

Electronic Supplementary Information

A Co-intercalation Enhanced V-based Cathode Material for Fast Charge Aqueous Zinc Ion Battery

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Experimental Section

Synthesis of $\text{HNaV}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$

$\text{HNaV}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$ (HSVO) was prepared via a simple one-step hydrothermal method. In brief, 0.5523g NaVO_3 (Aladdin, 99.8%) was dissolved in 60 ml deionized water at 80 °C. After, pH of the solution was adjusted to 2.0-3.0 by HCl (3M). Then, the solution was transferred to 100 mL autoclave and kept at 180 °C for 48 h. The product was collected and washed with distilled water and ethanol thoroughly for 3 times, respectively. The light green fiber was obtained after dried at 60°C for 8 h in air.

Synthesis of $\text{NaV}_6\text{O}_{15}$

$\text{NaV}_6\text{O}_{15}$ (SVO) was obtained by heating the $\text{HNaV}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$ at 500 °C in the air for 3 hours.

Material characterizations

The XRD patterns of the products were detected by Bruker D8 ADVANCE X-ray Diffractometer (XRD) with Cu-K_α radiation (Maximum voltage = 50 kV, Maximum current = 60 mA). The morphologies of the composite were observed by scanning electron microscopy (SEM, SU8010, Hitachi, Japan). TEM and HRTEM (JEM-2100F(URP), JEOL, Japan) were performed to learn the overall morphologies and internal structure. The elements distribution in the sample was scanned by energy dispersive spectrum (EDS). X-ray photoelectron spectroscopy (XPS, Esca lab 250Xi, Thermo Fisher, Britain) was used to analysis the combination status of elements.

Electrochemical characterizations

The HSVO electrode was prepared by mixing HSVO (70wt.%), conductive carbon additives (Super-P, 20 wt.%), and polyvinylidene fluoride (PVDF, 10 wt.%), then the mixed slurry was cast onto Ti foil and dried in a vacuum oven at 80°C for 8 h. Zinc foil and glass fiber membrane (Whatman, GF/D) were used as the anode and separator, respectively, and Zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$, 2 mol in 1L water, Aladdin, AR, 98.0%) solution was used as the electrolyte. A CR2032-type coin cell was assembled in the air atmosphere to evaluate the electrochemical performance on a LAND battery testing system (CT3001A). Cyclic voltammograms (CV) were test on a CHI600E electrochemical workstation. All of the tests were performed at room temperature ($25\pm 2^\circ\text{C}$).

calculation formula of theoretical specific capacity is as follows:

$$C_x = \frac{\frac{1g}{M_x} \cdot N_A \cdot E_x \cdot e}{3600s}$$

C_x : Theoretical specific capacity, $\text{mAh}\cdot\text{g}^{-1}$

M_x : Relative molecular mass

E_x : Number of electrons gain and loss per molecule

N_A : Avogadro constant (6.02×10^{23})

e : Elementary charge ($1.60\times 10^{-19}\text{C}$)

When the theoretical specific capacity was calculated by $\text{HNaV}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$, the M_x as 658 and E_x as 12, the values was $488.78 \text{mAh}\cdot\text{g}^{-1}$.

