Aqueous rechargeable zinc ion batteries are provided. The battery comprises a cathode comprising a V$_3$O$_7$·H$_2$O-grapheene composite, the composite comprising a plurality of V$_3$O$_7$·H$_2$O nanostructures in contact with grapheene, an anode in electrical communication with the cathode, the anode comprising zinc, and an aqueous electrolyte between the cathode and the anode, the aqueous electrolyte comprising zinc ions and an ether of a type and an amount selected to maximize a capacity retention value of the battery.
References Cited

OTHER PUBLICATIONS

Qiao et al., Synthesis of V$_2$O$_3$·H$_2$O nanobelts as cathode materials for lithium-ion batteries, Electrochemistry Communications 8, Nov. 15, 2005, pp. 21-26.


* cited by examiner
Coulombic efficiency (%) vs. Capacity (mAh g⁻¹) for the 20 C rate over Cycle number.
FIG. 2F

Energy density (Wh kg⁻¹) vs. Power density (W kg⁻¹)

- This work
- β-MnO₂ (ref 2f)
- Zn₀.₉₃V₂O₅.nH₂O (ref 2g)
- α-MnO₂ (ref 2e)
- Zn₃Mn₁Fe₃O₁₀/C (ref 11a)
- Zn₃Fe(CN)₆/Sc (ref 11c)
- Na₃V₂(PO₄)₃/C (ref 11b)
COMPOSITE ELECTRODE FOR AQUEOUS RECHARGEABLE ZINC ION BATTERIES

REFERENCE TO GOVERNMENT RIGHTS

This invention was made with government support under DE-SC0008711 awarded by the US Department of Energy. The government has certain rights in the invention.

BACKGROUND

The harvesting and utilization of clean and renewable energy, such as energy from solar and wind, have experienced a rapid evolution. Implementation of these intermittent energy resources requires large-scale energy storage systems to store and regulate the power output among peak and off-peak hours. As the most popular electrochemical energy storage device, lithium ion batteries (LIBs) are considered to be the most promising candidate due to their high energy density. However, in such large-scale applications, cost, lifetime and safety are particularly important factors to be considered. Compared to expensive and flammable non-aqueous LIBs, aqueous batteries with water-based electrolyte possess a natural advantage in these areas. Furthermore, they do not require strict oxygen- and water-controlled manufacturing environments and thus have much lower fabrication costs.

The development of aqueous battery systems has progressed rapidly in recent years, including monovalent Li⁺, Na⁺ and K⁺ and divalent Mg²⁺ and Zn²⁺ systems. Among them, aqueous rechargeable zinc ion batteries (ARZIBs) have attracted much attention due to the low price, rich global distribution, high stability, relatively low redox potential, and high theoretical capacity (825 mAh g⁻¹) of zinc metal. These merits of ARZIBs have substantially raised their application potential in large-scale energy storage systems and even in electric vehicles. Most recently, α-MnO₂, β-MnO₂, and Zn₀.₇₋₀.₅V₀.₃₋₀.₁O₂·nH₂O nanofibers have been applied to ARZIBs.

Although ARZIBs have been the focus of recent research, the lack of suitable cathode materials is a significant challenge to their commercial development. Although the radius of Zn²⁺ ions (0.74 Å) is almost the same as that of Li⁺ ions (0.76 Å), the larger atomic mass and stronger positive polarity result in poorer transport kinetics and lower solid-state solubility in bulk electrode. Thus, most electrode materials that can accommodate Li⁺ ions insertion/extraction are not suitable for ARZIBs. Only a few cathode materials have been demonstrated in a laboratory and most deliver limited specific capacities, poor rate capability and/ or bad cycling performance.

SUMMARY

The present disclosure provides aqueous rechargeable zinc ion batteries.

One embodiment of an aqueous rechargeable zinc ion battery comprises a cathode comprising a V₃O₇·H₂O-graphene composite, the composite comprising a plurality of V₃O₇·H₂O nanowires in contact with graphene, an anode in electrical communication with the cathode, the anode comprising zinc, and an aqueous electrolyte between the cathode and the anode, the aqueous electrolyte comprising zinc ions and an ether at an amount in a range of from 1 vol. % to 20 vol. %.

Other principal features and advantages of the invention will become apparent to those skilled in the art upon review of the following drawings, the detailed description, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Illustrative embodiments of the invention will hereafter be described with reference to the accompanying drawings.

FIGS. 1A-1F depict electron microscopy characterization of the H₂V₃O₈ NW/graphene composite. FIG. 1A is an SEM image showing the morphology of the as-prepared H₂V₃O₈/graphene composite. FIG. 1B is an SEM image depicting the intimate distribution of H₂V₃O₈ NWs and graphene film. FIG. 1C is a schematic illustration of the structure of the composite. FIG. 1D is a TEM image showing the uniform distribution of H₂V₃O₈ NWs on graphene films. FIG. 1E is a TEM image showing the rectangular shape of the NWs with a curved tip surface. FIG. 1F is an HRTEM image of the NW tip showing the single-crystalline lattice of H₂V₃O₈. The inset is the corresponding fast fourier transform (FFT) image.

FIGS. 2A-2F depict the electrochemical performance of the H₂V₃O₈/graphene electrode. FIG. 2A shows the galvanostatic charge-discharge profiles of the H₂V₃O₈/graphene cathode at a 1/3 C rate. FIG. 2B depicts the cycling performance and the corresponding coulombic efficiency at a 1 C rate after 5 cycles of activation at 1/3 C rate. FIG. 2C shows rate capability at varying C rates. FIG. 2D shows galvanostatic charge-discharge profiles at different C rates. FIG. 2E shows long cycling stability at a 20 C rate. FIG. 2F depicts a comparison of the energy and power density of the H₂V₃O₈ NW/graphene cathode with other reported materials for ARZIBs.

