

Supporting Information

High-capacity zinc-ion storage in an open-tunnel oxide for aqueous and nonaqueous Zn-ion batteries

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Synthesis of Microporous $\text{Mo}_{2.5+y}\text{VO}_{9+z}$

$\text{Mo}_{2.5+y}\text{VO}_{9+z}$ was prepared by a hydrothermal synthesis as previously reported.¹ Vanadyl sulfate $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$ (1.37 g, 5.18 mmol) and ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (3.68 g, 3.03 mmol) were dissolved in 50 mL of H_2O . The solutions were mixed in a 125-mL Teflon-lined Parr stainless steel autoclave for 10 min and then purged with nitrogen for 3 min before heating at 190 °C for 2 days. A gray solid was obtained from the reaction, washed with water, and dried overnight at 100 °C. The solid was then stirred in 0.4 M oxalic acid solution for 30 min at 60 °C (2 g solid in 50 mL of the acid solution) to remove an amorphous byproduct, followed by washing with water and drying at 100 °C overnight. The solid was heated at 400 °C for 2 h in air to remove water and NH_4^+ ions from the channels of the structure.

Microwave-assisted Chemical Insertion

The microwave-assisted chemical insertion of Zn ions was performed in air. Appropriate equivalents of zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), 12 mL of diethylene glycol (DEG), and 0.15 g of the host material $\text{Mo}_{2.5+y}\text{VO}_{9+z}$ were stirred in a 30-mL borosilicate reaction vessel for 20 min. The reaction vessel was placed in an Anton Parr Monowave 300 microwave reactor, and heated as fast as possible with a maximum power of 850 W to a set temperature (in less than 3 min). The reaction time was varied between 10 and 30 min, with stirring at 1000 rpm to keep the solid particles suspended uniformly. After the reaction, the mixture was washed several times by centrifugation with acetone and water to remove unreacted species and DEG. The metal-inserted product was dried in air at 100 °C.

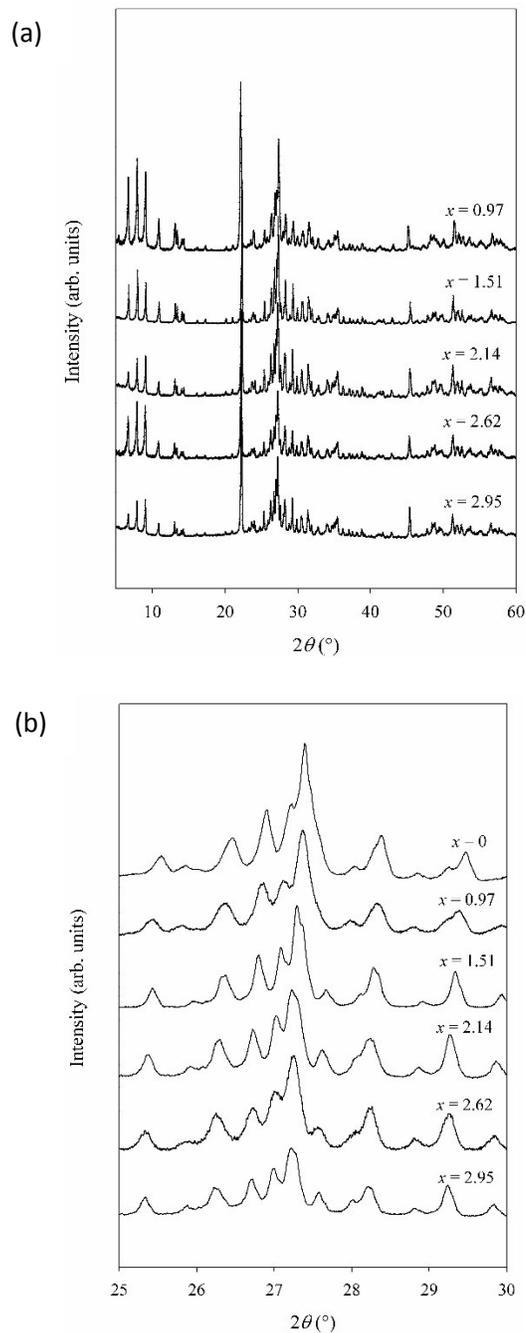


Fig. S1 Powder X-ray diffraction patterns of the Zn-inserted products $\text{Zn}_x\text{Mo}_{2.5+y}\text{VO}_{9+z}$: (a) 2θ range = 5 – 60, (b) 2θ range = 25 – 30, showing a shift in the peak positions as a function of Zn content (x).

