



Coupling active polymer networks with solubility-driven gradients for augmented hydrogel thermocells

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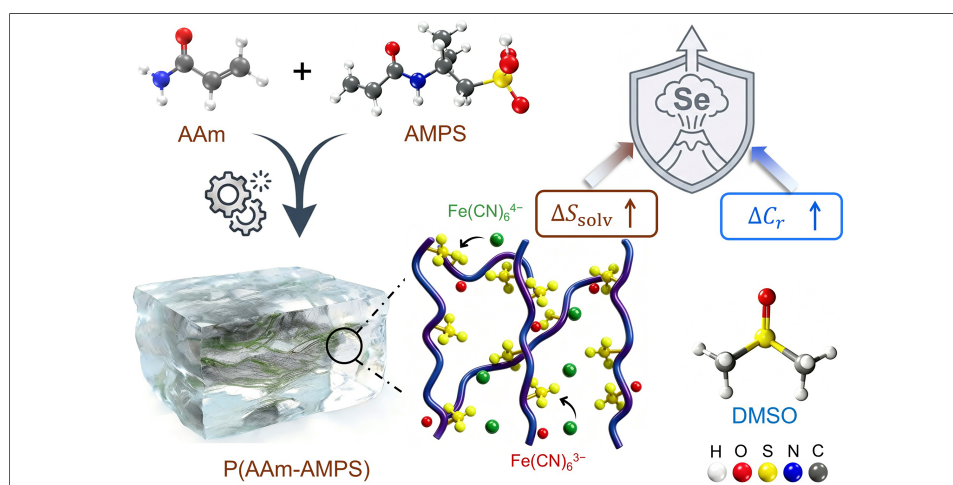
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Abstract

Quasi-solid-state thermocells (QTECs) convert low-grade heat into electricity via temperature-dependent redox reactions, but their rational design is hindered by an incomplete understanding of ion-solvent and ion-polymer interactions. Herein, precise control over these interactions is exploited in a binary strategy that simultaneously engineers the local solvation environment and a solubility gradient. Copolymerization of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) with acrylamide (AAm) creates a stretchable network. The charged network selectively interacts with $\text{Fe}(\text{CN})_6^{4-}$ ions, while the introduction of dimethyl sulfoxide (DMSO) breaks the solubility symmetry of the redox couple to establish a concentration gradient. This interplay between the active hydrogel and the solvent-induced gradient raises the Seebeck coefficient from 1.31 to 2.30 $\text{mV}\cdot\text{K}^{-1}$ while maintaining favorable thermal and ionic conductivities. Moreover, various spectroscopic and *in-situ* characterizations elucidate the contrasting roles of active and inert polymer networks in cooperating with this gradient. Together, these results demonstrate that coupling an active polymer network with a solvent-induced concentration gradient is an effective strategy for boosting thermoelectrochemical performance, which offers an unexplored design path for improved QTECs.



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INTRODUCTION

As the demand for sustainable recovery of low-grade waste heat ($< 100\text{ }^{\circ}\text{C}$) intensifies, quasi-solid-state thermocells (QTECs) have attracted growing attention^[1-5]. Comprising an elastic hydrogel electrolyte swollen with ionic solutions and inert electrodes, QTECs exploit continuous thermally driven redox reactions to directly convert heat into electricity^[6-9]. Their inherent stretchability and leakage-free operation make them particularly suitable for self-powered wearable electronics and sensors^[10,11]. The energy conversion capability of a QTEC is measured by its thermopower (Seebeck coefficient, S_e), which reflects the voltage generated per unit temperature difference. The magnitude of S_e is governed by two principal thermodynamic contributions: the concentration-driven entropy difference (ΔC_r), arising from a non-equimolar distribution of oxidized and reduced ions across the temperature gradient, and the solvation-driven entropy difference (ΔS_{solv}), originating from the reorganization of ion solvation shells upon electron transfer^[12-14]. Although enhancing either parameter alone can increase S_e , simultaneously establishing both ΔC_r and ΔS_{solv} within a single hydrogel network, and making them act synergistically, remains an unresolved challenge.

A widely adopted strategy for boosting S_e is to amplify ΔC_r ^[15-17]. This concentration-dependent contribution is captured by^[18]:

$$S_e = \frac{R}{nF\Delta T} \left[T_H \ln \frac{\gamma_{ox,H}^A}{\gamma_{red,H}^B} + T_H \ln \frac{C_{ox,H}^A}{C_{red,H}^B} \right] - \frac{R}{nF\Delta T} \left[T_c \ln \frac{\gamma_{ox,c}^A}{\gamma_{red,c}^B} + T_c \ln \frac{C_{ox,c}^A}{C_{red,c}^B} \right] \quad (1)$$

where T_H and T_c denote the temperatures at the hot and cold electrodes, A and B denote the two distinct redox ions, n is the number of electrons transferred, F is the Faraday constant, R is the ideal gas constant, and γ and C represent the activity coefficients and molar concentrations, respectively. Subscripts *ox* and *red* denote the oxidized and reduced species, while *H* and *c* refer to the hot and cold sides. Early work exploited host-guest hydrophobic encapsulation between α -cyclodextrin and I_3^- to induce a ΔC_r between I^-/I_3^- redox ions, which raised S_e to $2.0\text{ mV}\cdot\text{K}^{-1}$ ^[19]. This concept was later extended by adding guanidinium salts to $\text{Fe}(\text{CN})_6^{4-/3-}$ electrolyte. The thermosensitive crystallization of guanidinium- $\text{Fe}(\text{CN})_6^{4-}$ complex generates a robust ΔC_r and markedly improves the power output^[20-24]. More recently, specific ion-solvent interactions have been employed to tune solubility of redox species and modulate ΔS_{solv} , leading to further gains in the thermoelectrochemical performance^[15,25-27]. Despite these advances, existing strategies rely almost exclusively on regulating the liquid phase. As a result, the polymer network in hydrogel electrolytes is treated merely as a passive scaffold, with its potential to actively enhance thermopower left largely unexplored.

