Supporting Information

A Deep-Cycle Aqueous Zinc-Ion Battery Containing an Oxygen-Deficient Vanadium Oxide Cathode

Meng Liao, Jiawei Wang, Lei Ye, Hao Sun, Yunzhou Wen, Chuang Wang, Xuemei Sun, Bingjie Wang,* and Huisheng Peng*

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1. Synthesis of $p$-VO, $O_d$-VO, and porous current collectors

*Preparation of rGO/carbon cloth porous current collector:* Graphene oxide (GO) solution was synthesized via a modified Hummer’s method. The rGO/carbon cloth porous current collector was prepared on a 1×1 cm$^2$ carbon cloth (WOS 1009, CeTech) by electrodeposition at room temperature using a CHI760 electrochemical workstation. The electrodeposition was carried out in an aqueous electrolyte containing 0.03 mg/mL GO and 0.1 mol/L EDTA·2Na. Carbon rod and Hg/HgO electrode were used as the counter and reference electrodes, respectively. A potential of −1.2 V vs. Hg/HgO electrode was applied for 120 s. After electrodeposition, the sample was washed with deionized water and freeze dried in vacuum overnight. In this work, the mass loading of rGO was ~0.2 mg·cm$^{-2}$ in the cathode. The weight ratio of rGO was ~9% based on rGO/$O_d$-VO or rGO/$p$-VO composite. Note that the synthetic route of $O_d$-VO, including the MnO$_2$ deposition process and heat treatment in reducing gas for oxygen vacancy introduction, had little effect on the properties of rGO/CC composite (details in Figure S14). The porous current collector was used to afford large specific area for loading active materials and enable the accelerated transport of electrons and ions.

*Fabrication of the nano-textileLiked $V_6O_{13}$ cathode ($p$-VO):* $p$-VO electrode was prepared by a two-step procedure. At Step 1, the precursor, $\alpha$-MnO$_2$, was synthesized onto the porous current collector through an electrodeposition method. The electrodeposition was performed in a three-electrode mode. Typically, MnO$_2$ was electrodeposited onto the porous current collector in an electrolyte containing 0.1 mol·L$^{-1}$ Mn(Ac)$_2$ and 0.1 mol·L$^{-1}$ Na$_2$SO$_4$ using pulse electrodeposition mode (1.5 V for 1 s and 0.7 V for 10 s) with a Pt counter electrode and an Ag/AgCl reference electrode. The formation of the MnO$_2$ nano-crystallites was produced by the following
reaction, i.e., \( \text{Mn}^{2+} + 2 \text{H}_2 \text{O} \rightarrow \text{MnO}_2 + 4 \text{H}^+ + 2e^- \), using the pulse electrodeposition method in a dilute Mn\(^{2+}\) (0.1 mol/L) electrolyte solution. At Step 2, the nano-textile-liked \( \text{V}_6\text{O}_{13} \) was synthesized through a self-assembly process.\(^1\) \( \text{MnO}_2 \) (serving as both oxidant and template) anchored at porous current collector (rGO/CC substrate) was soaked in a \( \text{VOSO}_4 \) solution (0.1 mol·L\(^{-1}\), working both as reducer and vanadium source) overnight at room temperature. The obtained sample was thoroughly washed with deionized water to remove the remnant impurities (including \( \text{Mn}^{2+} \) and \( \text{MnO}_2 \)) and then dried in air. A layer of \( \text{V}_6\text{O}_{13} \) was formed on the surface of rGO/carbon cloth porous current collectors. The formation of the nano-textile-liked \( \text{V}_6\text{O}_{13} \) was driven by the different redox potentials of \( \text{MnO}_2/\text{Mn}^{2+} \) and \( \text{VO}^{2+}/\text{VO}_2^+ \).

