Supplemental Information

A 1.51 V pH Neutral Redox Flow Battery towards Scalable Energy Storage

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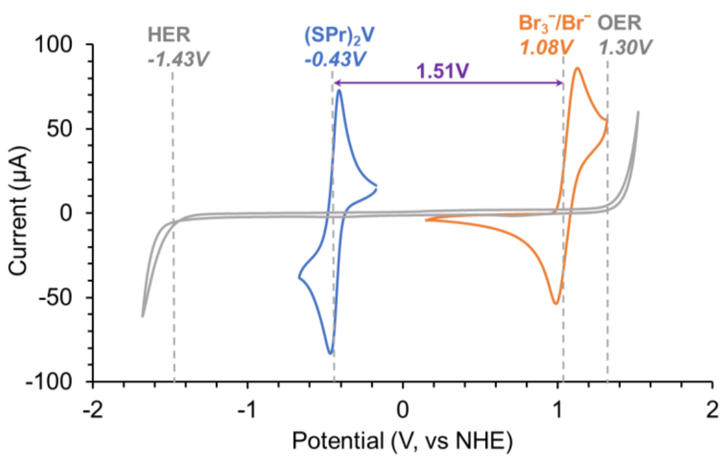

Figure S1. The cyclic voltammograms of $(SPr)_2V$ (-0.43 V) and NH_4Br (1.08 V) in 0.5M NH_4Cl aqueous electrolyte. Experiment conditions: 4.0 mM $(SPr)_2V$ or 50 mM NH_4Br, 100 mV/s scan rate, glassy carbon working electrode for $(SPr)_2V$, Pt working electrode for NH_4Br, glassy carbon counter electrode, Ag/AgCl reference electrode.

