WEARABLE DEVICES

Giant thermopower of ionic gelatin near room temperature

Cheng-Gong Han1,2†, Xin Qian3, Qiikai Li1,4, Biao Deng5, Yongbin Zhu1, Zhijia Han1, Wenqing Zhang5, Weichao Wang6, Shien-Ping Feng4, Gang Chen3†, Weishi Liu1,2†

Harvesting heat from the environment into electricity has the potential to power Internet-of-things (IoT) sensors, freeing them from cables or batteries and thus making them especially useful for wearable devices. We demonstrate a giant positive thermopower of 17.0 millivolts per degree Kelvin in a flexible, quasi-solid-state, ionic thermoelectric material using synergistic thermodiffusion and thermogalvanic effects. The ionic thermoelectric material is a gelatin matrix modulated with ion providers (KCl, NaCl, and KNO₃) for thermodiffusion effect and a redox couple [Fe(CN)₆⁴⁻/Fe(CN)₆³⁻] for thermogalvanic effect. A proof-of-concept wearable device consisting of 25 unipolar elements generated more than 2 volts and a peak power of 5 microwatts using body heat. This ionic gelatin shows promise for environmental heat-to-electric energy conversion using ions as energy carriers.

The need to power Internet-of-things (IoT) sensors without using cables or batteries has spurred intense research on energy harvesting from environment. One approach is thermoelectric energy conversion technology, which is based on the Seebeck effect and uses widely available waste heat to meet the power demands of IoT sensors from microwatts to megawatts (1, 2). Conventional electronic-thermoelectric (e-TE) materials are usually narrow-bandgap semiconductors that use electrons or holes as energy carriers. For a typical thermoelectric material, the thermopower (or Seebeck coefficient) is ~100 to 200 µV K⁻¹. As a result, generating a useful voltage of 1 to 5 V in a room temperature environment requires either the challenging integration of thousands or even tens of thousands of tiny, ~50-µm thermoelectric elements (3) or a DC-DC voltage booster to increase the voltage of a regular-sized device with millimeter legs up to 100 times (4).

An alternative route for direct energy harvesting from low-grade heat was reported in ionic systems by exploring two very different mechanisms. One mechanism is based on redox reactions at two electrodes maintained at two different temperatures. Devices using this mechanism are called thermogalvanic cells (5, 6). The other mechanism is ionic thermodiffusion under a temperature gradient without redox reaction, also known as the Soret effect (7, 8). Electricity can be generated continuously based on the thermogalvanic mechanism as the redox reagents are rebalanced by ionic diffusion (9). Thermodiffusion cells operate in a capacitive mode (10). After a temperature difference establishes a voltage difference, the charges stored on the electrodes can be discharged to an external load. The temperature gradient is removed for the system to recover and reapply for next cycle. Most research is based on either the thermogalvanic or the thermodiffusion cell configuration. For thermogalvanic cells, liquid electrolytes with redox couples such as cobalt(II/III) tris(bipyridyl) (11, 12), iron(II/III) (13), iodide/triiodide (14, 15), and ferro/ferricyanide [Fe(CN)₆⁴⁻/Fe(CN)₆³⁻] (9, 16–23) were reported to have an absolute temperature coefficient of a few millivolts per degree Kelvin. For example, one of the highest negative temperature coefficients of ~4.2 mV K⁻¹ was realized in an aqueous system using the Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ redox couple and chao- tropic guanidium salts (22). For the thermodiffusion cell configuration, a thermopower of +11 mV K⁻¹ was obtained using NaOH in a polyethylene oxide (PEO) solution (10). Liquid cells, however, have a drawback in use for wearable devices because of the challenges of encapsulation (24–26). Quasi-solid-state electrolytes have gained attention as an alternative (27–29). A temperature coefficient of ~1.09 and ~1.21 mV K⁻¹ was observed when using Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ as a redox couple in the poly(sodium acrylate) and polyvinyl alcohol matrix, respectively (27, 28), a value lower than that of the redox couple in liquid solutions. High thermodiffusive thermopower is observed in the quasi-solid-state polymer gel composite of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and polyethylene glycol (PEG) with ionic liquid as charge carriers, and the thermopower is tunable from ~4 to 14 mV K⁻¹ by tailoring the composition (29). Furthermore, a thermopower as high as +24 mV K⁻¹ was reported by using the high ionic selectivity of the NaOH–PEO aqueous solution in the confined nanocellulosic channels, such that Na⁺ is the major mobile ion (30). However, whether the thermodiffusion effect and thermogalvanic effect work together synergistically to boost the final thermopower in a single ionic thermoelectric (i-TE) system remains an open question because of their fundamentally different physical pictures.

