

Concentration-driven enhancement of low-grade thermal energy harvesting in electrochemical systems

Jia-Ning Zhang¹, Rui Wang², Hao-Nan Song¹, Miao Gao¹, Zhuo-Jian Yang¹, Jia-Yi Zhang¹, Fei-Fei Zhang¹(✉), Jun-Min Yan¹(✉)

¹ Key Laboratory of Automobile Materials, Ministry of Education, School of Materials Science and Engineering, Jilin University, Changchun 130022, China

² School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

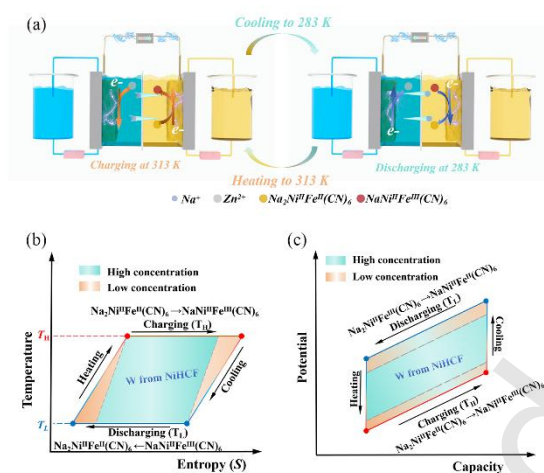
Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909001>

<https://www.sciopen.com/journal/1998-0124> on Jun. 27, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, *18*, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.



This study employed a combination of experimental characterization and simulation to investigate the influence of electrolyte concentration on the electrochemical performance and thermoelectric conversion efficiency of nickel hexachloroferrate (NiHCF) electrodes.

Concentration- driven enhancement of low- grade thermal energy harvesting in electrochemical systems

Jia-Ning Zhang¹, Rui Wang², Hao-Nan Song¹, Miao Gao¹, Zhuo-Jian Yang¹, Jia-Yi Zhang¹, Fei-Fei Zhang¹ , and Jun-Min Yan¹ 

¹ Key Laboratory of Automobile Materials, Ministry of Education, School of Materials Science and Engineering, Jilin University, Changchun 130022, China

² School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

Received: 7 April 2026; Revised: 2 June 2026; Accepted: 27 June 2026

 Address correspondence to Jun-Min Yan, junminyan@jlu.edu.cn; Fei-Fei Zhang, ffzhang@jlu.edu.cn

 Cite this article: Nano Research, 2026, 19, 94909001 <https://doi.org/10.26599/NR.2026.94909001>

ABSTRACT: Thermal regenerative electrochemical cycles (TRECs) represent a highly promising technology for the direct conversion of low-grade thermal energy (<373 K) into electrical energy. This study investigates the impact of electrolyte concentration on the electrochemical performance and thermoelectric conversion efficiency of nickel hexacyanoferrate (NiHCF) electrodes. The findings demonstrate that decreasing the electrolyte concentration not only increases the reaction entropy, but also reduces the interstitial water content within the NiHCF lattice, thereby amplifying the vibrational energy of the cyanide ligands. Ultimately, the synergistic effect of these two mechanisms yields an enhanced temperature coefficient (α). Leveraging the theory of concentration-driven temperature coefficients, a highly efficient TREC Zn–NiHCF flow cell was developed. Notably, this study represents the first elucidation of how supporting electrolyte concentration influences Prussian blue analogues in thermal energy recovery applications, offering a critical insight into the viability of TREC systems and establishing new avenues for optimizing their energy-harvesting capabilities.

KEYWORDS: energy storage, low-grade heat harnessing, redox flow batteries, prussian blue analogues, hydration entropy, structural vibration entropy

1 Introduction

The depletion of fossil fuels has spurred significant interest in energy conversion systems capable of harnessing waste energy to reduce consumption [1-3]. Low-grade thermal energy is widely available from sources including solar thermal, geothermal, and industrial waste heat [4-6]. However, its utilization remains challenging owing to low-grade heat's characteristically small temperature gradients and dispersed nature [7]. Conventional approaches, including solid-state thermoelectric generators (TEGs) [8-10] and organic Rankine cycle (ORC) systems [11, 12], have demonstrated potential for low-grade thermal energy harvesting, but their performance is fundamentally constrained by the limited temperature differences available.

Given these limitations, the isothermal energy-conversion technology would be more feasible compared with temperature-gradient-based technologies [13]. The thermal regenerative electrochemical cycle (TREC) has emerged as a promising technology for harvesting low-grade thermal energy by leveraging the temperature dependence of electrode potentials within an isothermal cycle. By strategically designing and controlling the system's temperature coefficient (α). By exploiting the distinct temperature coefficients of the cathode and anode, TREC systems can generate an additional voltage difference from a

temperature differential, thereby enabling supplementary electrical energy output that directly originates from low - grade thermal energy conversion. [14-17]. As α directly determines the theoretical voltage response to a temperature gradient, it is a critical parameter governing the thermoelectric performance of TRECs.

In a TREC system, the electrochemical temperature coefficient (α) can be defined as:

$$\alpha = \Delta E / \Delta T = \Delta S / nF \quad (1)$$

where ΔE is the voltage difference, ΔT is the temperature difference, ΔS is the entropy change, n is the number of electrons transferred in the reaction, and F is Faraday's constant [18]. For high-performance TREC systems, the temperature coefficient α is the most critical variable. Beyond modulating α through adjustments in ionic activity, a thorough understanding of the factors governing entropy change is equally essential for the rational design and development of electrode materials with larger temperature coefficients. [19, 20]. Prior studies indicate that modulating ΔS represents a viable strategy for significantly increasing the α . For example, Yu et al. developed a TGC using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ -GdmCl aqueous electrolytes, which could achieve a Seebeck coefficient of -3.73 mV K^{-1} through the formation and dissolution of thermosensitive crystals [21]. Lee et al, by leveraging the coordination properties of anions

to modulate entropy changes from desolvation and reorganization, demonstrated a full-cell temperature coefficient of -3.04 mV K^{-1} in an aqueous electrochemical system [22].

Recently, metal organic frameworks (MOFs) are increasingly applied in electrochemical systems. Their advantages, including a tunable porous structure, high specific surface area, and structural controllability, make them highly suitable for applications such as energy storage [23-25]. Prussian blue analogues (PBAs), a prominent subclass of MOFs [26, 27], have been actively investigated for their capacity to achieve higher α through the modulation of ΔS during intercalation reactions [28-32]. Consequently, the design of electrode materials with high α must prioritize the factors governing ΔS , a critical relationship established in prior studies [33, 34]. However, when applied to solid-electrode systems, entropy values reveal more nuanced behavior. The observed temperature coefficient is governed not only by ion activity but also by significant entropy contributions emerging from the electrode/electrolyte interface. These factors include:

$$\Delta S = \Delta S_{ion} + \Delta S_{phn} + \Delta S_{conf} + \Delta S_e + \Delta S_{other} \quad (2)$$

where ΔS_{ion} is the ion entropy, ΔS_{phn} is the phonon vibration entropy, ΔS_{conf} is the configuration entropy, ΔS_e is the electron entropy, and ΔS_{other} is related to other factors that affect the electrochemical reaction. A comprehensive understanding of the distinct entropy contributions is critical for manipulating the reaction entropy and thereby maximizing the thermal response of electrochemical systems. Studies have already shown that α of PBAs can be significantly enhanced by modulating hydration entropy via ionic coordination and varying the cationic species in the electrolyte. Lee et al. demonstrated through electrolyte testing that chaotropic anions ClO_4^- induces a higher thermoelectric potential in PBAs than hydrophilic anions such as NO_3^- and SO_4^{2-} . And they further showed that, when the thermoelectric properties of PBAs were measured in electrolytes containing different cations, larger cation radii were associated with higher hydration entropy. [22, 28, 35, 36].

Here, to clarify how electrolyte concentration influences the temperature coefficient of PBAs, the thermoelectric performance of a representative electrode material, nickel hexacyanoferrate (NiHCF), in NaCl electrolytes is evaluated across a range of concentrations. Electrochemical measurements reveal an inverse proportionality between the NaCl concentration and the α value of NiHCF. This relationship is further explained by using a combination of molecular dynamics (MD) simulations and density functional theory (DFT). Guided by this theoretical framework, we construct a TREC cell to convert thermal energy into electricity by pairing NiHCF cathode (negative temperature coefficient) and $\text{Zn}^{0/2+}$ anolyte (positive temperature coefficient, Fig S1 in the Electronic Supplementary Material (ESM)). In a TREC system, the theoretical overall α is governed by the difference between the temperature coefficients of the cathode and the anode. Consequently, to maximize the thermal-to-electrical conversion, it is highly advantageous to pair electrodes with temperature coefficients of opposite signs. The cell operates through a

four-step thermal cycle comprising heating, charging, cooling, and discharging (Fig 1(a)). The temperature-entropy (T-S) curved in Figs 1(b), 1(c) and Fig S2 in the ESM depict the thermodynamic evolution and the voltage-temperature relationship of the cathodic and the anodic side during TREC cycling. In step 1, the cell which is initially in the discharged state is heated up from T_L to T_H at open circuit. This thermal input increases the entropy of the NiHCF, an effect pronounced in low-concentration electrolytes, since that the α associated with this entropy contribution can be approximated as concentration-driven α . Given the negative α of NiHCF, the cathode potential decreases as temperature rises. Consequently, pairing this cathode with a Zn anode (positive α) causes the full cell's open-circuit voltage (OCV) to decrease significantly, as shown in the potential-capacity (P-C) curve. In step 2, the cell is charged at low voltage at T_H , and its entropy increases via endothermic electrochemical reactions. During step 3, the cell is disconnected and cooled from T_H to T_L , which increases the TREC system OCV. Finally, the cell discharges at T_L , returning the system to its initial state to complete the cycle.

Based on the principle that tuning the concentration-driven temperature coefficient could enhance low-grade heat recovery, a full-cell α of -1.08 mV K^{-1} is attained. Under a temperature difference of 30 K, the full-cell's electrical efficiency (η) approached 0.71% (equivalent to 7.41% of Carnot efficiency, η_C). This result demonstrates that NiHCF in a low-concentration NaCl electrolyte is a promising electrode material for high-efficiency TREC system.

2 Experimental

2.1 Chemicals and Materials Preparation

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Sodium ferrocyanide decahydrate ($\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$), sodium chloride (NaCl), and N-methylpyrrolidone (NMP) were purchased from Aladdin. Zinc chloride (ZnCl_2) was purchased from Sinopharm Chemical Reagent Co., Ltd. Acetylene black and polyvinylidene fluoride (PVDF) were purchased from Canrd. All reagents were of analytical grade and were used without additional purification. 5 mm thick carbon felt was purchased from Gansu Hao's Carbon Fiber Co., Ltd. Nafion 115 membranes and 0.3 mm zinc sheets were purchased from SCI Materials Hub. Pumps were purchased from Kamoer. Furthermore, all experiments utilized deionized water (DI water).

2.2 Synthesis of NiHCF Nanoparticle

A quantity of 100 mL of 20 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 100 mL of 10 mM $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ were dissolved in deionized water. A stirring bar was settled in the 250 ml beaker with the speed of 500 RPM. Then, these two solutions were dropped at the speed of 1 mL s^{-1} into the beaker. After aging for a night, the NiHCF powder was separated from water and washed by deionized water three times, and washed by ethanol in a centrifuge to remove the ions on the surface. Then, the powder of NiHCF was dried in a vacuum oven at 363 K for a night. Finally, the green color NiHCF powder was synthesized.

2.3 Electrochemical tests

Cyclic Voltammetry (CV) measurements were performed using a three-electrode construction composed of a platinum electrode clip working electrode, a carbon plate counter electrode, and an Ag/AgCl reference electrode (the α is approximately 0.11 mV K^{-1}). For CV test of NiHCF, the working electrode was a carbon paper coated with NiHCF powder, with carbon black as conducting additive and PVDF as binder at mass ratio of 7:2:1. Galvanostatic intermittent titration technique (GITT) was used to determine the overpotentials during charge and discharge. The GITT procedure consists of a series of current pulses, each with 2 minutes of galvanostatic charge/discharge, the current density was set to 0.2 mA cm^{-2} , followed by 5 minutes of relaxation. The electrochemical tests were conducted with an Autolab electrochemical workstation (CHI660E).

2.4 Characterization of materials

acquired using a Horiba LabRAM HR Evolution spectrometer equipped with a 532 nm laser. All samples were analyzed using the same instrumental parameters. X-ray photoelectron spectra (XPS) were obtained using a Thermo Scientific K-Alpha spectrometer with monochromatic Al K α radiation ($h\nu \frac{1}{4} 1486.6 \text{ eV}$).

