

Supporting Information

Enhancing Hydrophilicity of Thick Electrodes for High Energy Density Aqueous Batteries

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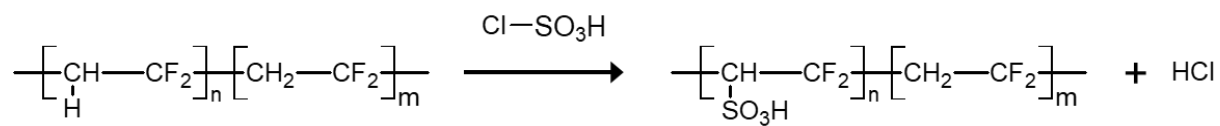


Fig. S1 A scheme to synthesize sulfonated PVdF (S-PVdF) from PVdF through simple chemical reaction.

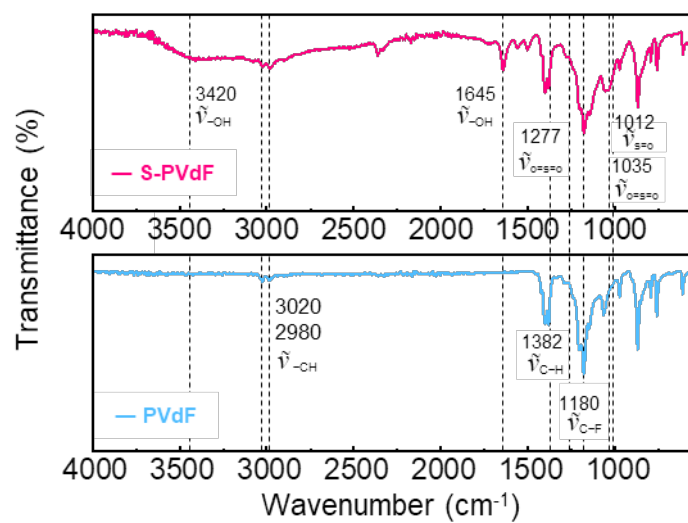


Fig. S2 FT-IR spectra of S-PVdF and PVdF binders.

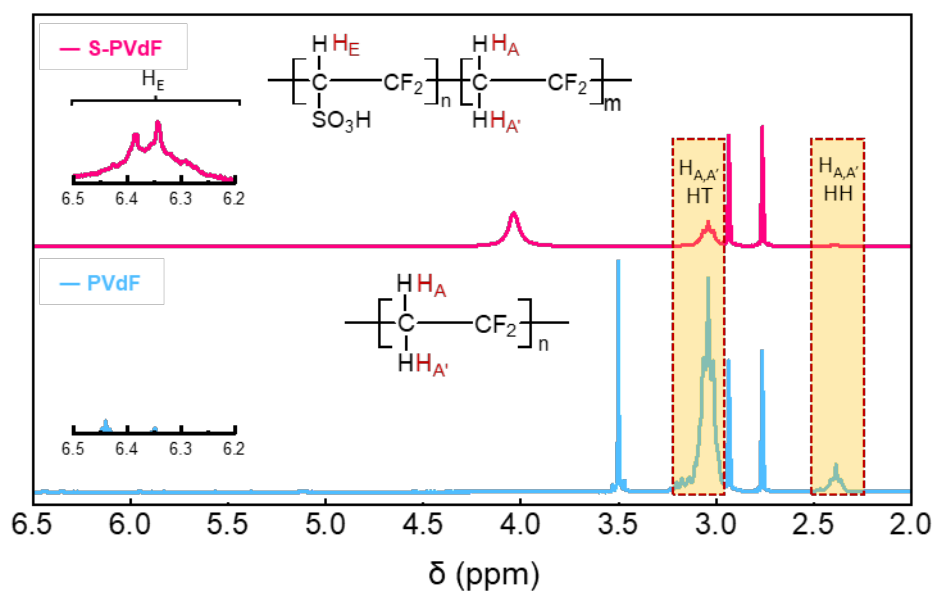


Fig. S3 ^1H NMR spectra of S-PVdF and PVdF binders.

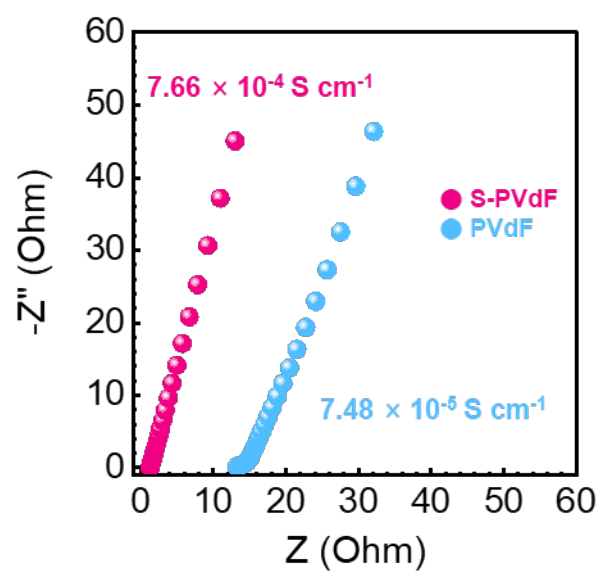


Fig. S4 Nyquist plots of S-PVdF and PVdF binders and their ionic conductivities.