Efforts to activate the polymer network in QTECs have centered on backbone functionalization. Polyacrylamide (PAAm) hydrogels serve as the most commonly used matrix owing to their excellent mechanical properties, high water retention, and ease of processing^[26,28-30]. However, the chemically inert PAAm backbone imposes a fundamental limitation. Without strong coordinating groups, it cannot engage in electrostatic or ion-dipole interactions with the redox ions, which severely restricts its ability to modulate ΔS_{solv} . To overcome this, recent studies have introduced tailored functional groups, such as zwitterionic sulfobetaine methacrylate, into the chains to establish selective ion-polymer interactions and to reshape the solvation environment of redox ions^[31-33]. These active networks increase the entropy difference of redox ions and improve the thermoelectrochemical performance of QTEC. Nevertheless, these advances have only addressed part of the challenge. The rational integration of active polymer sites and a favorable ΔC_r into a hydrogel electrolyte to amplify S_e has not been realized. Moreover, it remains unknown whether active and inert networks cooperate with ΔC_r in fundamentally different ways, a knowledge gap that directly hinders the design of truly optimized electrolytes. Bridging this gap demands a strategy that simultaneously engineers both the polymer network and the ionic environment.

Herein, we report an electrolyte design that couples polymer-network modification with a solvent-induced concentration gradient to address both limitations identified above. Copolymerizing a PAAm backbone with 2-acrylamido-2-methylpropanesulfonic acid (AMPS) converts the inert hydrogel matrix into an electrostatically active scaffold, while introducing dimethyl sulfoxide (DMSO) as a co-solvent to generate a pronounced solubility asymmetry between redox ions. The resulting copolymer network and DMSO-induced ΔC_r synergistically raise S_e from $1.31 \text{ mV}\cdot\text{K}^{-1}$ (in pristine PAAm) to $2.30 \text{ mV}\cdot\text{K}^{-1}$, with a high normalized power density of $0.32 \text{ mW}\cdot\text{m}^{-2}\cdot\text{K}^{-2}$. Importantly, the synergy between the active polymer network and ΔC_r enhances S_e through a nonlinear, volcano-shaped relationship. This work demonstrates that the rational coupling of polymer-network functionality with solvent-mediated concentration effects constitutes a viable strategy for high-performance QTECs.

EXPERIMENTAL

Materials and preparation of thermogalvanic hydrogel electrolytes

Potassium ferricyanide [$\text{K}_3\text{Fe}(\text{CN})_6$, $\geq 99.5\%$], potassium hexacyanoferrate [$\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$, $> 99.0\%$], DMSO ($\geq 99.9\%$), and AMPS (98%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Acrylamide (AAM, $\geq 99.9\%$), ammonium persulphate (APS, $\geq 96\%$), and *N,N'*-methylenebisacrylamide (MBAA, $\geq 99\%$) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Graphite plates were sourced from Qingdao Baofeng Graphite Produce Co., Ltd. All chemicals were used as received. Deionized water was employed throughout.

In a typical synthesis, AAm and AMPS (total mass of 2.0 g) were dissolved in 5.0 mL of deionized (DI) water at predetermined mass ratios to yield the desired copolymer compositions. Subsequently, 0.02 g of APS (initiator) and 0.02 g of MBAA (crosslinker) were added. After stirring at room temperature for 1 h at 300 rpm, the precursor was transferred into a polytetrafluoroethylene mold and polymerized at 60°C for 1 h to produce a hydrogel matrix. By varying the AAm/AMPS ratio, pAAm, p(AAm-AMPS), and pAMPS hydrogels were obtained.

The as-prepared hydrogel matrices were then immersed in a $0.4 \text{ M Fe}(\text{CN})_6^{4-/3-}$ aqueous solution at 60°C for 3 h to yield the thermogalvanic hydrogel electrolytes. Samples prepared without co-solvents were denoted as PAAm and P(AAm-AMPS). To establish a concentration gradient of the redox ions, DMSO was introduced into the immersion solution. The resulting DMSO-containing electrolytes were labeled as PAD-X and PSD-X for the PAAm and P(AAm-AMPS) systems, respectively, where X indicates the volume percentage (vol%) of DMSO.

Density functional theory calculation

Density functional theory (DFT) simulations were performed to evaluate electrostatic potentials (ESPs) and binding energy. For ESP analysis, geometry optimizations were carried out at the B3LYP/6-311G(d) level^[34,35], with an implicit solvent model using the Gaussian 16 package^[36]. Single-point energy calculations were then performed on the optimized structures to map ESP surfaces, followed by critical extrema analysis via the Multiwfn program. For binding energy calculations, simulations were conducted using the DMol3 module in Materials Studio 2023. The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional and double numerical plus polarization basis sets were employed. The convergence tolerances for energy, force, and displacement were set to 1×10^{-5} , $0.002 \text{ Ha}\cdot\text{\AA}^{-1}$, and $0.005 \text{ \AA}$, respectively. Individual ions and interacting pairs were fully relaxed before single-point energy calculations to determine the binding energy.

Material characterization

Fourier transform infrared (FTIR) spectra were collected using a Bruker Vertex 70V + Hyperion II spectrometer (Bruker, Germany) under vacuum in the range of $400\text{--}4,000 \text{ cm}^{-1}$. X-ray photoelectron spectroscopy (XPS) was performed on a PHI VersaProbe 4 system (ULVAC-PHI, Japan). Ultraviolet-visible

(UV-vis) absorption spectra were recorded from 200 to 500 nm with a PerkinElmer LAMBDA 1050+ spectrophotometer (PerkinElmer, USA). Thermal conductivity was measured using a Hot Disk TPS 2500S analyzer (Hot Disk AB, Sweden). X-ray diffraction (XRD) patterns were collected on a Malvern PANalytical diffractometer (Malvern PANalytical, UK) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over the 2θ range 10° – 60° . The morphology of the electrolyte was examined by scanning electron microscopy (SEM, Hitachi Regulus8100, Hitachi, Japan) at an acceleration voltage of 15 kV and an optical microscope (YM710TR, YUESCOPE, China). A universal testing machine (Instron 68TM, Instron, USA) equipped with a 50 N load cell was used to evaluate the mechanical properties at a deformation rate of $50 \text{ mm}\cdot\text{min}^{-1}$. Viscosity measurements were conducted using a Brookfield DV3T LV rheometer (AMETEK Brookfield, USA).

