Electronic Supplementary Information (ESI)

Carbothermal Reduction-Induced Oxygen Vacancy in Spinel Cathode for High-Performance Aqueous Zinc-Ion Battery

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**Scheme S1.** Schematic illustration of the synthesis of O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}.
**Fig. S1** High-resolution XPS Zn 2p (a), O 1s (b), and C 1s (c) profiles of O\textsubscript{2}-ZnV\textsubscript{2}O\textsubscript{4}-200.
Fig. S2 Thermogravimetric (TG) analyses illustrating the decomposition of precursors (Zn(CH$_3$COO)$_2$·2H$_2$O + NH$_4$VO$_3$) in the absence (a) and presence (b, c) varying amounts of sucrose and the formation of (a) O$_V$-ZnV$_2$O$_4$-0, (b) O$_V$-ZnV$_2$O$_4$-100, and (c) O$_V$-ZnV$_2$O$_4$-200.

TG analyses were performed with the mixture of the precursors (Zn(CH$_3$COO)$_2$·2H$_2$O + NH$_4$VO$_3$) in the presence of varying amounts of sucrose (0, 100, and 200 mg). Multi-step weight loss was observed in all cases. In the absence of sucrose, three distinct weight losses were observed (Fig. S2a). The second and third weight losses (200-350°C) overlap when sucrose is present. The initial weight loss in step I (<130°C) is attributed to the loss of H$_2$O from Zn(CH$_3$COO)$_2$·2H$_2$O (Fig. S2a, b and c). Step II (>130°C) corresponds to the loss of NH$_3$ and structural H$_2$O due to the decomposition of NH$_4$VO$_3$.\textsuperscript{1,2} The third weight loss can be attributed to the evolution of CO$_2$/O$_2$ and the final stable weight plateau observed above 450°C corresponds to the formation of carbon-supported ZnV$_2$O$_4$ as the final product. In the presence of sucrose, the well-defined plateau was not observed at the final stage possibly due to the presence of sucrose-derived carbon. The weight loss above 350°C in the presence of sucrose is associated with further loss of O$_2$. The quantitative analysis of the weight loss at various steps confirms that the final product has carbon and O$_V$-ZnV$_2$O$_4$. The % carbon content in the presence of sucrose is quantified to be 19.6% and 34.7% for the sample mixture analyzed in the presence of 100 and 200 mg of sucrose, respectively.
Fig. S3 EPR spectral profile of O$_V$-ZnV$_2$O$_4$-0, O$_V$-ZnV$_2$O$_4$-100, and O$_V$-ZnV$_2$O$_4$-200 at room temperature.
Fig. S4 (a) High-resolution XPS V 2p profile of \( \text{OV-ZnV}_2\text{O}_4-0 \), \( \text{OV-ZnV}_2\text{O}_4-100 \), and \( \text{OV-ZnV}_2\text{O}_4-200 \). (b) The bar diagram depicts the % of different oxidation states of V.
Fig. S5 High-resolution XPS O 1s profile of $O_{V}$-$ZnV_{2}O_{4}$-0 (a), $O_{V}$-$ZnV_{2}O_{4}$-100 (b), and (c) $O_{V}$-$ZnV_{2}O_{4}$-200.
Fig. S6 FESEM images of O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-0 (a), O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-100 (b), and (c) O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-200.
Fig. S7 HADDF image of O$_{V}$-ZnV$_{2}$O$_{4}$-200 and the corresponding STEM elemental mapping image illustrating the distribution of carbon.
**Fig. S8** (a) Galvanostatic charge-discharge profiles obtained for Zn||O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-200 ZIB at 100 mA g\textsuperscript{-1} and (b) Comparison of first charge profile at the current density of 100 and 500 mA g\textsuperscript{-1}.