Materials Characterization

Powder X-ray diffraction (XRD) data were collected on a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.54046 \text{ \AA}$, 40 kV, 44 mA). Synchrotron powder X-ray diffraction (SXRD) was performed at beamline 11-BM, Advanced Photon Source (APS), Argonne National Laboratory (ANL) through a mail-in program. The samples were packed into Kapton capillaries. The data collection was performed at $2\theta = 0.5 - 50^\circ$ with a 2θ step size of 0.001° using a monochromatic X-ray ($\lambda = 0.41417 \text{ \AA}$). The diffraction data were refined with the general structure analysis system (GSAS) with the graphical user interface (EXPGUI).² Scanning electron microscopy (SEM) was performed on a FEI Quanta 650. High-resolution transmission electron microscopy (HR-TEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDS) were performed with a JEOL 2010F TEM/STEM. Elemental Analysis was carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Varian 715-ES ICP-OES spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra DLD XPS system equipped with an Al K α source. Survey scans were collected from 0 to 1200 eV binding energy (pass energy 80 eV), followed by high-resolution scans of the C 1s, Mo 3d, V 2p, and Zn 2p regions (pass energy 20 eV) at 0.1 eV resolution. All spectra were charge-corrected relative to the C 1s component at 284.7 eV binding energy, and analyzed using CasaXPS software.

Electrochemical Measurements

The $Zn_xMo_{2.5+y}VO_{9+z}$ electrodes were prepared by mixing the active material (75 wt. %), super P conductive carbon (15 wt. %), and polyvinylidene fluoride (PVdF, 10 wt. %) in N-methyl-2-pyrrolidinone (NMP) solvent. For non-aqueous cells, the slurries were coated onto carbon discs. The electrodes were dried overnight at 120 °C under vacuum. Coin cells were assembled by using zinc foil as anode, glass fiber membrane as separator, and 0.2 M zinc triflate ($Zn(CF_3SO_3)_2$) in propylene carbonate (PC)/dimethylsulfoxide (DMSO) (1 : 4) as electrolyte.³⁻⁶ For aqueous cells, the slurries were coated onto carbon strips. A sealed glass cell having zinc metal as both counter and reference electrodes was flooded with an aqueous 0.5 M $Zn(CH_3COO)_2$ electrolyte.⁷⁻⁹ The electrochemical testing was carried out galvanostatically with an Arbin cycler at various current densities. Cyclic voltammetry (CV) was performed with a multi-potentiostat VMP3 Bio-Logic system.

