# Electronic Supplementary Information (ESI)

# Thermosensitive slurry electrolyte design for efficient electrochemical heat

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## **Supplementary Notes**

Note S1: Theoretical analysis of temperature coefficient ( $\alpha$ ) with thermosensitive crystallization For a half-cell reaction in a thermally regenerative electrochemical cycle (TREC) system, A + n e<sup>-</sup>  $\rightarrow$ B,  $\alpha$  represents the dependence of the potential difference ( $\Delta E$ ) on the temperature difference ( $\Delta T$ ), which can be expressed as:

$$\alpha = \frac{\partial E}{\partial T} = \frac{E_{\rm H} - E_{\rm L}}{T_{\rm H} - T_{\rm L}} \tag{S1}$$

where E is the electrode potential, T is temperature, the subscripts "H" and "L" indicate that the corresponding variables pertain to the TREC cell at high and low temperature. According to the Nernst equation, E of the redox reaction can be expressed as:

$$E = E^{0} + \frac{RT}{nF} \ln \frac{\gamma_{A}[A]}{\gamma_{B}[B]}$$
(S2)

where  $E^0$  is the standard potential, *R* is the ideal gas constant, *n* is the number of electrons transferred in the reaction, *F* is the Faraday's constant,  $\gamma_A$  and  $\gamma_B$  are the activity coefficient of species A and B, [A] and [B] are the concentration of the reactants A and products B in the redox reaction. In general, the electrolyte is thermodynamically stable and the concentration of redox ions do not change when the TREC system is heated up or cooled down, that is,  $[A]_H = [A]_L$  and  $[B]_H = [B]_L$ . If we neglect the change of  $\gamma$  with temperature, and apply equation S2 to S1, we have:

$$\alpha = \frac{R}{nF} \ln \frac{\gamma_{\rm A} \left[ {\rm A} \right]_{\rm L}}{\gamma_{\rm B} \left[ {\rm B} \right]_{\rm L}} = \frac{\Delta S}{nF}$$
(S3)

where  $\Delta S$  is the solvent-dependent entropy difference between the redox ions. Nevertheless, the concentration of redox ions at  $T_{\rm H}$  and  $T_{\rm L}$  are with a huge difference in the discussed half-cell system with redox ion-based thermosensitive crystallization<sup>1</sup>. Then equation S3 can be derived as:

$$\alpha = \frac{R}{nF} \ln \frac{\gamma_{A}}{\gamma_{B}} + \frac{R}{nF\Delta T} \left( T_{H} \ln \frac{[A]_{H}}{[B]_{H}} - T_{L} \ln \frac{[A]_{L}}{[B]_{L}} \right)$$

$$= \frac{R}{nF} \ln \frac{\gamma_{A} [A]_{L}}{\gamma_{B} [B]_{L}} + \frac{RT_{H}}{nF\Delta T} \left( \ln \frac{[A]_{H}}{[B]_{H}} - \ln \frac{[A]_{L}}{[B]_{L}} \right)$$

$$= \frac{\Delta S}{nF} + \frac{RT_{H}}{nF\Delta T} \left( \ln \frac{[A]_{H}}{[B]_{H}} - \ln \frac{[A]_{L}}{[B]_{L}} \right)$$
(S4)

Here, we define the entropy difference related to concentration gradient ( $\Delta C_r$ ) of species A and B between  $T_H$  and  $T_L$  as:

$$\Delta C_{\rm r} = \frac{RT_{\rm H}}{\Delta T} \left( \ln \frac{\left[ \mathbf{A} \right]_{\rm H}}{\left[ \mathbf{B} \right]_{\rm H}} - \ln \frac{\left[ \mathbf{A} \right]_{\rm L}}{\left[ \mathbf{B} \right]_{\rm L}} \right)$$
(S5)

Apply equation S5 to S4, we have:

$$\alpha = \alpha_{\Delta S} + \alpha_{\Delta C_r} = \frac{\Delta S}{nF} + \frac{\Delta C_r}{nF}$$
(S6)

whereas  $\alpha$  is divided into two terms, the first term  $\alpha_{\Delta S}$  is the temperature coefficient related with  $\Delta S$ , and the second term  $\alpha_{\Delta Cr}$  is the temperature coefficient related with  $\Delta C_r$ .

As a result,  $\alpha$  can be boosted by generating a large  $\Delta C_r$  using redox ion-based thermosensitive crystallization. For instance, in the Fe(CN)<sub>6</sub><sup>3-/4-</sup> half-cell with Fe(CN)<sub>6</sub><sup>4-</sup>-based thermosensitive crystallization, a sustainable positive concentration gradient of Fe(CN)<sub>6</sub><sup>4-</sup> can be achieved during heating, leading to a large  $\Delta C_r$  and thus a highly enhanced  $\alpha$ .

