of large amount of zinc results in pulverization of the electrode and rapid capacity fading and therefore was avoided. Moreover, a practical voltage window not only enable better cyclability, but also ensure lesser voltage polarization and an adequate operating voltage suitable for practical application.

Figures 8A and **8B** show the voltage polarization curves for the two electrodes at different current rates. A rate of 1C (the C-rate is a measure of rate at which the cell is discharged or charged relative to its maximum capacity; a 1C rate means that the discharge/charge current will discharge/charge the cell in 1 h) was defined as 350 mA g^{-1} and 300 mA g^{-1} for $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ respectively, based on the highest capacity achieved at a moderate current density. **Figure 8A** demonstrates the variation of cell voltage for $H_2V_3O_8$ electrode as a function of obtainable specific capacity. The voltage profile shows a small plateau delivering ~100 mAh g^{-1} of capacity at around 0.8 V, following which it varies in slope registering high specific capacity of 325 mAh g^{-1} and 270 mAh g^{-1} at high rates of 4C (1400 mA g^{-1}) and 8C (2800 mA g^{-}

^{1}), respectively. Depending on the applied current rates close to 1.5 to 2, Zn^{2+} ions are electrochemically intercalated during discharge. An average operating voltage of ~0.64 V is obtained for this electrode irrespective of the rate. On the contrary $Zn_{0.25}V_2O_5.H_2O$ electrode demonstrates a higher average operating voltage of ~0.8 V at all current densities (**Figure 8B**). This is most likely the consequence of higher average oxidation state of V in $Zn_{0.25}V_2O_5.H_2O$ ($V^{4.8+}$) compared to that in $H_2V_3O_8$ ($V^{4.66+}$) including the effect from structural energetics.

For $Zn_{0.25}V_2O_5.H_2O$, typical discharge-charge polarization curves display sloping behavior with some small plateau like feature, suggesting a dominant solid-solution type process associated with electrochemical zinc (de)insertion. Interestingly, at higher current rates, discharge-charge capacities increased with cycling, reaching highest value after some cycling. This is most likely related to the kinetic limitation of Zn^{2+} diffusion into the layered structure of the electrode, requiring multiple discharge-charge cycles to open up accessible intercalation sites, before optimal capacity could be achieved. The $Zn_{0.25}V_2O_5.H_2O$ electrodes registered a specific capacity of ~300 mAh g^{-1} (at C/6: 50 mA g^{-1}), which is slightly lower than the $H_2V_3O_8$ electrode. Typically, about 1.2 Zn^{2+} ions are intercalated per mole of $Zn_{0.25}V_2O_5.H_2O$ during the electrochemical discharge process. The high specific capacities obtained for both materials can be ascribed to the large specific surface area and short diffusion distances provided by the nanofiber morphology. It is also important to note that for both the electrodes the voltage polarization curves recorded in the subsequent cycles exhibit identical feature as the first cycle, indicating that the initial structure is recovered at the end of each charge cycle.

As a result of nanostructural morphology, flexible film like electrode architecture, and structural reversibility upon Zn^{2+} de(intercalation) both the electrodes demonstrate superior cyclability at high current rates. **Figures 9A** to **9D** show specific capacity and coulombic efficiency of the $H_2V_3O_8$ (**Figure 9A** and **Figure 9B**) and $Zn_{0.25}V_2O_5.H_2O$ (**Figure 9C** and **Figure 9D**) as a function of cycling at **4C** (**Figure 9A** and **Figure 9C**) and 8C (**Figure 9B** and **Figure 9D**) current rates (For the definition of C rate for $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ see above). As evident, the $Zn_{0.25}V_2O_5.H_2O$ based cell registered excellent cyclability at 8C rate, retaining 80% of the initial specific capacity after 1000 cycles. At 4C, a similar cell delivered 500 cycles with only 20% drop in the initial capacity. Whereas, identical $H_2V_3O_8$ cells demonstrated slightly inferior capacity retention delivering about 40% and 30% of the initial reversible capacity at the end of 300 and 500 cycles, when operated at current rate of 4C and 8C, respectively.

It is important to note that the $H_2V_3O_8$ cell showed distinctively better cycling behavior at higher current rate (8C). This can be linked to the comparatively lower amount Zn^{2+} intercalation per mole of $H_2V_3O_8$, leading to lesser structural strain, which ensures better cyclability. However this feature is not very prominent for the $Zn_{0.25}V_2O_5.H_2O$ based electrode, which suggests higher structural flexibility of $Zn_{0.25}V_2O_5.H_2O$ towards Zn^{2+} (de)intercalation. Higher structural flexibility granted by the presence of interlayer Zn^{2+} ions also ensures excellent electrochemical cyclability of the $Zn_{0.25}V_2O_5.H_2O$ cells. On the contrary, hydrogen bonded VO_x interlayer in $H_2V_3O_8$ lack structural rigidity and flexibility of $Zn_{0.25}V_2O_5.H_2O$, resulting in slightly poor capacity retention. For all the studies nearly 100% coulombic efficiency was registered as a function of cycling, which further confirms the high degree of reversibility of electrochemical Zn^{2+} (de)intercalation into the layered structure of presented vanadium oxide materials.

By virtue of 1D nanomorphology and film like compact yet flexible electrode architecture both the materials delivered splendid rate performance under variable current loading as a function of cycling. **Figure 10A** shows rate capability of $H_2V_3O_8$ and **Figure 10B** shows rate capability of $Zn_{0.25}V_2O_5.H_2O$ cell studied under variable current loading as a function of cycling. The corresponding coulombic efficiencies are also shown. The results are shown in **Figures 10A** and **10B** together with the corresponding coulombic efficiencies registered at variable rates. As expected, $Zn_{0.25}V_2O_5.H_2O$ electrode demonstrates better rate capability; starting with an initial capacity of 285 mAh g^{-1} at 1C rate, the cell delivers 260 mAh g^{-1} of durable capacity at 8C, which reverts back to 285 mAh g^{-1} of capacity at 1C rate, nearly identical to the initial 1C capacity. Whereas $H_2V_3O_8$, starting with a slightly higher initial 1C capacity of 335 mAh g^{-1} falls to 222 mAh g^{-1} of capacity at 8C rate, which doesn't completely recover at 1C at the end of variable current load test. Similar to electrochemical cyclability, better rate performance of $Zn_{0.25}V_2O_5.H_2O$ compared to the $H_2V_3O_8$ electrode is attributed to its more robust and flexible layered structure which is efficiently pillared by immobile Zn^{2+} ions. In both cases, coulombic efficiency increases with current load, which is expected as the unwanted side reactions are suppressed at higher current rates.

Based on the galvanostatic cycling and rate performance results, energy and power densities could be calculated and are presented in the Ragone plot shown in **Figure 11.** The specific energy density is the total energy that can be derived per unit mass of the active electrode material at the cathode. It is the product of specific discharge capacity (Q in mAh g^{-1}) based on the total mass of the active electrode material and the operating voltage in one full discharge. The power density is obtained from the product of current density and average operating voltage.

As evident, beside good cyclability and excellent rate capability, both the $H_2V_3O_8$ and $Zn_{0.25}V_2O_5.H_2O$ based cells delivers good energy density at high power density in comparison to α-MnO_2 (see reference 1) and $Zn_3[Fe(CN)_6]_2$, see reference 2. $Zn_{0.25}V_2O_5.H_2O$ exhibits the highest energy density of the three positive electrodes at high power and delivers a steady and high energy density over a wide range of power.

Conclusions

In summary, we have developed two novel layered vanadium oxide nanomaterials for highly reversible Zn^{2+} storage at high current rates and long term cyclability. Besides, a simple scalable microwave synthesis of vanadium oxide nanomaterials and a versatile water based environmentally green electrode fabrication process is presented. As has been found, presence of stable interlayer species, e.g., H_2O in $H_2V_3O_8$ and Zn^{2+} and/or H_2O in $Zn_{0.25}V_2O_5.H_2O$, plays pivotal role in stabilizing the layered structure against repeated Zn^{2+} de(intercalation), and thereby enables long term cyclability with high specific capacities. Although the average operating cell voltages (0.64 V for $H_2V_3O_8$ and 0.81 V for $Zn_{0.25}V_2O_5.H_2O$) are rather modest, high specific capacities of ~300 mAh g^{-1} ensure high energy density (230-280 Wh kg^{-1}), highest on record among the known aqueous Zn-ion batteries (see **Table 1** below). Good energy density, impressive rate performance and cyclability, cost effective scalable processing of raw materials and electrodes, and not the least high abundance and production of zinc metal make these aqueous zinc ion secondary cells viable candidates for large scale application like grid storage.

