INTRODUCTION

For many decades, thermoelectric materials have shown great potential for converting low-grade heat energy into electricity (the heat source temperature is less than 100°C). According to the types of carriers, the thermolectric materials can be divided into two types of electronic thermolectric (e-TE) materials and ionic thermolectric (i-TE) materials. The e-TE materials based on the Seebeck effect have excellent electrical conductivity, but their thermopower (or Seebeck coefficient) is usually much less than 1 mV/K, which is often complicated and difficult to achieve volt-level appliance voltage (1–4).

The i-TE materials are composed of two types, respectively. One is the thermogalvanic cell based on redox reaction (5, 6). The other type of i-TE materials is based on nonredox reaction and ionic thermodiffusion effect (or Soret effect) (7). Ionic heat-electric conversion devices are usually manufactured based on organic polymer materials. Recent studies have shown that using different electrolytes, through the interaction of the polymer network and the anion/cation, huge thermopower can be obtained. The thermophoretic mobility difference between the anions and cations of an electrolyte is the key to maximizing the thermally generated electric signal. In i-TE materials, the electrolytes include two types of inorganic electrolyte and organic ionic liquid electrolyte. Among them, the thermophoretic mobility difference of ions in inorganic electrolyte is mainly realized by the interaction between the weak polyelectrolyte network and the inorganic electrolyte. Manning’s “counterion condensation” theory and Boltzmann distribution theory of the anions and cations densities in the electric double layer together showed that the cations in the polyanionic electrolyte had the higher thermophoretic mobility than anions (8). Specifically, under temperature gradient, some cations tended to “condensate” along negatively charged polymer chains and impose frictional drags on the anions, while the other cations that were not condensated on the negative polymer backbones remained more thermophoretic mobile. Using NaOH to functionalize CH-OH of polyethylene oxide (PEO) and convert to CH-O-, the thermopower of +11 mV/K could be obtained (9).

Moreover, the nanocellulose channels were oxidized by 2,2,6,6-tetramethylpiperidine-1-oxyl, and enhanced the negative charge densities, they realized the thermopower of NaOH-PEO system as high as +24 mV/K (10). Similarly, it was reported that in a gelatin-hydrogel matrix with a negatively charged network, the use of synergistic thermodiffusion and thermodalvanic effects demonstrated a huge positive thermopower of +17.0 mV/K (11).

As for the interaction between polymer network and organic ionic liquids, the thin film based on ion-dipole interaction had a thermopower of +26.1 mV/K (12). In addition, by adjusting the composition of two type polymers, the controllable adjustment of thermopower from −4 mV/K to +14 mV/K was reported for the first time (13). Above all, we can see that the currently reported i-TE materials, n-type thermolectric materials with negative thermopower are fewer, and their thermopower is lower than the p-type thermolectric materials, which has a greater restriction on the design of ultra-sensitive ion thermopiles (14–17). Although the use of poly(34-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) and CuCl2 in electronic and ionic hybrid system has achieved a thermopower of −18.2 mV/K, the high-quality n-type i-TE materials (absolute thermopower, >10 mV/K) are still extremely rare (18, 19).

Alarmingly, as a typical interaction between ions and polymer networks, the application of coordination theory in i-TE materials has never been reported. The molecular dynamics simulation of the solid inorganic electrolyte pointed out that the Lewis basic polymer was conducive to slow cation and fast anion diffusion due to the stronger coordination interaction with cationic group, which is an essential signal for the design of n-type i-TE materials (20). In addition, the recent reports have also shown that adding inorganic electrolyte such as NaOH or NaCl into polyvinyl alcohol (PVA) solid thin films by the coordination interaction between —OH (PVA) and cations would cause cation/anion dissociation and improve the triboelectric properties of PVA blends (Fig. 1B) (21, 22). However, the thermophoretic mobility of NaOH in the solid polymer network is extremely lower than the organic ionic liquid electrolyte, which is why the thermolectric materials with inorganic electrolyte are usually dispersed in the hydrogel phase of high dielectric constant or liquid organic solvent of lower Tg (glass transition temperature) (9–11).

In this work, we combined synergistic coordination and hydration interactions to achieve high thermopower. Obviously, for the
RESULTS

Because of the water solubility, degradability, and biocompatibility, PVA is widely used in the field of biomedical hydrogels (23). We notice that through a higher-temperature dry-annealed process at 100°C, a certain amount of “permanent” PVA crystals can be made in the fully swollen PVA hydrogel (24, 25). If the coordination structure of cation can be interwoven in the stable crystalline PVA, then the water swelling resistance of the PVA crystal domain can be used to achieve a stable cation-PVA coordination relationship. That is to say, we preliminarily infer that a higher-temperature dry-annealed process may be used in PVA hydrogel to achieve crystalline PVA and a stable PVA-cation coordination interaction at the same time. Specifically, we speculate that the stable PVA crystal domain can play an important role in “anchoring the Na”-PVA coordination structure and stably exist in the hydrogel” (Fig. 1B). In all the following measurements, we first prepared the NaOH-PVA hydrogel by freeze-thawed processes, then dry-annealed the PVA hydrogel at 100°C, and lastly fully swelled the dry-annealed hydrogel in deionized water. Among them, we mainly studied the influence of annealing time at 100°C and the concentration of NaOH on the thermoelectric properties of PVA hydrogel.