2.5 Thermal test

The specific heat capacity (C_p) of the electrolyte and the NiHCF powder was measured using differential scanning calorimetry (DSC). For each measurement, a $10 \mu\text{L}$ aliquot of the electrolyte solution or a 5 mg sample of NiHCF powder was hermetically sealed in a Tzero pan. Two sample pans were loaded into the DSC furnace, with an empty Tzero pan used as the reference. The DSC furnace was equilibrated at 293 K and subsequently heated from 278 K to 343 K at a constant rate of 5 K min^{-1} . The specific heat capacity of the solutions was calculated based on the heat flow of the

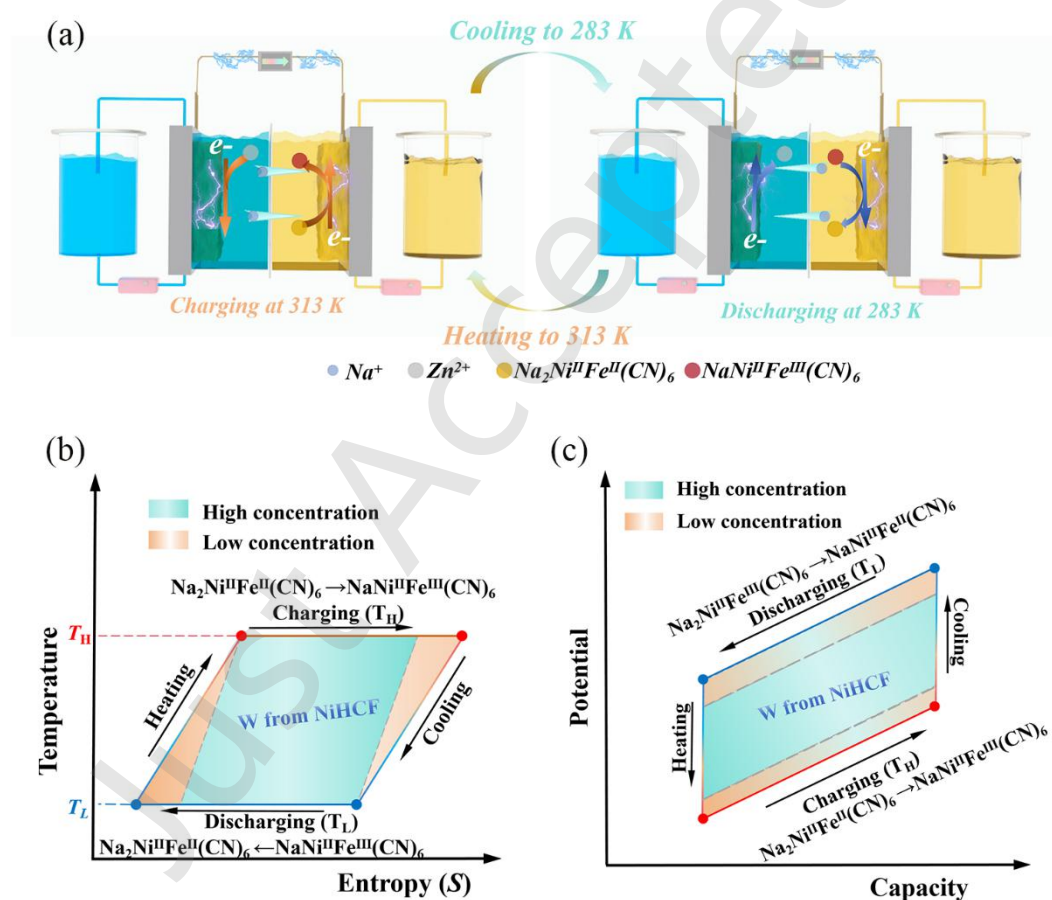


Figure 1. (a) Schematic of the thermal regenerative electrochemical cycle (TREC), comprising four consecutive steps: heating to the high temperature (T_H), charging at T_H , cooling to the low temperature (T_L), and discharging at T_L . (b) Temperature-entropy (T-S) and (c) potential-capacity (P-C) diagrams illustrating the thermodynamic and electrochemical processes of the cathode during the TREC cycle.

Fourier-transform infrared (FTIR) measurement was carried out with a PerkinElmer Frontier MIR/FIR system by the Attenuated Total Reflection (ATR) model. X-ray diffraction analysis (XRD) measurements were conducted on a Powder XRD Diffractometer System (DX-2700, China, Cu K α , $2\theta=10^\circ$ - 60°). The morphology and structure of the NiHCF nanoparticle were observed by field emission scanning electron microscopy (FE-SEM, JSM-7900F) and transmission electron microscope (JEOL JEM-F200). Raman spectra were

solution and water at different temperatures and the specific heat capacity of water, as shown in Fig S17 in the ESM. The moisture content of the NiHCF was determined by thermogravimetric analysis (TGA). In this analysis, the

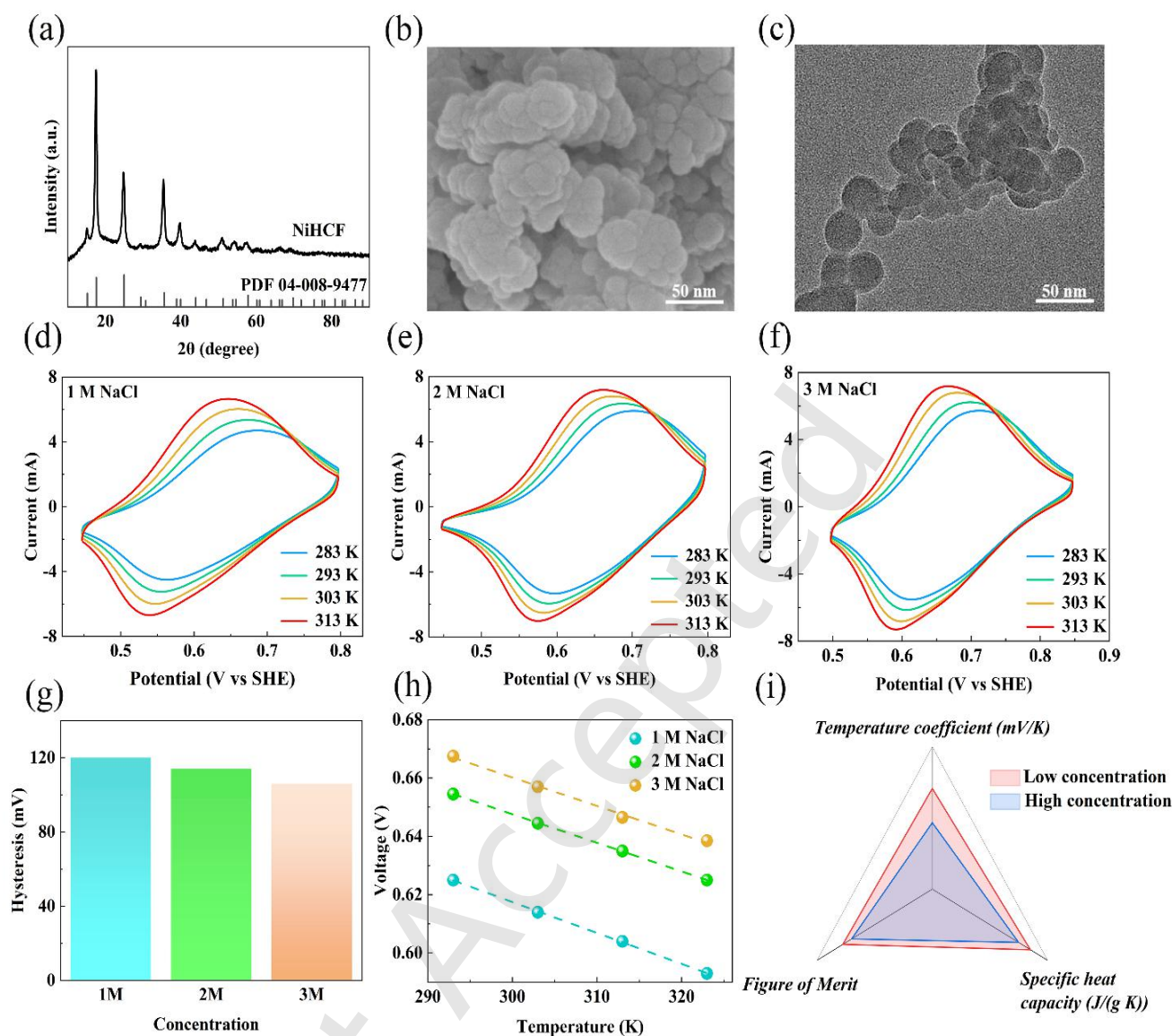


Figure 2. (a) XRD pattern, (b) SEM image and (c) TEM image of NiHCF. CV curves of the NiHCF electrode measured in (d) 1 M, (e) 2 M, and (f) 3 M NaCl solutions across a temperature range of 293 to 323 K at 1 mV s^{-1} . (g) Potential hysteresis and (h) temperature coefficient of the NiHCF electrode measured in three solutions. (i) Comparison of the NiHCF electrode in solutions of varying concentrations in terms of temperature coefficient α , specific heat capacity (cp), and Figure of Merit (Y).

sample was heated to 473 K at a rate of 1 K min^{-1} under a N_2 atmosphere.

2.6 Flow cell Tests

The slurry for the NiHCF electrode was prepared by mixing 70 wt% NiHCF powder, 20 wt% carbon black, and 10 wt% PVDF binder in NMP solvent. This slurry was drop-cast onto a carbon cloth substrate and subsequently dried under vacuum at 373 K for 10 hours. The resulting electrode had a geometric area of 5 cm^2 and a NiHCF active material mass loading of approximately 2 mg cm^{-2} . In the NiHCF/Zn flow cell, the active electrode area was 5 cm^2 . Graphite felt electrodes were used for both the positive and negative sides. These electrodes were thermally treated at 773 K in air for 10 hours prior to use. Peristaltic pumps circulated the catholyte and anolyte at a flow rate of 25 mL min^{-1} . The catholyte consisted of $n \text{ M NaCl}$ ($n = 1, 2, 3$), and the anolyte was 0.2 M ZnCl_2 with $n \text{ M NaCl}$. A Nafion 115 membrane ($127 \text{ }\mu\text{m}$ thick) separated the catholyte and anolyte

compartments. To improve the selective permeability of Nafion-115 to Na^+ , Nafion-115 membranes were treated prior to use. First, the membrane was treated with 5.0% H_2O_2 under 353 K for 0.5 h and then transferred to 5.0% H_2SO_4 at 353 K for 0.5 h. Next, 1 M NaOH aqueous solution was used to change the membranes from H-type (proton conductive) to Na-type (Na^+ conductive) under 80°C for 2 h. After that, the membrane was transferred to 3 M NaCl at 80°C for 2 h to further enhance the conductivity of Na^+ . The membrane was rinsed in deionized water for 30 min to wash away the chemicals after each step. For the cycling stability test, galvanostatic measurement was performed with an Arbin battery tester. A chiller (Huber cc 805) was used to control the temperature of the battery. A thermal imager was used to monitor the actual temperature of the battery.

2.7 Computational method

In this study, we employed the CP2K software package to perform first-principles calculations aimed at investigating

the entropy changes and unit cell deformations associated with the dehydration of sodium ions as they enter the Prussian Blue structure. For specific test methods, please refer to Supplemental Note 2 in the Electronic Supplementary Material.

3 Result and discussion

NiHCF powder was synthesized using a straightforward coprecipitation method [37, 38]. The X-ray diffraction (XRD) pattern (Fig 2(a)) confirms the highly crystalline monoclinic structure of the synthesized NiHCF (JCPDS card 04-008-9477) [39]. Scanning and transmission electron microscopy (SEM and TEM) images reveal that the NiHCF particles are quasi-spherical, with an average diameter of approximately 50 nm (Fig 2(b, c)). These particles exhibit uniform size distribution and dense packing. This monodispersity is attributed to the relatively low precursor concentration used during synthesis; this condition suppresses the nucleation

growth of the Fe^{3+} signature indicate the oxidation of Fe^{2+} to Fe^{3+} . In contrast, the Ni 2p spectra remain unchanged across the charge-discharge process, confirming that Ni^{2+} is electrochemically inactive, consistent with previous studies [42, 43].

To evaluate the influence of electrolyte concentration on the α , cyclic voltammetry (CV) is performed on NiHCF electrodes in NaCl solutions (1, 2, and 3 M) across a range of temperatures. The CV curves (Figs 2(d-f)) show a positive shift in equilibrium potential with increasing NaCl concentration. As evidenced in Fig 2(g), higher electrolyte concentrations reduce voltage hysteresis due to enhanced ionic conductivity and mitigated electrode polarization. The reaction kinetics of NiHCF also show slight improvement at higher concentrations. However, linear fitting of the equilibrium potential derived from CV curves (Fig 2(h)) reveals that the temperature coefficient (α) of NiHCF decreases markedly from -1.06 mV K^{-1} to -0.70 mV K^{-1} with

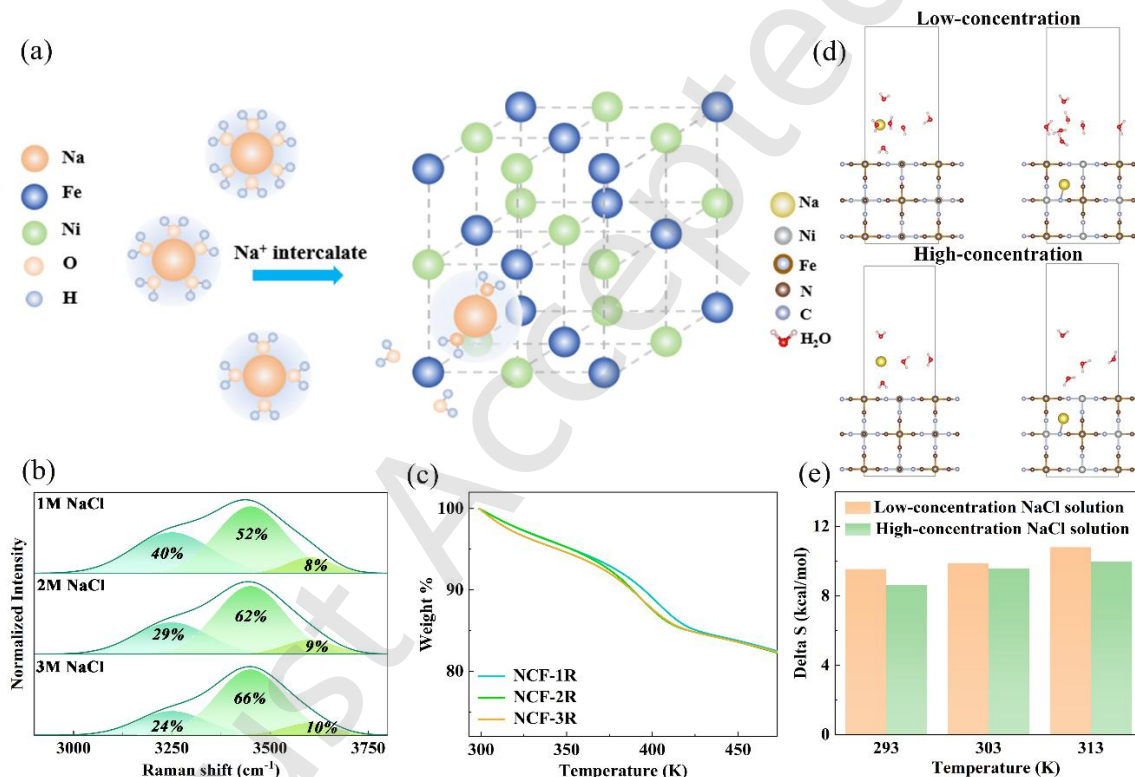


Figure 3. (a) Schematic of the dehydration mechanism accompanying the electrochemical intercalation of Na^+ with varying hydration states into the NiHCF framework. (b) Raman spectra of OH stretching bands for three different concentrations of NaCl solution. (c) TGA under an inert (N_2) atmosphere for NCF-1R, NCF-2R and NCF-3R. (d) MD of the electrochemical intercalation of Na^+ with varying hydration states into a NiHCF framework, and (e) the calculated entropy value.

rate and promotes homogeneous nucleation and uniform crystallization, ultimately yielding densely clustered particles [40, 41].

