Supplementary information

Solid-state n-type Thermodiffusion-assisted Thermogalvanic Cells with Unprecedented Thermal Energy Conversion

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Supplemental experimental procedures

Materials. PEDOT:PSS (Clevios P VP AI4083, solid content of 1.5 wt. %) was purchased from Heraeus. Iron(II) chloride tetrahydrate (98%), Iron (III) chloride (97%), Iron (II) perchlorate hydrate (98%), Iron (III) perchlorate hydrate (low chloride ($\leq 0.005\%$)), perchloric acid (ACS reagent, 70%), Iron(II) sulfate heptahydrate ($\geq 99.0\%$), Iron(III) sulfate hydrate (97%) were purchased from Sigma-Aldrich. All chemicals were used without further purification

Fabrication of solid-state Thermodiffusion-assisted TG cells. The molar concentration of $Fe(ClO_4)_{2/3}$ redox couples was calculated for the aqueous solvents in the PEDOT:PSS dispersion, ignoring the water molecules of hydration in the iron redox couples. The final PEDOT:PSS/Fe(ClO₄)_{2/3} solutions were obtained after stirring 6 h. at room temperature. Au electrodes were thermally evaporated onto UV-ozone-treated glass substrates (2.5 mm × 21 mm × 70 nm). Thin films were fabricated by drop-casting 30 μ l of the PEDOT:PSS/Fe(ClO₄)_{2/3} solutions onto the Au-patterned glass substrate. The drop-casted solution was air-dried at 23-25 °C and 50 – 60 % relative humidity (RH), to obtain a solid-state film. The device was configured in-plane with Au electrodes distanced 3.8 mm apart. The film thickness, measured using a stylus profiler (P-6, KLA Tencor), was approximately 30 μ m.

Ionic Seebeck coefficient. The S_i was measured using a custom-built system controlled by LabVIEW software (Fig. S16). Peltier devices attached to an aluminum heat sink were connected in series to a Keithley 2400 source meter to apply a temperature gradient across the sample. T-type thermocouples, which directly contact with electrode, connected to a Keysight 34970A data acquisition unit measured the temperature difference between the two

electrodes.¹ Thermovoltage-time curves were recorded using a Keysight 34465A digital multimeter. To standardize the S_i measurement, the Seebeck coefficient of a nickel plate was measured beforehand, yielding -19.96 μ V K⁻¹, consistent with the literature values. Measurements were conducted in a humidity-controlled chamber with adjustable humidity from 30% to 99.9% RH. The S_i was determined from the linear relationship between the thermovoltage and temperature difference, averaged over four experiments.

Power density output. The discharging power and energy were measured by recording the current-voltage curves as the voltage approached near saturation within 15 min. during the thermal charging. During the discharge, a Keithley 2400 meter obtained the current-voltage curves, and the output power was calculated using the formula $P_{max}/(\Delta T)^2 = V_{oc}J_{sc}/(2\Delta T)^2$, where V_{OC} is the open-circuit voltage, J_{SC} is the short-circuit current density, and ΔT is the temperature difference across the cell.

Thermal conductivity. Thermal diffusivity (${}^{D}_{thermal}$) was measured using a Laser Flash Diffusivity Tester (LFA457, Netzsch), and specific heat capacity (${}^{C}_{p}$) was measured using Differential Scanning Calorimetry (Q200, TA Instruments) at 298K. Thermal conductivity (κ) was calculated using the following equation: $\kappa = C_p \cdot D_{thermal} \cdot \rho$, where ρ is the density. The PEDOT:PSS/0.3 M Fe(ClO₄)_{2/3} sample (10 mm × 10 mm × 1.8 mm) exhibited a thermal conductivity of 1.087 W m⁻¹K⁻¹ at 298K under 60% RH, averaged over three experimental replicates.

Since the thermal conductivity of the sample depends on the % RH, the κ values of the sample under various % RH were obtained using the following equation ²:

 $\kappa_f = \kappa_i \emptyset_i + \kappa_w \emptyset_w$

where \emptyset is the volume fraction, and the subscripts f, i, and w correspond to the final state of hydrated PEDOT:PSS/Fe(ClO₄)_{2/3} at each % RH, the initial state of PEDOT:PSS/Fe(ClO₄)_{2/3} at the 60% RH, and water, respectively. Note that the κ value of water is 0.6 W m⁻¹K⁻¹. The volume fraction of the water was estimated using the equation below:

$$V_{total} = V_i + V_w = M_i / \rho_i + M_w / \rho_w$$

where V_{total} is the total volume at each % RH, V_i , M_i , and ρ_i are the volume, mass, and density of the sample at the initial 60 % RH, respectively. V_w , M_w , and ρ_w are the volume, mass, and density of the water at each % RH. V_w is obtained by dividing the mass of the absorbed water at different % RH by water density of 1 g ml⁻¹.