The PVA used in this experiment was prepared by alcoholysis of polyvinyl acetate with methanol as the solvent and NaOH as the catalyst (Eq. 1). The pH value of 15 weight % (wt %) PVA aqueous solution was about 8.5, which meant that the pure PVA hydrogel contained part of NaOH. Therefore, we initially selected pure PVA hydrogel to study the thermoelectric properties and used the residual NaOH in the purchased PVA raw materials as the inorganic electrolyte.

\[
\text{CH}_2\text{CH}_n + n\text{CH}_3\text{OH} \xrightarrow{\text{NaOH}} \text{CH}_2\text{CH}_n + n\text{CH}_3\text{COOCH}_3
\]  

(1)

Characterization of the crystalline morphology in PVA hydrogels

We first used x-ray diffraction (XRD) to characterize the crystallinity of fully swollen PVA hydrogels after different annealing times. The dry-annealed PVA hydrogels for 50 to 110 min show strong diffraction peaks at about 18.35 (Fig. 2A), and the red shift phenomenon occurs with the extension of the annealing time (fig. S2A). This is due to the self-association of –OH (PVA), which corresponds to the typical reflection crystal plane of (101) (26). The red shift phenomenon of the diffraction peak is due to the large amount of water in the PVA hydrogels. According to the Bragg’s law: \(2d\sin\theta = n\lambda\), (where \(d\) is the interplanar spacing, \(\theta\) is the angle between the incident x-ray and the corresponding crystal plane, \(\lambda\) is the x-ray’s wavelength, and \(n\) is the diffraction order). The longer the annealing time, the less water content in the swollen hydrogels (Fig. 2B) and the smaller the interplanar spacing \(d\). When \(n\lambda\) is a constant value, the diffraction peak will shift to the right side (for the solid PVA thin films, the diffraction peak of (101) crystal plane is 19.7°) (24). Moreover, the peak intensity of the diffraction peak gradually increases with the increase in the annealing time, and the crystallinity of PVA hydrogels also increases. Small peaks at about 21.71° are
also observed in the hydrogels dry-annealed for 90 and 110 min, which also indicate that the hydrogels with longer dry-annealed time have higher crystallinity (27).

Fourier-transform infrared (FTIR) spectroscopy was used to analyze the intermolecular interactions in PVA hydrogels (Fig. 2C). The peak at 3300 cm\(^{-1}\) is the \(\nu\)-OH stretching vibration of PVA and water, and the peaks at 1422 and 2925 cm\(^{-1}\) are attributed to the \(\nu\)-CH and \(\nu\)-CH\(_2\) stretching vibrations of PVA (28). In particular, 1142 cm\(^{-1}\) is the fingerprint of the crystallinity for PVA. It is the \(\nu\)-C\(\_\)C stretching vibration peak associated with the stretching vibration of C–O, that is, the symmetrical stretching vibration peak of O–C–C. The longer the dry-annealed time, the larger the peak value. This is the same as the XRD analysis results (29). The amorphous peak at 1087 cm\(^{-1}\) is the \(\nu\)-O stretching vibration peak related to the stretching vibration of C–C, that is, the antisymmetric stretching vibration peak of O–C–C. Not only does its peak increase but it is also accompanied by a more obvious red shift. This is due to the reduction of water content, which promotes the interaction between PVA chains in the amorphous region. This also suggests that, on the one hand, the dry-annealed process is beneficial to improve the crystallinity of PVA. On the other hand, it greatly increases the density of the amorphous region in the polymer network, which is likely to help achieve the coordination interaction of NaOH-PVA, and NaOH-H\(_2\)O hydration interaction at the same time (30). Moreover, during the dry-annealed process, the dehydration-crystallization process of the PVA/NaOH hydrogel was from the outside to the inside. That is, from the overall point of view of the sample, the crystallinity of the PVA/NaOH hydrogel was not uniform, and the closer to the outer layer of the sample, the higher the crystallinity of the hydrogel.

In this experiment, we only used the crystallinity of the outermost layer of the sample as the reference. However, it should be emphasized that although the sample does not have the overall uniformity, it has the uniform crystallinity in its symmetrical structure (fig. S2C). From the stress-strain curve of fully swollen PVA hydrogel dry-annealed for 90 min (Fig. 2D), we observed the sample with higher crystallinity obviously has better toughness and transparency (fig. S2B), which is important for the wearable i-TE devices.