Positive/Negative Electrodes	Average Operating Voltage (V)	Energy Density (Wh kg^{-1})	Capacity Retention (Rate)	Reference
α-MnO_2/Zn	1.3 V	225	75% After 100 cycles (6C rate)	**1**
Zinc-hexacyanoferrate/Zn	1.7 V	100	75% After 100 cycles (1C rate)	**2**
$H_2V_3O_8$/Zn	0.64 V	230	70% after 500 cycles (8C rate)	Present Work
$Zn_{0.25}V_2O_5.H_2O$/Zn	0.81 V	280	80% after 1000 cycles (8C rate)	Present Work

Table 1. Operating voltage, energy density, and cycling performance of different rechargeable aqueous Zn-ion batteries.

The foregoing description of the preferred embodiments of the present disclosure has been presented to illustrate the principles of the invention and not to limit the disclosure to the particular embodiments illustrated and described. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.

References

1. C. J. Xu, B. H. Li, H. D. Du, F. Y. Kang, Angew. Chem. Int. Ed. 2012, 51, 933.

2. Zhang, L.; Chen, L.; Zhou, X.; Liu, Z. Adv. Energy Mater. 2015, 5, 1400930.

THEREFORE WHAT IS CLAIMED IS:

1. A zinc ion battery, comprising:

a positive electrode compartment having enclosed therein an intercalation layered positive electrode material $M_xV_2O_5.\mathbf{n}H_2O$, wherein x is in a range from 0.05 to 1, **n** is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_2O_5 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

2. The zinc ion battery according to claim 1 wherein **n** is greater than 0 and less than 1.

3. The zinc ion battery according to claims 1 or 2 wherein some of the waters of hydration are hydrogen bonded to the layers.

4. The zinc ion battery according to claims 1, 2 or 3 wherein the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery.

5. The zinc ion battery according to claims 1, 2, 3 or 4 wherein the electrolyte has a pH in a range from about 1 to about 8.

6. The zinc ion battery according to any one of claims 1 to 5 wherein the electrolyte has a pH in a range from about 4 to about 8.

7. The zinc ion battery according to any one of claims 1 to 6 wherein the intercalation layered cathode material has a nanostructured morphology which is defined by an average particle size of less than or equal to 1000 nm in at least one particle dimension.

8. The zinc ion battery according to claim 7 wherein the average particle size is less than 500 nm in a direction of Zn ion transport through the particle.

9. The zinc ion battery according to any one of claims 1 to 8 wherein the intercalation layered positive electrode material has a particulate morphology being particles having a mean size in a range from about 5 nm to about 50 μm.

10. The zinc ion battery according to claim 9 wherein the particles are coated with electrically conducting material.

11. The zinc ion battery according to claim 10 wherein the electrically conducting material is any one or combination of carbon powder and conducting polymer.

12. The zinc ion battery according to claim 9 wherein the particles are embedded in an electrically conducting matrix.

13. The zinc ion battery according to claim 12 wherein the electrically conducting matrix comprises any one or combination of carbon and conducting polymer, and including a binder.

14. The zinc ion battery according to claim 13 wherein the binder is any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

15. The zinc ion battery according to any one of claims 1 to 14 wherein the negative electrode comprises zinc metal.

16. The zinc ion battery according to claim 15 wherein the negative electrode is a zinc metal electrode.

17. The zinc ion battery according to claim 15 wherein the negative electrode is a zinc alloy.

18. The zinc ion battery according to any one of claims 1 to 14 wherein the negative electrode comprises a current collector, and a surface of the current collector facing into the negative electrode compartment having a layer of zinc bound thereto.

19. The zinc ion battery according to claim 18 wherein the layer of zinc comprises powdered zinc metal.

20. The zinc ion battery according to claim 18 wherein the layer of zinc comprises a sheet of zinc metal.

21. The zinc ion battery according to claim 18, 19 or 20 wherein the current collector is comprised on any one or combination of carbon, boron, lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal.

22. The zinc ion battery according to any one of claims 1 to 14 wherein the negative electrode comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage.

23. The zinc ion battery according to any one of claims 1 to 22 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.01 to about 10 molar.

24. The zinc ion battery according to any one of claims 1 to 23 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.1 to about 4 M.

25. The zinc ion battery according to claim 23 wherein the salt of zinc comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide.

26. A zinc ion battery, comprising:

a positive electrode compartment having enclosed therein and intercalated layered positive electrode material $M_{\mathbf{x}}V_3O_7.\mathbf{n}H_2O$, wherein $\mathbf{x}$ is in a range from 0.05 to 1, $\mathbf{n}$ is greater than 0 and less than 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said V_3O_7 is a layered crystal structure having the metal ions M pillared between the layers, and waters of hydration coordinated to the metal ions M and/or hydrogen bonded to the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

27. The material according to claim 26 wherein **n** is greater than 0 and less than 1.

28. The zinc ion battery according to claims 26 or 27 wherein the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery.

29. The zinc ion battery according to claims 26, 27, or 28 wherein the electrolyte has a pH in a range from about 1 to about 8.

30. The zinc ion battery according to any one of claims 26 to 29 wherein the intercalation layered positive electrode material has nanostructured morphology which is defined by an particle size of less than or equal to 1000 nm in at least one particle dimension.

31. The zinc ion battery according to claim 30 wherein the average particle size is less than 500 nm in a direction of Zn ion transport through the particle.

32. The zinc ion battery according to any one of claims 26 to 30 wherein the

intercalation layered positive electrode material has a particulate morphology being particles having a mean size in a range from about 5 nm to about 50 µm.

33. The zinc ion battery according to claim 32 wherein the particles are coated with an electrically conducting material.

34. The zinc ion battery according to claim 33 wherein the electrically conducting material is any one or combination of carbon powder and conducting polymer.

35. The zinc ion battery according to claim 32 wherein the particles are embedded in an electrically conducting matrix.

36. The zinc ion battery according to claim 35 wherein the electrically conducting matrix comprises any one or combination of carbon and conducting polymer, and including a binder.

37. The zinc ion battery according to claim 36 wherein the binder is any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

38. The zinc ion battery according to any one of claims 26 to 37 wherein the negative electrode comprises zinc metal.

39. The zinc ion battery according to claim 38 wherein the negative electrode is a zinc metal electrode.

40. The zinc ion battery according to claim 38 wherein the negative electrode is a zinc alloy.

41. The zinc ion battery according to any one of claims 26 to 37 wherein the negative electrode comprises a current collector, and a surface of the current collector facing into the negative electrode compartment having a layer of zinc bound thereto.

42. The zinc ion battery according to claim 41 wherein the layer of zinc comprises powdered zinc metal.

43. The zinc ion battery according to claim 41 wherein the layer of zinc comprises a sheet of zinc metal.

44. The zinc ion battery according to claim 41, 42 or 43 wherein the current collector is comprised of any one or combination of carbon, boron, lead, vanadium,

chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal.

45. The zinc ion battery according to any one of claims 26 to 37 wherein the negative electrode comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage.

46. The zinc ion battery according to any one of claims 26 to 45 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.01 to about 10 Molar.

47. The zinc ion battery according to any one of claims 26 to 46 wherein the electrolyte further comprises water dissolved zinc present in a range from about 0.1 to about 4 M.

48. The zinc ion battery according to any one of claims 26 to 47 wherein the salt of zinc comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate, zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide.

49. A zinc ion battery; comprising:

a positive electrode compartment having enclosed therein an intercalated layered positive electrode material $M_xMoO_y.nH_2O$, wherein x is in a range from 0 to

1, y is in a range from 2 to 3, n is in a range from 0 to 2, wherein M is any one or combination of a d-block metal ion, f-block metal ion and alkaline earth ion, the metal M ion being in a +2 to +4 valence state, and wherein said MoO_y has a layer or tunnel crystal structure, and the metal ions M, if present, pillared between the layers, and waters of hydration coordinated to the metal ions M pillared between the layers;

a negative electrode compartment having enclosed therein a negative electrode for storing zinc;

a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and

an electrolyte comprising water and having a salt of zinc dissolved therein.

50. The zinc ion battery according to claim 49 wherein the negative electrode comprises zinc, and wherein the zinc ion battery is a zinc metal battery.

51. The zinc ion battery according to claims 49 or 50 wherein the electrolyte has a pH in a range from about 1 to about 8.

52. The zinc ion battery according to any one of claims 49 to 51 wherein the electrolyte has a pH in a range from about 4 to about 8.

53. The zinc ion battery according to any one of claims 49 to 52 wherein the intercalation layered positive electrode material has nanostructured morphology

which is defined by a particle size of less than or equal to 1000 nm in at least one particle dimension.

54. The zinc ion battery according to claim 53 wherein the average particle size is less than 500 nm in a direction of Zn ion transport through the particle.

55. The zinc ion battery according to any one of claims 49 to 54 wherein the intercalation layered positive electrode material has a particulate morphology being particles having a mean size in a range from about 5 nm to about 50 µm.

56. The zinc ion battery according to claim 55 wherein the particles are coated with electrically conducting material.

57. The zinc ion battery according to claim 56 wherein the electrically conducting material is any one or combination of carbon powder and conducting polymer.