# Note S2: Crystallization and dissolution over a thermal cycle and the corresponding higher net work in the thermosensitive crystallization-boosted TREC (TC-TREC)

The pristine TREC with a  $\alpha$  negative consists of four processes: heating up, charging, cooling down and discharging (Fig. S1). The cell is assembled in discharged state and heated from  $T_L$  to  $T_H$  at open circuit in process 1. The cathode potential ( $E_+$ ) decreases and the anode potential increases ( $E_-$ ) due to their negative  $\alpha_+$  and positive  $\alpha_-$ , respectively, resulting a decreased open circuit voltage (OCV). In process 2, the cell is charged at a low voltage at  $T_H$ . Then the cell is cooled from  $T_H$  to  $T_L$  at open circuit in process 3 and the OCV increases. Finally, the cell is discharged at a high voltage at  $T_L$  and returns to the original state. The cell generates a net-work (W) due to the higher average discharging voltage than average charging voltage.

In general, *W* can be expressed as:

$$W = \left[ \left( I_{\rm dis} V_{\rm dis} - I_{\rm ch} V_{\rm ch} \right) dt \right] \tag{S7}$$

where *I* and *V* are the current and voltage of the cell, the subscripts "dis" and "ch" indicate that the corresponding variables during discharging and charging,  $E_{loss}$  is the energy loss due to the internal resistance of the cell. Since we use the same current value during discharging and charging, the simplified *W* in equation S7 can be expressed as:

$$W = Q_{\rm c} \left( \overline{V_{\rm dis}} - \overline{V_{\rm ch}} \right)$$
  
=  $Q_{\rm c} \left| \overline{\alpha} \right| \Delta T - E_{\rm loss}$  (S8)

where  $Q_c$  is the charge capacity of the cell.

Therefore, a larger  $\alpha$  and  $q_c$  can lead to a higher W. In TC-TREC, four basic processes are the same as in TREC except the extra dissolution and crystallization processes (Fig. S2). When the cell is heated from  $T_L$  to  $T_H$ , the dissolution of KGdmFeCN crystals induce a large  $\Delta C_r$  and thus an extra negative  $\alpha_{\Delta Cr}$ , as discussed before. Different from dissolution, the crystallization process occurs during discharging instead of cooling, which means that  $\Delta C_r$  is close to zero during cooling and  $\alpha$  at charged state ( $\alpha_{ch}$ ) equals to  $\alpha_{\Delta S}$ . Overall, TC-TREC possess an enhanced  $\overline{\alpha}$ . Besides, specific charge capacity ( $q_c$ ) is also boosted by using thermosensitive crystallization since adequate crystals can be added to the system and reacted in the electrochemical reaction due to their fast crystallization and dissolution kinetics<sup>1</sup>. With both highly enhanced  $\alpha$  and  $q_c$ , TC-TREC can generate a higher W than pristine TREC (Fig. S3). If we approximate  $\overline{\alpha}$  as the average of  $\alpha_{dis}$  and  $\alpha_{ch}$  in equation S8, then we have:

$$W = Q_{c}\Delta T \left| \alpha_{dis} + \alpha_{ch} \right| / 2 - E_{loss}$$
  
=  $Q_{c}\Delta T \left| \alpha_{\Delta S} + \alpha_{\Delta C_{r}} + \alpha_{\Delta S} \right| / 2 - E_{loss}$   
=  $Q_{c}\Delta T \left| \overline{\alpha_{\Delta S}} \right| + Q_{c}\Delta T \left| \alpha_{\Delta C_{r}} \right| / 2 - E_{loss}$  (S9)

Since  $\Delta S = Q_c \left| \overline{\alpha_{\Delta S}} \right|$ , and case is the same for  $R \Delta C_r$ , we have:

$$W = \Delta T \left( \Delta S + R \Delta C_{\rm r} / 2 \right) - E_{\rm loss} \tag{S10}$$

Furthermore, we will derive the relationship between  $\Delta C_r$  and  $\Delta S_{sol}$  in an effort to essentially elucidate why thermosensitive crystallization with a large  $\Delta S_{sol}$  can endow TC-TREC with a remarkable high  $\alpha$ . For a crystal associated with ion A within the redox pair, the dissolution process can be expressed as:

$$Crystal \xrightarrow{dissolution} n_A A + n_O O$$
(S11)

where O is the other ions produced by the crystal during the dissolution. Considering a solution with crystal at  $T_L$  and the crystal dissolute at  $T_H$ , then the  $\Delta S_{sol}$  between  $T_H$  and  $T_L$  can be expressed as:

$$\Delta S_{\text{sol}} = \left( \begin{bmatrix} \mathbf{A} \end{bmatrix}_{\mathrm{H}} V - \begin{bmatrix} \mathbf{A} \end{bmatrix}_{\mathrm{L}} V \right) S_{\mathrm{A}} + \left( \begin{bmatrix} \mathbf{O} \end{bmatrix}_{\mathrm{H}} V - \begin{bmatrix} \mathbf{O} \end{bmatrix}_{\mathrm{L}} V \right) S_{\mathrm{o}} - \left( \begin{bmatrix} \text{crystal} \end{bmatrix}_{\mathrm{L}} V - \begin{bmatrix} \text{crystal} \end{bmatrix}_{\mathrm{H}} V \right) S_{\text{crystal}} = \left( \begin{bmatrix} \mathbf{A} \end{bmatrix}_{\mathrm{H}} V - \begin{bmatrix} \mathbf{A} \end{bmatrix}_{\mathrm{L}} V \right) \left( S_{\mathrm{A}} + \frac{n_{\mathrm{O}}}{n_{\mathrm{A}}} S_{\mathrm{o}} + \frac{1}{n_{\mathrm{A}}} S_{\text{crystal}} \right) = \left( \frac{\begin{bmatrix} \mathbf{A} \end{bmatrix}_{\mathrm{H}}}{\begin{bmatrix} \mathbf{A} \end{bmatrix}_{\mathrm{L}}} - 1 \right) \left( S_{\mathrm{A}} + \frac{n_{\mathrm{O}}}{n_{\mathrm{A}}} S_{\mathrm{o}} + \frac{1}{n_{\mathrm{A}}} S_{\text{crystal}} \right) \begin{bmatrix} \mathbf{A} \end{bmatrix}_{\mathrm{L}} V$$

$$(S12)$$

where  $S_A$  is the molar entropy of A, and other terms follow the same rule for explanation, V is the volume of the solution. Obviously,  $\Delta S_{sol}$  is dependent on the value of  $[A]_{H}/[A]_{L}$ .

As mentioned in Note S1,  $\Delta C_r$  is a parameter regarding the concentration-gradient entropy difference of redox pair A and B in electrolyte between  $T_H$  and  $T_L$ . In addition, since the crystal only generates ion A and the concentration of ion B does not change after heating, that is,  $[B]_H = [B]_L$ , then we have

$$\Delta C_{\rm r} = \frac{RT_{\rm H}}{\Delta T} \left( \ln \frac{\left[A\right]_{\rm H}}{\left[B\right]_{\rm H}} - \ln \frac{\left[A\right]_{\rm L}}{\left[B\right]_{\rm L}} \right)$$

$$= \frac{RT_{\rm H}}{\Delta T} \ln \frac{\left[A\right]_{\rm H}}{\left[A\right]_{\rm L}}$$
(S13)

Obviously,  $\Delta C_r$  is also dependent on the value of  $[A]_{H}/[A]_L$ . Therefore, based on equation S6, S12 and S13, it is obvious to obtain  $\alpha \propto \Delta C_r \propto \Delta S_{sol}$ . Therefore, crystal with large  $\Delta S_{sol}$  generates high  $\Delta C_r$  in the electrolyte upon heating and is beneficial for the enhancement of  $\alpha$ .

#### Note S3: Theoretical analysis and calculation method of efficiency of TC-TREC

To simplify the expression of equation, we assume a condition that crystals totally dissolve during the heating process of a thermal cycle, and all derivation below is based on this condition unless specified. Based on the *W* discussed before, the heat-to-electricity conversion efficiency ( $\eta$ ) of TC-TREC can be theoretically expressed as:

$$\eta = \frac{W}{Q_{\rm H} + Q_{\rm HX}} = \frac{\Delta T \left(\Delta S + \Delta C_{\rm r} / 2\right) - E_{\rm loss}}{T_{\rm H} \left|\overline{\alpha}\right| Q_{\rm c} + \left(1 - \eta_{\rm HX}\right) \left(C_{\rm p} \Delta T + \Delta H_{\rm sol}\right)}$$
(S14)

where  $Q_{\rm H}$  is the heat absorbed during the redox reaction at  $T_{\rm H}$ ,  $Q_{\rm HX}$  is the extra heat needed to heat

the cell up,  $C_p$  is the heat capacity of all active materials in the cell, and  $\eta_{\text{HX}}$  is the heat recuperation efficiency and 50–70% has been proven to be reasonable. In this equation,  $\Delta H_{\text{sol}}$  is positioned in the denominator, while  $\Delta C_r$ , which is proportional to  $\Delta S_{\text{sol}}$ , is in the numerator. Therefore, the crystal with a large  $\Delta S_{\text{sol}}$  and a small  $\Delta H_{\text{sol}}$  is beneficial for the enhancement of  $\eta$ . This is consistent with the demand for thermosensitive crystallization. Consequently, using thermosensitive crystallization can induce a considerably enhanced  $\eta$ .