**Thermoelectric properties of PVA hydrogel after different annealing times at 100°C**

Similar to the conventional e-TE, the thermopower or Seebeck coefficient of i-TE materials is defined as 

\[ S_i = -\frac{V(T_H) - V(T_C)}{T_H - T_C}, \]

where \(V(T_H)\) and \(V(T_C)\) are the voltages of hot electrode at \(T_H\) temperature and cold electrode at \(T_C\) temperature, respectively. We first tested the thermopower of PVA hydrogels that have been fully swollen after different annealing times at 100°C (Fig. 3A). It can be seen from the figures that the freeze-thawed PVA hydrogel (the annealing time is 0 min) has a lower positive thermopower, while the dry-annealed PVA hydrogels from 10 to 130 min all have larger negative absolute thermopower. In which, the lower positive thermopower is mainly due to the thermal diffusion of Na\(^{+}\) and OH\(^{-}\) in the hydrogel under the hydration interaction. As evidence, we also tested the thermopower of 0.1 mM NaOH aqueous solution (Fig. 3B), which has a
slightly smaller positive thermopower than the freeze-thawed PVA hydrogel. It has been reported in the typical (polar) aqueous solution that because the intrinsic interaction between anion and cation in pure substances was shielded by the hydration interaction, the thermopower was greatly weakened \((31)\). We can foresee that the infinitely diluted aqueous solution will have a much smaller than \(1 \text{ mV/K}\) thermopower. In theory, the thermopower is determined by the heat of transfer \(Q^*\) related to the ion transport, \(S_i = \frac{Q^*}{eF}\) \((F\) is the Faraday constant and \(T\) is the absolute temperature) \((32, 33)\). The \(Q^*\) value is associated with the interaction between anion and cation. Eastman pointed out that for highly concentrated solutions, the \(Q^*\) value was much larger \((34, 35)\). According to our experiment, compared with the aqueous solution in the flow state, the quasi-solid-state hydrogel was likely to have a slightly weaker hydration interaction on salt ions, thereby increasing the thermopower of the freeze-thawed NaOH-PVA hydrogel.

The negative thermopower depends on the annealing time, and with the extension of annealing time, the \(|S_i|\) (the absolute thermopower of \(S_i\)) first increases and then decreases in the negative thermopower direction. The factors affecting the \(Q^*\) value not only include the interaction between anion and cation but also include the interaction between ions and polymers. Obviously, the dry-annealed process promotes the interaction of \(Na^+\) and \(OH^-\) with the polymer network, and this process further promotes the conversion of limited

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**Fig. 3. Thermoelectric properties of PVA hydrogel.** The residual NaOH in the purchased PVA raw materials was used as inorganic electrolyte. (A) Thermopower of fully swollen PVA hydrogels after different annealing times at 100°C. (B) Thermopower of 0.1 mM NaOH aqueous solution and thermopower of fully swollen PVA hydrogels after air-drying at room temperature for 12 hours. (C) Na 1s XPS spectra of the PVA hydrogel dried at room temperature for 12 hours and the PVA hydrogel dry-annealed at 100°C for 90 min. (D) O 1s XPS spectra of the PVA hydrogel dried at room temperature for 12 hours and the PVA hydrogel dry-annealed at 100°C for 90 min. (E) The typical thermo-ionic charging and forward electronic working curve of fully swollen PVA hydrogel with annealing time of 90 min at 100°C.
positive thermopower to negative. This is an effective evidence for the formation of a stable PVA-cation coordination structure in the fully swollen hydrogel. We have also observed that the maximum negative thermopower is $-19.69 \text{ mV/K}$ with the annealing time of 90 min. On this account, in the next study to the influence of NaOH concentration on the thermoelectric properties of NaOH-PVA hydrogel, the annealing time is uniformly set to 90 min. We also dried the freeze-thawed PVA hydrogel at room temperature for 12 hours to form enough crystalline domains and then fully swelled it in de-ionized water to measure the thermopower (Fig. 3B). However, its thermopower is much smaller than the dry-annealed samples. This is because during the fully swollen process, the crystalline domains formed by air-drying are unstable. The temporary coordination relationship of $-\text{OH (PVA)}$ and $\text{Na}^+$ will be released again (24).

Correspondingly, we also tested the x-ray photoelectron spectroscopy (XPS) of the PVA hydrogel dried at room temperature for 12 hours and the PVA hydrogel dry-annealed at 100°C for 90 min. The XPS peaks observed near 1072.0 and 531.0 eV can be attributed to the core energy levels of Na 1s and O 1s, respectively (Fig. 3, C and D) (36). First, whether the sample dried at room temperature or dry-annealed, the electron binding energy of the Na 1s core level is slightly lower than its reference value, and the electron binding energy of the O 1s core level is slightly higher than its reference value. This is mainly due to the PVA film with loss of water, the coordination of the oxygen atoms on the $-\text{OH (PVA)}$, and metal ions ($\text{Na}^+$), which leads to an increase in the electron cloud density of the metal ions, an increase in the shielding effect, and the core level electron binding energy decline (37). Second, the coordination interaction of dry-annealed samples is notably stronger than that of samples dried at room temperature. This is mainly related to the stable and dense PVA crystal domains under the dry annealing process. Here, we have reasons to believe that a higher-temperature dry-annealed process may be an effective method for studying the coordination interactions in ionic hydrogel thermoelectric materials.

