Interlayer-Expanded $V_6O_{13-n}H_2O$ Architecture Constructed for an Advanced Rechargeable Aqueous Zinc-Ion Battery

Jianwei Lai,† Haihui Zhu,‡ XiuPing Zhu,‡ Harsha Koritala,§ and Ying Wang*,†

†Department of Mechanical & Industrial Engineering, Louisiana State University, Baton Rouge, Louisiana 70803, United States
‡Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, State College, Pennsylvania 16802, United States
§Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180-3522, United States

Supporting Information

ABSTRACT: Rechargeable aqueous zinc-ion batteries have been intensively studied as novel promising large-scale energy storage systems recently, owing to their advantages of high abundance, cost effectiveness, and high safety. However, the development of suitable cathode materials with superior performance is severely hampered by the sluggish kinetics of $Zn^{2+}$ with divalent charge in the host structure. In the present work, a highly reversible aqueous $Zn^{2+}$ battery is demonstrated in aqueous electrolyte using $V_6O_{13-n}H_2O$ hollow microflowers composed of ultrathin nanosheets. Benefiting from the synthetic merits of its favorable architecture and expanded interlamellar spacing that results from its structural water, the $V_6O_{13-n}H_2O$ cathode exhibits outstanding electrochemical performances with a high reversible capacity of 395 mAh g$^{-1}$ at 0.1 A g$^{-1}$, superior rate capability, and durable cycling stability with a capacity retention of 87% up to 1000 cycles. In addition, the reaction mechanism is significantly investigated in detail. This study demonstrates that the $V_6O_{13-n}H_2O$ nanostructure is emerging as a promising cathode material for the high-potential rechargeable aqueous zinc-ion battery, and it may shed light on the water-initiated effective interlayer engineering strategy for the construction of high-performance cathode materials for grid-scale energy storage devices.

Keywords: aqueous zinc-ion battery, $V_6O_{13-n}H_2O$ nanosheets, interlayer engineering, energy storage, electrochemical characterization

1. INTRODUCTION

The increasing demands for environmentally friendly large-scale energy storage devices with high energy density, high safety, and low cost have stimulated the development of advanced rechargeable batteries, due to the energy crisis and environmental pollution caused by traditional energy technology.1–5 Among various energy storage systems, lithium-ion batteries (LIBs) have been widely used in portable electrical devices and large-scale energy storage systems for several decades.7–10 However, the high cost, limited lithium resources, as well as safety concerns on flammable organic electrolytes greatly hinder their further development.11–14 Recently, rechargeable multivalent ion ($Zn^{2+}$, $Mg^{2+}$, $Ca^{2+}$, or $Al^{3+}$) batteries have been attracting great interest, as they are considered as both high-potential and high-safety energy storage devices when compared to expensive and unsafe Li-ion batteries.15–19 In this regard, rechargeable aqueous zinc-ion batteries (ZIBs) are particularly attractive due to their distinctive advantages, such as low cost, low redox potential of $Zn^{2+}/Zn$ (−0.76 V vs standard hydrogen electrode), high abundance, high stability in water, high theoretical capacity (820 mAh g$^{-1}$), as well as high energy density (5851 mAh mL$^{-1}$) in terms of zinc metals.20 The cost and environmental pollution can be greatly reduced by replacing traditional organic electrolytes with aqueous-based electrolytes. Such aqueous electrolytes can exhibit excellent ionic conductivity up to 1.0 S cm$^{-1}$, superior to the organic electrolytes, and may
effectively boost the high rate capabilities of aqueous ZIBs for grid-scale renewable energy storage systems.\textsuperscript{31,32} Recently, intensive research in designing the advanced materials of ZIBs has been conducted for large-scale energy storage.\textsuperscript{15,16} Significant efforts and investigations have contributed to the rapid development of reversible zinc-ion storage electrode materials, such as manganese-based oxides, Prussian blue analogs, and vanadium-based materials. Manganese oxides, including $\alpha$, $\beta$, $\gamma$, and $\delta-MnO_2$ have been studied as intercalation hosts for zinc ions.\textsuperscript{23–26} Unfortunately, $\text{MnO}_2$ suffers from poor rate performance and rapid capacity fading in aqueous electrolyte. For example, Kim et al. reported a $\delta$-$\text{MnO}_2$ nanoflake cathode with a capacity of 252 mAh g\(^{-1}\), and only 44% of the highest capacity can be retained after 100 cycles at 83 mAh g\(^{-1}\).\textsuperscript{26} Liu et al. reported a ZIB with improved energy density and cycling performance by employing MnSO\(_4\) as an additive for the effective suppression of Mn\(^{2+}\) when cycling.\textsuperscript{27} Attempts on the Prussian blue analogs delivered limited capacity ($\sim$50 mAh g\(^{-1}\)) and suffered from O\(_2\) evolution at a high operation voltage of $\sim$1.7 V.\textsuperscript{28}