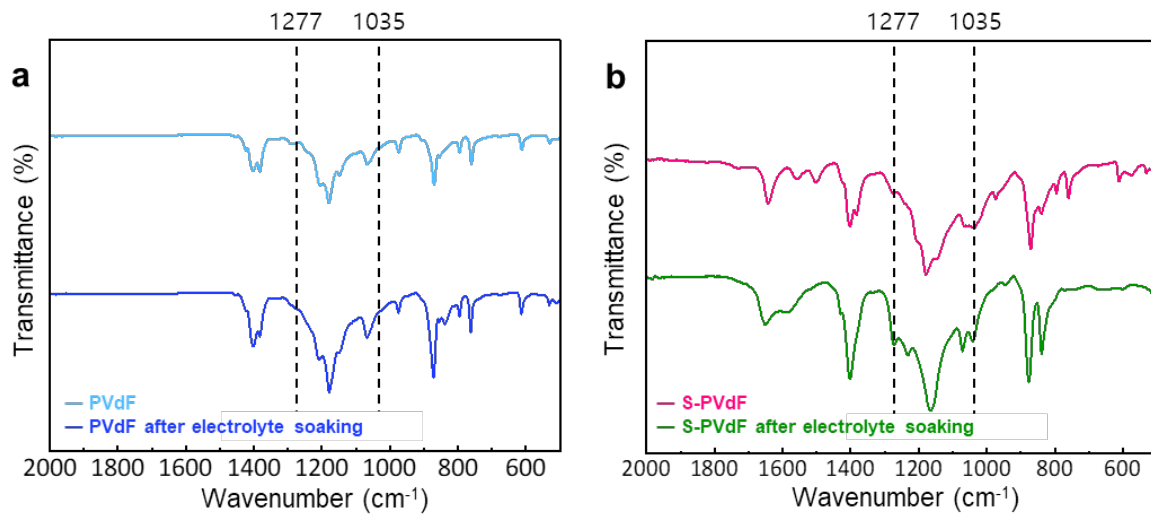


Fig. S5 FTIR spectra of binder before and after electrolyte soaking. **a** PVdF binders before and after electrolyte soaking. **b** S-PVdF binders before and after electrolyte soaking.

We have confirmed that the sulfonate groups in S-PVdF binders can provide abundant coordination sites with Zn^{2+} by Fourier transformation infrared spectrum (FTIR). After soaking in electrolyte for 24 h, the 1277 cm^{-1} symmetric O=S=O peak shifts to a wave number (1271 cm^{-1}) in S-PVdF binders, which suggests that the Zn^{2+} ions interact with sulfonate groups [1].

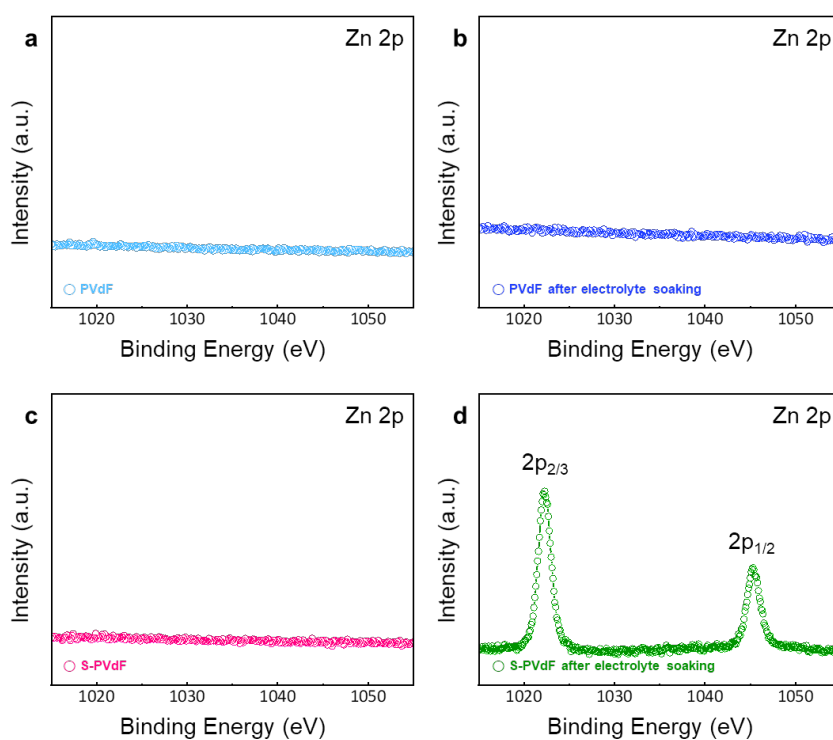


Fig. S6 XPS spectrum of Zn 2p in PVdF binders **a** before and **b** after electrolyte soaking. XPS spectrum of Zn 2p in S-PVdF binders **c** before and **d** after electrolyte soaking.

We also measured the binding energy of PVdF and S-PVdF to zinc ions via X-ray photoelectron spectroscopy (XPS). As can be seen in Fig. S6, XPS analysis exhibits the characteristic binding energies of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ of 1022.3 and 1045.4 eV in S-PVdF [2].