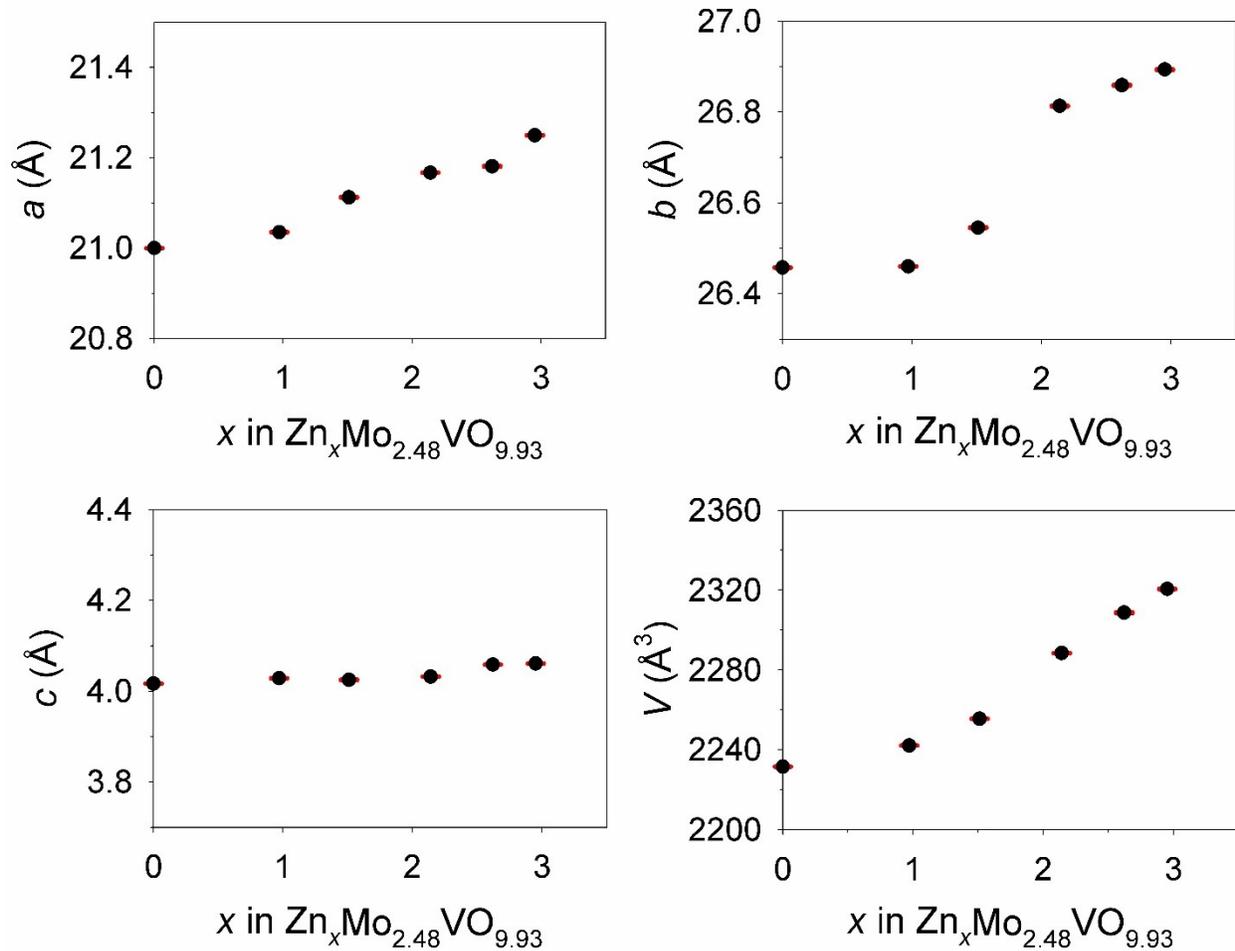
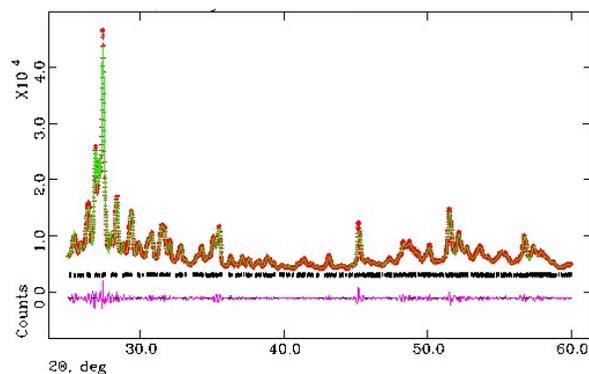
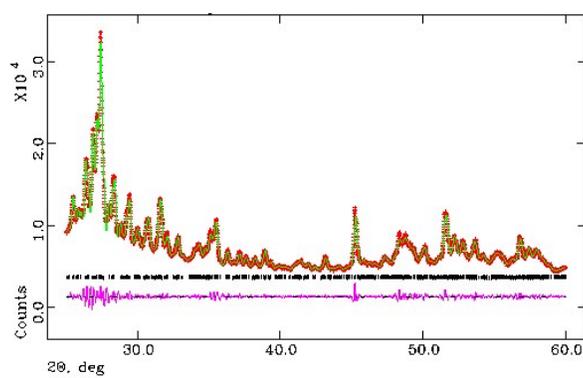


Fig. S2 Unit cell parameters of $\text{Zn}_x\text{Mo}_{2.5+y}\text{VO}_{9+z}$ ($0 \leq x \leq 3$) from Le Bail refinements (error bars in red).