Supplementary Figures

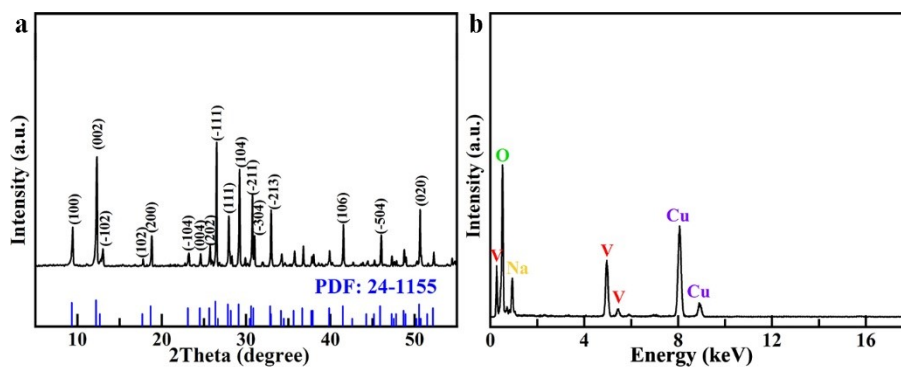


Fig. S1 (a) XRD, (b) EDS of SVO

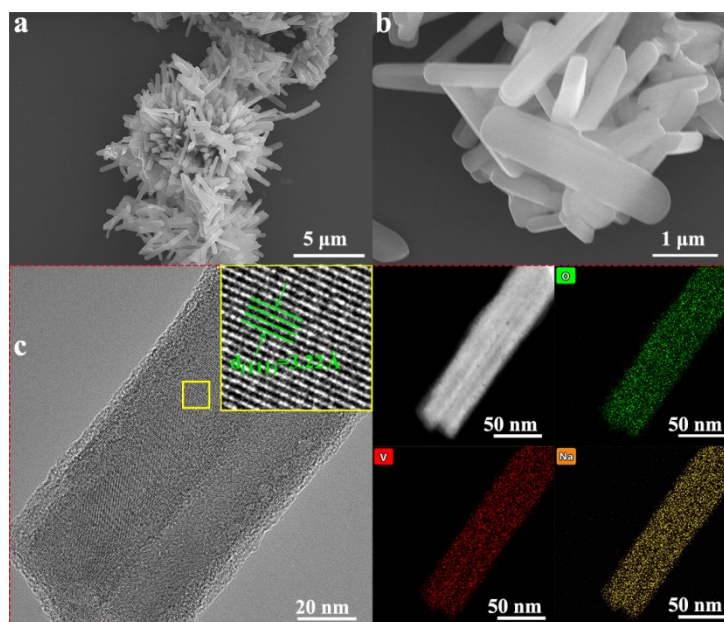


Fig. S2 (a,b) SEM, and (c) HRTEM -Element Mapping of SVO

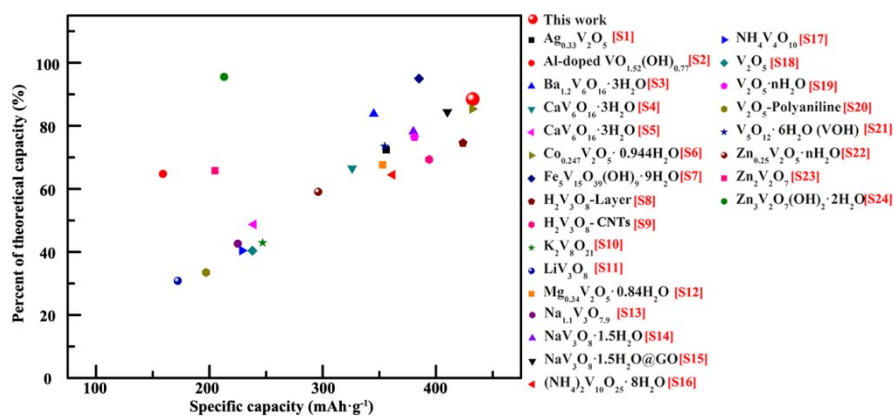


Fig. S3 Summary of the electrochemical performance of V-based cathode materials in AZIBs.^{S25}