The advantages of vanadium-based materials for ZIBs include high specific capacity, high safety, abundance resource, and low cost. Layered vanadium oxide bronzes show enhanced cycling stability and rate capability by employing cations or structural water as “pillars”.\textsuperscript{29–33} These pillars can effectively improve the structural stability during charge–discharge processes and provide a fast Zn\(^{2+}\) diffusion path. Mai et al. presented a $\text{V}_6\text{O}_{13}$·$\text{H}_2\text{O}$/graphene cathode with expanded interlayer spacing (1.26 nm) for ZIBs, which delivered a high specific capacity of $\sim$372 mAh g\(^{-1}\) at 0.3 A g\(^{-1}\) and retained 71% of the maximum capacity after 900 cycles at 6 A g\(^{-1}\).\textsuperscript{34} It should be noted that the intercalation kinetics of Zn\(^{2+}\) in metal oxides are sluggish due to the intensive polarization and large solvation sheath of Zn\(^{2+}\). Such good electrochemical performance of the $\text{V}_6\text{O}_{13}$·$\text{H}_2\text{O}$/graphene cathode can be attributed to the reduced effective charge in $\text{H}_2\text{O}$-solvated Zn\(^{2+}\). Mai et al. also reported a sodium-stabilized vanadium oxide (Na\(_{0.33}\)V\(_2\)O\(_5\)) nanowire cathode, showing a capacity of 367.1 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), and 93% capacity retention could be achieved after 1000 cycles at 1 A g\(^{-1}\).\textsuperscript{35} Nazar et al. developed a Na\(_{0.25}\)V\(_6\)O\(_{13}\)·$\text{H}_2\text{O}$ pillared by Zn\(^{2+}\) and crystalline water, exhibiting a capacity of $\sim$282 mAh g\(^{-1}\) at 0.3 A g\(^{-1}\) and 81% capacity retention after 1000 cycles at 2.4 A g\(^{-1}\).\textsuperscript{36} Kim et al. constructed a LiV\(_2\)O\(_3\) cathode with a capacity of $\sim$256 mAh g\(^{-1}\) at 16 A g\(^{-1}\) and 75% capacity retention after 65 cycles at 133 mA g\(^{-1}\).\textsuperscript{37} Liang et al. studied a variety of sodium vanadates, demonstrating that Na\(_{0.15}\)V\(_3\)O\(_5\) exhibited a high capacity of 281 mAh g\(^{-1}\) at 0.5 A g\(^{-1}\) and maintained 71% capacity over 2000 cycles at 4 A g\(^{-1}\).\textsuperscript{37} They also investigated NH\(_4\)V\(_4\)O\(_8\) cathode with $\sim$400 mAh g\(^{-1}\) at 0.3 A g\(^{-1}\) with negligible capacity loss up to 1000 cycles at 10 A g\(^{-1}\).\textsuperscript{38} Except for a few cathode candidates, most of the reported cathode materials of ZIBs are seriously hindered by low specific capacity, poor rate capability, and limited cycle life for future practical applications.\textsuperscript{11–43} Therefore, there is an urgent need to develop a novel vanadium-based oxide cathode material with high capacity, high durability, and excellent rate performance, which may play a crucial role in the breakthrough of achieving practical large-scale ZIBs.

Owing to its high specific capacity, wide availability, and low cost, the reaction mechanism and electrochemical performance of mixed-valence $\text{V}_6\text{O}_{13}$ have been explored in organic electrolytes for rechargeable alkali-ion-based batteries.\textsuperscript{39,40} For instance, Yu et al. reported the $\text{V}_6\text{O}_{13}$ nanotextiles evaluated as a cathode for LIBs, which delivered a high capacity of 326 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) and a reversible capacity of 134 mAh g\(^{-1}\) at 500 mA g\(^{-1}\), showing superior electrochemical performance and huge potential as high-energy cathode materials.\textsuperscript{44} However, the electrochemical reaction mechanisms of $\text{V}_6\text{O}_{13}$$\cdot\text{H}_2\text{O}$ in aqueous electrolytes with multivalent ions (e.g., Zn\(^{2+}\)) remain still unclear. The crystal structure of $\text{V}_6\text{O}_{13}$ is composed of corner and edge-sharing distorted VO\(_6\) octahedra, which form alternating single and double vanadium oxide layers connected by shared corners.\textsuperscript{45,46} There are three various vanadium environments noted as V(1), V(2), and V(3) in the crystal structure of $\text{V}_6\text{O}_{13}$. According to the valence bond sum calculations, the V(1) atoms in single layers and V(3) atoms in double layers are occupied by V\(^{4+}\), while the V(2) atoms in the double layers exhibit V\(^{5+}\). It should be noted that the crystal structure of $\text{V}_6\text{O}_{13}$ is fully connected in three dimensions, even though it is easy to understand the structure in respect of single and double layers. Based on the first principle calculations, previous study reveals that the water insertion in interlayer-expanded $\text{V}_6\text{O}_{13}$$\cdot\text{H}_2\text{O}$ is ascribed to the strong intercalation of water molecules and the lattice O ions between the single and double layers, forming hydroxyl radicals on each side. Such expanded interlayer spacing by water intercalation exhibited good rate capability and excellent cycling stability for lithium ion storage.\textsuperscript{43} Moreover, $\text{V}_6\text{O}_{13}$ with the mixed valences of V\(^{4+}\) and V\(^{5+}\) shows high electronic conductivity at room temperature, which is favorable for the ultrafast charge and discharge processes when applied in the battery system.\textsuperscript{44}

