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Supplemental information

A neutral polysulfide/ferricyanide

redox flow battery

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Figure S1. Cyclic voltammograms of the redox couples employed in the proposed neutral PFRFB system. (A) Cyclic voltammetry curves of 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 1.0 M KCl solution under different scan rates. (B) Linear fitting of the oxidation and reduction peak current densities of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ versus the square root of the sweeping rate, respectively. (C) Cyclic voltammetry curves of 0.1 M K_2S in 1.0 M KCl solution at different sweeping rates. (D) Linear fitting of oxidation and reduction peak current densities of $\text{S}^{2-}/\text{S}_2^{2-}$ versus the square root of the sweeping rate, respectively. Related to Figure 1.

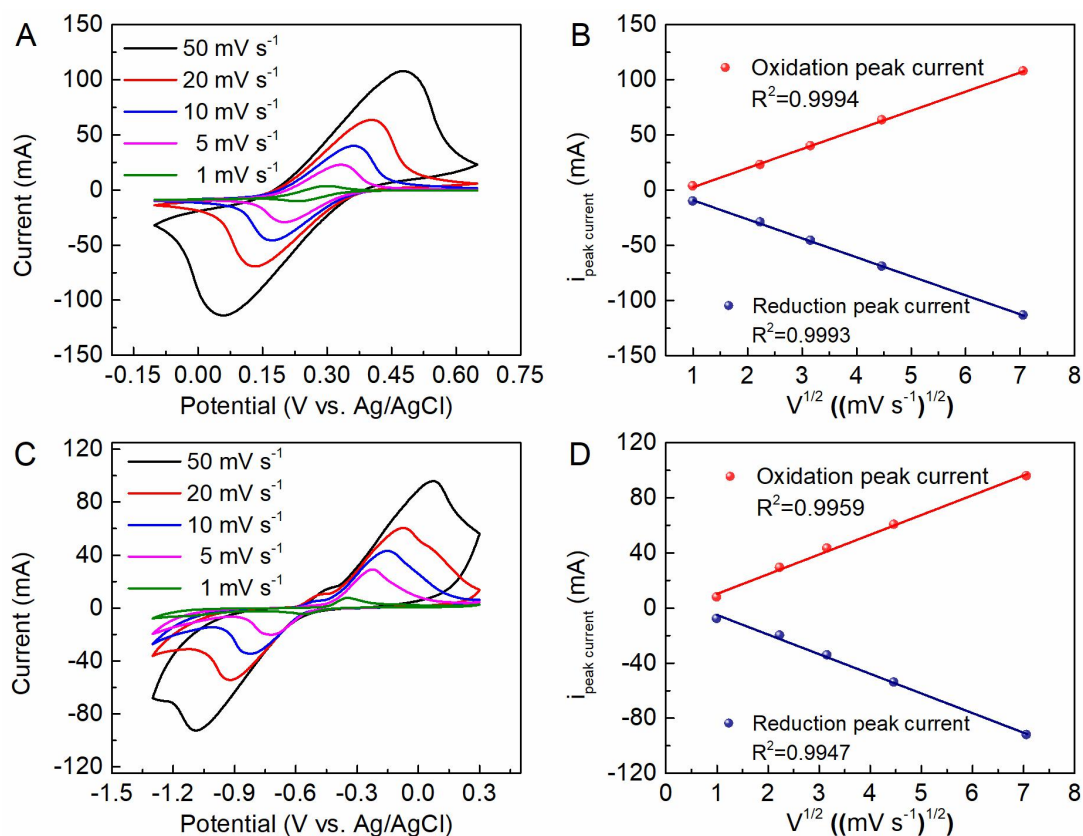


Figure S2. Electrochemical and chemical stability of the catholyte in PFRFB single cell over charging-discharging process. (A) Raman spectra of 500-fold diluted samples from the catholyte under 100% state of charge (SOC) taken at the end of 2nd, 100th, 200th, and 300th cycle. (B) Raman spectra of 500-fold diluted samples from the catholyte under 100% state of discharge (SOD) taken at the end of 2nd, 100th, 200th, and 300th cycle. (C) UV-vis spectra of 500-fold diluted samples from the catholyte under 100% SOC taken at the end of 2nd, 100th, 200th, and 300th cycle. (D) UV-vis spectra of 500-fold diluted samples from the catholyte under 100% SOD taken at the end of 2nd, 100th, 200th, and 300th cycle. Related to Figure 2.