X-ray photoelectron spectroscopy (XPS) is conducted on the NiHCF electrodes at 100% and 0% states of charge (SOC, Fig S3 in the ESM) to probe the redox behavior. The electrodes are fabricated from a slurry containing 70 wt% NiHCF powder, 20 wt% carbon black, and 10 wt% PVDF in NMP solvent. At 0% SOC, the Fe species primarily exist in the Fe^{2+} state, as evidenced by characteristic peaks at 708.3 eV (2p_{3/2}) and 721.3 eV (2p_{1/2}). Upon charging to 100% SOC, the attenuation of the Fe^{2+} peaks and the concomitant

increasing electrolyte concentration. Thus, although elevated concentrations provide a modest kinetic advantage, this benefit is outweighed by the substantial reduction in the thermoelectric response. Therefore, low-concentration electrolytes present a more viable pathway for efficient thermal energy conversion in TREC systems. To quantify the thermoelectric performance of the redox couple TREC system, we employ its Figure of Merit (Y), defined by the following expression:

$$Y = \frac{\alpha q_c \mu}{c_p} = \mu Y' \quad (3)$$

where q_c is the specific charge capacity of the cathodic or

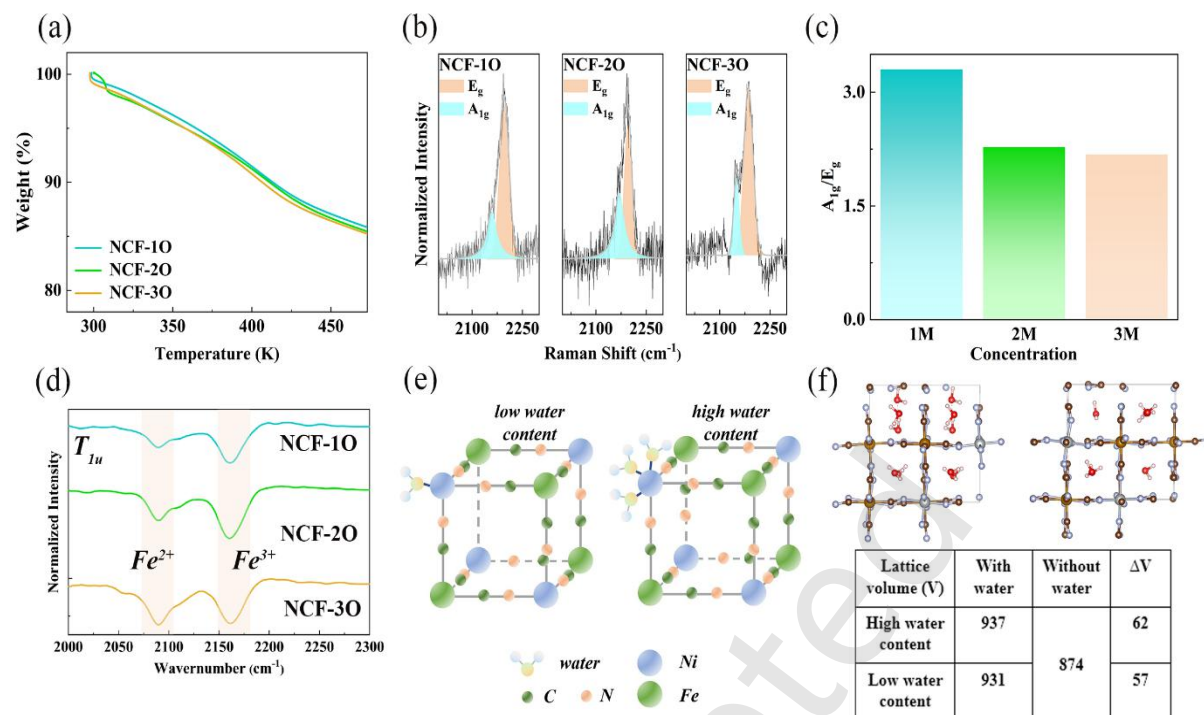


Figure 4. (a) TGA, (b) Raman spectra and (c) ratio of A_{1g} to E_g of NCF-10, NCF-20, and NCF-30. (d) FTIR spectra of the oxidation NiHCF samples (e) Schematic of the role of hydration in modulating the unit cell volume of NiHCF. (f) MD of NiHCF at Varied Hydration Levels and the Corresponding Calculated Unit Cell Volumes.

anodic redox couple, cp is the specific heat capacity of the whole system, and Y' is the Figure of Merit of the redox couple in electricity-assisted TREC systems [15, 44]. A larger $|Y|$ indicates better thermoelectric conversion performance. Fig 2(i) presents a comparison of the temperature coefficient, specific heat capacity, and Y for NiHCF in both low-concentration and high-concentration NaCl solutions. The data reveal that the NiHCF electrode achieves significantly enhanced thermoelectric performance in the low-concentration electrolyte, which suggests a larger entropy change under this condition.

It has been established that the hydration number of Na^+ decreases with increasing NaCl electrolyte concentration [45]. The restricted channel dimensions of the NiHCF framework necessitate partial desolvation of Na^+ for insertion during the reduction process (Fig 3(a)). The associated change in hydration entropy (ΔS_{hyd}) arises from the disruption of hydrogen-bond networks upon ion dehydration [22, 46]. This dehydration process increases molecular freedom, enhancing rotational, vibrational, and exchange dynamics of water molecules and ions, thereby generating a high entropy change. Solutions characterized by higher hydration numbers will exhibit more substantial entropy changes during dehydration. Consequently, Na^+ in low-concentration electrolytes, which maintain higher hydration numbers, are expected to yield a larger ΔS_{hyd} upon dehydration. This hypothesis is corroborated by analyzing the Raman spectra of aqueous NaCl solutions across a range of concentrations. The OH stretching vibration band of water is deconvoluted into three component bands centered at approximately 3250, 3450, and 3600 cm^{-1} , which correspond to strongly hydrogen-bonded, weakly hydrogen-bonded, and non-hydrogen-bonded water species, respectively (Fig S4 in the ESM) [47]. As evidenced in Fig

3(b), increasing NaCl concentration results in a blue-shift of the spectrum, indicating a significant reduction in the population of strongly hydrogen-bonded water species. This spectral evolution suggests that in low concentration NaCl solutions, water molecules and ions exhibit enhanced rotational, vibrational, and exchange freedom. This increased molecular mobility facilitates the release of water molecules during desolvation, thereby generating larger entropy changes.

The influence of electrolyte concentration on α is further investigated for both its oxidized and reduced states of NiHCF. Samples electrochemically oxidized or reduced in NaCl solutions of different concentrations ($x = 1, 2$, or 3 M) are denoted as NCF- xO or NCF- xR , where “O” and “R” stand for the oxidized and reduced states, respectively. To assess how Na^+ intercalation affects the internal water environment, thermogravimetric analysis (TGA) is performed on electrochemical reduced (Na-intercalated) NiHCF samples (NCF-1R to NCF-3R) (Fig 3(c)). At lower temperatures, the mass-loss profiles showed noticeable difference, which is attributable to distinct distributions of water molecules within the host structure. Once the samples are heated above 423 K, where both surface-adsorbed and interstitial water are removed, the curves converged [48]. The final weight losses recorded at 473 K for NCF-1R to NCF-3R are 17.54%, 17.60%, and 17.64%.

FTIR spectra of the reduced samples (NCF-1R to NCF-3R) exhibit no notable shifts as electrolyte concentration increases (Fig S5 in the ESM), indicating that the reduction process in electrolytes of varying concentration does not substantially alter the internal water environment of the PBA lattice. To further elucidate the effect of concentration, DFT is employed to investigate Na^+ insertion

thermodynamics under varying electrolyte concentrations and temperature gradients (Fig 3(d)). The simulation results reveal that, regardless of electrolyte concentration, Na^+ universally undergoes varying degrees of desolvation during framework insertion. And the insertion of Na^+ into NiHCF in low-concentration electrolytes yields a consistently larger ΔS across all tested temperatures (Fig 3(e)), thereby corroborating the proposed concentration-dependent ion-framework interaction mechanism.

Here, TGA analysis of NiHCF following complete Na^+ removal (specifically, NCF-10, NCF-20, and NCF-30) consistently revealed a progressive increase in residual moisture content with rising NaCl electrolyte concentration, despite the overall magnitude of variation remaining relatively small. The sample NCF-10 exhibits a smaller overall weight loss of 14.01%, compared to 14.41% and 14.61% for the other samples, suggesting that a larger proportion of moisture is co-removed during the Na^+ extraction process (Fig 4(a)). This phenomenon may be attributed to a spontaneous association between intercalated Na^+ and interstitial water molecules within the NiHCF framework. During Na^+ desorption, these weakly bound water molecules are co-desorbed. Conversely, at higher Na^+ concentrations, Na^+ ions with more stable solvation structures can slightly shield water molecules [49],

system comprising a NiHCF host structure and solvated Na^+ is constructed. Molecular dynamics simulations of Na^+ deintercalation from NiHCF at varying concentrations of NaCl yielded water co-desorption rates of 234 nmol/s (low concentration) and 169 nmol/s (high concentration).

Figure 4(b) presents the Raman spectra of NCF-10 to NCF-30. The data indicate that as the NaCl concentration increases, the E_g peak intensity rises while the A_{1g} intensity decreases. Consequently, the A_{1g}/E_g peak intensity ratio exhibits a gradual decrease (Fig 4(c)). Structural vibration entropy is considered a key variable parameter that significantly influences the PBA temperature coefficient, with its value being markedly affected by the internal moisture content of PBAs. The mechanism involves interstitial water molecules surrounding transition metal ions, which amplifies the influence of coordinated water. This effect alters the stretching vibrations of cyanide ligands, specifically the E_g and A_{1g} modes. Lower water content increases the covalent character of the Fe-C bonds, which enhances the overall symmetry of the PBA structure. This higher symmetry induces intense A_{1g} vibrational modes. The energy of these A_{1g} modes exceeds that of the E_g modes (activated by water), resulting in a net change in the phonon vibrational entropy, which is closely related to structural vibration.[50] This trend suggests that at lower NaCl

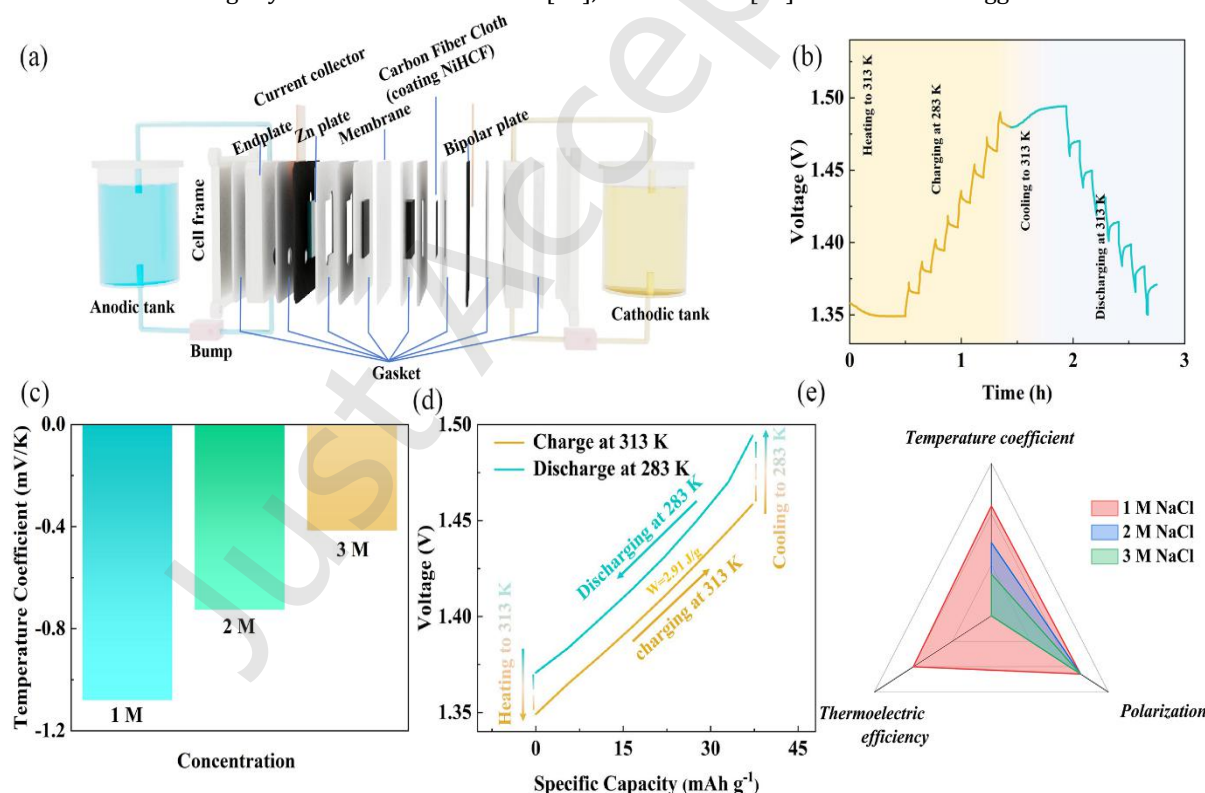


Figure 5. (a) Setup of the NiHCF/Zn^{0/2+} full cell. (b) GITT profile of a flow cell consisting of NiHCF as cathode, 1 M NaCl as catholyte, Zn metal as anode, 0.2 M ZnCl₂/1 M NaCl as anolyte during one TREC cycle at 283 K and 313 K. The current density was 0.2 mA cm⁻². (c) Comparison of temperature coefficients for full cells utilizing three different electrolyte concentrations. (d) The voltage plot of the above flow cell versus the specific capacity of the cathode. (e) Comparison of temperature coefficients, polarization, and thermoelectric efficiency in NiHCF/Zn TREC flow cell at different NaCl electrolyte concentrations.