Herein, a novel hydrated $\text{V}_6\text{O}_{13}$$\cdot\text{H}_2\text{O}$ (H-VO) material as a promising cathode has been developed for the construction of a high-performance aqueous rechargeable zinc-ion battery by employing an aqueous Zn(CF\(_3\)SO\(_2\))\(_2\) electrolyte and zinc foil anode, as illustrated in Scheme 1. Benefiting from the interlayer-expanded strategy through feasible water intercalation and the unique dandelion-like hollow architecture constructed by ultrananosheets, the particular $\text{V}_6\text{O}_{13}$$\cdot\text{H}_2\text{O}$ cathode can provide abundant accessible channels for fast kinetics of Zn\(^{2+}\) within the electrode, short transportation path for Zn\(^{2+}\) migration, and promote the rapid transfer of electrons. In addition, the in situ growth of a carbon layer on the

Scheme 1. Schematic Illustration of a Rechargeable Aqueous Zinc-Ion Battery Based on $\text{V}_6\text{O}_{13}$$\cdot\text{H}_2\text{O}$ Cathode and Metallic Zn Foil Anode

$\text{Zn}$ Anode $\rightarrow$ Separator $\rightarrow$ $\text{V}_6\text{O}_{13}$$\cdot\text{H}_2\text{O}$ Cathode
The morphology of as-synthesized H-VO was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 1a, the H-VO displays a hollow microflower structure with sizes of 2–7 μm. The high-resolution SEM image further presents that these hollow structures are constructed by two-dimensional ultrathin nanosheets with widths of 50–200 nm, which are entangled together (Figure 1b). In addition, the presences of V, O, and C in H-VO are confirmed in the energy dispersive X-ray spectrum (EDS) results, showing a carbon content of ~2.99 wt % (Figure S2). Furthermore, the TEM image in Figure 1c shows that the H-VO possesses the feature of ultrathin layers, consistent with the high-solution SEM image. From the high-resolution TEM image in Figure 1d, a single nanosheet exhibits distinct lattice fringe areas apart from areas without fringe, and it could be attributed to the carbon layer covered on the surface of the nanosheet, which was formed during the hydrothermal reaction. It should be noted that such in situ coating of carbon on the surface of the H-VO nanosheets would be beneficial to enhance the interfacial conductivity of the sample when evaluated in aqueous ZIB. The interplanar spacing of 0.583 nm is well matched with the (200) crystalline facet of H-VO. Such a favorable hollow structure of H-VO would be advantageous for the fast kinetics of Zn2+ intercalation and deintercalation. In order to determine the crystalline water content of H-VO, thermogravimetric analysis (TGA) was carried out in the temperature range of 30–500 °C under the nitrogen atmosphere as displayed in Figure 1e. The total weight loss is attributed to the evaporation of physically absorbed water (30–100 °C) and lattice water (100–350 °C). Based on a weight loss of 3.5 wt %, it can be estimated that there is approximately 1.1 structural water per V6O13 unit. The crystal structure of the as-prepared H-VO was characterized by X-ray diffraction (XRD) as presented in Figure 1f. The XRD pattern of H-VO can be well indexed to monoclinic V6O13 with the space group of C2/m (unit cell parameters of a = 11.9 Å, b = 3.671 Å, c = 10.122 Å, and β = 100.87°; JCPDS no. 01-072-1278). Based on Bragg’s equation (d = 0.5λ/ sin θ), the diffraction peak located at lower angles indicates a larger interlayer distance. The diffraction peak of H-VO at 2θ = 7.8° from facet (001) is attributed to the water insertion with expanded interlayer, and the corresponding interlayer spacing is calculated to be 1.13 nm, which is larger than the 0.99 nm value at 2θ = 8.9° from the standard PDF card. The larger lattice spacing of 1.13 nm may provide more diffusion channels for the migration of Zn2+, and the expanded interlamellar spacing is comparable to the V2O5·nH2O cathode,48 which is more electrochemically superior to previously reported VS2,40 zinc pyrovanadate,41 and Na2V6O16·3H2O.49 In addition, the expanded interlayer of H-VO at (001) plane is in good agreement with a previous report.48 After the sample was annealed at 400 °C under Ar flow for 2 h, the dehydrated V6O13 (VO) was obtained. The diffraction peak attributed to the interlayer spacing of 1.13 nm is divided into two peaks at 9.1° and 12.4°, indicating the decreased lattice space. The peak position change suggests that the interlayer expansion is mainly attributed to the water intercalation.

The electrochemical performances of H-VO and VO as cathode materials were evaluated using 3 M Zn(CF3SO3)2 aqueous solution as the electrolyte and metallic zinc foil as the anode assembled in 2032 coin-type cells. The initial three
cyclic voltammogram (CV) curves of H-VO in the voltage range of 0.2−1.4 V (vs Zn/Zn²⁺) at a scan rate of 0.1 mV s⁻¹ are displayed in Figure 2a. During the first cathodic scan, there are five cathode perks located at 1.07, 0.90, 0.76, 0.63, and 0.44 V, and the small peak at 1.07 V may be caused by some irreversible reactions occurring in the initial cycle, which will be discussed later. The remaining four cathode peaks are slightly different from the peak positions at 0.91, 0.77, 0.65, and 0.46 V in the subsequent cycles of the reduction scan. The reduction peak shifting could be ascribed to the activation of H-VO during the discharge process. From the initial three anodic scans, they exhibit completely overlapping peaks at 0.52, 0.78, 0.95, and 1.10 V. In addition, the CV curves in the initial three cycles show good similarity and repeatability with the exclusion of a small deviation in the first cathodic CV curves, suggesting the good structural stability and excellent reversibility of the Zn/H-VO battery. Over four distinct pairs of reduction/oxidation peaks are clearly observed, implying a four-step reaction mechanism corresponding to the Zn²⁺ insertion/extraction. Such CV curves of the H-VO are quite different from many reported vanadium-based cathodes for aqueous ZIBs with only two pairs of redox peaks, such as V₂O₅·nH₂O,34 Zn₂V₂O₇,39 and H₂V₃O₈.43 For the VO electrode, five reduction peaks of the first cathodic scan at 1.10, 0.78, 0.62, 0.56, and 0.50 V are noticeably different from three cathode peaks at 0.85, 0.65, and 0.49 V in the following two cycles, and three oxidation peaks at 0.59, 0.76, and 1.00 V can be observed in these initial three cycles (Figure S3a). Furthermore, the selected second CV curves comparison at 0.1 mV s⁻¹ between H-VO and VO show significant differences based on the number of peaks and corresponding peak positions (Figure S3b).

