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H₂V₃O₈ Nanowires as High-Capacity Cathode Materials for Magnesium-Based Battery

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Supporting Information

ABSTRACT: Magnesium-based batteries have received much attention as promising candidates to next-generation batteries because of high volumetric capacity, low price, and dendrite-free property of Mg metal. Herein, we reported $H_2V_3O_8$ nanowire cathode with excellent electrochemical property in magnesium-based batteries. First, it shows a satisfactory magnesium storage ability with 304.2 mA h g⁻¹ capacity at 50 mA g⁻¹. Second, it possesses a high-voltage platform of ~2.0 V vs Mg/Mg²⁺. Furthermore, when evaluated as a cathode material for magnesium-based hybrid Mg²⁺/Li⁺ battery, it exhibits a high specific capacity of 305.4 mA h g⁻¹



at 25 mA g⁻¹ and can be performed in a wide working temperature range (-20 to 55 °C). Notably, the insertion-type ion storage mechanism of $H_2V_3O_8$ nanowires in hybrid Mg^{2+}/Li^+ batteries are investigated by ex situ X-ray diffraction and Fourier transform infrared. This research demonstrates that the $H_2V_3O_8$ nanowire cathode is a potential candidate for high-performance magnesium-based batteries.

KEYWORDS: $H_2V_3O_8$, nanowires, cathode materials, magnesium ions storage, high capacity, hybrid Mg^{2+}/Li^+ battery

INTRODUCTION

With the rapid development of industry and popularization of automobiles, depletion of fossil fuels was tremendously excessive over the past decades. To solve the global issue, the exploitation of smart grids and electric vehicles have attracted a great deal of attention. New types of high-performance secondary batteries as the energy storage system not only are important to a smart grid but also play an indispensable role for electric vehicles.^{1–7} At present, lithium ion batteries as one of the most promising rechargeable batteries have been widely applied to portable electronics due to its high energy density and long cycle life.^{8–12} But the expensive price of Li source and Li dendritic growth impede its further development.

In comparison, Mg source is abundant in the earth and Mg metal has been identified to be dendrite-free on the surface during electrochemical deposition.¹³ On the other hand, Mg metal has a much higher volumetric capacity, about 3833 mA h cm⁻³ compared to the 2205 mA h cm⁻³ of Li metal.¹³ Mg metal also exhibits high chemical stability in different atmosphere and it is easier to handle with low reactivity.¹⁴ Therefore, high-performance rechargeable magnesium-based batteries are potential candidates for next-generation new-type batteries because of the unique advantages of Mg metal.^{15–17} Nonetheless, the intense polarization nature of divalent Mg²⁺ ions results in sluggish intercalation kinetics, which exacerbates the

difficulty in finding an appropriate cathode material and the compatible electrolyte. 18,19

At present, to avoid the intractable safety problem in traditional lithium batteries, magnesium-based hybrid Mg²⁺/Li⁺ batteries are designed, which could integrate the unique characteristics of Mg metal and the rapid diffusion kinetics of Li⁺ ions.²⁰⁻²³ Recently, one of the major challenges for improving the energy density of hybrid Mg²⁺/Li⁺ batteries is to find a high-capacity cathode material.²⁴ Layered vanadium oxides could deliver large specific capacity owing to the multielectron reaction, which have attracted much attention in the field of lithium-ion intercalation host.²⁵⁻²⁷ Moreover, vanadium oxides possess abundant reserves and low price. Among them, $H_2V_3O_8$ is an important member, which has large interlayer spacing between V₃O₇ layers connected by hydrogen bonds. These special hydrogen bonds can buffer the structure expanding/shrinking when ions insert into or extract from the interlamination of $H_2V_3O_8$.^{28,29} The V_3O_7 layer is composed of VO_5 trigonal bipyramids and VO_6 octahedrons, sharing edges and corners by oxygen atoms.³⁰ On the other hand, the $V^{5+/4+}$ mixed valence can optimize the electron conductivity and

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Figure 1. (a) XRD pattern, (b) Raman spectrum, and (c) TEM images of $H_2V_3O_8$. (d) CV curve of $H_2V_3O_8$ at the scan rate of 0.2 mV s⁻¹ in threeelectrode cell. (e) Voltage profiles of $H_2V_3O_8$ and Mo_6S_8 . (f) Cycling performance of $H_2V_3O_8$ at the current density of 50 mA g⁻¹ for magnesium storage.

provides more redox sites during the electrochemical reaction.^{31–33} Thus, $H_2V_3O_8$ holds high promise to become a high-performance cathode for magnesium-based batteries.