thereby inhibiting their co-desorption, reserving the interstitial water in the PBA. Consequently, NiHCF retains moisture more effectively at elevated NaCl concentrations. To validate this theory, we conduct MD simulations to model sodium ion dehydration (Figs S6, S7 in the ESM). A model

concentrations, Na^+ desorption promotes a transition to a higher-symmetry state in NiHCF, a change that is correlated with a reduction in internal water content. Figure 4(d) illustrates the FTIR spectra for samples NCF-10 to NCF-30. Here, the cyanide stretching peaks for Fe(II) (2097 cm⁻¹) and

Fe(III) (2173 cm^{-1}) display systematic redshifts. This shift indicates a corresponding decrease in CN bond strength, revealing an inverse relationship between bond strength and NaCl concentration. As the T_{1u} vibration mode is not directly associated with the covalent character of the framework, the observed spectral shift is likely attributable to a higher CN bond energy in samples with desorbed Na^+ ions at lower concentrations [51]. This enhanced CN bond energy suggests an increase in the local symmetry of the NiHCF framework at low Na^+ concentrations. To verify the above findings, we calculated the integrated Crystal Orbital Hamilton Population (ICOHP) values to examine how variations in trace water content influence the bonding characteristics of the Ni–N and Fe–C bonds in the vicinity of NiHCF vacancies (see Note S2 in the ESM for further information). As shown in Figure S8, under conditions of slightly reduced water content, the average –ICOHP value of the Fe–C bonds decreased, while that of the Ni–N bonds increased in the region surrounding the vacancy. Specifically, the covalency of the Fe–C bonds is weakened, whereas that of the Ni–N bonds is enhanced. This gives rise to a more uniform distribution of bond strengths [36], which in turn drives the vibrational modes to shift toward the A_{1g} mode. Consequently, the system exhibits a higher structural vibrational entropy, further corroborating the aforementioned conclusions.

The lattice volume of NiHCF exhibits a strong positive correlation with its internal water content. Figure 4(e) demonstrates the lattice dilation of the NiHCF framework resulting from increased water content. The theoretical lattice volume of NiHCF versus its hydration degree is determined using DFT. As shown in Fig 4(f), the escape of water molecules from highly hydrated NiHCF induces a greater volumetric change, which corresponds to a larger entropy change (Figs S6, S7 in the ESM). Consequently, this pronounced volumetric change underlies the material's enhanced temperature coefficient at lower NaCl concentration electrolyte. It is consistent with the trend of lattice parameter measurements from *ex-situ* XRD analysis of NCF-10 to NCF-30 (Fig S9 in the ESM). Collectively, these results demonstrate that elevated electrolyte concentrations suppress the escape of water from the NiHCF framework, the water content within the NiHCF remains elevated following the reaction. Based solely on the temperature coefficient, NiHCF demonstrates superior thermoelectric conversion performance in low-concentration electrolytes.

A complete TREC flow cell with a negative temperature coefficient is fabricated (Fig 5(a)) to verify the feasibility of thermal energy conversion. The system consists of a Zn anode and a NiHCF cathode (0.1 g NiHCF on carbon cloth) separated by a Nafion 115 membrane. The anolyte is 0.2 M ZnCl_2 and n M NaCl ($n=1, 2, 3$), while the catholyte is simply n M NaCl. The system demonstrates stable operation and sustains extended cycling at room temperature (Fig S10 in the ESM).

The galvanostatic intermittent titration technique (GITT) is employed to determine the overpotentials during charge and discharge. Figure 5(b) depicts the cell voltage as a function of time during a single thermal cycle. The temperature first increases from 298 K to 313 K. Owing to

the system's negative temperature coefficient, the open-circuit voltage (OCV) consequently decreases. Subsequently, the cell is charged galvanostatically at 0.2 mA cm^{-2} (step 2), during which $[\text{Fe}(\text{CN})_6]^{4-}$ is fully oxidized to $[\text{Fe}(\text{CN})_6]^{3-}$. Following charging, the temperature is reduced to 283 K (step 3), resulting in an OCV increase of 14.5 mV. Finally, the cell is discharged galvanostatically until its voltage returns to the initial value measured at the beginning of step 1 (step 4).

Figure S11 in the ESM presents the IR-corrected cell voltage as a function of the SOC, demonstrating that the discharge voltage at 283 K is markedly higher than the charge voltage at 313 K. And the calculated temperature coefficient of the full cell in a 1 M NaCl solution is approximately -1.08 mV K^{-1} . The temperature coefficient of the full cell is also measured across a range of concentrations (Figs S12, S13 in the ESM). As illustrated in Fig 5(c), the coefficient decreases markedly with increasing electrolyte concentration, the measured full-cell temperature coefficients in 2 M and 3 M NaCl solutions are merely -0.72 mV K^{-1} and -0.41 mV K^{-1} , respectively. Although higher concentrations enhance electrolyte conductivity, thereby marginally reducing full-cell polarization, the associated precipitous drop in the temperature coefficient ultimately inhibits the effective conversion of thermal energy into electrical energy (Fig S14 in the ESM). Therefore, optimal performance of the TREC system is best achieved by operating at low current densities within a low-concentration electrolyte solution.

In principle, a larger temperature differential promotes a greater voltage divergence between the charge and discharge curves, which enlarges the area enclosed by the hysteresis loop and thus enhances the net energy output. However, at elevated temperatures, parasitic side reactions cause the observed charging capacity to fall substantially below the theoretically predicted value, and the subsequent discharge capacity is substantially lower than the preceding charge capacity, yielding a reduced Coulombic efficiency for the thermal cycle. Consequently, a temperature range of 283–313 K is chosen to accommodate both cell operation and thermoelectric conversion. Figure 5(d) illustrates the practical operation of the TREC, wherein low-grade heat is harvested through a cycle of charging at 313 K and discharging at 283 K at a current density of 1 mA cm^{-2} , thereby converting thermal energy into electrical energy.

Previous analyses indicate that electrolyte concentration has a comparatively minor influence on electrochemical hysteresis during isothermal charge-discharge cycles (Fig S15 in the ESM). However, its effect on the temperature coefficient is more substantial, becoming the dominant factor under large thermal gradients. Consequently, the temperature coefficient's influence on system performance is greatest at lower concentrations. At elevated concentrations (2 M and 3 M), the low temperature coefficient is insufficient to overcome the significant ohmic polarization, thereby precluding efficient thermal energy conversion. At a 1 M NaCl concentration, the NiHCF electrode yields a net output of 2.91 J g^{-1} over the full SOC range (0–100%), and the TREC system achieved an absolute thermal energy conversion efficiency of 0.71% without heat

recuperation, which corresponds to a relative efficiency of 7.41% of the Carnot efficient (Note S1).

Fig 5(e) compares the full-cell temperature coefficient (α), electrochemical polarization, and the thermoelectric efficiency for the NiHCF/Zn flow cells at three electrolyte concentrations. Since polarization is dominated by the ion permeability of the separator, its value remains similar across all three concentrations. Consequently, the 1 M cell, with its significantly higher temperature coefficient, is the only configuration that achieves effective thermoelectric conversion. Furthermore, the system demonstrates stable cycling capacity, indicating that the influence of electrolyte concentration on the entropy change of NiHCF is both reversible and persistent, rather than a transient effect (Fig S16 in the ESM). While the NiHCF cathode demonstrates a favorable thermal response and a high temperature coefficient, it experiences a certain degree of capacity decay. We attribute this to localized structural degradation from lattice distortions and active material shedding under flow-cell conditions. Furthermore, system efficiency and power density can be improved by mitigating zinc side reactions and utilizing advanced membranes with low polarization. Consequently, the NiHCF/Zn TREC system exhibits significant potential for low-grade thermal energy harvesting compared to other thermoelectric systems (Fig S18 in the ESM), particularly at low electrolyte concentrations.

4 Conclusion

In summary, this work demonstrates that electrolyte concentration is a decisive parameter governing the thermoelectric conversion performance of NiHCF. Comprehensive characterization reveals that electrolyte concentration not only increases the reaction entropy but also modulates the hydration state of intercalating cations and the water content within the NiHCF framework. To elucidate the mechanism through which electrolyte concentration drives the temperature coefficient of NiHCF, combined MD and DFT simulations are employed to model the electrochemical environment across a range of temperatures and concentrations, enabling the quantification of changes in lattice parameters and entropy. To verify the practical effect of this concentration-driven temperature coefficient on TREC performance, flow cells incorporating NiHCF cathode and Zn anode are constructed and evaluated using electrolytes of different concentrations. When at a lower concentration, the system achieves an absolute thermal energy conversion efficiency of 0.71%, corresponding to 7.41% of the Carnot efficiency, under an applied ΔT of 30 K. However, at a high electrolyte concentration, efficient thermoelectric conversion is hindered. Therefore, optimizing the electrolyte concentration enhances the electrode's temperature coefficient, thereby improving low-grade heat harvesting. This work underscores the critical role of electrolyte concentration in amplifying the thermoelectric potential of electrode materials to achieve efficient TREC systems. These findings provide a valuable foundation for the future development of TREC systems.

Electronic Supplementary Material: Supplementary material (structural characterization, simulation calculations, electrochemical testing of the control group).

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the ESM. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was supported by National Key R&D Program of China (No. 2022YFA1504100) and the Scientific and Technological Developing Project of Jilin Province (20260102105JC).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution statement

J. N. Z.: Data curation, validation, writing manuscript, experimental design. R. W.: Writing manuscript. H. N. S.: Experimental design, validation. M. G., Z. J. Y., J. Y. Z.: Validation. F. F. Z.: Project administration, validation, writing manuscript, experimental design, writing – reviewing and editing. J. M. Y.: Project administration, writing – reviewing and editing. All the authors have approved the final manuscript.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

References

- [1] Bell, L. E. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. *Science* 2008, 321, 1457-1461.
- [2] Bonaccorso, F.; Colombo, L.; Yu, G. H.; Stoller, M.; Tozzini, V.; Ferrari, A. C.; Ruoff, R. S.; Pellegrini, V. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* 2015, 347, 10, 1246501.
- [3] Chu, S.; Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* 2012, 488, 294-303.
- [4] Colonna, P.; Casati, E.; Trapp, C.; Mathijssen, T.; Larjola, J.; Turunen-Saaresti, T.; Uusitalo, A. Organic Rankine Cycle Power Systems: From the Concept to Current Technology, Applications, and an Outlook to the Future. *J. Eng. Gas. Turbines Power-Trans. ASME* 2015, 137, 19, 100801.
- [5] Saboori, A.; Gallo, D.; Biamino, S.; Fino, P.; Lombardi, M. An Overview of Additive Manufacturing of Titanium Components by Directed Energy Deposition: Microstructure and Mechanical Properties. *Appl. Sci.-Basel* 2017, 7, 23, 883.
- [6] Zhu, L. L.; Ding, T. P.; Gao, M. M.; Peh, C. K. N.; Ho, G. W. Shape Conformal and Thermal Insulative Organic Solar Absorber Sponge for Photothermal Water Evaporation and Thermoelectric Power Generation. *Adv. Energy Mater.* 2019, 9, 7, 1900250.
- [7] Han, C. G.; Qian, X.; Li, Q. K.; Deng, B.; Zhu, Y. B.; Han, Z. J.; Zhang, W. Q.; Wang, W. C.; Feng, S. P.; Chen, G.; Liu, W. S. Giant

thermopower of ionic gelatin near room temperature. *Science* 2020, 368, 1091-+.

