

Supplementary information for

Balanced-State Electrolytes Overcome Crossover in Vanadium Redox Flow Batteries

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1. Calculation of the net flux in VRFBs

Fick's law is written as below:

$$J = -D\nabla C \quad (\text{Eq. S1})$$

where, J is the amount of substance per unit area per unit time; D is the diffusion coefficient; ∇C is the concentration gradient between the two sides of the membrane.

Based on Fick's law, adjusting the concentration of vanadium ions can effectively control the net flux between the positive and negative sides caused by crossover. The effects of electrolytes' concentration and state of charge (SOC) on the net flux were quantitatively calculated under transient conditions, using the diffusion rates listed in Table S1.^{S2}

Table S1 The diffusion rate of vanadium ions across Nafion membranes.

Vanadium ions	V ²⁺	V ³⁺	VO ²⁺	VO ₂ ⁺
Diffusion coefficient/ cm ² min ⁻¹	5.261 × 10 ⁻⁶	1.933 × 10 ⁻⁶	4.095 × 10 ⁻⁶	3.538 × 10 ⁻⁶

2. Side reactions

2.1 Side reaction induced by crossover

In VRFBs, the vanadium ions transported from one side to the other side induce side reactions that cause an imbalance in electrolyte valence on the positive and negative sides, as illustrated below.^{S1}



Reactions associated with vanadium ion transport from the positive side to the negative side:



As shown in Eqs. (S5) - (S10), the crossover of V^{3+} and VO^{2+} consumes equivalent amounts VO_2^+ and V^{2+} , respectively. While the crossover of V^{2+} and VO_2^+ ultimately consumes twice as much as VO_2^+ and V^{2+} , respectively. Combine with the diffusion rates of vanadium ions across the Nafion series membranes ($V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$).^{S2}; this results in a net flux of V^{2+} transport from the negative to the positive side during cycling, accompanied by twice the expected consumption of VO_2^+ . Consequently, crossover leads to the accumulation of surplus V^{2+} on the negative side, whereas a deficiency of VO_2^+ arises on the positive side.

2.2 Side reaction induced by air and charging



V^{2+} is highly sensitive to oxygen and is readily oxidized to V^{3+} by air. The oxidation of V^{2+} with air increases V^{3+} content, thereby improving the concentration of VO_2^+ on the positive side during charging.



The HER generates more VO_2^+ on the positive side than the amount of V^{2+} on the negative side during the charge process. The air-induced V^{2+} oxidation and HER elevate the average vanadium valence of electrolytes during cycling.

3. Average vanadium valence of electrolytes after adding vanadyl sulfate

The average vanadium valence of the electrolytes (A_v) after adding $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ into $\text{V}^{3.5+}$ electrolyte can be calculated as below:

$$A_v = (1.70 \times 3.5 + (C_e - 1.70) \times) \times \frac{V_c}{1.70 \times 40} \quad (\text{Eq. S10})$$

where C_e is the concentration of prepared electrolyte, and V_c is the electrolyte volume.

By solving Eq. S13, we can obtain the average vanadium valence of electrolytes with concentrations of 1.81, 1.83, 1.91, 1.93, 2.01, and 2.03 M as 3.53, 3.54, 3.55, 3.56, 3.58, and 3.58, respectively.

The equivalent amount of surplus $1.7 \text{ M VO}_2^+ (E_5)$ in electrolytes with the concentrations of 1.81, 1.83, 1.91, 1.93, 2.01, and 2.03 M was calculated as 1.15, 1.42, 2.19, 2.44, 3.08, and 3.26 mL via Eq. S14.

$$E_5 = \frac{m_c}{163 + 5 \times 18} \times \frac{1}{2 \times 1.70} \quad (\text{Eq. S11})$$

where m_c is the weight of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ required to prepare the electrolyte with concentrations of 1.81, 1.83, 1.91, 1.93, 2.01, and 2.03 M.

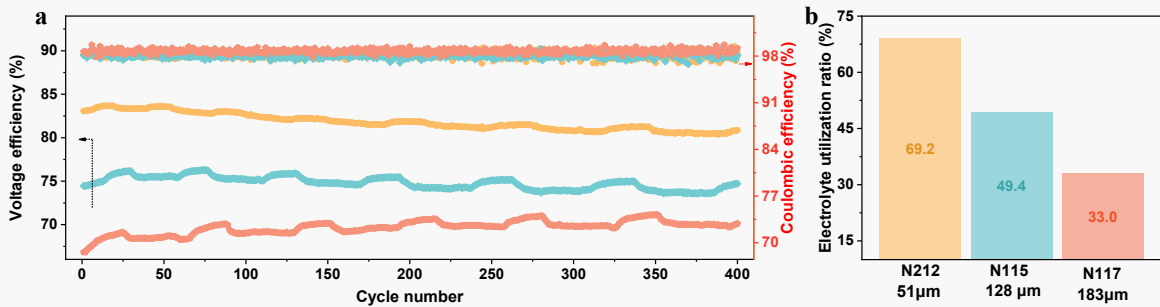


Fig. S1 Performance comparison of VRFBs with Nafion 212/115/117. **a**, Voltage efficiency/coulombic efficiency of VRFBs during cycling (operated at $28 \pm 3^\circ\text{C}$). **b**, The maximum electrolyte utilization ratio of VRFBs under the conditions: current density 200 mA cm^{-2} , flow rates 2.5 ml min^{-1} .

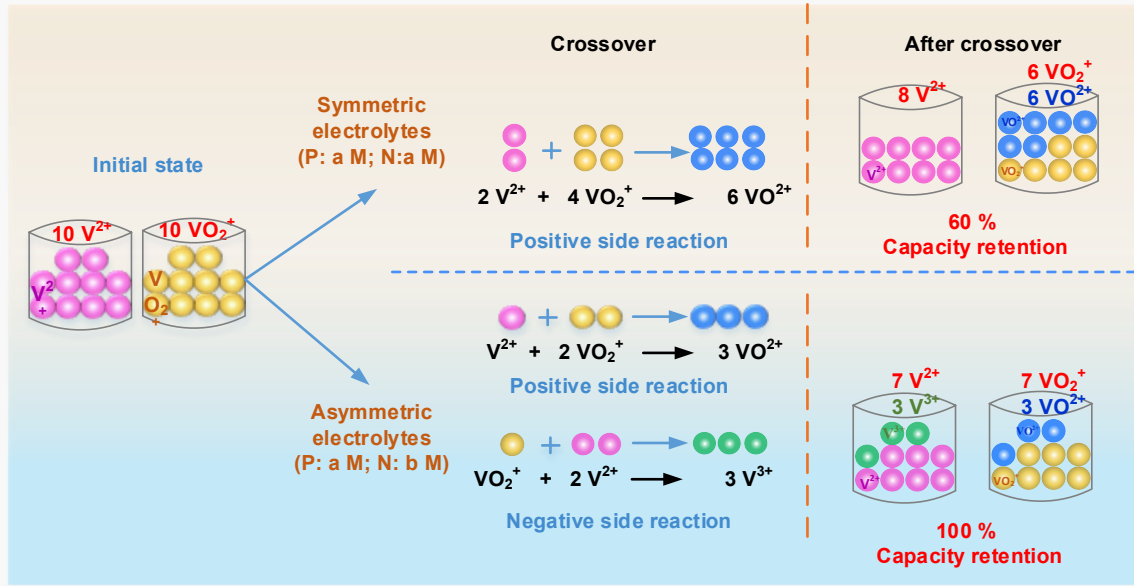


Fig. S2 Schematic illustration of the enhanced discharge capacity in a VRFB employing an asymmetric electrolyte (Note: P and N denote the positive and negative electrolytes, respectively).

As depicted in Fig. S2, the initial state assumes 10 V^{2+} and 10 VO_2^+ on the negative side and positive sides, respectively. In a VRFB operated with symmetric electrolytes, crossover leads to the transport of two V^{2+} ions from the negative to the positive side, accompanied by the consumption of 4 VO_2^+ ions. This imbalance in vanadium-ion content and valence across the two sides consequently reduces the capacity to 60%. By contrast, in the VRFB working with asymmetric electrolytes, the amount of V^{2+} transport from the negative to the positive side is counterbalanced by an equivalent flux of VO_2^+ in the opposite direction. Therefore, the contents and valence of vanadium ions on the positive and negative sides remain balanced, preserving 100% capacity despite crossover.

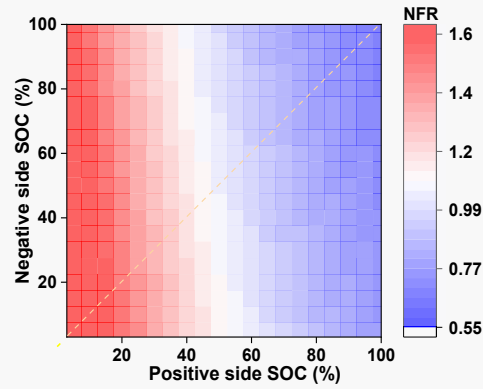


Fig. S3 Electrolyte net flux ratio between the positive and negative sides (NFR) under different SOC. Vanadium ion crossover in VRFBs is predominantly governed by diffusion, with net convective and migratory fluxes being negligible.^{S3} Therefore, in this work, we treated the diffusion rates of vanadium ions across Nafion series membranes—derived from the experimental results (Table S1) reported by Professor Zhang^{S2}—as their effective permeabilities. These values were used in the crossover analysis presented in Figs. 2a and S3.

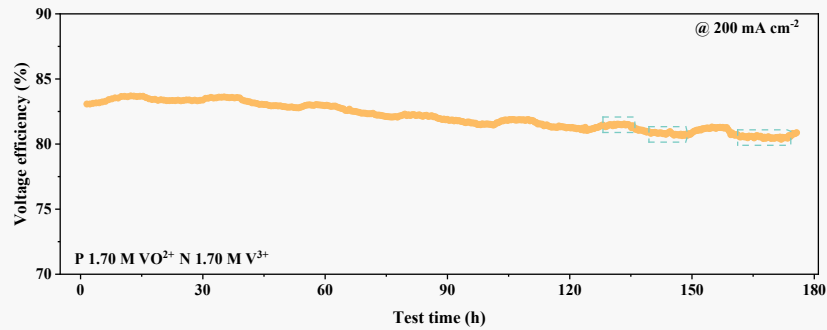


Fig. S4 Voltage efficiency changes with test time (operated at 28 ± 3 °C).

4. Hydraulic pressure effects on suppressing the capacity decay of VRFBs

Changing the concentration of electrolytes can significantly influence the osmotic and hydraulic pressure. Therefore, this work investigates how these pressures contribute to the suppression of capacity decay. The relationship between electrolytes' concentration and osmotic pressure can be expressed as:^{S4}

$$\Delta P_{os} = \left((C_2 + C_3) - (C_4 + C_5) + (C_{H^+ - P} - C_{H^+ - N}) \right) \times R \times T \quad (\text{Eq. S12})$$

where ΔP_{os} is the osmotic pressure; C_2 , C_3 , C_4 , and C_5 represent the vanadium concentrations of related valence. R is the universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), and T is the temperature (K).