As shown in the figures, the potential-induced transformation of the cathode began at ~1.32 V at the low current density of 100 mA g\textsuperscript{-1} in contrast to 1.52 V at 500 mA g\textsuperscript{-1} (Fig. 3b). The conversion/ transformation took a longer time at the lower current density. The cathode delivers a maximum capacity of 374.5 mAh g\textsuperscript{-1} (at 500 mA g\textsuperscript{-1}) after 10 charge-discharge cycles at a current density of 500 mA g\textsuperscript{-1}, whereas a maximum capacity of 600.1 mAh g\textsuperscript{-1} (100 mA g\textsuperscript{-1}) after 3 charge-discharge cycles at 100 mA g\textsuperscript{-1} was achieved. It is worth pointing out here that the specific capacity at a particular current density after activation remains the same irrespective of the current density (low or high) at which the cathode is activated.
Fig. S9 (a) Galvanostatic charge-discharge profile of Zn||Ov-ZnV$_2$O$_4$-200 ZIB at different current densities. Plot illustrating the cycling stability of Ov-ZnV$_2$O$_4$-200 at the current densities of (b) 100 mA g$^{-1}$ and (c) 2000 mA g$^{-1}$.
**Fig. S10** Galvanostatic charge-discharge profile (a) and plot illustrating the cycling stability of $\text{O}_x\text{V}_2\text{O}_4$-0, $\text{O}_x\text{V}_2\text{O}_4$-100, and $\text{O}_x\text{V}_2\text{O}_4$-200 at 500 mA g$^{-1}$ (b). (c) Nyquist plots at open circuit voltage and a table summarizing the charge transfer resistance.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$R_{ct}$ (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_x\text{V}_2\text{O}_4$-0</td>
<td>260.8</td>
</tr>
<tr>
<td>$\text{O}_x\text{V}_2\text{O}_4$-100</td>
<td>214.3</td>
</tr>
<tr>
<td>$\text{O}_x\text{V}_2\text{O}_4$-200</td>
<td>180.1</td>
</tr>
</tbody>
</table>
Note S1: Analysis of Galvanostatic Intermittent Titration Technique (GITT) study

\[ D = \frac{4}{\pi \tau} \left( \frac{n_m V_m}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2 \]  

(1)\textsuperscript{3,4}

D is the diffusion coefficient, \( n_m \) and \( V_m \) are the number of moles of the active material and the molar volume, respectively, and S is the contact area between the electrode and electrolyte. \( \tau \) is the time duration of the pulse. \( \Delta E_s \) and \( \Delta E_t \) are the quasi-equilibrium and battery voltage changes, respectively.

**Fig. S11** GITT profile of a single step during the discharge of Zn||O\textsubscript{2}-ZnV\textsubscript{2}O\textsubscript{4}-200.
**Fig. S12** Plots illustrating the diffusion coefficient vs ion insertion state for O$_{\text{V}}$-ZnV$_2$O$_4$-0 (a), and O$_{\text{V}}$-ZnV$_2$O$_4$-100 (b).
**Fig. S13** Nyquist plot at OCV (1.1 V) and after different cycles in charge state at 1.8 V (Ov-ZnV$_2$O$_4$-200 cathode). Table summarizing the charge transfer resistance. The equivalent circuit is shown in the inset: $R_s$: solution resistance, $R_{ct}$: charge transfer resistance, CPE: constant phase element, and W: Warburg impedance.

<table>
<thead>
<tr>
<th>State</th>
<th>$R_{ct}$ (ohm)</th>
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</thead>
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<tr>
<td>OCV</td>
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<tr>
<td>1$^{st}$ charge to 1.8 V</td>
<td>94.2</td>
</tr>
<tr>
<td>2$^{nd}$ charge to 1.8 V</td>
<td>14.1</td>
</tr>
<tr>
<td>10$^{th}$ charge to 1.8 V</td>
<td>12.4</td>
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<tr>
<td>30$^{th}$ charge to 1.8 V</td>
<td>12.1</td>
</tr>
</tbody>
</table>
Fig. S14 Nyquist plot at OCV (1.1 V) and after different cycles in discharge state at 0.2 V (O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-200 cathode). Table summarising the charge transfer resistance.