Based on such highly reversible CV curves of these two cathodes, their cycling performances are further investigated by employing the galvanostatic charge−discharge method. As presented in Figure 2b, H-VO delivers a remarkable and stable initial discharge capacity of 383 mAh g⁻¹ at a current density of 0.1 A g⁻¹ and corresponding charge capacity of 392 mAh g⁻¹ with a high initial Coulombic efficiency of 97.6%. The favorable Coulombic efficiency implies good reversibility of Zn²⁺ ingress/egress. In the following 15 cycles, the specific capacity gradually increases, which is ascribed to the activation process of the H-VO electrode, and then stabilizes in the range of 390−395 mAh g⁻¹ with an overall Coulombic efficiency over 99.5%. It should be noted that the H-VO can maintain the high and stable capacities of ~390 mAh g⁻¹ when applied a low current density of 0.1 A g⁻¹ during the whole 50 cycles, which outperforms many previous reported cathodes that suffered from severe capacity fade under the same current density in the initial few cycles,35,41,43 indicating the high reversibility and stability nature of the H-VO electrode. Based on the high discharge capacity of 390 mAh g⁻¹, the number of electrons transfer during electrochemical reaction is calculated to be ~7.7, corresponding to 3.85 Zn²⁺ migration. Notably, the vanadium ions in H-VO can be reduced to V³⁺ with eight electrons transferring, so its theoretical capacity can be calculated to be 401.6 mAh g⁻¹. As discussed above, the CV curves of H-VO electrode show multistep Zn²⁺ intercalation/deintercalation behaviors (Figure 2a). According to Figure 2c, H-VO delivers a capacity of 104.2 mAh g⁻¹ at 0.3 A g⁻¹ in the
voltage range of 0.8–1.4 V during the discharge process, corresponding to one Zn2+ (two electrons transfer) insertion. Subsequently, H-VO displays a capacity of 278.8 mAh g−1 in 0.2–0.8 V, corresponding to ~2.77 Zn2+ (5.54 electrons transfer) intercalation. Notably, there are two V3+ and four V4+ ions for each V2O5·1.1H2O. Therefore, we speculate that two V3+ ions are reduced to V2+ (two electrons transfer) during 0.8–1.4 V, and 5.54 V4+ are further reduced to V3+ (5.54 electrons transfer) during 0.2–0.8 V. Similarly, H-VO presents a capacity of 282.8 mAh g−1 between 0.2 and 0.93 V during charge process, corresponding to the oxidation of 5.63 V3+ to V4+. In the voltage range of 0.93–1.4 V, a capacity of 104.3 mAh g−1 is shown, relevant to the oxidation of 2 V4+ to V5+. Thus, 5.63 V3+ are oxidized to V4+ during 0.2–0.93 V, and 2 V4+ are oxidized to V5+ during 0.93–1.4 V. It should be noted that H-VO exhibits a discharge capacity of 211 mAh g−1 during 0.6–1.4 V, and a discharge capacity of 175.6 mAh g−1 during 0.2–0.6 V at 0.3 A g−1, which shows ~54.6% capacity contribution in 0.6–1.4 V, and 45.4% (<50%) capacity is obtained in 0.2–0.6 V (Figure 2c). These results are similar to the previously reported VOG sample having a capacity contribution of 59% in 0.6–1.6 V and 41% in 0.2–0.6 V.44 However, for the dehydra VO electrode, although it provides higher first discharge capacity of 434 mAh g−1 at the same current density of 0.1 A g−1 due to the elimination of structural water, VO displays a significantly reduced initial charge capacity of 404 mAh g−1, indicating a poorly reversible process. The capacity of VO dramatically decreases to 323 mAh g−1 with further charge–discharge after 20 cycles and then gradually increases to 370 mAh g−1, which may be ascribed to the activation and stabilization of VO by water intercalation and irreversible Zn2+ as pillars trapped in the interlayer during cycling. Such relatively unstable cycling performance of VO largely hinders its practicability for gridscale energy storage devices. Moreover, the comparison of typical galvanostatic charge–discharge curves at the selected cycle with a current density of 0.1 A g−1 between H-VO and VO manifests a reversibly high capacity of ~395 mAh g−1 achieved for H-VO, while an unfavorable capacity of ~323 mAh g−1 is presented for VO (Figure S4).

Furthermore, the excellent rate performance is of significance for large-scale aqueous ZIBs to address the ever-growing demands for practical energy storage systems. However, many previous reported cathodes for aqueous ZIBs display undesirable rate behaviors, which are largely hampered by the high polarization of Zn2+ with divalent charge in the host structure. In the presented H-VO electrode, it shows exceptionally satisfactory capacity even under severe galvanostatic tests. The comparison of rate capabilities and corresponding charge–discharge curves with a voltage range of 0.2–1.4 V starting from a current density of 0.3 to 20 A g−1 are illustrated in Figure 2c, d. Extraordinarily, via increasing the current density from 0.3 up to 10 A g−1, the H-VO electrode exhibits impressive capacities of 386 and 270 mAh g−1, respectively, with only ~30% capacity loss. Even when the highest current rate of 20 A g−1 is applied, a considerable capacity of 97 mAh g−1 still can be obtained. The corresponding discharge or charge time is as short as ~17.5 s, demonstrating ultrafast charge transfer kinetics of the H-VO electrode and superior rate capability. More importantly, as the current density abruptly returns back to 0.8 A g−1, the reversible discharge capacity restores to 364 mAh g−1, which is comparable to the specific capacity of 372 mAh g−1 under the same current density in previous cycles, manifesting a strong endurance for rapid Zn2+ insertion/extraction and good structural reversibility. In contrast, the rate behavior of VO applied with identical increasing current rates is severely inferior, displaying an initial discharge capacity of 398 mAh g−1 at 0.3 A g−1, drastically declining to 61 mAh g−1 at 10 A g−1 with corresponding capacity fading over 80%, and declining further to 16 mAh g−1 at 20 A g−1 (Figures 2d and S5). Such a significant rate performance difference implies that the water intercalation in H-VO plays a vital role in remarkably improving the rate capability. The superior capacities of H-VO under a series of current densities probably benefit from the enlarged interlamellar spacing (1.13 nm), which provides abundant accessible channels and simultaneously facilitates rapid transportation of electrolyte ions through the electrode. In addition, the unique hollow-microflower structure of H-VO assembled from ultrathin nanosheets can not only effectively shorten the diffusion path lengths of Zn2+ ingress/egress but also possess the volume flexibility to buffer the volume change during cycling. Furthermore, H-VO with mixed valence states of V4+ and V5+ shows metallic characteristics, which can increase the electrical conductivity of the electrode and enable the fast electron transfer. Therefore, the excellent rate performance of the Zn/H-VO battery could not only realize high capacity but also achieve ultrafast charge/discharge processes.