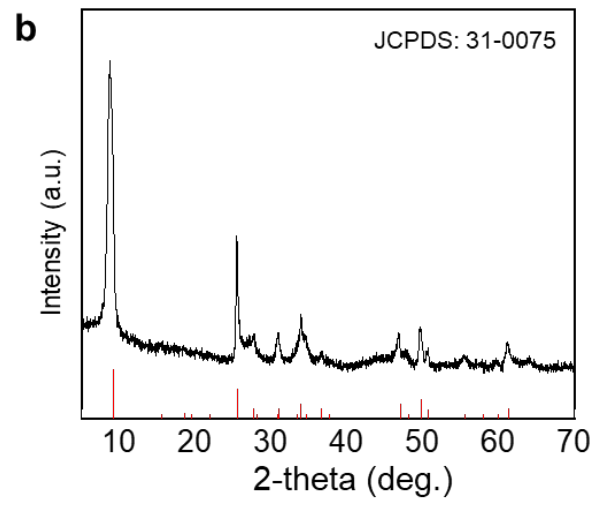
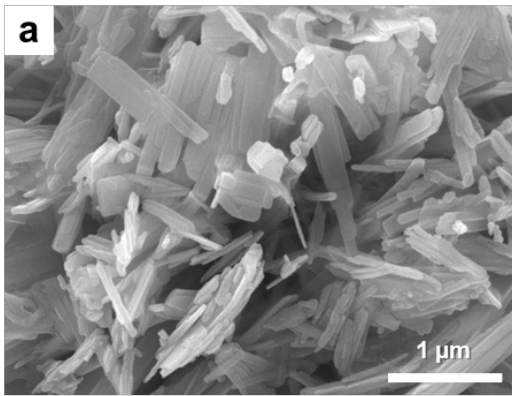


Fig. S7 a SEM image and **b** XRD pattern of $\text{NH}_4\text{V}_4\text{O}_{10}$ (NHVO).

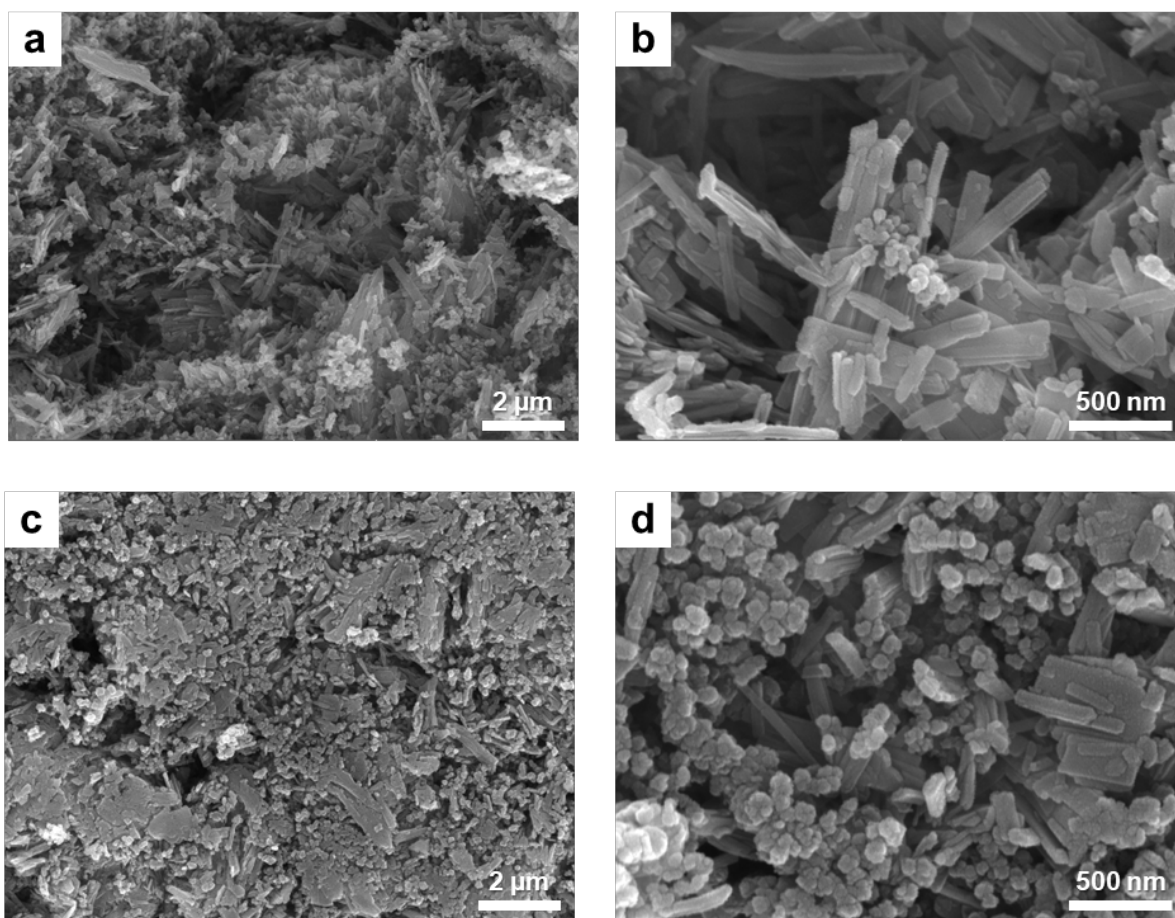


Fig. S8 Cross-sectional SEM image of a cathode with **a** S-PVdF binders and **b** its magnification. Cross-sectional SEM image of a cathode with **c** S-PVdF binders and **d** its magnification after the calendaring process.