<table>
<thead>
<tr>
<th>State</th>
<th>( R_{ct} ) (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV</td>
<td>180.1</td>
</tr>
<tr>
<td>1\textsuperscript{st} discharge to 0.2 V</td>
<td>192.1</td>
</tr>
<tr>
<td>2\textsuperscript{nd} discharge to 0.2 V</td>
<td>196.2</td>
</tr>
<tr>
<td>10\textsuperscript{th} discharge to 0.2 V</td>
<td>229.5</td>
</tr>
<tr>
<td>30\textsuperscript{th} discharge to 0.2 V</td>
<td>205.8</td>
</tr>
</tbody>
</table>
Fig. S15 The calculated partial density of states (PDOS) of O$_3$ZnV$_2$O$_4$. 
**Fig. S16** Zn$^{2+}$ ion interaction with (a) pristine ZnV$_2$O$_4$, and (b) O$_V$-ZnV$_2$O$_4$, and the calculated values of interaction energy. [Color code: grey sphere for Zn, red (big) sphere for V, and red (small) sphere for O].

![Diagram of ZnV$_2$O$_4$ and O$_V$-ZnV$_2$O$_4$ with calculated interaction energies.](image)
Note S2. Limitations of our calculation:

Our current level of theory (PBE-GGA) has limitations in accurately describing the electronic structure of systems containing transition metals, lanthanides, and actinides. To address these limitations, we recommend using advanced approaches incorporating U+V corrections. Standard DFT, particularly with local or semi-local exchange-correlation functionals like LDA or GGA, often fails to accurately describe systems with strong electron-electron correlations, such as transition metal oxides, lanthanides, and actinides. U+V corrections help account for these strong correlations by introducing on-site (U) and inter-site (V) Coulomb interactions. The Hubbard U term corrects the self-interaction error in DFT, better describing the localized d or f electrons in transition metals and rare earth elements. It effectively increases the energy gap and corrects the electronic structure by accounting for electron-electron repulsion within the same atomic site. The inter-site V term extends the correction to include interactions between electrons on different sites, crucial for materials where electron correlation effects involve neighboring atoms or ions.

By including U+V corrections, DFT can more accurately predict electronic properties such as band gaps, magnetic moments, and charge transfer insulators, often underestimated by standard DFT methods.
**Fig. S17** Cyclic voltammograms of O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-0, O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-100, and O\textsubscript{V}-ZnV\textsubscript{2}O\textsubscript{4}-200.
**Note S3: Determining the capacitive and diffusion-controlled contributions:**

The voltammogram was quantitatively analysed to understand the \( \text{Zn}^{2+} \) storage kinetics according to the eqn (1):\(^5\)

\[
i = a v^b
\]

where, ‘a’ and ‘b’ are the adjustable parameters and the value of b ranges from 0.5 to 1.0. The b-value is obtained from log\((i)\)-log \((v)\) plots and the value of ‘b’ for the four peaks A, B, C and D are calculated to be 0.63, 0.69, 0.71 and 0.67, respectively, suggesting a diffusion-dominated process. The capacitive contribution is further calculated according to the following eqn (2)

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

where, \(i\) refers to current (mA), the \(k_1\) and \(k_2\) are two potential dependent constant and \(v\) the scan rate mV \(s^{-1}\). The \(k_1\) and \(k_2\) were calculated by plotting \(i\) vs. \(v^{1/2}\) and \(k_1v\) and \(k_2v^{1/2}\) correspond to the contribution from the capacitive and diffusion control process, respectively.
**Fig. S18** Cyclic voltammograms at different scan rates (a), plot illustrating $b$-value and log($i$)-log($v$) plot (b), cyclic voltammogram illustrating the capacitive contribution at the scan rate of 1 mV s$^{-1}$ (c), and plot illustrating the capacitive and diffusion-controlled contribution at various scan rate (d).
**Fig. S19** Capacitive and diffusion-controlled current contribution at 1 mV s$^{-1}$ of O$_V$-ZnV$_2$O$_4$-0, O$_V$-ZnV$_2$O$_4$-100, and O$_V$-ZnV$_2$O$_4$-200.
Fig. S20 (a) High-resolution ex-situ XPS V 2p profile of Oₓ-ZnVₓO₄·200 at different charge and discharge states. (b) The bar chart represents the % of different oxidation states of V at different states of charge-discharge.
Fig. S21 (a) Cyclic voltammograms (first three cycles) of Zn||Ov-ZnV$_2$O$_4$-200 at 3 mV s$^{-1}$, and (b) galvanostatic charge-discharge profiles at 500 mA g$^{-1}$. Electrolyte: Zn (CF$_3$SO$_3$)$_2$ in dry acetonitrile.
Fig. S22 FESEM (a, d), TEM (b, e), and HRTEM (c, f) images of O\textsubscript{y}-Zn\textsubscript{x}V\textsubscript{2}O\textsubscript{4-200} cathode when charged to 1.8 V (a-c) and discharged to 0.2 V (d-g). STEM elemental mapping (Zn, V, O, C, S, and F) of the cathode at the discharge state (0.2 V). The inverse FFT image is shown in the inset of (f).
**Fig. S23** High-resolution XPS C1s profile of $\text{O}_7\text{Zn}_5\text{O}_{14}$ cathode at pristine, fully charged, and discharged states.
Fig. S24 Schematic illustration of the charge-storage with O$_V$-ZnV$_2$O$_4$-200.
Fig. S25 Digital photograph of OCV of a single coin cell and ZIB-powered LCD panel of digital hygrometer.
Table S1. ZIB performance of low valent vanadium-based spinel cathode.

