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**Electronic Supplementary Information** 

## Flow battery recharging by thermoresponsive liquid–liquid phase separation

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Fig. S1 The relationship between the redox potential of  $Fe(CN)_{6^{4-/3-}}$  and volume ratio of the additive (LT or BE).



**Fig. S2** Cyclic voltammograms of the diluted additive-rich and lean phases after phase separation in the water–LT system (Fig. 4a). The Pt disk electrode, Pt spiral electrode, and Ag|AgCl electrode (in saturated KCl aqueous solution) were employed as the working, counter, and reference electrodes, respectively. The additive-rich and lean phases were diluted 10 times by 0.1 mol L<sup>-1</sup> KCl aqueous solution. The scanning rate was 0.1 V s<sup>-1</sup>. The obvious anodic and cathodic peaks of  $Fe(CN)_6^{4-/3-}$  were observed for the diluted additive-lean phase, which were much larger than those for the diluted additive-rich phase.

The concentration of  $Fe(CN)_{6^{3-}}$  in the diluted aqueous solution ( $c_{dil}$ ) was calculated according the following equation (1').

$$c_{dil} = \frac{\iota_{cp}}{0.4463nFD^{1/2} \left(\frac{nFv}{RT}\right)^{1/2}}$$
(1')

Then the concentration of  $Fe(CN)_{6}^{3-}$  in the additive-lean or additive-rich phases ( $c_{0}$ ) were calculated according the following equation (2').

$$c_0 = 10c_{dil} \tag{2'}$$

As a result,  $c_0$  was 0.015 mol L<sup>-1</sup> in the additive-lean phase and 0.0012 mol L<sup>-1</sup> in the additive-rich phase.

## Table S1 Parameters used for the calculation of the concentration of Fe(CN)63-.

	Parameters	Unit
Reduction peak current density ( <i>i</i> <sub>cp</sub> )	3.45×10 <sup>-4</sup> (Diluted additive-lean phase)	A cm <sup>-2</sup>
	2.72×10 <sup>-5</sup> (Diluted additive-rich phase)	
Number of the electron transferred (n)	1	-
Faraday constant (F)	96485	C mol <sup>-1</sup>
Diffusivity of $Fe(CN)_6^{3-}(D)$	7×10 <sup>-6</sup>	cm <sup>2</sup> s <sup>-1</sup>
Scanning rate (v)	0.1	V s <sup>-1</sup>
Gas constant ( <i>R</i> )	8.31	J mol <sup>-1</sup> K <sup>-1</sup>
Temperature (T)	296	К



Fig. S3 Effect of the heating temperature of the discharged anolyte on the difference in the concentration of the additive between the additive-rich and lean phases. The heating temperature in the right panel (T<sub>H2</sub>) is higher than that in the left panel (T<sub>H1</sub>).



Fig. S4 Structure of the prototype flow cell.



Fig. S5 Schematic of the charge-discharge cycle using the experimental setup in this work.



**Fig. S6** Estimation of the molar ratio of LT in the electrolytes in the initial condition of the charge–discharge cycle test for the water–LT system. The estimation is based on the phase diagram of the water–LT system in Fig. 4b. The clouding point was evaluated at the molar ratio of 0.01, 0.025, 0.05, 0.10, 0.15 and 0.20. The molar ratio of LT in the anolyte was equivalent to that in the electrolyte with high concentration of LT in the panel (0.10). The molar ratio of LT in the catholyte was equivalent to that in the electrolyte with low concentration of LT in the panel (0.01), which can be estimated from the phase diagram.



**Fig. S7** Potential of the anolyte and catholyte in the initial condition of the charge–discharge cycle test for the water–LT system. The difference in the potentials between the anolyte and catholyte was 46 mV, which was consistent with the initial open circuit voltage of the flow cell in Fig. 5c (44 mV).



**Fig. S8** Charge–discharge cycles of the water–BE system. The horizontal axis represents the total discharged quantity during the four discharging processes. For the initial analyte, the molar ratio of BE was 0.10, and the concentrations of  $(NH_4)_4Fe(CN)_6$  and  $(NH_4)_3Fe(CN)_6$  were both 0.025 mol L<sub>water</sub><sup>-1</sup>. The initial catholyte was prepared according to the procedure in the experimental section. The discharged electrolytes were regenerated by utilizing 70°C of hot water and room-temperature water (approximately 23°C). The discharging current density was 2.6 A m<sup>-2</sup>. For the second, third, and fourth discharges, the flow cell was discharged at the constant voltage of 1 mV after the constant-current discharge to adjust the discharged quantity.



**Fig. S9** Estimation of the molar ratio of BE in the electrolytes in the initial condition of the charge–discharge cycle test for the water–BE system. The estimation is based on the phase diagram of the water–BE system with 0.025 mol  $L_{water}^{-1}$  of (NH<sub>4</sub>)<sub>4</sub>Fe(CN)<sub>6</sub> and (NH<sub>4</sub>)<sub>3</sub>Fe(CN)<sub>6</sub>. The clouding point was evaluated at the molar ratio of 0.01, 0.012, 0.015, 0.025, 0.05, 0.10, 0.15 and 0.20. The clouding point was not observed at the molar ratio of 0.01 in the range between 23 and 70°C. The molar ratio of BE in the anolyte was equivalent to that in the electrolyte with high concentration of BE in the panel (0.10). The molar ratio of BE in the catholyte was equivalent to that in the electrolyte with low concentration of BE in the panel, which was estimated to be between 0.01 and 0.012 from the phase diagram. According to the result in Fig. 3b, the difference in the potential generated by the difference in the additive concentration between the anolyte and catholyte was estimated to be between 14 and 37 mV, which is consistent with the initial OCV of the flow cell (22 mV).



Fig. S10 Polarization curve and power density of the water-BE system in the fully charged condition.



**Fig. S11** Schematic of the assumption on the heat recovery. The total thermal energy input to induce the liquid–liquid phase separation of the discharged anolyte can be described with the sum of  $C_p\Delta T$  and  $\Delta H_{LLPS}$ . In this figure,  $C_p$ ,  $\Delta T$ , and  $\Delta H_{LLPS}$  denote the heat capacity of the electrolyte, the temperature difference between high- and low-thermal reservoirs, and the change in enthalpy by the thermoresponsive liquid–liquid phase separation respectively. On the basis of the assumption in the paper, the former ( $C_p\Delta T$ ) can be covered by the heat exchange with the discharged anolyte after the liquid–liquid phase separation. Hence, the thermal energy received from the high-temperature thermal reservoir equals  $\Delta H_{LLPS}$ , analyzed by the DSC measurement.



Fig. S12 Schematic of electrolytes in fully charged and fully discharged conditions.