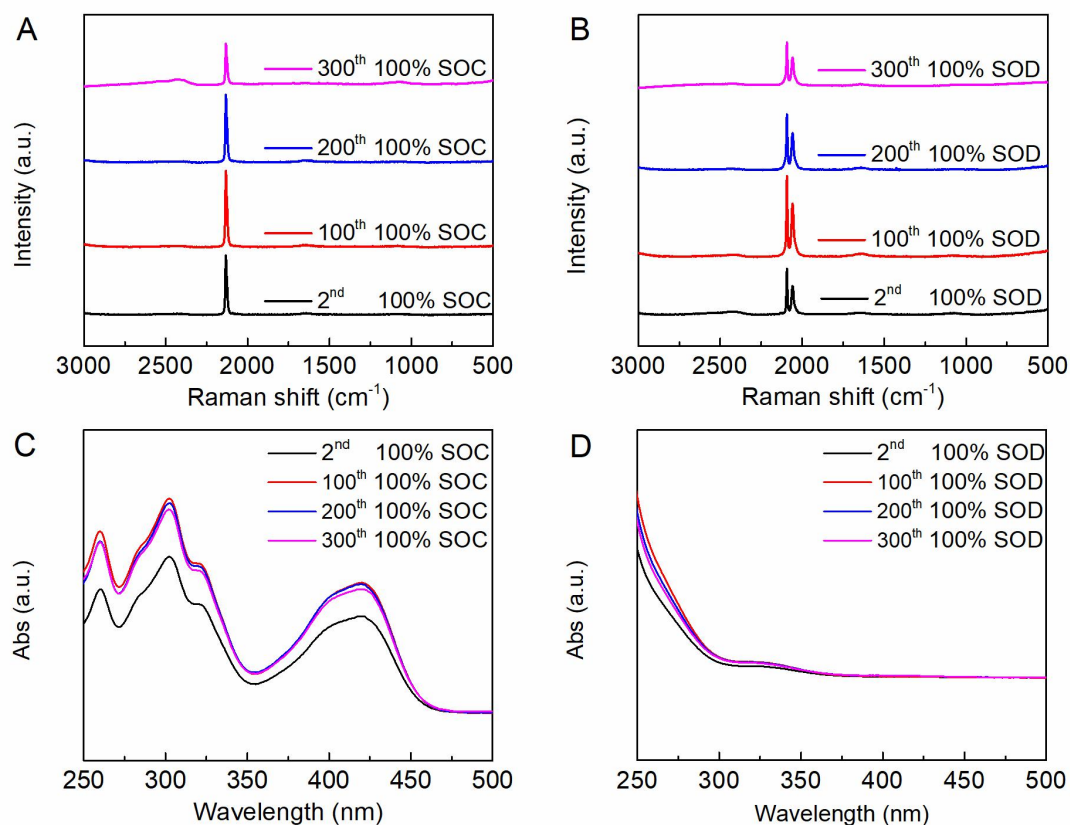


Figure S3. Photographs of concentrated-solutions of K_2S and $[Fe(CN)_6]^{4-}$, respectively. (A) Concentrated K_2S solutions in H_2O and 1.0 M KCl solution, respectively. (B) Mixtures of $K_4[Fe(CN)_6]$ and $Na_4[Fe(CN)_6]$ with equimolar varying from 0.8 M to 1.0 M at an interval of 0.1 M in 1.0 M KCl solution. K_4 and Na_4 are short forms of $K_4[Fe(CN)_6]$ and $Na_4[Fe(CN)_6]$ for clarity, respectively. Related to Figure 4.