In the i-TE materials, ionic conductivity is the sum of anion and cation mobility. In contrast, thermopower mainly characterizes the thermophoretic mobility difference of anions and cations. When the ionic concentration is constant, the coordination interaction in PVA hydrogel greatly limits the mobility of cations. Therefore, the ionic conductivity ($\sigma_1$) of these samples gradually decreases with the the dry-annealed process (fig. S5B). On the other hand, the loss of high--dielectric constant water content is also one of the reasons for the decrease in total ionic conductivity. In addition, the dry-annealed process to a certain extent also gradually enhances the weak coordination of OH$^-$ (NaOH) to $-\text{CH}$ and $-\text{CH}_2$ in the PVA polymer network, which also leads to the reduction of negative thermopower at 110- and 130-min annealing (20).

These devices also exhibit the nearly ideal rectangular shapes in the representative cyclic voltammetry (CV) curves (fig. S5C), which indicates purely capacitive behavior, and the changes in surface capacitance are consistent with the change of ionic conductivity (34). The ionic hydrogels with high TE properties were used in i-TE capacitors for the thermo-ionic charging and electronic discharging. The ionic hydrogel was sandwiched between two carbon electrodes for testing purposes. The sealed device was exposed to an external temperature difference of 1 K (fig. S1, A and B). The thermo-ionic charging state was continuously measured for 3 min, and the forward electronic working was tested by connecting an external load of 20 kilohms (Fig. 3E). The NaOH-PVA hydrogel was charged to 19.69 mV with a response time of ~180 s, and the time to completely forward electronic working was 10 s. Further, as the external load resistance increased, the discharge time gradually became longer. On the basis of the effective medium theory of composite, we also estimated the thermal conductivity of PVA hydrogels (table S2) (35). The thermal conductivity of fully swollen PVA hydrogel with annealing time of 90 min is calculated to be 0.42 W/m-K, which is consistent with report in the literature (30).

In addition, the transient response time of the thermal charging process is an important measure for the practical applications. When we studied the thermoelectric properties of PVA hydrogels after different dry-annealing times at 100°C, the thickness of the freeze-thawed hydrogel obviously decreased gradually (decreased from the original thickness of 3 to 0.88 mm in table S1) with the increase in the annealing time. Therefore, we also took the PVA hydrogels under different dry-annealing times as the examples to discuss the influence of sample thickness on the transient charging behavior of PVA hydrogels (fig. S4). We noticed that the freeze-thawed PVA hydrogel only needed 13 s to reach the maximum thermal charging voltage. In addition, the freeze-thawed PVA hydrogel also showed the decrease in the thermovoltage after reaching the maximum value. In this experiment, we used the maximum thermovoltage of the freeze-thawed sample as the reference, although it was not reasonable to calculate the thermopower. However, it took about 3 min for all dry-annealed PVA hydrogels to reach the maximum thermal charging voltage, which was much slower than the response time of the freeze-thawed sample. Obviously, the thickness was not the main factor that determines the response time of the sample. Here, we attribute it to the faster ion diffusion dynamics process in the freeze-thawed PVA hydrogel. Moreover, the thermal charging time was set as 3 min in the following experiments to unify the transient charging behavior of the dry-annealed PVA hydrogels, although part of the dry-annealed PVA hydrogels did not reach the maximum thermovoltage at this time.

**Mechanism of the synergistic coordination and hydration interactions**

Molecular dynamic simulations of Lewis basic polymers and the impact of ionic fillers on PVA blends’ triboelectric performance both showed the coordination interaction of $-\text{OH (PVA)}$ and $\text{Na}^+$ generally occurred in the “dewatered” solid electrolyte (20--22). For the Lewis basic structure $-\text{OH (PVA)}$, the oxygen atom contains two pairs of lone-pair electrons and more concentrated negative Lewis formal charges, which leads to the strong coordination of $\text{Na}^+$ in PVA. Further, the strong coordination interaction is reflected in the helical distortion of the polymer structure about the cation and strongly peaked distribution of coordination structures [here, we mainly take the PVA typical coordination relationship as an example with four number of $-\text{OH (PVA)}$ to coordinate one number of $\text{Na}^+$] (38). In the PVA monomer structure, the more dispersed positive Lewis formal charges of $-\text{CH}_2$ and $-\text{CH}$ are both used to balance the negative Lewis formal charges of $-\text{OH (PVA)}$, which leads to the extensive weak coordination interaction of OH$^-$ (NaOH) with more numbers of $-\text{CH}_2$ and $-\text{CH}$.

In i-TE materials of NaOH-PVA hydrogel, the number of anions and cations with bipolar thermodiffusion is equal ($n^+_0 = n^-_0$), and there is no intermolecular redox reaction. Therefore, on the basis of the Onsager transport theory and the Einstein correlation of thermodiffusion, the total thermopower of symmetrical electrolyte can be expressed as follows (11)
The ion species weakens the intrinsic interaction between Na\(^+\) and OH\(^-\), showing a sign in the hydrogel at this time. Moreover, the presence of water and the charge mobility under temperature gradient.