Cyclic voltammetry (CV) and isothermal electrochemical cell. Cyclic voltammetry and the isothermal electrochemical cell measurements were conducted using an electrochemical workstation (COMPACTSTAT, IVIUM technologies) with a three-electrode system: platinum disc and wire electrodes as the working and counter electrodes, respectively, and a saturated calomel electrode (SCE) as the reference electrode. The open-circuit voltage of 0.3 M Fe(ClO₄)_{2/3} in deionized water in response to temperature was measured to be 1.95 mV K⁻¹. Given that the temperature coefficient of SCE itself is -0.47 mV K⁻¹, the temperature coefficient of 0.3 M Fe(ClO₄)_{2/3} in deionized water can be calculated to be 1.48 mV K⁻¹.

Ionic conductivity. The ionic conductivity (σ) of the solid-state TD-assisted TG cells was measured using impedance spectroscopy (COMPACTSTAT, IVIUM technologies) with a two-point probe. An AC voltage of 0.1V was applied over a frequency range of 3 MHz to 0.1 Hz. The ionic conductivity was calculated using the formula $\sigma = d/R \cdot A$, where d, R, and A represent the inter-electrode distance, resistance, and cross-sectional area of TG cells,

respectively. Ionic resistance was determined by fitting the Nyquist plot, and film thickness was measured using a stylus profiler (P6, KLA Tencor). All measurements were conducted at 80% RH, and results from three experimental replicates were averaged.

Materials characterization. X-ray photoelectron spectroscopy (XPS) spectra were measured using ESCALAB 250XI (Thermo Fisher Scientific) with an Al K α X-ray source. The PEDOT:PSS/Fe(ClO₄)_{2/3} solutions were drop-casted onto a pre-cleaned Si wafer and air-dried at 23 - 25 °C under 50 - 60 % RH. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy was analyzed using an IR spectrophotometer (model 670/620, Varian). Raman spectra were measured using a Raman spectrometer (alpha300R, WITec) with a 532 nm He-Ne laser source at 0.1 mW power output. The drop-casted PEDOT:PSS/Fe(ClO₄)_{2/3} films onto a glass substrate were measured at 23 - 25 °C under 50 -60 % RH. To investigate thermodiffusion of ClO₄⁻ counterions within the PEDOT:PSS matrix, samples were subjected to a temperature gradient for a sufficient duration. The vibrational peak corresponding to ClO₄⁻, located near 933 cm⁻¹, was monitored. Following thermal treatment, the sample was physically cut in half to separate the hot and cold regions, thereby preventing further ion migration prior to Raman analysis. UV-Vis spectroscopy was performed using a UV-Vis and NIR spectrophotometer (Cary5000, Agilent) within the wavelength range of 200-800 nm. To prevent absorption saturation, 50 μl of 25 mM Fe³⁺ solution and 100 μl of 0.1 M Fe²⁺ solution were each diluted to a final volume of 3 ml. HClO₄ was added to observe the absorption features of Fe independently of the acid anion effect. At lower pH, peaks centered around 240 nm, attributed to hydrated Fe ions ($[Fe(H_2O)_6]^{2+/3+}$), were predominant, while absorption peaks at higher wavelengths, associated with Fe complexes such as $[Fe(OH)]^{+/2+}$, diminished. The pH of 25 mM Fe³⁺ aqueous solution with

0.2 M HClO₄ was approximately 2.48, higher than the reported pH range of 1.0-2.0 for PEDOT:PSS (AI4083).

Serially connected modules and their applications. A module comprising 16 single devices connected in series was fabricated (Fig. S10). A 70 nm thick Au electrode was designed for serial connection and deposited onto a pre-cleaned PET substrate (32.4 mm × 128.1 mm) using a thermal evaporator. Films were produced by drop-casting a PEDOT:PSS/Fe(ClO₄)_{2/3} solution onto the Au electrodes on the PET substrate, treated with UV-Ozone cleaning. The drop-cast solution was air-dried under ambient conditions (22 – 25 °C under 40 – 60 %). The resulting module generated sufficient output power of 360 μW to directly operate external electronic devices, such as LEG arrays, thermohydrometer, and a digital watch without external voltage boosters or capacitors.