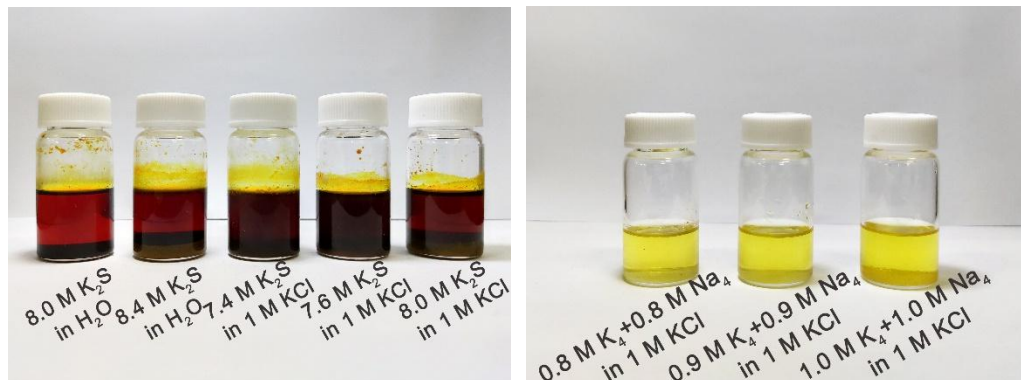


Figure S4. Electrochemical performance of the PFRFB stack with refresh catholyte and anolyte over extended cycling tests. The PFRFB stack consists a 20.0 L solution of 0.3 M $K_3[Fe(CN)_6]$ + 1.0 M KCl as the catholyte and a 20.0 L solution of 1.0 M K_2S + 1.0 M KCl as anolyte under a current of 17 A for the tests. Related to Figure 5.

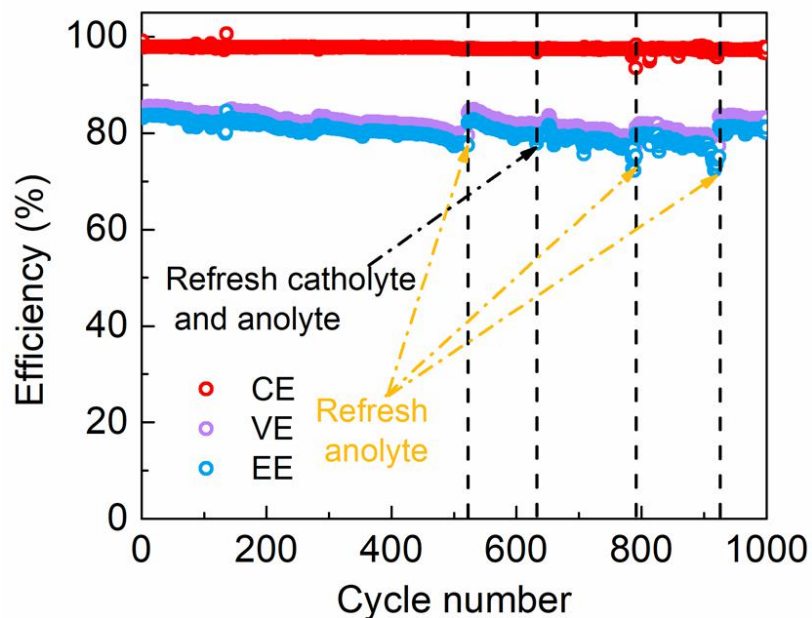


Table S1. Kinetic parameters of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ from CV dates. Related to Figure 1 and Figure S1.

V (mV s^{-1})	E_a (V)	E_b (V)	i_{Pa} (mA)	i_{Pc} (mA)	$ i_{Pa}/i_{Pc} $
1	0.300	0.229	3.64	-10.24	0.36
5	0.333	0.201	22.91	-29.24	0.78
10	0.361	0.173	40.03	-45.77	0.87
20	0.403	0.132	63.46	-69.43	0.91
50	0.479	0.058	107.84	-113.81	0.95

Table S2. Kinetic parameters of S^{2-}/S_2^{2-} from CV dates. Related to Figure 1 and Figure S1.

V ($mV s^{-1}$)	E_a (V)	E_b (V)	i_{Pa} (mA)	i_{Pc} (mA)	$ i_{Pa}/i_{Pc} $
1	-0.247	-0.568	7.72	-4.48	1.73
5	-0.223	-0.720	29.15	-20.13	1.45
10	-0.151	-0.822	43.23	-34.46	1.25
20	-0.073	-0.924	60.56	-54.37	1.11
50	-0.072	-1.088	95.91	-92.57	1.04

Method S1. Cost calculations. Related to Figure 5.

According to the methodology proposed by Chiang et. al (*Joule* **1**, 306-327, 2017), the chemical cost of storage (CCS) for PFRFB system was calculated on the equations given below:

$$CCS \left(\frac{US\$}{kWh} \right) = \frac{\text{Cost of Catholyte (US\$)} + \text{Cost of Anolyte (US\$)}}{\text{Voltage (V)} \cdot 1 \text{ (Ah)} \cdot 0.001 \left(\frac{kWh}{Wh} \right)} \quad (1)$$

in which the CCS (US\$/KWh) refers to the cost in US dollars of electrolyte per kilowatt hour, while the cost of catholyte and anolyte (US\$) involves the cost of redox species and supporting species. Voltage (V) represents the open circuit voltage of the cell. Note that the solvent cost is negligible.

