Zn/V2O5 Aqueous Hybrid-Ion Battery with High Voltage Platform and Long Cycle Life

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ABSTRACT: Aqueous zinc-ion batteries attract increasing attention due to their low cost, high safety, and potential application in stationary energy storage. However, the simultaneous realization of high cycling stability and high energy density remains a major challenge. To tackle the above-mentioned challenge, we develop a novel Zn/V2O5 rechargeable aqueous hybrid-ion battery system by using porous V2O5 as the cathode and metallic zinc as the anode. The V2O5 cathode delivers a high discharge capacity of 238 mAh g−1 at 50 mA g−1, 80% of the initial discharge capacity can be retained after 2000 cycles at a high current density of 2000 mA g−1. Meanwhile, the application of a “water-in-salt” electrolyte results in the increase of discharge platform from 0.6 to 1.0 V. This work provides an effective strategy to simultaneously enhance the energy density and cycling stability of aqueous zinc-ion-based batteries.

KEYWORDS: vanadium pentoxide, aqueous hybrid-ion battery, high voltage platform, high energy density, “water-in-salt” electrolyte

INTRODUCTION

Aqueous zinc-ion batteries (ZIBs) have attracted significant scientific and technical interests due to their high safety, colossal ionic conductivity, and high rate performance.1−10 A series of ZIB cathode materials, including manganese-based materials,14,15 Prussian blue,9,11−13 and vanadium-based materials,14,15 have been developed. Among these cathode materials, MnO2 was reported first. However, the MnO2 cathode suffers from significant capacity fading in aqueous electrolyte. The low capacity and poor cycle life limit its practical application. Recently, a series of new Mn-based nanomaterials have been reported to improve the energy density and cycling performance of ZIBs. Kang’s group assembled a battery with an α-MnO2 cathode and ZnSO4/Zn(NO3)2 aqueous electrolyte, and the α-MnO2 can deliver a high discharge capacity of 210 mAh g−1.1,3 Liu et al. adopted a MnSO4 electrolyte additive in aqueous Zn/MnO2 battery to suppress the dissolution of Mn5+ and achieved significantly improved energy density and cycling stability.7 For Prussian blue, the limited capacity (∼50 mAh g−1) and O2 evolution at a high operating voltage hinder its practical applications.

Vanadium-based materials are very attractive for aqueous ZIBs due to the advantages of abundant resources, low cost, and good safety.14−25 He et al. reported a VS2 cathode material for ZIBs. The VS2 cathode exhibited a high specific discharge capacity of 190.3 mAh g−1 and long-term cyclic stability.14 Nazar’s group reported a vanadium oxide bronze pillared by Zn2+ and crystalline water (Zn0.25V2O5·nH2O), which demonstrated a capacity retention of more than 80% after 1000 cycles.15 However, the voltage platform of the vanadium-based cathodes (VS2, Zn0.25V2O5·nH2O, LiV3O8...) for ZIBs is not high enough, resulting in less competitive advantages in energy density.

Recently, it has been demonstrated that “water-in-salt” electrolyte is able to retard the hydrogen and oxygen evolution at a high electrochemical window in aqueous electrolyte (∼3.0 V).26−31 Xu et al. first constructed a full aqueous Li-ion battery with LiMn2O4 cathode, MoS2 anode, and 21 m lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) as the electrolyte; such an aqueous battery demonstrated an open-circuit voltage of 2.3 V.26 Since then, a series of “water-in-salt” electrolytes have been reported for aqueous ion batteries, enabling relatively high voltage and energy density.27−31 Chen et al. assembled a Zn/LiMn2O4Fe2O4 aqueous hybrid-ion battery based on a “water-in-salt” electrolyte, which obtained a high energy density of 183 Wh kg−1 and a high operating voltage exceeding 1.8 V.32 Given that the use of “water-in-salt” electrolyte can enhance the energy density of aqueous metal ion