In this paper, large layered $H_2V_3O_8$ nanowires exhibit excellent Mg^{2+} ions storage property, exhibiting 304.2 mA h g^{-1} capacity at 50 mA g^{-1} with a high-voltage platform of 2.0 V (vs Mg/Mg^{2+}). On the other hand, as cathode materials for magnesium-based hybrid Mg^{2+}/Li^+ batteries, $H_2V_3O_8$ nanowires can also achieve a high specific capacity of 305.4 mA h g^{-1} . Furthermore, the outstanding rate capacity and wide working temperature range make this material more competitive. To illuminate the reason for excellent electrochemical property, ions storage mechanism and structure change of $H_2V_3O_8$ nanowires at different electrochemical statuses are studied.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern (Figure 1a) is obtained to investigate the crystallographic structure of H₂V₃O₈ nanowires. All the peaks can be indexed to the orthorhombic $H_2V_3O_8$ (JCPDS No.01-085-2401, space group: *Pnam*, *a* = 16.9298 Å, *b* = 9.3598 Å, c = 3.6443 Å), which demonstrates the high purity of H₂V₃O₈ nanowires. Remarkably, the sharp diffraction peaks indicate good crystallinity of H₂V₃O₈ nanowires, and the lowangle (200) peak reveals the large interlamellar spacing of about 8.5 Å of structure. Raman spectrum of the $H_2V_3O_8$ nanowires (Figure 1b) is further detected to confirm the bonds in materials. The absorption bonds located at 145 and 197 cm⁻¹ come to the stretching mode of $(V_2O_2)_n$ relating to the layered structure. The peaks at 286, 410, and 996 cm^{-1} can be attributed to the V=O bonds. The peak located at 505 and 696 cm⁻¹ associated with the V–O bonds.³⁴ To further identify the states of the vanadium element, the nanowires are characterized by X-ray photoelectron spectroscopy (XPS). The V 2p spectra of $H_2V_3O_8$ is shown in Figure S1a of the Supporting Information. The 2p core level spectrum of vanadium manifests two asymmetrical peaks, relating to V 2p_{3/2} and V 2p_{1/2} orbitals, respectively. The signals of V $2p_{3/2}$ can be divided into two

different peaks of V⁴⁺ (516.3 eV) and V⁵⁺ (517.8 eV), respectively. The calculated V⁵⁺/V⁴⁺ ratio is 2.02, which is close to the theoretical value of V⁵⁺/V⁴⁺ ratio in H₂V₃O₈ (2.00).^{35,36} Scanning electron microscopy (SEM) (Figure S1b) image shows the nanowire morphology of H₂V₃O₈ and the distribution of V and O in the H₂V₃O₈ nanowires have been observed in element mapping images (Figure S1c). The transmission electron microscopy (TEM) image of a single nanowire (Figure 1c) shows that the diameter of the nanowire is about 60 nm. Besides, the lattice fringe with the spacing of 0.467 nm is observed in high-resolution TEM (HRTEM) image (inset of Figure 1c), which matches well with the (020) plane of H₂V₃O₈.