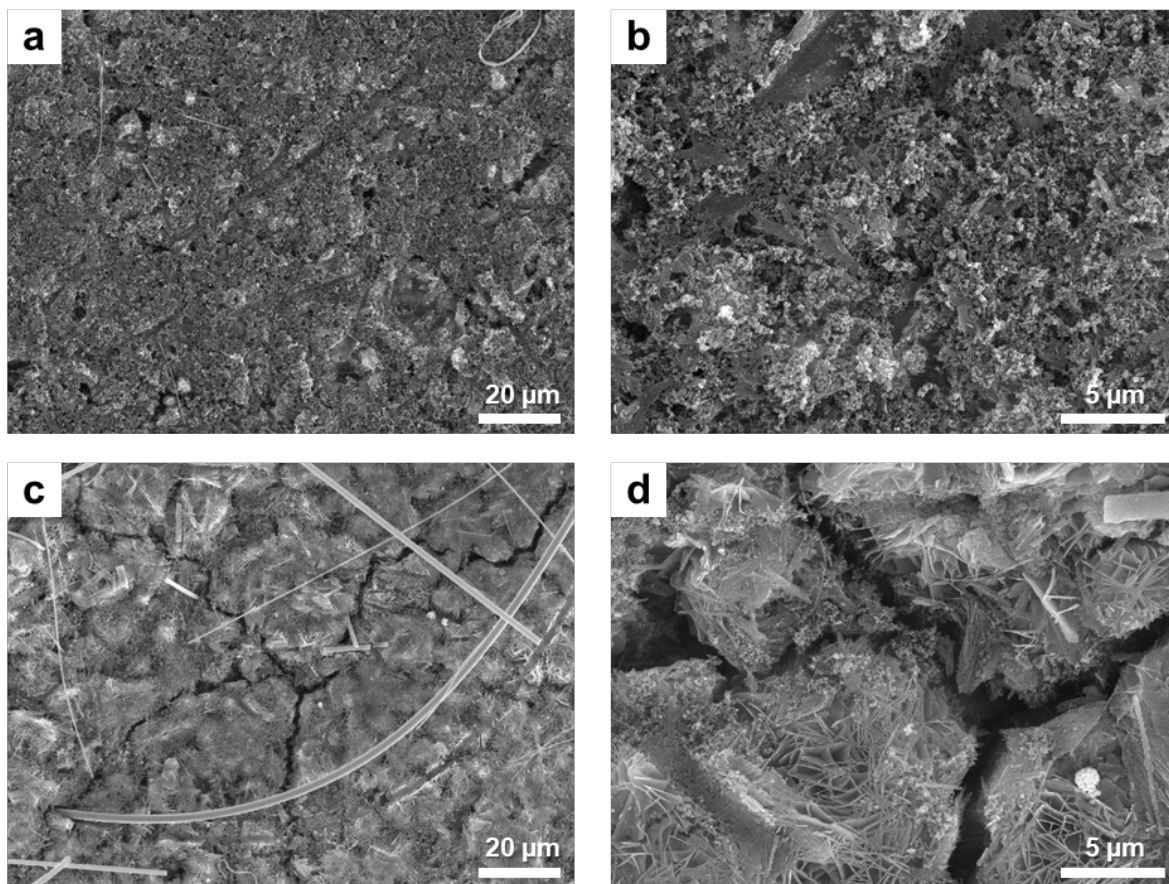


Fig. S9 **a** SEM images of cathodes with S-PVdF binders and **b** its magnification. SEM images of cathodes with **c** PVdF binders and **d** its magnification.

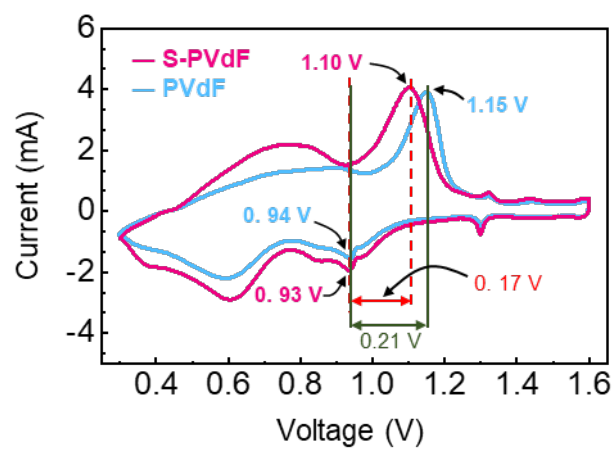


Fig. S10 CV profiles of full cells with S-PVdF and PVdF binders at 0.2 mV s^{-1} .