Thermoelectrochemical performance measurements

The QTEC was assembled in a sandwich configuration of platinum (Pt)|hydrogel electrolyte ($3 \times 1 \times 0.3 \text{ cm}$)|Pt. Two thermocouples were attached to both electrodes to monitor the temperature gradient (ΔT). The temperature of these plates was precisely regulated by a circulating water-cooling system (HRC2 Lite, IKA, Germany). The S_e was determined from the slope of the steady-state voltage vs. ΔT plots, with the thermoelectrochemical voltage and ΔT monitored by a Keithley DAQ6510 sourcemeter (Keithley Instruments, USA). Current–voltage and power–voltage characteristics were captured using a Keithley 2450 sourcemeter (Keithley Instruments, USA) by sweeping the voltage from the open-circuit value down to 0 V, with the load resistance determined from the recorded current at each voltage step. Discharge-charge cycles were performed using a protocol consisting of thermal charging (open circuit), galvanic discharge, and thermal recovery. Ionic conductivity (σ) was determined by electrochemical impedance spectroscopy (EIS, PARSTAT 3000A, AMETEK, USA) and calculated as $\sigma = L/(RA)$, where L , R , and A respectively denote the hydrogel electrolyte thickness, bulk resistance, and electrode-electrolyte contact area.

RESULTS AND DISCUSSION

Properties of P(AAm-AMPS) electrolyte

Figure 1A schematically compares the network structures of the pristine PAAm and P(AAm-AMPS) hydrogel electrolytes. The PAAm backbone is non-electroactive and provides minimal electrostatic interaction with redox ions. In contrast, copolymerization with AMPS monomers introduces abundant sulfonate groups ($-\text{SO}_3^-$) that act as fixed anionic centers. ESP maps confirm that the AMPS monomer carries a strongly negative charge distribution localized on the sulfonate moiety, whereas the AAm unit remains essentially neutral [Figure 1B]. This concentrated negative charge creates a strong local electric field, which offers a driving force for valence-selective interactions with the redox ions.

FTIR spectra verify the integration of both polymer components [Figure 1C]. The peak at $\sim 1,450 \text{ cm}^{-1}$ corresponds to the $-\text{CH}_2$ bending vibration of the PAAm segments^[37,38], while the bands at $1,042$ and $1,195 \text{ cm}^{-1}$ are assigned to the stretching vibrations of the S–O and S=O groups in AMPS chains^[39,40]. The coexistence of these characteristic bands confirms the successful formation of P(AAm-AMPS) copolymer networks. XPS spectra further corroborate this result through the emergence of a distinct S 2p signal in the P(AAm-AMPS) electrolyte [Figure 1D]. Moreover, the high-resolution N 1s spectra [Figure 1E] display a clear change in line shape for the C–NH $_2$ and O–NH–C components^[41,42], consistent with the altered chemical environment expected for the copolymer. The P(AAm-AMPS) hydrogel also exhibits good mechanical robustness and stretchability, as confirmed by its resistance to twisting, folding, and stretching without structural failure [Figure 1F and Supplementary Figure 1]. This mechanical integrity ensures that the as-prepared QTECs can accommodate complex deformation during operation without electrolyte leakage.