In this work, to calculate the pressure drop between the positive and negative sides of the VRFBs, the half-cells are simplified as a pipe cross-section. Hence, the pressure drop on the positive and negative sides is calculated using the following equation:^{S5}

$$\Delta p_p = f_d \frac{L}{d} \cdot \frac{\rho v^2}{2} \quad (\text{Eq. S13})$$

$$f_d = \frac{64}{Re} \quad (\text{Eq. S14})$$

$$Re = \frac{\rho d Q}{\mu A} \quad (\text{Eq. S15})$$

where f_d is the Darcy friction factor, L and d are the length and diameter of the pipe, separately, ρ and v denote the density and viscosity of the flowing electrolyte. Q and A are the flow rate (L s^{-1}) and the cross-sectional area of electrodes (m^2), respectively. Therefore, the pressure drops (ΔP_p) induced by changes in electrolyte viscosity can be expressed as Eq. (S 19).

$$\Delta p_p = 32v \frac{L}{d^2} (\mu_{P1} - \mu_{N1}) \quad (\text{Eq. S16})$$

where μ_{P1} and μ_{N1} are the dynamic viscosity of traditional electrolytes on the positive and negative sides, respectively. Thus, the pressure drop difference caused by the prepared electrolytes can be achieved by adjusting the flow rate of electrolytes on the positive and negative sides, as shown in Eq. (S20).

$$32v \frac{L}{d^2} (\mu_{P1} - \mu_{N1}) = 32 \frac{L}{d^2} (\mu_P v_P - \mu_N v_N) \quad (\text{Eq. S17})$$

where μ_P , μ_N , v_P , and v_N are the viscosity and flow rate of traditional electrolytes on the positive and negative sides. Based on the viscosity (Fig. S5a) and flow rate (51 rpm) of the traditional

electrolytes and prepared electrolytes, the equivalent pressure drop across both sides is calculated via Eq. (S21):

$$32v \frac{L}{d^2} (4.7966 - 3.1199) = 32 \frac{L}{d^2} (3.68212v_P - 5.23054v_N) \quad (\text{Eq. S18})$$

where v_P and v_N are the flow rates on the positive and negative sides. To maintain equal pressure drops, the flow rate on the positive side must be 1.88 times (95.67 rpm) that on the negative side (51 rpm).

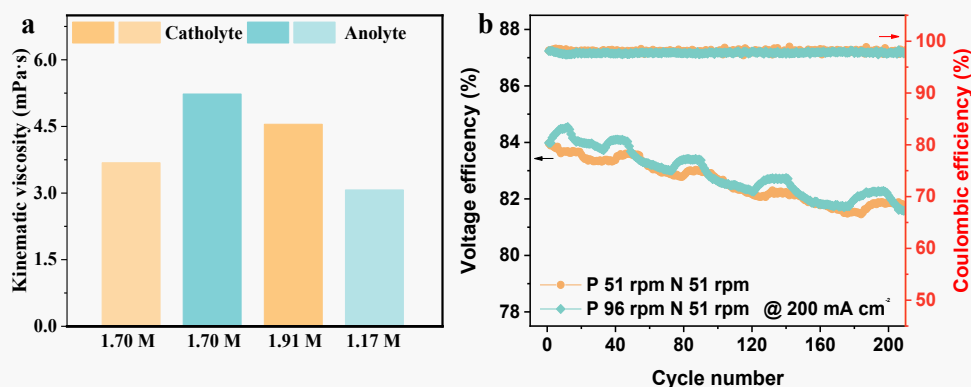


Fig. S5 Electrolyte viscosity and its impact on VRFB performance. **a**, Viscosity of electrolytes at different concentrations (measured at 23 ± 0.5 °C). **b**, Effect of flow rate on the voltage and coulombic efficiencies of VRFBs (operated at 28 ± 3 °C).

Fig. S5b shows that the VRFB operated at pump speeds of P96/N51 rpm exhibits higher voltage efficiency than that at P51/N51 rpm, owing to improved mass transfer. However, the capacity decay rate follows a comparable trend in both cases (Fig. 2g). This indicates that increasing the hydraulic pressure gradient between the membranes has no obvious effect on suppressing capacity decay during long-term cycling.

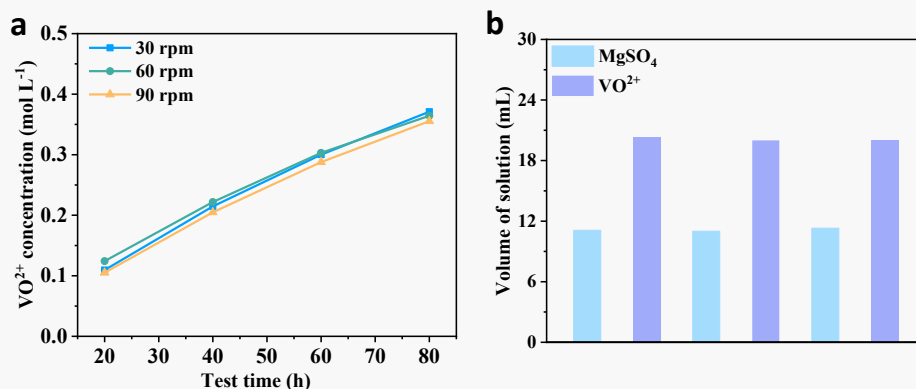


Fig. S6 Pressure drop effects on vanadium ions crossover across the membrane (measured at 28 ± 3 °C). **a**, Concentration of VO^{2+} varies with time at different symmetric flow rates. **b**, Volume of MgSO_4 and VO^{2+} solution after 80 hours (Note: The reported volume of MgSO_4 solution excludes the volume removed for sampling).

In Fig. S6 tests, a flow battery cell assembled with N212 membrane was employed. Two pieces of electrodes with a size of $20.00 \times 20.00 \text{ mm}^2$ were used as the electrodes. 20.00 mL of 1.70 M MgSO_4 and 1.70 M VOSO_4 solution were pumped into the two sides of the cell using a peristaltic pump, Longer BT100. Hydraulic pressure differences were generated and studied by changing the pump speed from 30 to 90 rpm.

As shown in Fig. S6, neither the VO^{2+} concentration in the MgSO_4 solutions nor the solution volumes changed significantly over the tested flow rates, indicating that the effect of pressure drop differences on vanadium ion crossover is negligible.

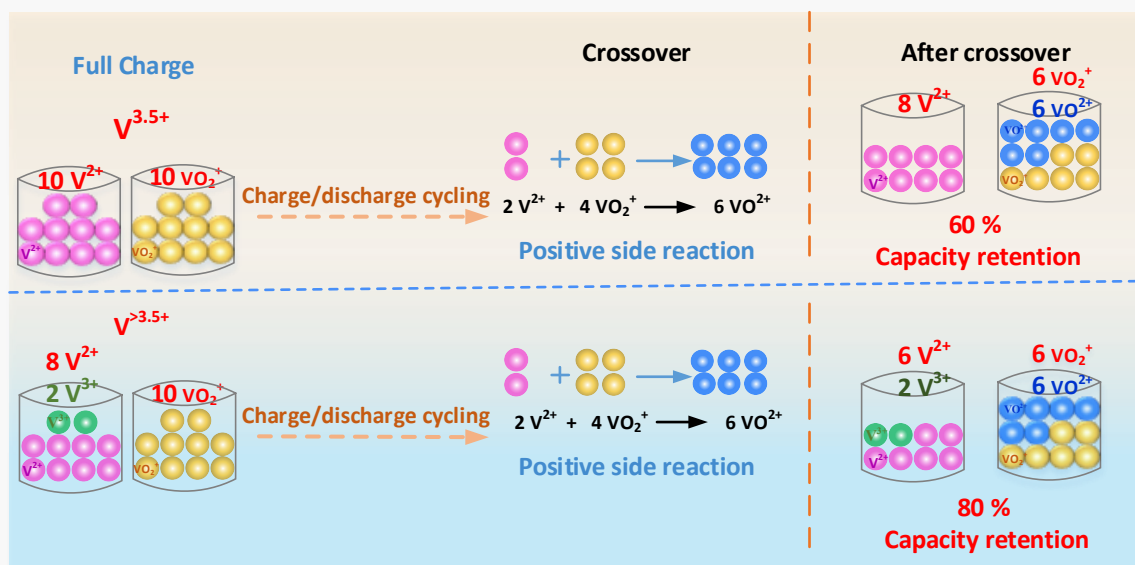


Fig. S7 Schematic of surplus VO_2^+ for suppressing capacity decay.

Fig. S7 demonstrates that increasing the average vanadium valence of the electrolyte improves the balance between the positive and negative electrolytes under equivalent crossover conditions, thereby substantially reducing the capacity decay rate.

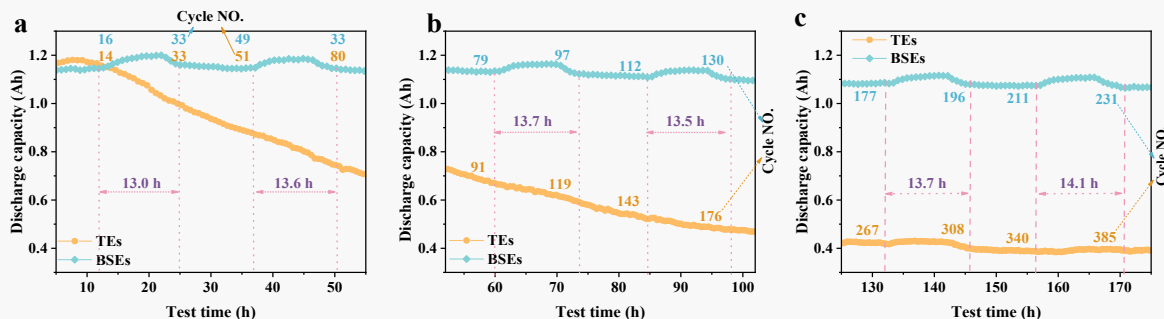


Fig. S8 Fluctuation of discharge capacity with test time (operated at $28 \pm 3^\circ\text{C}$). a–c, Discharge capacity profiles for the VRFBs using TEs and BSEs during different testing periods: 0–55 h (a), 50–102 h (b), and 125–175 h (c). The corresponding cycle numbers and specific time intervals are indicated within the panels.

The peaks of discharge capacity consistently appear within similar time intervals, demonstrating the strong regulation of temperature changes in one day. The VRFB employing BSEs operated for 289.49 hours over 400 cycles, which is significantly longer than the 175.67 hours achieved by the VRFB with TEs.

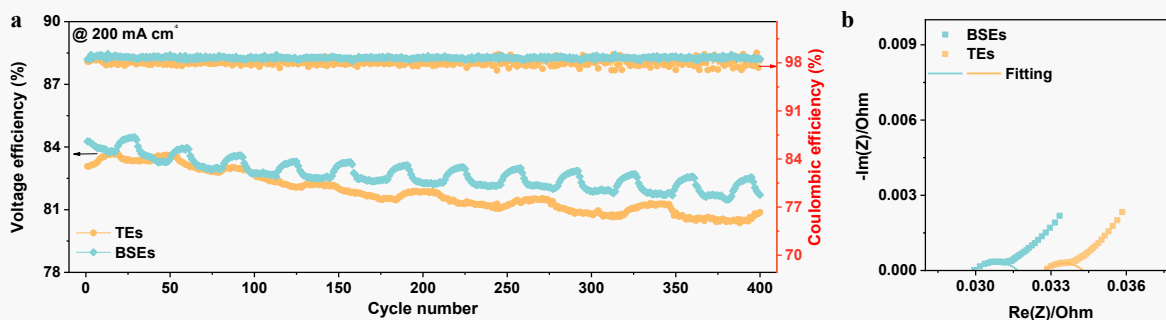


Fig. S9 Performance comparison of VRFBs with balanced-state electrolytes (BSEs) and traditional electrolytes (TEs). Comparison of a, the voltage/coulombic efficiency (operated at $28 \pm 3^\circ\text{C}$) and b, electrochemical impedance spectroscopy (EIS) spectrum (measured at $23 \pm 0.5^\circ\text{C}$).

