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Supplementary Information

Reversible redox chemistry of disulfide/thiol for aqueous organic flow batteries

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Experimental

Chemicals and materials

Pyridyl disulfide (PySSPy), diphenyl disulfide (PhSSPh), and 2-mercaptopyridine (PySH) were received from TCI. Sulfuric acid (H_2SO_4, 98%) and hydrochloric acid (HCl, 37%) were received from Luoyang Chemical Reagents Ltd. Dimethyl sulfoxide-d_6 (DMSO-d_6) and zinc oxide (ZnO) were received from Adamas. Zinc foil with a thickness of 100 μm was received from Canrd. Sodium sulfate (Na_2SO_4) and sodium hydroxide (NaOH) were received from Greagent. Nafion 117 membrane was received from Dupont. Carbon plates, graphite felt, and polybenzimidazole (PBI) membrane were received from Zhongke Energy. Anion exchange membrane (AEM 8040) was received from Huamotech. All solvents were used directly without any treatment.

Preparation and characterization of *Dp*-PySSPy catholyte

Dp-PySSPy was prepared by mixing PySSPy with an acid solution. Specifically, to prepare 10 mL of 10 mM *Dp*-PySSPy, 22 mg PySSPy was added to 10 mL HCl/H_2O, and the mixture was ultrasonicated for 1 h at room temperature. The preparation process for *p*-PySH is similar to that of *Dp*-PySSPy. UV-vis spectra were recorded by Agilent Carry 100. Raman spectra were tested in a Horiba Scientific LabRAM HR spectrometer at 532 nm. ^1H NMR spectra were recorded on a 600 MHz Bruker Ascend instrument. All the samples were first added to a capillary tube and then put into an NMR tube containing DMSO-d_6.

Electrochemical measurements

Rotating disk electrode measurements were performed on an electrochemical workstation CHI760E, and a pine-modulated speed rotator. During the test, a three-electrode system with Ag/AgCl as the reference electrode, glassy carbon (diameter 5 mm) as the working electrode, and Pt wire as the counter electrode was used. The concentration of *Dp*-PySSPy in 1 M HCl was 1 mM, and the rotation rates were set from 100 to 2700 r.p.m. at a scan rate of 5 mV s^{-1}. The following Levich equation was used to calculate the diffusion coefficient (D).

$$i = 0.620nFACD^{2/3}\omega^{1/2}\upsilon^{-1/6}$$

Where i is limiting current, n is the number of electrons transferred (2), F is Faraday constant (96485 C mol^{-1}), A is electrode area (0.196 cm^2), C is the concentration of *Dp*-PySSPy (1 mM), D is the diffusion coefficient, ω *is* the rotation rate, and v is the kinetic viscosity of 1 M HCl (~1 cP).

Cyclic voltammetry measurements were conducted on a CHI760E electrochemical workstation with a three-electrode system, glassy carbon (diameter 3 mm, working electrode), Ag/AgCl (reference electrode), and Pt wire (counter electrode). During the test, the concentration of *Dp*-PySSPy in 1 M HCl was 2.5 mM, and the scan rates were set from 50 to 2000 mV s^{-1}. The diffusion coefficient (*D*) was calculated according to the Randles-Sevcik equation:

$Ip = 269000 \times n^{1.5}AD^{0.5}v^{0.5}C$

Where *Ip* is the peak current, n is the number of electrons transferred (2), *A* is the electrode area (0.071 cm^2), *D* is the diffusion coefficient, *v* is the scan rate, and *C* is the concentration of *Dp*-PySSPy (2.5 mM).

***In situ* Raman characterization**

An *in situ* Raman test was performed on a self-designed battery with one quartz window. One piece of graphite felt (Ø20 mm), and 0.8 mL 0.5 M *p*-PySH were added into the anode side, followed by adding a PBI membrane with a diameter of 25 mm. On the cathode side, one piece of graphite felt (Ø20 mm), and 0.8 mL 0.25 M *Dp*-PySSPy were added into a polytetrafluoroethylene channel, followed by one quartz window.