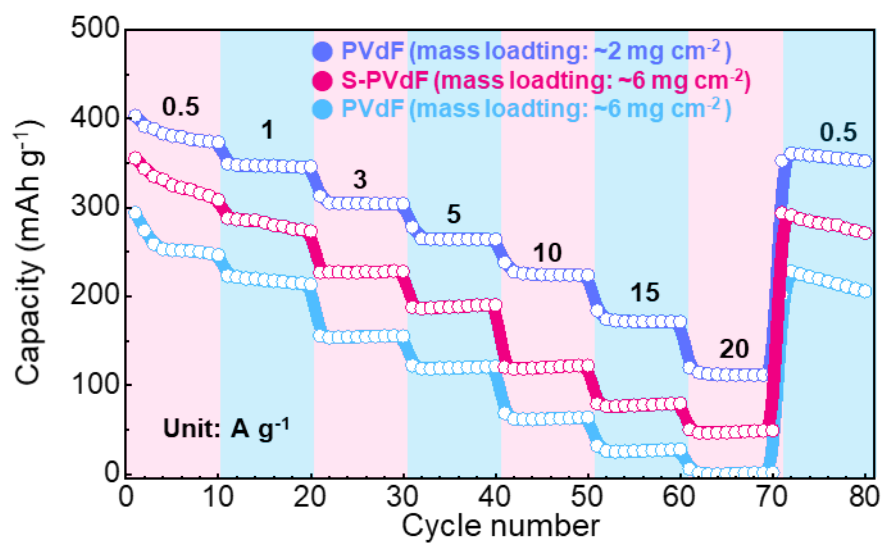


Fig. S11 Rate capability of cathodes with different binders.

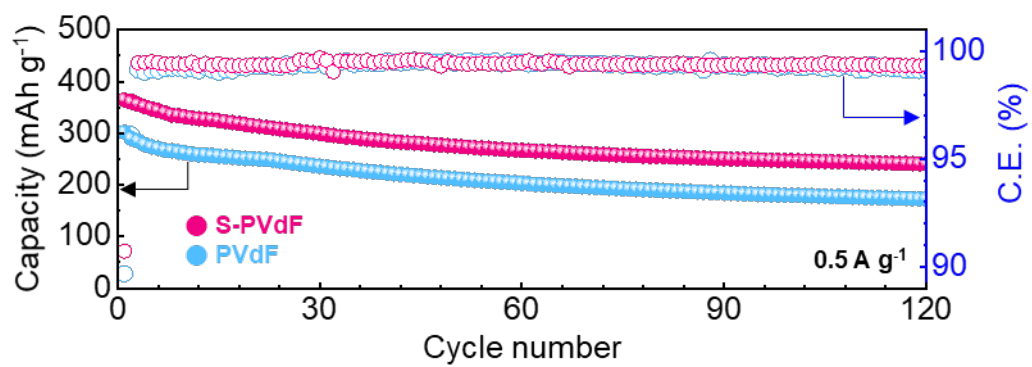


Fig. S12 Cycling performances of full cells with different binders at a low current density of 0.5 A g^{-1} ($\sim 0.1 \text{ C}$).

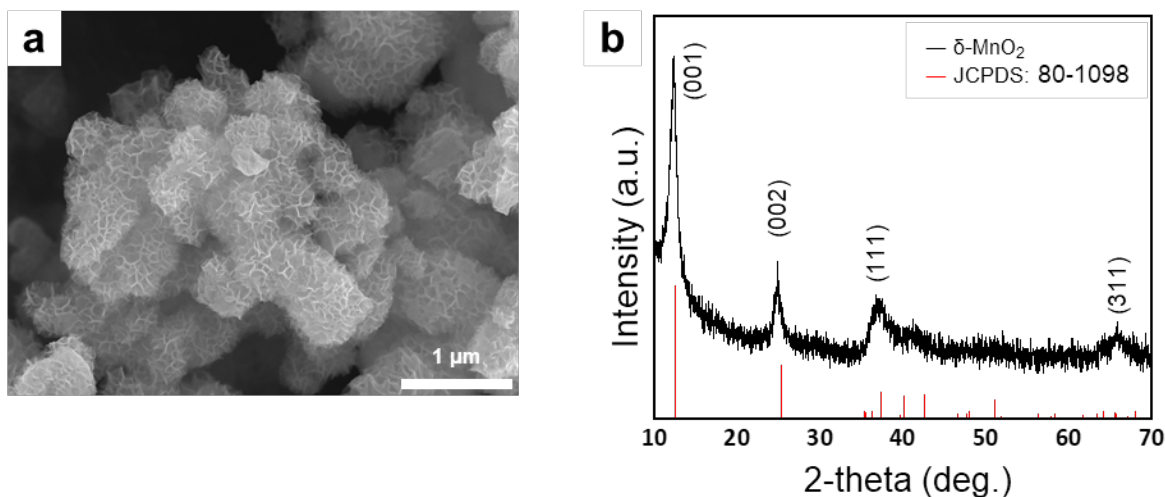


Fig. S13 a SEM image and **b** XRD pattern of δ -MnO₂.