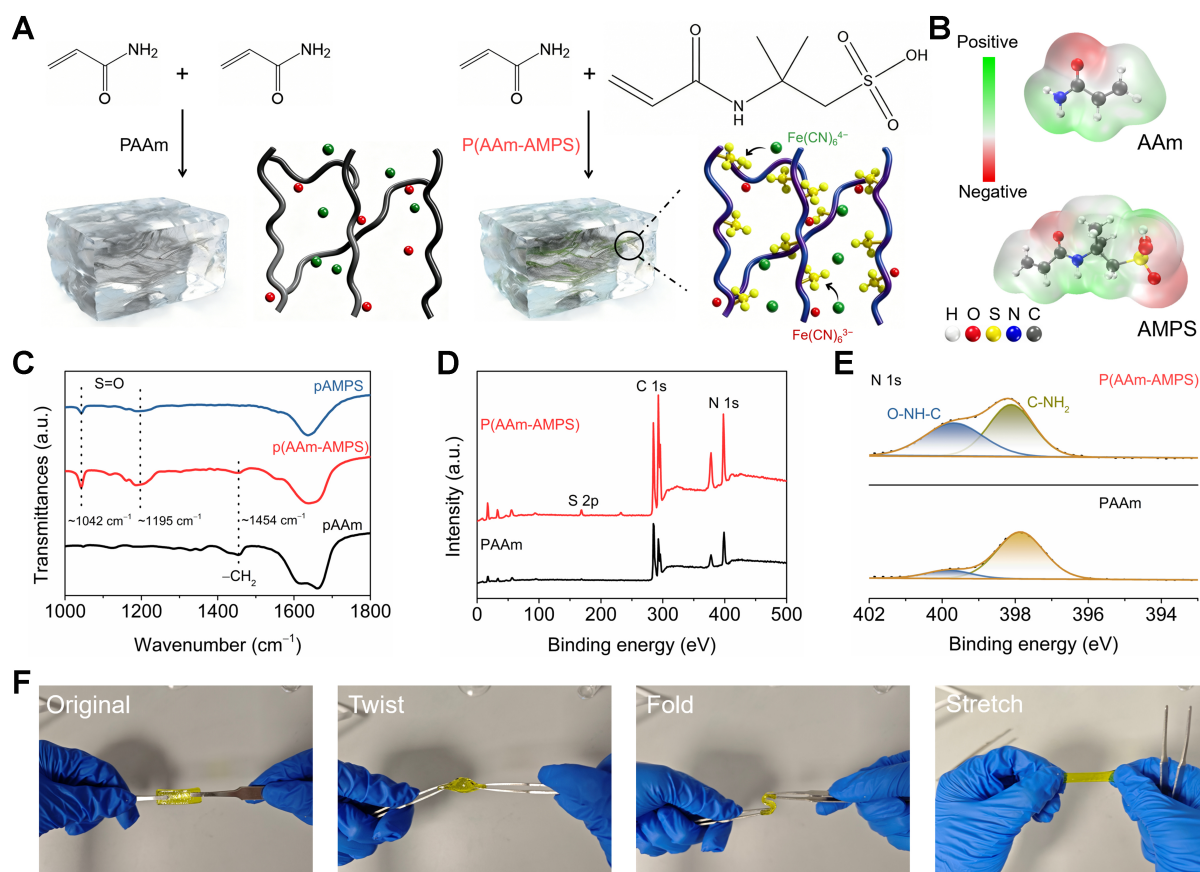


Figure 1. Design and chemical characterization of the thermogalvanic hydrogel electrolytes. (A) Schematic of the synthesis and network structure of PAAm and P(AAm-AMPS) electrolytes; (B) ESP maps of AAm and AMPS chain segments; (C) FTIR spectra of different hydrogel matrices; (D) XPS full spectra and (E) high-resolution N 1s spectra of PAAm and P(AAm-AMPS) electrolytes; (F) Digital photographs of the as-prepared P(AAm-AMPS) electrolyte. PAAm: Polyacrylamide; AAm: acrylamide; AMPS: 2-acrylamido-2-methylpropanesulfonic acid; ESP: electrostatic potential; FTIR: Fourier transform infrared; XPS: X-ray photoelectron spectroscopy.

Activating the polymer network

The heat-to-electricity conversion in the QTEC relies on temperature-dependent redox reactions of the $\text{Fe}(\text{CN})_6^{4-/3-}$ couple [Figure 2A]. At the hot electrode, $\text{Fe}(\text{CN})_6^{4-}$ oxidizes to $\text{Fe}(\text{CN})_6^{3-}$ and releases an electron; this electron travels through the external circuit to the cold electrode, where it reduces $\text{Fe}(\text{CN})_6^{3-}$ back to $\text{Fe}(\text{CN})_6^{4-}$. To evaluate the effect of network composition, Figure 2B and Supplementary Figure 2 examine the S_e of the P(AAm-AMPS) electrolytes as a function of the AAm/AMPS mass ratio. The pristine PAAm electrolyte (1:0 ratio) exhibits an S_e of $1.31 \text{ mV}\cdot\text{K}^{-1}$, consistent with previous reports^[26,30]. Incorporation of AMPS markedly influences S_e , an effect attributable to emerging ion-polymer interactions. S_e reaches a maximum of $1.61 \text{ mV}\cdot\text{K}^{-1}$ at a 1:1 mass ratio, approximately a 23% improvement over PAAm. Further increasing AMPS content to a 1:3 ratio, however, reduces S_e to $1.42 \text{ mV}\cdot\text{K}^{-1}$. Excess AMPS chains saturate the local coordination environment and consequently provide little additional solvation contrast between the redox ions. The overcrowded sulfonate groups also introduce steric hindrance and induce electrostatic chain aggregation, which further reduces ΔS_{solv} . This non-monotonic dependence highlights the need for a balanced copolymer composition.

To elucidate the origin of thermopower enhancement in P(AAm-AMPS) electrolytes, we performed UV-vis spectroscopy to probe the specific interactions between AMPS-containing polymer and two redox ions. As shown in Figure 2C, the characteristic absorption peak of $\text{Fe}(\text{CN})_6^{3-}$ remains unchanged upon the addition of

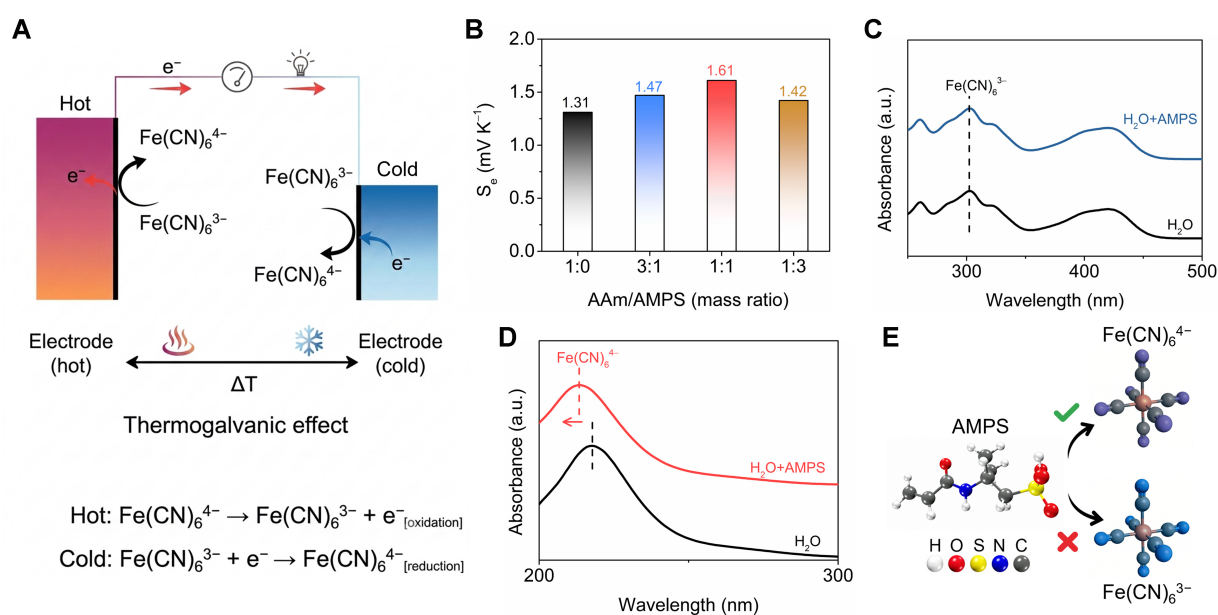


Figure 2. Thermogalvanic mechanism and microscopic interactions in the P(AAm-AMPS) electrolyte. (A) Schematic illustration of the thermogalvanic mechanism in a $\text{Fe}(\text{CN})_6^{4-/3-}$ -based thermocell; (B) Thermopower of P(AAm-AMPS) electrolytes as a function of the AAm/AMPS mass ratios; UV-vis spectra of (C) $\text{K}_3\text{Fe}(\text{CN})_6$ and (D) $\text{K}_4\text{Fe}(\text{CN})_6$ solutions with and without AMPS; (E) Schematic illustration of the microscopic interactions between AMPS segments and redox ions. AAm: Acrylamide; AMPS: 2-acrylamido-2-methylpropanesulfonic acid; UV-vis: ultraviolet-visible.