The higher voltage efficiency of the VRFB (Fig. S9a) with the balanced state electrolytes benefits from its lower resistance (Fig. S9b) compared with that using traditional electrolytes.

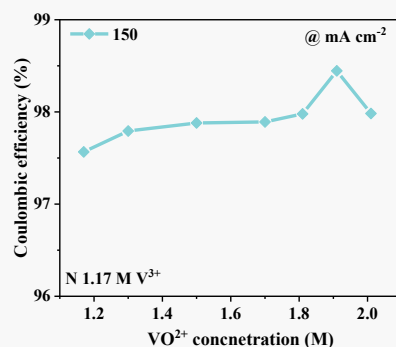


Fig. S10 Effects of VO^{2+} concentration on the coulombic efficiency of VRFBs at 150 mA cm^{-2} (operated at $28 \pm 3^\circ \text{C}$).

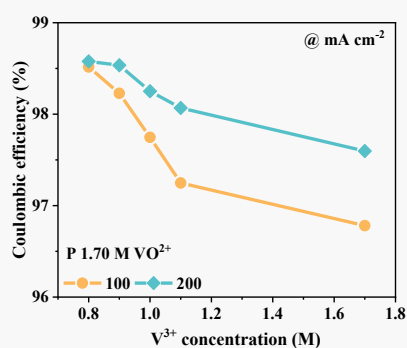


Fig. S11 Effects of V^{3+} concentration on the coulombic efficiency of VRFBs at 100 and 200 mA cm^{-2} (operated at $28 \pm 3^\circ \text{C}$).

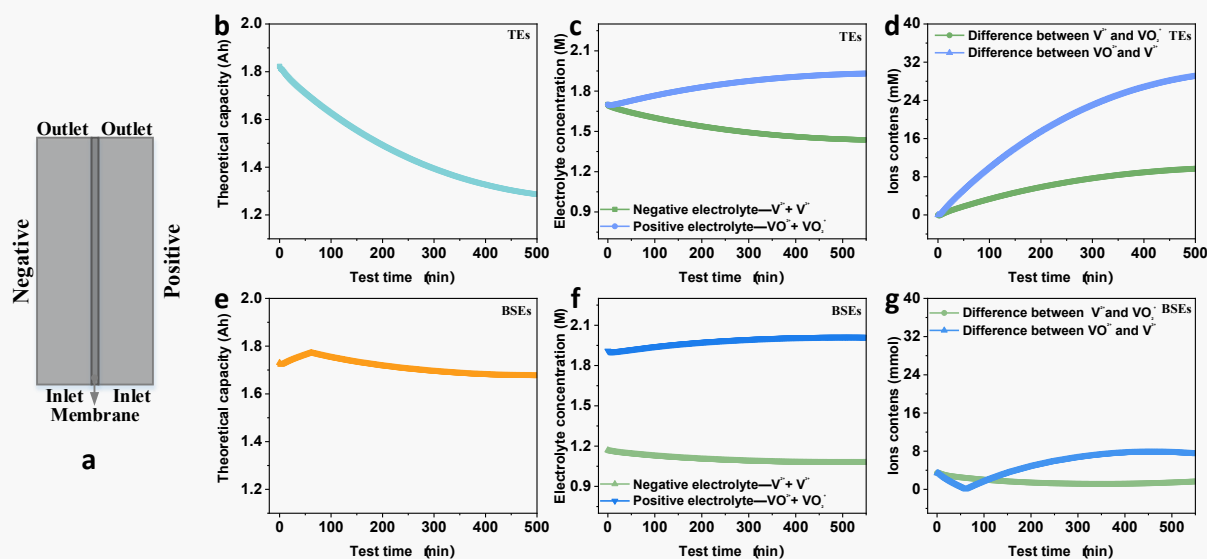


Fig. S12 Simulated cell performance using the TEs (P $1.70 \text{ M V}^{3.50+}$; N $1.70 \text{ M V}^{3.50+}$) and BSEs (P $1.91 \text{ M V}^{3.55+}$; N $1.170 \text{ M V}^{3.50+}$) (simulated at 25°C). **a**, 2D model built with Comsol software. **b-d**, Theoretical capacity, electrolyte concentration on the positive and negative sides, and difference between V^{2+} and VO_2^+ ,

as well as V^{3+} and VO^{2+} in the VRFB with TEs at different times. **e-g**, Theoretical capacity, electrolyte concentration on the positive and negative sides, and difference (absolute value) between V^{2+} and VO_2^+ as well as V^{3+} and VO^{2+} in the VRFB with BSEs at different times.

Fig. S12b illustrates that the theoretical capacity of a VRFB with TEs decreases significantly over time owing to crossover. This stems from the substantially disparate diffusion rates of vanadium ions across Nafion membranes ($V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$), which results in the net flux of electrolyte transport from the negative to the positive sides, producing a steadily increasing concentration disparities between the two sides (Fig. S12c). Specifically, the contents of V^{2+} and VO_2^+ diminish substantially over time, whereas those of V^{3+} and VO^{2+} increase, driven by crossover coupled with side reactions. Hence, enhancing vanadium ion transport from the positive to the negative side while reducing the reverse flux can mitigate crossover-induced capacity loss. In a VRFB using BSEs, crossover is well effectively counteracted by elevating the positive-side electrolyte concentration and lowering that on the negative side, reflected in its stable theoretical capacity over time (Fig. S12e). Electrolyte concentrations on both sides likewise remain invariant over time within the BSE-equipped VRFB (Fig. S12f). In contrast to the progressively widening disparities in V^{2+}/VO_2^+ and VO^{2+}/V^{3+} contents over time in the VRFB with TEs (Fig. S12d), the contents in the VRFB with BSEs were stably maintained at a high matching value (Fig. S12g).

The initially lower theoretical capacity of the BSE-based VRFB compared with the TE-based system arises from the elevated average vanadium valence ($V^{3.55+}$), which results in a reduction of capacity. Nevertheless, long-term testing reveals that raising the average vanadium valence from 3.50 to 3.55 enhances VRFB stability, as evidenced in Fig. S13. These results align closely with the experimental data.^{S6}

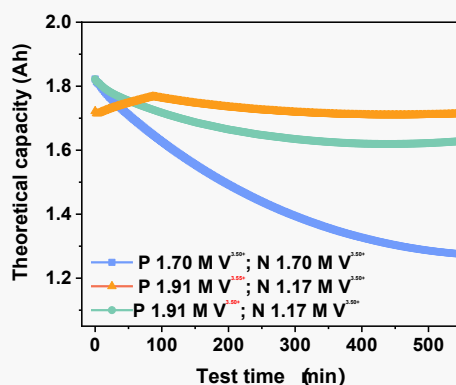


Fig. S13 Effect of elevating the average vanadium valence of electrolytes on capacity decay (simulated at 25 °C).

All simulations in Figs. S12 and S5 were performed at 50 states of charge (SOC). A comparative analysis of VRFB performance using TEs and BSEs across different SOC is presented in Fig. S14. Experimental results indicate that the SOC for a VRFB equipped with an N212 and operated at 200 mA cm⁻² ranges from about 10 to 80 (Fig. 2c). Accordingly, we compared the theoretical capacity of VRFBs using BSEs after 250 and 500 min to that employing TEs over this SOC range, as depicted in Fig. S14a-b. The data reveal that BSEs deliver superior performance to TEs over most of the SOC range, particularly at high SOC. At SOC of 10 and 20, the crossover from the positive to the negative side dominates vanadium ion flux across the membrane, consequently resulting in lower performance than that observed with TEs. Throughout the entire charge–discharge process, the net crossover in VRFBs with BSEs was minimized between the positive and negative sides, which enabled a stable discharge capacity over time.

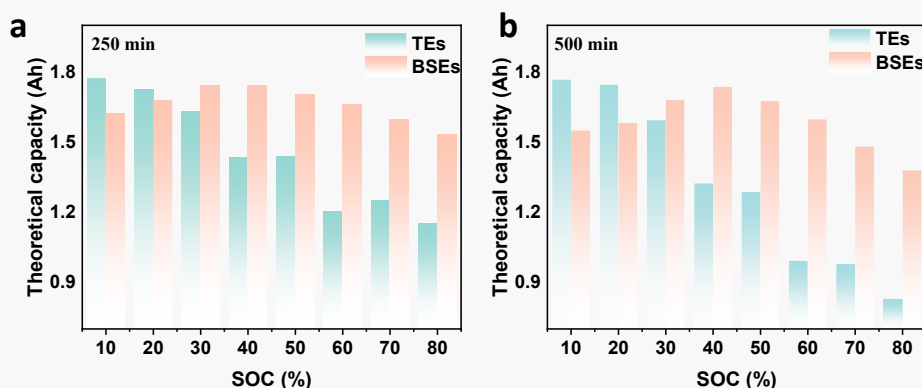


Fig. S14 Performance comparison of VRFBs using TEs and BSEs at different SOC (simulated at 25 °C). Battery performance after a, 250 and b, 500 min.

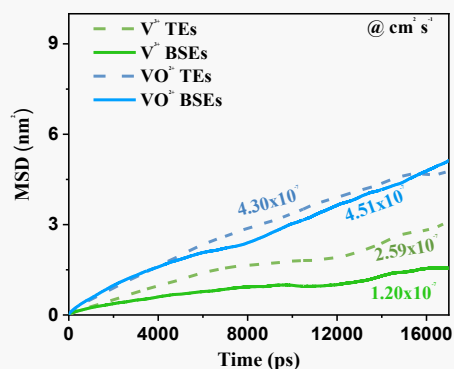


Fig. S15 MSD simulation results of V^{3+} and VO^{2+} in Nafion membrane with the balanced-state electrolytes (BSEs) and traditional electrolytes (TEs) (simulated at 25 °C).

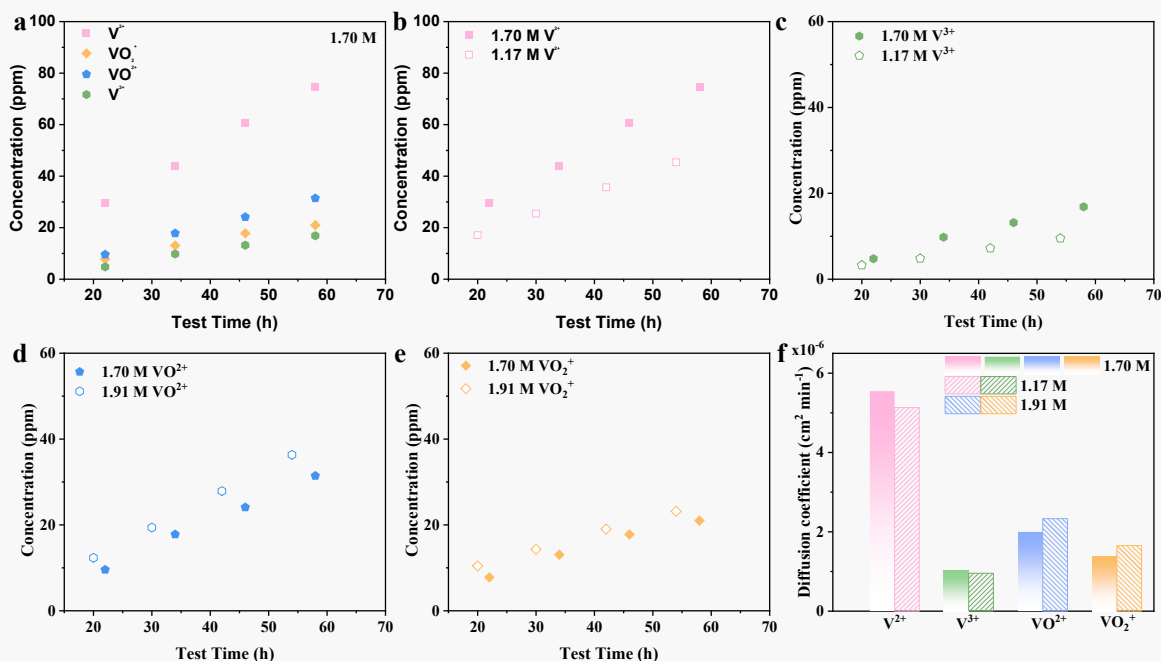


Fig. S16 Vanadium ion diffusion tests across an N212 membrane (operated at 28 ± 3 °C). **a**, Diffusion fluxes of various vanadium ions in 1.70 M electrolyte. **b-c**, Effect of reducing electrolyte concentration from 1.70 to 1.17 M on the diffusion fluxes of V^{2+} and V^{3+} . **d-e**, Effect of increasing electrolyte concentration from 1.70 to 1.91 M on the diffusion fluxes of VO^{2+} and VO_2^+ . **f** Variation of vanadium ion diffusion coefficients with electrolyte concentration. All tests were conducted at 28 ± 3 °C.

As shown in Fig. S16a, the flux of V^{2+} exhibits the highest value followed by those of VO^{2+} , VO_2^+ , and V^{3+} , which is consistent with a previous report.^{S2} Moreover, Fig. S16b-e demonstrates that

decreasing the electrolyte concentration profoundly reduces vanadium ion flux across the Nafion membrane, whereas increasing the concentration markedly enhances the flux. These results confirm that the transport of vanadium ions across the Nafion membrane can be approximated by Fick's law.^{S7}

The diffusion coefficients of vanadium ions across a Nafion 212 membrane were calculated using the following equation:^{S2}

$$\ln\left(\frac{C_A}{C_A - C_B}\right) = D \frac{A}{V_B L} t \quad (\text{Eq. S19})$$

where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), A is the effective membrane area (m^2), L is the membrane thickness (m), C_A is the vanadium ion concentration on the enrichment side (mol L^{-1}), C_B is the vanadium ion concentration on the deficiency side (mol L^{-1}), and t is the test time (s). In this calculation, the volume of deficiency side (V_B) and C_A were assumed constant.

The resulting values (Fig. S16f) exhibit good agreement with independent measurements reported previously.^{S2} These results further demonstrate that modulating the concentration of vanadium ions alters their diffusion rate across the Nafion membrane.

In these experiments, a flow battery cell equipped with a Nafion 212 membrane and two electrodes with a size of $40.00 \times 40.00 \text{ mm}^2$ was employed. The diffusion test for V^{2+} was conducted under N_2 protection to avoid the influence of air-induced V^{2+} oxidation. For each test, 20 mL of vanadium electrolyte was circulated on one side of the cell, while an equimolar MgSO_4 solution in 3 M H_2SO_4 served as the counter electrolyte on the opposite side. Both solutions were pumped at a flow rate corresponding to 51 rpm using a Longer BT100-2J peristaltic pump.

The paired electrolyte compositions were as follows:

- 1) Standard concentration (1.70 M): 1.70M V^{2+} , V^{3+} , VO^{2+} , or VO_2^+ in 3 M H_2SO_4 versus 1.70 M MgSO_4 in 3 M H_2SO_4 .
- 2) Reduced concentration (1.17 M): 1.17 M V^{2+} or V^{3+} in 3 M H_2SO_4 versus 1.17 M MgSO_4 in 3 M H_2SO_4 .
- 3) Increased concentration (1.91 M): 1.91 M VO^{2+} or VO_2^+ in 3 M H_2SO_4 versus 1.91 M MgSO_4 in 3 M H_2SO_4 .

Vanadium ion concentrations were determined using an Inductively Coupled Plasma–Optical Emission Spectrometer (Avio-200, PerkinElmer). Samples (0.2 ml) were withdrawn and diluted

7500-fold (for vanadium electrolytes) or 750-fold (for counter solutions) with deionized water prior to analysis.

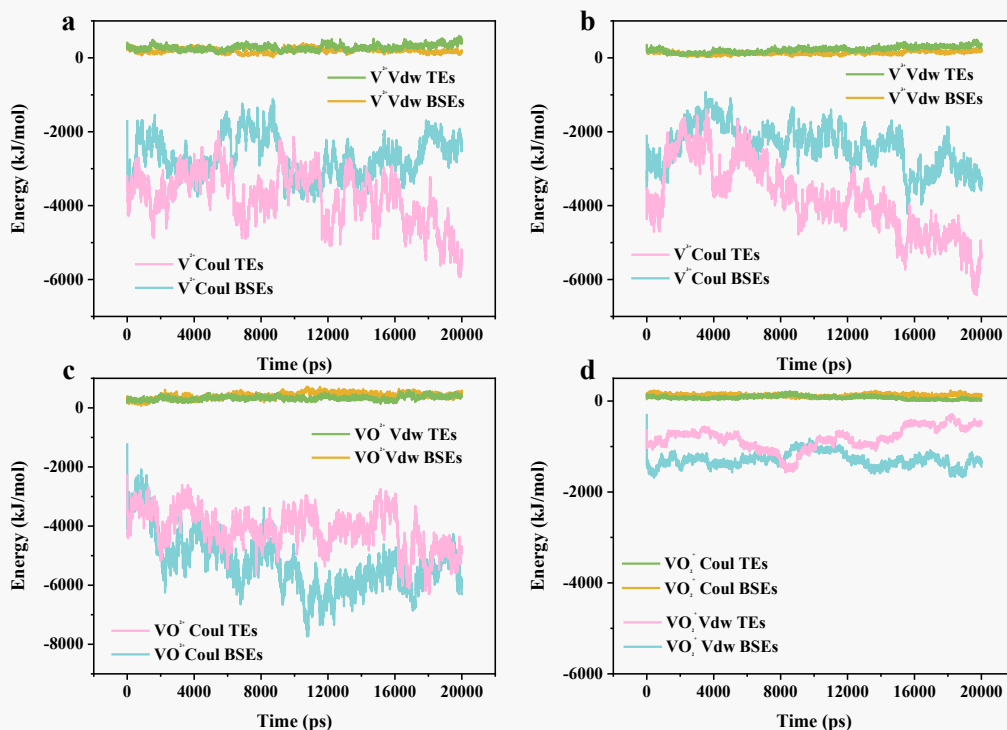


Fig. S17 Energies of vanadium ions in the Nafion membrane (simulated at 25 °C). The van der Waals and coulombic energy between **a**, V^{2+} , **b**, V^{3+} , **c**, VO^{2+} , **d**, VO_2^+ and sulfonic acid groups in Nafion membrane with the balanced-state electrolytes (BSEs) and traditional electrolytes (TEs).

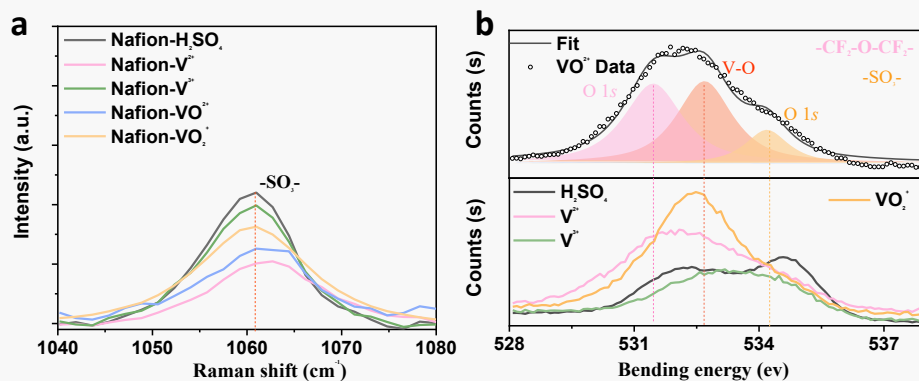


Fig. S18 Interactions between vanadium ion and sulfonic acid groups (operated at 23 ± 0.5 °C). **a**, Raman and **b**, XPS spectra of Nafion 212 immersed in different solutions.

In these tests, Nafion 212 was immersed separately for 5 days in 3.0 M H_2SO_4 , 1.7 M V^{2+} , V^{3+} , VO^{2+} , and VO_2^+ . As depicted in Fig. S17a, the Raman peak position of sulfonic acid groups shifts upon immersion of the Nafion membrane in vanadium electrolytes, demonstrating the interactions between vanadium ions and sulfonic acid groups.^{S8} It is more evident in the XPS results (Fig. S17b), where both the position and intensity of the O 1s peak attributable to the sulfonic acid groups (534.89 eV) markedly shift to lower values after introducing vanadium ions into Nafion membranes.^{S8,S9}

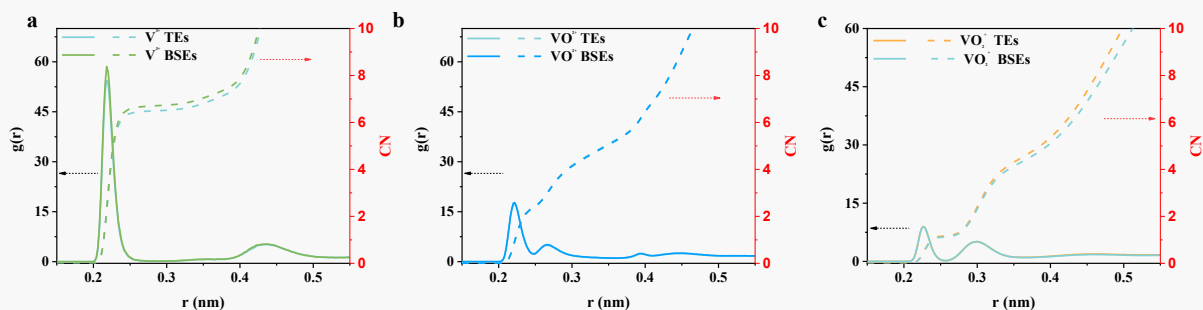


Fig. S19 Solvent structures of vanadium ions in Nafion membranes immersed in different electrolytes (simulated at 25 °C). The radial distribution function/coordination numbers of **a**, V^{3+} , **b**, VO^{2+} , and **c**, VO_2^+ in Nafion membrane with the balanced-state electrolytes (BSEs) and traditional electrolytes (TEs).