**Synthesis of the oxygen deficient \( \text{V}_6\text{O}_{13} \) cathode (\( \text{O}_{\text{d}}\)-VO):** \( \text{O}_{\text{d}}\)-VO electrode was produced by annealing \( p\)-VO at 250 °C for 3 h with H\(_2\)/N\(_2\) mixed gas flow (volume ratio: 3/1). The flow rate is 200 sccm, and the heating rate is 2 °C per min. The mass loading of \( \text{O}_{\text{d}}\)-VO was measured to be \( \sim 2 \text{ mg·cm}^{-2} \) by an electronic macro-balance (BT25S, 0.0001 mg). The amounts of oxygen defects in \( \text{O}_{\text{d}}\)-VO could be controlled by tuning the temperature of synthesis. In this work, the heating temperature of 250 °C was utilized, and the according calculated amount of oxygen defects in the sample was \( \sim 37\% \) based on the fitting areas of two peaks in O 1s XPS spectra.

**Synthesis of the flexible Zn anode for the construction of flexible Zn/\( \text{O}_{\text{d}}\)-VO batteries:** A flexible Zn anode was prepared by a facile electrodeposition approach on the carbon cloth (WOS 1009, CeTech) as a flexible matrix. A typical two-electrode setup was used for Zn electroplating, in which the carbon cloth was used as a working electrode, whereas a zinc plate (purity >99.99%, Sigma) was used as both counter and reference electrode. Aqueous solution containing 1 mol·L\(^{-1}\) ZnSO\(_4\) (AR grade, Sigma) and 1 mol·L\(^{-1}\) KCl (AR grade, Sigma) was used as electrodeposition electrolyte. Electroplating was performed at -0.8 V versus Zn foil for 1000–2000 s using an electrochemical workstation (CHI 760). The Zn-coated carbon cloth was then washed
with deionized water for several times and dried at room temperature in vacuum for 6 h before use.

2. Electrochemical measurement

The electrochemical performances of the samples were carried out via stainless-steel coin cells (CR 2032). The free-standing $O_d$-VO ($\sim 1 \text{ cm}^2$) was directly used as cathode. Polished zinc foil and glass fiber membrane were used as the anode and separator, respectively. For control experiments, $p$-VO samples were annealed in $N_2$ at 250 °C for 3 h to avoid the effect of thermal treatment before battery fabrication. 3 M zinc trifluoromethanesulfonate ($\text{Zn(TFSI)}_2$) aqueous solution was used as the electrolyte. Flexible Zn/$O_d$-VO batteries were assembled by separating the $O_d$-VO cathode and the flexible Zn anode with 3 M Zn(TFSI)$_2$ gelation electrolyte, and then packing with commercial aluminum plastic films. Galvanostatic charge/discharge data were recorded on an Arbin electrochemical station (MSTATS-5V/10 mA/16Ch). The current density and specific capacity were based on the mass of synthesized $O_d$-VO or $p$-VO in each electrode. Electrochemical impedance spectroscopy (EIS) test was performed on a CHI 660D electrochemical workstation with an AC voltage of 5 mV amplitude at the frequency range of 100 kHz to 10 mHz. Full cell reaction of $p$-VO/$O_d$-VO was listed below: $V_6O_{13} + xZn^{2+} \leftrightarrow Zn_xV_6O_{13}$ (the theoretical capacity is 413 mAh·g$^{-1}$ when $x=4$).

3. CV study

Figure S16 displayed the CV curves of the Zn/$O_d$-VO batteries at increasing scan rates ranged from 0.1 to 1.0 mV·s$^{-1}$ with a voltage window from 0.2 to 1.5 V. There were two pairs of redox peaks in the CV curves. The obtained peak currents ($i$) and scan rates ($v$) were assumed to follow the equation as below$^{2}$

$$i = av^b,$$

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which could also be represented as

\[ \log(i) = b \log(v) + \log(a), \]

where \( b \) represented the slope of \( \log(i) \) versus \( \log(v) \) curve. If \( b \) value was calculated to be 0.5, the electrochemical process was controlled by ion diffusion. And when \( b \) value was calculated to be 1, the electrochemical process was dominated by the pseudocapacitance. By fitting the plots of \( \log(i) \) versus \( \log(v) \), the \( b \) values of Peaks 1, 2, 3, and 4 in this work were calculated to be 0.753, 0.735, 0.677 and 0.680, respectively, suggesting that the charge/discharge processes of the Zn/\( O_d \)-VO cell were synchronously controlled by ionic diffusion and pseudocapacitance. The above results were responsible for the high rate capabilities of the obtained Zn/\( O_d \)-VO cells. In addition, the capacitive contribution could be further determined by the equation as below:

\[ i = k_1 v + k_2 v^{1/2}, \]

which could also be represented as

\[ \frac{i}{v^{1/2}} = k_1 v^{1/2} + k_2, \]

where \( i \), \( k_1v \), and \( k_2v^{1/2} \) represented the current response, capacitive, and ionic diffusion contribution, respectively. The \( k_1 \) value could be obtained by fitting the \( i/v^{1/2} \) versus \( v^{1/2} \) plots, the capacitive contribution in Zn/\( O_d \)-VO was calculated to be 48.2% at 0.1 mV·s\(^{-1}\). Upon the increasing scan rates, the percentages of capacitive contribution accordingly increased to 59.1%, 66.9%, 72.7% and 77.6% at scan rates of 0.2, 0.5, 0.8 and 1.0 mV·s\(^{-1}\), respectively, indicating that the Zn/\( O_d \)-VO cells showed facilitated charge transfer kinetics.

4. Galvanostatic intermittent titration study

The thermodynamic voltage-composition relationship that reflected the equilibrium phase diagram in Zn/\( O_d \)-VO system was determined by the galvanostatic intermittent titration technique (GITT). The \( Zn^{2+} \) diffusion coefficients (\( D_{Zn^{2+}} \)) in \( O_d \)-VO were fitted from the obtained GITT data. In the GITT method the transient voltage generated
due to the application of current pulse was monitored as a function of time.\(^3\) The solid diffusion coefficient was calculated according to the equation below:

\[
D = \frac{4L^2}{\pi \tau} \left(\frac{\Delta E_S}{\Delta E_t}\right)^2,
\]

where \(t\), \(\tau\), and \(\Delta E_S\) represented the duration of the current pulse (s), the relaxation time (s), and the steady-state potential change (V) by the current pulse, respectively. \(\Delta E_t\) was the potential change (V) during the constant current pulse after eliminating the IR drop. \(L\) was the according ion diffusion length (cm). For compact electrode in this case, it could be equal to the thickness of electrode.

5. Computational method and model

All calculations were carried out by using the projector augmented wave method in the framework of the density functional theory (DFT),\(^4\) as implemented in the Vienna \textit{ab-initio} Simulation Package (VASP). The generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) exchange functional were used here. The plane-wave energy cutoff was set to 500 eV, and the Monkhorst–Pack method with \(2\times4\times1\) was employed for the Brillouin zone sampling of the unit cell of \(V_6O_{13}\) monolayer.\(^5\) The convergence criterions of energy and force calculations were set to \(10^{-5}\) eV per atom and 0.01 eV·Å\(^{-1}\), respectively. To explore the interactions between Zn and \(V_6O_{13}\) monolayer, the adsorption energies of Zn on the \(1\times2\times1\) supercell of the perfect and O vacancy \(V_6O_{13}\) monolayer were calculated. Here, the adsorption energies (\(E_a\)) were calculated by the energy difference of the system after and before adsorption:\(^6\) \(E_a = E(Zn-V_6O_{13}) - E(Zn) - E(V_6O_{13})\), where \(E(Zn-V_6O_{13})\), \(E(Zn)\) and \(E(V_6O_{13})\) represented the DFT energies of the Zn adsorbed perfect or O vacancy \(V_6O_{13}\) monolayer, the energy of an isolated Zn atom and the energy of perfect or O vacancy \(V_6O_{13}\) monolayer, respectively.