Wearable module. The wearable module, consisting of 100 single devices connected in series, was constructed in a Lego-like configuration. Each module array consisted of 5 single devices, and 10 arrays were vertically assembled on a PET board to facilitate heat conduction in the in-plane direction of the module. Two assemblies, containing 100 single devices, were affixed to the human body using copper tape to enhance heat conduction from the body to the devices. The device, designed in a Lego-like configuration, was sufficiently flexible to conform to the curvature of human arms. A thermovoltage of 1.5 V was harvested from low-grade natural body heat.



Fig. S1. Ionic conductivity measurements under isothermal conditions with an applied amplitude of 0.1 V. (a, b) Nyquist plots and (b) equivalent circuit model at varying concentrations of $Fe(CIO_4)_{2/3}$ in PEDOT:PSS.



Fig. S2. Thermovoltage response under cycling temperature gradients. (a) Raw data from realtime thermovoltage measurements under repeated changes in temperature gradients. (b) Plot of thermovoltage versus temperature gradient, showing a linear relationship used to determine the Seebeck coefficient from the slope of the fitted line.



● Fe²⁺ ● Fe³⁺ ♥ ClO₄⁻ ● Additional ions

Fig. S3. Working mechanisms of various TG cells. (a) Conventional liquid TG cell, (b) Thermodiffusion-combined TG cell by additional ions, and (c) Solid-state Thermodiffusion-assisted TG cell developed in this study, in which the galvanic couple synergistically promotes both the TG and thermodiffusion effect simultaneously.



Fig. S4. Open circuit voltage vs. saturated calomel electrode (SCE) in response to temperature in an isothermal 3-electrode half-cell. The temperature coefficient (α) was measured to be (a) 1.48 mV K⁻¹ in deionized water and (b) 2.527 mV K⁻¹ in PEDOT:PSS solution.



Fig. S5. Cyclic voltammetry (CV) curves of $Fe(ClO_4)_{2/3}$ (0.3 M) (**a**) in deionized water, (**b**) in aqueous PEDOT:PSS solution scanned at 50, 150, and 250 mV s⁻¹. (**c**) Plots of the peak-to-peak potential separation (ΔE_p) between anodic and cathodic peaks from the CV curves of PEDOT:PSS/ Fe(ClO₄)_{2/3} (0.05, 0.1, 0.3, 0.5 M) scanned at 50 – 250 mV s⁻¹.



Fig. S6. XPS spectra for Fe 2p binding energy of pristine $Fe(ClO_4)_2$, $Fe(ClO_4)_3$, PEDOT:PSS/Fe(ClO₄)₂ (0.3 M) and PEDOT:PSS / Fe(ClO₄)₃ (0.3 M).



Fig. S7. UV-vis spectra of (**a**) $Fe(ClO_4)_2$ and (**b**) $Fe(ClO_4)_3$ in aqueous solution with addition of $HClO_4$ ranging from 0 to 0.2 M. $HClO_4$ was added to observe the absorption features of $Fe^{2+/3+}$ independent of the acid anion effect. At lower pH values, the peaks centered ~240 nm, attributed to hydrated Fe ions ($[Fe(H_2O)_6]^{2+/3+}$), became predominant, while the peaks centered ~300 nm, associated with Fe complexes, such as $[Fe(OH)]^{+/2+}$, diminished.



Fig. S8. (a) XPS spectra for O 1s binding energy of PEDOT:PSS with increasing concentrations of $Fe(ClO_4)_{2/3}$ from 0 to 0.3 M. Three primary O 1s peaks (b) in pristine PEDOT:PSS and (c) in PEDOT:PSS/Fe(ClO₄)_{2/3} (0.3 M).



Fig. S9. XPS spectra for Fe 2p binding energy in PEDOT:PSS/Fe(ClO_4)₃ (0.05, 0.1 and 0.3 M).



Fig. S10. Raman spectra showing the vibrational modes of the PEDOT moiety by incorporating $Fe(ClO_4)_{2/3}$ at 0.05, 0.1, 0.3 M in PEDOT:PSS.