58. The zinc ion battery according to claim 55 wherein the particles are embedded in an electrically conducting matrix.

59. The zinc ion battery according to claim 58 wherein the electrically conducting matrix comprises any one or combination of carbon and conducting polymer, and including a binder.

60. The zinc ion battery according to claim 59 wherein the binder is any one or combination of styrene butadiene rubber (SBR), sodium carboxymethylcellulose (CMC), polyvinyl acetate (PVAc), polyethylene glycol (PEG), polybutyl acrylate (PBA), polyurethane, acrylonitrile, polypyrrole, polyaniline, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), perfluorosulfonic acid (PFSA), and poly(3,4-ethylenedioxythiophene) (PEDOT).

61. The zinc ion battery according to any one of claims 49 to 60 wherein the negative electrode comprises zinc metal.

62. The zinc ion battery according to claim 61 wherein the negative electrode is a zinc metal electrode.

63. The zinc ion battery according to claim 61 wherein the negative electrode is a zinc alloy.

64. The zinc ion battery according to any one of claims 49 to 60 wherein the negative electrode comprises a current collector, and a surface of the current collector facing into the negative electrode compartment having a layer of zinc bound thereto.

65. The zinc ion battery according to claim 64 wherein the layer of zinc comprises powdered zinc metal.

66. The zinc ion battery according to claim 64 wherein the layer of zinc comprises a sheet of zinc metal.

67. The zinc ion battery according to claim 64, 65 or 66 wherein the current collector is comprised on any one or combination of carbon, boron, lead, vanadium, chromium, manganese, iron, cobalt, nickel, cadmium, tungsten, bismuth, tin, indium, antimony, copper, titanium, and zinc metal.

68. The zinc ion battery according to any one of claims 49 to 67 wherein the negative electrode comprises a material that can store elemental zinc by any one or combination of intercalation, conversion, and capacitive storage.

69. The zinc ion battery according to any one of claims 49 to 68 wherein the electrolyte further comprises water said dissolved zinc present in a range from about 0.01 to about 10 molar.

70. The zinc ion battery according to any one of claims 49 to 69 wherein the electrolyte further comprises water said dissolved zinc present in a range from about 0.1 to about 4 M.

71. The zinc ion battery according to any one of claims 49 to 70 wherein the salt of zinc comprises any one or combination of zinc sulfate, zinc acetate, zinc citrate,

zinc iodide, zinc chloride, zinc perchlorate, zinc nitrate, zinc phosphate, zinc triflate, zinc bis(trifluoromethanesulfonyl)imide, zinc tetrafluoroborate, and zinc bromide.

72. The zinc ion battery according to any one of claims 49 to 71 wherein n is greater than 0 and less than 2.

73. The zinc ion battery according to any one of claims 49 to 72 wherein some of the waters of hydration are hydrogen bonded to the layers.

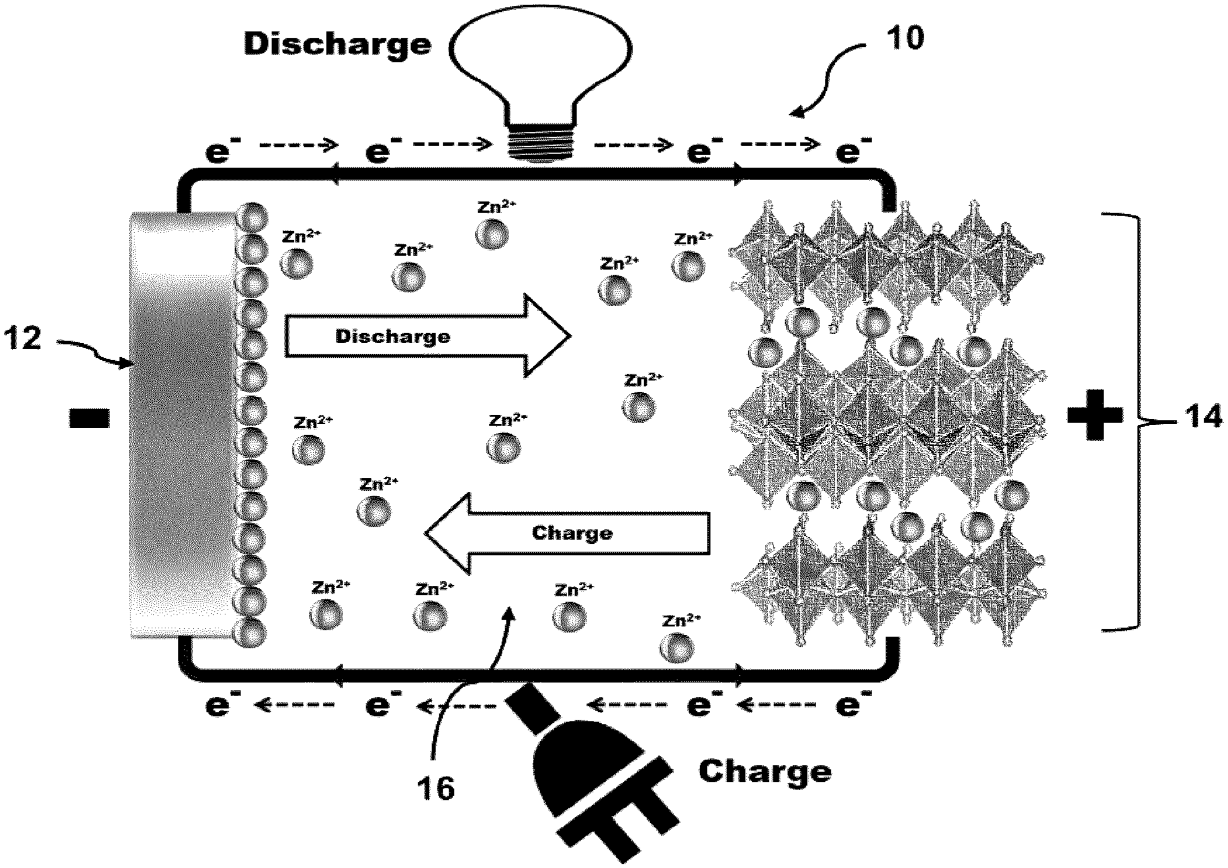


Figure 1A

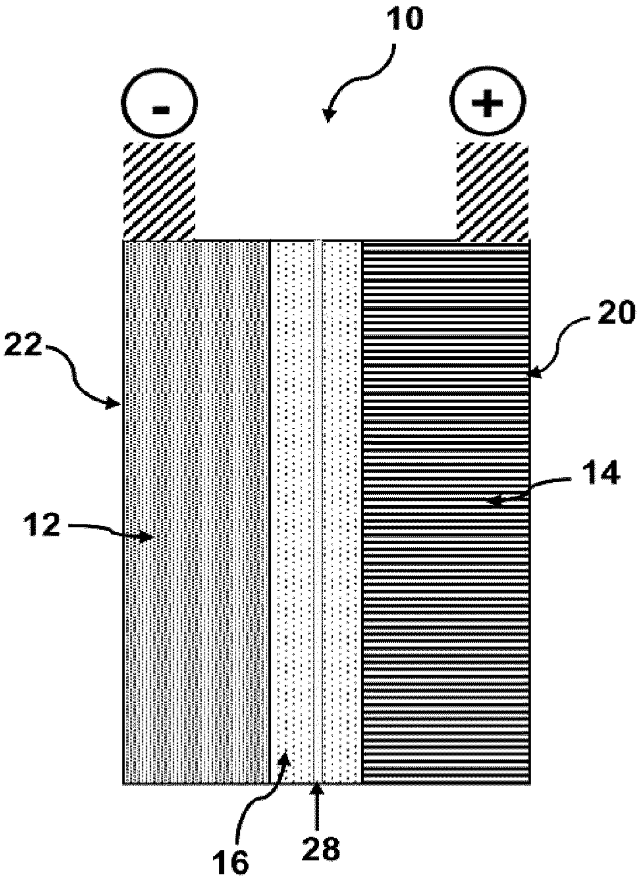
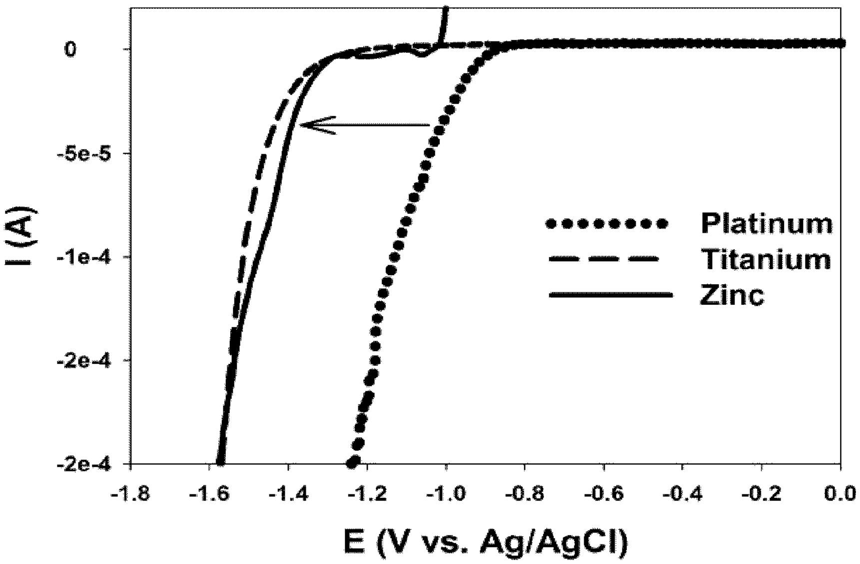
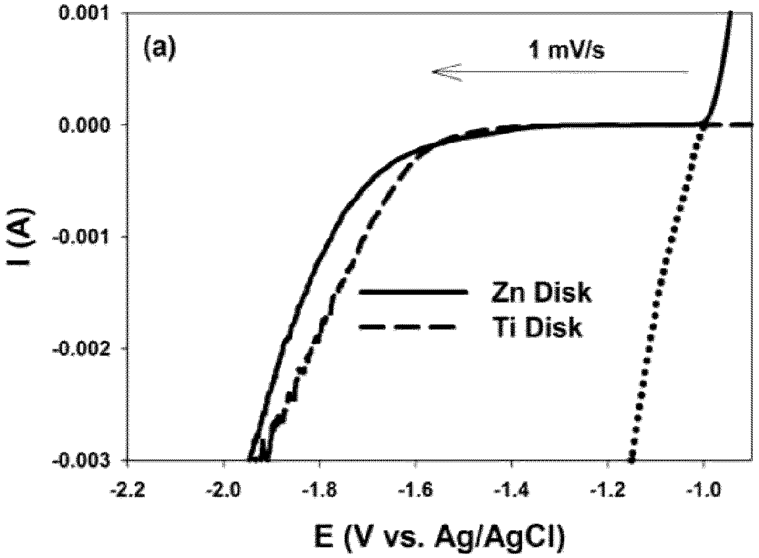