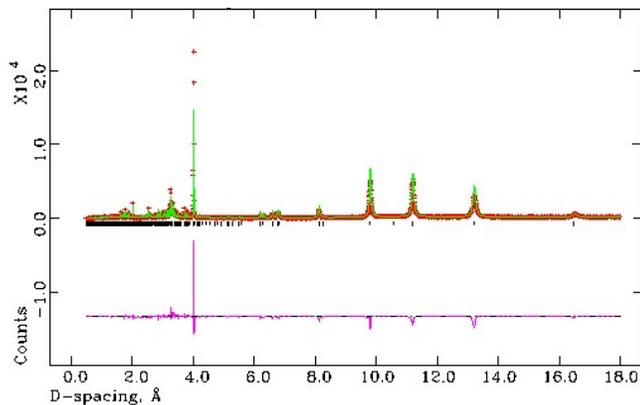


(a)

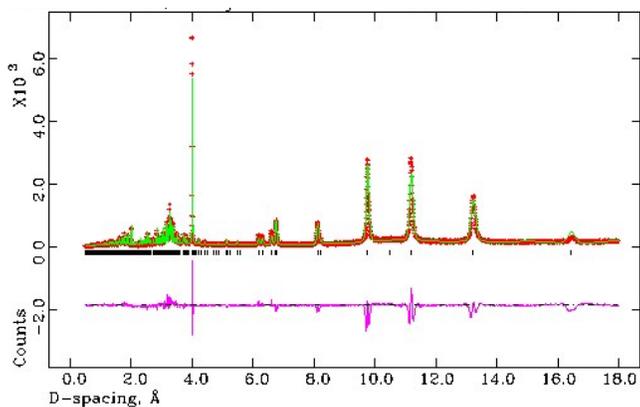


(b)

Fig. S3 Le Bail PXRD refinements of (a) pristine $\text{Zn}_x\text{Mo}_{2.5+y}\text{VO}_{9+z}$ ($x = 0$, orthorhombic space group ($Pba2$), $a = 21.0505(3)$ Å, $b = 26.3766(5)$ Å, $c = 4.0144(1)$ Å, $wR_p = 2.87\%$) and (b) Zn-inserted $\text{Zn}_x\text{Mo}_{2.48}\text{VO}_{9.93}$ ($x = 2$), prepared by the microwave-assisted chemical insertion: $Pba2$, $a = 21.1668(1)$ Å, $b = 26.8135(1)$ Å, $c = 4.0321(2)$ Å, $wR_p = 2.70\%$ (measured: orange; calculated: green; difference: pink; Bragg reflections: vertical tick marks).



(a)



(b)

Fig. S4 Refinements of the SXR D data of (a) pristine $Zn_xMo_{2.5+y}VO_{9+z}$ ($x = 0$, orthorhombic space group $Pba2$), $a = 21.0401(3)$ Å, $b = 26.4012(2)$ Å, $c = 4.0128(1)$ Å, $\chi^2 = 5.97$, $wRp = 13.57\%$) and (b) Zn-inserted $Zn_xMo_{2.48}VO_{9.93}$ ($x = 1$), prepared by the microwave-assisted chemical insertion: $Pba2$, $a = 21.0322(3)$ Å, $b = 26.4525(1)$ Å, $c = 4.0381(2)$ Å, $\chi^2 = 3.341$, $wRp = 14.29\%$, (measured: orange; calculated: green; difference: pink; Bragg reflections: vertical tick marks).