The magnesium ions storage performance of $H_2V_3O_8$ nanowires are investigated by a three-electrode cell with 0.5 M $Mg(ClO_4)_2$ acetonitrile (CH₃CN) electrolyte. Activated carbon clothes are both used as counter and reference electrodes, which reach up to 2.4 V vs Mg/Mg²⁺ in CH₃CNbased electrolyte after potential calibrated.³⁷ First, cyclic voltammetry (CV) is measured at the scan rate of 0.2 mV s^{-1} with the potential range from 1.2 to 3.1 V vs Mg/Mg²⁺ (Figure 1d). One cathodic peak is observed around 2.0 V and two anodic peaks are situated at 2.3 and 2.5 V, which ascribed to the insertion and extraction potential of magnesium ions. Galvanostatic charge and discharge curves of H₂V₃O₈ nanowires are shown in Figure 1e; $H_2V_3O_8$ nanowires possess a high working voltage platform of about 2.0 V which is almost twice the voltage of classical Mo_6S_8 materials. Moreover, the high specific capacity of 304.2 mA h g^{-1} (at the current density of 50 mA g^{-1}) are possessed by $\rm H_2V_3O_8$ nanowires which is almost 3 times as much as the capacity of Mo_6S_8 (at 20 mA g⁻¹).¹³ In particular, the energy density of H₂V₃O₈ nanowires can reach about 520 W h kg⁻¹, much higher than the energy density of Mo_6S_8 of about 90 W h kg⁻¹. The cycling performance of H₂V₃O₈ nanowires is illustrated in Figure 1f; a high capacity of 261.2 mA h g⁻¹ still remained after 20 cycles. To sum up, $H_2V_3O_8$ nanowires exhibit excellent magnesium ions storage



Figure 2. (a) Schematic illustration of hybrid Mg^{2+}/Li^+ battery. (b) CV curves of APC and hybrid electrolyte at the scan rate of 100 mV/s. (c) Voltage–time cycling curves of electrolyte and (d) an enlarged view of it.



Figure 3. (a) CV curves of $H_2V_3O_8$ nanowires at scan rate of 0.1 mV s⁻¹ and (b) cycling performance of $H_2V_3O_8$ nanowires at the current density of 50 mA g⁻¹ in hybrid Mg^{2+}/Li^+ battery and Mg battery; (c) rate capability of $H_2V_3O_8$ nanowires in hybrid Mg^{2+}/Li^+ battery. (d) Cycling performance of $H_2V_3O_8$ nanowires at the current density of 100 and 200 mA g⁻¹.

ability and hold a high potentiality to act as high-perfomance cathode materials in magnesium batteries.

Unfortunately, magnesium is unable to reversibly deposit/ dissolve in $Mg(ClO_4)_2-CH_3CN$ electrolyte and common electrolyte of all-phenyl-complex (APC, (PhMgCl)_2-AlCl₃ in THF) is incompatible with the $H_2V_3O_8$ nanowires (proved in following content). To take full advantage of unique characteristics of magnesium and make use of excellent electrochemistry property of $H_2V_3O_8$ nanowires, hybrid Mg^{2+}/Li^+ batteries are applied, which is inspired by the Daniell-type batteries. The work mechanism of the hybrid Mg^{2+}/Li^+ battery is exhibited in Figure 2a. In this hybrid battery, the electrolyte that 1 M LiCl dissolved in APC provides Mg^{2+} ions and Li^+ ions and APC display low overvoltage, large electrochemical windows and highly reversible Mg deposition/stripping efficiency of about 100%.³⁸ The electrolyte plays an important part that Mg element will form the $[Mg_2Cl_3(THF)_6]^+[AlCl_2Ph_2]^-$ to counteract the serious polarization effect and make the Mg plating/stripping smooth.^{38,39} During the discharge process, Li⁺ ions can insert into the cathode materials with large diffusion coefficient and Mg anode will dissolve into electrolyte. Meanwhile, in the charging process, Li⁺ ions will extract from the cathode and Mg^{2+} ions will deposit on the anode smoothly.



Figure 4. (a) Cycling performance of $H_2V_3O_8$ nanowires at 55 °C at current density of 100 mA g⁻¹. (b) GITT curves of $H_2V_3O_8$ nanowires at a small current density of 25 mA g⁻¹. (c) Specific capacity comparison between $H_2V_3O_8$ nanowires and previously reported materials in hybrid Mg²⁺/Li⁺ battery. (d) Diffusion coefficient of Li⁺ ions in the $H_2V_3O_8$ nanowires at different discharge state.