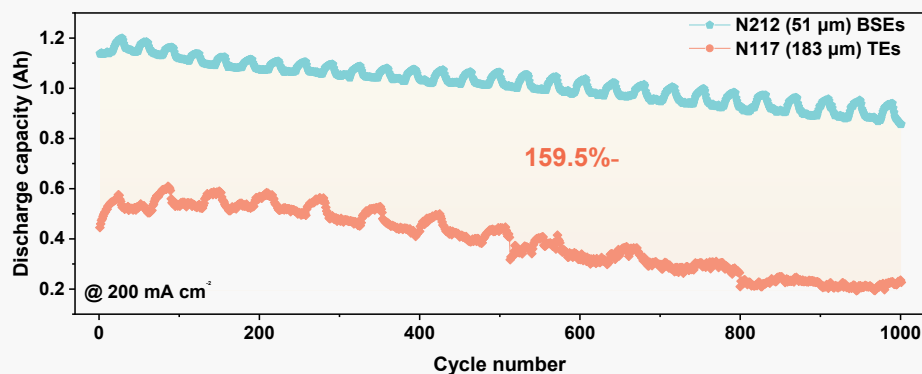


Fig. S20 Comparison of VRFBs with BSEs (P 1.91 M $\text{V}^{3.55+}$; N 1.17 M $\text{V}^{3.50+}$), combining with N212 (51 μm) and TEs (P 1.70 M $\text{V}^{3.50+}$; N 1.70 M $\text{V}^{3.50+}$), combining with N117 (183 μm) in discharge capacity vs. cycle number (operated at 28 ± 3 °C).

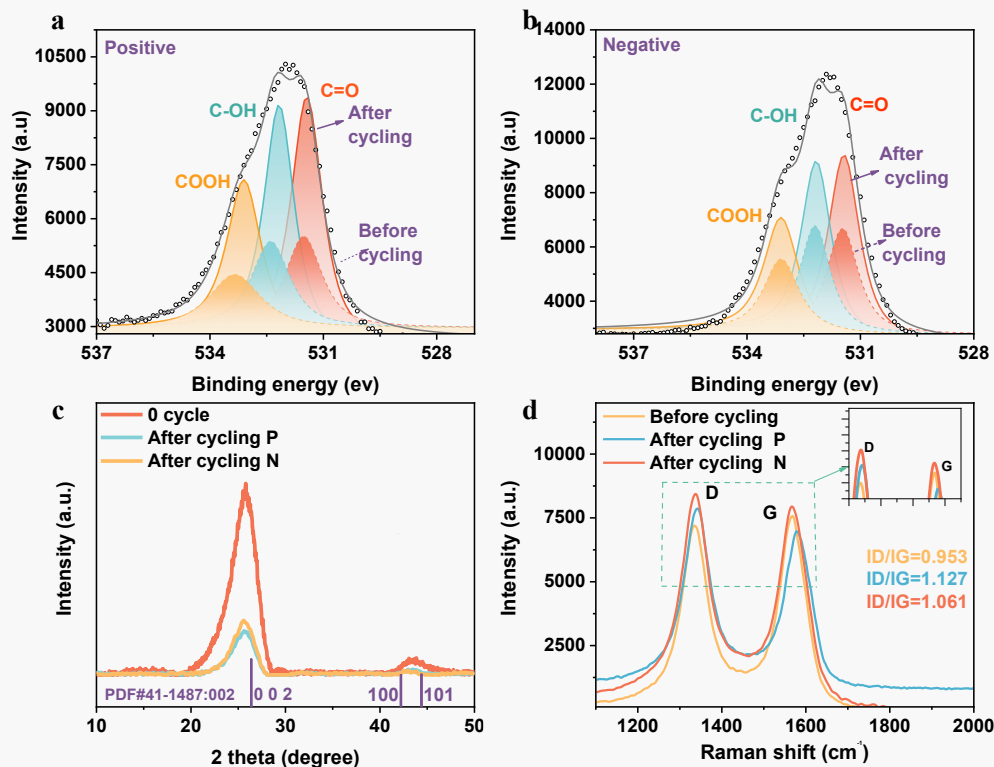


Fig. S21 Electrode degradation in VRFBs with BSEs after cycling. a-b, XPS spectra of the electrode on the positive and negative sides before and after cycling. c, XRD and d, Raman spectra of electrodes before and after cycling. (The electrodes were obtained by disassembling the VRFB after operating at 200 mA cm^{-2} for 1000 cycles and were subsequently dried in air. All tests were conducted at $23 \pm 0.5 \text{ }^{\circ}\text{C}$).

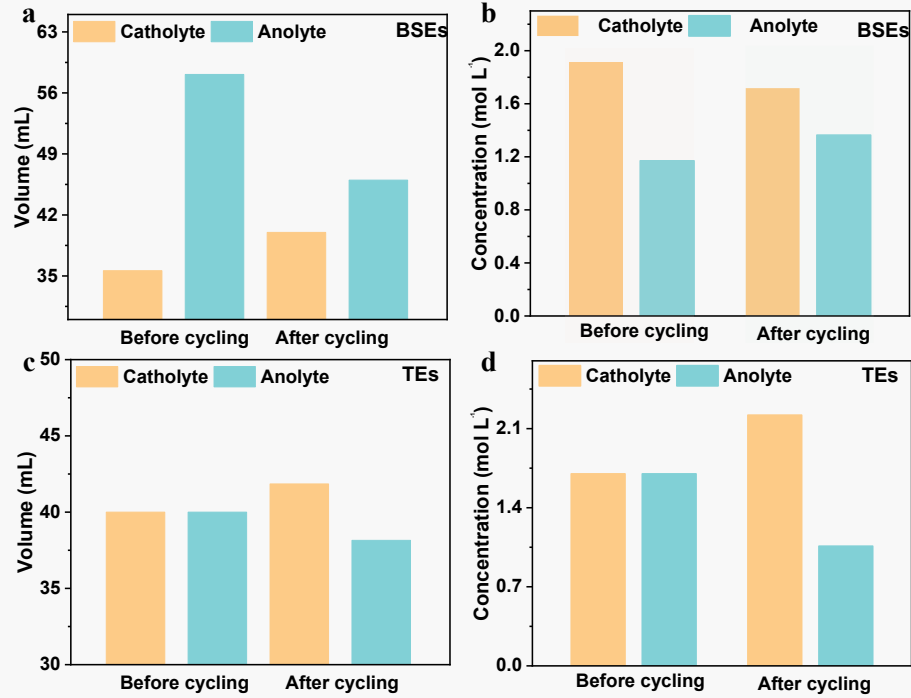


Fig. S22 Changes in electrolytes before and after cycling. a-b, Volume and concentration changes in VRFBs with BSEs (P 1.91 M $V^{3.55+}$; N 1.17 M $V^{3.50+}$). c-d, Volume and concentration changes in VRFBs with TEs (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$). (The electrolyte volumes of the VRFBs using TEs and BSEs were measured after cycling at 200 mA cm^{-2} for 400 cycles and 1000 cycles, respectively. The concentrations of the electrolytes were determined using a Lambda 365 UV-Visible Spectrophotometer (PerkinElmer, USA) at 23 ± 0.5 °C.

In the VRFB with BSEs, the amount of vanadium ions net flux from the negative to the positive sides can be calculated based on the variation of electrolytes' volume and concentration before and after cycling (Fig. S21a-b), as shown below:

$$(40 \times 1.72 - 46 \times 1.36) \times \frac{1}{2} / (0 \times 1.70) \text{ 儼 } 4.59\% \quad (\text{Eq. S20})$$

Similarly, in the VRFB with traditional electrolytes, the net flux of vanadium ions from the negative to the positive sides (Fig. S21c-d) can be obtained as below:

$$(42 \times 2.22 - 38 \times 1.06) \times \frac{1}{2} / (0 \times 1.70) \text{ 儼 } 38.94\% \quad (\text{Eq. S21})$$



Fig. S23 Electrolyte net flux between the positive and negative sides in VRFBs with BSEs (P 1.91 M $V^{3.55+}$; N 1.17 M $V^{3.50+}$) and TEs (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$) combining with N212 before and after cycling.

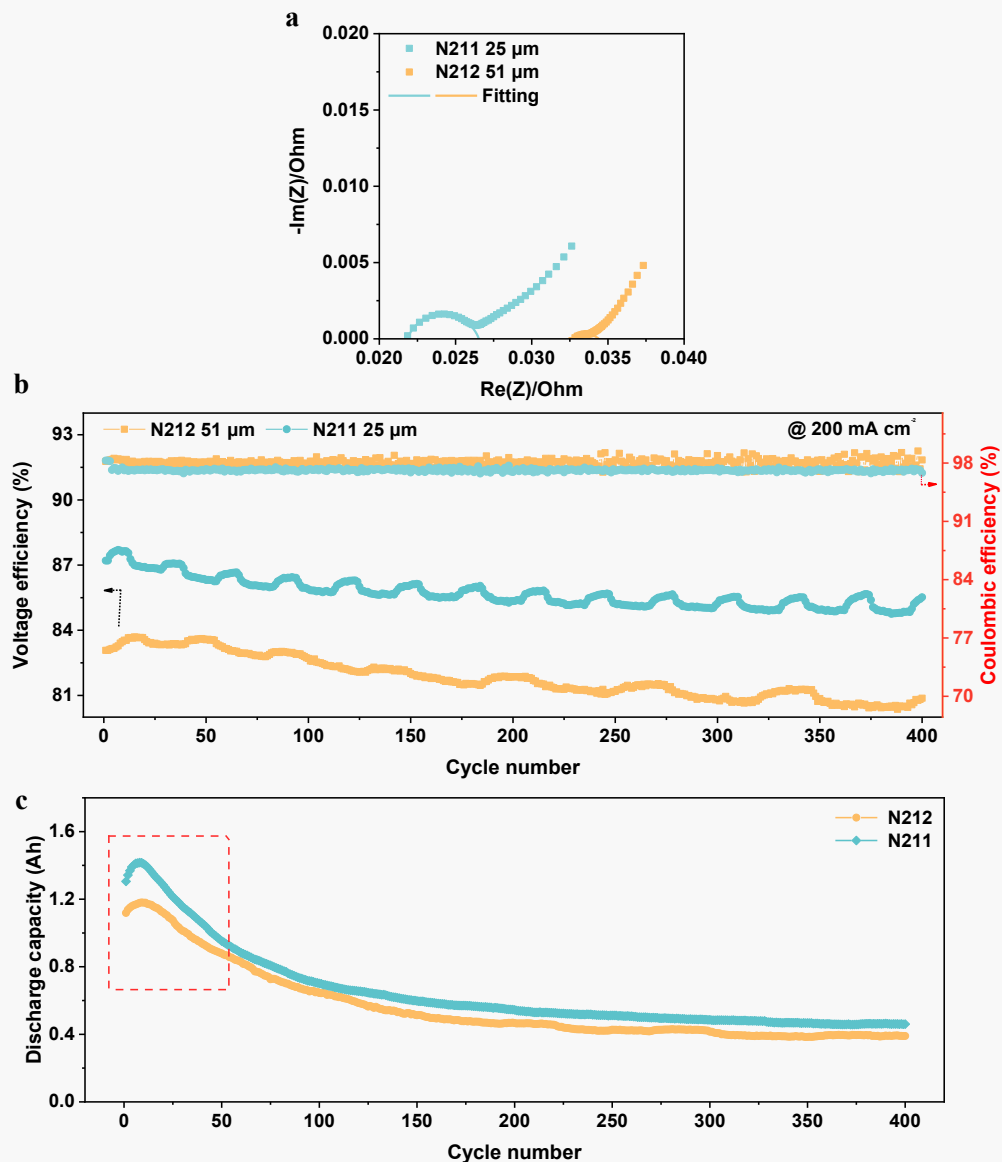


Fig. S24 Performance comparison of VRFBs employing N212 and N211 membranes with traditional electrolytes. a, The EIS spectrum **b**, voltage/coulombic efficiency, and **c**, discharge capacity of VRFBs using N212 and N211 membranes over cycling. Tests were conducted at 28 ± 3 °C for battery cycling and 23 ± 0.5 °C for EIS.