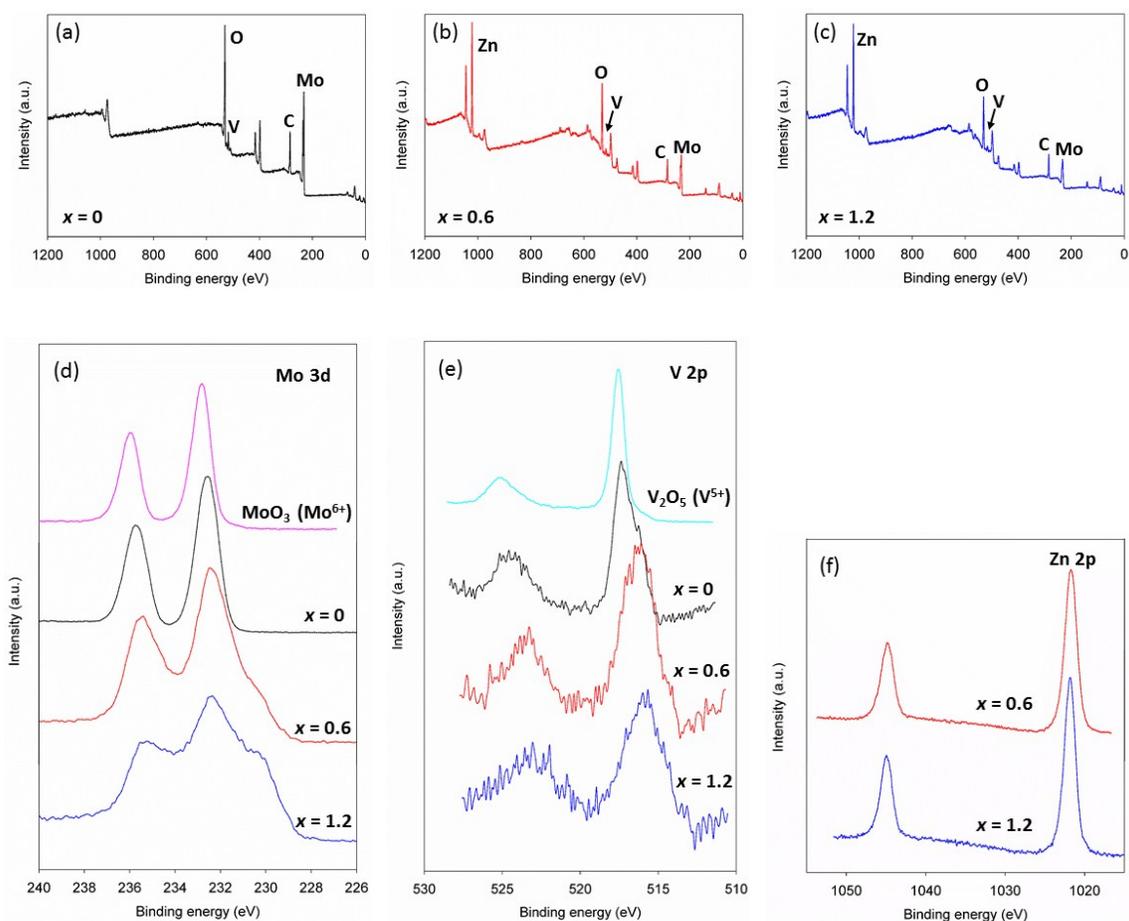


Fig. S5 X-ray photoelectron spectroscopy (XPS) data of $\text{Zn}_x\text{Mo}_{2.5+y}\text{VO}_{9+z}$: (a, b, c) low-resolution surveys of $x = 0, 0.6,$ and 1.2 . (d, e, f) high-resolution core level spectra for Mo 3d, V 2p, and Zn 2p regions of $\text{Zn}_x\text{Mo}_{2.5+y}\text{VO}_{9+z}$ (with MoO_3 and V_2O_5 as reference compounds), respectively. All of the survey spectra reveal characteristic peaks of Mo, V, C, and O. Zn characteristic peaks are only present in the spectra of Zn-inserted compounds ($x = 0.6$ and 1.2). Compared to MoO_3 (Mo^{6+} observed at 232.6 eV), the high-resolution Mo 3d spectra of the pristine compound ($x = 0$) and Zn-inserted compounds ($x = 0.6$ and 1.2) show a significant shift towards a lower binding energy corresponding to Mo ions being reduced. Likewise, the high-resolution V 2p spectra of the Zn-inserted products ($x = 0.6$ and 1.2) are significantly downshifted with respect to V_2O_5 (V^{5+} observed at 517.5 eV) suggesting the reduction of V ions. Two characteristic peaks of Zn $2p_{1/2}$ and