Fig. 4. Mechanism of the coordination and hydration interactions. Schematic figure of the interactions in the as-fabricated i-TE materials of NaOH-PVA hydrogels under the temperature gradient.

\[ S_{\text{d(thermodiffusive)}} = \frac{(\hat{\mathcal{S}}_i D_i) - (\hat{\mathcal{S}}_j D_j)}{e(D_e + D_j)} = \frac{(\mu_{i}^T) - (\mu_{j}^T)}{(\mu_{i}^{q}) + (\mu_{j}^{q})} \quad (2) \]

where \( \hat{\mathcal{S}} \) is the Eastman transfer entropy, \( e \) is the element charge, \( D \) is the mass diffusion coefficient of the “+” or “−” ions, the thermal mobility of the ions \( \mu_{i}^T = \frac{D_i \hat{\mathcal{S}_i}}{k_B T} \) (\( \mu_i \) is the electrochemical potential of the ion species \( i \), \( k_B \) is Boltzmann constant, and \( T \) is temperature) and the charge mobility \( \mu_{i}^{q} = \frac{q_i D_i}{k_B T} \). We can see that the difference between the thermal mobility of Na\(^+\) and OH\(^-\) determines the sign of the thermopower and the thermal mobility is simultaneously determined by the mass diffusion coefficient \( D \) and the Eastman entropy \( \hat{\mathcal{S}} \) of transfer. The type of interaction between the solute NaOH and the surrounding solvent PVA/H\(_2\)O determines \( \hat{\mathcal{S}} \), and \( \hat{\mathcal{S}} \) reflects the dependence of Gibbs free energy and temperature.

On the basis of the above two points, according to the types of interaction between NaOH-H\(_2\)O-PVA, our experimental processes and schematic can be divided into three steps (Figs. 1 and 4). In the first step, before dry-annealing, the low-concentration NaOH electrolyte is fully dispersed in freeze-thawed PVA hydrogel due to the hydration interaction. As Na\(^+\) and OH\(^-\) are wrapped by the solvation shell of water, which hinders the contact of anions and cations with the polymer network. That is, the NaOH-H\(_2\)O interaction is dominant in the hydrogel at this time. Moreover, the presence of water weakens the intrinsic interaction between Na\(^+\) and OH\(^-\), showing a small positive thermopower. In the second step of dry-annealed process at a higher temperature, the water is continuously evaporated, and the NaOH electrolyte continuously “breaks away” from the water phase. Part of the PVA chain is coordinated with NaOH, and the other part of the PVA chain further forms a stable PVA crystal domain. At this stage, the dominant NaOH-H\(_2\)O interaction is effectively reversed, and the process is similar to the preparation of dewatered solid electrolytes. Among them, the cation has a strong coordination relationship with the Lewis basic structure OH (PVA) than the anion. In the third step, for the fully swollen PVA hydrogels, Na\(^+\) with strong coordination interaction is slightly weakened by solvation effect of water. While OH\(^-\) (NaOH) is regulated by the next two interactions, which are the stronger hydration interaction, and the weaker coordination interaction of −CH\(_2\) and −CH. Different from the swollen sample after air-drying at room temperature, it is obvious that the stable coordination of Na\(^+\) in the polymer network after dry-annealing is the key to realize the giant negative thermopower.

**Thermoelectric properties of PVA hydrogel with different concentrations of NaOH**

We further discussed the thermopower of fully swollen PVA hydrogels before and after dry-annealing at 100°C for 90 min by adjusting the concentration of NaOH. The freeze-thawed sample has a slightly larger positive thermopower with the increase in NaOH concentration (Fig. 5A). As for the dry-annealed samples, they have the oppositely negative thermopower, and the maximum thermopower of −37.61 mV/K appears at 0.9 mM NaOH (Fig. 5B), which is twice as much the thermopower of n-type i-TE materials currently reported (Fig. 5C). This is mainly due to the stable coordination interaction between more numbers of Na\(^+\) and −OH (PVA) with the increasing of NaOH concentration. In addition, it also leads to the more number of hydration interaction OH\(^-\) (NaOH) thermophoretic migration under temperature gradient and the increasing of ion conductivity (Fig. 5B). In addition, when the NaOH concentration continues to increase from 0.9 to 1.2 mM, its negative absolute thermopower occurs to decrease. We believe that the strength of the coordination interaction between Na\(^+\) and −OH (PVA) not only depends on the dry-annealed temperature and time but also depends on the number of coordination −OH (PVA). Obviously, the lower the amount of Na\(^+\), the helical twist of polymer network around Na\(^+\) is more severe (Fig. 4) because of coordination interaction and the more stable coordination interaction between Na\(^+\) and −OH (PVA) at fully swollen process. Under the condition that the thickness of the hydrogel remains unchanged, we further characterized the influence of the large temperature difference on the transient charging behavior of the PVA hydrogel (Fig. S8) for the sample that was dry-annealed.
for 90 min and the NaOH concentration of 0.9 mM. Similarly, the thermal charging voltage was first tested for about 3 min in our experiment. In the higher temperature range of 0 to 5 K, the average thermopower of the sample was −26.58 mV/K. It was obvious that the thermal charging voltage of the sample under the large temperature difference showed a nonlinear behavior, compared with the thermal charging behavior in the temperature range of 0 to 1 K. By extending the thermal charging time to 8 hours, we have also tested the thermal charging voltage stability of the sample under the temperature difference of 5 K (fig. S9). On the one hand, under the large measurement temperature difference of 5 K, the PVA-NaOH hydrogel needs about 2.3-hour thermal charging time to reach the stable value of the maximum open circuit voltage. By fitting with the thermal charging voltage in the 1-K temperature range, the open-circuit voltage-temperature difference curve recovered a good linear behavior (goodness of fit, 99.916%). This fact that the thermal charging voltage increased with the increasing of the temperature difference was probably related to the thermal sensitivity of the PVA hydrogel crystal domains. It is well known that the crystal domains of PVA hydrogels prepared by hydrogen bond physical cross-linking have the reversible characteristics of the higher-temperature melting and the lower-temperature solidification. On the other hand, our device also exhibited a stable voltage retention of at least 6 hours, which was important to ensure the practicality of the device for long-term operation.

