



US009780412B2

(12) **United States Patent**  
**Adams et al.**

(10) **Patent No.:** **US 9,780,412 B2**  
(45) **Date of Patent:** **Oct. 3, 2017**

(54) **ELECTRODE MATERIALS FOR RECHARGEABLE ZINC CELLS AND BATTERIES PRODUCED THEREFROM**

(71) Applicant: **Brian D. Adams**, Mitchell (CA)

(72) Inventors: **Brian D. Adams**, Mitchell (CA); **Dipan Kundu**, Kitchener (CA)

(\* ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **15/461,849**

(22) Filed: **Mar. 17, 2017**

(65) **Prior Publication Data**  
US 2017/0207492 A1 Jul. 20, 2017

**Related U.S. Application Data**  
(63) Continuation of application No. PCT/CA2016/050613, filed on May 31, 2016.  
(60) Provisional application No. 62/230,502, filed on Jun. 8, 2015.

(51) **Int. Cl.**  
**H01M 4/66** (2006.01)  
**H01M 4/62** (2006.01)  
**H01M 4/485** (2010.01)  
**H01M 10/36** (2010.01)

(52) **U.S. Cl.**  
CPC ..... **H01M 10/36** (2013.01); **H01M 4/485** (2013.01); **H01M 4/623** (2013.01); **H01M 4/625** (2013.01); **H01M 4/661** (2013.01); **H01M 4/663** (2013.01); **H01M 2300/0002** (2013.01)

(58) **Field of Classification Search**  
CPC ..... H01M 10/36; H01M 4/50; H01M 4/244; H01M 4/485; H01M 4/66; H01M 4/62  
See application file for complete search history.

(56) **References Cited**  
U.S. PATENT DOCUMENTS

5,336,572 A 8/1994 Koksang  
8,663,844 B2 3/2014 Kang et al.  
2013/0157138 A1 6/2013 Mettan et al.  
(Continued)

FOREIGN PATENT DOCUMENTS

CN 102110858 6/2011  
WO 2013112660 8/2013

OTHER PUBLICATIONS

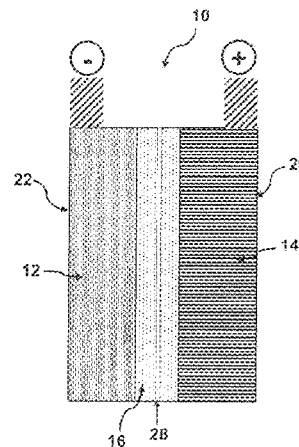
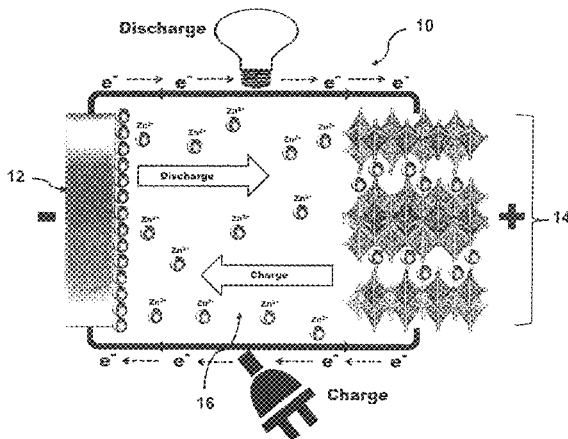
"Manganese vanadium oxides as cathodes for lithium batteries", Heai-Ku Park, Solid State Ionics, 176, p. 307-312, 2005.\*  
(Continued)

*Primary Examiner* — Kenneth Douyette  
(74) *Attorney, Agent, or Firm* — Bereskin & Parr LLP

(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<sup>2+</sup> 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<sup>2+</sup> 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.

**16 Claims, 14 Drawing Sheets**



(56)

**References Cited**

## U.S. PATENT DOCUMENTS

2014/0050970 A1\* 2/2014 Li ..... H01M 4/26  
429/163

## OTHER PUBLICATIONS

“Structure and properties of layered manganese-vanadium oxide as a cathode material for lithium secondary batteries”, Lu et al., *Electrochemistry Communications* 6, p. 672-677, 2004.\*

Le et al., “Intercalation of Polyvalent Cations into V<sub>2</sub>O<sub>5</sub> Aerogels”, *Chemistry of Materials*, 1998, pp. 682-684, vol. 10 (3).