Fig. S11. Raman spectroscopy analysis confirming thermodiffusion of ClO_4^- counterions within the PEDTO:PSS matrix. A vibrational peak near 933 cm⁻¹, corresponding to ClO_4^- , was observed. The higher intensity of this peak on the cold side compared to the hot side indicates directional ion migration driven by the thermal gradient.



Fig. S12. a-c, FT-IR spectra of the O-H stretching modes of water peaks in PEDOT:PSS with increasing concentrations from 0 to 0.3 M for (a) $Fe(ClO_4)_{2/3}$, (b) $FeCl_{2/3}$, and (c) $Fe(SO_4)/Fe_2(SO_4)_3$.



Fig. S13. Effect of humidity on the kinetics of solid-state TD-assisted TG cell. (a) Seebeck coefficient and (b) Current density and power density measured under varying relative humidity conditions from 40% to 80%.



Fig. S14. Schematic illustration of the quasi-continuous operation of the solid-state TDassisted TG cell in 4 steps: (a) Thermal charging in an open circuit, (b) electrical discharging in a short circuit with the maximum current output, (c) thermal recharging in an open circuit, and (d) Homogeneous distribution of ions by removing the temperature gradient.



Fig. S15. Ionic conductivity depending on the concentrations of $Fe(ClO_4)_{2/3}$ in PEDOT:PSS.



Fig. S16. The configuration of the custom-built Seebeck measurement setup.

Table S1

Ionic conductivity depending on the concentrations of $Fe(ClO_4)_{2/3}$ in PEDOT:PSS. The value was the average of three experimental replicates measured at 80% RH.

| Fe(ClO ₄) _{2/3} concentration | 0 M | 0.02 M | 0.05 M | 0.1 M | 0.2 M | 0.3 M |
|--|-------|--------|--------|-------|-------|-------|
| Ionic conductivity (S cm ⁻¹) | 0.212 | 2.443 | 0.737 | 0.386 | 0.292 | 0.269 |
| Standard deviations | 0.015 | 0.125 | 0.057 | 0.019 | 0.041 | 0.014 |

Table S2

Comparison of the S_i, P_{max} normalized to $(\Delta T)^2$, and thermal energy conversion efficiency (η_r) of TG cells reported in the literature. In the mechanism column, "Diff." and "Galv." represent thermodiffusion and thermogalvanic, respectively. In the state of electrolyte column, "Liq." and "Quasi-S" indicate the liquid and quasi-solid states, respectively.

| Mechanism | State of electrolyte | Electrolyte | Electrode | Sign | Si | $P_{max}/\Delta T^2$ | η_r | Ref. |
|---------------|----------------------|--|-------------------------------|-------|------------------|----------------------|----------------|----------------|
| Diff. / Galv. | Liq. / Quasi-S | | | P / N | mV/K | mW/m^2K^2 | % | |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in PVA | Au/Cr | Р | 1.21 | 0.012 | - | 3 |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in PVA | Pt | Р | 1.4 | 0.2 | - | 4 |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in PVA | Pt | Р | 6.5 | 1.97 | 2.66 | 5 |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in anisotropic PVA | Pt wire | Р | 1.5 | 0.22 | - | 6 |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in PAAm | Ti | Р | 1.2 | 0.007 | - | 7 |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in PAAm | Graphite | Р | 1.37 | 0.31 | - | 8 |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in acryloyl glycinamide | Pt | Р | 2.17 | 0.23 | - | 9 |
| Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in cellulose | Ni | Р | 1.38 | 0.06 | - | 10 |
| Diff. / Galv. | Quasi-S | $K_{3/4}[Fe(CN)_6]$ in gelatin + KCl $K_{3/4}[Fe(CN)_6]$ in gelatin + KCl $K_{3/4}[Fe(CN)_6]$ in gelatin/GTA + KCl | Cu/Au 3D Cu/Au 3D Cu/Au | Р | 17 17 24.7 | 0.66 8.9 9.6 | 0.01 - - | 11 12 13 |