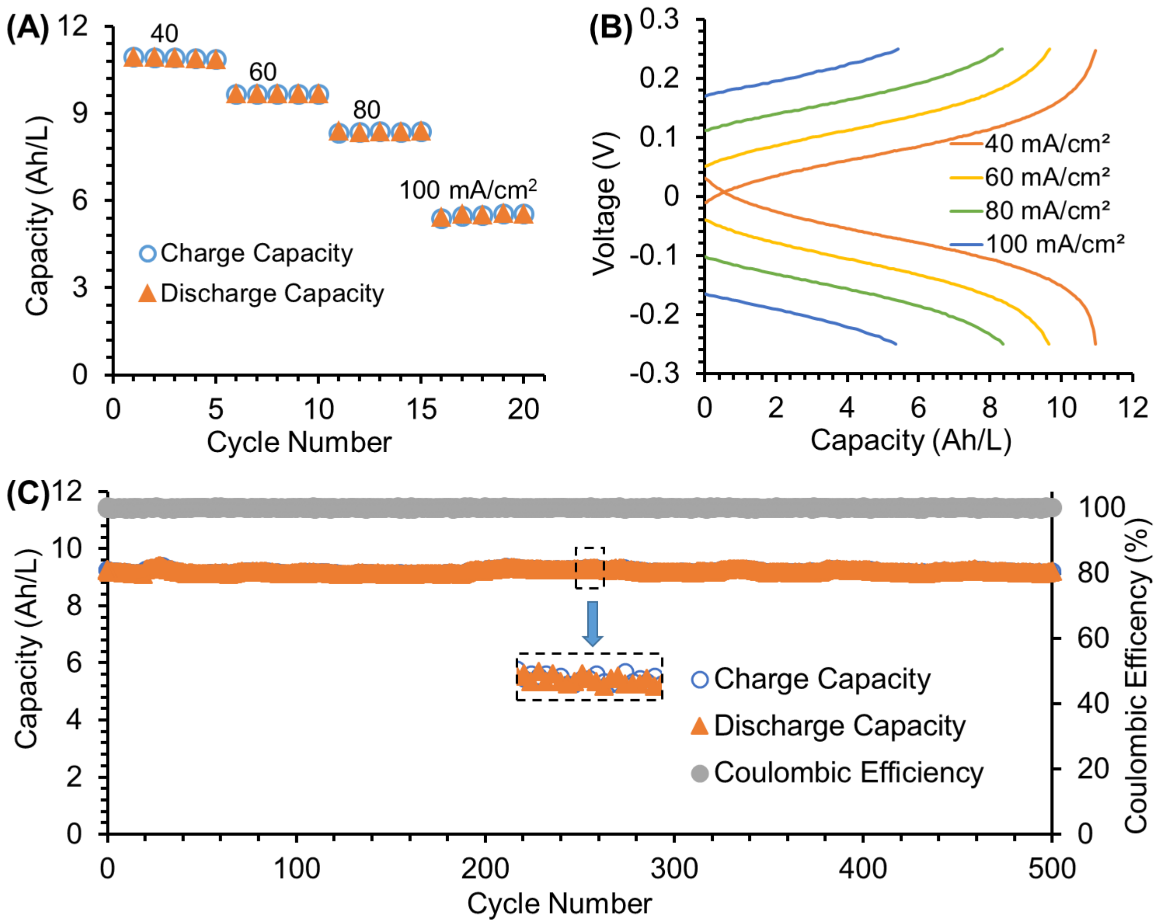

Figure S2. (A) Plot of battery capacity versus cycling numbers of the $(SPr)_2V/(SPr)_2V^{-\cdot}$ half-cell RFB at current densities from 40 to 100 mA/cm^2. (B) Representative charge and discharge curves at current densities from 40 to 100 mA/cm^2 for the half-cell RFB. (C) Extended 500 cycle data of the half-cell RFB showing charge capacity, discharge capacity, and Coulombic efficiency versus cycle number at 60 mA/cm^2 current density. Conditions: anolyte, 0.5 M $(SPr)_2V$ in 1.0 M NH_4Cl; catholyte, 0.5 M $(SPr)_2V^{-\cdot}$ in 1.0 M NH_4Cl; Nafion® 212 cation-exchange membrane, pH = 7.0, 25 ^{o}C.

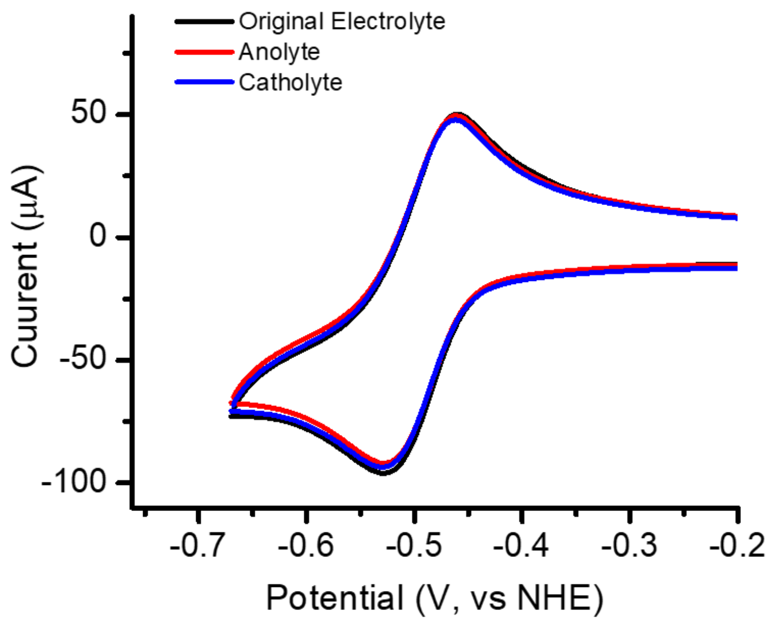

Figure S3. Post CV analysis of the $(SPr)_2V/(SPr)_2V^{-\cdot}$ half-cell RFB after the cycling test.