The thermo-ionic charging and electronic discharging behaviors of the ionic conductor was then evaluated (the working principle was described in fig. S10). During the heating process, ions of opposite electrical properties gather on the electrodes to generate a voltage between the two electrodes. The stage I is called thermo-ionic charging (Fig. 5D). When the hot side of the ion thermoelectric capacitor connects an external load in the circuit, the current can flow through the external load to balance the voltage generated by the ions and the voltage drops for about 15 s during loading. The stage II is called electronic discharging. Once the external circuit is disconnected, the voltage returns to the same level after about 130 s, and this process is repeatable (Fig. 5E). The stage III is the thermionic discharging stage, in which the heater is turned off and the external load is disconnected. The anions and cations gathered on the two electrodes return to their original state due to the retraction of temperature gradient. Meanwhile, because of the disconnection of the external circuit, the electrons at stage II still stay at the electrode, and so, the open circuit voltage becomes negative. The stage IV is the reverse electronic working stage, in which the external load is reconnected to the electrode, the electrons gathered on the electrode flow out, and the absolute voltage on the external load drops to 0. We have also repeatedly obtained a high thermal charging voltage for half a month (fig. S11), which showed that the thermoelectric capacitor can be reused, instead of a disposable energy source. Last, the thermopower could be notably improved by modularizing the NaOH-PVA hydrogels (Fig. 5F). In our tests, the largest thermopower of 213 mV/K was observed for the module composed of six NaOH-PVA hydrogel elements.

In particular, for the practical use of ion thermoelectric devices, stacking multiple pairs of p-type and n-type ion thermoelectric materials to build a complete power generation module is also another method to achieve high thermopower. The high-performance ion thermoelectric module not only needs to have a higher thermopower but also needs to have a matching ion conductivity. In the experiment, the ion conductivity of our sample with the largest
thermopower is 7.36 × 10⁻⁵ S/cm. Among the reported p-type i-TE materials (table S3), we have noticed that the i-TE material functionalized with PEO by NaOH, which the thermopower of +11 mV/K and the ion conductivity of 8.13 × 10⁻⁸ S/cm can be obtained. The ionic conductivity of this p-type i-TE material has matching characteristics with the n-type i-TE material we reported. Specifically, four pairs of ion thermoelastic modules stacked with PEO-NaOH samples and PVA-NaOH hydrogels have a maximum thermopower of 183 mV/K (fig. S12).

In the future work, how to effectively improve the ionic conductivity and maintain a higher thermal voltage is bound to be our research focus. In the ionic hydrogel thermolectric devices, the improvement of ionic conductivity is mainly achieved by increasing the ionic concentration. However, when the ionic thermopower reaches a certain maximum value, it usually decreases as the ionic concentration increases (13). Therefore, if we want to increase the ionic conductivity while ensuring the high thermopower, then we must increase the concentration of salt ions while finding other ways to continue to increase the interaction between the polymer and the ions. Among them, the challenging work is how to further effectively increase the interaction between polymers and ions. As we all know, the number of Gutmann donor for H₂O molecules is 18 (39). Because of the ionic hydration, this severely hinders the interaction between the ions and the polymer. However, for the organic monomer reagents such as dimethyl sulfoxide and pyridine, the number of Gutmann donor is as high as about 30 (fig. S13B). This makes the H₂O molecules in the ion solvation sheath easier to be replaced by the organic reagents with high Gutmann donor numbers (fig. S13A) (40). On the basis of our work, if we continue to use the chemically catalyzed reactions to graft organic functional groups with the high Gutmann donor number onto the molecular chain of PVA, then it is likely to further enhance the cation-polymer coordination interaction (fig. S13C). In this way, the PVA hydrogel can accept more salt ions under the premise of ensuring the high thermopower, thereby increasing the ionic conductivity.

DISCUSSION
We have demonstrated a giant negative thermoelectric effect in an ionic hydrogel material of PVA and NaOH, which synergistically combines the coordination and hydration interactions. High thermopower of −19.69 to 37.61 mV/K was achieved by comprehensively optimizing the annealing time (90 min) and the NaOH concentration (0.9 mM), and we have also demonstrated that the higher-temperature (100°C) dry-annealed process has a great feasibility for studying the stable coordination structure in the i-TE hydrogel. This PVA-based ionic conductor hydrogel with flexible, transparent, and cost-effective properties can be used in wearable energy storage devices to enable large-scale manufacture.