RFB assembly

Symmetric *Dp*-PySSPy/*p*-PySH RFB. RFB mold consists of two chambers, two tanks, two pumps, and two graphite end plates. Specifically, two carbon felts (3 × 3 cm) without pretreatment were added into positive and negative chambers, and a PBI membrane was soaked in working electrolytes for over 24 hours, separating the two chambers. For the 0.1/1 M *Dp*-PySSPy catholyte in 3 M H_2SO_4, the volume is 8 mL. The anolyte is 8 mL of 0.2/2 M *p*-PySH 3 M H_2SO_4. Both electrolytes were flowed at a rate of 15 mL min^{-1} by a peristaltic pump (Lead fluid). For 2 M *Dp*-PySSPy catholyte, to ensure PySSPy is fully protonated, the H_2SO_4 concentration was set to 6 M. Flow battery tests were conducted on a Neware battery test system. The symmetric *Dp*-PySSPy/*p*-PySH RFB was cycled from -0.6 to 0.6 V.

Zn-*Dp*-PySSPy RFB. The Zn-*Dp*-PySSPy RFB was conducted by a dual-membrane and three-electrolyte configuration, Nafion 117 membrane on the anolyte side, AEM 8040 as SO_4^{2-} exchange membrane on the catholyte side, and 1.5 M Na_2SO_4 as middle electrolyte. Before use, AEM 8040 and Nafion 117 were immersed in 1.5 M Na_2SO_4 solution for 48 hours, respectively. Specifically, for a Zn-*Dp*-PySSPy RFB, 8 mL of 0.1 M *Dp*-PySSPy in 3 M H_2SO_4 was used as catholyte. The middle electrolyte was 1 mL of 1.5 M Na_2SO_4. An excess amount of $Zn/Zn(OH)_4^{2-}$ as anolyte, 10 mL of 0.2 M $[Zn(OH)_4]^{2-}$ was formed by adding ZnO to 4 M NaOH, and a Zinc plate was added in the anolyte side. The flow rate of both anolyte and catholyte was 15 mL min^{-1}.

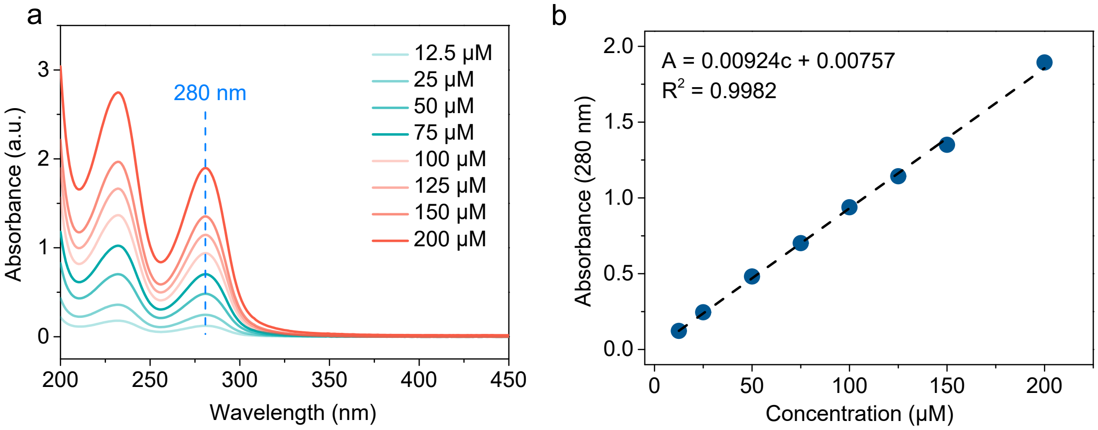

Fig. S1 (a) UV-vis spectra of PySSPy at different concentrations, (b) Relationship between absorbances at 280 nm and concentrations of PySSPy, and the data were linearly fitted to obtain the standard curve equation of PySSPy.

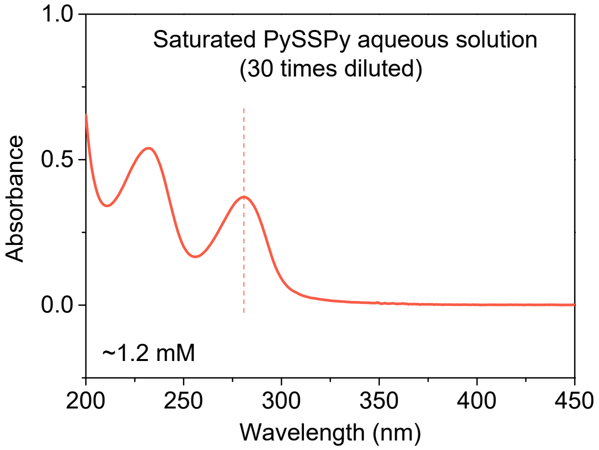

Fig. S2 UV-vis spectra of saturated PySSPy solution, the solubility of PySSPy can be calculated by the absorbance at 280 nm into the above standard curve equation.