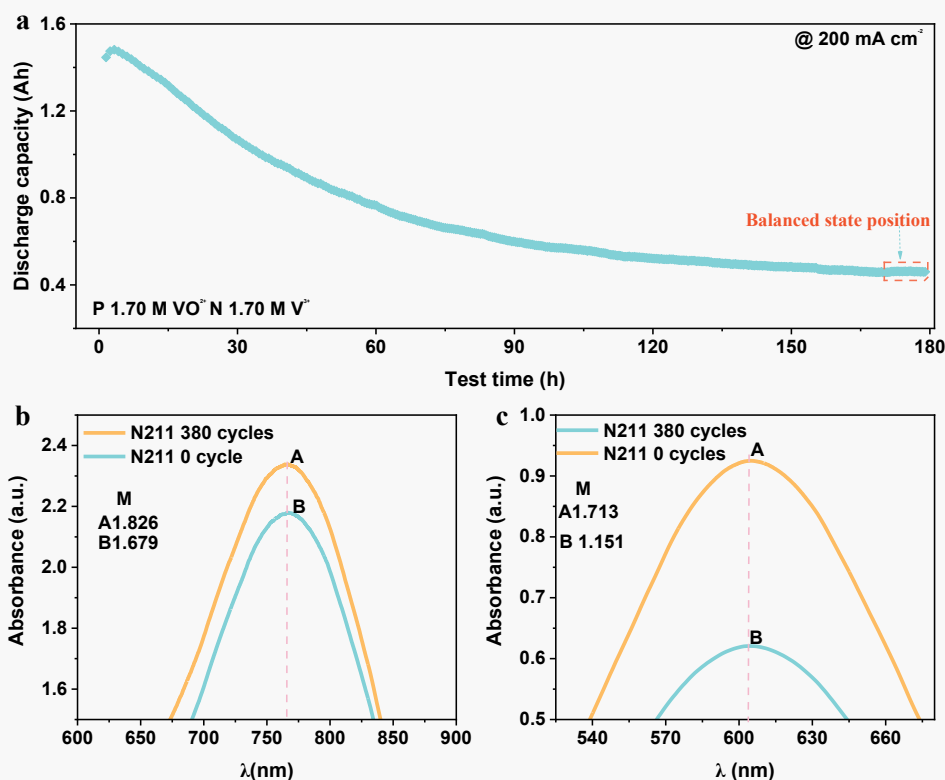


Fig. S25 Electrolyte concentration in VRFB with N211 at the balanced state. a, Discharge capacity varies with test time. UV spectra of electrolytes at the balanced state on the b, positive and c, negative sides. (The concentrations of the electrolytes were measured using a UV-visible spectrophotometer at 23 ± 0.5 °C after 180 cycles.) Tests were conducted at 28 ± 3 °C for battery cycling and 23 ± 0.5 °C for UV-Vis.

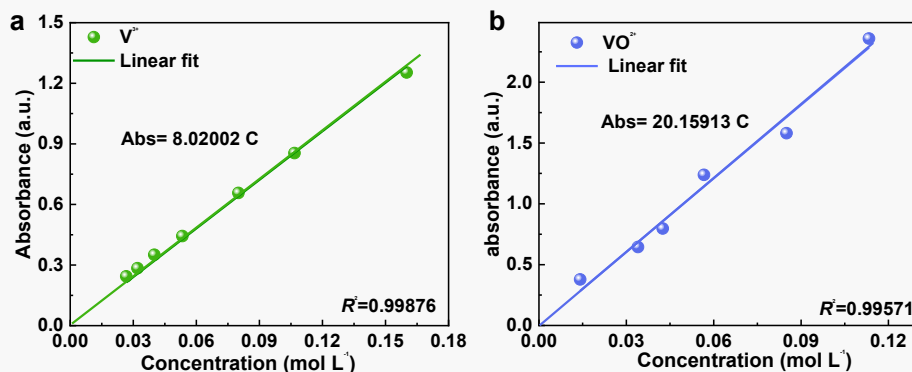


Fig. S26 UV-Vis calibration curves. a-b Calibration curves for V³⁺ and VO²⁺ after 15-fold dilution with deionized water. Tests were conducted at 23 ± 0.5 °C.

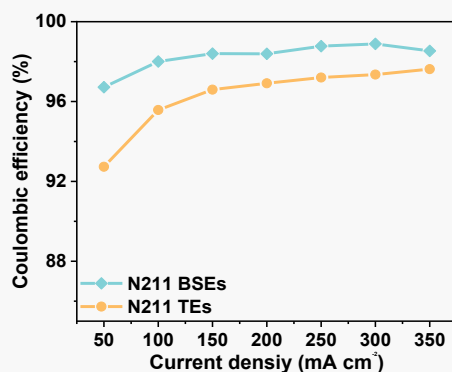


Fig. S27 Effects of BSEs on improving the coulombic efficiency of the VRFB with N211 (conducted at 28 ± 3 °C).

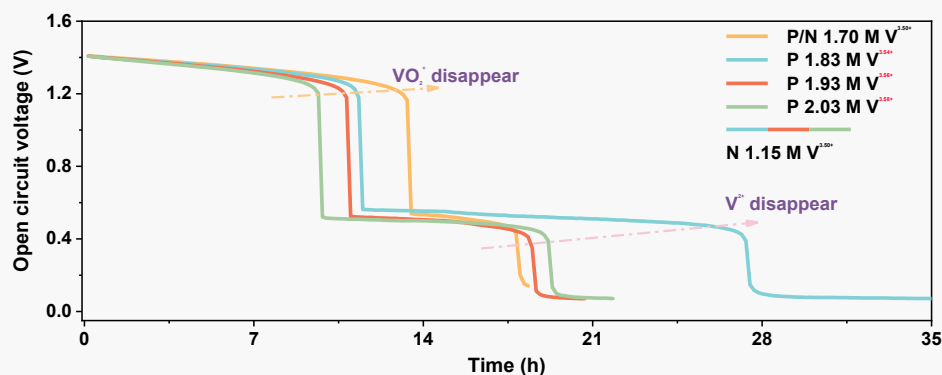


Fig. S28 Self-discharge curves of VRFBs with the N211 membrane and different electrolytes (operated at 28 ± 3 °C).

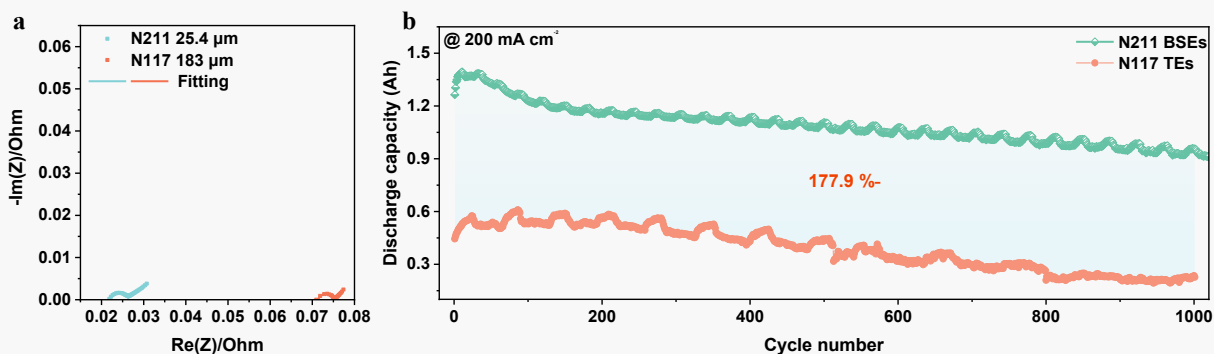


Fig. S29 Comparison of resistance and discharge capacity in VRFBs using N211 and N117 membranes. **a**, EIS spectrum and **b**, discharge capacity of the VRFB with N211/BSEs and N117/TEs. Tests were conducted at 28 ± 3 °C for battery cycling and 23 ± 0.5 °C for EIS.

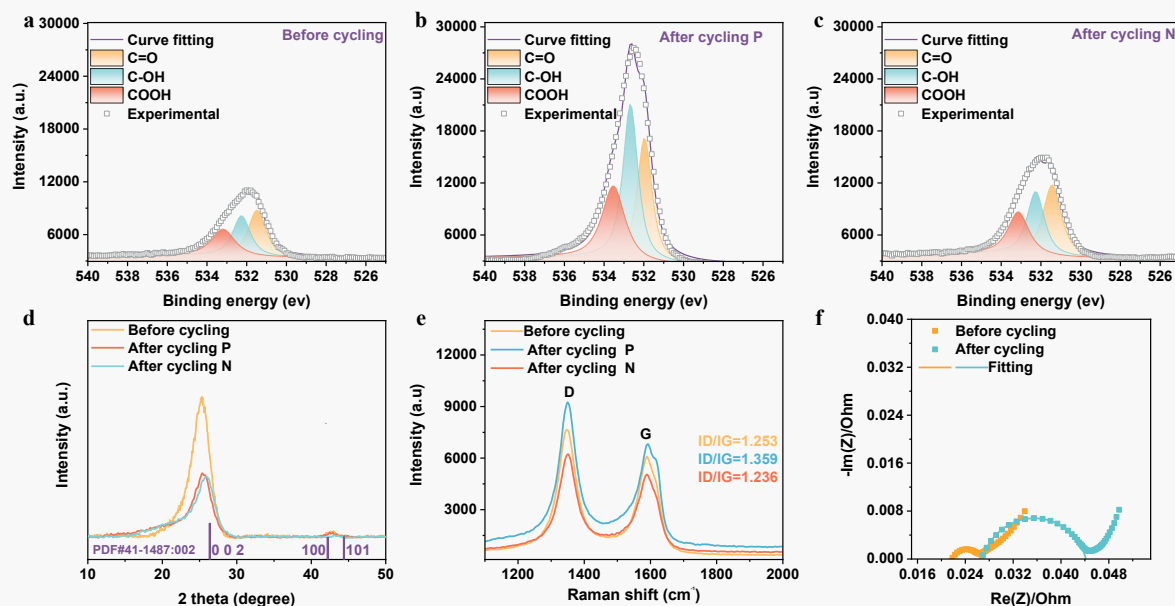


Fig. S30 Electrode changes in the VRFB with N211/BSEs after cycling. **a-c**, XPS, **d**, XRD, and **e**, Raman spectra of electrodes on the positive and negative sides before and after 1000 cycles. **f**, EIS spectrum of the VRFB with N211 combined with BSEs before and after 1000 cycles. (The electrodes were obtained by disassembling the VRFB after operating at 200 mA cm^{-2} for 1000 cycles and were subsequently dried in air. All tests were conducted at $23 \pm 0.5^\circ \text{C}$).

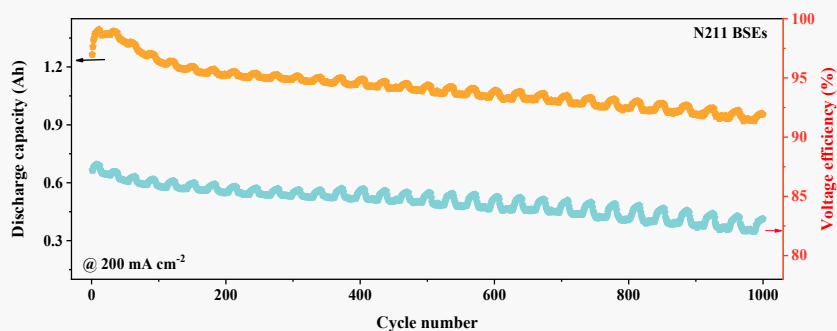


Fig. S31 Discharge capacity and voltage efficiency of the VRFBs using N211 combined with BSEs (operated at $28 \pm 3^\circ \text{C}$).