The working mechanism is exhibited in the following equations:

cathode: $H_2V_3O_8 + xLi^+ + xe^- \leftrightarrow Li_xH_2V_3O_8$

anode: $2Mg + 3Cl^{-} + 6THF$ $\leftrightarrow [(\mu-Cl)_3Mg_2(THF)_6]^+ + 4e^{-}$

Above all, the electrolyte property is one of the most important factors for the electrochemical performance of batteries.^{40,41} Therefore, the stability of electrolyte APC and 1 M LiCl in APC (LiCl/APC) are measured by CV which range from -1 to 2 V (vs Mg/Mg²⁺) at the scan rate of 100 mV/s (Figure 2b, Figure S2a). Obviously, APC and LiCl/APC electrolyte both remain stable in the voltage of 2 V. The shape of the curve repeats in three cycles, which means the Mg/Mg²⁺ deposition/ dissolution stability is very well. On the other hands, the presence of LiCl enhances the corresponding current intension from 0.7 to 2.2 mA cm⁻². Thus, LiCl/APC electrolyte has the stable Mg/Mg²⁺ deposition/dissolution property and faster reaction rate compared with pure APC electrolyte. To further investigate the overpotential of electrolyte, two Mg foils both as positive and negative electrodes are assembled by CR2016 coin cells. Figure 2c demonstrates the galvanostatic charging/ discharging testing at current intensity of 20 µA. Figure 2d reveals the difference of cycles in detail, in which the Mg/Mg²⁺ dissolution/deposition in LiCl/APC electrolyte repeat well after many cycles and the overpotential (0.05 V) is weaker than that in APC (0.1 V).

To explore the electrochemical performance of $H_2V_3O_8$ nanowires in hybrid Mg^{2+}/Li^+ batteries, coin cells with metallic magnesium as anode are assembled. The CV curves of $H_2V_3O_8$ nanowires are measured at 0.1 mV s⁻¹ in the potential range of 0.5–2.0 V vs Mg/Mg^{2+} (Figure 3a). In the first cycle, two cathodic peaks are situated at 1.5 and 1.1 V, whereas there is only a little anodic peak observed in the 1.5 V. The curve of the first cycle is different from the next cycles, which might result from the irreversible interaction of ions to the $H_2V_3O_8$ nanowires. For the next cycles, two weak cathodic peaks appear at potentials of 1.7 and 1.1 V and there is an anodic peak situated at the potential of 1.5 V. The CV curves of materials with pure APC electrolyte are also explored, which exhibits weak current response and no existing cathodic or anodic peak, meaning that Mg²⁺ ions are hard to intercalate into the materials. The electrochemical performance is tested via galvanostatic charging/discharging measurement (Figure 3b). The H₂V₃O₈ nanowires achieve a high specific capacity of 282 mA h g^{-1} at the current density of 50 mA g^{-1} , which corresponds to 2.98 mol of lithium insertion per unit formula of $H_2V_3O_8$. The high capacity is attributed to the big interlayer spacing and enough activated position for Li⁺ ions insertion/ extraction. However, H₂V₃O₈ nanowires in pure APC electrolyte deliver no capacity at the same current density, which corresponds well to the CV results. It indicates that Mg²⁺ ions are difficult to insert into H₂V₃O₈ in APC electrolyte. To further evaluate the electrochemical behavior, rate capability is measured ranging from 50 to 500 mA g^{-1} (Figure 3c). The H₂V₃O₈ nanowires deliver the discharge capacity of 273, 209, 153, and 88 mA h g^{-1} at the current densities of 50, 100, 200, and 500 mA g^{-1} , respectively. After the relative high rate measurement, the current density is returned to 50 mA g^{-1} , and the discharge capacity can also recover about 240 mA h g^{-1} , demonstrating a high rate stability. The charge and discharge profiles of the H₂V₃O₈ nanowires at the different current densities are shown in Figure S2b in which the average discharge voltage is 1.4 V, and there is almost no capacity in pure APC. The cycling performance of H₂V₃O₈ nanowires at 100 and 200 mA g⁻¹ are displayed in Figure 3d. High specific capacities of 219 and 185.1 mA h g⁻¹ have been obtained. After 50 cycles, the specific capacities of 129.6 and 104.5 mA h g^{-1} remained, respectively. The high-temperature performance is also important to practical application. At 55 °C, the H₂V₃O₈ nanowires exhibit a high specific capacity of 249.6 mA h g⁻¹ at 100 mA g^{-1} (Figure 4a). Compared to that in room