Figure 1B



0
-5e-5
-1e-4
-2e-4
-2e-4
I (A)
-1.8
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
E (V vs. Ag/AgCl)
Platinum
Titanium
Zinc

Figure 2



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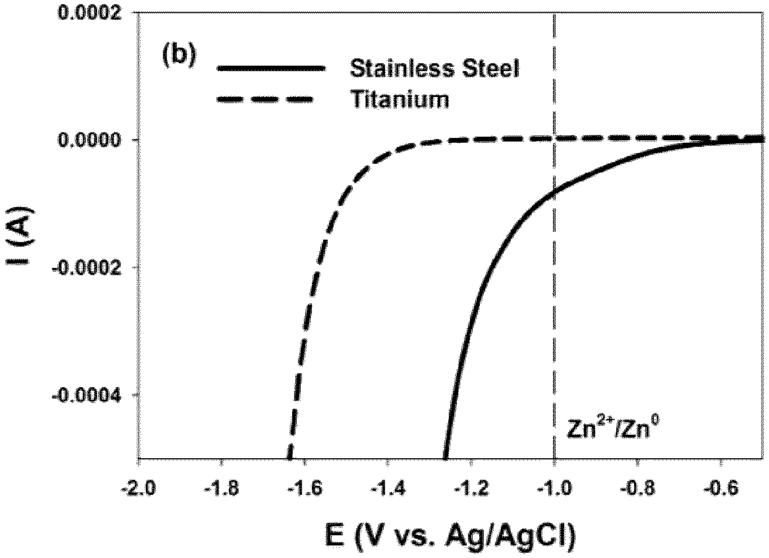

Figure 3B

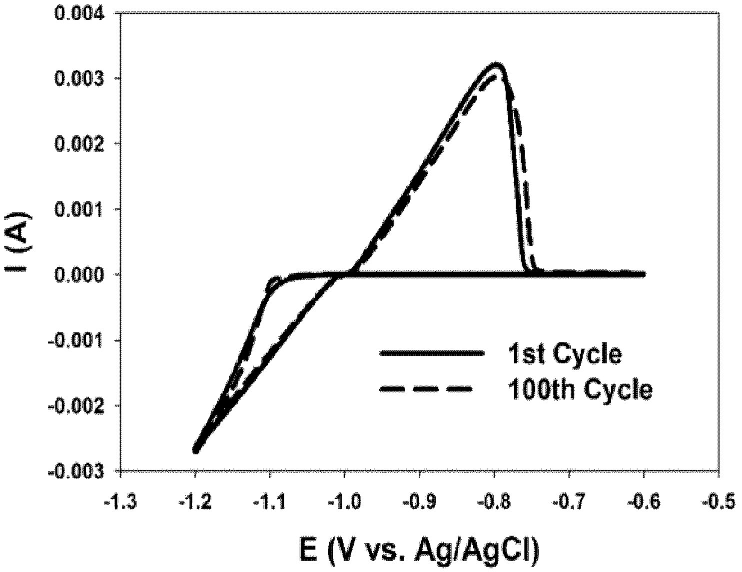

Figure 4A

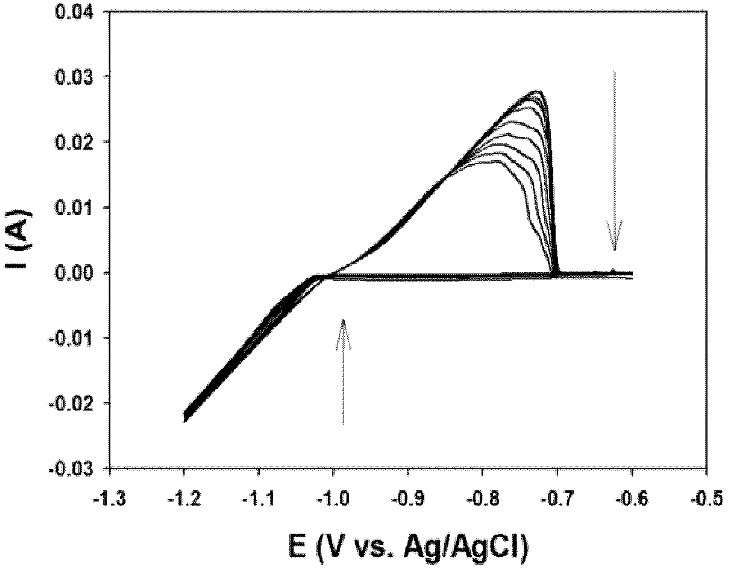

Figure 4B

6/14

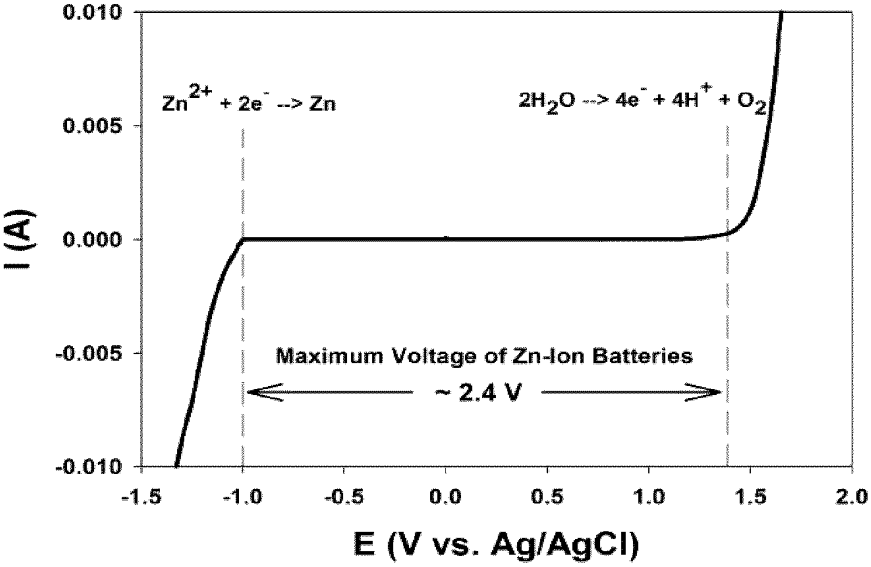
0.010
0.005
0.000
-0.005
-0.010
I (A)
$Zn^{2+} + 2e^{-} \rightarrow Zn$
$2H_2O \rightarrow 4e^{-} + 4H^{+} + O_2$
Maximum Voltage of Zn-Ion Batteries
~ 2.4 V
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
E (V vs. Ag/AgCl)