Zn $2p_{3/2}$ were observed at 1021.7 and 1044.8 eV in both the $x = 0.6$ and 1.2 samples, indicating the presence of Zn^{2+} in the Zn-inserted compounds. Based on the V 2p and Mo 3d spectra (Mo^{6+} : 232.6 eV; Mo^{5+} : 232.0 eV; Mo^{4+} : 230.0 eV; V^{5+} : 517.5 eV; V^{4+} : 516.2 eV; V^{3+} : 515.0 eV), the reduction of Mo and V ions coincides with the appearance of Zn 2p signal confirming the Zn-insertion process.^{10–14}

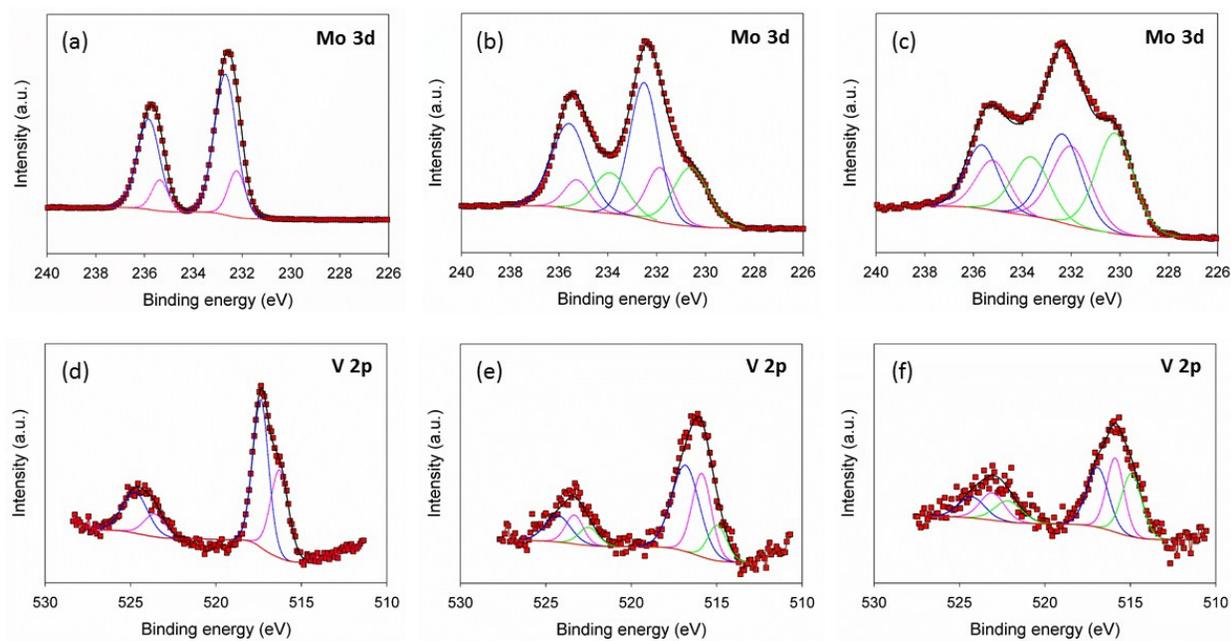


Fig. S6 Deconvolution of the $Zn_x Mo_{2.5+y} VO_{9+z}$ XPS spectra: (a, b, c) Mo $3d_{5/2}$ and $3d_{3/2}$ peaks of $x = 0, 0.6,$ and $1.2,$ respectively (blue: Mo^{6+} ; pink: Mo^{5+} ; green: Mo^{4+}). (d, e, f) V $2p_{3/2}$ and $2p_{1/2}$ peaks of $x = 0, 0.6,$ and $1.2,$ respectively (blue: V^{5+} ; pink: V^{4+} ; green: V^{3+}).