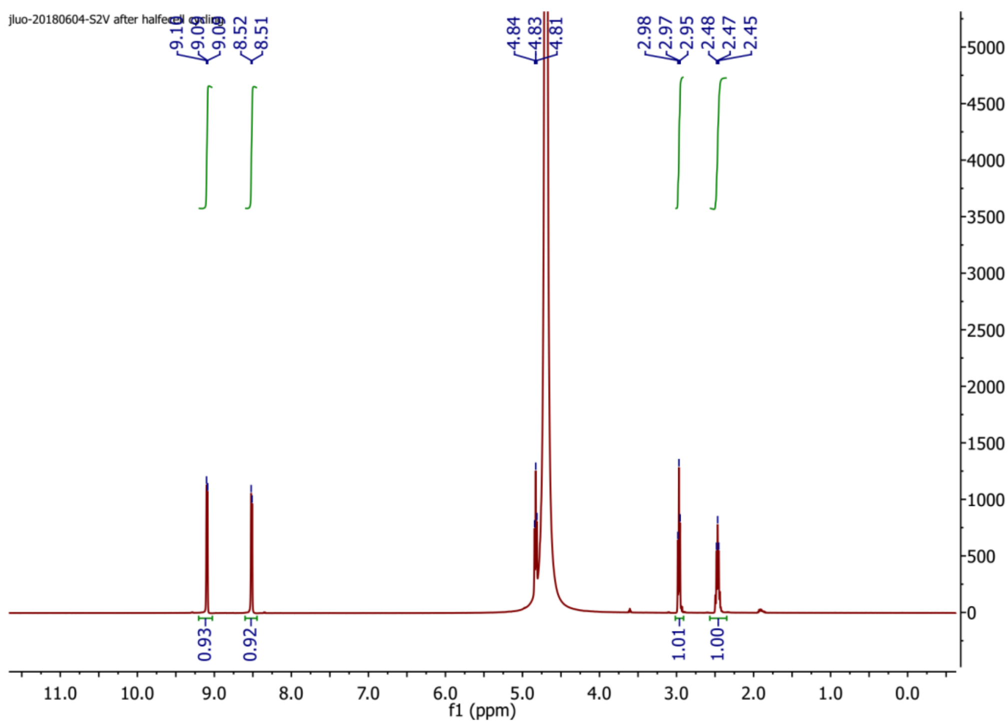

Figure S4. Post ^{1}H-NMR analysis of the $(SPr)_2V/(SPr)_2V^{-\cdot}$ half-cell RFB after 500 charge/discharge cycles.

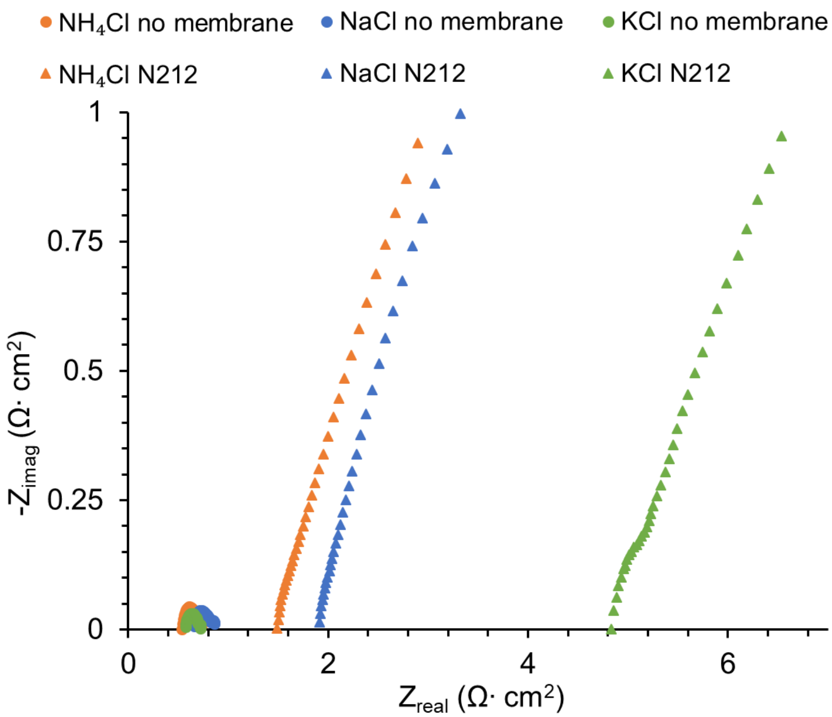

Figure S5. EIS curves of flow batteries without membrane and with a Nafion 212 membrane in the presence of 1.0 M NH_4Cl, 1.0 M NaCl, or 1.0 M KCl as supporting electrolyte.

***Notes for Figure S5*:** To compare the cation conductivity of ammonium electrolytes with the widely used sodium and potassium electrolytes in the Nafion 212 membrane, the area resistance of the Nafion 212 membrane was tested in 1.0 M NH_4Cl, 1.0 M NaCl, and 1.0 M KCl solutions by electrochemical impedance spectroscopy (EIS) measurements (Figure S5). In a general procedure, two flow batteries, one with a membrane and one without the membrane, are circulated with a same electrolyte and are measured by EIS to get their area resistances. Then the membrane area resistance was calculated as the difference between the area resistances of two flow batteries. The Nafion 212 membrane displayed lowest area resistance in NH_4Cl solution (0.95 Ω•cm^2), which is much smaller than that of NaCl (1.25 Ω•cm^2) and KCl (4.26 Ω•cm^2) solutions. And the trend of the area resistance of the Nafion 212 membrane is NH_4Cl < KCl < NaCl. These results indicate that NH_4^+ cation has the highest ion conductivity among these three cations in the Nafion 212 membrane.