Figure 5. (a) Ex situ XRD patterns and (b) FTIR spectra of $H_2V_3O_8$ nanowires in different statuses in the first cycle.

temperature, the specific capacity rises about 14% due to the enhanced ions diffusion kinetics and electrochemical activity. On the other hand, the $H_2V_3O_8$ nanowires also deliver a specific capacity of 77.5/59.5/34.5 mA h g⁻¹ in 10/-5/-20 °C at 100 mA g⁻¹ (Figure S3).

The kinetics of Li⁺ ions in the hybrid electrolyte and cathode materials is an important element to the origin of the large capacity and the high-rate performance. Galvanostatic intermittent titration technique (GITT) is used to research the diffusion of Li⁺ ions, which provides insight into the interaction between materials and diffusion ions.^{42,43} The GITT result is shown in Figure 4b; $H_2V_3O_8$ nanowires reach a specific capacity as high as 305.4 mA h g^{-1} , which corresponds to 3.22 mol of lithium insertion per unit formula of H₂V₃O₈. To the best of our knowledge, this capacity is excellent among the reported cathode materials in hybrid Mg²⁺/Li⁺ battery (Figure 4c).²¹ This result demonstrates that H₂V₃O₈ nanowire is a promising cathode material for hybrid Mg²⁺/Li⁺ battery. An et al. reported $H_2V_3O_8$ exhibits the same specific capacity of 325 mA h g⁻¹ at low current density in lithium ion batteries.³¹ Wang et al. reported H₂V₃O₈ exhibits specific capacity of only 160 mA h g^{-1} at low current density in sodium ion batteries, which might be caused by the large ion radius and polarization effect of sodium ion.²⁹ Moreover, the Li⁺ ions diffusivity (D^{GITT}) can be calculated from the slight potential response (Figure S4) using the formula in Scheme 1 in the Supporting Information. Figure 4d exhibits average Li⁺ diffusivity of about 1×10^{-10} cm² s⁻¹ in the $H_2V_3O_8$ cathode over the whole intercalation process. During the discharging process, Li⁺ ions diffusivity decline from $1.15 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ to $4.8 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, which may result from the intense electrostatic repulsion when the Li⁺ ions concentration increases in the host materials.

Theoretical exploration on the reaction mechanism of materials is important for improving the performance of batteries. To investigate the Li⁺ ions storage mechanism of the H₂V₃O₈ nanowires in the hybrid battery, ex situ XRD measurements are performed at different charge and discharge states in the first cycle (Figure 5a). The patterns of the (200) diffraction are magnified, from which the slightly reversible shifts occur during the cycle. When the battery discharged to 1.7 V (II), the peak shifts apparently to a higher degree from 10.5° to 10.9° , which indicates the decrease of interlayer distance. It might result from the intercalation of Li⁺ ions that enhances the coordination reaction with oxygen.⁴⁴ When the battery discharged to 0.5 V (V), the peak shifts back slightly to lower degrees, corresponding to the extension of layer space, which may be due to the high concentration of Li⁺ ions. After the battery charged back to 2 V (VIII), the (200) diffraction shifts back. It does not revert to the initial stage but locates at