| Galv. | Quasi-S | KI/I ₂ in methylcellulose + KCl | Graphite | Р | 9.62 | 0.36 | - | 14 |
|------------------|---------|---|------------------------|---|-------|--------|------|----|
| Diff. / Galv. | Quasi-S | K _{3/4} [Fe(CN) ₆] in PDMAA + EMIM:DCA | SWCNT | Р | 32.4 | 25.84 | 0.04 | 15 |
| Galv. | Liq. | K _{3/4} [Fe(CN) ₆] in aq. sol + GdmCl | Carbon fabric | Р | 3.73 | 7.08 | 11.1 | 16 |
| Galv. | Liq. | $K_{3/4}[Fe(CN)_6]$ in aq. sol + Urea + GdmCl | Graphite | Р | 4.2 | 1.10 | - | 17 |
| Galv. | Liq. | K _{3/4} [Fe(CN) ₆] in methanol | SWCNT | Р | 2.9 | 0.64 | - | 18 |
| Galv. | Liq. | $K_3[Fe(CN)_6]/(NH_4)_4[Fe(CN)_6]$ in aq. Sol | Activated carbon cloth | Р | 1.88 | 1.8 | - | 19 |
| Galv. | Liq. | K _{3/4} [Fe(CN) ₆] in aq. sol | CNT aerogel sheet | Р | 1.43 | 0.16 | 3.95 | 20 |
| Galv. | Quasi-S | FeCl _{2/3} in PVA | Au/Cr | N | -1.02 | 0.033 | - | 3 |
| Galv. | Quasi-S | FeCl _{2/3} in PVA | 3D porous PEDOT:PSS | N | -0.85 | 0.17 | - | 21 |
| Galv. | Quasi-S | FeCl _{2/3} in PAAm + DMAEA-Q | Cu | N | -2.02 | 0.1 | - | 22 |
| Galv. | Quasi-S | Fe(ClO ₄) _{2/3} in PAAm | Graphite | N | -1.65 | 0.43 | - | 8 |
| Galv. | Quasi-S | Fe(ClO ₄) _{2/3} in PAAm + TLS | Carbon cloth | N | -2.49 | 0.0005 | - | 23 |
| Galv. | Quasi-S | KI/I ₂ in methylcellulose + KCl | Graphite | Ν | -8.18 | 0.12 | - | 14 |
| Diff. + Galv. | Quasi-S | FeCl _{2/3} in Chitosan + Melamine | Ni | N | -7.24 | 7.23 | - | 24 |

| Galv. | Liq. | $Fe(CF_3SO_3)_{2/3}$ $Fe(NO_3)_{2/3}$ | Au Au | Ν | -1.46 -1.38 | 0.099 0.159 | - | 25 |
|-------|------|--|----------------------------|---|----------------|----------------|---|----|
| Galv. | Liq. | $Fe(ClO_4)_{2/3}$ in aq. sol + HCl | Pt | Ν | -1.74 | 0.95 | - | 26 |
| Galv. | Liq. | Cu/Cu(SO ₄) ₂ | 3D multi- structured Cu | Ν | -1.66 | 0.71 | - | 27 |
| Galv. | Liq. | $KI/I_2 + \alpha - CD + KCl$ | Pt wire | Ν | -2.0 | 0.0063 | - | 28 |

Table S3

Thermal energy conversion efficiency in relation to Carnot-relative efficiency (η_r) . The value was the average of three experimental replicates.

| | Temperature (°C) | Thermal Diffusivity (α) (mm^2/s) | Specific heat capacity (C _p) (J/g·K) | Thermal Conductivity (κ) (W/m·K) | Carnot- relative efficiency (η _r) |
|-----------|---------------------|--|--|--|---|
| Mean: | 25.0 | 0.376 | 2.351 | 1.087 | 0.2420/ |
| Std. Dev: | 0.0 | 0.004 | 0.000 | 0.010 | 0.242% |

Supplemental Notes

Quasi-continuous operation and reactivation of the TD-assisted TG cells

Time-voltage and time-current curves were simultaneously measured using a Keysight 34465A and a Keithley 2400. Energy density curves with different resistors were calculated from corresponding current and voltage values over time.

The quasi-continuous operation of the solid-state TD-assisted TG cells followed these steps (Fig. S11):

(A) Thermal charging in an open circuit

Initially, all the mobile ions within the TD-assisted TG cell are distributed homogeneously, resulting in no electrode potential difference. When a temperature gradient is applied, the redox reaction of the $Fe^{2+/3+}$ ions induces an electrochemical potential generating faradaic currents, and concurrently, the liberated ClO_4^- ions migrate towards the colder electrode, contributing to the generation of electrical potential (electromotive force) and capacitive (non-faradaic) currents.