To calculate  $\eta$ , we do not use equation S14 since there are several items that cannot be easily measured or calculated such as  $E_{\text{loss}}$  and  $C_{\text{p}}$ . Therefore, W is calculated based on equation S7, that is, the experimental area of the loop in the V- $q_{\text{c}}$  diagram, and the effects of IR drops and Coulombic efficiency are both taken into account. As for  $C_{\text{p}}$ , it is a variable due to the continuous dissolution of crystals during heating. For the sake of convenience, we define the effective heat capacity of the electrolyte considering the heat absorption of crystal dissolution ( $C_{\text{p,eff}}$ ) as:

$$C_{\rm p,eff} = \frac{C_{\rm p}\Delta T + \Delta H_{\rm sol}}{\Delta T}$$
(S15)

The numerator term can be directly measured based on the differential scanning calorimetry (DSC) test (Fig. S15) and the equation of  $\eta$  for calculation can be expressed as:

$$\eta = \frac{\int (I_{\rm dis}V_{\rm dis} - I_{\rm ch}V_{\rm ch})dt}{T_{\rm H} \left|\overline{\alpha}\right| Q_{\rm c} + (1 - \eta_{\rm HX})C_{\rm p,eff}\Delta T}$$
(S16)

Note that equation S14–S16 is applicable only when the dissolution of crystal is endothermic, which applies to both crystals utilized in this study based on our DSC test (Fig. S15).

## Note S4: Calculation on the efficiency of electrically assisted TC-TREC

In the electrically assisted TC-TREC, active materials consists of  $Fe(CN)_6^{3-/4-}$  solution, KGdmFeCN crystals, GdmCl anolyte, and Ag/AgCl anode. At discharged state, they are specifically 50 mM K<sub>3</sub>Fe(CN)<sub>6</sub>/2 M GdmCl/2 M KCl solution, 45 wt% KGdmFeCN crystals, 4 M GdmCl solution, and AgCl electrode. Although excess anolyte and anode are used to study the  $Fe(CN)_6^{3-/4-}$  half-cell, only enough amount of them are counted into the calculation of  $\eta$ , which is reasonable in an electrically assisted TREC (Fig. S12). Besides, some KGdmFeCN crystals dissolve during charging instead of heating since they are quite a lot, while the  $Fe(CN)_6^{3-}$ -based crystallization occurs. We assume that

the endotherm of dissolution and the exotherm of crystallization complement each other during charging. In our experiment, W is calculated to be 525.915 mJ (14.6 J mL<sup>-1</sup>) when temperature is varied from 20 to 70 °C as shown in Fig. 3c. The volume of Fe(CN)<sub>6</sub><sup>3-/4-</sup> solution is 20 µL, and the mass of KGdmFeCN crystals is 18.769 mg. Our experiments show that

$$Q_{\rm c} = 1.1652 \text{ mAh}$$
,  $\rho_{\rm Fe(CN)_6^{3-/4-} \text{ solution}} = 1.147 \text{ g mL}^{-1}$ ,  $\rho_{\rm anolyte} = 1.092 \text{ g mL}^{-1}$   
 $\rho_{\rm crystal} = 1.49 \text{ g mL}^{-1}$ ,  $\rho_{\rm AgCl} = 5.56 \text{ g mL}^{-1}$ 

Total mass of GdmCl needed at charged state is

$$m_{\rm GdmCl} = \frac{3.6M_{\rm GdmCl}Q_{\rm c}}{nF} = \frac{3.6 \times 95.53 \times 1.1652}{1 \times 96485} \times 1000 = 4.153 \,\rm{mg}$$

Based on the solubility of GdmCl in water at 20 °C (228 g/100 mL), and the water content in 4 M GdmCl (72.35 wt%), the mass of 4 M GdmCl anolyte needed at discharged state is

$$m_{\text{anolyte}} = \frac{4.153}{2.28 \times 0.7235} = 2.518 \text{ mg}$$

The specific charge capacity of AgCl  $(q_{c, AgCl})$  is

$$q_{c,AgCl} = \frac{nF}{3.6M_{AgCl}} = \frac{1 \times 96485}{3.6 \times 143.35} = 186.965 \text{ mAh g}^{-1}$$

where  $M_{AgCl}$  is the molecular weight of AgCl. Then the mass of AgCl needed for charging is

$$m_{\rm AgCl} = \frac{Q_{\rm c}}{q_{\rm c, AgCl}} = \frac{1.1652}{186.965} \times 1000 = 6.232 \,\rm mg$$

Total volume of all active materials is

$$V_{\text{total}} = V_{\text{Fe(CN)}_{6}^{3-/4-} \text{ solution}} + V_{\text{crystal}} + V_{\text{anolyte}} + V_{\text{Ag/AgCl}}$$
$$= 20 + 18.769 / 1.49 + 2.518 / 1.092 + 6.232 / 5.56$$
$$= 36.023 \ \mu\text{L}$$

The mass of catholyte is

$$m_{\text{catholyte}} = m_{\text{Fe(CN)}_6^{3-/4-} \text{ solution}} + m_{\text{crystal}} = 20 \times 1.147 + 18.769 = 41.709 \text{ mg}$$

Our DSC tests (Fig. S15a) show that

$$c_{\rm p,anolyte} = 3.481 \,\mathrm{J} \,\mathrm{g}^{-1} \,\mathrm{K}^{-1}, \ c_{\rm p,AgCl} = 0.353 \,\mathrm{J} \,\mathrm{g}^{-1} \,\mathrm{K}^{-1}$$
 (see Reference<sup>2</sup>),  $Q_{\rm HX,catholyte} = 181.027 \,\mathrm{J} \,\mathrm{g}^{-1}$ 

In total,  $Q_{\rm HX}$  is calculated as

$$Q_{\rm HX} = (m_{\rm anolyte} c_{\rm p,anolyte} + m_{\rm AgCl} c_{\rm p,AgCl}) \Delta T + m_{\rm catholyte} Q_{\rm HX,catholyte}$$
  
= (2.518×3.481+6.232×0.353)×50+41.709×181.027  
= 8098.708 mJ

As shown in Figs. 3a and S13, we have

$$\overline{\alpha_{\text{Fe}(\text{CN})_6^{3-/4-}}} = (\alpha_{\text{ch}} + \alpha_{\text{dis}}) / 2 = -2.458 \text{ mV K}^{-1}, \ \overline{\alpha_{\text{Ag/AgCl}}} = 0.187 \text{ mV K}^{-1}$$

Then  $Q_{\rm H}$  is calculated as

$$Q_{\rm H} = T_{\rm H} \left| \overline{\alpha} \right| Q_{\rm c}$$
  
=  $T_{\rm H} \left| \overline{\alpha}_{\rm Fe(CN)_6^{3-/4-}} - \overline{\alpha}_{\rm Ag/AgCl} \right| Q_{\rm c}$   
=  $343.15 \times (2.458 + 0.187) \times 1.1652 \times 3.6$   
=  $3807.261 \,\rm mJ$ 

Finally, the efficiency without heat recuperation is calculated as

$$\eta = \frac{W}{Q_{\rm H} + Q_{\rm HX}} = \frac{525.915}{3807.261 + 8098.708} \times 100\% = 4.417\%$$

With 50% heat recuperation efficiency, efficiency is calculated as

$$\eta = \frac{W}{Q_{\rm H} + (1 - \eta_{\rm HX})Q_{\rm HX}} = \frac{525.915}{3807.261 + (1 - 0.5) \times 8098.708} \times 100\% = 6.694\%$$

The Carnot-relative efficiencies with and without 50% heat recuperation efficiency are calculated to be 30% and 46%, respectively. The simulation of  $\eta$  with different values of crystal content is based on the same calculation process.

#### Note S5: Calculation on the efficiency of charging-free TC-TREC

In the charging-free TC-TREC, active materials consist of  $Fe(CN)_6^{3-/4-}$  solution, KGdmFeCN crystals, and  $I_3^-/I^-$  anolyte. At charged state, they are specifically 0.8 M K<sub>3</sub>Fe(CN)<sub>6</sub>/1.5 M GdmCl catholyte, 0.15 g mL<sup>-1</sup> KGdmFeCN crystals, and 0.1 M I<sub>2</sub>/2.5 M KI/1.5 M GdmCl anolyte. Since using excess electrolyte while calculating only enough of them will lead to an exaggerated  $\eta$  in charging free TREC (Fig. S12), catholyte and anolyte with the same charge capacity are used here. In our experiment, *W* is calculated to be 187.766 mJ (5.87 J mL<sup>-1</sup>) when temperature is varied from 28 to 70 °C as shown in Fig. 4d. The volumes of Fe(CN)<sub>6</sub><sup>3-/4-</sup> solution and anolyte are 20 and 10 µL, respectively, and the mass of KGdmFeCN crystals is 3 mg. Total volume of all active materials is

$$V_{\text{total}} = V_{\text{Fe}(\text{CN})_{6}^{3-/4-} \text{ solution}} + V_{\text{crystal}} + V_{\text{anolyte}}$$
  
= 20 + 3 / 1.49 + 10  
= 32.013 µL

Our experiments show that

$$Q_{\rm c} = 0.336 \text{ mAh}, \ \rho_{\rm Fe(CN)_6^{3-/4-} \text{ solution}} = 1.167 \text{ g mL}^{-1}, \ \rho_{\rm anolyte} = 1.364 \text{ g mL}^{-1}$$

The mass of anolyte, and catholyte & crystal are

$$m_{\text{anolyte}} = 10 \times 1.364 = 13.64 \text{ mg}, \quad m_{\text{catholyte}} = 20 \times 1.167 + 3 = 26.34 \text{ mg}$$

Our DSC tests (Fig. S15b) show that

$$c_{\rm p,anolyte} = 2.897 \text{ J g}^{-1} \text{ K}^{-1}, \ Q_{\rm HX,catholyte} = 163.753 \text{ J g}^{-1}$$

In total,  $Q_{\rm HX}$  is calculated as

$$Q_{\rm HX} = m_{\rm anolyte} c_{\rm p,anolyte} \Delta T + m_{\rm catholyte} Q_{\rm HX,catholyte}$$
$$= 13.64 \times 2.897 \times 42 + 26.34 \times 163.753$$
$$= 5972.887 \text{ mJ}$$

As shown in Fig. 4b, we have

$$\overline{\alpha_{_{\text{Fe}(\text{CN})_6^{3-/4-}}}} = -3.188 \text{ mV K}^{-1}, \ \overline{\alpha_{_{\text{I}_3/\text{I}^-}}} = 0.449 \text{ mV K}^{-1}$$

Therefore,  $Q_{\rm H}$  is calculated as

$$Q_{\rm H} = T_{\rm H} \left| \overline{\alpha} \right| Q_{\rm c}$$
  
=  $T_{\rm H} \left| \overline{\alpha}_{\rm Fe(CN)_6^{3-/4-}} - \overline{\alpha}_{\rm I_3^-/I^-} \right| Q_{\rm c}$   
= 343.15×(3.188+0.449)×0.336×3.6  
= 1509.625 mJ

Finally, the efficiency without heat recuperation is calculated as

$$\eta = \frac{W}{Q_{\rm H} + Q_{\rm HX}} = \frac{187.766}{1509.625 + 5972.887} \times 100\% = 2.509\%$$

With 50% heat recuperation efficiency, efficiency is calculated as

$$\eta = \frac{W}{Q_{\rm H} + (1 - \eta_{\rm HX})Q_{\rm HX}} = \frac{187.766}{1509.625 + (1 - 0.5) \times 5972.887} \times 100\% = 4.176\%$$

The Carnot-relative efficiencies with and without 50% heat recuperation efficiency are calculated to be 20% and 34%, respectively.

#### Note S6: Cycling test of the electrically assisted TC-TREC

To substantiate the stability of the electrically assisted TC-TREC system, we cycled a cell for 40 hours. For an expedited test, 15 wt% KGdmFeCN crystals were used and the cell was charged to 50% SOC. The cell was cycled between 20 and 70°C with a current density of 0.51 mA cm<sup>-2</sup>, and it exhibited a stabilized CE of ~99.4%. Normalized  $\eta$  is calculated based on the same process as in Note S4, and no significant change was observed in the cyclic curve (Fig. S17).

## Note S7: Estimation of the enthalpy change ( $\Delta H_{sol}$ ) during dissolution of KGdmFeCN

We use DSC tests to calculate the integral enthalpy of dissolution<sup>3</sup>. Measurements are performed for the reference and experimental systems. The reference system consists of 0.4 M K<sub>3</sub>Fe(CN)<sub>6</sub>/3 M GdmCl solution without crystal, and the experimental system consists of 0.4 M K<sub>3</sub>Fe(CN)<sub>6</sub>/3 M GdmCl solution with 0.1 g mL<sup>-1</sup> KGdmFeCN. The heat flow versus temperature plots are gained from the DSC tests. Since the heat is normalized in the two systems, we multiply the heat in the experimental system by the corresponding coefficient and get the heat versus temperature plots to calculate  $\Delta H_{sol}$ . The integration area is obtained by making a tangent at the point where two curves are offset, and the calculated  $\Delta H_{sol}$  from it is 207.9 J g<sup>-1</sup>.

# **Supplementary Figures**



Fig. S1 Schematic of thermally regenerative electrochemical cycle (TREC) with a negative temperature coefficient ( $\alpha$ ). The four surrounding diagrams contain four states of the cell and four processes of a thermal cycle, including heating the cell up, charging at high temperature ( $T_{\rm H}$ ), cooling the cell down, and discharging at low temperature ( $T_{\rm L}$ ). The yellow column height represents the relative value of electrode potential. The voltage-charge capacity diagram is in the center. The four dots correspond to the four surrounding diagrams, and the net energy (W) generated over one cycle is the area of the loop.



Fig. S2 Schematic of the change of electrolyte and  $Fe(CN)_6^{4-}$ -associated crystallization and dissolution processes within a thermal cycle in the thermosensitive crystallization-boosted TREC (TC-TREC) containing  $Fe(CN)_6^{3-/4-}$ .



Fig. S3 Schematic of the higher W of TC-TREC. a Voltage-specific charge capacity  $(q_c)$  diagram of the TREC (black) and TC-TREC (red). The TC-TREC generate a higher W due to its larger  $\Delta C_{r}$ based  $\alpha$  and larger  $q_c$  compared with TREC. b Temperature-entropy (*T-S*) diagram of the TREC (black) and TC-TREC (red). The TC-TREC generate an extra W due to  $\Delta C_r$ . The analysis result of both (a) and (b) illustrate that TC-TREC can generate a higher W than pristine TREC.