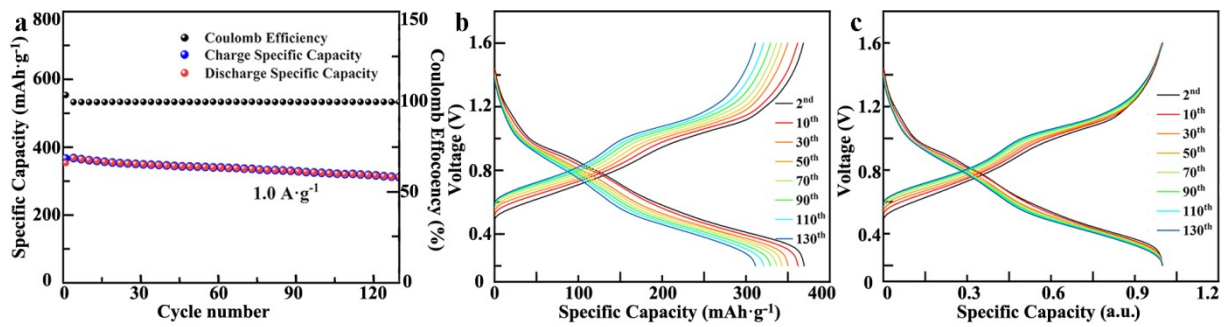


Fig. S4 (a) cycling performance and the corresponding coulombic efficiency, (b) GCD curves at $1.0 \text{ A}\cdot\text{g}^{-1}$; (c) Normalization GCD curves of HSVO at $1.0 \text{ A}\cdot\text{g}^{-1}$ HSVO electrode.

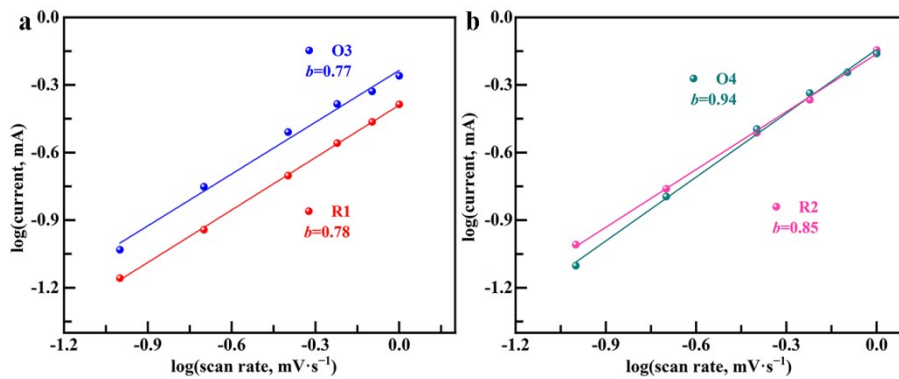


Fig. S5 Log(i) vs. log(v) plots at specific peak currents HSVO electrode in **Fig. 3a**

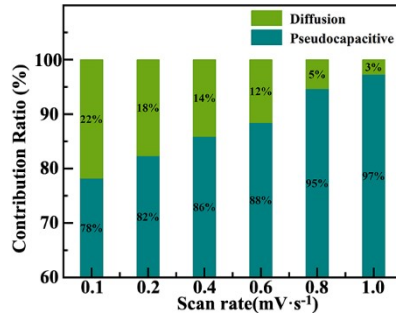


Fig. S6 Bar chart showing the percent of calculated pseudocapacitive contribution of HSVO electrode at $0.1\text{-}1.0 \text{ mV}\cdot\text{s}^{-1}$

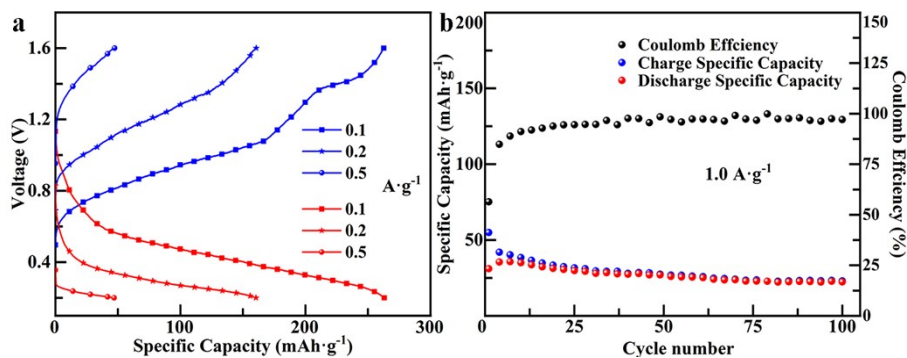


Fig. S7 (a) GCD curves at 0.1 and $1.0 \text{ A}\cdot\text{g}^{-1}$, (b) cycling performance and the corresponding coulombic efficiency at $1.0 \text{ A}\cdot\text{g}^{-1}$ of SVO