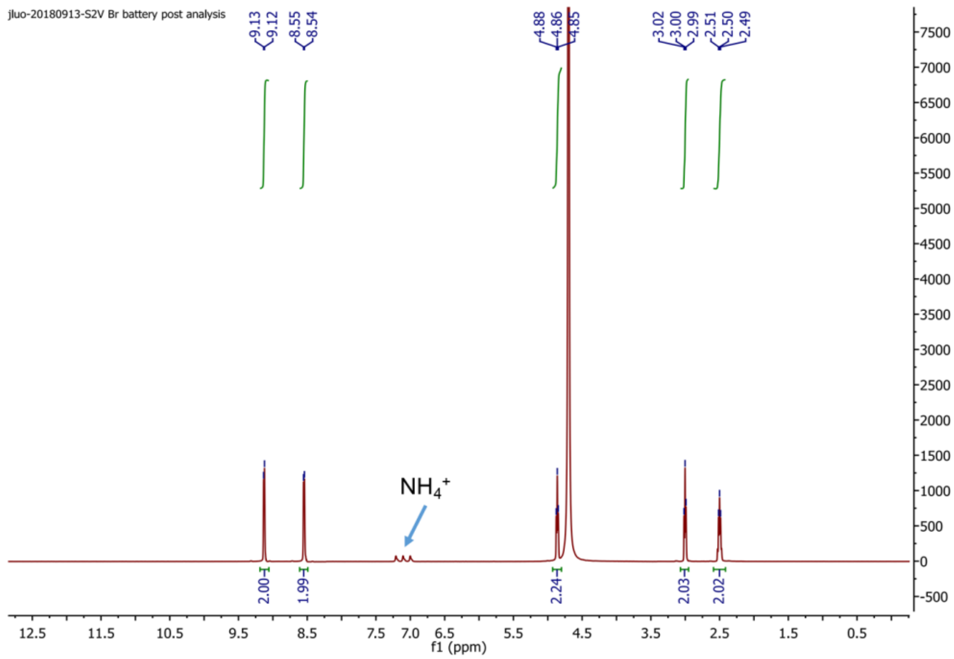

Figure S6. Post [1]H-NMR analysis of $(SPr)_2V$ anolyte in the 1.0 M $(SPr)_2V$/Br full-cell AORFB after 50 charge/discharge cycles. (The triplet peak between 6.8~7.2 ppm is [1]H-NMR signals of NH_4^+ cation.)