Figure 5

7/14

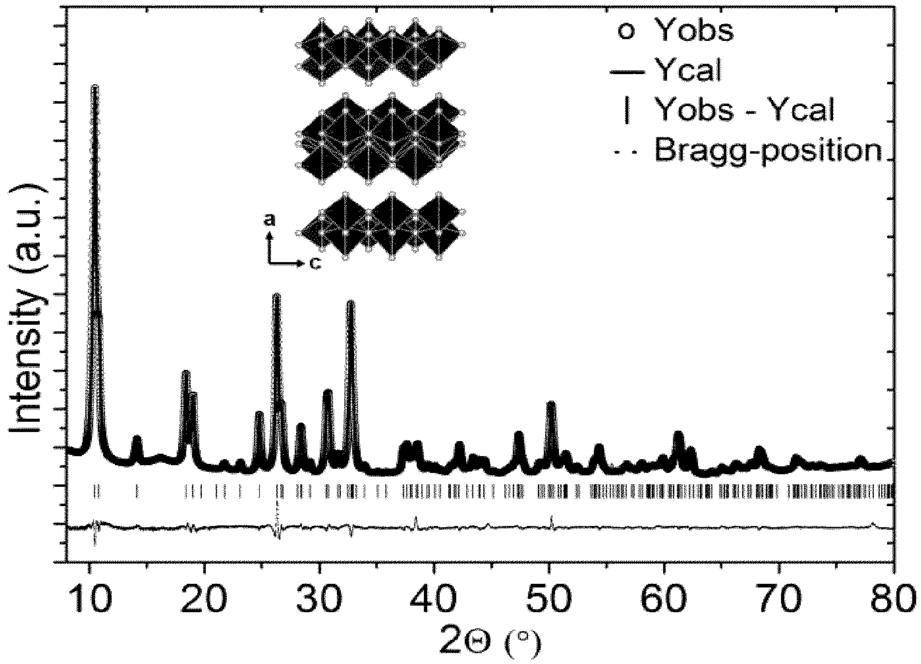

Figure 6A

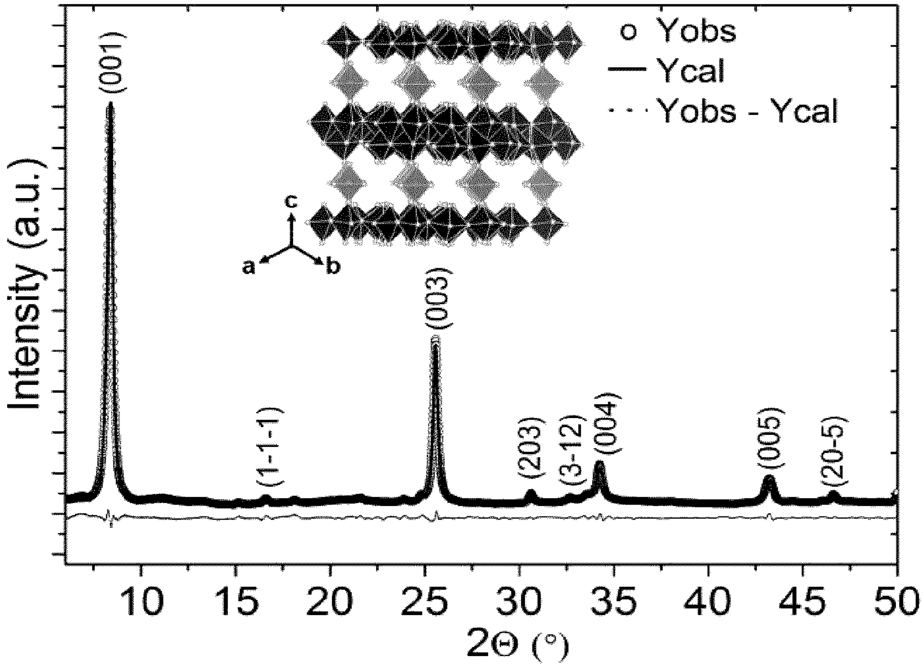

Figure 6B

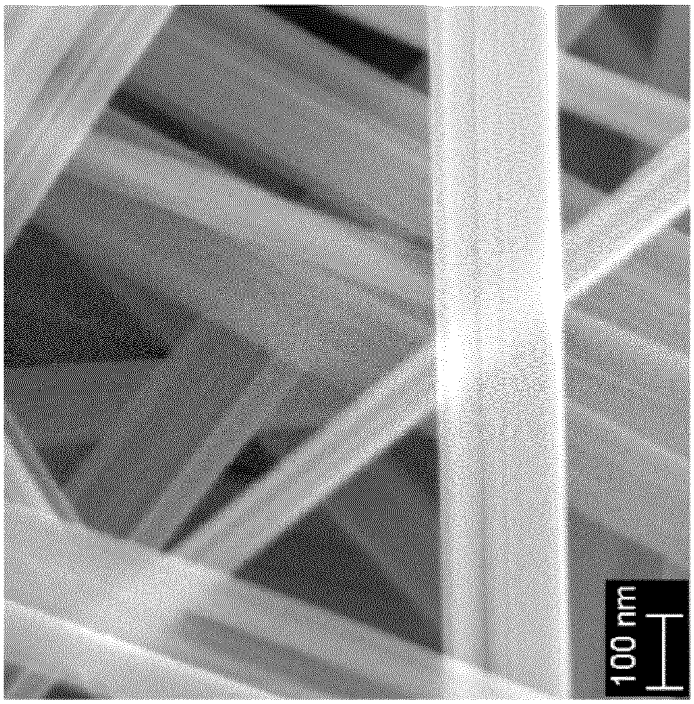

Figure 7B

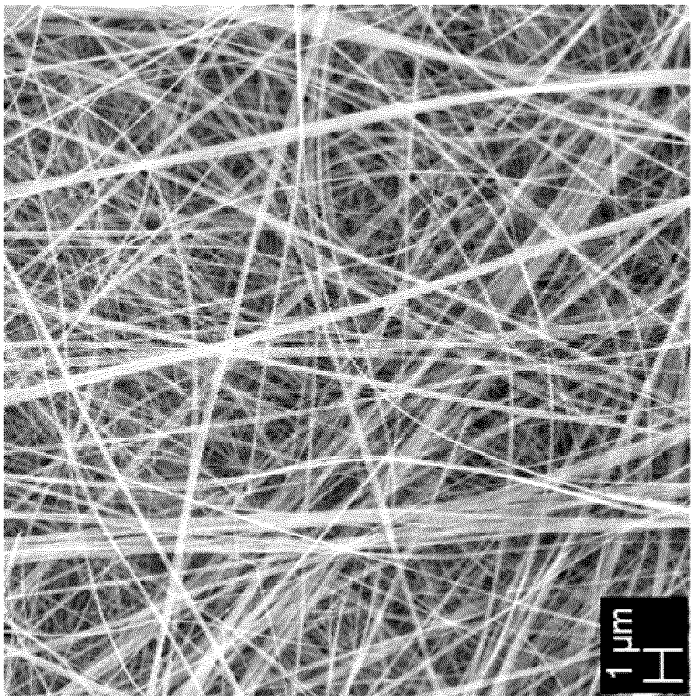

Figure 7A

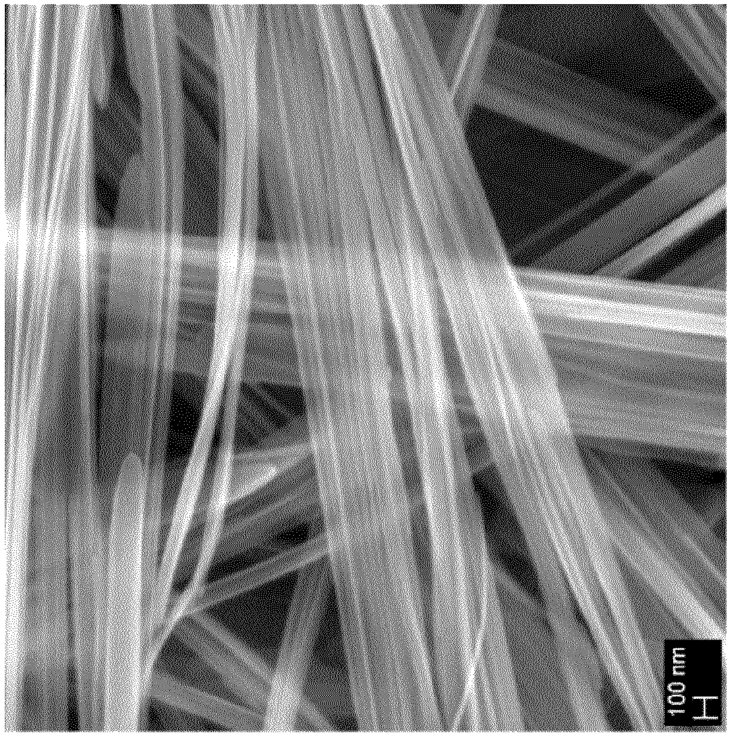

Figure 7D

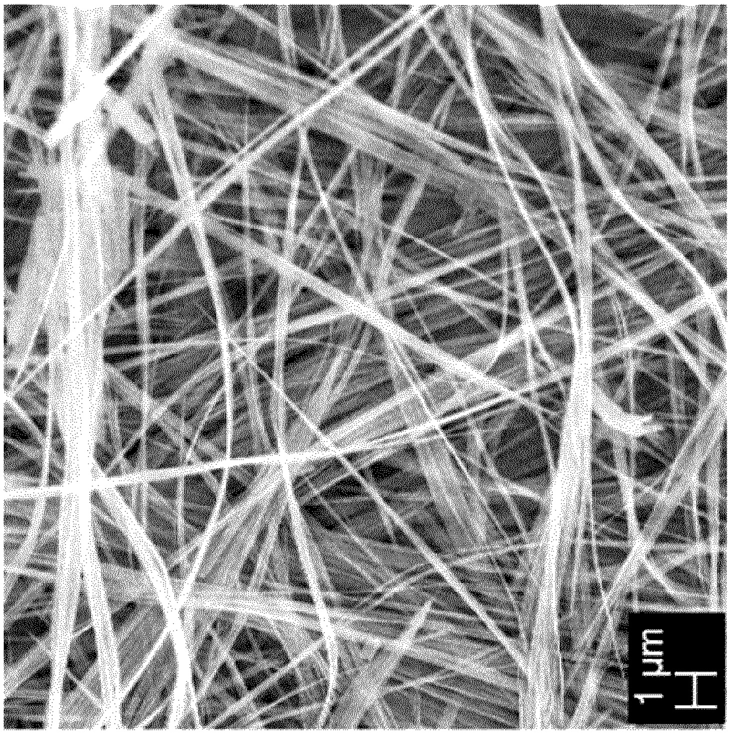

Figure 7C

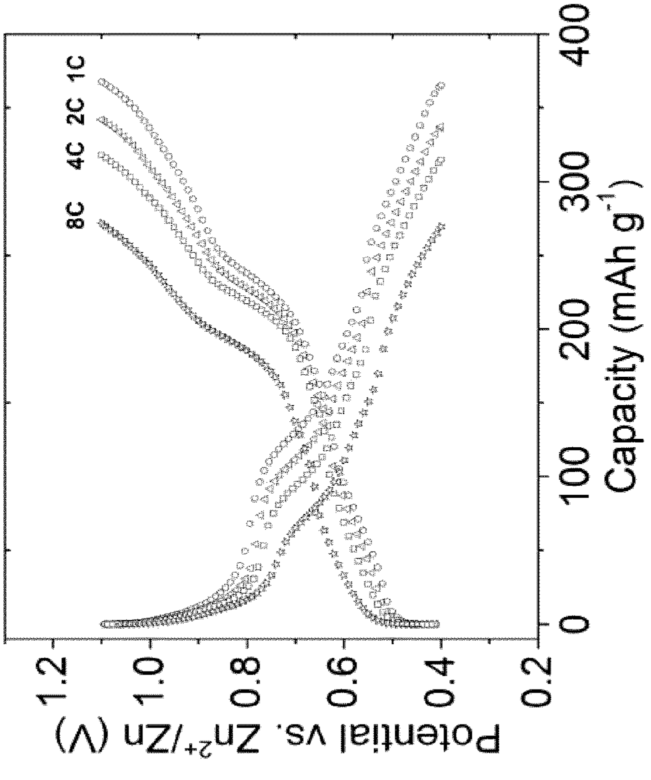

Figure 8A

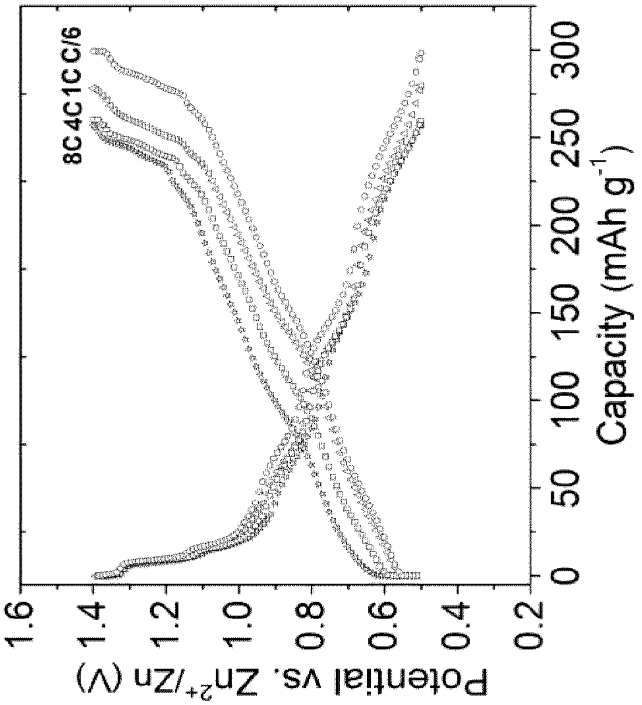

Figure 8B

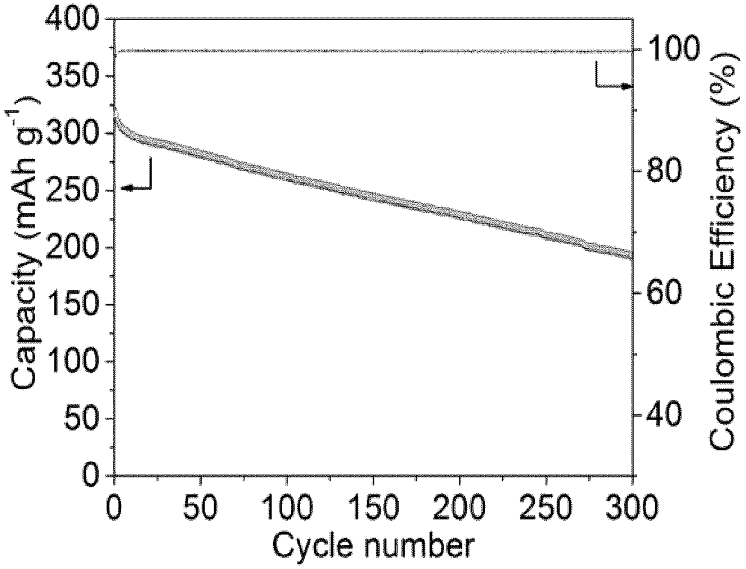

Figure 9A

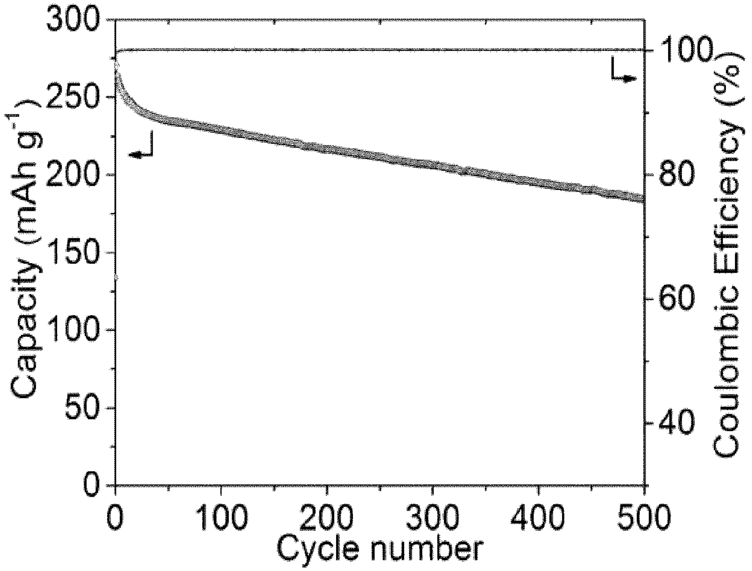

Figure 9B

12/14

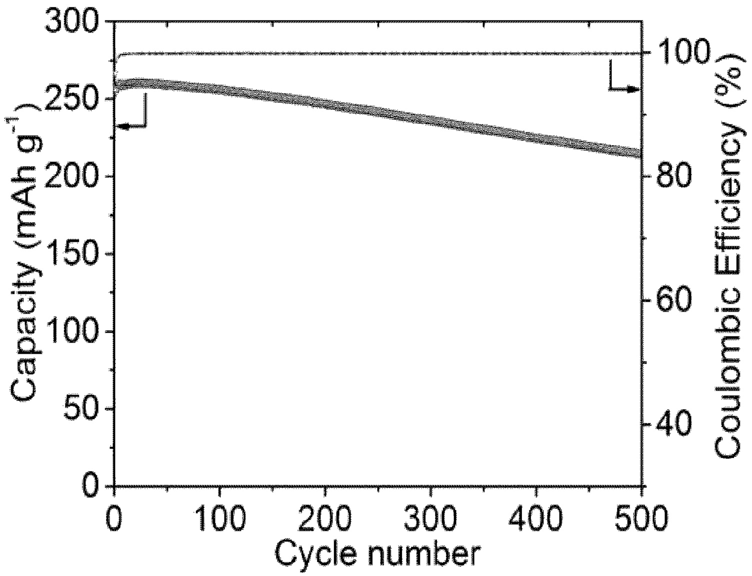

Figure 9C

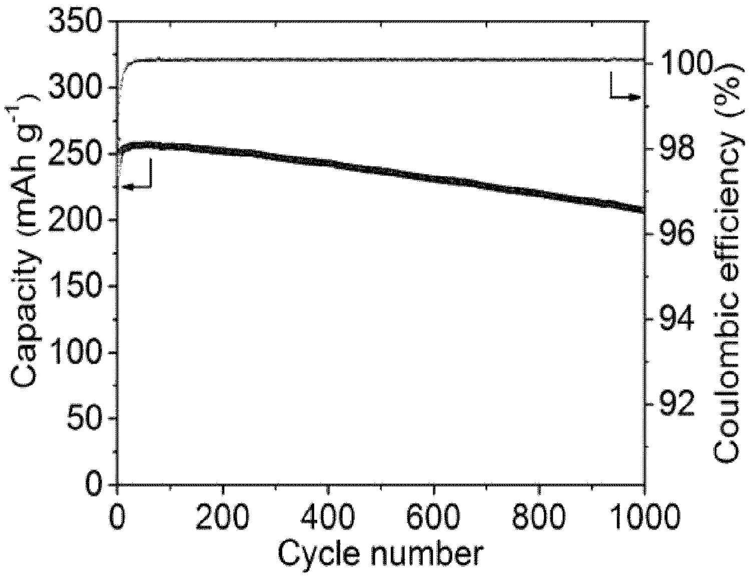

Figure 9D

13/14

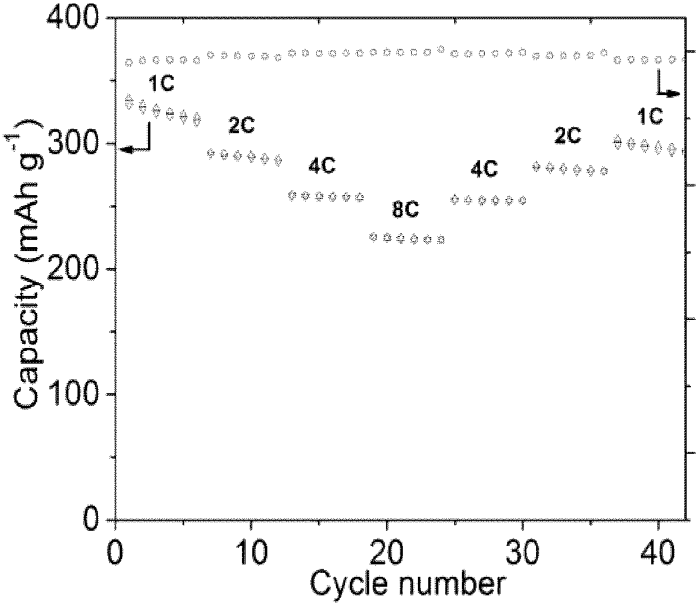

Figure 10A

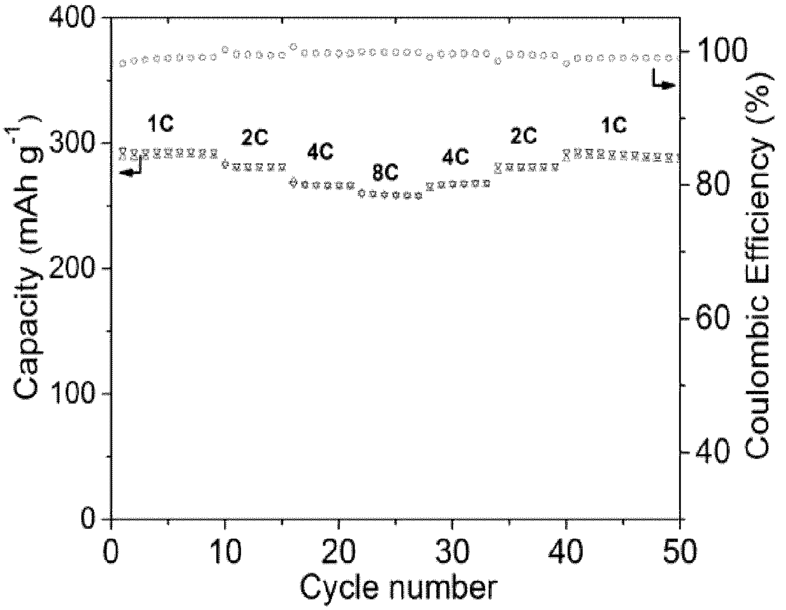

Figure 10B

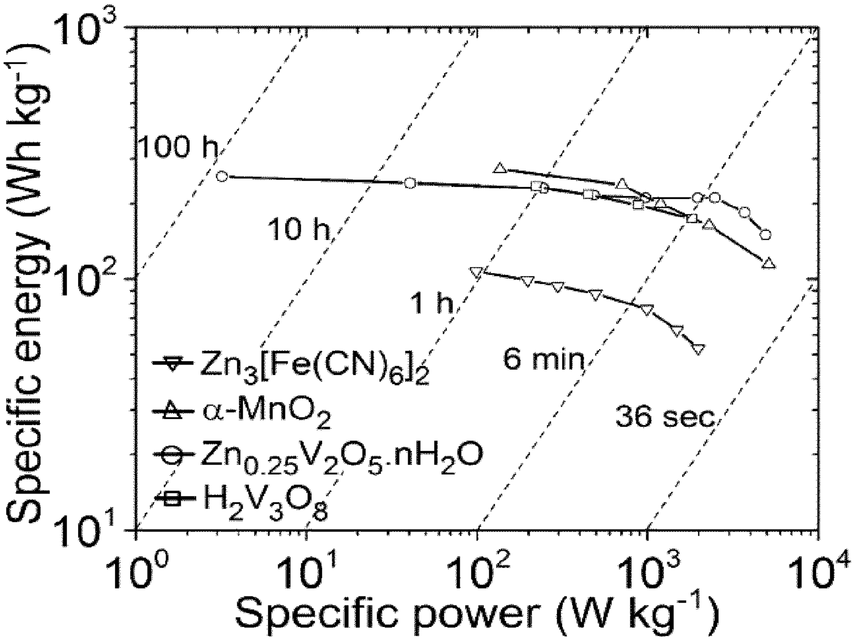
10^3
10^2
10^1
Specific energy (Wh kg^{-1})
10^0
10^1
10^2
10^3
10^4
Specific power (W kg^{-1})
100 h
10 h
1 h
6 min
36 sec
$Zn_3[Fe(CN)_6]_2$
α-MnO_2
$Zn_{0.25}V_2O_5.nH_2O$
$H_2V_3O_8$

Figure 11

OPIC Notes de l'examen / CIPO Examination Notes

Ce document est un supplément d'information aux RRI et OE / This document is a supplement to the information contained in the ISR and WO.