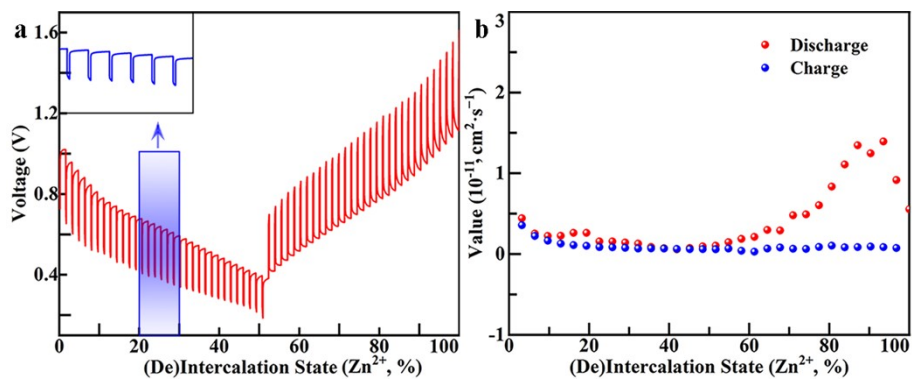


Fig. S8 (a) GITT measurements and (b) corresponding Zn²⁺ diffusion coefficient of SVO at 50 mA·g⁻¹

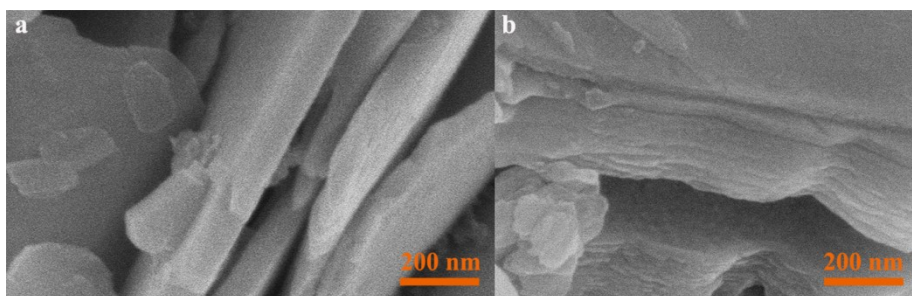


Fig. S9 SEM image of HSVO electrodes at full charge (a) and discharge (b)

Supplementary Notes

Notes S1^{S26}

We systematically studied the pseudocapacitive behavior through the analysis of CV curves within the scan rate of 0.1-1.0 mV·s⁻¹. There is a power law that links the scan rate with the current, which is

$$i=a \cdot v^b$$

$$\log(i)=b \cdot \log(v)+\log(a)$$

If the value of **b** is 0.5, we can summarize that the capacity is fully contributed by diffusion process, while if the **b** value is 1, we can conclude that the capacity is ruled by the capacitive effect.

Notes S2^{S27}

The reversible capacity in the cycles can be divided into pseudocapacitive contribution and diffusion contribution according to:

$$i=k_1v+k_2v^{1/2}$$

$$i'v^{1/2}=k_1v^{1/2}+k_2$$

where the pseudocapacitive contribution and the diffusion contribution are measured with k_1 and k_2 , respectively

Notes S3^{S28}

Galvanostatic intermittent titration technique (GITT) measurement has been taken to further investigate the kinetics of the Zn²⁺ solid-state diffusion of the HSVO electrode at 0.05 A·g⁻¹, in which the diffusion coefficient (D) of Zn²⁺ can be calculated from the parameters and voltage changes during the testing, according to:

$$D = \frac{4l^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

where t and τ represent the duration of current pulse (s) and relaxation time (s), respectively. l corresponds to the Zn²⁺ diffusion length (equal to the thickness of electrode, ≈ 0.001 cm). ΔE_s and ΔE_t are the steady-state voltage change (V) by the current pulse and voltage change (V) during the constant current pulse (eliminating the voltage changes after relaxation time), respectively.

Supplementary References

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