AMPS. In contrast, the $\text{Fe}(\text{CN})_6^{4-}$ signal exhibits a noticeable shift from 218 to 214 nm [Figure 2D], indicating a stronger interaction with the AMPS chains^[43–45]. DFT calculations further support this interpretation. The AMPS- $\text{Fe}(\text{CN})_6^{4-}$ complex exhibits a substantially more negative ESP minimum than AMPS- $\text{Fe}(\text{CN})_6^{3-}$ [Supplementary Figure 3], along with a more favorable binding energy [Supplementary Figure 4]. The pronounced UV-vis divergence, together with DFT calculations, demonstrates that the copolymer network preferentially interacts with $\text{Fe}(\text{CN})_6^{4-}$ over $\text{Fe}(\text{CN})_6^{3-}$ [Figure 2E]. Such valence-selective ion-polymer interactions effectively alter ΔS_{solv} to boost S_e .

Polar solvent-boosted concentration gradient

Introducing a ΔC_r of the redox ions provides an effective route to boost S_e [as captured by Equation (1)]. Since this strategy hinges on the solubility contrast between the two redox species, we incorporated DMSO as an organic co-solvent to tune their dissolution thresholds [Supplementary Figures 5 and 6]. The S_e of PAAm and P(AAm-AMPS) electrolytes were then systematically examined with varying DMSO contents. Figure 3A and Supplementary Figure 7 depict S_e as a function of the DMSO volume fraction for the two hydrogel matrices. For the PAAm-based electrolyte containing DMSO (denoted PAD-X), S_e rises almost linearly with increasing DMSO concentration. In contrast, the P(AAm-AMPS)-based counterparts (denoted PSD-X) shows a non-monotonic, volcano-shaped dependence. The S_e reaches a maximum of 2.30 mV·K⁻¹ at 10 vol% DMSO, clearly surpassing that of PAD-10 (2.02 mV·K⁻¹), while maintaining excellent mechanical properties [Supplementary Figure 8]. In addition to the in-plane performance, the cross-plane S_e was also measured [Supplementary Figure 9].

This enhancement arises from the interplay between the selective ion-polymer interaction in the P(AAm-AMPS) network and the DMSO-induced ΔC_r . Minor DMSO addition mainly enhances ΔC_r through differential solubility between redox ions, with minimal impact on ΔS_{solv} . At higher content, DMSO increasingly enters the solvation shell of redox ions and competes with sulfonate groups for ion coordination, potentially diminishing their ΔS_{solv} contribution. Excess DMSO (> 10 vol%) also induces

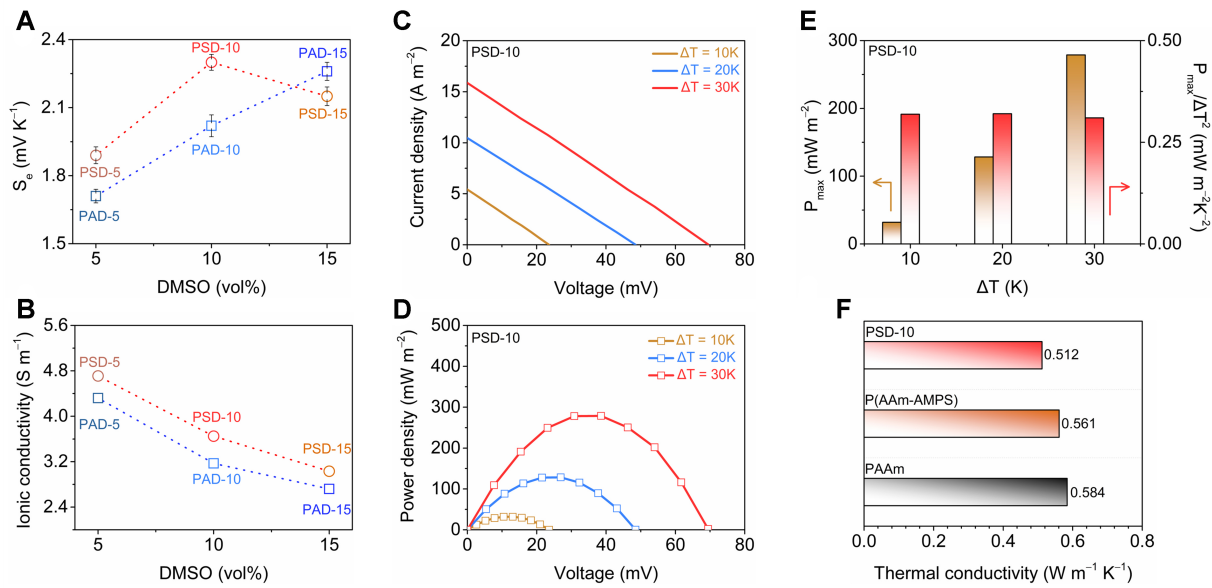


Figure 3. Thermoelectrochemical performance optimization and power output characterization. (A) Thermopower and (B) ionic conductivity of PAAm and P(AAm-AMPS) electrolytes as a function of DMSO volume fractions; (C) Current density-voltage and (D) power density curves of the optimized PSD-10 electrolyte measured under different ΔT ; (E) Maximum power density (P_{max}) and the normalized power density ($P_{max}/\Delta T^2$) under the corresponding ΔT ; (F) Thermal conductivity of different hydrogel electrolytes. PAAm: Polyacrylamide; AAm: acrylamide; AMPS: 2-acrylamido-2-methylpropanesulfonic acid; DMSO: dimethyl sulfoxide.

shrinkage of the hydrogel matrix [Supplementary Figure 10], which further restricts the local coordination space. The resulting loss in ΔS_{solv} outweighs the gain in ΔC_r , thereby dictating the non-monotonic trend in S_e . The PAD-X electrolytes, by contrast, lack active functional groups, so S_e follows the monotonic increase in ΔC_r .