(B) Electrical discharge in a short-circuit

Upon closing the circuit, electrons flow from the cold side to the hot side, rapidly discharging the voltage to 0V with the maximal current, comprising non-faradaic and faradaic currents.

(C) Thermal recharge in an open circuit

Reopening the circuit under a temperature gradient thermally recharges the thermovoltage within 3 minutes. Continuous electrochemical reactions consume transported electrons, regenerating the electrode potential differences. These charge-discharge cycles can repeat over

50 times, though output power decays over time due to electrode polarization. Removing the temperature gradient while short-circuiting the electrodes reactivates the device for the next cycle.

Simultaneous contribution of thermodiffusion and TG effects to ionic thermopower

When ions are introduced into an aqueous system, the surrounding water molecules rearrange to accommodate them. This process involves enthalpy-entropy compensation between water-water and water-ion interactions, leading to changes in structural entropy during ion transport. The ionic Seebeck coefficient induced by thermodiffusion effect (S_{TD}) can be described by Onsager relations as:

$$S_{TD} = \frac{\Delta V}{\Delta T} = \frac{\sum_{i} q_i n_i^0 \hat{S}_i D_i}{\sum_{i} q_i^2 n_i^0 D_i}$$

where q_i , n_i , S, D_i and T denote electrical charge, concentration, Eastman entropy of transfer, diffusion coefficient of ion species i, and temperature, respectively. The Einstein's relation for

thermodiffusion defines the thermal mobility (μ_i^T) as: $\mu_i^T = \frac{D_i \hat{S}_i}{k_B T}$. The differences in thermal mobilities between the cations and anions determine the sign of the S_{TD} .

Sign convention of TG cells

In ionic thermoelectric materials based on thermodiffusion, the ionic Seebeck coefficient can be defined as the ratio between thermovoltage induced by the internal electric field and the temperature gradient, expressed as:

$$S_{TD} = \frac{\Delta V}{\Delta T} = -\frac{V(T_H) - V(T_C)}{T_H - T_C}$$

Where $V(T_H)$ and $V(T_C)$ are the voltage of the electrode held at T_H and T_C , respectively. The sign of S_{TD} is determined by the type of charges with higher thermal mobility in the system. In p-type ionic TE materials, cations, which are the major charge carriers, thermodiffuse from the hot to the cold electrode along with heat flux. Therefore, a higher potential at the cold electrode is generated, inducing an internal electric field directed from the cold electrode to the hot electrode.

In TG cells, the standard electrode potential for the electrochemical reaction $xO + ne^- \leftrightarrow yR$ depends on the temperature. The variations of the standard electrode potential with temperature in an isothermal half-cell are known as the "temperature coefficient" in electrochemistry and are fundamentally related to the entropy difference for the redox reaction. The temperature coefficient can be defined as:

$$\alpha_R = \frac{\partial E^0}{\partial T} = \frac{\Delta S_{rxn}}{nF} = \frac{S_R - S_O}{nF}$$

where n, F, s_R, s_O, E^0, T and ΔS_{rxn} denote the number of electrons involved in the redox reaction, Faraday's constant, the molar entropy of redox species, standard electrode potential, temperature, and the entropy changes of the redox reaction, respectively. According to the Nernst equation, the equilibrium potential of the redox reaction can be expressed as:

$$E = E^0 - \frac{RT}{nF} ln \frac{a_R^y}{a_O^x}$$

Where a_R and a_O are the activities of oxidant and reductant, n is the number of electrons

transferred in the redox reaction, F is Faraday's constant and R is the ideal gas constant. As the concentrations of the oxidized species (O) and reduced species (R) are equal, the second term can be neglected. Therefore, the measured voltage of the cell under a temperature gradient can be simplified as:

$$S_{TD} = -\frac{V(T_H) - V(T_C)}{T_H - T_C} \approx -\frac{E^0(T_H) - E^0(T_C)}{T_H - T_C} = -\alpha_R$$

From this equation, we can see that the definition of temperature coefficient has the opposite sign of S_{TD} .