6. X-ray photonelectron spectroscopy (XPS) analysis
XPS analysis was used to probe the electrochemical reaction of Zn/O\textsubscript{d}-VO batteries. Figure S22a displayed the Zn 2p XPS spectra of the pristine, fully discharged and fully charged O\textsubscript{d}-VO electrodes. No detectable signal from Zn was observed at the pristine state. In the fully discharged state, the electrode displayed two Zn 2p\textsubscript{3/2} components located at 1023.4 and 1021.9 eV, which could be ascribed to two kinds of intercalated Zn\textsuperscript{2+} in O\textsubscript{d}-VO via different insertion as discussed in the main text (Figure 5).\textsuperscript{7} Upon charging, the O\textsubscript{d}-VO showed only one Zn 2p\textsubscript{3/2} component, which could be attributed to the remaining surface absorption in the sample. The O 1s XPS region in the pristine electrode could be deconvoluted into two peaks (Figure S22b) as discussed in Figure 2. Upon discharge, two newly emerged broad peaks appeared at binding energies of 529.9 and 532.5 eV. Figure S22c demonstrated the evolution of the V 2p signal during battery operation. The V\textsuperscript{5+} component (2p\textsubscript{3/2}: 517.3 eV) accompanied by the V\textsuperscript{4+} signal (2p\textsubscript{3/2}: 516.2 eV) was observed at the pristine state.\textsuperscript{8} At the fully discharged state, the signal of V\textsuperscript{4+} intensified strongly, and the component of V\textsuperscript{3+} clearly appeared as a result of Zn\textsuperscript{2+} ion insertion. When the electrode was charged to 1.5 V, the pristine V 2p spectrum appeared again.

7. Characterization

The morphologies of O\textsubscript{d}-VO, p-VO and Zn foil electrodes were characterized by scanning electron microscopy (SEM, Zeiss FE-SEM Ultra 55 operated at 3 kV), transmission electron microscopy (TEM, JEOL JEM-2100F operated at 200 kV), Raman spectroscopy (Dilor LabRam-1B, He-Ne laser of 4 mW, excitation wavelength of 532 nm), X-ray diffraction (Bruker AXSD8), and X-ray photoelectron spectroscopy (PHI5000C & PHI5300, Mg, 250 W, 14 kV). The electrochemical performances were obtained from an Arbin electrochemical station (MSTATS-5V/10 mA/16Ch) and CHI 760D electrochemical workstation. Photographs were taken by a camera (SONY A6000, Japan).
Figure S1. Schematic illustration to the synthetic procedure of oxygen-deficient V₆O₁₃ cathode (Oₓ-VO).
**Figure S2.** EDS elemental mappings and element compositions of the as-prepared, freestanding $O_{d^r}$-VO cathode.
**Figure S3.** The bright-field TEM image showing the uniform loading of as-synthesized $O_d$-VO on rGO layer.
Figure S4. (a) and (b). The dark-field TEM image and selected area electron diffraction pattern of p-VO, respectively.
Figure S5. O K-edge XANES spectra of $O_{\delta}$-VO.
Figure S6. Raman spectra of $O_d$-VO and $p$-VO.
Figure S7. XRD patterns of $O_\delta$-VO and $p$-VO.
Figure S8. CV curves for the first three cycles of the as-prepared $O_{r=}$ VO.
Figure S9. The typical charge/discharge curves of $O_d$-VO at current density of 50 mA·g$^{-1}$. 