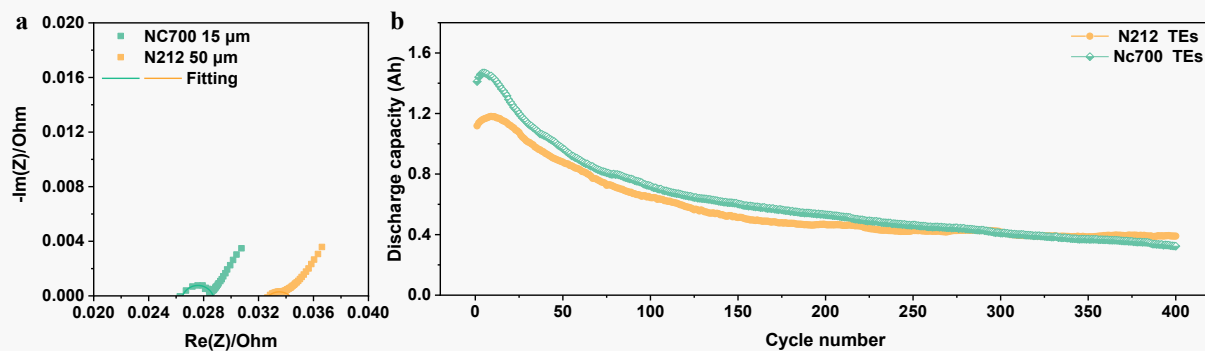


Fig. S32 Comparison of VRFBs with NC700 and N212. **a**, EIS spectrum and **b**, discharge capacity of VRFBs with NC700 and N212 tested with the TEs (P 1.70 M $\text{V}^{3.50+}$; N 1.70 M $\text{V}^{3.50+}$) at 200 mA cm^{-2} . Tests were conducted at 28 ± 3 °C for battery cycling and 23 ± 0.5 °C for EIS.

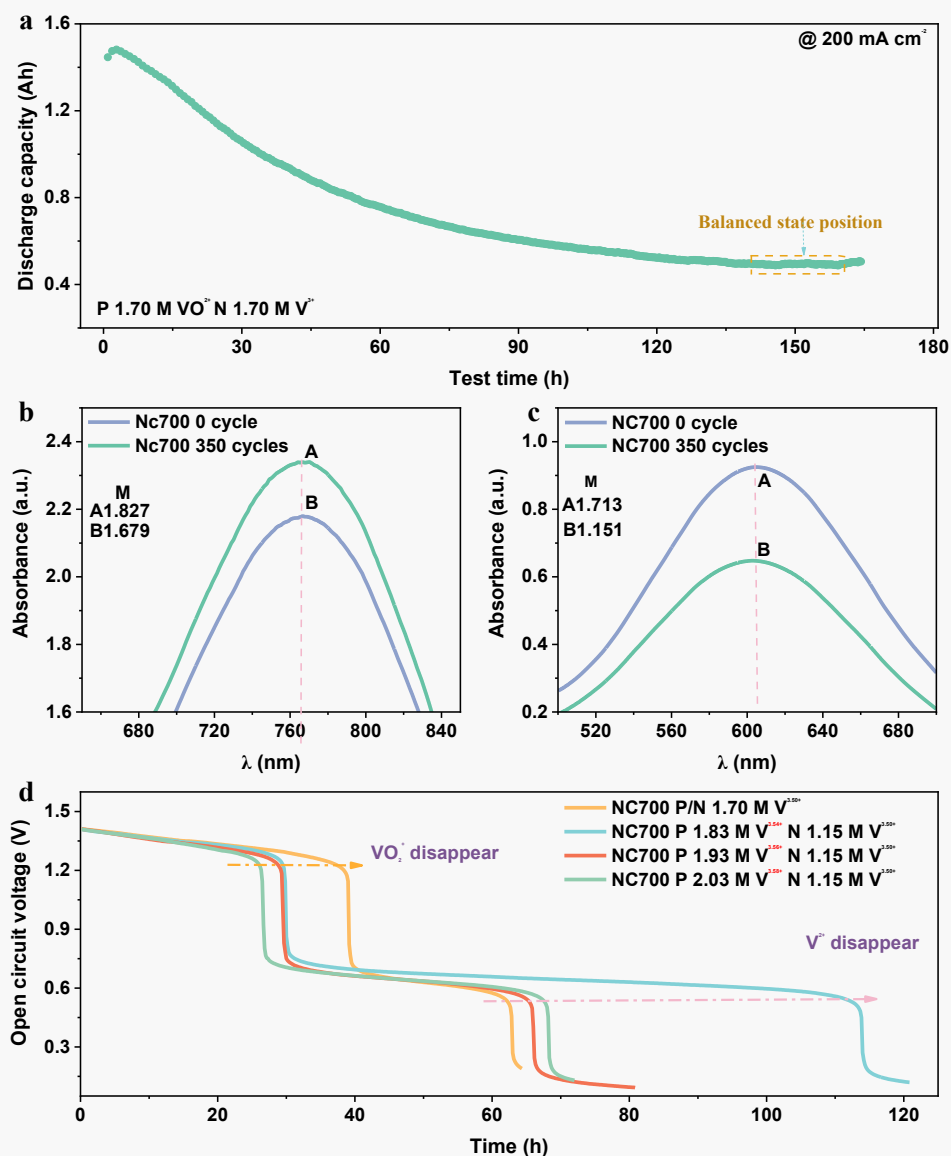


Fig. S33 Concentrations of the VRFB with NC700 at balanced state. **a**, Discharge capacity variation with test time in the VRFB using TEs ($\text{P } 1.70 \text{ M V}^{3.50+}$; $\text{N } 1.70 \text{ M V}^{3.50+}$). UV spectra of the VRFB electrolytes at the balanced state on **b**, the positive and **c**, negative sides. **d**, Self-discharge curves of VRFBs with different concentrations of electrolyte. Tests were conducted at $28 \pm 3^\circ \text{C}$ for battery cycling and Self-discharge. The concentrations of the electrolytes were measured using a UV-visible spectrophotometer at $23 \pm 0.5^\circ \text{C}$ after operating at 200 mA cm^{-2} for 150 cycles.

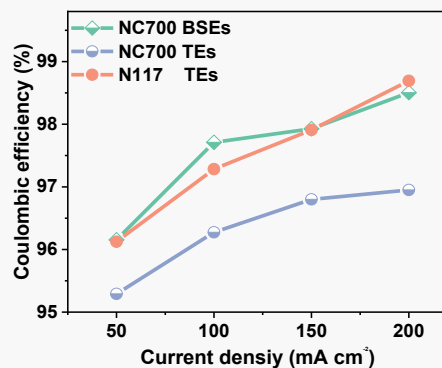


Fig. S34 Effects of BSEs on improving the coulombic efficiency of the VRFB with an NC700 (operated at $28 \pm 3^\circ\text{C}$).

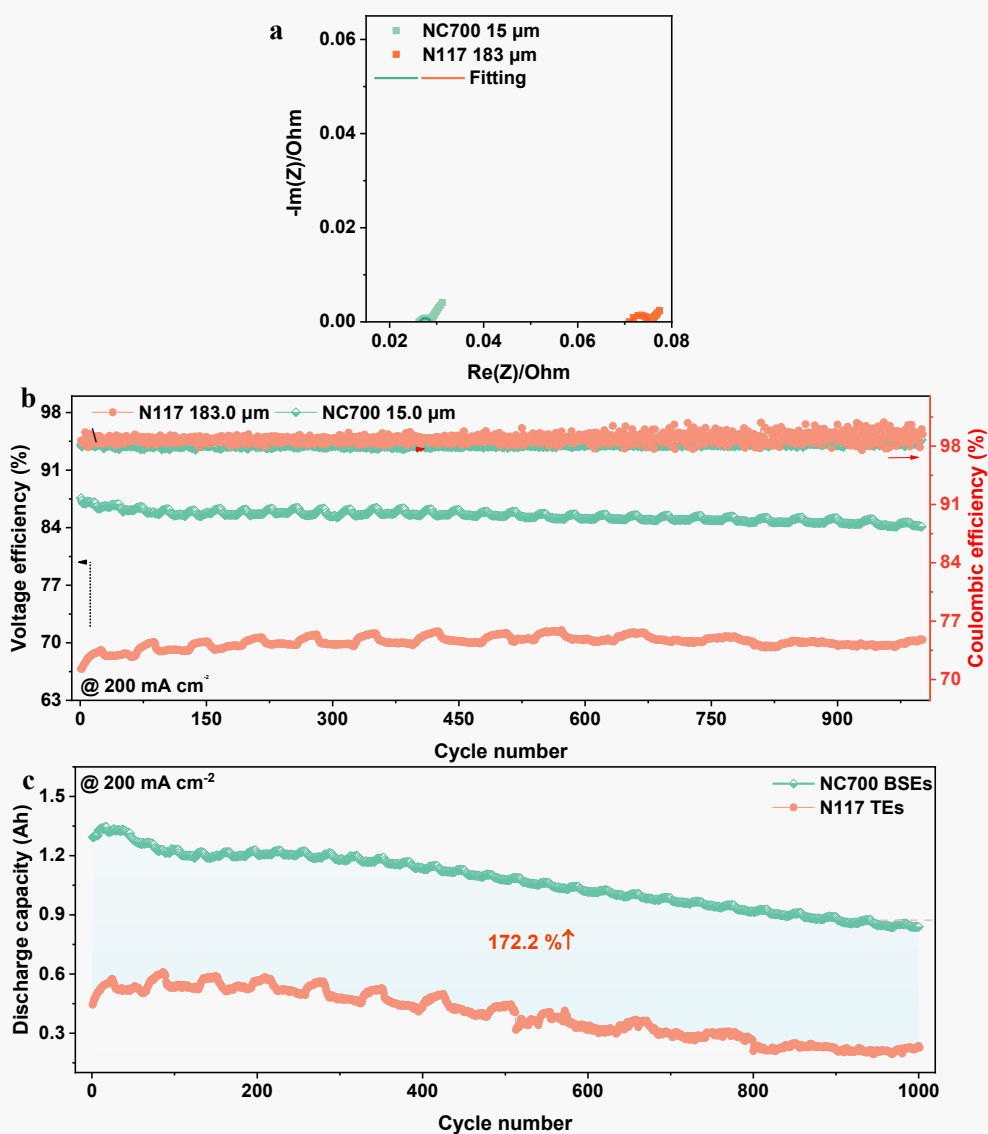


Fig. S35 Performance comparison of VRFBs with NC700 and N117. **a**, EIS spectrum, **b**, voltage/coulombic efficiency, and **c**, discharge capacity of VRFBs with NC700 combined with the BSEs (P

1.83 M $V^{3.54+}$, N 1.15 M $V^{3.50+}$) and that with N117 combined with the TEs (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$). Tests were conducted at 28 ± 3 °C for battery cycling and 23 ± 0.5 °C for EIS.