The long-term cycling properties at a high current density of 5 A g−1 are further examined to reveal the superiority of H-VO as opposed to VO in Figures 2e and S6. H-VO delivers an initial desirable discharge capacity of 300 mAh g−1, with a corresponding high Coulombic efficiency over 95%. Benefiting from the water incorporation synthetic strategy, H-VO can impressively maintain a high capacity of 262 mAh g−1 even after 1000 cycles with a capacity retention of 87% under the critical high current density, and the cumulative high Coulombic efficiencies over 99% are achieved except for the first cycle. Furthermore, a marked distinction in cycle life between H-VO and VO is clearly observed, showing that the average capacity of H-VO is 292 mAh g−1 while VO only displays a 151 mAh g−2 average capacity. The significant gap is as large as 141 mAh g−1, almost comparable to the average capacity of VO. Such magnificent cycling performance should be attributed to the unique architecture of the H-VO cathode, where the expanded interlayer at plane (001) through the structural reversibility. In contrast, the rate behavior of VO under a series of current densities probably benefit from the enlarged interlamellar spacing (1.13 nm), which provides abundant accessible channels and simultaneously facilitates rapid transportation of electrolyte ions through the electrode. In addition, the unique hollow-microflower structure of H-VO assembled from ultrathin nanosheets can not only effectively shorten the diffusion path lengths of Zn2+ ingress/egress but also possess the volume flexibility to buffer the volume change during cycling. Furthermore, H-VO with mixed valence states of V4+ and V5+ shows metallic characteristics, which can increase the electrical conductivity of the electrode and enable the fast electron transfer. Therefore, the excellent rate performance of the Zn/H-VO battery could not only realize high capacity but also achieve ultrafast charge/discharge processes.

The electrochemical kinetics of the H-VO electrode are further investigated through CV measurements and the galvanostatic intermittent titration technique (GITT).30 Figure S7a presents the CV profiles of the H-VO electrode at the scan rate of 0.1 and 0.2 mV s−1. There are four pairs of redox peaks at 0.1 mV s−1, as discussed above. When the scan rate increases to 0.2 mV s−1, the CV curves show two pairs of distinct redox peaks, and the other two small redox peaks become broad due to the larger scan rate. The capacitive response can be calculated by employing the equation of \( i = \alpha f \), where both \( a \) and \( b \) are adjustable parameters. This equation can be rearranged to \( \log i = \log b + \log v + \log a \). The coefficient \( b \) value of ~0.5 represents a diffusion control process, while a \( b \) value of ~1 indicates a capacitive process. As shown in Figure S7b,
the relationships between log \(i\) and log \(v\) are plotted, and the \(b\) values of the four peaks are determined to be 0.92, 1.20, 1.06, and 0.83, which suggests that the charge storage behaviors are mainly controlled by a pseudocapacitive process. Furthermore, the ratio of capacitive contribution can be decided by the equation of \(i = k_1v + k_2v^{1/2}\) at a specific potential, where \(k_1v\) is the capacitive effect and \(k_2v^{1/2}\) represents the diffusion control process. At the scan rate of 0.1 mV s\(^{-1}\), \(\sim\)62.9% capacity is attributed to the capacitive process, which implies that the capacitive contribution is dominant. This 62.9% capacitive contribution of the H-VO electrode is comparable to the 61.4% contribution in the previously reported VS\(_2\) at the same scan rate.\(^{40}\) Moreover, the Zn\(^{2+}\) diffusion coefficient (\(D_{Zn^{2+}}\)) can be calculated based on the following equation:

\[
D_{Zn^{2+}} = \frac{4L^2}{\pi\tau} \left( \frac{\Delta E_s}{\Delta E_i} \right)^2 \tag{1}
\]

where \(L\) is the diffusion length (cm) of Zn\(^{2+}\) which is equal to the thickness of the electrode, \(\tau\) is the relaxation time (s), \(\Delta E_s\) is the steady-state potential change (V) by the current pulse during a single-step GITT experiment, and \(\Delta E_i\) represents the potential change (V) during the constant current pulse of a single-step GITT experiment after eliminating the iR drop. As displayed in Figure 3, the overall calculated diffusion coefficients of Zn\(^{2+}\) (\(D_{Zn^{2+}}\)) during the entire discharge process in the H-VO cathode are higher than the \(D_{Zn^{2+}}\) values in the VO cathode, demonstrating the faster kinetics of the as-synthesized H-VO electrode. The average \(D_{Zn^{2+}}\) values of H-VO in the discharge process are 1.3 times larger than those of VO. The higher ionic diffusivity of H-VO is ascribed to its enlarged lattice spacing (1.13 nm in (001)), which can not only provide a more effective diffusion path for Zn\(^{2+}\) migration but also effectively reduce the electrostatic interactions in the crystal structure of H-VO during the electrochemical intercalation process. It is worth noting that the Zn\(^{2+}\) diffusion coefficients of H-VO in the graph under different insertion states keep stable except for the fully intercalation state, indicating the excellent stability of its structure during the ingress of Zn\(^{2+}\). The lower \(D_{Zn^{2+}}\) value when approaching 0.2 V...
results from the increased electrostatic repulsion in the H-VO electrode upon Zn\textsuperscript{2+} insertion. The above GITT analysis result can convincingly support the superior rate capability and remarkable cycling stability of the H-VO electrode instead of VO.