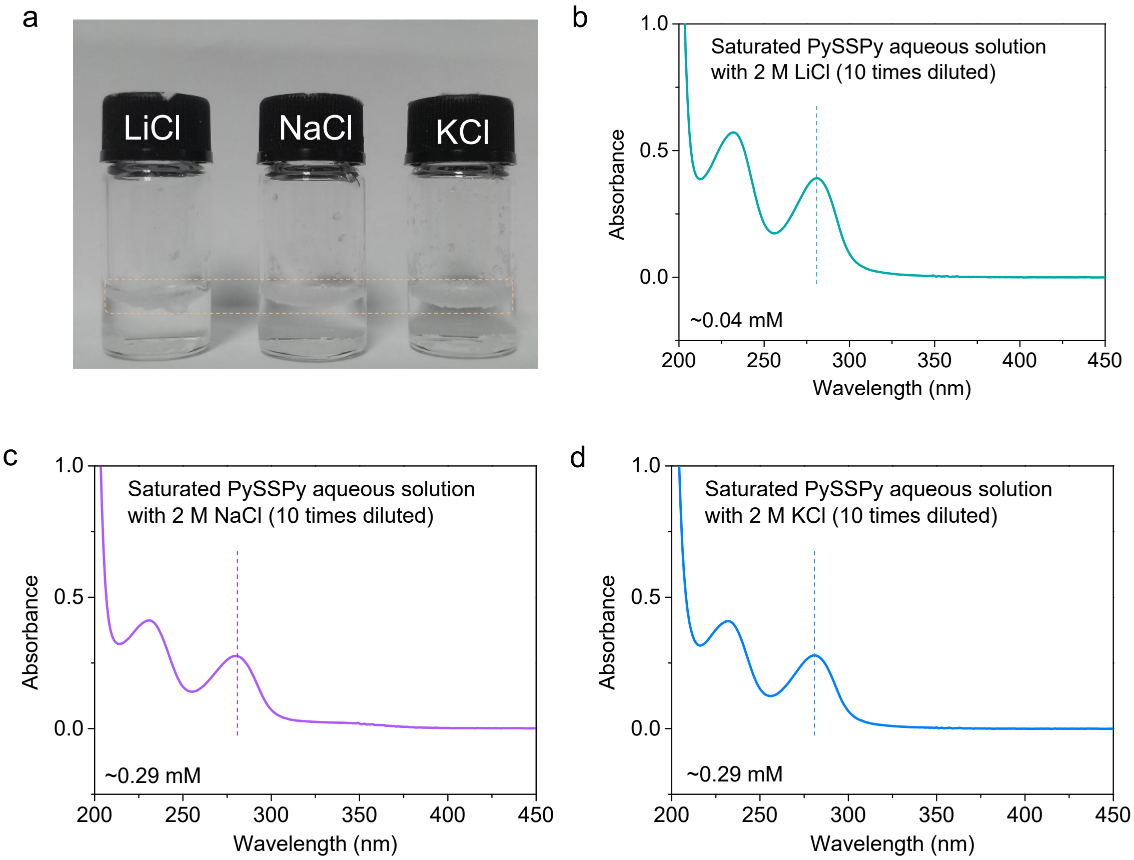

Fig. S3 Solubility test of PySSPy in 2 M Li/Na/KCl, and the corresponding UV-vis spectra. The solubility of PySSPy in 2 M Li/Na/KCl can be obtained from the above method.