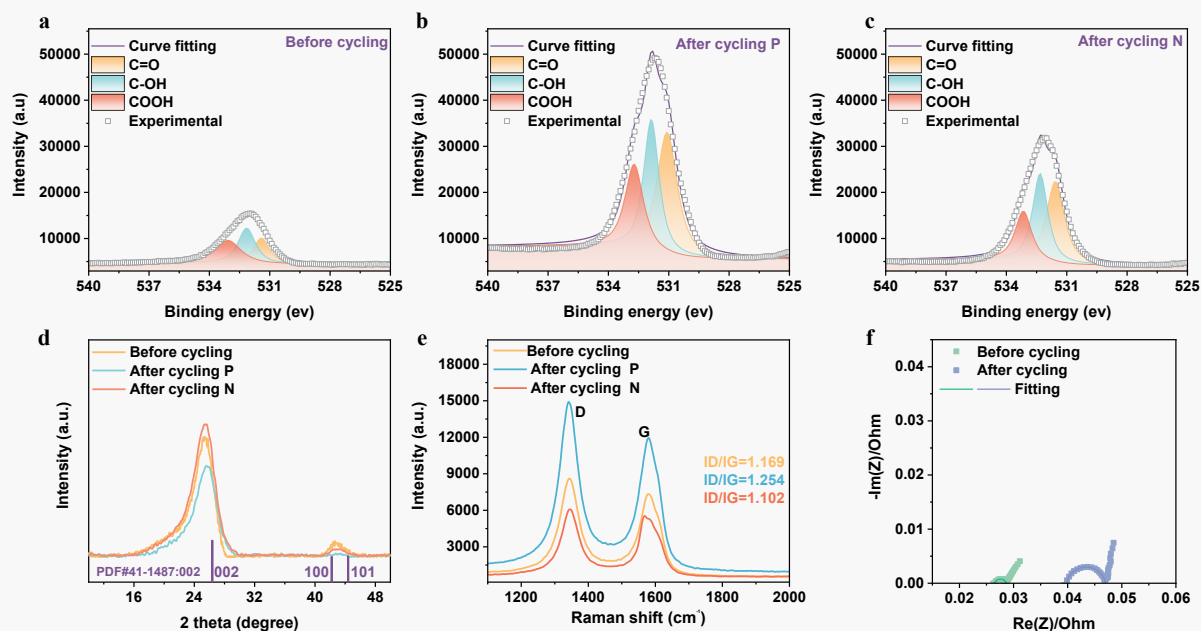


Fig. S36 Electrode changes in the VRFB with NC700/BSEs after cycling. **a-c** XPS spectra of pristine electrodes and electrodes on the positive and negative sides before and after 1000 cycles. **d**, XRD and **e**, Raman spectra of electrodes on the positive and negative sides before and after 1000 cycles. **f**, EIS spectrum of the VRFB before and after 1000 cycles. (The electrodes were obtained by disassembling the VRFB after operating at 200 mA cm^{-2} for 1000 cycles and were subsequently dried in air. All tests were conducted at 23 ± 0.5 °C.

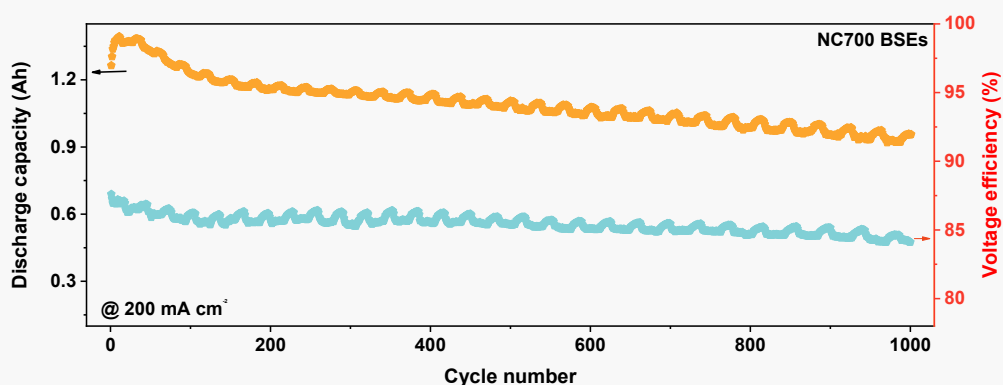


Fig. S37 Discharge capacity and voltage efficiency of VRFBs with NC700 and BSEs (operated at $28 \pm 3^\circ\text{C}$).

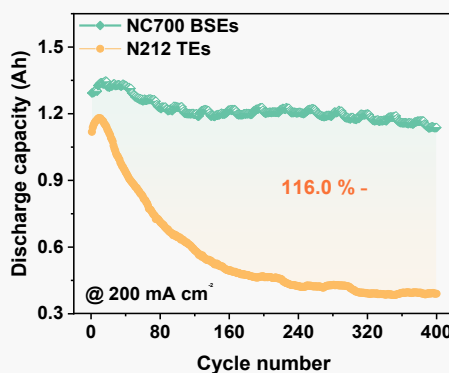


Fig. S38 Comparison of capacity retention rates between VRFBs employing NC700/BSEs and those with N212/TEs (operated at $28 \pm 3^\circ\text{C}$).

5. Cost model

Table S2 Electrolyte utilization in VRFBs with different systems.

VRFB system	Accumulated discharge capacity over 400 cycles (Ah)	Discharge capacity over 400 cycles ($\text{Ah cycle}^{-1} \text{mol}^{-1}$)
Current advanced system	225.10281	4.137919301
System with BSEs	486.2741	8.938862132

The discharge capacity of electrolytes per cycle per mol ($D_{\text{CP}} / \text{Ah mol}^{-1}$) is calculated as follows:

$$D_{\text{CP}} = \frac{D_{\text{AC}}}{C_{\text{NO}}} \times \frac{1000}{V_{\text{E}} \cdot E_{\text{C}}} \quad (\text{Eq. S22})$$

where D_{AC} , C_{NO} , V_E , and E_C represent the accumulated discharge capacity (Ah), the cycle number, the electrolyte volume (mL), and the electrolyte concentration (M), respectively.

The capital cost reduction for a VRFB system using BSEs and NC700 can be calculated as below:

$$C_{Cr} = (C_{R-M} + C_{R-E}) - (C_{R-M} \times M_{CR} + C_{R-E} \times E_{CR}) \quad (\text{Eq. S23})$$

where, C_{Cr} is the capital cost reduction ratio; C_{R-M} and C_{R-E} are the cost ratios of membrane (10.08%) and electrolyte (62.79%), respectively, over the capital cost of a current advanced 1 MW/4 MWh VRFB system;^{S10} M_{CR} and E_{CR} are the corresponding cost ratios of the membrane and electrolyte in the BSEs and NC700 based system^{S11} relative to a currently advanced VRFB system.

$$M_{CR} = \frac{472.281}{2329.825} \quad (\text{Eq. S24})$$

$$E_{CR} = \frac{4.137919}{8.938862} \quad (\text{Eq. S25})$$

Hence, the capital cost reduction for a VRFB system with BSEs compared to the current advanced VRFB system can be obtained:

$$C_{Cr} = (10.08 + 62.79) - \left(10.08 \times \frac{472.281}{2329.825} + 62.79 \times \frac{4.137919}{8.938862} \right) = 41.76 \quad (\text{Eq. S26})$$

The specific costs of electrolyte and membrane in different VRFB systems are listed in Table S3.

Table S3 Membrane and electrolyte costs as a proportion of the capital cost in a 1 MW/4 MWh VRFB system. ^{S10, S11}

	Membrane type	Membrane cost/ m ² (\$)	Membrane to capital cost ratio	Discharge capacity over 400 cycles (Ah cycle ⁻¹ mol ⁻¹)	Electrolyte to capital cost ratio
Current advanced system	N212	2329.825	10.80%	4.14	62.79%
System with BSEs	NC700	472.281	2.19%	8.94	29.08%

Table S4 Performance comparison between this work and other studies published in top journals in the past five years. (Note: P, N present electrolyte on the positive and negative sides)

Membrane type	Thickness (μm)	Capacity decay rate per cycle	EE	Electrolyte concentration/M	Related work
Nafion NC700 (Pristine Commercial Membrane)	15	0.015% during 1000 cycles at 200 mA cm⁻²	85.7% at 200 mA cm⁻²	P 1.91M N1.17 M	This work
ZN-based composite membranes	46	0.065% during 1000 cycles at 200 mA cm ⁻²	Around 80% at 200 mA cm ⁻²	P/N 1.5 M	Nat. Sustain. 2022, 5(12): 1080-1091.
Trimesoyl chloride (TMC) and m-phenylenediamine (MPD) composite membranes	40	0.14% during 100 cycles at 80 mA cm ⁻²	Around 83% at 200 mA cm ⁻²	P/N 1.5 M	Nat. Commun. 2020, 11(1): 13
PFSA-based hybrid membrane	46 ± 1	0.07% during 600 cycles at 120 mA cm ⁻²	79% at 200 mA cm ⁻²	P/N 1.25 M	Adv. Funct. Mater. 2022, 32(8): 2109427.
Cyanuric chloride (CC), CC and 2,4,6-tris(4-aminophenyl)-s-triazine as monomers for the self-standing COP membrane	54	0.142 % during 100 cycles at 200mA cm ⁻²	83 % at 200 mA cm ⁻²	P/N 1.7 MV	Angew.Chem, 2025, 64(1): e202413046.
Fluoroalkyl-grafted polyoxometalate (POMs) nanoclusters modified Nafion	70	0.11 % during 200 cycles at 120mA cm ⁻²	84.3% at 200 mA cm ⁻²	P/N 1.5 M	Angew.Chem, 2024, 136(36): e202409006.
Sulfonated covalent organic frameworks Nafion	24	0.13 % during 500 cycles at 100 mA cm ⁻²	77.5% at 200 mA cm ⁻²	P/N 1.5 M	Energy Storage Mater. 2024, 67: 103293
Hybrid membranes incorporated sulfonated-pCTF (s-pCTF)	40 ± 2	0.14% during 350 cycles at 120 mA cm ⁻²	78.53% at 200 mA cm ⁻²	P/N 1.5 M	Adv. Funct. Mater. 2023, 33(21): 2300138.

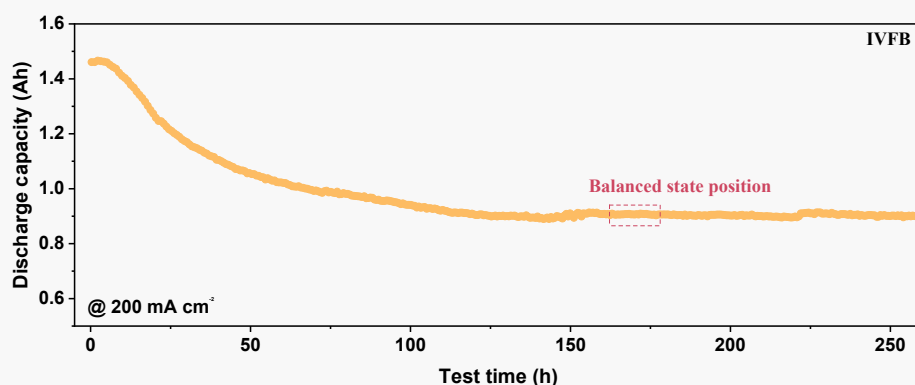


Fig. S39 Discharge capacity variation with test time in the IVFB using TEs (P 1.70 M $\text{Fe}^{3.0+}$; N 1.70 M $\text{V}^{2.0+}$) (operated at 28 ± 3 °C).

6. Data and script

All data for the figures in the main text and the script for Fig. 2b are available via the following link.

<https://doi.org/10.6084/m9.figshare.28938164>

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