Beyond S_e , the ionic conductivity (σ) of the hydrogel electrolytes also depends strongly on composition. At each DMSO concentration, the PSD electrolytes consistently outperform their PAD counterparts in σ [Figure 3B]. This improvement originates from anionic sulfonate groups in the P(AAm-AMPS) network, which promotes dissociation of redox ions and elevates effective charge carrier density^[46]. With increasing DMSO content, σ declines for all electrolytes, a trend attributable to combined effects of reduced ion concentration and increased viscosity [Supplementary Figure 11]. Despite this modest reduction in conductivity, the PSD-10 electrolyte delivers superior power output under various ΔT . The voltage-current and voltage-output power density curves of the PSD-10 based-QTEC exhibit characteristic linear V-I and parabolic V-P relationships [Figure 3C and D]. At a ΔT of 10 K, the device yields a short-circuit current density of $\sim 5.4 \text{ A}\cdot\text{m}^{-2}$, an open-circuit voltage of $\sim 23.3 \text{ mV}$, and a maximum power density (P_{max}) of $\sim 31.9 \text{ mW}\cdot\text{m}^{-2}$. When ΔT is raised to 30 K, P_{max} increases to $\sim 278.8 \text{ mW}\cdot\text{m}^{-2}$. The normalized power density ($P_{max}/\Delta T^2$) of PSD-10 based-QTEC remains stable at approximately $0.32 \text{ mW}\cdot\text{m}^{-2}\cdot\text{K}^{-2}$ over the tested temperature range [Figure 3E]. This composition is confirmed as the optimal DMSO content [Supplementary Figure 12], at which the overall power density is maximized driven by the S_e and σ trends shown in Figure 3A and B. A comparison with recently reported QTECs [Supplementary Table 1] reveals that our design strategy yields competitive thermoelectrochemical performance.

Beyond these gains in thermoelectrochemical performance, the design also effectively suppresses thermal conductivity (κ). A low κ is essential to sustain a stable ΔT across the QTEC. Specifically, the value drops from $0.584 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for pristine PAAm electrolyte to $0.561 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for P(AAm-AMPS) electrolyte, and reaches a minimum of $0.512 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for PSD-10 [Figure 3F]. Swelling measurements [