To prove the universality of the binder, δ -MnO₂ was prepared. First, 1.2g of KMnO₄ and 0.215 g of MnSO₄ were dissolved in 130 ml DIW. Then, the solution was put into a Teflon-contained autoclave and heated at 160 °C for 12 h. After cooling and centrifugation, the product was rinsed with DIW several times. Finally, δ -MnO₂ was obtained after drying in a convection oven at 80 °C for 12 h. Next, the δ -MnO₂ was cast on stainless (SUS) foil and composed of three components: active material, conductive materials, and binders in the weight ratio of 7:2:1. Denka black was selected as the conductive material. Slurries containing the three components in N-methyl-2-pyrrolidone (NMP) were cast onto SUS foil (20 μ m thick) via the doctor blading method, followed by a drying step at 80 °C for 12 h under vacuum. The active mass loadings for the cathode materials were $\sim 3 \text{ mg cm}^{-2}$. The full cell with S-PVdF binders showed a higher reversible capacity (282 mAh g⁻¹) than those with PVdF binders (237 mAh g⁻¹) at the same mass loading of 3 mg cm⁻² at a current density of 0.2 A g⁻¹. Moreover, the full cell with S-PVdF showed higher reversible capacities in the cycle test. More importantly, it retained a highly improved capacity of $\sim 185 \text{ mAh g}^{-1}$ with a durable capacity retention of 66% after 200 cycles at 0.2 A g⁻¹. On the other hand, only a 20% capacity (49 mAh g⁻¹) was obtained in the full cell with PVdF binders after the cycle test.

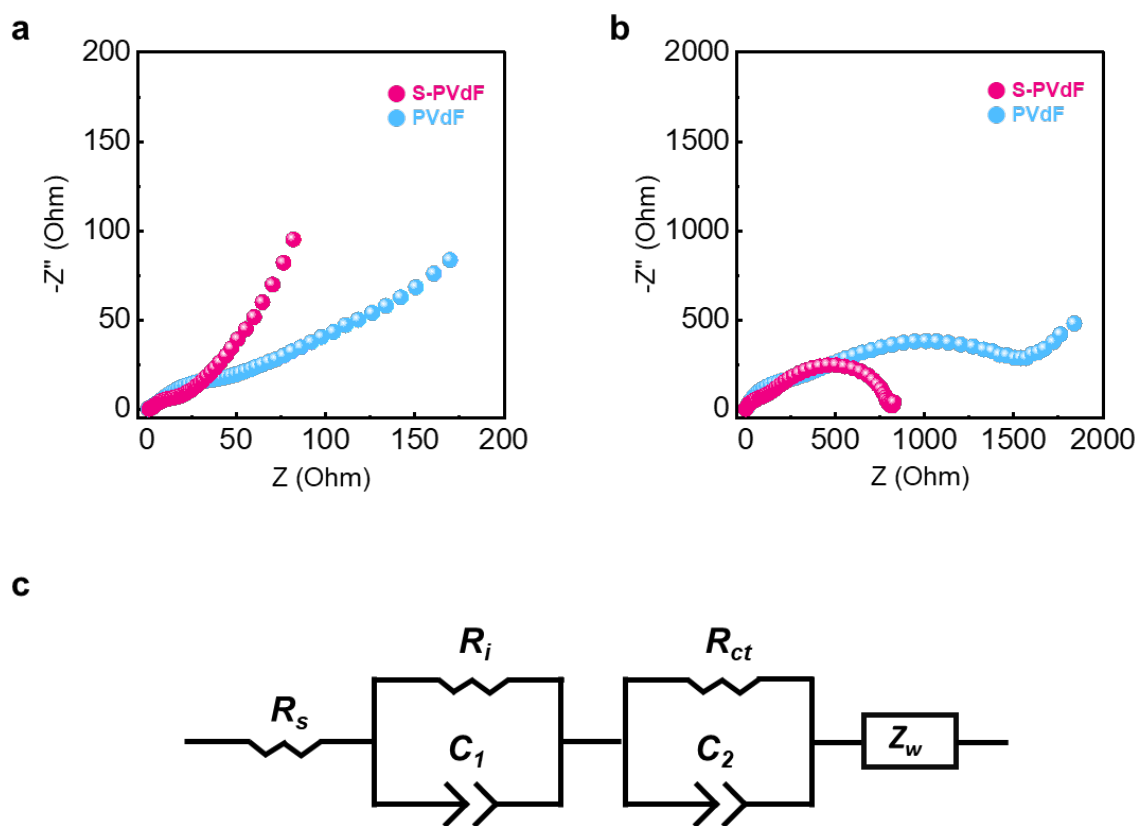


Fig. S14 EIS spectra of **a** before and **b** after long-term cycling (3000 cycles at 10 A g^{-1}). **c** Corresponding equivalent circuit. R_i and R_s are the ohmic resistance of solution and electrodes. R_{ct} is the charge-transfer resistance. C_1 and C_2 are the constant phase element of the double-layer capacitance, respectively. Z_w is the Warburg impedance.