Preparation of NaOH-PVA hydrogels by dry-annealed process
All of our NaOH-PVA hydrogels were first synthesized from NaOH with different molar masses (i.e., 0, 0.3, 0.6, 0.9, or 1.2 mM) and 15 wt % PVA solution. The solution was heated in a water bath at 100°C with stirring for 12 hours. After mixing and defoaming, the NaOH-PVA solution were poured into a mold, frozen at −20°C for 12 hours, and thawed at 25°C for 12 hours to fabricate freeze-thawed NaOH-PVA hydrogels. The freeze-thawed hydrogels were further dry-annealed at 100°C for a controlled time (i.e., 0, 10, 30, 50, 70, 90, 110, or 130 min). Last, the dry-annealed NaOH-PVA hydrogels were fully cooled at room temperature and then immersed in water to achieve their equilibrium-swollen state.

Preparation of NaOH-PVA hydrogels by air-drying process
First, the 15 wt % PVA hydrogel was prepared according to the above method, and the residual NaOH in the purchased PVA raw materials was used as the inorganic electrolyte. Then, the prepared NaOH-PVA hydrogel was dried at room temperature for 12 hours. Last, we put the dried hydrogel in water to be fully swollen.

Fabrication of the i-TE module
The conductive carbon paste (JW-001, DELIOU, China) was printed onto polyethylene terephthalate (PET) substrates (thickness of 0.7 mm) by a screen print method using a homemade mask to control the its geometry, and the printed PET thin films were dried at 80°C for 6 hours. The length of the carbon paste was 6 cm, and the width was 1 cm. The square resistance of the carbon electrodes was around 40 ohms. A layer of dielectric elastomer (3M-VHB4905) was cut into a square plate with a square hole at the center using a laser cutter (universal) with a size of 8 mm by 8 mm by 1 mm, followed by laminating onto one layer carbon electrode. Then, the NaOH-PVA hydrogel was added into the square hole. Last, we laminated another carbon electrode to the other side of the VHB tape. In addition, to achieve good contact between the electrode and NaOH-PVA hydrogel, we also used a thick glass plate weighing 10 kg to press the assembled i-TE device for 3 hours before testing various thermoelectric parameters.

Characterization of chemical properties
XRD (PANalytical/Areis) was used to analyze the crystallinity of NaOH-PVA hydrogels. We used a Thermo Fisher Scientific/Nicolet iS50 series spectrometer to record FTIR attenuation total reflection spectrum. XPS analysis was conducted on a VG ESCALAB MKII spectrometer. All the spectra were calibrated to the binding energy of the adventitious C 1s peak at 284.8 eV.

Characterization of mechanical properties
The NaOH-PVA hydrogels were loaded on a material testing machine (100-N load cell, Instron 5966, Instron, Norwood, MA) at room temperature for testing.

Characterization of electrochemical properties
The NaOH-PVA hydrogel was sandwiched between two conductive carbon electrodes, and an electrochemical workstation (CHI660E, Shanghai Chenhua Instrument Co. Ltd.) was used to measure the CV curves in the range of 0 to 0.2 V. Moreover, the NaOH-PVA hydrogel was sandwiched between two stainless steel electrodes, and electrochemical AC impedance spectroscopy was used to characterize the resistance of the NaOH-PVA hydrogel with the voltage amplitude of 5 mV and the frequency from 100 kHz down to 0.1 Hz. In addition,
the ionic resistance is obtained from the intercept of a straight line on the
abscissa, and the ionic conductivity can be obtained by the linear
extrapolation. The ionic conductivity \( \sigma_i = \frac{d}{R \times S} \), where \( \sigma_i \) is the ionic
conductivity, \( d \) is the thickness of the sample, \( R \) is the volume resistance,
and \( S \) is the contact area between the sample and the electrodes.

**Characterization of thermopower**

The thermopower and temperature gradient (0.2, 0.4, 0.6, 0.8, and
1 K) were determined from a homemade setup using a Keithley 2400
voltmeter and the TEC temperature control module TCM-X107
purchased from China’s Sichuan Yexian Technology, respectively.
The temperature sensitivity of the temperature control module was
0.002°C. For the general measurement, two Peltier devices attached
to an aluminum heat sink linked by a thermal paste were used to
generate the temperature gradient.