1. Renseignements généraux / General Information			
No. de la demande/ Application No.	**PCT/CA2016/050613**	Date de dépôt / Filing Date	31 May 2016 (31-05-2016)
No. de référence / Reference Number	672-001-P	Date de priorité / Priority Date	08 June 2015 (08-06-2015)
Déposant / Applicant	ADAMS, BRIAN D. ET AL		
CIB / IPC	IPC: ***H01M 10/36*** (2010.01) , ***H01M 4/42*** (2006.01) , ***H01M 4/485*** (2010.01)		
Titre / Title	ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM		

2. Détails de la recherche / Search Details		**Ch. I**
	(Cocher toutes les cases pertinentes) / (check all that apply)	*Commentaires / Comments*
restrictions de dates / date restrictions	● Date de dépôt / Filing ○ Aucune / None	*(détails / details)*
Antériorités relevées par le déposant ont été considérées / prior art noted by applicant considered	● Oui / Yes ○ SO / N/A	*(détails / details)*
Divulgations antérieures par le déposant et l'inventeur(s) ont été considérées / applicant and inventor(s) prior disclosures considered	● Oui / Yes ○ SO / N/A	*(détails / details)*

3. Documentation de la recherche / Search Documentation

(Indiquer clairement les bases de données /les outils de recherche utilisés et ajouter les chaînes de recherche/l'historique de recherche/stratégies de recherche) / (Clearly identify database(s) /search tool(s) used and append search strings/search history/search strategy)

SEARCH STRATEGY:
Check references cited in application that may be relevant
Search relevant databases listed below
Generally, do a broad search by keywords and then narrow by keywords and/or classification
Limit search date to filing date of application
Search inventor or applicant in at least CPD

KEYWORDS
battery, cell, electrochemical
zinc
vanad* or vanadium oxide or vanadium pentoxide or v2o5 or znxv2o5 or znv2o5 or mxv2o5
cathode, positive
aqueous, water, alkaline

IPC (2010.01): H01M 10/36, H01M 4/485; IPC (2006.01): H01M 4/42

DATABASES:
Databases: QUESTEL, Canadian Patent Database, CIPO Library Discovery Tool

Keywords: battery, cell, electrochemical, zinc, vanadium, vanadium oxide, vanadium pentoxide, znxv2o5 or znv2o5 or mxv2o5 cathode, positive, aqueous, water, alkaline

MINIMUM SEARCHING DONE USING THE ABOVE DATABASES ARE SHOWN BELOW.