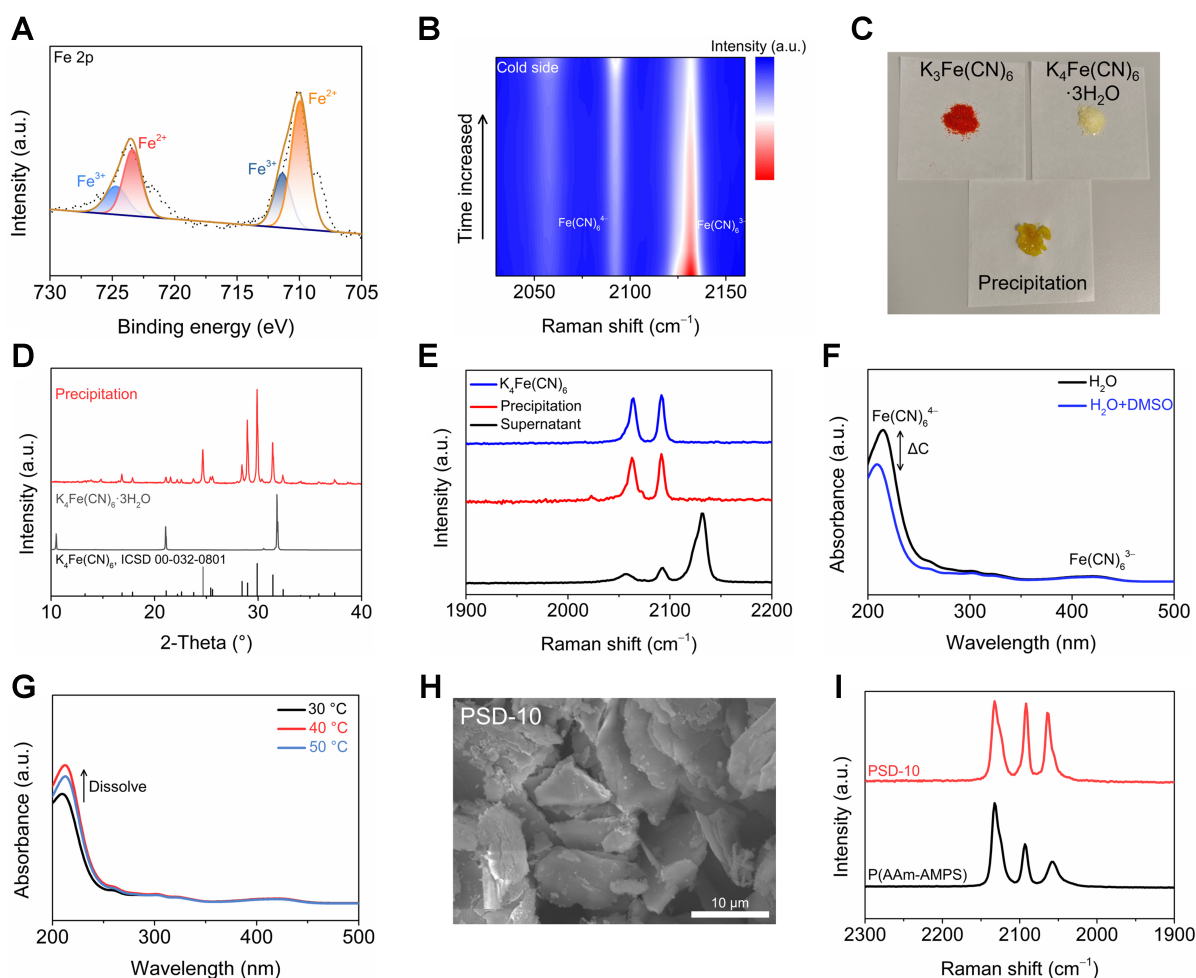


Figure 4. Investigation of the solubility-induced concentration gradients. (A) High-resolution XPS Fe 2p spectrum of the PSD-10 electrolyte; (B) Time-resolved *in situ* Raman spectra at the cold side of the PSD-10 electrolyte under a ΔT ; (C) Optical images of precipitation in DMSO/H₂O/K₃Fe(CN)₆/K₄Fe(CN)₆ solution and solids of K₃Fe(CN)₆ and K₄Fe(CN)₆·3H₂O (photographed by the authors); (D) XRD patterns and (E) Raman spectra of the precipitate and supernatant in the DMSO/H₂O/K₃Fe(CN)₆/K₄Fe(CN)₆ solution; (F) UV-vis absorption spectra of redox species with varying DMSO volume fractions and (G) temperature-dependent UV-vis spectra of redox species in DMSO/H₂O solutions; (H) Morphological characterization of the PSD-10 electrolyte (SEM image); (I) Raman spectra of P(AAm-AMPS) and PSD-10 electrolytes. XPS: X-ray photoelectron spectroscopy; DMSO: dimethyl sulfoxide; XRD: X-ray diffraction; UV-vis: ultraviolet-visible; SEM: scanning electron microscopy; AAm: acrylamide; AMPS: 2-acrylamido-2-methylpropanesulfonic acid.

Supplementary Figure 10] reveal the expansion of the polymer matrix after moderate DMSO (≤ 10 vol%) incorporation. This looser network architecture reduces continuous heat conduction pathways and adds polymer-solvent interfaces that enhance phonon scattering. This effect, together with the elevated viscosity induced by DMSO, contributes to the more pronounced decrease in thermal conductivity after DMSO addition compared with copolymerization [47,48].

Mechanism of solubility-driven concentration gradient

XPS analysis confirms the successful integration of the Fe(CN)₆^{4-/3-} in PSD-10. The high-resolution Fe 2p spectrum shows coexisting Fe²⁺ and Fe³⁺ states, a prerequisite for the thermogalvanic effect [Figure 4A]. During the operation of PSD-10-based-QTEC, the dynamic migration of redox ions under a ΔT was monitored by *in situ* Raman spectroscopy [Figure 4B]. The characteristic peaks at 2,058 and 2,093 cm⁻¹ correspond to Fe(CN)₆⁴⁻, whereas the 2,132 cm⁻¹ signal belongs to Fe(CN)₆³⁻ [49]. At the cold side, the Fe(CN)₆³⁻ stretching vibration gradually loses intensity, consistent with its reduction to Fe(CN)₆⁴⁻. The spectral features of two redox ions evolve in distinctly anti-correlated trends, a direct reflection of ΔT -driven ion migration and the accompanying redox reactions at the electrodes.

To establish the link between S_e enhancement and ΔC_r , we examined the precipitate formed in the DMSO-containing electrolytes. All characterizations consistently identify that the precipitate contains $\text{Fe}(\text{CN})_6^{4-}$ as the anionic component. It exhibits a yellow appearance identical to that of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ rather than the red hue characteristic of $\text{K}_3\text{Fe}(\text{CN})_6$ [Figure 4C]; the XRD pattern matches the standard reference of $\text{K}_4\text{Fe}(\text{CN})_6$ [Figure 4D]; Raman peaks are identical to those of pristine $\text{K}_4\text{Fe}(\text{CN})_6$ [Figure 4E]. Together, these observations demonstrate that only $\text{Fe}(\text{CN})_6^{4-}$ selectively crystallizes.

UV-vis spectroscopy of the supernatant quantitatively corroborates the above selective crystallization. The $\text{Fe}(\text{CN})_6^{4-}$ concentration drops substantially after DMSO incorporation, whereas $\text{Fe}(\text{CN})_6^{3-}$ content remains nearly unchanged [Figure 4F]. This solubility disparity arises from differential ion-solvent interactions between the two redox ions^[15,50], and the resulting thermodynamic equilibrium is highly temperature-sensitive. Temperature-dependent UV-vis profiles [Figure 4G] capture a prominent recovery of $\text{Fe}(\text{CN})_6^{4-}$ absorbance upon heating, indicating that the precipitated $\text{K}_4\text{Fe}(\text{CN})_6$ crystals redissolve as temperature rises. Direct visual confirmation is provided by optical microscopy images [Supplementary Figure 13]. This reversible crystallization–dissolution transition establishes ΔC_r under a ΔT , which directly contributes to the observed S_e enhancement.

The DMSO-induced crystallization of $\text{Fe}(\text{CN})_6^{4-}$ ions is physically confined within the PSD-10 hydrogel matrix. SEM images reveal micrometer-sized crystals embedded throughout the polymer network [Figure 4H]. The corresponding Raman spectra also display markedly stronger $\text{Fe}(\text{CN})_6^{4-}$ signals compared to the P(AAm-AMPS) electrolyte [Figure 4I]. This signal enhancement is attributable to physical scattering from the DMSO-induced solid $\text{Fe}(\text{CN})_6^{4-}$ precipitates. The localization of such precipitates within the hydrogel framework, consequently, facilitates a stable ΔC_r across the electrolyte.

Operational durability and device integration

The long-term stability of the PSD-10-based QTEC was evaluated under a quasi-continuous discharge mode [Figure 5A and B]. Upon applying a $\Delta T = 10$ K, the open-circuit voltage rises to approximately 23.1 mV within a thermal accumulation period of about 10 min. The subsequent repeated discharge-recovery cycles show only a gradual, minimal voltage decay, attributed primarily to polarization effect^[51]. After 200 consecutive cycles, the voltage stabilizes at ~21.2 mV, corresponding to a retention rate of 91.8%. The power output remains highly stable over 200 cycles as well [Supplementary Figure 14]. Although the device remains stable over this timescale, gradual ion redistribution is inevitable over extended use, and intermittent operation with resting periods could potentially further improve the cycling performance. Figure 5C demonstrates that the output voltage remains stable during a continuous 10-hour operation under a constant ΔT . After encapsulation with polyimide tape, the assembled QTEC also maintained good performance retention when tested daily over 7 days [Supplementary Figure 15]. These results highlight the excellent operational durability of the PSD-10-based QTECs for sustained low-grade heat harvesting.