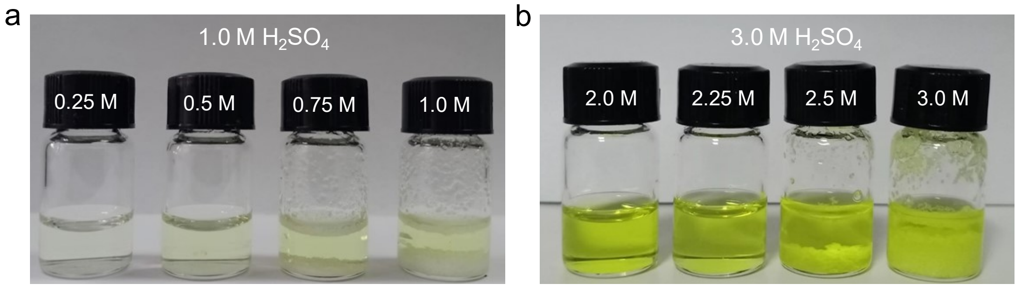

Fig. S4 Solubility test of PySSPy in 1 M and 3 M $H_2SO_{4.}$

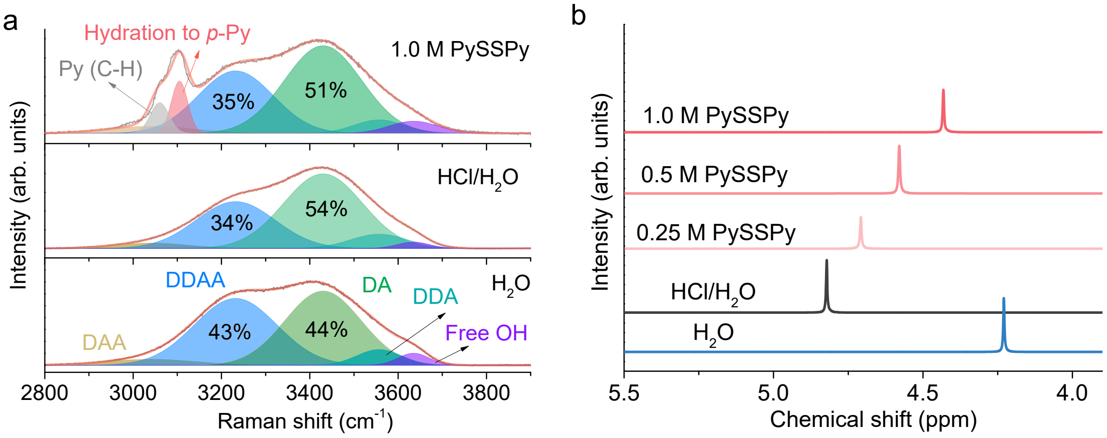

Fig. S5 (a) Raman OH stretching bands of H_2O, HCl/H_2O, and 1 M PySSPy. (b) Chemical shifts of H_2O in different samples. The concentration of HCl in HCl/H_2O is 2 M. DDAA: double donor-double acceptor. DDA: double donor-single acceptor. DAA: single donor-double acceptor. DA: single donor-single acceptor.