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batteries, the extension of “water-in-salt” electrolyte in aqueous Zn/vanadium-based material batteries may give rise to a higher energy density as well. Herein, we designed a novel Zn/V2O5 aqueous hybrid-ion battery (Figure 1 a) with “water-in-salt” electrolyte (21 m LiTFSI and 1 m Zn(CF3SO3)2). The employment of this strategy can lead to great improvements in both voltage platform and cycling stability. The porous V2O5 cathode exhibits a high discharge capacity (238 mAh g−1 at 50 mA g−1), superior rate capability (156 mAh g−1 at 1000 mA g−1), and long-term cyclability (80% capacity retention after 2000 cycles at 2000 mA g−1) based on the “water-in-salt” electrolyte. Our study highlights that the employment of “water-in-salt” electrolyte is an effective way to boost the energy density and cyclability of aqueous zinc ion-based batteries.

■ RESULTS AND DISCUSSION

The porous V2O5 microplates are synthesized via a simple organics-assisted strategy. The X-ray diffraction (XRD) pattern of the porous V2O5 prepared at 350 °C clearly displays a high degree of crystallization. All the diffraction peaks of the prepared sample can be assigned to orthorhombic V2O5 (JCPDS 41-1426) (Figure 1b).16 Field-emission scanning electron microscopic (FESEM) images show that the V2O5 exhibits a quasi-hexagonal microplate morphology with plenty of mesopores (Figures 1c and S1a–d). The highly porous
V2O5 exhibits a high speciation feature of V2O5 can be further confirmed by transmission electron microscopy (TEM) as shown in Figure 1d. The lattice spacing of 0.577 nm matches well with the interplanar distance of the (200) plane (Figure 1e). To investigate the valence states of V and O in the V2O5, the X-ray photoelectron (XPS) spectrum of the V2O5 is shown in Figure 1f. For the V 2p spectrum, the binding energies for V 2p1/2 and V 2p3/2 are located at 524.7 and 517.0 eV, respectively, matching well with those of V2O5.33,34 For the O 1s spectrum, the binding energy measured by nitrogen sorption (Figure S2).

The cyclic voltammogram (CV) curves collected in different electrolytes at 0.1 mV s−1 are shown in Figure 2a and Figure S3. In Zn(CF3SO3)2 (Figure 2a), three reduction peaks (0.52, 0.93, and 0.98 V) and four oxidation peaks (0.71, 0.95, 1.22, and 1.43 V) can be observed in the second CV curve, which are caused by the zinc ion intercalation/deintercalation during the charge/discharge processes. In LiTFSI (Figure S3), three pairs of cathodic/anodic peaks can be observed at 0.56/0.90 V, 0.95/1.08 V, and 1.17/1.22 V, which are associated with Li+ insertion/extraction in the V2O5. In Zn(CF3SO3)2−LiTFSI, two pairs of redox peaks appear at 0.90/1.08 V and 1.12/1.25 V, which is similar to the result obtained in LiTFSI to some extent. This suggests that the lithium ions may actually be involved in the electrochemical processes of Zn/V2O5 batteries with hybrid Zn(CF3SO3)2−LiTFSI electrolyte.

When 1 m Zn(CF3SO3)2 is used as the electrolyte, the Zn/V2O5 battery shows unstable charge/discharge plateau and cycling performance (Figure S4a). In sharp contrast, quite stable working plateaus and cyclability can be achieved when Zn(CF3SO3)2−LiTFSI “water-in-salt” electrolyte is used (Figure S4b). The Zn/V2O5 battery with Zn(CF3SO3)2−LiTFSI electrolyte shows two pairs of charge (1.06 and 1.23 V) and discharge (0.90 and 1.10 V) plateaus, which are much higher than those with Zn(CF3SO3)2 electrolyte (Figure 2b). In addition, the overpotential of the Zn/V2O5 battery with Zn(CF3SO3)2−LiTFSI is lower than that with Zn(CF3SO3)2. This is because the Li+ intercalation/deintercalation in Zn(CF3SO3)2−LiTFSI is more feasible than the Zn2+ insertion/extraction in Zn(CF3SO3)2. The working voltage is also increased when a low-concentration LiTFSI electrolyte (1 m) was used. However, it is not stable during the charge/discharge processes and the capacity fades quickly (Figure S5).