FIGS. 3A-3F depict an electron microscopy investigation of the post-cycling H₂V₃O₈ NW/graphene electrodes. FIGS. 3A-3C show results after 150 cycles at 1/3 C rate. FIGS. 3D-3F show results after 2000 cycles at 20 C rate. FIGS. 3A and 3D are SEM images showing the morphology of the electrode after 150 cycles at a 1/3 C rate. FIGS. 3B and 3E are SEM images showing the graphene conductive network in the electrode. FIGS. 3C and 3F are HRTEM images of the H₂V₃O₈ NW crystals.

FIGS. 4A-4F show the spectroscopy investigation of the electrochemical reaction mechanism. FIG. 4A shows the charge/discharge curve of the first operation cycle. Sampling points for XRD and Raman characterizations were marked with corresponding dots. FIG. 4B shows an ex-situ XRD measurement during the first electrochemical cycle showing the reversible evolution of the H₂V₃O₈ NW crystal structure. FIG. 4C shows the Raman spectrum in the wavelength range of 50-1200 cm⁻¹ of the electrodes. FIGS. 4D-4F show a comparison of the XPS of different elements in the composite electrode when charged to 1.6 V (top panel), discharged to 0.2 V (middle panel) and as pristine (bottom panel), for Zn (FIG. 4D), O (FIG. 4E), and V (FIG. 4F) elements. Experimental data are shown by black lines; overall fitted data are shown by pink lines; and fitted individual peaks are shown by other colors.
FIGS. 5A-5J depict an atomic-level study of the Zn$^{2+}$ intercalation in H$_2$V$_3$O$_8$ NWs. FIG. 5A depicts EELS mapping of a pristine H$_2$V$_3$O$_8$ NW. The white box shows the region used for EELS mapping. FIG. 5B depicts EELS mapping of a zinc-intercalated H$_2$V$_3$O$_8$ NW discharged to 0.2 V. The white box shows the region used for EELS mapping. FIG. 5C is a TEM image of a H$_2$V$_3$O$_8$ NW discharged to 0.2 V. FIG. 5D is an HRTEM image of the new phase within the NW. The intensity profile along the dashed line is shown in FIG. 5E. FIG. 5F is an HRTEM image of the unchanged H$_2$V$_3$O$_8$ phase region. FIG. 5G shows a high-resolution HAADF STEM image of a H$_2$V$_3$O$_8$ NW discharged to 0.2 V. FIG. 5H shows a cross-sectional image of the nanowire along the [100] direction and along the [001] direction (FIG. 5E) and along the [001] direction (FIG. 5F).

FIG. 6 is a schematic illustration of an aqueous rechargeable zinc ion battery according to an illustrative embodiment.

DETAILED DESCRIPTION

The present disclosure provides aqueous rechargeable zinc ion batteries. In an embodiment, an aqueous rechargeable zinc ion battery comprises a cathode comprising a V$_2$O$_5$.H$_2$O-graphene composite, an anode in electrical communication with the cathode, and an aqueous electrolyte between the cathode and the anode. At least some embodiments of the batteries are characterized by superior specific capacities, rate capabilities and cycling performance as compared to conventional aqueous rechargeable zinc ion batteries.

The composite of the battery comprises nanostructured V$_2$O$_5$.H$_2$O and graphene. By "nanostructured," it is meant that the V$_2$O$_5$.H$_2$O material has nanoscale morphology exhibiting structural feature(s) on the order of about 100 nm or less. The type of nanostructure is not particularly limited. In embodiments, the V$_2$O$_5$.H$_2$O is in the form of nanowires, elongated nanostructures each having a length 1 that is significantly greater than the other two dimensions of the nanowire. These other two dimensions may have similar magnitudes in which case the dimensions perpendicular to the length 1 may be referred to as a diameter d. However, the cross-sectional shape of the nanowire is not limited to a circular shape. The length 1 and diameter d are also not particularly limited. These dimensions may be reported as an average value as determined from a representative number of nanowires. In embodiments, the nanowires are characterized by an average length 1 having a value in the range of from about 1 µm to about 10 µm, from about 2 µm to about 8 µm, or from about 3 µm to about 5 µm. In embodiments, the nanowires are characterized by an average diameter d having a value in the range of from about 1 nm to about 200 nm, from about 10 nm to about 50 nm, or from about 20 nm to about 100 nm. The dimensions may be determined from SEM images. (See FIGS. 1A, 1B.) Other types of nanostructures include nanoparticles, nanorods, nanotubes, nanosheets, nanoflakes, and nanospheres.

The V$_2$O$_5$.H$_2$O nanostructures may be characterized as being single-crystalline by which it is meant that the lattice structure throughout the nanostructures as determined from HRTEM images (see FIG. 1F) is closest to that of a single-crystal phase.

The composite of the battery also comprises graphene in contact with the V$_2$O$_5$.H$_2$O nanostructures. By "in contact" it is meant that surface(s) of the V$_2$O$_5$.H$_2$O nanostructures are sufficiently close (e.g., in direct contact) to graphene surfaces(s) to facilitate the transport of electrons between the two types of materials. The contact may involve the formation of chemical bonds between the V$_2$O$_5$.H$_2$O nanostructures and the graphene. The distribution of the V$_2$O$_5$.H$_2$O nanostructures within the graphene (and vice versa) may be homogeneous by which it is meant that discrete regions within the composite have approximately equal ratios of nanostructures:graphene. (See FIG. 1A, 1B, 1D.) However, this does not mean that the distribution is perfectly homogeneous. When the V$_2$O$_5$.H$_2$O nanostructures are in the form of nanowires (or similar elongated nanostructures), the nanowires may be aligned with their lengths approximately parallel to the graphene surface(s) with which they are associated. (See FIG. 1C, 1D.) However, this does not mean that the orientation is perfectly parallel. Otherwise, as shown in FIGS. 1A-1D, the orientation of the nanowires with respect to the graphene surfaces (and with respect to one another) is random. The nature of the association between graphene and the V$_2$O$_5$.H$_2$O nanostructures may be determined from SEM and TEM images.