The outstanding Zn\textsuperscript{2+} intercalation/deintercalation performance of the H-VO electrode is further reflected in comparison to previously reported vanadium-based cathodes for aqueous ZIBs. As presented in Table S1, our developed H-VO electrode demonstrates the highest specific capacity of 395 mAh g\textsuperscript{−1} and the superlative retained capacity of 262 mAh g\textsuperscript{−1} with an impressive capacity retention over 87\%, which outperforms these published cathode materials, showing its high potential for practical energy storage devices.

Ex situ X-ray diffraction (XRD) is performed to investigate the structural evolution and corresponding reaction mechanisms of the H-VO cathode upon selected charge and discharge states during the first two cycles. As displayed in Figure 4a–c, the reflection pattern of the H-VO electrode at the initial state can match well with the as-synthesized V\textsubscript{6}O\textsubscript{13}·nH\textsubscript{2}O, with the exclusion of the peak ascribed to the PTFE binder at 18\°. When first discharged to 0.2 V at the current density of 0.2 A g\textsuperscript{−1}, the characteristic diffraction peak located at 7.8\° representing the (001) plane with an interlayer spacing of 1.13 nm shifts to a lower angle at 6.6\° with a calculated d-spacing of 1.33 nm, and a series of new diffraction peaks appears at the 2θ angles of 13.1\°, 17.2\°, 19.6\°, and 30.6\°, indicating that a phase transition occurs. Notably, the interlamellar spacing expands from 1.13 to 1.33 nm upon in-depth discharge process, which is ascribed to the insertion of Zn\textsuperscript{2+} shielded by water molecules with reduced effective charge into the interlayer of the H-VO. Such a favorable water shielding layer provides an electrostatic shielding effect for Zn\textsuperscript{2+}, which can lower the activation energy for its ingress into the host structure, thus contributing to effectively facilitating the fast Zn\textsuperscript{2+} diffusion. Furthermore, the peak intensity of the (001) facet shows a dramatic increase, which manifests the change of crystallinity initiated by the intercalation of Zn\textsuperscript{2+} during the initial discharge process. At the following fully charged state, a slight contraction from 1.33 to 1.07 nm is observed due to the deintercalation of Zn\textsuperscript{2+}, and the new peaks initially formed during the previous first discharge process remain with slight shifts to 12.3\°, 16.9\°, 20.9\°, and 30.1\°, respectively. As shown in Figure S8, these remaining four new peaks can be well indexed to the pure phase of Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O (JCPDS no. 01-087-0417, space group: P\textsuperscript{3}m\textsuperscript{1}), revealing an irreversible phase transition from V\textsubscript{6}O\textsubscript{13}·nH\textsubscript{2}O to Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O (x > 3) during the previous discharge process, which is in accordance with the irreversible reduction peak at 1.07 V from the first cathodic CV curve. It should be noted that the V–O–V pillars support the zinc oxide layers to form the layered Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O with a porous crystal framework, which is advantageous for Zn\textsuperscript{2+} migration in its lattice. Subsequently, when discharged a second time to 0.8 V, the major peak of V\textsubscript{6}O\textsubscript{13}·nH\textsubscript{2}O attributed to the (001) plane repeatedly shifts to the same lower angle of 6.6\°, while the peak of Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O at 12.3\° slightly shifts to 13.1\° with the corresponding lattice spacing only decreased by 6\%. It is speculated that the expanded interlayer of V\textsubscript{6}O\textsubscript{13}·nH\textsubscript{2}O is ascribed to the insertion of water-shielding layer of Zn\textsuperscript{2+} with reduced effective charge as mentioned above, while the interlayer contraction of Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O is induced by the intense electrostatic interaction between bare Zn\textsuperscript{2+} and vanadium–oxygen layers, as supported by a related reported V\textsubscript{2}O\textsubscript{5}·1.63H\textsubscript{2}O cathode\textsuperscript{51} in aqueous ZIBs, respectively. Reversibly, the fully charged electrode at 1.4 V at the second cycle showed the same XRD pattern as the electrode after the first cycle, suggesting the reversible transformation between Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O and Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O (a > b > x > y) after the first cycle. As revealed by the ex situ XRD, the electrochemical reaction is different between the first discharge process and subsequent discharge process. Notably, this difference can be observed from a small, irreversible reduction peak at 1.07 V in the initial cathodic CV curve. We speculate that this irreversible reduction peak is so small that the difference in the charge–discharge profiles may not be obviously observed. In addition, the structural change of H-VO after a series of cycles at fully charged states is further investigated. As displayed in Figure S9, the major peak of V\textsubscript{6}O\textsubscript{13}·nH\textsubscript{2}O at 8.3\° negatively shifts to 6.5\°, while the major peak of Zn\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O at 12.4\° positively shifts to 13.1\° after the first cycle, indicating a specific amount of water molecules and Zn\textsuperscript{2+} from electrolyte may be trapped in the crystal structure, which accounts for the structural change and gradual capacity decay. After 200 cycles, the XRD patterns of H-VO show no obvious difference, implying the good structure preservation with high durability, consistent with its desirable long-term cycling stability.