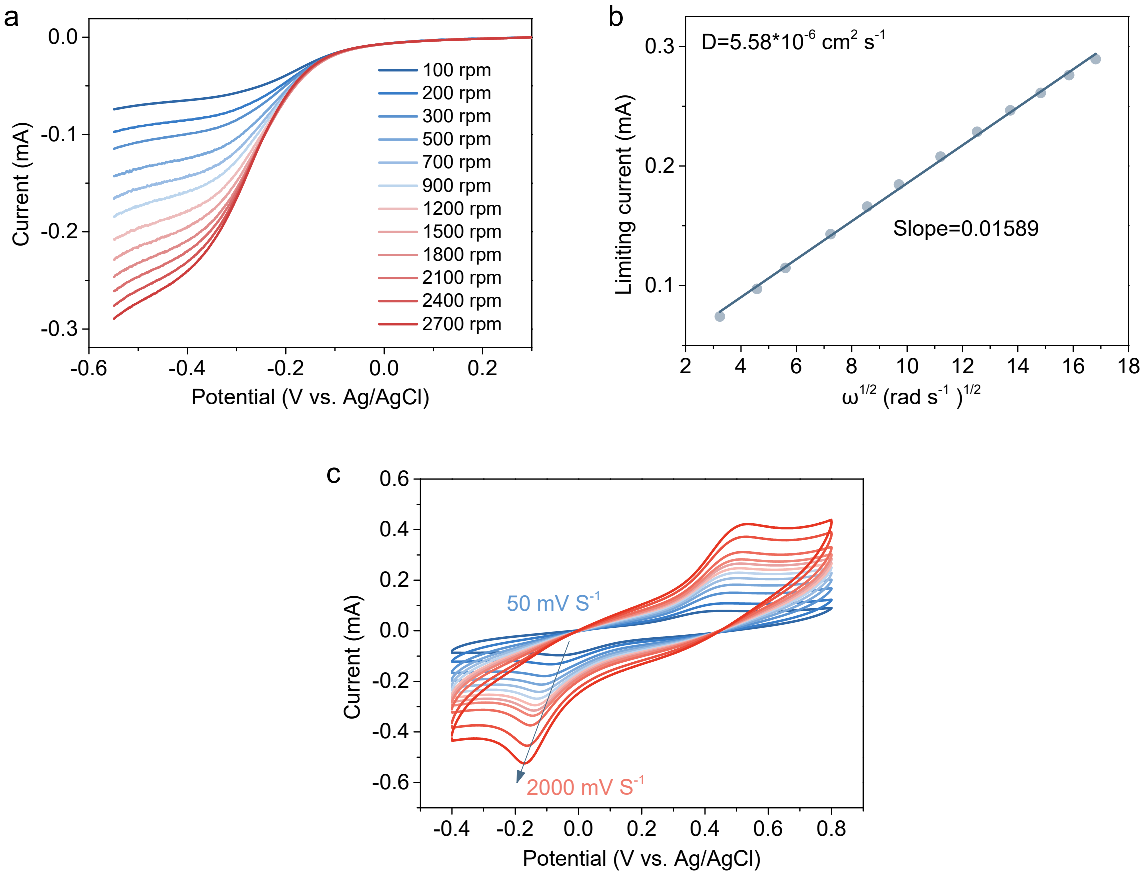

Fig. S6 Rotating disk electrode curves from 100 to 2700 rpm at 5 mV s^{-1} (a) and the corresponding plots of i vs. $\omega^{1/2}$ (b) for 1 mM *Dp*-PySSPy in 1 M HCl. (c) Cyclic voltammograms of 2.5 mM *Dp*-PySSPy in 1 M HCl at different scan rates.

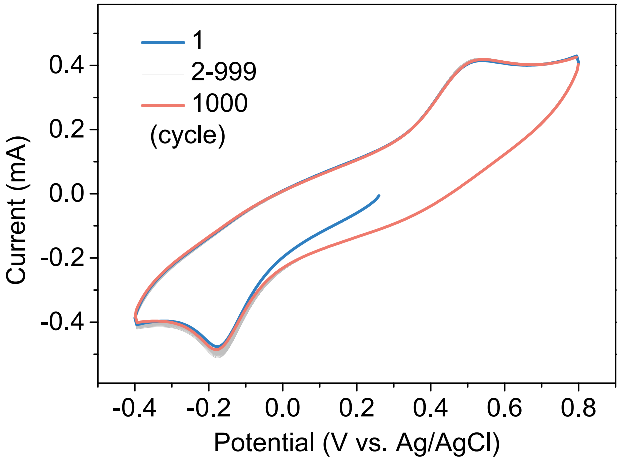

Fig. S7 Cyclic voltammograms of 2.5 mM *Dp*-PySSPy in 1 M HCl at 2000 mV s^{-1}.

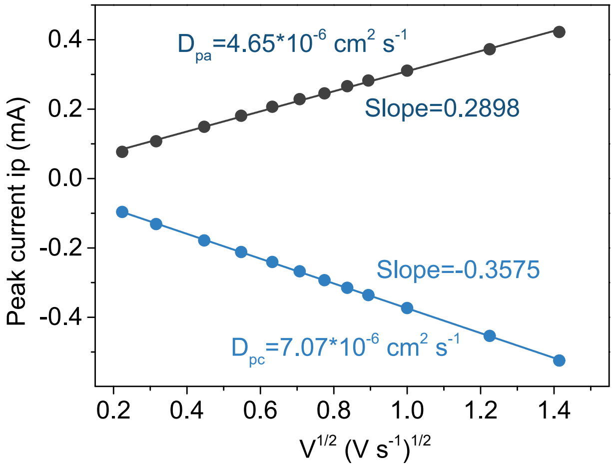

Fig. S8 Linearly fitted Randles-Sevcik plots for 2.5 mM *Dp*-PySSPy.