- [8] Du, Y.; Xu, J. Y.; Paul, B.; Eklund, P. Flexible thermoelectric materials and devices. *Appl. Mater. Today* 2018, 12, 366-388.
- [9] Jaziri, N.; Boughamoura, A.; Müller, J.; Mezghani, B.; Tounsi, F.; Ismail, M. A comprehensive review of Thermoelectric Generators: Technologies and common applications. *Energy Rep.* 2020, 6, 264-287.
- [10] Siddique, A. R. M.; Mahmud, S.; Van Heyst, B. A review of the state of the science on wearable thermoelectric power generators (TEGs) and their existing challenges. *Renew. Sust. Energ. Rev.* 2017, 73, 730-744.
- [11] Quoilin, S.; Broek, M. V. D.; Declaye, S.; Dewallef, P.; Lemort, V. Techno-economic survey of Organic Rankine Cycle (ORC) systems. *Renewable and Sustainable Energy Reviews* 2013, 22, 168-186.
- [12] Van Erdeweghe, S.; Van Bael, J.; Laenen, B.; D'haeseleer, W. Design and off-design optimization procedure for low-temperature geothermal organic Rankine cycles. *Applied Energy* 2019, 242, 716-731.
- [13] Yang, Y.; Loomis, J.; Ghasemi, H.; Lee, S. W.; Wang, Y. J.; Cui, Y.; Chen, G. Membrane-Free Battery for Harvesting Low-Grade Thermal Energy. *Nano Letters* 2014, 14, 6578-6583.
- [14] Gao, C. T.; Lee, S. W.; Yang, Y. Thermally Regenerative Electrochemical Cycle for Low-Grade Heat Harvesting. *ACS Energy Lett.* 2017, 2, 2326-2334.
- [15] Lee, S. W.; Yang, Y.; Lee, H. W.; Ghasemi, H.; Kraemer, D.; Chen, G.; Cui, Y. An electrochemical system for efficiently harvesting low-grade heat energy. *Nat. Commun.* 2014, 5, 6, 3942.
- [16] Zhang, H.; Wang, Q. Thermally regenerative electrochemical cycle for low-grade heat harnessing. *Chem. Phys. Rev.* 2021, 2, 11.
- [17] Zhang, J. N.; Li, J.; Yu, K. F.; Wang, Q.; Zhang, H.; Zhang, F. F.; Yan, J. M. Charging-free redox flow battery for continuous high-power electricity generation from low-grade heat. *Nano Research Energy* 2025, 4.
- [18] Hochbaum, A. I.; Chen, R. K.; Delgado, R. D.; Liang, W. J.; Garnett, E. C.; Najarian, M.; Majumdar, A.; Yang, P. D. Enhanced thermoelectric performance of rough silicon nanowires. *Nature* 2008, 451, 163-U165.
- [19] Zhang, H.; Lek, D. G.; Huang, S. Q.; Lee, Y. M.; Wang, Q. Efficient Low-Grade Heat Conversion and Storage with an Activity-Regulated Redox Flow Cell via a Thermally Regenerative Electrochemical Cycle. *Adv. Mater.* 2022, 34, 10, 2202266.
- [20] Liu, P.; Yu, B. Y.; Zeng, Y. L.; Zhang, Y. F.; Cai, X.; Long, X.; Jiang, H.; Yang, W. D.; Gui, S. Y.; Guo, J. H.; Li, J.; Zhou, J.; Duan, J. J. Thermosensitive slurry electrolyte design for efficient electrochemical heat harvesting. *Energy Environ. Sci.* 2025, 18, 2852-2860.
- [21] Yu, B. Y.; Duan, J. J.; Cong, H. J.; Xie, W. K.; Liu, R.; Zhuang, X. Y.; Wang, H.; Qi, B.; Xu, M.; Wang, Z. L.; Zhou, J. Thermosensitive crystallization-boosted liquid thermocells for low-grade heat harvesting. *Science* 2020, 370, 342-+.
- [22] Li, X. Y.; Wu, A. Y.; Li, J.; Li, Z. K.; Lee, D.; Lee, S. W. Anion Effects on Thermopower of Electrochemical Systems for Low-Grade Heat Harvesting. *ACS Energy Lett.* 2023, 8, 4061-4068.
- [23] Sun, T. T.; Zhao, Z. F.; Xu, Z. K.; Lin, S. Y. Anchoring Fe(OH)₃ nanoparticles on Ni-MOF nanosheets for efficient electrocatalytic oxygen evolution. *Rare Metals* 2023, 42, 1453-1459.
- [24] Wang, L.; Zhang, X.; Kong, Y. Y.; Li, C.; An, Y. B.; Sun, X. Z.; Wang, K.; Ma, Y. W. Metal-organic framework-derived CoSe₂@N-doped carbon nanocubes for high-performance lithium-ion capacitors. *Rare Metals* 2024, 43, 2150-2160.
- [25] Wu, Z. Z.; Xia, T.; Liang, Y.; Li, Y. P.; Sui, Z. Y.; Feng, L. J.; Wu, D. X.; Tian, X. L.; Chen, Q. Metal complexes of bipyridine-functionalized covalent organic frameworks as efficient electrocatalysts for oxygen evolution reaction. *Rare Metals* 2024, 43, 3096-3106.
- [26] Liu, C. L.; Bai, Y.; Li, W. T.; Yang, F. Y.; Zhang, G. X.; Pang, H. In Situ Growth of Three-Dimensional MXene/Metal-Organic Framework Composites for High-Performance Supercapacitors. *Angewandte Chemie-International Edition* 2022, 61, 11, e202116282.
- [27] Wang, X.; Yu, L.; Guan, B. Y.; Song, S. Y.; Lou, X. W. Metal-Organic Framework Hybrid-Assisted Formation of Co₃O₄/Co-Fe Oxide Double-Shelled Nanoboxes for Enhanced Oxygen Evolution. *Adv. Mater.*

2018, 30, 29, 1801211.

- [28] Gao, C. T.; Liu, Y. Z.; Chen, B. B.; Yun, J. H.; Feng, E. X.; Kim, Y. G.; Kim, M.; Choi, A.; Lee, H. W.; Lee, S. W. Efficient Low-Grade Heat Harvesting Enabled by Tuning the Hydration Entropy in an Electrochemical System. *Adv. Mater.* 2021, 33, 9, 2004717.
- [29] Huo, D. X.; Tian, H.; Wang, W. G.; Shu, G. Q. Effect of electrolytes on performance of CuHCF electrode of thermally regenerative electrochemical cycle system for harvesting low-grade heat. *Energy Conv. Manag.* 2022, 255, 9, 115306.
- [30] Li, J.; Li, X. Y.; Lee, D.; Yun, J.; Wu, A. Y.; Jiang, C.; Lee, S. W. Engineering of Solvation Entropy by Poly(4-styrenesulfonic acid) Additive in an Aqueous Electrochemical System for Enhanced Low-Grade Heat Harvesting. *Nano Letters* 2023, 23, 6164-6170.
- [31] Li, X. Y.; Li, J.; Yun, J. H.; Wu, A. Y.; Gao, C. T.; Lee, S. W. Continuous thermally regenerative electrochemical systems for directly converting low-grade heat to electricity. *Nano Energy* 2022, 101, 11, 107547.
- [32] Wang, W. G.; Tang, L.; Yan, Z. Q.; Li, Z. Z.; Huo, D. X.; Tian, H.; Shu, G. Q. Charging-free thermally regenerative electrochemical cycles with high temperature coefficients for heat-to-electricity conversion. *J. Mater. Chem. A* 2025, 10.1039/d5ta03351a, 12, 2050-7496.
- [33] Gao, C. T.; Yin, Y. L.; Zheng, L.; Liu, Y. Z.; Sim, S.; He, Y. M.; Zhu, C.; Liu, Z.; Lee, H. W.; Yuan, Q. H.; Lee, S. W. Engineering the Electrochemical Temperature Coefficient for Efficient Low-Grade Heat Harvesting. *Adv. Funct. Mater.* 2018, 28, 7, 1803129.
- [34] Reynier, Y.; Graetz, J.; Swan-Wood, T.; Rez, P.; Yazami, R.; Fultz, B. Entropy of Li intercalation in Li_xCoO₂ - art. no. 174304. *Phys. Rev. B* 2004, 70, 7, 174304.
- [35] Liu, Y. Z.; Gao, C. T.; Yun, J.; Kim, Y.; Kim, M.; Li, J.; Lee, S. W. Tuning the Hydration Entropy of Cations during Electrochemical Intercalation for High Thermopower. *Adv. Energy Sustain. Res.* 2022, 3, 6, 2100176.
- [36] Choi, A.; Song, Y. Y.; Kim, J.; Kim, D.; Kim, M. H.; Lee, S. W.; Seo, D. H.; Lee, H. W. Enhancing Efficiency of Low-Grade Heat Harvesting by Structural Vibration Entropy in Thermally Regenerative Electrochemical Cycles. *Adv. Mater.* 2023, 35, 38, 2303199.
- [37] Kjeldgaard, S.; Dugulan, I.; Mamakhel, A.; Wagemaker, M.; Iversen, B. B.; Bentien, A. Strategies for synthesis of Prussian blue analogues. *R. Soc. Open Sci.* 2021, 8, 13, 201779.
- [38] Sun, Y. P.; Xu, Y. L.; Xu, Z.; Sun, Y.; Xu, X. W.; Tu, J.; Xie, J.; Liu, S. Y.; Zhao, X. Long-life Na-rich nickel hexacyanoferrate capable of working under stringent conditions. *J. Mater. Chem. A* 2021, 9, 21228-21240.
- [39] Wessells, C. D.; Peddada, S. V.; Huggins, R. A.; Cui, Y. Nickel Hexacyanoferrate Nanoparticle Electrodes For Aqueous Sodium and Potassium Ion Batteries. *Nano Letters* 2011, 11, 5421-5425.
- [40] Omarova, M.; Koishybay, A.; Yesibolati, N.; Mentbayeva, A.; Umirov, N.; Ismailov, K.; Adair, D.; Babaa, M. R.; Kurmanbayeva, I.; Bakonov, Z. Nickel Hexacyanoferrate Nanoparticles as a Low Cost Cathode Material for Lithium-Ion Batteries. *Electrochim. Acta* 2015, 184, 58-63.
- [41] Wei, C.; Fu, X. Y.; Zhang, L. L.; Liu, J.; Sun, P. P.; Gao, L.; Chang, K. J.; Yang, X. L. Structural regulated nickel hexacyanoferrate with superior sodium storage performance by K-doping. *Chem. Eng. J.* 2021, 421, 8, 127760.
- [42] Fan, L. Y.; Shu, G. C.; Liu, Y. W.; Yu, H. X.; Yan, L.; Zhang, L. Y.; Shu, J. Cu-substituted nickel hexacyanoferrate with tunable reaction potentials for superior ammonium ion storage. *J. Mater. Sci. Technol.* 2024, 169, 19-27.
- [43] Gao, Y. N.; Yang, H. Y.; Wang, X. R.; Bai, Y.; Zhu, N.; Guo, S. N.; Suo, L. M.; Li, H.; Xu, H. J.; Wu, C. The Compensation Effect Mechanism of Fe-Ni Mixed Prussian Blue Analogues in Aqueous Rechargeable Aluminum-Ion Batteries. *ChemSusChem* 2020, 13, 732-740.
- [44] Zhang, H.; Wang, Z. Y.; Li, H. G.; Salla, M.; Song, Y. X.; Huang, S. P.; Huang, S. Q.; Wang, X.; Liu, K. P.; Xu, G. Q.; Huang, J. G.; Qu, C. W.; Wang, Q. Continuous electricity generation from solar heat and darkness. *Joule* 2023, 7, 1515-1528.
- [45] Mancinelli, R.; Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. Hydration of sodium, potassium, and chloride ions in solution and the concept of structure maker/breaker. *J. Phys. Chem. B* 2007, 111, 13570-

13577.

[46] Chen, Y. C.; Huang, Q. Q.; Liu, T. H.; Qian, X.; Yang, R. G. Effect of solvation shell structure on thermopower of liquid redox pairs. *EcoMat* 2023, 5, 12, e12385.

[47] Ahmed, M.; Namboodiri, V.; Singh, A. K.; Mondal, J. A.; Sarkar, S. K. How Ions Affect the Structure of Water: A Combined Raman Spectroscopy and Multivariate Curve Resolution Study. *J. Phys. Chem. B* 2013, 117, 16479-16485.

[48] Pasta, M.; Wessells, C. D.; Liu, N.; Nelson, J.; McDowell, M. T.; Huggins, R. A.; Toney, M. F.; Cui, Y. Full open-framework batteries for stationary energy storage. *Nat. Commun.* 2014, 5, 9, 3007.

[49] Guo, Q. B.; Han, S.; Lu, Y. X.; Xiao, R. J.; Li, J.; Hao, Q. L.; Rong, X. H.; Weng, S. T.; Niu, Y. S.; Ding, F. X.; Yang, Y.; Xia, H.; Wang,

X. F.; Xie, F.; Zhou, L.; Hou, X. Y.; Li, H.; Huang, X. J.; Chen, L. Q.; Hu, Y. S. Cation-self-shielding strategy promises high-voltage all-Prussian-blue-based aqueous K-ion batteries. *Nat. Commun.* 2025, 16, 13, 4707.

[50] Wei, W. J.; Li, W.; Butler, K. T.; Feng, G. Q.; Howard, C. J.; Carpenter, M. A.; Lu, P. X.; Walsh, A.; Cheetham, A. K. An Unusual Phase Transition Driven by Vibrational Entropy Changes in a Hybrid Organic-Inorganic Perovskite. *Angewandte Chemie-International Edition* 2018, 57, 8932-8936.

[51] Andonova, S.; Akbari, S. S.; Karadas, F.; Spassova, I.; Paneva, D.; Hadjiivanov, K. Structure and properties of KNi-hexacyanoferrate Prussian Blue Analogues for efficient CO₂ capture: Host-guest interaction chemistry and dynamics of CO₂ adsorption. *J. CO₂ Util.* 2021, 50, 13, 101593

Electronic Supplementary Material

Concentration- driven enhancement of low- grade thermal energy harvesting in electrochemical systems

Jia-Ning Zhang¹, Rui Wang², Hao-Nan Song¹, Miao Gao¹, Zhuo-Jian Yang¹, Jia-Yi Zhang¹, Fei-Fei Zhang¹ , and Jun-Min Yan¹ 

¹ Key Laboratory of Automobile Materials, Ministry of Education, School of Materials Science and Engineering, Jilin University, Changchun 130022, China

² School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

 Address correspondence to Jun-Min Yan, junminyan@jlu.edu.cn; Fei-Fei Zhang, ffzhang@jlu.edu.cn

Supporting information to <https://doi.org/10.26599/NR.2026.94909001>

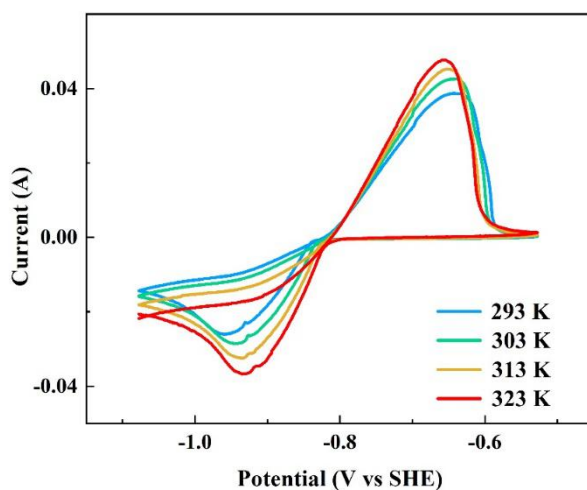


Figure S1. Cyclic Voltammetry (CV) curves of 0.2 M ZnCl_2 /1M NaCl at different temperatures.

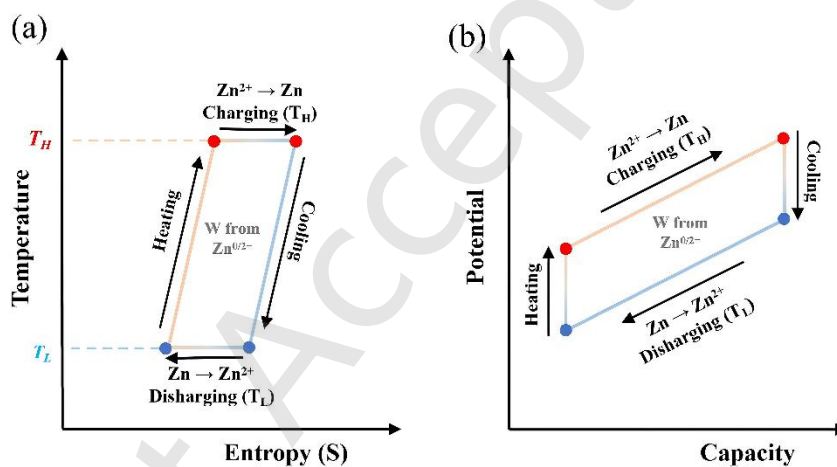


Figure S2. (a) Temperature-entropy (T-S) diagram and (b) potential-capacity (P-C) diagram of the TREC cycle for anodic side.

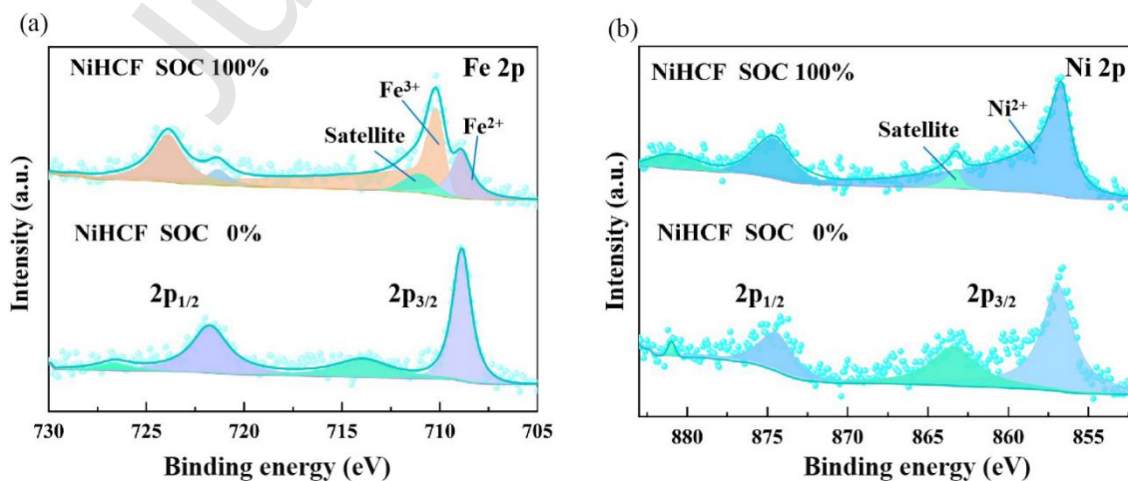


Figure S3. Ex-situ X-ray photoelectron spectra (XPS) spectra of (a) Fe 2p, and (b) Ni 2p of the NiHCF electrode at different states of charge (SOC).

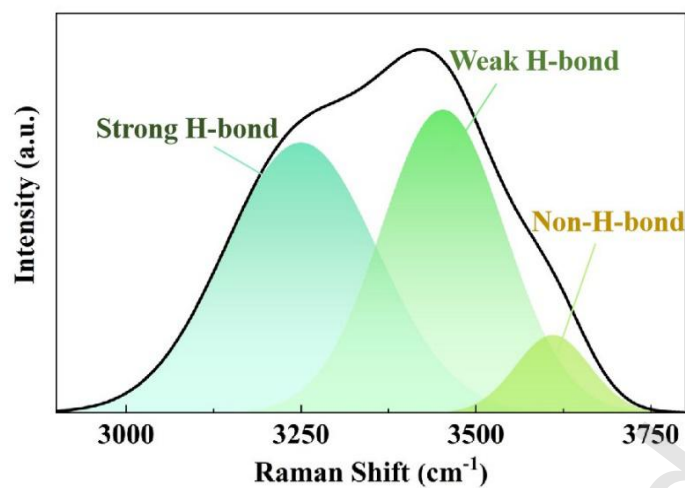


Figure S4. Raman spectra of OH stretching bands for deionized water.

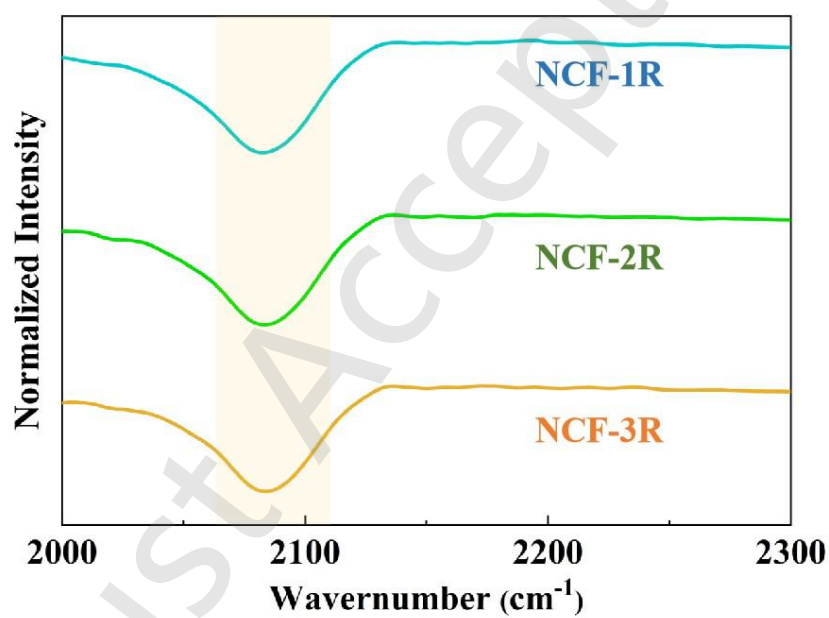


Figure S5. Fourier-transform infrared (FTIR) spectra of the NCF-1R, NCF-2R, and NCF-3R.

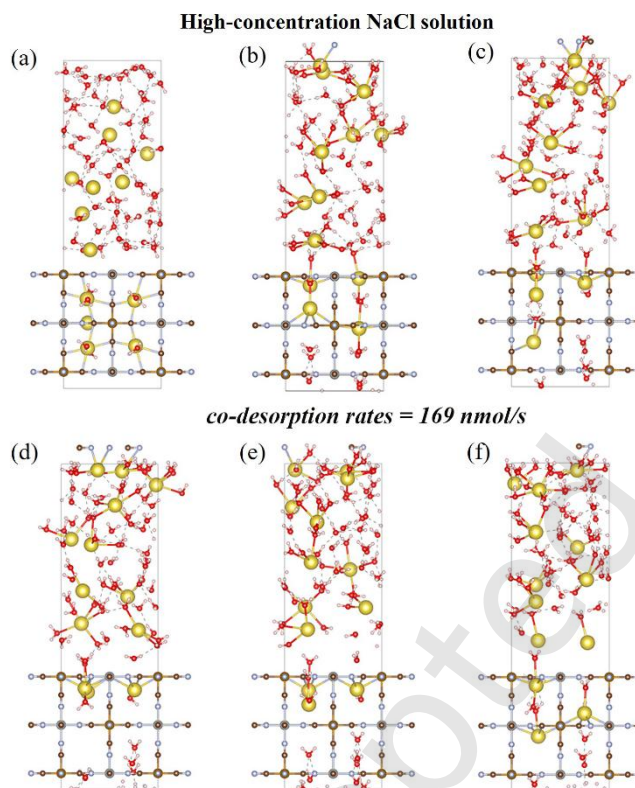


Figure S6. (a-f) Molecular dynamics (MD) simulation snapshot of Na^+ deintercalation from NiHCF framework into high concentration NaCl solution. (Co-desorption rate: 169 nmol/s)

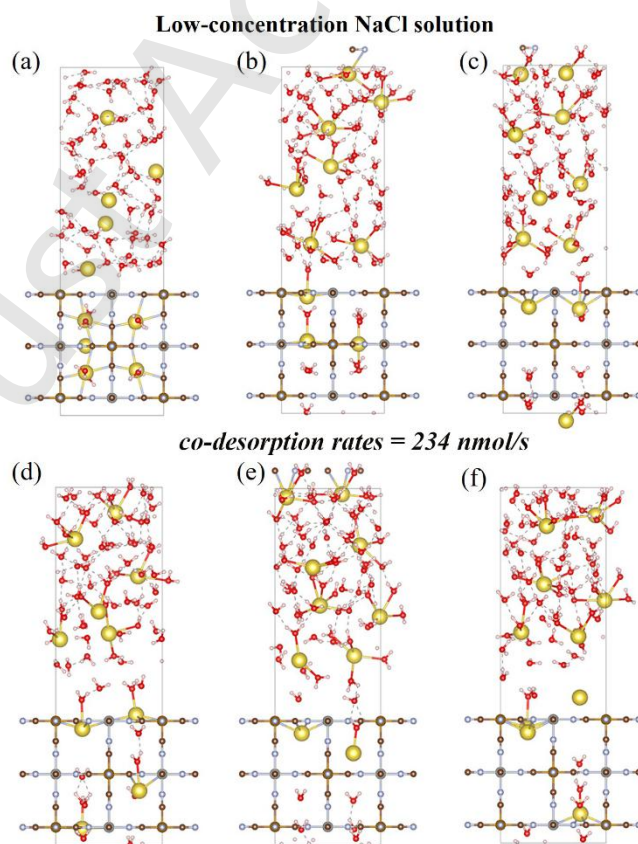


Figure S7. (a-f) MD simulation snapshot of Na^+ deintercalation from NiHCF framework into low concentration NaCl solution. (Co-desorption rate: 234 nmol/s)

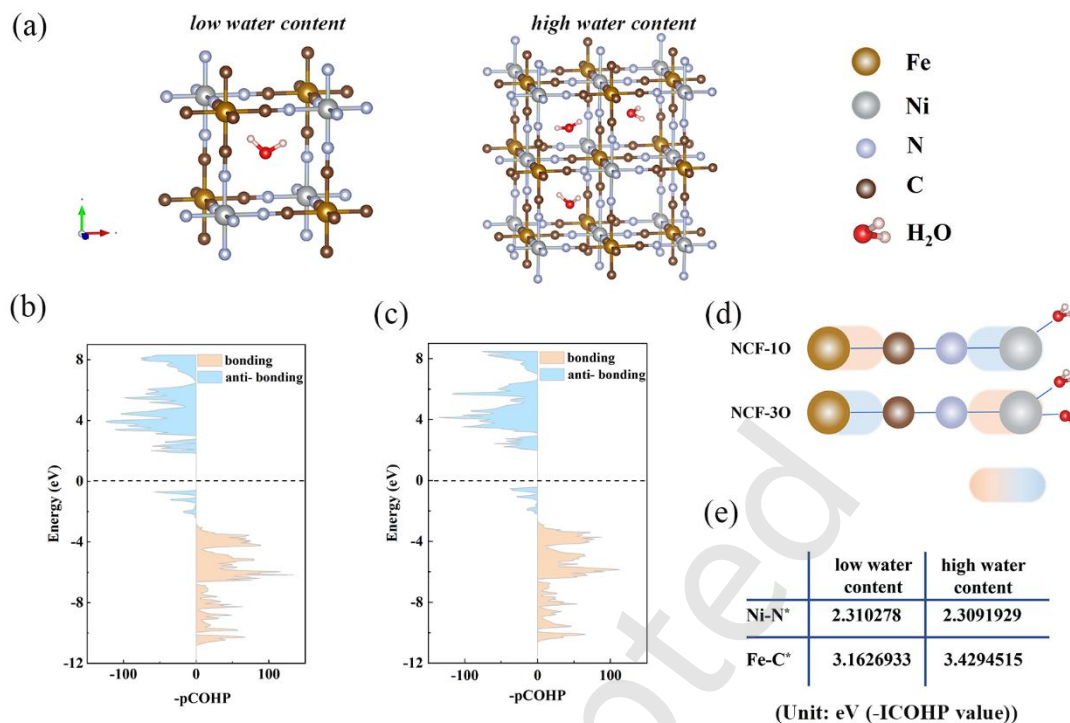


Figure S8. (a) Structural model of NiHCF with different water contents. Projected Crystal Orbital Hamilton Population (-pCOHP) diagrams of NiHCF with (b) low and (c) high water content. The Fermi level is set to 0 eV. (d) Schematic illustration of the effect of water molecules on the bond covalency of Ni—N and Fe—C bonds. (e) Effect of water content on the bond covalency of NiHCF (-ICOHP, eV). The average -ICOHP values of Ni—N and Fe—C bonds under two conditions are presented for comparison.