TG reaction and synergistic thermopower improvement

In the $Fe^{2+/3+}$ redox couple, Fe^{3+} has a higher charge density and lower solvation entropy compared to Fe²⁺, resulting in a more tightly packed hydration shell. When exposed to a temperature gradient, Electrochemical reactions with increasing entropy are thermodynamically favored at higher temperatures, while reactions with decreasing entropy are favored at lower temperatures. Consequently, the higher electrode potential at the hot electrode results in a temperature coefficient (α_R), producing a voltage with the same sign as the n-type S_i from thermodiffusion effects. Therefore, combining TG cells with positive temperature coefficients with thermodiffusion-based ionic thermoelectric materials having negative S_i can synergistically improve overall thermopower.

Carnot-relative efficiency

The thermal-to-electrical energy conversion efficiency (η) of a thermoelectric device is defined as the ratio of the maximum power density output (P_{max}) to the heat power (P_{heat}) input. The Carnot efficiency $(\eta_c = \Delta T/T_{hot})$ represents the theoretical maximum efficiency of a heat engine operating between two temperatures. The Carnot-relative efficiency (η_r) , used as a performance evaluation criterion, is calculated by:

$$\eta_r = \frac{\eta}{\eta_{carnot}} = \frac{P_{max}/P_{heat}}{\Delta T/T_{hot}} = \frac{\frac{P_{max}}{\kappa A \frac{\Delta T}{d}}}{\frac{\Delta T}{T}/T_{hot}}$$

Where κ , A, d, and ΔT are the thermal conductivity, electrode area, inter-electrode distance, and the temperature difference between the electrodes. Since our system operates transiently compared to conventional TG cells, the Carnot-relative efficiency (η_r) for the solid-state TDassisted TG cell is expressed by the following equation ¹¹:

$$\eta_r = \frac{\eta}{\eta_{carnot}} = \frac{\int_0^{\tau_{dis}} P(t)dt \left/ \left\{ \kappa A \frac{\Delta T}{d} (\tau_{ch} + \tau_{dis}) \right\}}{\Delta T/T_{hot}} = \frac{\left(\frac{\tau_{dis}}{\tau_{ch} + \tau_{dis}} \right)^{P_{avg}} / \kappa A \frac{\Delta T}{d}}{\Delta T/T_{hot}}$$

Here, P(t) is the output power during discharge with a fixed resistance, and P_{avg} is the average output power. τ_{ch} and τ_{dis} are the thermal charging and electrical discharging times, respectively. κ , A, d, and ΔT denote the thermal conductivity, electrode area, inter-electrode distance, and the temperature difference between the electrodes. The n-type solid-state TDassisted TG cell of PEDOT:PSS/Fe(ClO₄)_{2/3} (0.3M) was thermally charged for 15 min. and discharged for 60 min. with a constant resistance of 1000 ohms at a temperature difference of approximately 3.2 K. Consequently, the conversion efficiency was around $\eta_r = 0.242\%$, significantly higher than reported p-type combined systems ($\eta_r = 0.01\%$) and superior to previously reported n-type TG cells (Table S2). However, with the commercialization threshold for η_r is estimated as ~5%, further promising strategies need to be developed in future studies.

Comparative mechanisms of TG cells: from conventional liquid-state TG cell to n-type solid-state TD-assisted TG cell

In conventional liquid TG cells (Fig. S1(a)), composed of galvanic couples dissolved in aqueous or organic solvents, there is no mobility difference between cations and anions. Consequently, the thermovoltage is generated solely based on the electrochemical potential under temperature gradients, resulting in a small voltage due to the minimal entropy difference of redox species at different temperatures.

In a thermodiffusion-combined TG cell (Fig. S1(b)), galvanic couples with externally added ions, such as KCl, were developed to improve the ionic Seebeck coefficient of the TG cell. The added ions within the hydrogel matrix thermally diffuse and induce an internal electric field based on the thermodiffusion effect, enhancing the thermovoltage by combining the electrical potential induced by the internal electric field with the electrochemical potential of the redox couple. However, the high internal resistance limits the cell, resulting in low power density output.

A solid-state TD-assisted TG cell (Fig. S1(c)) was developed through the strategic design of a polymer complex, featuring electrostatic interactions between the polymer matrix and the galvanic couple. This design liberates counter ions of the galvanic couple, enhancing the thermodiffusion effect of counter ions along with the TG effect of redox species. This dual functionality of the galvanic couple in the polyelectrolyte remarkably improves the ionic Seebeck coefficient and power density output. Notably, this pioneering strategy realizes the

simultaneous TD effect in a TG cell without needing externally added ions.

Supplemental References

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