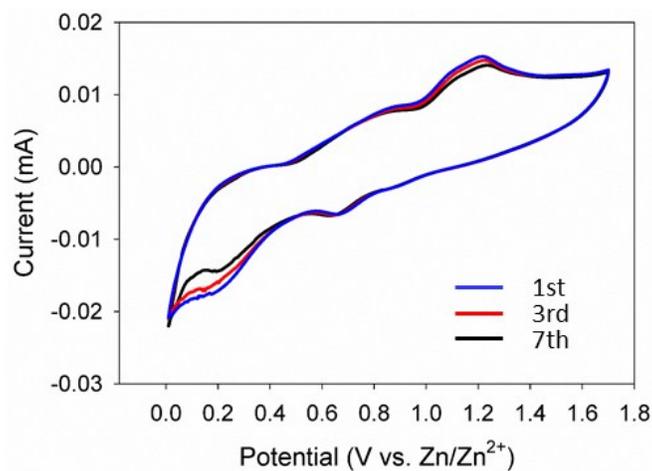


Fig. S7 CV curves of the Zn/Zn₂Mo_{2.5+y}VO_{9+z} cell in 0.2 M Zn(CF₃SO₃)₂ in propylene carbonate (PC)/dimethylsulfoxide (DMSO) (1 : 4) electrolyte at a scanning rate of 0.1 mV s⁻¹ within the potential range of 0.01 – 1.7 V at room temperature.

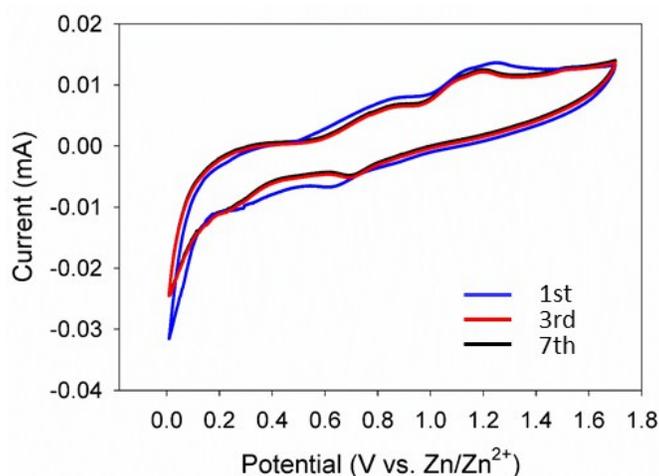


Fig. S8 CV curves of a 3-electrode Zn₂Mo_{2.5+y}VO_{9+z} aqueous cell with 0.5 M Zn(CH₃COO)₂ electrolyte at a scanning rate of 0.1 mV s⁻¹ within the potential range of 0.01 – 1.7 V at room temperature.

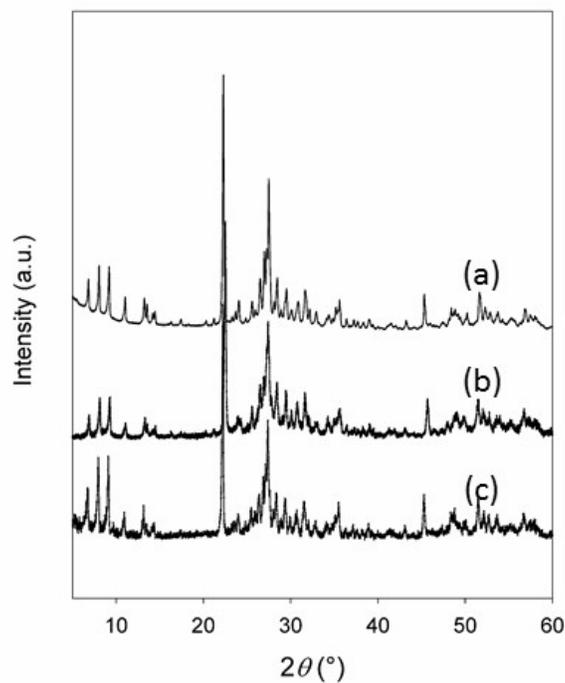


Fig. S9 Comparison of the X-ray diffraction patterns of (a) $\text{Zn}_2\text{Mo}_{2.5+y}\text{VO}_{9+z}$ and the electrode mixtures recovered from (b) a non-aqueous cell and (c) an aqueous cell after 35 cycles.

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