The relative amount of graphene and V$_2$O$_5$.H$_2$O nanostructures in the composite may vary and may be adjusted to optimize battery performance (i.e., capacity, rate capability, capacity retention, etc.). In embodiments, the amount of graphene in the composite is in the range of from about 1% to about 30% by weight as compared to the total weight of the composite. This includes embodiments in which the amount of graphene is in the range of from about 1% to about 5%.

The V$_2$O$_5$.H$_2$O-graphene composite may be combined with other cathode materials. By way of illustration, an additional conductive material, e.g., carbon black, may be used. A polymeric binder, e.g., polyvinylidene difluoride (PVDF), may be used. The types of additional conductive material and/or polymeric binder are not particularly limited. The relative amounts of the composite, the additional conductive material and the polymeric binder may be adjusted to optimize battery performance. Illustrative suitable amounts are provided in the Example below.

The V$_2$O$_5$.H$_2$O-graphene composite and if present, the other cathode materials, may be provided on an electrically conductive support. A variety of conductive supports may be used, e.g., a metal foil such as Ti foil. Carbon-based materials or foils may be used, e.g., a graphite foil or a graphene film.

The anode comprises zinc. However, the form of the zinc is not particularly limited, e.g., the form may be as a film, foil, etc. The anode may be composed entirely of zinc or the zinc may be provided on an electrically conductive support.

The aqueous electrolyte comprises water and a zinc salt. The type of zinc salt, its concentration and the pH of the aqueous electrolyte are not particularly limited. An illustrative aqueous electrolyte is described in the Example below. Other illustrative zinc salts include Zn(CF$_3$SO$_3$)$_2$, ZnSO$_4$, Zn(NO$_3$)$_2$, and Zn(ClO$_4$)$_2$. The zinc salt dissolves in the aqueous electrolyte to provide zinc ions. The pH of the aqueous electrolyte may be, e.g., less than 7, less than 5, in the range of from about 1 to about 5 or from about 3 to about 5.
The battery may include an ether, e.g., within the aqueous electrolyte, of a type and in an amount selected to maximize the capacity retention of the battery. By “maximize” it is meant that the capacity retention is increased to an approximately maximum value as measured as set forth in “Electrochemical measurements” in the Example below, using the electrochemical cell configuration and conditions described therein. This does not mean that the capacity retention has to be at the perfect maximum, but may be within, e.g., ±10%, ±5% or ±2% of the maximum value. The inventors have found that certain water-soluble ethers (e.g., diethyl ether, dimethyl ether, and tetrahydrofuran) when present within the aqueous electrolyte in amounts of 5 vol. % to 10 vol. % significantly improve the capacity retention of the present batteries as compared to the same batteries without the ether. By “vol. %” it is meant the volume percent of the ether as compared to the total volume of the aqueous electrolyte. In other embodiments, the ether is present in the aqueous electrolyte, but the amount is no more than 20 vol. %, no more than 18 vol. %, no more than 16 vol. %, no more than 15 vol. %, or no more than 12 vol. %. In embodiments, the ether is not tetraethylene glycol dimethyl ether. In embodiments, the ether is not diethylene glycol dimethyl ether.

The battery may comprise additional components typically associated with aqueous rechargeable batteries, e.g., a separator between the anode and the cathode. An illustrative battery is shown in FIG. 6.

Illustrative methods for forming the V₃O₇.H₂O-graphene composite and the aqueous rechargeable zinc batteries are provided in the Example below.

The battery may be characterized by a variety of properties, including one or more of the following properties: specific capacity, energy density, rate capability, and power density. Each of these properties may be referenced with respect to a selected C-rate. A C-rate of 1 C refers to the complete discharge/charge of the battery in one hour. These properties may be measured as set forth in “Electrochemical measurements” in the Example below, using the electrochemical cell configuration and conditions described therein.

In embodiments, the battery is characterized by a specific capacity of at least 50 mAh g⁻¹ at 1/3 C, at least 100 mAh g⁻¹ at 1/3 C, at least 350 mAh g⁻¹ at 1/3 C, at least 375 mAh g⁻¹ at 1/3 C, at least 400 mAh g⁻¹ at 1/3 C, at least 425 mAh g⁻¹ at 1/3 C or in the range of from 375 mAh g⁻¹ to 450 mAh g⁻¹ at 1/3 C. In embodiments, the battery is characterized by an energy density of at least 50 Wh kg⁻¹ at 1/3 C, at least 100 Wh kg⁻¹ at 1/3 C, at least 200 Wh kg⁻¹ at 1/3 C, at least 225 Wh kg⁻¹ at 1/3 C, at least 250 Wh kg⁻¹ at 1/3 C, at least 275 Wh kg⁻¹ at 1/3 C, at least 300 Wh kg⁻¹ at 1/3 C or in the range of from 225 Wh kg⁻¹ to 300 Wh kg⁻¹ at 1/3 C. In embodiments, the battery is characterized by a rate capability of at least 50 mAh g⁻¹ at 20 C, at least 100 mAh g⁻¹ at 20 C, at least 200 mAh g⁻¹ at 20 C, at least 225 mAh g⁻¹ at 20 C, at least 250 mAh g⁻¹ at 20 C, at least 275 mAh g⁻¹ at 20 C, at least 300 mAh g⁻¹ at 20 C or in the range of from 250 mAh g⁻¹ to 275 mAh g⁻¹ at 20 C. In embodiments, the battery is characterized by a power density of at least 100 W kg⁻¹ at 20 C, at least 500 W kg⁻¹ at 20 C, at least 1000 W kg⁻¹ at 20 C, at least 3000 W kg⁻¹ at 20 C, at least 3250 W kg⁻¹ at 20 C, at least 3500 W kg⁻¹ at 20 C, at least 3750 W kg⁻¹ at 20 C or in the range of from 3250 W kg⁻¹ to 4000 W kg⁻¹ at 20 C.