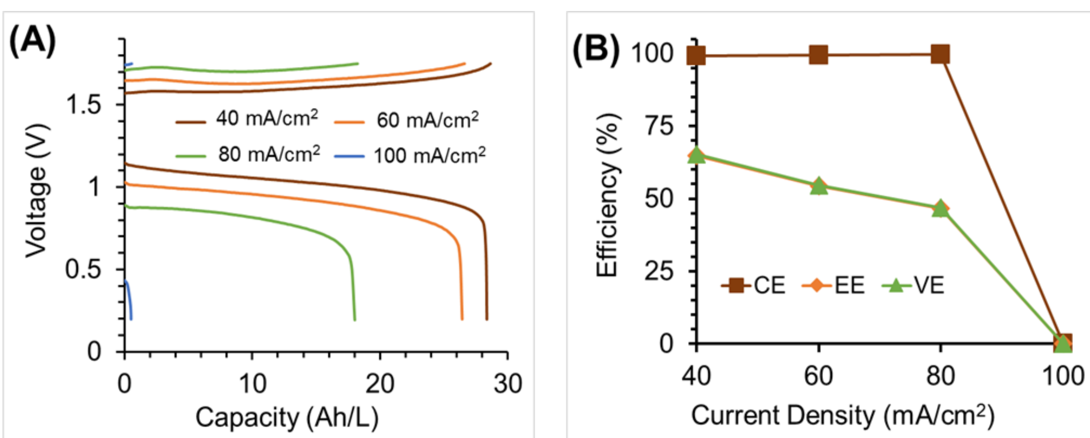

Figure S7. (A) Representative charge and discharge curves at current densities from 40 mA/cm^2 to 100 mA/cm^2 for the 1.5 M $(SPr)_2V$/Br AORFB. (B) Plots of average Coulombic efficiency (CE), energy efficiency (EE), and voltage efficiency (VE) at different operational current densities. Conditions: anolyte, 1.5 M $(SPr)_2V$ in 1.0 M NH_4Br; catholyte, 4.0 M NH_4Br with 0.2 M Br_2; Nafion 115 cation-exchange membrane, bare GF as anode and cathode, pH = 7.0, 25 ^oC.

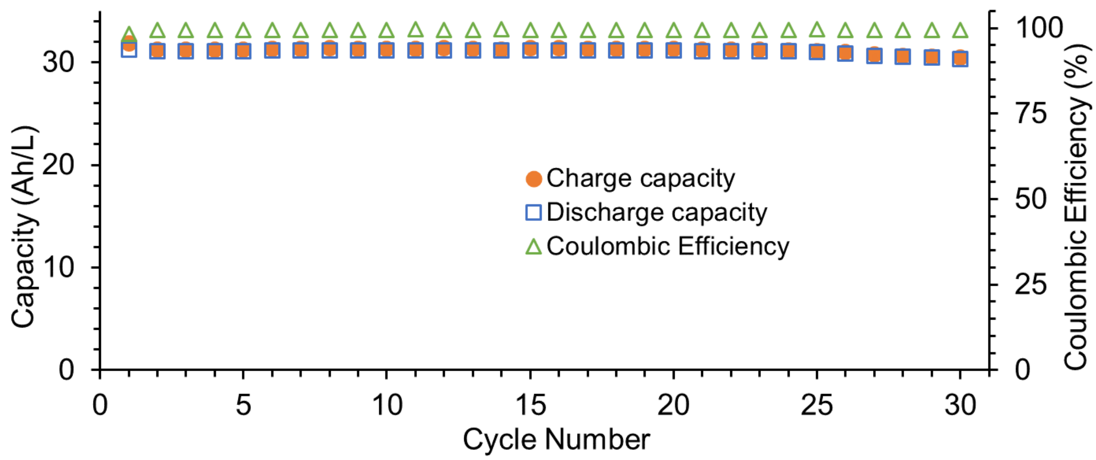

Figure S8. Extended 30 cycle data of the 1.5M $(SPr)_2V$/Br AORFB showing charge capacity, discharge capacity, and CE versus cycle number at 80 mA/cm^2 current density. Testing conditions: 1.5 M $(SPr)_2V$ in 1.0 M NH_4Br and 4.0 M NH_4Br with 0.2 M Br_2; Nafion 115; pH 7.0.

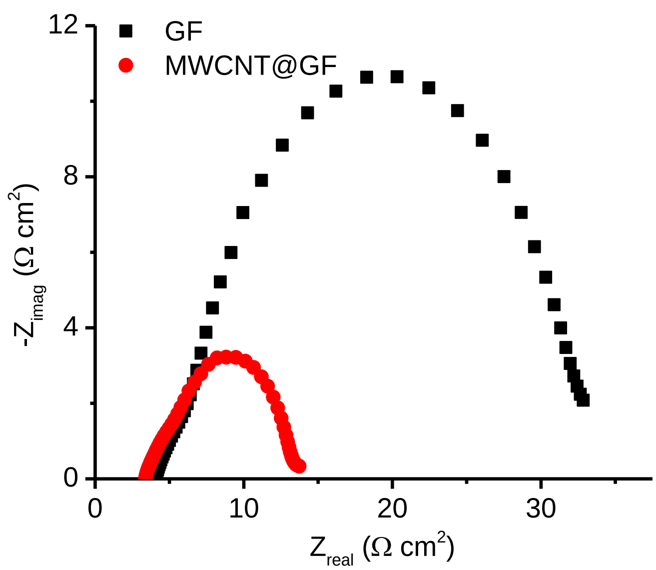

Figure S9. EIS measurements of the 1.5 M $(SPr)_2V$/Br AORFB by using bare GF (black) and MWCNT@GF (red) as cathode electrode.