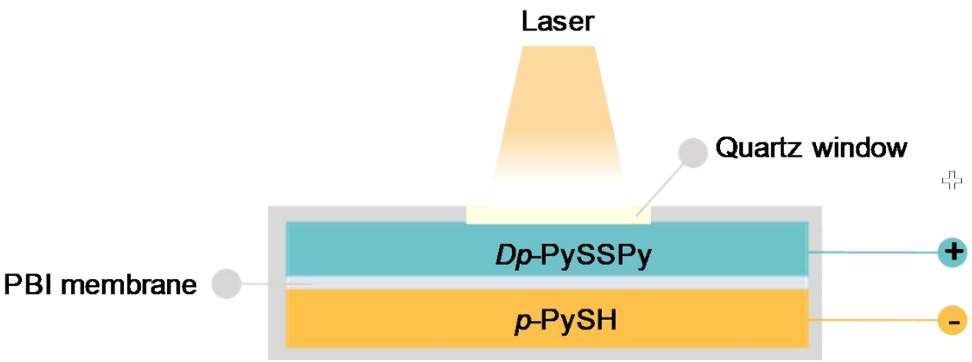

Fig. S9 Diagram of an *in situ* Raman test device.

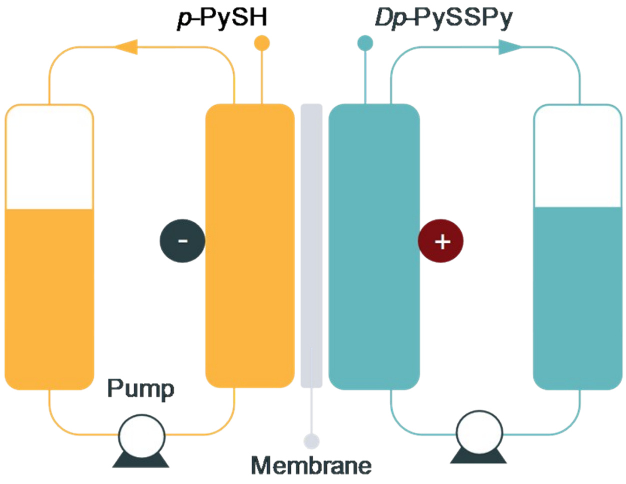

Fig. S10 Diagram of a symmetric RFB using *Dp*-PySSPy as the catholyte material and *p*-PySH as the anolyte material.