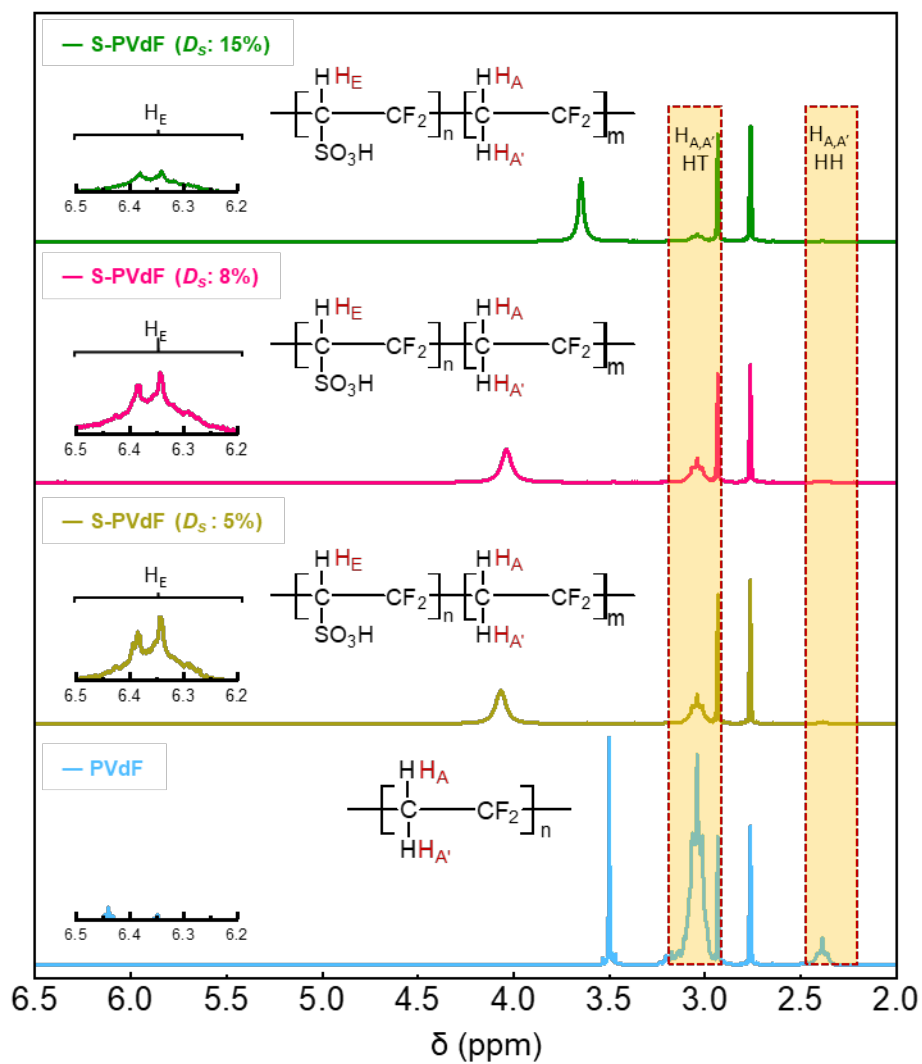


Fig. S15 ^1H NMR spectra of binders with different sulfonation degrees.

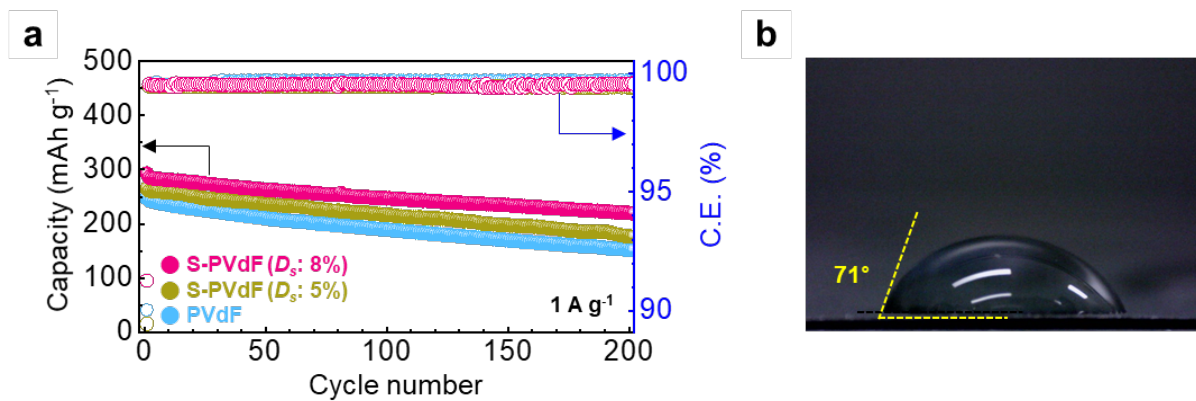


Fig. S16 a Galvanostatic cycling performances of cathodes with different binders at a current density of 1 A g^{-1} . **b** Contact angle of the cathode with S-PVdF binder (low sulfonation degree of 5%).