Jiahong et al., “AC Impedance Study of the Aqueous Zn/V<sub>2</sub>O<sub>5</sub> Secondary Battery”, *Acta Physicochimica Sinica*, 2000, pp. 454-458; vol. 16, No. 5.

Giorgetti et al., “Identification of an unconventional zinc coordination site in anhydrous Zn<sub>x</sub>V<sub>2</sub>O<sub>5</sub> aerogels from x-ray absorption”, 1999, pp. 2257-2264, vol. 11(8).

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*, 1998, pp. 367-372, vol. 496.

Xu et al., “Reversible Insertion Properties of Zinc Ion into Manganese Dioxide and Its Application for Energy Storage”, *Electrochemical and Solid-State Letters*, 2009, pp. A61-A65, vol. 12(4). International Search Report and Written Opinion for PCT/CA2016/050613 dated Sep. 21, 2016.

Joint Center for Energy Storage Research, downloaded from: <https://www.jcesr.org/research/multivalent-intercalation/>, Retrieved on Jul. 19, 2017.

Levi et al., “A review on the problems of the solid state ions diffusion in cathodes for rechargeable mg batteries.” *Journal of Electroceramics*, 2009, 22(1-3), 13-19.

Rong et al., “Materials Design Rules for Multivalent Ion Mobility in Intercalation Structures” *Chemistry of Materials*, 2015, 27(17), 6016-6021.

Xu et al., Supporting Information for “Energetic Zinc Ion Chemistry: The Rechargeable Zinc Ion Battery” *Angewandte Chemie*, 2012, 51, 933-935.

Paulsen et al., “Layered Li—Mn-Oxide with the O<sub>2</sub> Structure: A Cathode Material for Li-Ion Cells Which Does not Convert to Spinel” *Journal of The Electrochemical Society*, 1999, 146(10), 3560-3565.