In consequence, the schematic illustration of Zn\textsuperscript{2+} storage mechanism is shown in Figure 5. The corresponding electrochemical mechanism of the Zn/H-VO rechargeable battery is displayed as follows.

Anode:
\[ \text{Zn} \leftrightarrow \text{Zn}^{2+} + 2\text{e}^{-} \]

Cathode:
\[
\begin{aligned}
\text{VO}_3\text{H}_2\text{O} + (a + x)\text{Zn}^{2+} + 2(a + x)\text{e}^- + (m - n + 2)\text{H}_2\text{O} \\
\leftrightarrow \text{Zn}_n\text{V}_m\text{O}_{3y}\text{H}_x\text{O} + \text{Zn}_n\text{V}_m\text{O}_y(\text{OH})_z \cdot 2\text{H}_2\text{O} \\
(\text{first discharge process})
\end{aligned}
\]
\[
\begin{aligned}
\text{Zn}_n\text{V}_m\text{O}_{3y}\text{H}_x\text{O} + \text{Zn}_n\text{V}_m\text{O}_y(\text{OH})_z \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Zn}_n\text{V}_m\text{O}_{3y}\text{H}_x\text{O} \\
+ \text{Zn}_n\text{V}_m\text{O}_y(\text{OH})_z \cdot 2\text{H}_2\text{O} + (a + x - b - y)\text{Zn}^{2+} \\
+ 2(a + x - b - y)\text{e}^- \quad (\text{subsequent cycles})
\end{aligned}
\]

### 3. CONCLUSIONS

In summary, we designed and developed a novel aqueous rechargeable ZIB based on the H-VO cathode with a high potential for large-scale and cost-effective production. Owing to numerous transportation channels offered by large interlaminar spacing (1.13 nm) and short diffusion pathways benefiting from the unique hollow microflower structure, the H-VO cathode delivers a high specific capacity of 395 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), excellent rate capability with a considerable capacity of 97 mAh g\(^{-1}\) at an extremely high current density of 20 A g\(^{-1}\), and excellent cycle durability with a high capacity retention of 87% up to 1000 cycles at 5 A g\(^{-1}\). Our results demonstrate that the \(\text{VO}_3\text{H}_2\text{O}\) with greatly enhanced electrochemical performances possesses high potential for large-scale practical ZIB application and may shed light on the construction of high-performance promising cathode materials in a zinc-ion storage system.

### ASSOCIATED CONTENT

- **Supporting Information**
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b02054.

- **Synthesis method, materials characterization, electrochemical characterization, synthetic scheme, EDS spectrum of H-VO, cyclic voltammograms of VO at 0.1 mV s\(^{-1}\), CV curves comparison of H-VO and VO at 0.1 mV s\(^{-1}\), galvanostatic discharge/charge curves of H-VO and VO at 0.1 A g\(^{-1}\), discharge/charge profiles of VO at different current densities, discharge/charge curves of H-VO and VO at 5 A g\(^{-1}\), CV profiles of H-VO at various scan rates and corresponding plots of log \(i\) versus log \(v\), XRD pattern of H-VO at the fully charged state after the first cycle, XRD patterns of H-VO after various cycles at fully charged states, and comparison of our present work with previously reported vanadium-based cathodes (PDF)

- **AUTHOR INFORMATION**

  **Corresponding Author**
  *E-mail: ywang@lsu.edu.*

  **ORCID**
  Xuping Zhu: 0000-0002-2767-4211
  Ying Wang: 0000-0003-4650-9446

  **Notes**
  The authors declare no competing financial interest.

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### REFERENCES


(33) Ming, F.; Liang, H.; Lei, Y.; Kandambeth, S.; Eddaoudi, M.; Alshareef, H. Layered Mg\textsubscript{2}V\textsubscript{2}O\textsubscript{5}\textsuperscript{δ−} as Cathode Material for High-Performance Aqueous Zinc Ion Batteries. **ACS Energy Lett.** 2018, 3, 2602–2609.