The cost of electrolyte including both catholyte and anolyte was separately obtained by following equations:

$$\text{Cost of Catholyte (US\$)} = \left\{ P_c \left(\frac{US\$}{mol} \right) \cdot C_c \left(\frac{mol}{L} \right) + \sum \left[P_{e,s} \left(\frac{US\$}{mol} \right) \cdot C_{e,s} \left(\frac{mol}{L} \right) \right] \right\} \frac{1 \text{ Ah}}{CaP_c \left(\frac{Ah}{L} \right)} \quad (2)$$

$$\text{Cost of Anolyte (US\$)} = \left\{ P_a \left(\frac{US\$}{mol} \right) \cdot C_a \left(\frac{mol}{L} \right) + \sum \left[P_{a,s} \left(\frac{US\$}{mol} \right) \cdot C_{a,s} \left(\frac{mol}{L} \right) \right] \right\} \frac{1 \text{ Ah}}{CaP_a \left(\frac{Ah}{L} \right)} \quad (3)$$

Where, $P_c \left(\frac{US\$}{mol} \right)$ and $P_a \left(\frac{US\$}{mol} \right)$ are the cost of redox active molecules per molar in catholyte and anolyte and $C_c \left(\frac{mol}{L} \right)$ and $C_a \left(\frac{mol}{L} \right)$ represent the concentration of redox active molecules in catholyte and anolyte, respectively. $P_{c,s} \left(\frac{US\$}{mol} \right)$ and $P_{a,s} \left(\frac{US\$}{mol} \right)$ are the cost of supporting species per molar in catholyte and anolyte, $C_{c,s} \left(\frac{mol}{L} \right)$ and $C_{a,s} \left(\frac{mol}{L} \right)$ represent the concentration of supporting species in catholyte and anolyte, separately. $CaP_c \left(\frac{Ah}{L} \right)$ and $CaP_a \left(\frac{Ah}{L} \right)$ refers to the volume specific capacities of catholyte and anolyte, respectively.

The CCS of reported RFBs, such as PSIFB (*Ind. Eng. Chem. Res.* **56**, 9783–9792, 2017), DHAQ/Fe (*Science* **349**, 15929-1532, 2015), MV/4-HO-TEMPO (*Adv. Energy Mater.* **6**, 1501449-1501457, 2016), FcNCl/MV (*J. Am. Chem. Soc.* **139**, 1207-1214, 2017), ZIFB (*Angew. Chem. Int. Ed.* **5**, 11171-11176, 2018) and (SPr)₂V/(NH₄)₄[Fe(CN)₆] (*Joule* **3**, 149-163, 2019) RFBs were also calculated according to above equations for comparison. CCS of DBEAQ/Fe (*Joule* **2**, 1894-1906, 2018), Zn/Fe (*Angew. Chem. Int. Ed.* **56**, 14953-14957, 2017), Fe/Na₂S₂ (*J. Electrochem. Soc.* **163**, A5150, 2016), All-V and SIFB (*Nano Energy*, **30**, 283–292, 2016), AQDS/Br and Sulfur/air (*Joule* **1**, 306-327, 2017) were obtained from respective references.

Table S3. Cost of catholyte. Related to Figure 5.

Chemical	$P \left(\frac{US\$}{mol} \right)$	$C \left(\frac{mol}{L} \right)$	$C_a P_p \left(\frac{Ah}{L} \right)$	Cost (US\$)
K ₃ [Fe(CN) ₆]	0.329 ^[a]	0.80	21.44	0.0127
KCl	0.019 ^[b]	0.50	--	

[a] quoted from Anhui Jinao Chemical Co., Ltd

[b] From reference (Xie et al., 2017)

Table S4. Cost of anolyte. Related to Figure 5.

Chemical	$P \left(\frac{US\$}{mol} \right)$	$C \left(\frac{mol}{L} \right)$	$C_a P_a \left(\frac{Ah}{L} \right)$	Cost (US\$)
K ₂ S	0.493 ^[c]	2.0	53.6	0.0188
KCl	0.019 ^[b]	1.0	--	

[c] Quoted from Wuxi Zhanwang Chemical Reagent Co., Ltd.

$$CCS (US\$/kWh) = \frac{(0.0127 + 0.0188)}{0.97 \times 1 \times 0.001} US\$/kWh = 32.47 US\$/kWh$$