\* cited by examiner

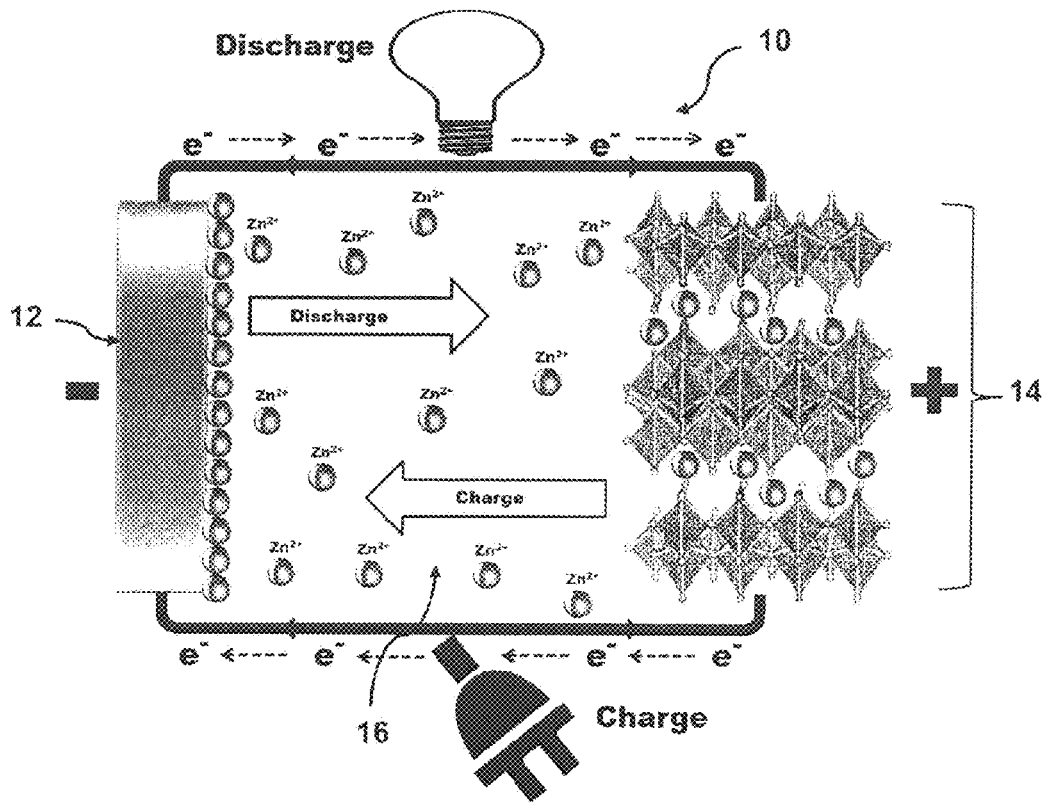


Figure 1A

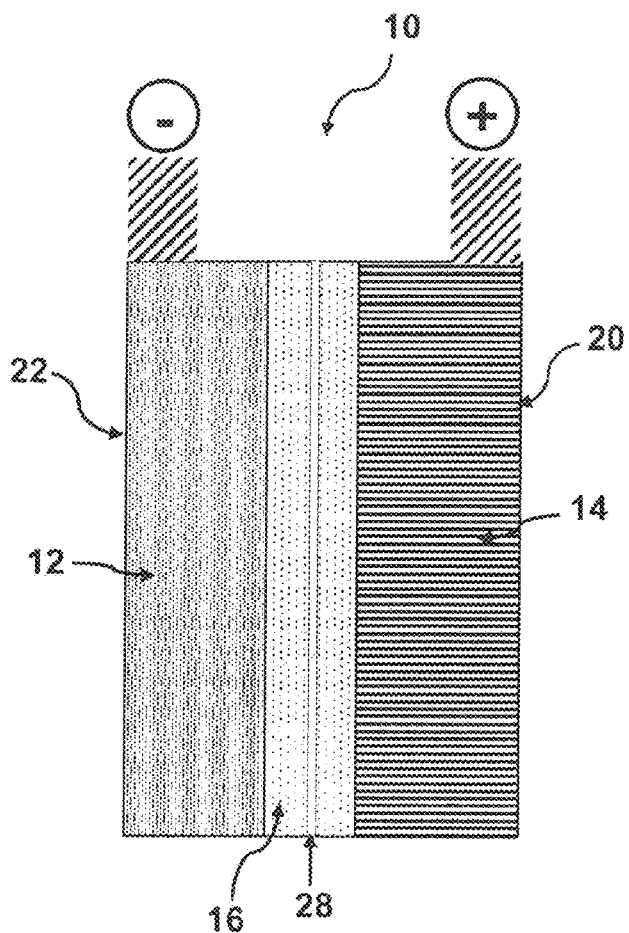


Figure 1B

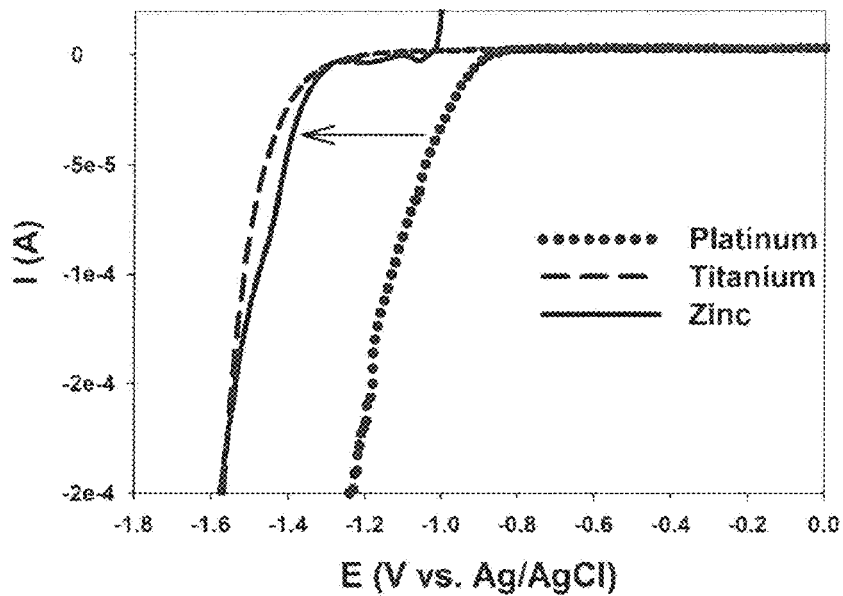


Figure 2

# Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

## Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

## Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

## Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

## API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

## LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

## FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

## E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.