The porous V2O5 delivers an initial discharge capacity of 215 mAh g−1 at 100 mA g−1 in Zn(CF3SO3)2−LiTFSI with a high Coulombic efficiency (CE) of 97% (Figure S6), indicating a highly reversible ion insertion/extraction process (Figure 2c). After 160 cycles, 95% (204 mAh g−1) of the highest capacity can be maintained, demonstrating the excellent cycling stability. In 1 m Zn(CF3SO3)2, the V2O5 delivers an initial discharge capacity of 201 mAh g−1. The capacity increases to 292 mAh g−1 at the first fifth, after which the capacity decreases continuously to 73 mAh g−1 after 90 cycles. When cycled in 21 m LiTFSI, the V2O5 exhibits an initial discharge capacity of 178 mAh g−1 (Figure S7). However, the capacity fades quickly with cycling, and only 58% of the initial capacity is retained after 50 cycles. A possible reason for the poor cyclability of V2O5 in 21 m LiTFSI is the lack of Zn ions, making the electrodeposition of Zn on anode during the charge process difficult. The cycling performance of the battery in Zn(CF3SO3)2−LiTFSI electrolyte with both lithium and zinc ions outperforms that in either Zn(CF3SO3)2 or LiTFSI electrolyte, implying a synergistic effect may exist in the Zn/V2O5 battery with Zn(CF3SO3)2−LiTFSI.

At a high current density of 500 mA g−1, 85% of the initial discharge capacity of the V2O5 in Zn(CF3SO3)2−LiTFSI can be retained after 240 cycles (Figure 2d), while for V2O5 in Zn(CF3SO3)2, only 58% of the initial capacity was retained. The CE also differs significantly. With Zn(CF3SO3)2−LiTFSI electrolyte, the CE stabilizes in the range of 99−101%, and with
Zn(CF$_3$SO$_3$)$_2$, the CE fluctuates between 97% and 115% (Figure S6). The porous V$_2$O$_5$ in Zn(CF$_3$SO$_3$)$_2$−LiTFSI (Figure 3a, b) also exhibits better rate capability than that in Zn(CF$_3$SO$_3$)$_2$ (Figure S8). In Zn(CF$_3$SO$_3$)$_2$−LiTFSI, the porous V$_2$O$_5$ delivers high capacities of 242, 217, 192, 171, and 156 mAh g$^{-1}$ at 50, 100, 200, 500, and 1000 mA g$^{-1}$, respectively (Figure 3b). When the current density returns to 50 mA g$^{-1}$, about 88% of the initial discharge capacity can be regained. After 50 cycles, a discharge capacity of 213.4 mAh g$^{-1}$ can be retained, which is much higher than the capacity of V$_2$O$_5$ in Zn(CF$_3$SO$_3$)$_2$ (79 mAh g$^{-1}$, Figure S8). Electrochemical impedance spectroscopy (EIS) characterization was also carried out. The formation of thicker and more protective solid electrolyte interphase (SEI) layer in LiTFSI−Zn(CF$_3$SO$_3$)$_2$ leads to lower electrical conductivity and ion diffusion than that in Zn(CF$_3$SO$_3$)$_2$ (Figure S9). The excellent cycling stability at high rate is the most appealing property of the Zn/V$_2$O$_5$ aqueous hybrid-ion battery. At a high current density of 2000 mA g$^{-1}$, 80% of the initial capacity can be retained after 2000 cycles (Figure 3c). From the above results, it is safe to conclude that the employment of Zn(CF$_3$SO$_3$)$_2$−LiTFSI “water-in-salt” electrolyte greatly improves the cycling stability and energy density of the Zn/V$_2$O$_5$ batteries. To the best of our knowledge, the Zn/V$_2$O$_5$ shows one of the most promising electrochemical performances in terms of combined high rate capability and long-term cycling stability. Most importantly, when compared to the recently reported vanadium-based ZIB cathode materials, the porous V$_2$O$_5$ manifests one of the highest capacities with moderately high voltage platforms (Figure 3d), demonstrating the great potential for energy storage applications.