higher degrees, indicating the irreversible shrink of layer space. To further explore the structure changes, Fourier transform infrared (FTIR) spectra of the H₂V₃O₈ cathode in three different statuses are measured (Figure 5b). The peak located at 552 cm^{-1} is attributed to the Vs (V–O–V) stretching vibration bonds and it remains unchanged during the cycling process which demonstrates the stability of the structure.²⁹ The absorption bands of about 970 and 1020 cm⁻¹ correspond to the symmetric stretching of $V^{4+}=O$ and $V^{5+}=O$ bonds, respectively.²⁹ In the initial stage (I), those two peaks are sharp and easy to distinguish. But after the battery discharged to 0.5 V (V), the peaks become vague and red-shift, which might be caused by the reduction of V^{5+} and V^{4+} . In the recharged stage (VIII), these peaks become sharp again but do not recover the initial status (I). Thus, a part of the reduced vanadium does not convert to the oxidation state. Meanwhile, a few Li⁺ ions might intercalate into the H₂V₃O₈ layers and remain in the spacing. The bands located at 1629 and 3427 cm⁻¹ come from the vibration of water molecules and H-O-H bonds and they remain stable in different stages.²⁹ The absorption bands at 1154 and 1210 cm⁻¹ are attributed to the symmetric and asymmetric stretching of -CF2- which come from the PTFE in the cathode sheet.

To explore the reason for the capacity decay of hybrid batteries, the Mg anode and the H₂V₃O₈ cathode materials at various stages have been investigated. Figure S5a-d show the SEM patterns of the Mg anode, whose surface is smooth in the initial stage, and then it becomes rough after some cycles, but there is no dendritic crystal. In addition, the morphology change of H₂V₃O₈ cathode materials also have been investigated (Figure S6a-d), there is no visible degeneration and H₂V₃O₈ nanowires maintain intact micromorphology after 100 cycles. Therefore, decay of the capacity might be caused by the gradual crystal structure degeneration, which is proved by the ex situ XRD (Figure S7). There are the XRD patterns about the cathode materials in the initial stage and after 50 and 100 cycles individually. The crystal structure of the cathode after 50 cycles is the same as that in the initial stage. But after 100 cycles, the major peaks at 10° and 32° weaken and other peaks disappeared, indicating the irreversible deformation of crystal structure of H₂V₃O₈. Therefore, the capacity decay may result from the collapse of the crystal structure.

In summary, the excellent electrochemical performance of $H_2V_3O_8$ nanowires for magnesium-based battery are reported. The $H_2V_3O_8$ nanowires as a cathode material exhibit a high-voltage platform of about 2.0 V and high specific capacity of 304.2 mA h g⁻¹ at 50 mA g⁻¹, which is outstanding performance in a magnesium battery. Furthermore, $H_2V_3O_8$ nanowires also exhibit a high specific capacity of 305.4 mA h g⁻¹ at 25 mA g⁻¹ in a magnesium-based hybrid Mg²⁺/Li⁺ battery. To the best of our knowledge, it is excellent among the reported cathode materials for hybrid Mg²⁺/Li⁺ batteries. Moreover, it shows the wide temperature adaptability (>250 mA h g⁻¹ at 55 °C and >30 mA h g⁻¹ at -20 °C) and rapid insertion kinetics of Li⁺ ions. In addition, the Li⁺ ions storage mechanism of $H_2V_3O_8$ as cathode for hybrid Mg²⁺/Li⁺ battery is demonstrates that the high-capacity $H_2V_3O_8$ nanowires are promising cathode materials for next-generation, high-performance magnesium batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b09924.

Additional figures S1–S7. XPS spectrum, SEM image, and elemental mapping images of $H_2V_3O_8$; CV curves of APC on SS working electrode and charge/discharge profiles of the $H_2V_3O_8$ nanowires at different current densities; discharge and charge specific capacity of $H_2V_3O_8$ nanowires at low temperatures; GITT potential feedback curve with time and other details; SEM images of Mg anode and $H_2V_3O_8$ nanowires after different cycles; XRD patterns of $H_2V_3O_8$ at various states (PDF)

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Notes

The authors declare no competing financial interest.

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