The battery may also be characterized by a capacity retention (%) at a selected rate and a selected number of cycles. In embodiments, the battery is characterized by a capacity retention of at least 60% at 20 C and after 2000 cycles, at least 75% at 20 C and after 2000 cycles, of at least 85% at 20 C and after 2000 cycles, at least 90% at 20 C and after 2000 cycles, at least 95% at 20 C and after 2000 cycles, at least 98% at 20 C and after 2000 cycles, or in the range of 85% to 95% at 20 C and after 2000 cycles.

The performance values described above may be reported with reference to room temperature (about 25°C) and a pH in the range of 2 to 7.

A schematic of an illustrative battery is shown in FIG. 6. The battery comprises a cathode 602 comprising a V₃O₇.H₂O-graphene composite. In this embodiment, the V₃O₇.H₂O nanostructures of the composite are nanowires and the composite is combined with carbon black and a polymeric binder. The cathode materials are deposited on an electrically conductive support. The battery 600 comprises an anode 604 (e.g., Zn foil) and an aqueous electrolyte 606 between the cathode 602 and the anode 604. In this embodiment, the aqueous electrolyte 606 comprises a zinc salt and 5 vol. % diethyl ether. The battery 600 also comprises a separator 608 between the cathode 602 and the anode 604.

The present batteries may be used as a source of power in a variety of electrical circuits comprising an electrical load or an electrical component that draws current from the battery. In their discharged state, the present batteries may be electrically connected to another power source for recharging.

In the present disclosure, the V₃O₇.H₂O-graphene composite of the battery is described with respect to its fully charged state (i.e., free of zinc ions). However, it is understood that the present batteries which comprise “cathodes comprising V₃O₇.H₂O-graphene composites” encompass the batteries in other states, e.g., a discharged state in which zinc ions may be incorporated into the V₃O₇.H₂O-graphene composite.

EXAMPLE

Introduction

Aqueous rechargeable zinc ion batteries are considered a promising candidate for large scale energy storage owing to their low cost and high safety nature. However, the lack of proper cathode materials with considerable specific capacity and good durability impedes practical application for these batteries. This example outlines the development of a composite material comprised of H₃V₂O₇ nanowires (NWs) wrapped by graphene sheets which is used as the cathode material for aqueous rechargeable zinc ion batteries. Owing to the synergistic merits and desirable structural features of H₃V₂O₇ NWs and the high conductivity of its graphene network, the H₃V₂O₇ NW/graphene composite exhibited superior zinc ions storage performance, including high capacity of 394 mAh g⁻¹ at 1/3 C, high rate capability of 270 mAh g⁻¹ at 20 C, and excellent cycling stability of up to 2000 cycles with a capacity retention of 87%. The battery offered a high energy density of 250 Wh kg⁻¹ at 1/3 C and a high power density of 3300 W kg⁻¹ at 20 C. Systematic structural and elemental characterization confirmed the reversible Zn²⁺ and water co-intercalation electrochemical reaction mechanism. This example demonstrates the potential of this material for designing high-performance aqueous rechargeable zinc ion batteries for grid-scale energy storage.

Experimental

Material synthesis: Graphene oxide (GO) was produced from natural graphite (<20 mm; Sigma-Aldrich) using a modified Hummers method. Graphite powder (2.0 g) was added to a mixture of H₂SO₄ (98 wt. %, 8 mL), K₂S₂O₈ (1.67 g), and P₂O₅ (1.67 g). This mixture was kept at 80°C for 5 h. Subsequently, the mixture was cooled to room
ments were performed using 2016 coin cells in the voltage range from 0.01 to 2.5 V at a current density of 200 mA g$^-1$. The specific capacitance was calculated using the formula $C = \frac{Q}{m \cdot \Delta V}$, where $Q$ is the charge delivered, $m$ is the mass of the active material, and $\Delta V$ is the potential window.

In a typical synthesis, V$_2$O$_5$ powder (0.364 g) was added to DI water (20 mL) and then ultrasonically dispersed for 2 h. After ultrasonication, the suspension was washed several times with ethanol and DI water, and freeze-dried. For preparing GO solution, 50 mg of the as-synthesized GO powder was dispersed in 21 mL DI water uniformly under ultrasonic for 2 h.

H$_2$V$_3$O$_8$ NWs and H$_2$V$_3$O$_8$ NW/graphene composite were prepared by a hydrothermal method. In a typical synthesis, V$_2$O$_5$ powder (0.364 g) was added to DI water (20 mL) and then stirred vigorously. Then, H$_2$O$_2$ (4 mL) was added to the mixture, which was then washed with HCl followed by DI water. The GO powder was finally obtained after centrifugation, copious washing with DI water, and freeze-drying. For preparing GO solution, 50 mg of the as-synthesized GO powder was dispersed in 21 mL DI water uniformly under ultrasonic for 2 h.

Characterizations: XRD (Bruker D8, Bruker, Mass., USA) was utilized to study the crystal structure. Scanning electron microscope (SEM) observations were performed on a Zeiss Leo 1530 field-emission microscope and transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) measurements were conducted on a FEI TF30 microscope. Raman scattering data were collected on a Thermo Scientific FT-Raman spectrometer using an Nd-line laser source. Nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2010 instrument. X-ray photoelectron spectroscopy (XPS) scan was acquired using a Thermo Scientific K-alpha XPS instrument. Scanning tunnel electron microscope (STEM) and electron energy loss spectroscopy (EELS) experiments were performed on a FEI Titan microscope with a CEDOS probe aberration-corrector operated at 200 keV. The probe semi-angle is 24.5 mrad and the probe current is -25 pA. High angle annular dark field (HAADF) STEM imaging was collected by a Fischione Model 3000 detector spanning 84 to 160 mrad in scattering angles. In these conditions, the estimated probe size is less than 1 Å. EELS spectrum images were recorded with GIF 865 spectrometer, with energy dispersion of 1 eV/pixel, which allows for the simultaneous visualization of the V L$_3$, O K, and Zn L$_2$EELS edges. The energy resolution was 1.2 eV, measured from the full width at half maximum of zero-loss peak. Thermogravimetric analysis (TGA) was measured by a TA Q500 thermogravimetric analyzer. The pH of the electrolyte was measured using a PHS-300 pH meter.

Electrochemical measurements: Electrochemical experiments were performed using 2016 coin cells in the voltage window of 1.6-0.2 V and a metallic Zn foil used as the counter-electrode. The working electrode was composed of 70 wt. % active material, 20 wt. % Super P conductive additive, and 10 wt. % polyvinylidene difluoride (PVDF) binder, and was coated on a Ti foil current collector. The electrode was cut into pieces 5x5 mm$^2$ in size and loaded with ~1.0 mg of active material. The working and counter electrodes were separated by a Whatman GF/C glass fiber filter. The electrolyte was 3 M Zn(CF$_3$SO$_3$)$_2$ aqueous solution (pH=3.55) because much better electrochemical performance has been discovered from the Zn(CF$_3$SO$_3$)$_2$ electrolyte compared to other Zn salts such as ZnSO$_4$, Zn(NO$_3$)$_2$ and Zn(ClO$_4$)$_2$.

Galvanostatic charge-discharge cycling was performed on a Land-2100 battery tester. Electrochemical impedance spectroscopy (EIS) was obtained by applying an AC voltage of 10 mV in the frequency range from 1 MHz to 1 Hz using an Autolab PGSTAT302N station. The electrodes for XRD and XPS measurements were prepared by grinding 70 wt. % active material, 20 wt. % Super P conductive additive and 10 wt. % PTFE binder and rolling to a sheet. The sheet was cut into 5x5 mm$^2$ pieces and loaded with ~1.0 mg of active material. Before the X-ray diffraction (XRD) and XPS measurements, the free-standing electrodes at different charge/discharged stages were immersed and washed thoroughly in DI water and dried at 60°C in air.

Density functional theory (DFT) calculations: DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) using a plane wave basis set, the GGA-Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the projector augmented wave (PAW) method. Rotationally invariant in GGA+U was employed to correct the strong electronic correlation among localized states.

In DFT calculations, 2x1x1 104 atom supercell was used with kinetic energy cutoff of 520 eV and 4x4x2 Monkhorst-Pack k-mesh. The Hellmann-Feynman forces were converged to 0.001 eV/Å. This DFT relaxation gave the potential ground state of Zn2+ ions. Therefore, this DFT calculation cannot give precise atomic location of the kinetically stabilized system. Instead, it provides a support to validate the interaction sites of Zn$_2^+$ ions.

Characterization of H$_2$V$_3$O$_8$ NW/Graphene Composite. H$_2$V$_3$O$_8$ NW/graphene composite was synthesized via a single-step hydrothermal method (see experimental details in the Method section). The crystallinity of the composite was firstly studied by XRD, where the characteristic peaks matched well to the orthorhombic crystalline phase of H$_2$V$_3$O$_8$ (space group: Pnma, JCPDS No. 85-2401, data not shown). No peaks from impurities of other vanadium oxides could be detected, indicating the high phase purity of the as-synthesized NWs. SEM images show the morphology and microstructure of the composite (FIGS. 1A and 1B).

H$_2$V$_3$O$_8$ NWs exhibited uniform sizes and a large aspect ratio, with lengths of 3.5 μm and diameters of 50-100 nm. Graphene sheets were well blended within the randomly oriented NWs, forming a homogeneous mixture. The C 1s XPS spectra of H$_2$V$_3$O$_8$ NW/graphene exhibited fewer oxygen-containing functional groups compared to graphene oxide (GO) (data not shown), confirming the reduction of GO to graphene. This architecture ensured large contact and minimal charge traveling distance between H$_2$V$_3$O$_8$ NWs and graphene (FIG. 1C), which were favorable for optimizing the charge transport properties of the composite. TEM images further revealed the H$_2$V$_3$O$_8$ NWs were anchored intimately on the graphene surface (FIG. 1D). Each NW exhibited a uniform contrast showing high-quality.
crystallinity and no indication of additives or impurities (FIG. 1E). A HRTEM image of the H$_2$V$_3$O$_8$ NW displayed a clear single-crystal lattice with sharp edges, and no amorphous layer could be observed on the NW surface (FIG. 1F).

The corresponding fast Fourier-transform (FFT) pattern (inset of FIG. 1F) revealed a d-spacing of 0.34 nm, which was in good agreement with the d$_{002}$ distance of H$_2$V$_3$O$_8$. H$_2$V$_3$O$_8$ NWs were also synthesized without adding graphene in the precursor to investigate the influence of graphene to the crystal growth. As confirmed by XRD (data not shown), the pristine H$_2$V$_3$O$_8$ NWs exhibited the same crystalline phase and lattice parameters with H$_2$V$_3$O$_8$ NW/graphene composite (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
</tr>
</thead>
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<tr>
<td>H$_2$V$_3$O$_8$/graphene</td>
<td>1.693(1)</td>
<td>0.936(5)</td>
<td>0.364(5)</td>
</tr>
<tr>
<td>Pristine H$_2$V$_3$O$_8$</td>
<td>1.693(2)</td>
<td>0.935(7)</td>
<td>0.364(6)</td>
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</table>

SEM and TEM images revealed a small increase of NW thickness (~50 nm in average) when no graphene was present, indicating the NW growth was slightly limited with graphene coverage (data not shown). In addition, nitrogen adsorption-desorption isotherms characterization revealed that the Brunauer-Emmett-Teller (BET) surface area of the H$_2$V$_3$O$_8$ NW/graphene composite was 21.5 cm$^2$ g$^{-1}$, which was much larger than the 14 cm$^2$ g$^{-1}$ of the pristine H$_2$V$_3$O$_8$ NWs (data not shown). A larger surface area can increase the contact area between the electrolyte and active material.

When dispersed in conductive additive pile for electrode preparation, the intimate contact between H$_2$V$_3$O$_8$ NWs and graphene was well preserved (data not shown), forming a three-dimensional conductive graphene network with a large quantity of active materials embedded inside. The mass fraction of graphene in H$_2$V$_3$O$_8$ NW/graphene composite was estimated to be ~3.7 wt. % by Thermogravimetric Analysis (TGA) (data not shown).

Electrochemical Performance of H$_2$V$_3$O$_8$ NW/Graphene in ARZIBs

The electrochemical performance of the H$_2$V$_3$O$_8$ NW/graphene composite electrodes was evaluated between 0.2-1.6 V (versus Zn/Zn$^{2+}$) in coin-cell-type batteries using 3M Zn(CF$_3$SO$_2$)$_2$ aqueous solution as the electrolyte and zinc metal foil as the anode electrode. The first three charge-discharge profiles of the H$_2$V$_3$O$_8$/graphene electrode at a current rate of 1/3 C (1 C=300 mA g$^{-1}$), based on the stable capacity of ~300 mAh g$^{-1}$ at 300 mA g$^{-1}$ as shown in FIG. 2A. The first discharge capacity was 394 mAh g$^{-1}$. The charge capacity was 386 mAh g$^{-1}$ with an initial coulombic efficiency of 98%. The high coulombic efficiency indicated good reversibility of the Zn$^{2+}$ ions insertion/extraction process. The discharge profiles exhibited two distinct voltage plateaus between 0.8-0.6 V and 0.6-0.4 V, respectively. In the following charging processes, these two voltage plateaus remained in every profile. This phenomenon suggested that the electrochemical reactions might occur without irreversible crystal structure change in the subsequent cycles.

The cycling performance of the H$_2$V$_3$O$_8$ NW/graphene cell at a current rate of 1 C after three cycles activation at 1/3 C is shown in FIG. 2B. The activation process was implemented to ensure the charge/discharge reactions would occur deep (or fully) inside the electrode material lattice and thus avoid the capacity increase phenomenon during the initial cycles. The cell could deliver a specific discharge capacity of 336 mAh g$^{-1}$ with a 100% coulombic efficiency after 150 cycles, which is so far the highest capacity value among all reported zinc ion batteries with mild-acidic aqueous electrolyte (pH=3.55). The rate capability of the H$_2$V$_3$O$_8$ NW/graphene electrode was evaluated by increasing the current rate from 1/3 C to 10 C gradually (FIG. 2C).

When the current rate was increased to 5 C, the cell could still deliver a capacity as high as 240 mAh g$^{-1}$. Impressively, when the current rate continued to be increased from 6 C to 10 C, the capacity almost remained nearly at the same value as 5 C. The specific capacities were 232, 227, 222, 218 and 215 mAh g$^{-1}$ from 6 C to 10 C, respectively. The discharge profiles at different current rates, especially at higher current rates, showed the same shape and small polarization (FIG. 2D), which was evidence of the fast charge transfer kinetics of the electrode. The durability and long cycling stability at a very high current rate (20 C) of the cell was studied after the rate capability test (FIG. 2E). In the first 700 cycles, the capacity gradually increased from ~200 mAh g$^{-1}$ to 270 mAh g$^{-1}$ and was maintained ~400 cycles. Then, the capacity slowly decreased to 240 mAh g$^{-1}$ from the 1030$^{th}$ to the 2000$^{th}$ cycle, representing a high-capacity retention of 87% with respect to the highest value (276 mAh g$^{-1}$ at 1030$^{th}$ cycle). Compared to other state-of-the-art ARM systems (FIG. 2F),[12-26] the H$_2$V$_3$O$_8$ NW/graphene composite exhibited a very competitive electrochemical performance. Specifically, the H$_2$V$_3$O$_8$ NW/graphene cathode was able to deliver 180 W h kg$^{-1}$ at a very high power density of 3800 W kg$^{-1}$ (calculated based on the cathode weight only) and a high volumetric energy density of 485 Wh L$^{-1}$ (calculated based on the cathode electrode only, data not shown). The weight energy density was significantly higher than other conventional aqueous energy storage systems, including a supercapacitor (<10 W h kg$^{-1}$),[12] aqueous lithium battery (50-80 W h kg$^{-1}$),[13] and an Ni-MH (20-80 W h kg$^{-1}$) battery. Compared to the excellent electrochemical performance of the H$_2$V$_3$O$_8$ NW/graphene composite, the pristine H$_2$V$_3$O$_8$ NW only electrode showed an inferior performance, including lower discharge capacity of 230 mAh g$^{-1}$ at 1/3 C current rate after 60 cycles and poor rate performance of only 58.4 mAh g$^{-1}$ at 5 C (data not shown). This comparison revealed that graphene grafting not only improved the cyclic stability and rate capability of H$_2$V$_3$O$_8$ NWs, but also increased the discharge capacity by ~30 mAh g$^{-1}$. This enhancement can be attributed to the improved electrochemical kinetics of the electrode and the capacitive effect from the high specific area of the graphene sheet.[15, 16]

To reveal why the H$_2$V$_3$O$_8$ NW/graphene composite exhibited such a good electrochemical performance, the electrode configuration and crystal structure of the H$_2$V$_3$O$_8$ NW after different numbers of cycle were investigated by SEM and TEM. It was found that the composite configuration and NW morphology were preserved very well after short (FIGS. 3A and 3B) and long (FIGS. 3D and 3E) charge/discharge cycles, showing only reduced NW length after the cycles. The graphene sheets could be clearly observed after 200 cycles, retaining a sound distribution within the NW network (FIGS. 3B and 3E). HRTEM images further showed that both cycled H$_2$V$_3$O$_8$ NWs retained the same high quality crystal lattice as the pristine samples (FIGS. 3C and 3F for 150 cycles at 1 C and 2000 cycles at 20 C, respectively). The XRD spectrum of the electrode after 2000 cycles still exhibited sharp diffraction peaks, indicating the high crystallinity of the electrode material was maintained (data not shown), which ensured high capacity reten-
tion during repeated charge/discharge processes. The reduced peak intensity of the (002) peak could be a result of the NW morphology change after long-term cycling (FIG. 3F), where most NWs turned into much shorter and fatter rods.

Electrochemical impedance spectroscopy (EIS) was then employed to understand the electrochemical kinetics of the composite electrodes (data not shown). Nyquist plots of the H$_2$V$_3$O$_8$ NW/graphene composite and pristine H$_2$V$_3$O$_8$ NW electrodes at the end of the first and 150th discharge all showed one semicircle, which could be assigned to the charge transfer resistance ($R_c$) between the electrode interface and the electrolyte. The line slope could be attributed to ion diffusion in the bulk electrode. After the first discharge, the semicircle radius of the H$_2$V$_3$O$_8$ NW/graphene electrode was only slightly smaller than that of the pristine H$_2$V$_3$O$_8$ electrode. After 150 cycles, $R_c$ of the H$_2$V$_3$O$_8$ NW/graphene electrode was almost twice smaller than that of pristine H$_2$V$_3$O$_8$ NW. Such a big difference demonstrated that the graphene conductive network played a significant role in improving the charge transfer kinetics of the electrode especially after large cycling numbers.

Mechanism of the Electrochemical Reaction
Ex-situ XRD spectra recorded at different cut-off voltages were used to investigate the structure evolution of the H$_2$V$_3$O$_8$ NW/graphene electrode during one charge/discharge cycle (FIGS. 4A and 4B). When the electrode was discharged to 0.8 V, no detectable shift of any diffraction peaks could be observed. This suggested that the structure of the electrode material during this operation period experienced no appreciable change when subjected to only a small amount of Zn$^{2+}$ ion insertion. With more Zn$^{2+}$ ions intercalated into the electrode from 0.6 V to 0.2 V, a shift of peaks toward a higher degree was observed. Magnified XRD curves of the (200) peak were examined (data not shown). The corresponding reduction of the interlayer distance from 0.84 nm to 0.81 nm is believed to be a result of the enhanced electrostatic attraction between two negatively charged V$_2$O$_5$ interlayers by positively charged Zn$^{2+}$ ions intercalation.[17, 18] Interestingly, when discharged to 0.5 V and 0.2 V, a few new peaks appeared gradually at 6.6°, 13°, 33.6° and 38.4°. The peak located at 6.6° corresponded to the (002) peak. After 150 cycles, the peak area ratio of the (002) peak was 1:2 (Table 2).

TABLE 2

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Pristine electrode</th>
<th>Discharged to 0.2 V</th>
<th>Charged to 1.6 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn atom/V atom</td>
<td>0</td>
<td>2.11/3</td>
<td>0.30/3</td>
</tr>
</tbody>
</table>

The high efficiency of Zn$^{2+}$ insertion/extraction into/from the electrode agreed with the high coulombic efficiency of the batteries. In the pristine and fully charged electrodes, the O 1 s region could be fitted into three peaks as shown in FIG. 4D. The peaks located at lower energy of 529.9 and 530.9 eV could be assigned to the O 1 s in VO$_6$ octahedrons and VO$_4$ trigonal bipyramids, respectively. The other at 532.6 eV could be assigned to the V---O layers.[19] However, a new broad peak appeared at 533.1 eV when the electrode was discharged to 0.2 V. The new peak could be assigned to the O 1 s in H$_2$O.[20] In accordance with the insertion of water molecules in the crystal, which did not contribute to the capacity. Moreover, as shown in FIG. 4E, the V 2p$_{3/2}$ signal in the pristine electrode could be divided into two peaks at 515.9 and 517.4 eV, corresponding to V$^{4+}$ and V$^{5+}$, respectively. The peak area ratio of V$^{4+}$ and V$^{5+}$ was 1:2, which agreed well with the theoretical value. With the intercalation of Zn$^{2+}$, a new peak located at 515.1 eV corresponding to V$^{2+}$ appeared and the proportion of V$^{4+}$ increased as the V$^{5+}$ component decreasing. The average valence of vanadium, calculated based on the area ratio, was reduced from 4.67 to 3.7. Therefore, 2.91 charges per formula unit were accessible for electrochemical reactions, which were responsible for the large zinc storage capacity (~280 mA·h g$^{-1}$). Additional capacity could come from the emergence of new phase and surface adsorption.

An atomic-level study of the Zn$^{2+}$ intercalation was conducted by TEM, STEM and EELS to further understand the high rate performance of the H$_2$V$_3$O$_8$ NW/graphene electrode. In a pristine H$_2$V$_3$O$_8$ NW, as shown in FIG. 5A, EELS mapping showed a uniform elemental distribution of both O and V elements, confirming the good stoichiometry of the NW structure. No Zn signal was detected from the pristine NW. For a Zn$^{2+}$ ion-intercalated NW (charged to 0.2 V, FIG. 5B), while both O and V elements still remained the same intensity distribution, significant amount of Zn signal element was detected across the entire NW body with an obviously high concentration along the NW edge, indicating more Zn$^{2+}$ ions were stored on the surface and along the edge of the NW. TEM of the NW after the first discharge
showed that the NW was composed of two different phases (FIG. 5C). A new phase with an interlayer distance of 1.34 nm was observed distributing longitudinally along the NW axial direction (FIG. 5D). HRTEM studies revealed that it was the typical structure of bilayered $\text{H}_2\text{V}_2\text{O}_5\cdot \text{H}_2\text{O}$ [26, 27]. As schematically shown in FIG. 5E, the $\text{Zn}^{2+}$ ions and water molecules were inserted between the $\text{V}_2\text{O}_5$ bilayers. Other parts of the NW still remained the original $\text{H}_2\text{V}_2\text{O}_5$ phase, with negligible change of the lattice spacing (FIG. 5F). This was in good agreement with the insignificant XRD peak shift. High-precision, high-angle annular dark field (HAADF) STEM experiments were further acquired from the $\text{H}_2\text{V}_2\text{O}_5$ phase region following approaches developed by Yankovich [28]. The STEM image series was acquired, including 300 frames using 512x512 pixels and the pixel dwell time was ~2 μs. As shown in FIG. 5G, additional HAADF signals could be observed inside some quasi-hexagons of V atoms (yellow arrows). FIG. 5G shows the intensity line scan along the dashed line in the HAADF image. Clear shoulders could be observed adjacent to the V dumbbells, which were likely to be intercalated $\text{Zn}^{2+}$ sites. DFT calculations showed that $\text{Zn}$ was stable at the center of the vacant sites, with slight distortion to neighboring V atoms (FIGS. 5I and 5J). This was also observed in the HAADF image. From a 2D Gaussian fitting with projected interatomic distances marked (data not shown), additional Zn HAADF signal could be located inside the V quasi-hexagon, together with a slight distortion of neighboring V atoms. STEM analysis and DFT calculation suggested that the rows of vacancy sites between V—O octahedrons could accommodate the intercalation of $\text{Zn}^{2+}$ ions with very small lattice distortion, offering fast $\text{Zn}^{2+}$ diffusion channels with minimal kinetic energy barrier, and thus the ultra-high rate capability.