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Cathode Material</th>
<th>Electrolyte</th>
<th>Reaction mechanism</th>
<th>Voltage (V) vs. Zn²⁺/Zn</th>
<th>Specific capacity</th>
<th>Energy density</th>
<th>Power density</th>
<th>Capacity retention / cycles/ current density</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Electroactivation-induced spinel ( \text{ZnV}_2\text{O}_4 )</td>
<td>2M ( \text{Zn(ClO}_4)₂</td>
<td>0.2–1.4</td>
<td>312 mAh g⁻¹ at 0.5 C</td>
<td>84% / 1000 / 10 C</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( \text{ZnO/ZnV}_2\text{O}_4 ) composite hollow microspheres</td>
<td>3M ( \text{Zn(CF}_3\text{SO}_3)₂</td>
<td>0.2–1.8</td>
<td>338 mAh g⁻¹ at 100 mA g⁻¹</td>
<td>79% / 2000 / 4000 mA g⁻¹</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Porous structure ( \text{ZnV}_2\text{O}_4/C-N composite} )</td>
<td>2M ( \text{ZnSO}_4 )</td>
<td>0.5–1.8</td>
<td>301 mAh g⁻¹ at 300 mA g⁻¹</td>
<td>/ 1000 / 200 mA g⁻¹</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Act–( \text{ZnV}_2\text{O}_4 )</td>
<td>3M ( \text{ZnSO}_4 )</td>
<td>Insertion/extrahtaion of ( \text{Zn}^{2+} )</td>
<td>0.4–1.6</td>
<td>242 mAh g⁻¹ at 500 mA g⁻¹</td>
<td>83% / 2000 / 4000 mA g⁻¹</td>
<td>9</td>
<td></td>
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</tr>
<tr>
<td>5</td>
<td>Urchin-like ( \text{MgV}_2\text{O}_4 )</td>
<td>2M ( \text{Zn(CF}_3\text{SO}_3)₂ ( \text{N}_2)₂</td>
<td>Insertion/extrahtaion of ( \text{Zn}^{2+} )</td>
<td>0.2–1.4</td>
<td>272 mAh g⁻¹ at 200 mA g⁻¹</td>
<td>171.5 / 140.6</td>
<td>10</td>
<td></td>
<td></td>
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<tr>
<td>6</td>
<td>Sea-urchin-like oxygen-deficient ( \text{ZnV}_2\text{O}_4 )</td>
<td>3M ( \text{Zn(CF}_3\text{SO}_3)₂</td>
<td>Co-insertion/extrahtaion of ( \text{Zn}^{2+} ) and ( \text{H}^+ )</td>
<td>0.2–1.8</td>
<td>599.6mA h g⁻¹ at 100 mA g⁻¹</td>
<td>371.8 / 62.1</td>
<td>57.5%/2300/4000 this work</td>
<td></td>
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</tr>
</tbody>
</table>
References:


