Electronic Supplementary Information (ESI)

Simultaneous energy harvesting and storage via solar-driven regenerative electrochemical cycles[†]

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Supplementary Information Text

The test of Seebeck coefficient of redox species

The method to test the Seebeck coefficient of redox species is the same as reported works. A threeelectrode setup was adopted in a three-neck flask, with the Ag/AgCl/4M KCl as reference electrode, platinum wire as the counter electrode. The flask was put in a water bath, and the hermetically sealed thermalcouple tip was placed next to the working electrode to monitor the temperature. The open circuit voltage of different redox species versus Ag/AgCl electrode was recorded at different temperatures, ranging from 30 °C to 60 °C. The Seebeck coefficient of Ag/AgCl electrode has been measured in reported papers as 0.12 ± 0.02 mV K⁻¹. A variety of solutions with different redox species dissolved in water were prepared for the test, including 0.1 M K₃Fe(CN)₆/0.1 M K₄Fe(CN)₆, 0.1 M Kl₃/0.1M Kl, 0.1 M CuSO₄, 0.01 M H₂BQ/0.01 M BQ/0.05 M H₂SO₄, 0.01M 4-OH-TEMPO⁺/0.01M 4-OH-TEMPO/0.6 NaCl, and 0.01 FcN⁺Cl/0.01 FcNCl/0.6 NaCl. To prepare the 0.01M 4-OH-TEMPO⁺/0.01M 4-OH-TEMPO/0.6 NaCl, a H-cell was used to electrolyze 0.02 M 4-OH-TEMPO paired with 0.05 M BQ/0.6M NaCl to get equimolar 4-OH-TEMPO⁺ and 4-OH-TEMPO. The 0.01 FcN⁺Cl/0.01 FcNCl/0.6 NaCl solution was prepared similarly. The Seebeck coefficient was then obtained by perform a liner fit between the open circuit voltage an temperature after taking account of the Seebeck coefficient of Ag/AgCl reference electrode.

The measurement of specific heat capacity

The test of the specific heat capacity was based on the DSC method between the temperature range of 25 ~ 75 °C, with a heat rate of 5 °C min⁻¹ and a N₂ flow of 50 mL min⁻¹. The measurement conditions for the empty crucible, the reference sample, and the prepared samples are the same. The measurement of the empty crucible was performed first, following by water as the reference sample, and the 0.5 M $K_3Fe(CN)_6/0.1$ M $K_4Fe(CN)_6$ solution and 0.1 M $I_2/2$ M KI soluiton as the prepared samples. The calculation of the specific heat capacity is based on the equation:

$$Cp = \frac{H}{H_r} \times \frac{m_r}{m} \times Cp_r,$$

where Cp is the specific heat capacity of the prepared sample, H is the heat flow of the prepared sample, H_r is the heat flow of the reference sample with known specific heat capacity, m is the weight of the prepared sample, m_r is the weight of the reference sample, Cp_r is the specific heat capacity of the reference sample.



Fig. S1. The Seebeck coefficient measurement of inorganic redox species: CuSO₄/Cu solution.



Fig. S2. The Seebeck coefficient measurements of organic redox species. (A) BQ/H_2BQ solution; (B) TEMPO⁺/TEMPO solution.



Fig. S3. The Seebeck coefficient measurements of organometallic redox species: FcN⁺Cl/FcNCl solution.



Fig. S4. Tafel plots of redox species. (A) K₃Fe(CN)₆/K₄Fe(CN)₆ solution and **(B)** KI₃/KI solution.



Fig. S5. The cell structure. (**A**) Schematic of the cell components. (**B**) Top-view photograph of the cell. (**C**) Side-view photograph of the cell.



Fig. S6. The open circuit voltage profile of the cell employing a $CuSO_4$ (0.2M)/Cu-based cathode and a Ag/AgCl –based anode at different temperatures.



Fig. S7. DSC results of the electrolytes. (A) DSC test and (B) the calculated specific heat capacity of electrolytes.



Fig. S8. Energy efficiency comparison. Comparison of energy conversion efficiencies (η_r : the energy conversion efficiency versus Carnot efficiency) in this work with reported thermogalvanic cells with redox species dissolved in solvents.(1-3)



Fig. S9. SEM image of the carbon felt.



Fig. S10. Raman spectra of different samples.



Fig. S11. XPS spectra of absorbers. (A) XPS spectra of CF and CF-rGO; **(B)** the curve fitting of C1s spectra of CF; **(C)** the curve fitting of C1s spectra of CF-rGO.



Fig. S12. Photographs of the cell structures. Images of **(A)** the cuvettes with a rectangular hole and **(B)** the assembled device with a Nafion membrane sandwiched between two cuvettes.



Fig. S13. SEM images of the PVDF coating on absorbers. (A) Top-view and **(B)** cross-sectional SEM images of the PVDF coating on CF-rGO.



Fig. S14. Image of the CF, CF-rGO, and CF-rGO-PVDF absorbers.



Fig. S15. The galvanostatic discharge voltage profiles of the solar-driven regenerative electrochemical cell with or without solar illumination at a simulated open circuit voltage the same as that in Fig. 4H.



Fig. S16. UV-vis spectra of (A) the $K_3Fe(CN)_6/K_4Fe(CN)_6$ catholyte and (B) the KI_3/KI anolyte before and after operation at 65 °C for 4 days.



Fig. S17. (A) SEM image of CF-rGO and energy dispersive X-ray (EDX) elemental mapping of (B) C, (C) O and (D) N before the cell operation.



Fig. S18. (A) SEM image of CF-rGO and EDX elemental mapping of (B) C, (C) O and (D) N after the cell operation.

Table S1. Summary of Seebeck coefficients of a v	variety of redox species.
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Redo x species	K₃Fe(CN)₅/ K₄Fe(CN)₅	KI ₃/KI	CuSO₄/ Cu	BQ/ H₂BQ	4-ОН-ТЕМРО⁺/4- ОН-ТЕМРО	FcN⁺Cl/FcN Cl
α (mV/K)	-1.42	0. 53	0.78	0.38	-0.02	-0.056

Electroly	0.5 M	Satura	19.	12.80	6.40	3.20 wt%
tes	K ₃ Fe(CN) ₆ /0.1 M	ted CuSO ₄	20	wt%	wt%	$CuSO_4$ in H_2O
	K ₄ Fe(CN) ₆ vs. 0.1	in H₂O	wt%	CuSO ₄ in	CuSO ₄ in	
	M I ₂ /2 M KI		$CuSO_4$	H₂O	H ₂ O	
			in H₂O			
α	1.8	0.75	0.7	0.76	0.71	0.83
			7			
(mV K⁻¹)						
Referenc	This work	Ref.8	Ref	Ref.8	Ref.8	Ref.8
е			.8			
Electroly	0.64 wt%	3.36 M	3.3	3.36	0.1 M	0.585 M
tes	CuSO ₄ in H ₂ O	KBr, 1	6 M	M KBr,	Fe(CN) ₆ ^{3-/4}	LiCl, 0.415 M
		wt% Br_2	KBr, 2	saturated	-	KCl, 0.01 M
			wt%	Br ₂		LiH
			Br ₂			
α	1.32	0.69	1.1	1.55	1.43	0.39~0.61
			9			
(mV K⁻¹)						
Referenc	Ref.8	Ref.8	Ref	Ref.8	Ref.8	Ref.8
е			.8			
Electroly	copper	KFeFe(0.4	NiHCF	0.5 M	0.35 M
tes	hexacyanoferrate	CN) ₆ vs.	M I⁻/	vs.	Fe(CN) ₆ ^{3-/4}	Cu(HCOO) ₂
	(CuHCF) vs. 3 M	0.3 M	l₃ [–] in	Ag/AgCl	⁻ vs. 0.125	in H ₂ O
	$Cu(NO_3)_2$ in H_2O	K₃Fe(CN) ₆	H ₂ O		М	
		/0.5 M			Cu ⁺ /Cu ²⁺	
		K₄Fe(CN) ₆			in H ₂ O	
		in H ₂ O				
		-				
α	1.2	1.45	0.5	0.74	2.9	1.2
			3			
(mV K⁻¹)						
Referenc	Ref.50	Ref.50	Ref	Ref.5	Ref.50	Ref.6
е			.8	0		

Table S2. The Seebeck coefficients of reported thermogalvanic cells.

Table S3. Comparison of the energy conversion efficiencies at different current densities.

Current density	(I) W	Q _н (J)	η (%)	η _r (%)
(µA cm⁻²)				
100	0.0551	0.57	1.23	11.9
200	0.0436	0.47	1.0	9.7

Table S4. The bulk prices for the electroactive materials and absorbers of the solar-driven regenerative electrochemical cell. Most of the information is either from Alibaba.com or related reports.

The cell in this work	K₃Fe(C N)₀	K₄Fe(CN) ₆	l ₂	KI	KCI	Carbon felt	Grap hite
Bulk price (US\$/kg)	0.8	0.9	1	0.23	0.1	0.8	0.75
Solar cell	Polysili con	Single crystal silicon	GaAs	N719 dye	Perov skite layer (CH ₃ NH ₃ I)		
Bulk price (US\$/kg)	20	100	200	69000	450		
Thermoelec trics	Bi ₂ Te ₃	SiGe	Mg ₂ Si _{0.85} Bi 0.15	CeFe ₄ Sb ₁₂	InGaZ nO	Na0. ₇ C οO _{2-δ}	
Bulk price (US\$/kg)	110	679	6.67	37	511	36	
Redox flow battery	VOSO ₄	FeCl ₂	Zn	HBr			
Bulk price (US\$/kg)	10.2	2.53	3	3.33			

References

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