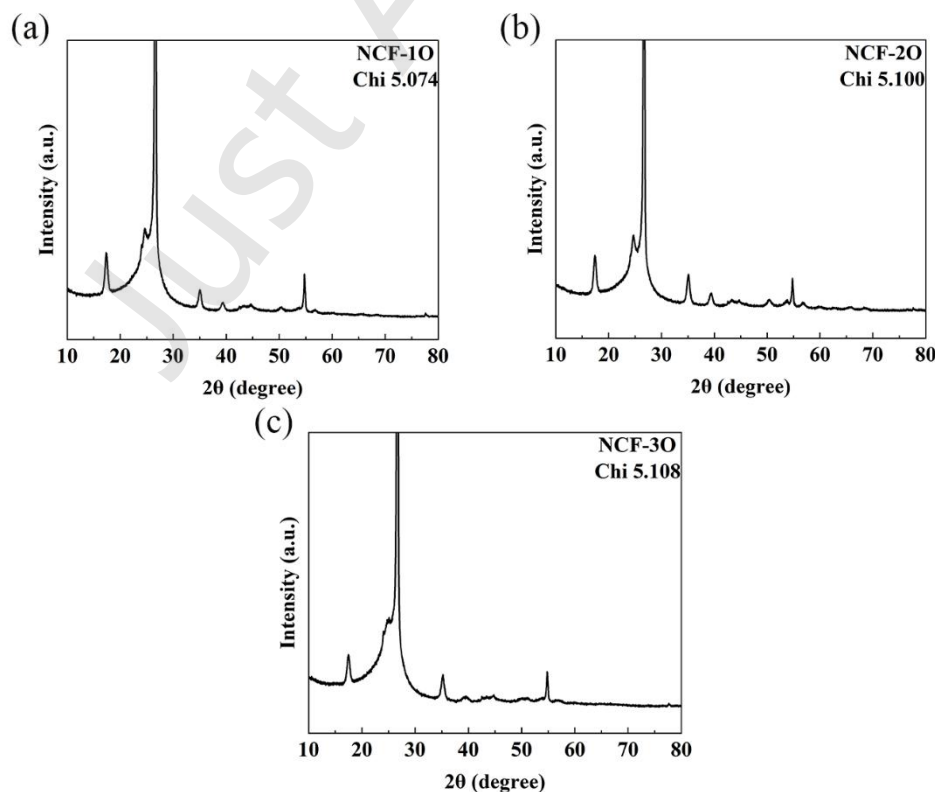


Figure S9. X-ray diffraction analysis (XRD) patterns of (a) NCF-10, (b) NCF-20, (c) NCF-30 and their corresponding lattice constants.

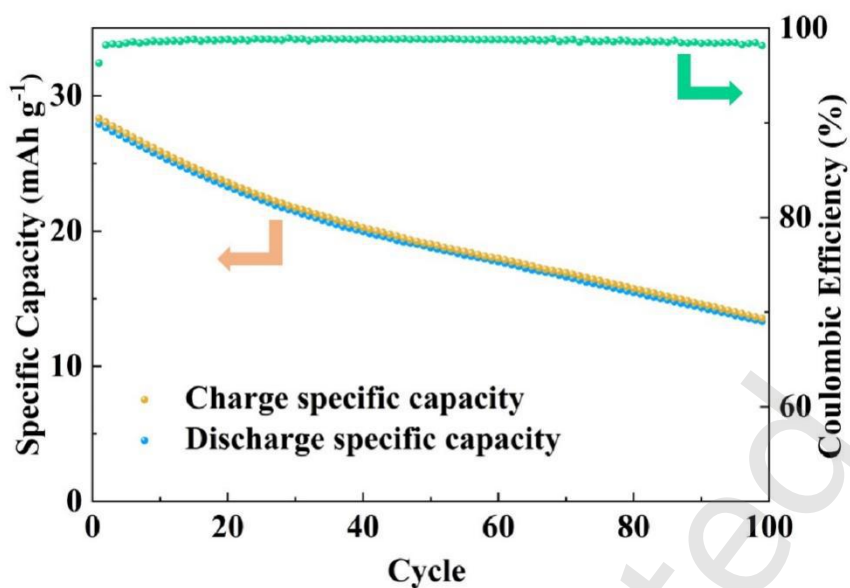


Figure S10. Cycling performance of a flow cell consisting of 1M NaCl as catholyte and 0.2 M ZnCl₂/1 M NaCl as anolyte.

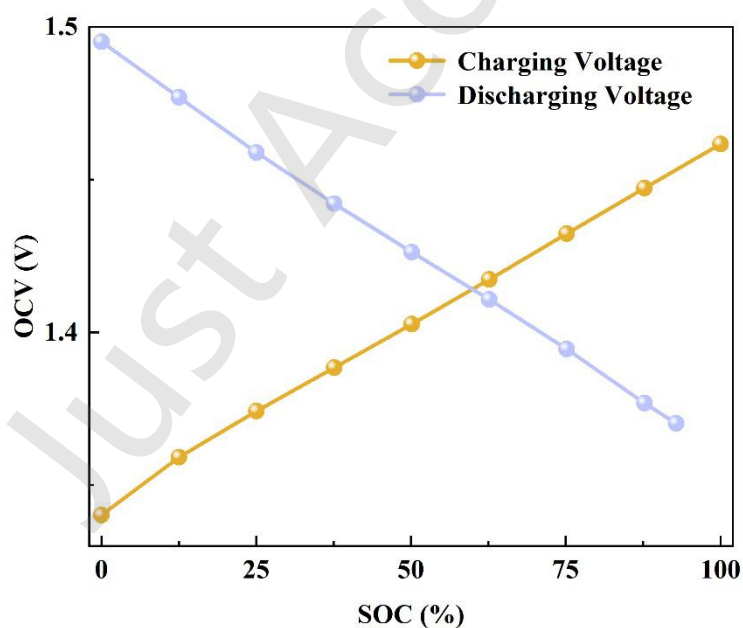


Figure S11. Open circuit voltage (OCV)-SOC plot of the of a flow cell consisting of NiHCF as cathode, 1 M NaCl as catholyte, Zn metal as anode, 0.2 M ZnCl₂/1 M NaCl as anolyte after IR correction during one TREC cycle at 283 K and 313 K.

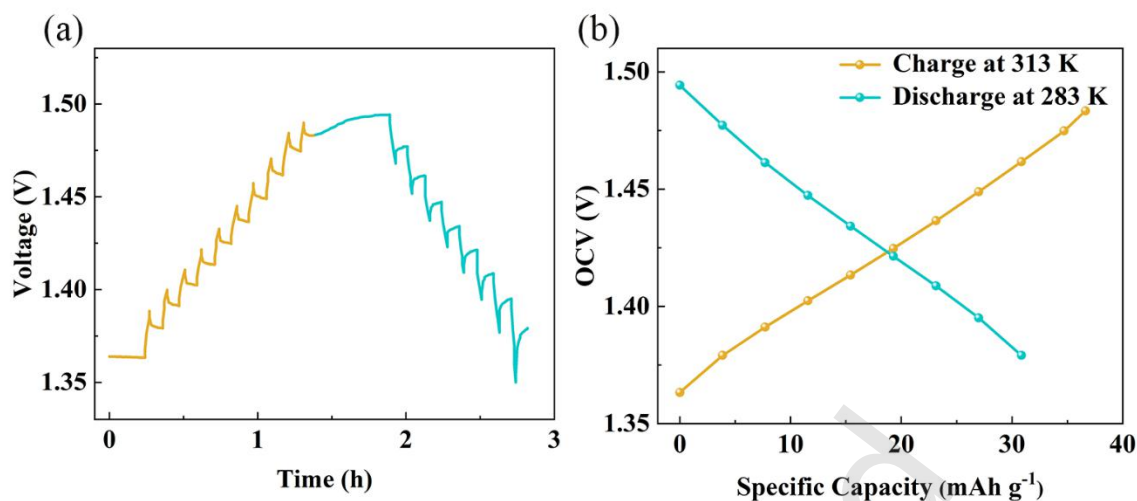


Figure S12. (a) Galvanostatic intermittent titration technique (GITT) profile of a flow cell consisting of NiHCF as cathode, 2 M NaCl as catholyte, Zn metal as anode, 0.2 M ZnCl₂/1 M NaCl as anolyte during one thermal regenerative electrochemical cycling (TREC) cycle at 283 K and 313 K. (b) OCV-SOC plot of the cell after IR correction during one TREC cycle.

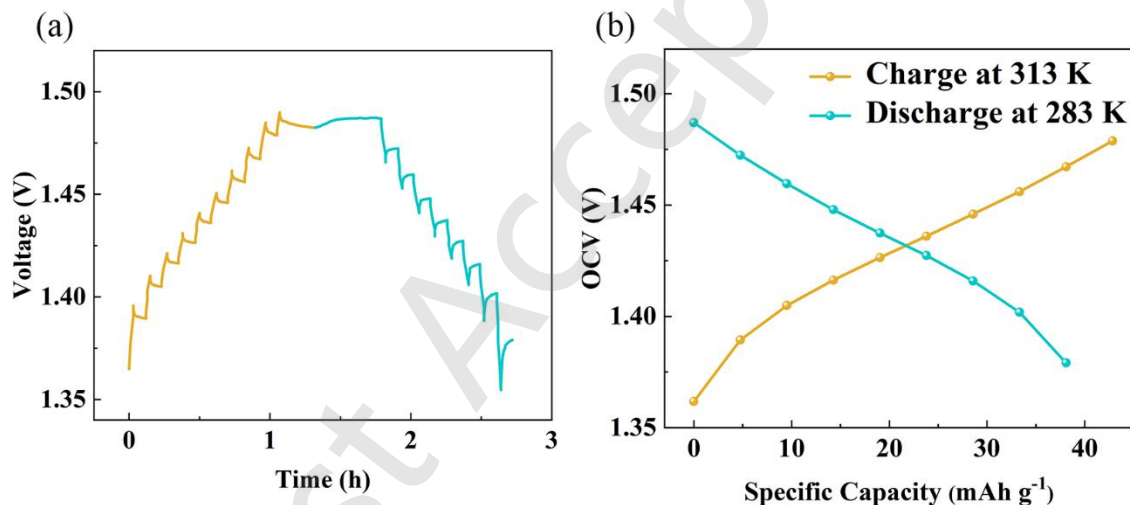


Figure S13. (a) GITT profile of a flow cell consisting of NiHCF as cathode, 3 M NaCl as catholyte, Zn metal as anode, 0.2 M ZnCl₂/1 M NaCl as anolyte during one TREC cycle at 283 K and 313 K. (b) OCV-SOC plot of the cell after IR correction during one TREC cycle.

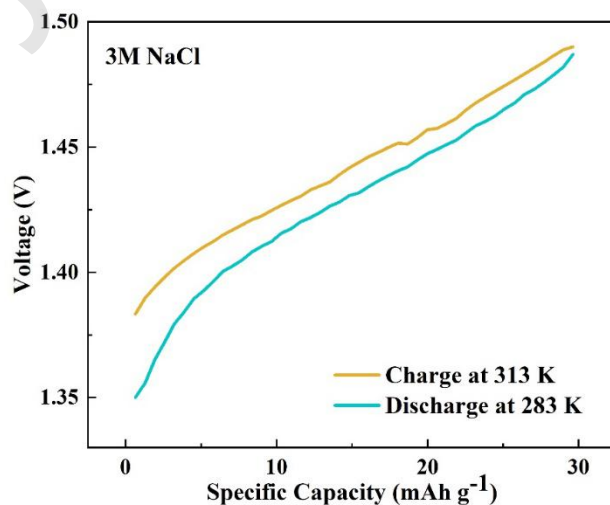


Figure S14. The voltage plot of the above flow cell with an electrolyte concentration of 3 M vs. the specific capacity of the cathode.

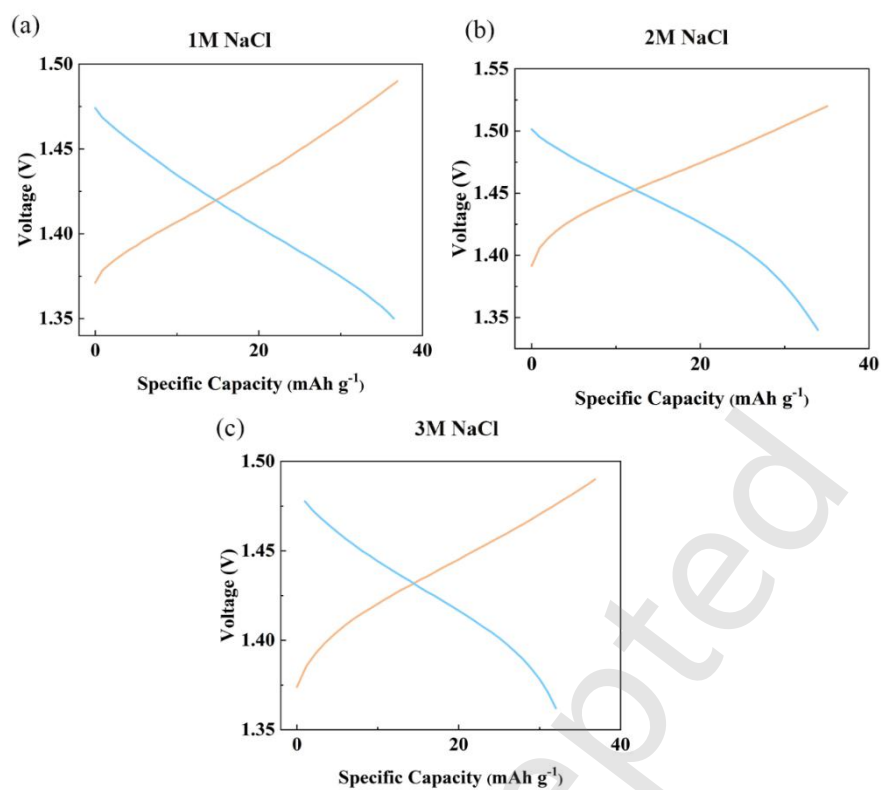


Figure S15. Voltage profiles of a flow cell consisting of (a) 1 M, (b) 2 M, (c) 3 M NaCl as catholyte, NiHCF as cathode, 0.2 M ZnCl_2/n M NaCl ($n=1,2,3$) as anolyte, and Zn plate as anode.