1 Questel

((zinc)/TI/AB/IW/CLMS/DESC/ODES/OBJ/ADB/ICLM/KEYW/TX AND (vanad+ or vanadium_oxide or vanadium_pentoxide)/TI/AB/IW/CLMS/DESC/ODES/OBJ/ADB/ICLM/KEYW/TX AND (batter+)/TI/AB/IW/CLMS/DESC/ODES/OBJ/ADB/ICLM/KEYW/TX) AND PD <= 2016-05-31

17108 hits

((batter+ or cell+)/TI/AB/IW/CLMS/DESC/ODES/OBJ/ADB/ICLM/KEYW/TX AND (zinc)/TI/AB/IW/CLMS/DESC/ODES/OBJ/ADB/ICLM/KEYW/TX AND (VANAD+ OR VANADIUM_OXIDE OR VANADIUM_PENTOXIDE)/TI/AB/IW/CLMS/DESC/ODES/OBJ/ADB/ICLM/KEYW/TX AND (water or aqueous)/TI/AB/IW/CLMS/DESC/ODES/OBJ/ADB/ICLM/KEYW/TX) AND (H01M)/IPC AND PD <= 2016-05-31

8341 hits

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1645 hits, checked all

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603 hits, Checked all

2. CIPO Library Discovery Tool

S3 (batter* or cell*) AND zinc* AND (VANAD* OR V2O5 or znxv2o5 or znv2o5) AND (aqueous or water or alkaline) Expanders - Apply related words; Apply equivalent subjects

288

S2 (batter* or cell*) AND zinc* AND (VANAD* OR V2O5 or znxv2o5 or znv2o5) AND (electrode or cathode or positive) Expanders -

Apply related words; Apply equivalent subjects

239

S1 (batter* or cell*) AND zinc* AND (VANAD* OR V2O5 or znxv2o5 or znv2o5) Expanders - Apply related words; Apply equivalent subjects

1,165

3. GOOGLE

Used all keywords

4. INTELLECT (Canadian Patent Database)

(filing-date <= 2016-05-31) and (H01M* <IN> ipc) and (BATTER* OR CELL OR CELLS OR ELECTROCHEMICAL) and zinc* and (VANAD* OR V2O5 OR ZNXV2O5 OR ZNV2O5 OR MXV2O5)

517 hits

(filing-date <= 2016-05-31) and (H01M* <IN> ipc) and (BATTER* OR CELL OR CELLS OR ELECTROCHEMICAL) and zinc* and (VANAD* OR V2O5 OR ZNXV2O5 OR ZNV2O5 OR MXV2O5) and (aqueous or water or alkaline)

470 hits

(filing-date <= 2016-05-31) and (H01M 10/* or H01M 4/* <IN> ipc) and (BATTER* OR CELL OR CELLS OR ELECTROCHEMICAL) and zinc* and (VANAD* OR V2O5 OR ZNXV2O5 OR ZNV2O5 OR MXV2O5) and (aqueous or water or alkaline)

359 hits

(filing-date <= 2016-05-31) and (H01M* <IN> ipc) and (BATTER* OR CELL OR CELLS OR ELECTROCHEMICAL) and zinc* and (VANAD* OR V2O5 OR ZNXV2O5 OR ZNV2O5 OR MXV2O5) AND ((ADAMS <IN> INVENTOR) or (KUNDU <IN> INVENTOR) or (NAZAR <IN> INVENTOR))

2 hits

RATIONALE FOR STOPPING SEARCH:

Reasonable time has been spent

4. Documents pertinents identifiés / Relevant Documents Found

(En plus des documents cités par le RRI, d'autres documents qui pourraient s'avérer pertinents lors d'un traitement supplémentaire (p.ex., Chapitre II) peuvent être inclus. Les documents devraient être identifiés en tant que document X, Y ou A. Cependant, une explication supplémentaire de chaque document n'est pas nécessaire. / In addition to the documents cited in the ISR, other documents which may be considered relevant in further prosecution (e.g. Ch. II) may be included. Documents should be identified as either X, Y or A document, however, no further explanation of each document is necessary.)

---

1. Reference Cited

X document

D1: WO 2013/112660 A1 (ADAMSON at al.) 1 August 2013 (01-08-2013)

D1 discloses a zinc ion battery comprising a positive electrode (cathode), a negative electrode (anode), a separator and an electrolyte. The cathode comprises a layered material comprising zinc metal oxide or a mixed metal oxide, for example, MnV2O5 (paragraphs 0012-0014). Some of the oxides have water of hydration (paragraph 0015). The cathode further comprises carbon and binder which includes polytetrafluoroethylene (paragraphs 0017-0020). The cathode is present in powdered form and disclosed size of powders includes less than 100 nm (paragraph 0170). The anode comprises a material for storing zinc, for example, zinc or manganese or a combination and the zinc can be in the form of a powder (paragraphs 0019, 0022, 0135 and 0196). The cathode and anode materials are coated on a current collector comprising conductive metals, for example, copper (paragraph 0179). The electrolyte comprises a salt of zinc, for example zinc sulfate. Disclosed concentration of the salt includes 1 mole to 2 moles per kilogram of solution. Disclosed pH of the electrolyte solution includes 3-8 (paragraphs 0181-0186).

A documents

US 5,336,572 (KOKSBANG) 9 August 1994 (09-08-1994)

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CN 102110858 (WANG et al.) 29 June 2011 (29-06-2011)

LE et al., “Intercalation of Polyvalent Cations into V2O5 Aerogels”, Chemistry of Materials, Volume 10 (3) (1998), Pages 682–684.

JIAHONG et al., “AC Impedance Study of the Aqueous Zn/V2O5 Secondary Battery”, ACTA PHYSICOCHIMICA SINICA, Volume 16, No. 5 (2000), Pages 454-458.

GIORGETTI et al., “Identification of an unconventional zinc coordination site in anhydrous ZnxV2O5 aerogels from x-ray absorption”, Chemistry of Materials, Volume 11(8) (1999), Pages 2257-2264.

ZHANG et al., “Hydrothermal synthesis and characterization of a series of novel zinc vanadium oxides as cathode materials”, Materials Research Society Symposium - Proceedings, Materials for Electrochemical Energy Storage and Conversion II - Batteries, Capacitors and Fuel Cells, 496 (1998), Pages 367-372) .

The inventive concept appears to be a zinc- ion battery, comprising a positive electrode compartment having enclosed therein an intercalation layered positive electrode material MxV2O5.nH2O, a negative electrode compartment having enclosed therein a negative electrode for storing zinc; a separator electrically insulating and permeable to zinc ions separating the positive and negative compartments; and an electrolyte comprising water and having a salt of zinc dissolved therein.

2. Novelty – PCT Article 33(2)

Claims 1, 4-9 and 12-25 lack novelty in view of D1 pursuant to PCT Article 33(2).

Claims 2-3 and 10-11 are novel and thus comply with PCT Article 33(2).

3. Inventive Step – PCT Article 33(3)

As claims 1, 4-9 and 12-25 are not novel in view of D1, they cannot be considered to involve an inventive step and thus do not comply with PCT Article 33(3).

Claims 2-3 and 10-11 do not comply with PCT Article 33(3) having regard to D1 in view of common knowledge in the art. The subject matter of claims 1, 4-9 and 12-25 is disclosed in D1. The additional features specified in claims 2-3 (that is, the presence of water of hydration in the oxide) cannot be considered to involve an inventive step since D1 further teaches that some oxides have water of hydration present, and also the use of metal oxides with water of hydration present in electrode materials is an option that is within the purview of a person skilled in the art. Furthermore, coating the particles with electrically conducting material as specified in claims 10-11 is also a design option that is within the purview of a person skilled in the art, since coating electrode materials with carbon is commonly practiced in the art, thus, the subject matter of claims 10-11 cannot be considered to involve an inventive step.

4. Industrial Applicability – PCT Article 33(4)

The subject matter of claims 1-25 is considered to be industrially applicable and thus complies with the requirements of PCT Article 33(4).

5. CIB additionels / Additional IPCs