To monitor the structural change of porous V$_2$O$_5$ in different electrolytes during the charge/discharge processes, ex-situ XRD experiments were carried out. The V$_2$O$_5$ in Zn(CF$_3$SO$_3$)$_2$−LiTFSI behaves quite differently from that in Zn(CF$_3$SO$_3$)$_2$. In hybrid Zn(CF$_3$SO$_3$)$_2$−LiTFSI electrolyte, the (001) diffraction peak, which is originally located at 20.2°, shifts toward lower angles at the initial discharge process and then shifts back to its original position in the subsequent charge process, indicating...
the highly reversible expansion/extraction of the corresponding lattice distance (Figure 4a, 4b). In Zn(CF3SO3)2, the (001) diffraction located at ~20.2° and (110) diffraction located at ~26.2° shift toward higher angles during the discharge process (Figure 4c). Both peaks shift toward lower angles slightly during the subsequent charge process; however, neither of them can recover to their initial positions. In addition, a new peak appears at 18.2° during the initial discharge, and it does not disappear upon charge. The ex-situ XRD results demonstrate that the V2O5 in Zn(CF3SO3)2 suffers from serious irreversible structural change during charge/discharge processes.

To investigate whether the Zn ions can insert into or extract from the V2O5 reversibly in Zn(CF3SO3)2-LiTFSI, ex-situ XPS and TEM characterizations were carried out (Figure 4d–f). No signal of Zn can be detected in the XPS spectrum of V2O5 (Figure 4d). When discharged to 0.2 V, the Zn ions can be successfully intercalated into V2O5 as demonstrated by the obvious Zn 2p 3/2 spin-orbit doublet. However, not all the Zn ions can be deintercalated after recharging to 1.6 V. It is speculated that the trapped Zn ions may act as the interlayer pillars and stabilize the layered structure of V2O5 during the charge/discharge processes, which is similar to the effects of preintercalated metal ions (Li+, Na+, K+, Zn2+, ...) in V2O5.15,38

The HRTEM images display a slight lattice spacing change of the (200) plane during the charge/discharge processes (Figure 4e, 4f). When discharged to 0.2 V, the (200) lattice spacing increases by 2.43% compared to that of the original state, confirming the intercalation reaction mechanism and agreeing well with the ex-situ XRD results.

To provide further insight into the structural change of the porous V2O5 in Zn(CF3SO3)2-LiTFSI during charging and discharging, in-situ XRD was performed as well (Figure 5). The 2θ range is recorded from 15 to 38°, a range which can well reflect the structural changes of the V2O5. As observed in the in-situ XRD study, the (200) diffraction shifts leftwards and rightwards during discharge and charge, respectively. In addition, the (301) and (011) diffraction peaks merge into one peak during discharge, and the new peak splits into two peaks during charge. These changes are completely reversible during cycling, suggesting the highly reversible electrochemical reactions. Interestingly, the in-situ XRD results show great similarity to those of Li/V2O5 batteries in nonaqueous electrolyte (LiPF6/EC/DEC = 1:1:1 vol/vol/vol),39 implying the insertion and extraction of Li ions in V2O5 play a significant role in the Zn/V2O5 battery with Zn(CF3SO3)2-LiTFSI electrolyte. Considering both the Zn ions and Li ions involved in the electrochemical processes of the Zn/V2O5 battery, we term it hybrid-ion batteries rather than ZIBs.

**CONCLUSION**

In conclusion, we develop a novel Zn/V2O5 rechargeable aqueous hybrid-ion battery. The application of Zn(CF3SO3)2-LiTFSI “water-in-salt” electrolyte enables the Zn/V2O5 battery with high discharge platform and outstanding cycling performance. In/ex-situ characterizations demonstrate that both the Zn ions and Li ions are involved in the electrochemical processes. This work highlights that the hybrid “water-in-salt” electrolyte is a promising strategy to enhance the energy density and long-term cycling stability of zinc-ion-based aqueous batteries.