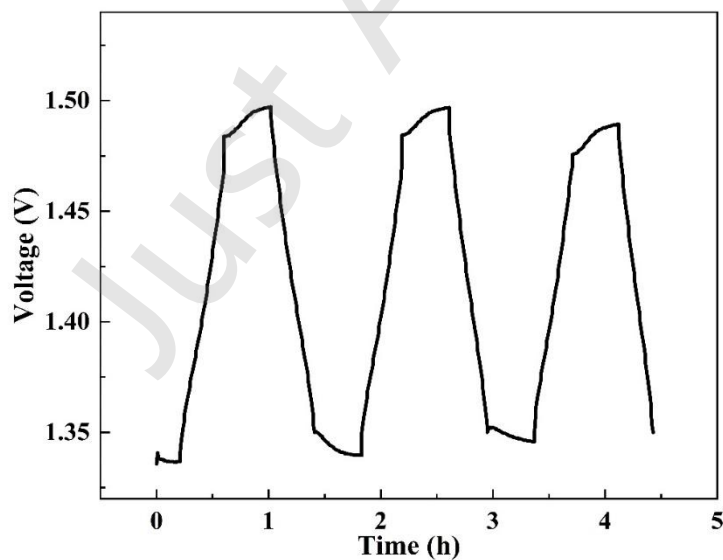


Figure S16. Continuous TREC operation of the flow cell. The flow cell with express NiHCF as cathode, Zn plate as anode, 1 M NaCl as the catholyte, and 0.2M $\text{ZnCl}_2/1$ M NaCl as the anolyte. The current density is 0.2 mA/cm^2 .

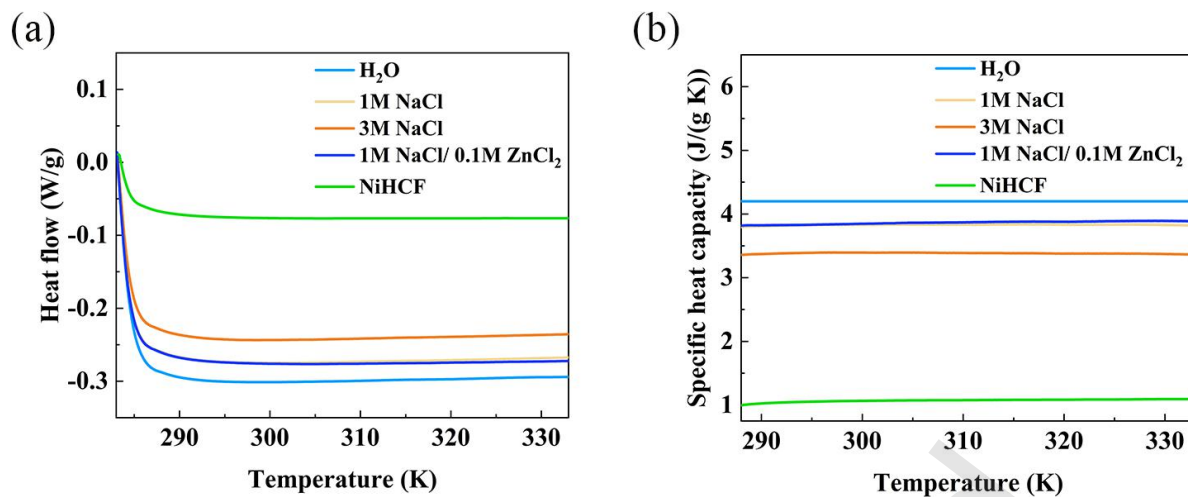


Figure S17. Specific heat capacity of electrolytes. (a) Heat flow and (b) the calculated specific heat capacity of electrolytes heating from 283 to 343 K in DSC.

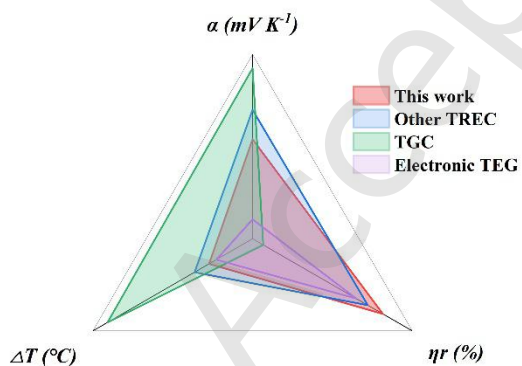


Figure S18. Comparison of the performance to the other systems [1-3] in terms of temperature coefficient, apparent thermoelectric efficiency and operating temperature range.

NOTE S1 Efficiency calculation of the TREC

The absolute thermoelectric conversion efficiency of this TREC flow cell (assuming the coulombic efficiency of the system is 100%) is

$$\eta = \frac{W_{TTE}}{Q_H + Q_{HX}} = \frac{W_{TTE}}{T_H |\alpha_{cell}| q_c + c_p \Delta T (1 - \eta_{HX})} \quad S1$$

Where W_{TTE} (TTE means “thermal-to-electrical”) is the work generated by harnessing low-grade heat in one TREC cycle. Q_H is the heat absorbed at high temperature (T_H), Q_{HX} is the external energy required to heat up the system. ΔT is the temperature difference between T_H and T_L . c_p is the specific heat capacity of the system. q_c is the theoretical total charge of the redox couple. $|\alpha_{cell}|$ is the temperature coefficient of the full cell. η_{HX} is the efficiency of the heat recuperation system, which is the ratio of the thermal energy recuperated by the heat recuperation system and the whole thermal energy rejected in the cooling process. Note that the efficiency reported here is an intrinsic cell-level metric used to evaluate thermodynamic performance, and it intentionally excludes auxiliary energy losses such as pumping power (about 1 W). A comprehensive system-level efficiency evaluation for practical applications would necessarily need to incorporate these pumping and balance-of-plant energy consumptions. [4, 5]

In this work, 1M NaCl is the catholyte and NiHCF is cathode, while 0.2 M $ZnCl_2/1$ NaCl is used as the anolyte and Zn metal is anode. The measured density of the catholyte and anolyte is 1.1 and 1.12 g/mL, and specific capacity of catholyte, cathode, anolyte and Zn plate is 3.89, 1.09, 3.83 and 0.39 J/(g K), respectively. Based on the theoretical voltage profile of the NiHCF/Zn based TREC cell during TREC in Fig 5e. The utilized capacity is 37.2 mAh/g, corresponding to 37.2 mAh for 1 g NiHCF. The volume of the required anolyte is 3.47 mL, then the required catholyte (1M NaCl) is 2.78 mL.

$$\begin{aligned} c_p &= m_{catholyte} c_{p_{catholyte}} + m_{cathode} c_{p_{cathode}} + m_{anolyte} c_{p_{anolyte}} + m_{anode} c_{p_{anode}} \\ &= 2.78 * 1.1 * 3.89 + 1 * 1.09 + 3.47 * 1.12 * 3.83 + 0.35 * 0.39 \\ &= 28.01 \text{ J/K} \end{aligned}$$

$$\begin{aligned} W_{TTE} &= \Delta T |\alpha_{cell}| q_c \\ &= 30 * 0.00108 * 0.0372 * 3600 \\ &= 4.34 \text{ J} \end{aligned}$$

$$\begin{aligned} Q_H &= T_H |\alpha_{cell}| q_c \\ &= 313 * 0.00108 * 0.0372 * 3600 \\ &= 45.27 \text{ J} \end{aligned}$$

$$\text{So without heat recuperation, } \eta = \frac{4.34}{45.27 + 28.01 * 30} = 0.49\%$$

$$\text{The Carnot efficiency is } \eta_c = \frac{30}{313} = 9.58\%$$

$$\text{The relative efficiency is } \eta_r = \frac{0.49}{9.58} = 5.12\%$$

Note: The NiHCF mass of 1 g was used only as a normalization basis for the efficiency calculation. This value does not represent the actual cathode mass used in a single experimental cell.

NOTE S2 Computational Method

In this study, we employed the CP2K software package to perform first-principles calculations aimed at investigating the entropy changes and unit cell deformations associated with the dehydration of sodium ions as they enter the Prussian Blue structure. The calculations were rooted in the framework of density functional theory (DFT), utilizing the PBE functional to handle electron exchange and correlation effects. This functional has demonstrated both good accuracy and reliability in studies involving transition metal complexes and ion transport phenomena. A plane-wave basis set with an energy cutoff of 400 Ry was employed to ensure an adequate description of the electron density.

The Brillouin zone integration was carried out using the Γ -point sampling method, which is well-suited for the periodic system sizes under investigation. The interactions between ionic cores and valence electrons were effectively described using the Goedecker-Teter-Hutter (GTH) pseudopotentials. All calculations were performed under periodic boundary conditions to mimic an infinitely extended crystalline environment. During the geometry optimization process, both atomic positions and unit cell parameters were fully relaxed until the Hellmann-Feynman forces converged to less than 0.0004 Hartree/Bohr.

To simulate the dehydration process of sodium ions, a model system was constructed that included both the Prussian Blue host structure and solvated sodium ions. By progressively constraining the distances between the sodium ions and the surrounding water molecules, umbrella sampling in conjunction with the weighted histogram analysis method (WHAM) was employed to compute the free energy changes associated with the entry of sodium ions from an aqueous solution into the Prussian Blue lattice. Particular attention was given to the entropic contributions during this process. The unit cell deformations were analyzed by

comparing the lattice parameters and volume changes before and after the incorporation of sodium ions. Unless otherwise specified, all computational parameters adhered to the default settings of the CP2K software to ensure the reproducibility and comparability of the results.

And for ICOPH simulation, all the calculations are performed in the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package[6]. The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof is selected for the exchange-correlation potential [7]. The cut-off energy for plane wave is set to 600 eV. The energy criterion is set to 10^{-7} eV in iterative solution of the Kohn-Sham equation. The spin polarizations are applied to elements due to the magnetic nature of Ni and Fe. For bulk calculations, Brillouin-zone integrations were carried out using a Monkhorst-Pack k-point mesh, while a reduced k-point grid was $2 \times 2 \times 2$. All the structures are relaxed until the residual forces on the atoms have declined to less than 0.01 eV/Å.

The bonding information was derived from the electronic wavefunctions using a Γ -centered $3 \times 3 \times 3$ k-point grid. The LOBSTER (Local Orbitals Basis Suite Toward Electronic-Structure Reconstruction) code was used to calculate the Crystal Orbital Hamilton Population, which allowed for evaluating the contributions of electrons to individual bonds [8-10].

NOTE S3 Temperature coefficient tests

Cyclic voltammetry (CV) was employed to determine the temperature coefficients of NiHCF and the Zn/Zn^{2+} redox couple. All measurements were conducted using a three-electrode configuration, comprising a platinum mesh electrode as the working electrode, a carbon plate as the counter electrode, and an Ag/AgCl electrode as the reference. For NiHCF characterization, the working electrode was prepared by coating carbon paper with a slurry of NiHCF powder, conductive carbon black, and PVDF binder at a mass ratio of 7:2:1.

To evaluate the temperature coefficient of the TREC system, the overpotential during charge and discharge was quantified via the galvanostatic intermittent titration technique (GITT). The GITT protocol consisted of repeated current pulses, each involving 2 min of constant-current charge or discharge followed by a 5 min open-circuit relaxation period, thereby allowing the cell to reach a quasi-equilibrium potential unaffected by resistive (IR) drop contributions.

The slight deviation between the measured and theoretically derived α may originate from non-ideal full-cell effects. Specifically, the CV-derived half-cell temperature coefficient characterizes NiHCF only at a specific SOC and thus primarily serves to illustrate the overall trend across different electrolyte concentrations. In contrast, the full-cell temperature coefficient represents an average over all SOC and may therefore be lower than that obtained from half-cell measurements.

Reference

- [1] Zhang, L.; Kim, T.; Li, N.; Kang, T. J.; Chen, J.; Pringle, J. M.; Zhang, M.; Kazim, A. H.; Fang, S. L.; Haines, C.; Al-Masri, D.; Cola, B. A.; Razal, J. M.; Di, J. T.; Beirne, S.; MacFarlane, D. R.; Gonzalez-Martin, A.; Mathew, S.; Kim, Y. H.; Wallace, G.; Baughman, R. H. High Power Density Electrochemical Thermocells for Inexpensively Harvesting Low-Grade Thermal Energy. *Adv. Mater.* **2017**, *29*.
- [2] Yang, Y.; Lee, S. W.; Ghasemi, H.; Loomis, J.; Li, X. B.; Kraemer, D.; Zheng, G.; Cui, Y.; Chen, G. Charging-free electrochemical system for harvesting low-grade thermal energy. *Proceedings of the National Academy of Sciences of the United States of America* **2014**, *111*, 17011-17016.
- [3] Ying, P. J.; He, R.; Mao, J.; Zhang, Q. H.; Reith, H.; Sui, J. H.; Ren, Z. F.; Nielsch, K.; Schierning, G. Towards tellurium-free thermoelectric modules for power generation from low-grade heat. *Nat. Commun.* **2021**, *12*.
- [4] Zhang, H.; Lek, D. G.; Huang, S. Q.; Lee, Y. M.; Wang, Q. Efficient Low-Grade Heat Conversion and Storage with an Activity-Regulated Redox Flow Cell via a Thermally Regenerative Electrochemical Cycle. *Advanced Materials* **2022**, *34*.
- [5] Ali, E.; Kwon, H.; Kim, J.; Park, H. Numerical study on serpentine design flow channel configurations for vanadium redox flow batteries. *Journal of Energy Storage* **2020**, *32*.
- [6] Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758-1775.
- [7] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77*, 3865-3868.
- [8] Maintz, S.; Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R. Analytic projection from plane-wave and PAW wavefunctions and application to chemical-bonding analysis in solids. *Journal of Computational Chemistry* **2013**, *34*, 2557-2567.
- [9] Dronskowski, R.; Bloechl, P. E. Crystal orbital Hamilton populations (COHP): energy-resolved visualization of chemical bonding in solids based on density-functional calculations. *The Journal of Physical Chemistry* **1993**, *97*, 8617-8624.
- [10] Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R. Crystal Orbital Hamilton Population (COHP) Analysis As Projected from Plane-Wave Basis Sets. *Journal of Physical Chemistry A* **2011**, *115*, 5461-5466.