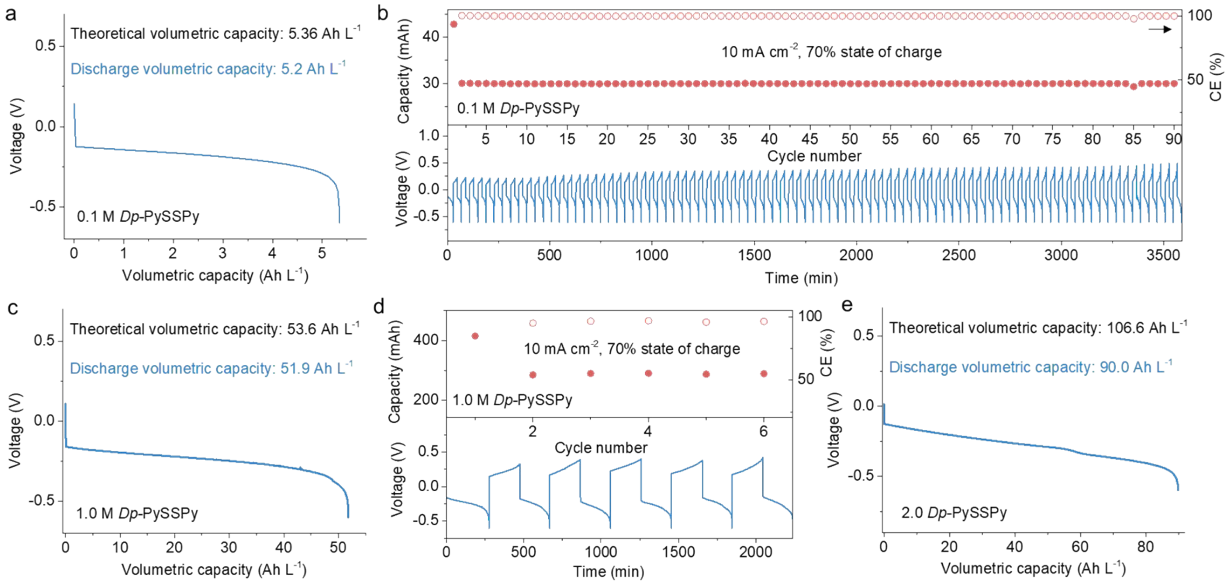

Fig. S11 First discharge profile (a), Coulombic efficiency and charge-discharge profiles (b) of a symmetric RFB with 0.1 M *Dp*-PySSPy. First discharge profile (c), Coulombic efficiency and charge-discharge profiles (d) of a symmetric RFB using a 1 M *Dp*-PySSPy catholyte. (e) Discharge profile of 2 M *Dp*-PySSPy in a symmetric RFB at 20 mA cm^{-2}.

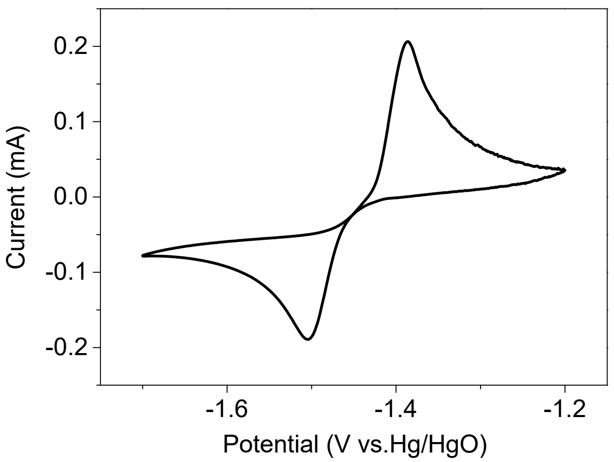

Fig. S12. Cyclic voltammogram of 25 mM ZnO in 4 M NaOH using a HgO/Hg reference electrode at 5 mV s^{-1}.

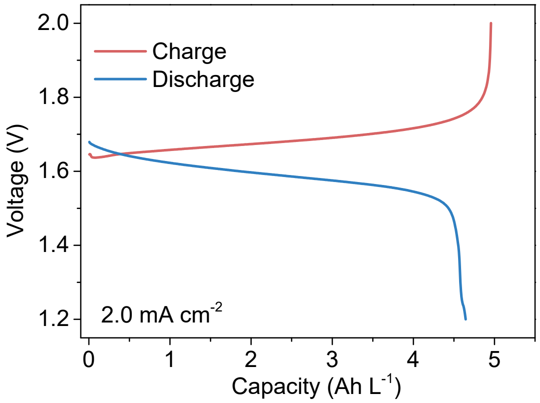

Fig. S13 Charge-discharge profiles of a Zn-*Dp*-PySSPy RFB with 0.1 M *Dp*-PySSPy as catholyte and an excess amount of Zn/Zn$(OH)_4^{2-}$ anolyte.

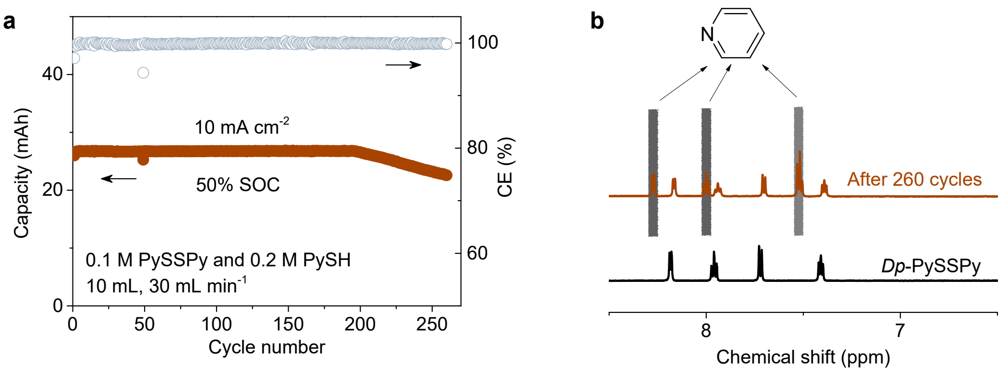

Fig. S14. (a) Cycling performance of a symmetric RFB. (b) ^{1}H NMR spectrum of a catholyte before and after 260 cycles. Three peaks in the ^{1}H NMR spectrum are attributed to pyridine, indicating that the electrochemical conversion of *Dp*-PySSPy is unstable.