**Thermopower by synergistic hydration and
coordination interactions**

On the basis of the interaction between the polymer network, water,
and the electrolyte anion/cation, we have also partially supplemented
and simplified the thermopower formula i-TE material (11, 41). The
Onsager theory believes that all irreversible processes are the result of
generalized thermodynamic flow driven by a certain generalized
thermodynamic force. For the thermodynamic process in the linear
nonequilibrium region, the relationship between thermodynamic force and flow can be described approximately by the linear
phenomenological heat-transfer law

\[
J_p = \sum_{j=1}^{f} L_{pj} X_j
\]

where \( J_p \) is the \( p \)th generalized thermodynamic flow in the irre-
versible process, \( X_j \) is the \( j \)th generalized thermodynamic force in
the irreversible process, \( L_{pj} \) or \( L_{jp} \) is the linear phenomenological
coefficient, also known as the correlation coefficient, and \( f \) is the
number of independent generalized flows or forces. When there are
multiple irreversible factors in the thermodynamic process, regardless
of whether these generalized forces are of the same nature or different
properties, in principle, each generalized flow is driven by various
generalized forces existing in the system.

Furthermore, Onsager proved that the matrix of phenomeno-
logical coefficients in the linear phenomenological law relation is
symmetric, that is, each phenomenological coefficient satisfies the
“reciprocity relations,” which can be expressed as

\[
L_{pj} = L_{jp}
\]

Under the temperature gradient, the ionic flow \( J_i \) is the sum of
the diffusion flow caused by the negative gradient of chemical poten-
tial (\( X_i \)) and the heat conduction flow caused by the gradient of
temperature potential (\( X_Q \))

\[
J_i = L_{ii} X_i + L_{iq} X_Q = L_{ii} \frac{\nabla(-\mu_i)}{T} + L_{iq} \frac{1}{T}
\]

Among them, \( i \) is the ion type, and \( \mu_i \) is the electrochemical
potential.

1) The linear phenomenological coefficient \( L_{ii} = \frac{D_i}{k_B} \) (\( D_i \) is
the ionic diffusion constant, \( k_B \) is the Boltzmann constant).

2) The electrochemical potential \( \mu_i \) is a function of the concen-
tration distribution \( n_i(r) \) and the temperature distribution \( T(r) \) and
\( \mu_i = \mu \left[ \frac{n_i(r)}{T(r)} \right] + q_i V \). In addition, in an ideal solution,
the electrochemical potential is related to the pure system of ions: \( \mu_i = \mu_i^{\text{pure}} + k_B T \ln \frac{n_i}{N^\text{pure}} \) (\( N \) is the total number of molecules and \( \mu_i^{\text{pure}} \) is
the chemical potential of the pure system \( n_i \)). Therefore, it can be
derived as \( \frac{\partial \mu_i}{\partial n_i} = \frac{k_B T}{n_i} \). Moreover, according to the Maxwell relation,
the partial derivative of free energy with respect to concentration is partial
entropy \( S_i = \frac{\partial \mu_i}{\partial n_i} \).

Under the open circuit condition, the ion does not carry a net current,
then

\[
\sum q_i J_i = - \sum q_i J_i = - \sum q_i J_i = 0
\]

In fully cooled and close to equilibrium state i-TE materials,
\( n_i(r) = n_i^0 + \delta n_i(r) = n_i^0 \). In addition, the open-circuit voltage and
temperature changes are small enough, so

\[
\sum q_i J_i = - \sum q_i J_i = - \sum q_i J_i = 0
\]

Furthermore, the thermopower based on temperature gradient and
electrostatic potential gradient can be expressed as

\[
S_{\text{td(thermodiffusive)}} = \frac{\nabla V}{\nabla T} = \frac{\sum q_i \mu_i^0 q_i \bar{S}_i q_i D_i}{\sum q_i \mu_i^0 q_i \bar{S}_i q_i D_i} \nabla T
\]

In the i-TE material of NaOH-PVA hydrogel, the number of
anions and cations of bipolar thermal diffusion are equal (\( n_{\text{an}} = n_{\text{cat}} \)),
and there is no intermolecular redox reaction. The thermopower of
the symmetric electrolyte can be expressed as

\[
S_{\text{td(thermodiffusive)}} = \frac{\bar{S}_+ D_+ - \bar{S}_- D_-}{e(D_+ + D_-)}
\]

In addition, when there is no electric field and concentration
gradient, the ionic flow is related to the “thermal diffusion rate,”

\[
J_i = - n_i \frac{D_i \bar{S}_i}{k_B T} \nabla T = - n_i \mu_i \nabla T
\]

Therefore, the thermopower of the symmetrical electrolyte can also be expressed as

\[
S_{\text{td(thermodiffusive)}} = \frac{\mu_+ \nabla T - \mu_- \nabla T}{\mu_+ + \mu_-}
\]

Therefore, we can see that the difference in thermal mobilities of
the cations and anions determines the thermopower, and the

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hydration and coordination interactions jointly determine the ionic thermal mobilities in the NaOH-PVA hydrogel.

Characterization of thermal conductivity

On the basis of the effective medium theory of composite, we can also estimate the thermal conductivity of NaOH-PVA hydrogels. At room temperature, the thermal conductivity of pure PVA (0.2 W/m·K) and water (0.6 W/m·K) is known, through the formula $k = k_p \phi_p + k_w \phi_w$ ($k$ and $\phi$ are thermal conductivity and weight ratio, the subscripts $c$, $p$, and $w$ correspond to the PVA hydrogel, PVA, and water, respectively).

SUPPLEMENTARY MATERIALS

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