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

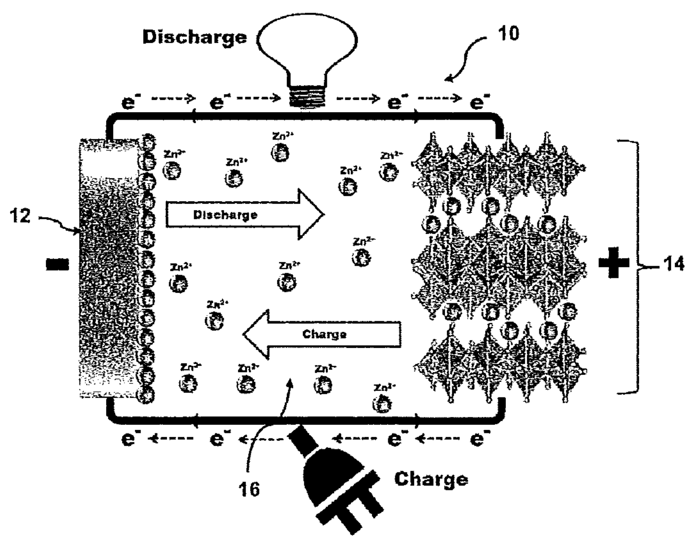

Figure 1A

(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.

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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 $M_xV_3O_7.\mathbf{n}H_2O$, wherein **x** is in a range from 0.05 to 1, **n** is greater than 0 and less than 2, 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

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