Fig. S4 Schematic of synthesizing KGdmFeCN crystals.



Fig. S5 Photographs of the TC-TREC electrolyte before and after heating up.



Fig. S6 Specific charge capacity ( $q_c$ ) and Coulombic efficiency of the Fe(CN) $_6^{3-/4-}$  half-cell with different values of KGdmFeCN crystal content. The  $q_c$  increases with an increase in crystal content, while the Coulomb efficiency is maintained at approximately 100%.



Fig. S7 The  $q_c$  of different Fe(CN) $6^{3-/4-}$  half-cell systems.



Fig. S8 The effective specific heat capacity ( $c_{p,eff}$ ) of KFeCN solution and KGdmFeCN systems with 45 wt% and 100 wt% crystal content. The  $c_{p,eff}$  of KGdmFeCN system with 45 wt% crystal content is calculated from the DSC plot in Fig. S15.



Fig. S9 Electrical conductivity of (a) Fe(CN)6<sup>3-/4-</sup> electrolyte with & without crystal, and (b) KCl & GdmCl electrolyte at different temperatures.



Fig. S10 Schematics of the (a) electrically assisted and (b) charging-free TC-TREC cells configuration and operation within a thermal cycle. The catholyte and anolyte are separated by a Nafion 115 membrane.



**Fig. S11 Fabrication of the electrically assisted TC-TREC cell. a** Schematic of the electrically assisted TC-TREC cell. **b** Components used in the cell. **c** Side-view photograph of the cell



Fig. S12 Schematic of thermal cycles in (a) electrically assisted and (b) charging-free TREC when using capacity-symmetric cell and capacity-asymmetric cell. The solid lines represent the real voltage-charge capacity plot over a thermal cycle when using capacity-symmetric cell, while the dashed lines represent the changed one when using capacity-asymmetric cell. Obviously, the net works are the same when using two types of cells in electrically assisted TREC, which is opposite in charging-free TREC. Therefore, it is reasonable to use a capacity-asymmetric cell and count only the necessary amount of active materials into the calculation of efficiency ( $\eta$ ) for the electrically assisted TREC. However, a capacity-symmetric cell is essential for the charging-free TREC, otherwise all the excess active materials should be considered, because the using of them can induce gentler charge and discharge curves and thus a higher *W* and  $\eta$ .



Fig. S13 The absolute value of  $\alpha$  of the electrically assisted TC-TREC cell at different state of charge (SOC). The decrease of  $|\alpha|$  arises from the consumption of KGdmFeCN crystals during charging process.



Fig. S14 The current-voltage curves and their corresponding power densities for (a) electrically assisted and (b) charging-free TC-TRECs.



Fig. S15 The heat flow versus sample temperature plots in differential scanning calorimetry (DSC) tests of electrolyte in (a) electrically assisted and (b) charging-free TC-TRECs. The specific heat energy needed to heat the catholyte up is calculated from the area between the curve and the abscissa. The calculated specific heat capacity ( $c_p$ ) of anolyte in electrically assisted and charging-free TC-TRECs are 3.481 and 2.897 J g<sup>-1</sup> K<sup>-1</sup>, respectively.



Fig. S16 The  $\eta$  of electrically assisted TC-TREC operating at different temperature differences. The cell was tested by maintaining  $T_{\rm H}$  at 70°C and varying  $T_{\rm L}$  to ensure an adequate supply of Fe(CN)<sub>6</sub><sup>4-</sup> for the reaction.



Fig. S17 Cycling performance of the electrically assisted TC-TREC system. a Voltage-time plot of the electrically assisted TC-TREC cell during cycling. The cell is cycled between 20 and 70 °C with the current density of 0.51 mA cm<sup>-2</sup>. b Coulombic efficiency and normalized heat-to-electricity conversion efficiency ( $\eta$ ) per cycle during the cycling test.



Fig. S18 Estimation of the enthalpy change ( $\Delta H_{sol}$ ) during dissolution of KGdmFeCN based on DSC tests. The black solid line represents the reference system without crystal (0.4 M K<sub>3</sub>Fe(CN)<sub>6</sub>/3 M GdmCl, 1 g in total), the red solid line represents the experimental system with crystal (0.4 M K<sub>3</sub>Fe(CN)<sub>6</sub>/3 M GdmCl with 0.1 g mL<sup>-1</sup> KGdmFeCN, 1.088 g in total), and the red dashed line is obtained by tangent at the point where the two solid lines are offset. The calculated  $\Delta H_{sol}$  from the red area is 207.9 J g<sup>-1</sup>.

