Supporting Information

Stabilization of VOPO₄·2H₂O voltage and capacity retention in aqueous zinc batteries with a hydrogen bond regulator

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Experimental Procedures

VOPO$_4$·2H$_2$O was synthesized by a reflux process. Typically, 0.8 g of V$_2$O$_5$, 4.4 mL of H$_3$PO$_4$ (85%) and 30 mL of H$_2$O were refluxed for 8 h. The precipitation was filtered, washed with ethanol and deionized water for several times and dried at 60 °C in a vacuum oven.

Characterizations

X-ray diffraction (XRD) data was collected on a PANalytical Empyrean diffractometer with Cu-Kα radiation. Morphologies were characterized by a scanning electron microscope equipped with an energy dispersive X-ray spectroscopy (EDS) detector (SU8010, HITACHI, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an XPS spectrometer with Al-Kα radiation (8.34 Å) as the excitation source (ESCALAB 250Xi, Thermo Scientific Escalab, USA). The Fourier transform infrared (FT-IR) spectra were collected on Lambda 650S (UK PerkinElmer). Raman spectra were obtained on a LabRAM HR Evolution series high-resolution Raman spectrometer (Nano Wizard Ultra Speed & inVia Raman, Germany) with a laser wavelength of 633 nm.

Electrochemical Measurements

VOPO$_4$·2H$_2$O and Ketjen Black were mixed with a weight ratio of 2:1 in water and drop casted on carbon paper substrates. Galvanostatic charge-discharge was carried out in coin cells with VOPO$_4$·2H$_2$O and Zn foil as the cathode and anode, respectively. Electrochemical impedance spectroscopy (EIS) was recorded in three-electrode cells with Zn as the counter and reference electrodes. Electrochemical studies were performed on the Bio-logic VMP3 or Land CT-2001A battery cyclers.
Figure S1. a) XRD pattern and b) SEM image of VOPO₄·2H₂O.

Figure S2. a) Zn plating/stripping behavior in the symmetric cell at current density of 1 mA cm⁻² and capacity of 1 mA h cm⁻². b) XRD of Zn electrode after 20 cycles.

Figure S3. Differential capacity curves of VOPO₄·2H₂O in 4 m Zn(OTf)₂/5.5 m Glu electrolyte at various current densities.
Figure S4. a) Charge-discharge and b) differential capacity curves of VOPO$_4$·2H$_2$O in 4 m Zn(OTf)$_2$ electrolyte at various current densities.

Figure S5. Charge-discharge curves of VOPO$_4$·2H$_2$O at different cycles in 4 m Zn(OTf)$_2$/5.5 m Glu at a) 0.74 C and b) 7.4 C.
Figure S6. Characterizations of the VOPO₄·2H₂O cathode at different states of the 30th cycle in the 4 m Zn(OTf)₂/5.5 m Glu electrolyte: a) XRD, SEM images of the b) charged and c) discharged electrodes, d) EDS Zn/V ratios.

Figure S7. V 2p₃/₂ XPS of VOPO₄·2H₂O cathode at different states of the 30th cycle in the 4 m Zn(OTf)₂/5.5 m Glu electrolyte.
Figure S8. Differential scanning calorimetry (DSC) curve of the 4 m Zn(OTf)$_2$/5.5 m Glu solution.

Figure S9. Nyquist plots and the fitted curves of the VOPO$_4$·2H$_2$O electrode in the 4 m Zn(OTf)$_2$/5.5 m Glu electrolyte at different temperatures.

Table S1. The $R_{ct}$ values from the fittings of Nyquist plots.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>-20</th>
<th>-15</th>
<th>-10</th>
<th>5</th>
<th>0</th>
<th>5</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{ct}$ (Ω)</td>
<td>4620</td>
<td>3477</td>
<td>2012</td>
<td>1427</td>
<td>945</td>
<td>786</td>
<td>321</td>
</tr>
</tbody>
</table>
Figure S10. CV curves of VOPO₄·2H₂O in the 4 m Zn(OTf)₂/5.5 m Glu electrolyte at different scan rates under -20 °C.