![Graph showing typical charge/discharge curves of $O_d$-VO](image)
Figure S10. Comparison of the Ragone plot of the Zn/$O_x$-VO and Zn/p-VO batteries.
Figure S11. a, Galvanostatic discharge and charge profiles of $O_{x}$-VO cathode at a current density of 500 mA g$^{-1}$. b, Cycling performance of $O_{x}$-VO in terms of specific capacity (red) and the corresponding Coulombic efficiency (blue) at current density of 500 mA g$^{-1}$. 
Figure S12. **a**, Galvanostatic discharge and charge profiles of $O_d$-VO cathode at a current density of 2 A·g$^{-1}$. **b**, Cycling performance of $O_d$-VO in terms of specific capacity (red) and the corresponding Coulombic efficiency (blue) at current density of 2 A·g$^{-1}$. 
Figure S13. Surface morphology of cycled \( O_f \)-VO electrode.
Figure S14. a, Raman spectra of G1 (as-prepared rGO), G2 (setting G1 at the potential of 1.5 V for 20 min, the same as the applied potential in electrochemical deposition of MnO₂) and G3 (setting G2 by heat treatment at 250 °C with reducing gas of H₂/N₂ for 3 h). The relative intensities of the D and G bands (D/G) from G1-G3 were 1.24, 1.23 and 1.26, respectively. b, Galvanostatic charge-discharge curves of G1-G3 at increasing current densities from 0.2 to 1.0 A·g⁻¹. The contribution of capacity (<1.5 mAh·g⁻¹) from the introduction of current collector (G1-G3) was ignorable compared with that of Od-VO (~400 mAh·g⁻¹ at 0.2 A·g⁻¹). c, Comparison on capacity retention of Od-VO and p-VO without the introduction of rGO at 0.2 A·g⁻¹. d, Rate capability of Od-VO and p-VO without the introduction of rGO at increasing current densities from 0.2 to 2.0 A·g⁻¹.
Figure S15. a, Charge distribution of perfect V$_6$O$_{13}$ (p-VO). b-d, Charge distribution of different types of oxygen-deficient V$_6$O$_{13}$ (O$_d$-VO).
Figure S16. (a) and (b) The calculated charge differences for $p$-VO and $O_d$-VO, respectively. The light yellow and blue represent electron dissipation and accumulation, respectively. (c) and (d) The charge transfers along z-direction for Zn/$p$-VO and Zn/$O_d$-VO surfaces, respectively.
Figure S17. CV curves of $O_{2}$-VO at increasing scan rates from 0.1 to 1.0 mV s$^{-1}$. 
**Figure S18.** CV curves displaying the capacitive contribution (deep blue region) to the total current at 1 mV·s⁻¹ of Oₓ-VO.
Figure S19. Schematic illustration to selected steps of the GITT curve during discharging.
**Figure S20.** a, Galvanostatic charge/discharge profiles of $p$-VO and $O_d$-VO at 200 mA·g$^{-1}$. b, Nyquist plots at open circuit potential (OCP), 0.91 V (the first discharging plateau labelled in a) and 0.57 V (the second discharging plateau) vs. Zn of $p$-VO and $O_d$-VO.
Figure S21. Mott-Schottky plots of $O_d$-VO and $p$-VO samples. The carrier density was inversely proportional to the absolute value of the slope.\textsuperscript{9}
Figure S22. XPS spectra of Zn 2p, O 1s and V 2p regions at the pristine, 1st discharged (0.2 V), and 1st charged (1.5 V) states in O_{δ}-VO cathodes.
**Figure S23.** (a) and (b) EDS elemental distributions of the fully charged and the fully discharged O$_{x}$-VO electrodes, respectively.
**Figure S24.** (a) and (b) Surface morphology of as-fabricated flexible Zn anodes at low and high magnifications, respectively.
Figure S25. (a) and (b) Galvanostatic cycling profiles and hysteresis evolution in symmetric cells composed of flexible Zn/Zn at 2 and 4 mAh·cm⁻², respectively.
Table S1. The calculated adsorption energies for Zn$^{2+}$ on the surface of perfect V$_6$O$_{13}$ and oxygen-deficient V$_6$O$_{13}$.

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<th>Location</th>
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<td>Perfect</td>
<td>-2.868</td>
<td>-2.872</td>
<td>-2.877</td>
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<tr>
<td>Defect</td>
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<td>-0.026</td>
<td>-0.034</td>
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Table S2. Comparison of utilization and cycle life of vanadium-based cathode materials for AZIBs with mild aqueous electrolyte.

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<th>Capacity (mAh·g$^{-1}$)</th>
<th>Utilization</th>
<th>Cycle life (mA·g$^{-1}$)</th>
<th>Current density (mA·g$^{-1}$)</th>
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<td>V$_2$O$_5$</td>
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<td>36%</td>
<td>160</td>
<td>100</td>
<td>21 M LiTFSI + 1 M Zn(CH$_3$F$_3$SO$_3$)$_2$</td>
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<td>11</td>
<td>Na$_{0.33}$V$_2$O$_5$</td>
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<td>200</td>
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<td>100</td>
<td>100</td>
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<td>Oxygen-deficient V$<em>6$O$</em>{13}$</td>
<td>398</td>
<td>95%</td>
<td>200</td>
<td>200</td>
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<td>337</td>
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References