# **Supplementary Tables**

Operating mode	Electrically assisted	Charging-free			
Cathodic half-cell	Fe(CN) <sub>6</sub> <sup>3-/4-</sup>				
Anodic half-cell	Ag/AgCl	I <sub>3</sub> <sup>-</sup> /I <sup>-</sup>			
Temperature range(°C)	20–70	28–70			
$\alpha$ (mV K <sup>-1</sup> )	-3.96	-3.64			
$q_{\rm c}$ for the full cell (Ah L <sup>-1</sup> )	32.34	10.5			
$W(J mL^{-1})$	14.6	5.87			
η(%)	4.42	2.51			
$\eta$ with 50% $\eta_{\rm HX}$ (%)	6.69	4.18			

 Table S1 Characteristics of the electrically assisted and charging-free TC-TREC systems.

Operating mode	Cell configuration (  : ion exchange membrane)	$ \alpha $ (mV K <sup>-1</sup> )	W (J g <sup>-1</sup> /J mL <sup>-1</sup> )	η (%)	$\eta$ with 50% $\eta_{\rm HX}$ (%)	Temperature range (°C)	Ref.
Electrically assisted	Graphite/KGdmFeCN   GdmCl/Ag/AgCl	3.96	$14.6 \text{ J mL}^{-1}$	4.42	6.69	20–70	This work
	CuHCFe/NaNO <sub>3</sub>    Cu(NO <sub>3</sub> ) <sub>2</sub> /Cu	1.2	8.93 J g <sup>-1</sup>	3.7	5.7	10–60	4
	NiHCF/KCl/Ag/AgCl	0.74	$2.34 \text{ J g}^{-1}$	1.6	2.6	15–55	5
	CoHCF-pp/NaCl	0.89	$2.05 \ \mathrm{J} \ \mathrm{g}^{-1}$	2.65	3.65	10–50	6
	LMO/LiNO <sub>3</sub> +KNO <sub>3</sub> /CuHCFe	1.16	$0.97 \ \mathrm{J} \ \mathrm{g}^{-1} \ *$	1.8	2.6	10–40	7
	$\frac{\text{Ni}_{0.2}\text{Co}_{0.8}(\text{OH})_2}{\text{KFe}(\text{CN})_6^{3-/4-}}$	1.46	$11.74 \text{ J mL}^{-1} *$	3.61	-	25–55	8
	CuHCFe/RbNO <sub>3</sub> +Cu(NO <sub>3</sub> ) <sub>2</sub> /Cu	1.71	$7.81 \text{ J g}^{-1}$	1.57	2.74	10–50	9
	NiHCF/K2SO4/Zn	1.58	5.83 J g <sup>-1</sup> *	2.40	3.77	10-40	10
	NiHCF/K <sub>2</sub> SO <sub>4</sub>    (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> +NH <sub>3</sub> ·H <sub>2</sub> O/Zn	2.27	9.89 J g <sup>-1</sup> *	2.17	3.58		
	Graphite/KFe(CN) <sub>6</sub> <sup>3-/4-</sup> +GdmCl  ZnCl <sub>2</sub> /Zn	3.28	$1.82 \text{ J mL}^{-1} *$	1.15	1.84	25–50	11
	CuHCFe/PSS+RbNO <sub>3</sub> +Cu(NO <sub>3</sub> ) <sub>2</sub> /Cu	2.01	8.06 J g <sup>-1</sup> *	1.82	2.99	10-40	12
	CuHCFe/NaClO <sub>4</sub>    Fe <sup>2+/3+</sup> ClO <sub>4</sub> /Graphite	3.04	14.28 J g <sup>-1</sup> *	4.11	6.26	10–60	13
	CuHCFe/NaNO <sub>3</sub> (Half cell)	0.755	2.88 J g <sup>-1</sup> *	3.8	-	15–55	14
Charging- free	Graphite/KGdmFeCN   KI3 <sup>-</sup> /I <sup>-</sup> /Graphite	3.64	$5.87 \text{ J mL}^{-1}$	2.51	4.18	28–70	This work
	CC/KFe(CN)6 <sup>3-/4-</sup>    KNO3/PB	1.4	4.55 J g <sup>-1</sup> *	0.52	0.8	20–60	15
	$\frac{\text{CF-rGO/KFe}(\text{CN})_6^{3-/4-}}{\text{KI}_3^-/\text{I}^-/\text{CF-rGO}}$	1.8	-	1.23	-	30–65	16
	CP/LiFe(CN)6 <sup>3-/4-</sup>    LiCl/FP	1.84	$3.816 \text{ J mL}^{-1} *$	1.81	2.97	27–57	17

**Table S2** Comparison of  $\alpha$ , W and  $\eta$  values for various reported TREC systems with and without50% heat recuperation efficiency ( $\eta_{\text{HX}}$ ).

\* Only the studied half-cell's active materials are counted into the calculation of energy density.

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