To meet practical voltage requirements under small temperature gradients, multiple QTEC units were connected in series using segmented PSD-10 hydrogel electrolytes, adjacent graphite electrodes, and copper ribbons interconnects [Figure 5D]. Increasing the number of series-connected units from 2 to 12 raises the thermovoltage from 39.1 to 294.7 mV at $\Delta T = 10$ K, which confirms the scalability of the device. Elevated temperature gradients enhance the power generation capability, as demonstrated by the ~0.73 V output of the 12-unit module at $\Delta T = 40$ K within a short time [Figure 5E]. Combined with a voltage amplifier, this module can power a small electronic device [Figure 5F], which demonstrates the practical applicability of the PSD-10 electrolyte. The hydrogel electrolyte is easy to prepare and can be fabricated at scale, which makes it compatible with advanced packaging technologies. These features highlight its potential for large-scale ionic thermoelectric energy harvesting.

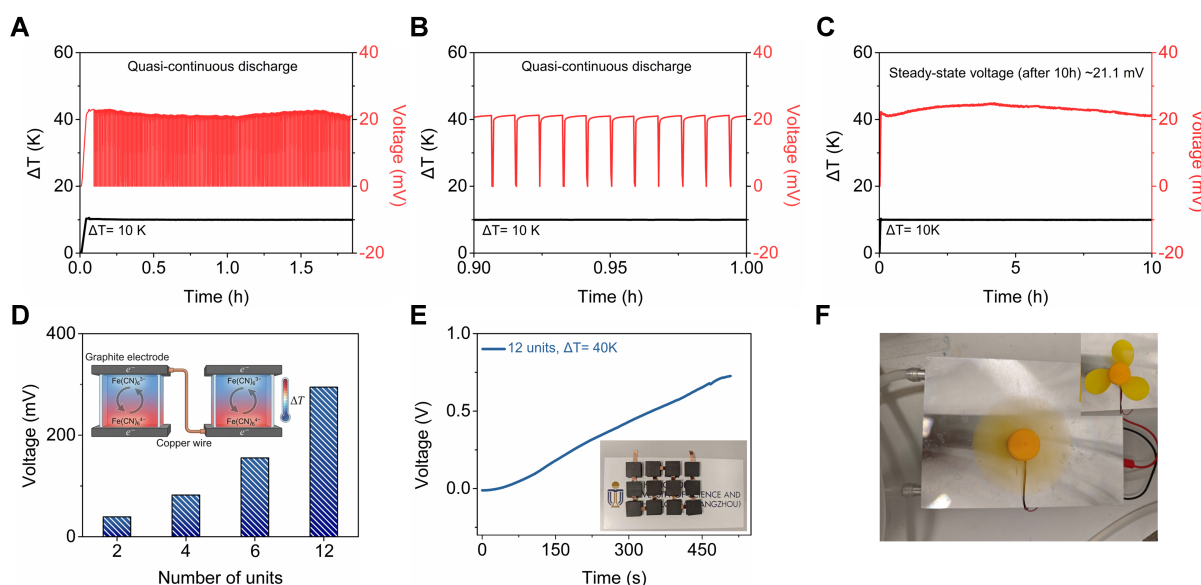


Figure 5. Long-term stability and device integration. (A) Quasi-continuous discharge profiles of the PSD-10-based thermocell at a $\Delta T = 10$ K; (B) Magnified view of the discharge cycles from 0.9 to 1.0 h in (A); (C) Voltage evolution of PSD-10-based thermocell during prolonged operation at a $\Delta T = 10$ K; (D) Output voltage as a function of the number of series-connected units under a constant ΔT ; (E) Voltage-time curve of an integrated module consisting of 12 series-connected units at $\Delta T = 40$ K; and (F) Optical image of the module powering a small fan (photographed by the authors).

CONCLUSION

In summary, this work presents a QTEC with enhanced thermoelectrochemical performance via the integrated design of an electrostatically active polymer network and a polar co-solvent. At an optimal AAm/AMPS mass ratio of 1:1, the copolymer network selectively interacts with $\text{Fe}(\text{CN})_6^{4-}$ over $\text{Fe}(\text{CN})_6^{3-}$ ions to effectively modulate the solvation entropy difference (ΔS_{solv}). The subsequent introduction of DMSO breaks the solubility symmetry of the redox couple, which establishes a concentration gradient (ΔC_r) that further boosts the thermopower. A non-monotonic dependence of S_e on DMSO content reveals a competition between the two mechanisms. A maximum of $2.30 \text{ mV} \cdot \text{K}^{-1}$ is reached at 10 vol% DMSO, while favorable thermal and ionic conductivities are retained. The DMSO-introduced concentration gradient originates from the selective crystallization of $\text{Fe}(\text{CN})_6^{4-}$ and the resulting precipitates are physically confined within the hydrogel network to sustain a stable ΔC_r under the temperature gradient. Under quasi-continuous discharge, the optimized PSD-10-based QTEC retains 91.8% of its initial voltage after 200 cycles and maintains stable output over 10 h of continuous operation.

This work highlights that the polymer network, when functionalized with charged groups, actively enhances thermopower through selective ion coordination. The active network alone delivers a modest yet meaningful gain through polymer-based solvation entropy modulation, a design strategy that has remained largely unexplored in thermogalvanic electrolytes. More importantly, the active contribution can be effectively coupled with a solvent-induced concentration gradient. This strategy, which establishes the polymer network as an active and tunable component, expands the design landscape of QTECs beyond common single-mechanism approaches. Further exploration of alternative polymer architectures, for instance from block copolymers to phase-separated morphologies, may broaden this optimization space and raise the efficiency limits of next-generation QTECs.

DECLARATIONS

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Authors' contributions

Conceptualization, visualization, investigation, methodology, data curation, writing - original draft: Lin, W.
Software, visualization, investigation, methodology, data curation: Zheng, D.
Validation: Wu, S.; He, P.
Conceptualization, writing - review and editing, supervision, resources, project administration: Fang, C.

Availability of data and materials

The original contributions presented in this study are included in the article/[Supplementary Materials](#). Further inquiries can be directed to the corresponding author(s).

AI and AI-assisted tools statement

During the preparation of this manuscript, the AI tool Gemini (Google) (version 3.1 Pro, released 2026-02-10) was used solely for language editing. The tool did not influence the study design, data collection, analysis, interpretation, or the scientific content of the work. All authors take full responsibility for the accuracy, integrity, and final content of the manuscript.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Supplementary Materials

[Supplementary Materials](#)

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