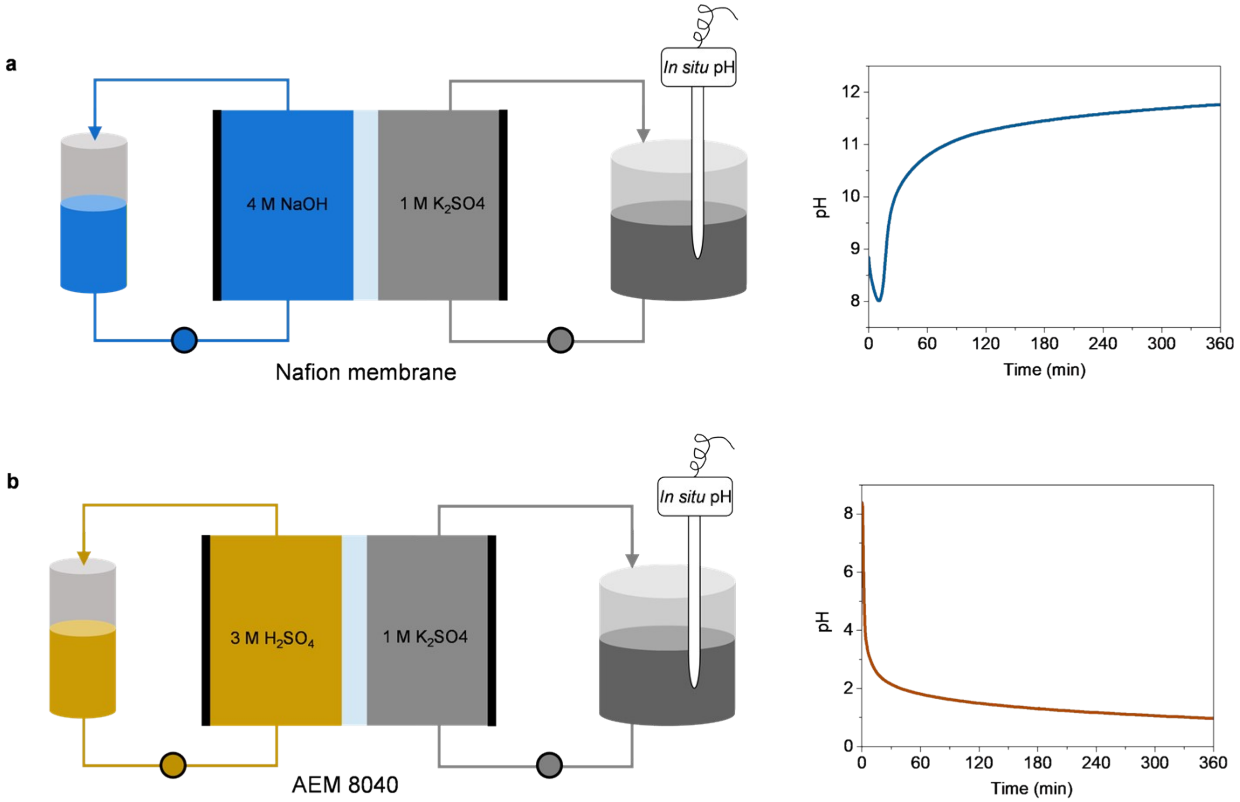

Fig. S15. (a) An *in situ* pH device to measure the OH^- crossover and the corresponding pH change in the K_2SO_4 side. 20 mL of 4 M NaOH and 20 mL of 1 M K_2SO_4 were added to two tanks, respectively. Flow rate of both solutions: 15 mL min^{-1}. (b) An *in situ* pH device to measure the H^+ crossover and the corresponding pH change in the K_2SO_4 side. 20 mL of 3 M H_2SO_4 and 20 mL of 1 M K_2SO_4 were added to two tanks, respectively. Flow rate of both solutions: 15 mL min^{-1}. The results indicate that both H^+ and OH^- are readily permeable through CEM or AEM membranes.