CONCLUSION

In this example, a novel $\text{H}_2\text{V}_2\text{O}_5$ NW/graphene composite was developed as a cathode material for ARZIBs. The composite was synthesized by a one-step hydrothermal method, offering a great potential for low-cost and large-scale manufacturing. This one-step synthesis strategy enabled a uniform mixture and intimate contact between the $\text{H}_2\text{V}_2\text{O}_5$ NWs and graphene surfaces, which significantly improved the charge transfer kinetics and stability of the composite electrode. The high quality $\text{H}_2\text{V}_2\text{O}_5$ NW crystal structure allowed rapid and reversible $\text{Zn}^{2+}$ intercalation/ extraction. Therefore, the $\text{H}_2\text{V}_2\text{O}_5$ NW/graphene composite exhibited a large specific capacity of 394 mAh g$^{-1}$ at 1/3 C, a high-rate capability of 270 mAh g$^{-1}$ at 20 C, and excellent cycling stability of more than 2000 cycles. The crystal evolution and electrochemical mechanism of $\text{Zn}^{2+}$ and water co-intercalation were systematically investigated by ex-situ XRD, Raman and XPS spectra. HRTEM image revealed the emergence of a new bilayered phase as a result of heavy co-insertion of $\text{Zn}^{2+}$ ions and water molecules. STEM analysis suggested that the $\text{Zn}^{2+}$ ions were located at the vacancy sites between V—O octahedrons, which might be responsible for the ultra-high rate capability. Combining the advantages of zinc metal anode and mild-acidic aqueous electrolyte, this ARM system holds great potential for large-scale energy storage applications with low price, excellent safety and high durability.

REFERENCES

What is claimed is:

1. An aqueous rechargeable zinc ion battery comprising: a cathode comprising a V$_3$O$_7$·H$_2$O-graphene composite, the composite comprising a plurality of V$_3$O$_7$·H$_2$O nanostructures in contact with graphene, an anode in electrical communication with the cathode, the anode comprising zinc, and an aqueous electrolyte comprising zinc ions and an ether of a type and providing a total amount of ether in the aqueous electrolyte, the type and the total amount selected to maximize a capacity retention value of the battery wherein the total amount of ether is in a range from 1 vol. % to 5 vol. %.

2. The battery of claim 1, wherein the V$_3$O$_7$·H$_2$O nanostructures are V$_3$O$_7$·H$_2$O nanowires.

3. The battery of claim 1, wherein the ether is selected from diethyl ether, dimethyl ether, and tetrahydrofuran.

4. The battery of claim 1, wherein the ether is selected from diethyl ether, dimethyl ether, and tetrahydrofuran and the amount of ether is in a range of from 1 vol. % to 5 vol. %.

5. The battery of claim 1, wherein the capacity retention value of the battery is at least 80% at 20 C and after 2000 cycles.

6. The battery of claim 1, wherein the capacity retention value of the battery is at least 85% at 20 C and after 2000 cycles.

7. The battery of claim 6, wherein the battery is characterized by one or both of: a specific capacity of at least 375 mAh g$^{-1}$ at 1/3 C and a rate capability of at least 250 mAh g$^{-1}$ at 20 C.

8. The battery of claim 7, wherein the battery is characterized by both the specific capacity of at least 375 mAh g$^{-1}$ at 1/3 C and the rate capability of at least 250 mAh g$^{-1}$ at 20 C.

9. An aqueous rechargeable zinc ion battery comprising: a cathode comprising a V$_3$O$_7$·H$_2$O-graphene composite, the composite comprising a plurality of V$_3$O$_7$·H$_2$O nanowires in contact with graphene, an anode in electrical communication with the cathode, the anode comprising zinc, and an aqueous electrolyte between the cathode and the anode, the aqueous electrolyte comprising zinc ions and an ether providing a total amount of ether in the aqueous electrolyte in a range of from 1 vol. % to 5 vol. %.

10. The battery of claim 9, wherein the ether is selected from diethyl ether, dimethyl ether, and tetrahydrofuran.

11. The battery of claim 9, wherein the battery is characterized by a capacity retention value of at least 80% at 20 C and after 2000 cycles.

12. The battery of claim 9, wherein the battery is characterized by a capacity retention value of at least 85% at 20 C and after 2000 cycles.

13. The battery of claim 12, wherein the battery is characterized by one or both of: a specific capacity of at least 375 mAh g$^{-1}$ at 1/3 C and a rate capability of at least 250 mAh g$^{-1}$ at 20 C.

14. The battery of claim 13, wherein the battery is characterized by both the specific capacity of at least 375 mAh g$^{-1}$ at 1/3 C and the rate capability of at least 250 mAh g$^{-1}$ at 20 C.

15. The battery of claim 1, wherein the ether is diethyl ether.

16. The battery of claim 9, wherein the ether is diethyl ether.