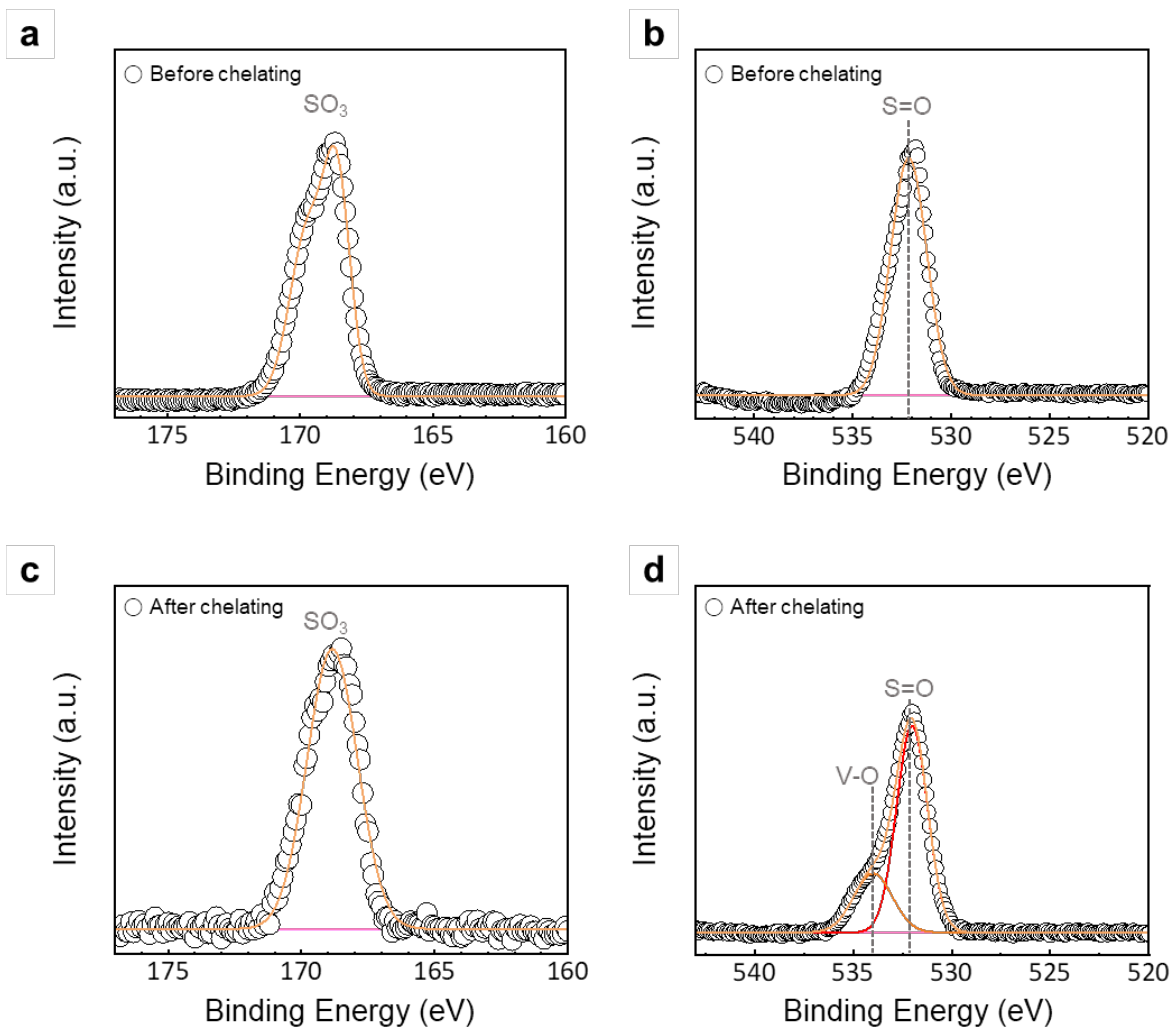


Fig. S17 High-resolution XPS spectra of S-PVdF films before and after being immersed into cathode-dissolved electrolytes. **a** S2p and **b** O1s spectra peaks of immersed S-PVdF film before being immersed into cathode-dissolved electrolytes. **c** S2p and **d** O1s spectra peaks S-PVdF film after being into cathode-dissolved electrolytes.

To clarify the suppression of vanadium dissolution of vanadium-based active materials, we prepared cathode-dissolved electrolyte. First, 0.1 g of the vanadium-based active materials ($\text{NH}_4\text{V}_4\text{O}_{10}$) were immersed into 10 ml of 2 M ZnSO_4 aqueous electrolytes. Then, the solution was kept in an oven for 24 h at 70 °C and purified via filtration by 0.45 μm syringe filter. S-PVdF films for measuring ionic conductivities were also used here. The films were immersed into the yellowish cathode-dissolved electrolyte for 24 h at room temperature. Then, the films

were rinsed with DIW and ethanol several times. Finally, the films were dried in a convection oven at 80 °C for 12 h.

Supplementary References

- [S1] H. Fan, M. Wang, Y. Yin, Q. Liu, B. Tang, et al., Tailoring interfacial Zn²⁺ coordination via a robust cation conductive film enables high performance zinc metal battery. *Energy Storage Materials*. **49**(380-389 (2022)).
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- [S2] Y. Yang, C. Liu, Z. Lv, H. Yang, Y. Zhang, et al., Synergistic manipulation of Zn²⁺ ion flux and desolvation effect enabled by anodic growth of a 3d ZnF₂ matrix for long-lifespan and dendrite-free zn metal anodes. *Advanced Materials*. **33**(11), 2007388 (2021).
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