We combined thermogalvanic and thermodiffusion effects to achieve high thermopower. Before moving on, however, it is necessary to clarify our terminologies because the literature has created some confusion. Similar to conventional e-TE materials, the thermodiffusive thermopower (or Seebeck coefficient) of ions is defined as $S_\text{ion} = \frac{V(T_H) - V(T_C)}{T_H - T_C}$, where $V(T_H)$ and $V(T_C)$ correspond to the voltage of the hot electrode at temperature $T_H$ and the cold electrode at temperature $T_C$, respectively. We clarify later that the sign of $S_\text{ion}$ is determined by the type of charge with higher thermal mobility in a solution, and thus is a transport property. In electrochemistry, the temperature dependence of the standard electrode potential for a reduction reaction ($E^\circ$) at the isothermal condition is referred to as the “temperature coefficient” as $\alpha_R = \frac{dE^\circ}{dT}$ (31, 32), where $\alpha_R$ is a thermodynamic property. For a redox reaction $O + ner = R$, where the oxidized species $O$ is converted into the reduced species $R$ with a mole of electrons ($e^-$) transferred per unit mole of reaction, the temperature coefficient is $\alpha_R = \frac{s_R}{T} - \frac{s_O}{T}$, where $s_O$ and $s_R$ are partial molar entropies of the species $O$ and $R$, respectively, and $F$ is the Faraday constant. In a thermogalvanic cell under a temperature gradient, the redox reaction contribution to the measured voltage is $V(T_H) - V(T_C) = \alpha_R (T_H - T_C)$, which means that the sign of $\alpha_R$ is opposite to the sign convention of the Seebeck coefficient (33). In addition to the redox contributions, the thermodiffusional redox species under a temperature gradient also contributes to the total voltage, which is usually negligible (~10 µV K⁻¹) in aqueous solutions (33). We report a giant thermopower of 17.0 mV K⁻¹ in a quasi-solid-state i-TE material by combining the thermodiffusion effect of KCl and the temperature coefficient of a Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ redox couple. The general strategy is to use a negative temperature coefficient (i.e., $\alpha_R < 0$) and a p-type thermodiusionthermopower (i.e., $S_\text{ion} > 0$) to generate a high differential thermal voltage $S_t$. Using such materials, a high output voltage of 2.2 V is achieved using body heat in a wearable and flexible i-TE device with only 25 unipolar elements in series working in a quasi-continuous
Giant thermopower of i-TE materials

We denote the as-fabricated i-TE materials as Gelatin-x MX-m/n FeCN^{4+/3-} (MX = KCl, NaCl, KNO₃, where x and m/n are the molar concentrations of MX and K₆[Fe(CN)₆]•xK₃[Fe(CN)₆], respectively, where Fe(CN)₆^{3-}/Fe(CN)₆^{4-} serves as the redox couple (hereafter abbreviated as FeCN^{4+/3-}) and the ion provider MX further boosts the thermodiffusive thermopower. We chose organic gelatin for the matrix because of its abundance, low cost, high bio-compatibility, and mechanical flexibility. We found that thermodiffusion of ionic species under a temperature gradient, together with the thermogalvanic effect of redox couple FeCN^{4+/3-}, contributes to the high thermopower of i-TE materials of Gelatin-x KCl-m/n FeCN^{4+/3-}. We observed an improved thermopower from 4.8 to 12.7 mV K⁻¹ by increasing the concentration of KCl from x = 0 M to x = 0.8 M in the as-fabricated Gelatin-x KCl-0.42/0.25 M FeCN^{4+/3-} (Fig. 1A and fig. S1). We achieved a further improved thermopower from 12.7 to 17.0 mV K⁻¹ by tailoring the volume ratio of water to gelatin (Fig. 1A). This value is much higher than other reported gel-based i-TE materials by using either a thermodiffusion effect or a thermogalvanic effect (Fig. 1B and table S1).

The thermodiffusion of KCl in gelatin showed a p-type thermopower. We then used the FeCN^{4+/3-} redox couple, which has a negative temperature coefficient, to achieve a synergistic effect. Because α_T is related to the entropy change of reduction reaction, the negative temperature coefficient α_T = −(∂S/∂T)_P < 0 indicates that FeCN^{4+} has lower solvation entropy than FeCN^{3-}, which is consistent with the solvation shell being more tightly packed around FeCN^{4+} because of its higher valence charge (35). At the hot electrode, the oxidation reaction FeCN^{3-} → e⁻ + FeCN^{4+} is thermodynamically favorable and injects electrons into the hot electrode, increasing its electrochemical potential (i.e., lower voltage) and generating a thermopower (33) that is consistent with the thermodiffusion contributions of KCl. At the cold side, the reduction reaction FeCN^{3-} + e⁻ → FeCN^{4+} is thermodynamically favored, with electrons attracted from the electrode, resulting in a decreased electrochemical potential (i.e., higher voltage). The redox couple therefore works together synergistically to achieve the high p-type thermopower in the as-fabricated i-TE materials of Gelatin-x KCl-m/n FeCN^{4+/3-}.

Optimization of thermopower

The optimization of the as-fabricated i-TE materials of Gelatin-x MX-m/n FeCN^{4+/3-} involved tuning of the concentration of the ion providers (MX = KCl, KNO₃, and NaCl), the redox couple (FeCN^{4+/3-}), and the volume ratio of water to gelatin. We obtained a thermopower of 1.4 mV K⁻¹ from V(T_H) - V(T_C) and T_H - T_C measurements (fig. S1) for the FeCN^{4+/3-} redox couple in an aqueous electrolyte with Cu foils as the symmetric electrodes (Cu | aqueous FeCN^{4+/3-} | Cu). Our measurements were in good agreement with the previously reported value (1.4 mV K⁻¹) (9). We observed a leap in thermopower from 1.4 to 4.8 mV K⁻¹ in Gelatin-FeCN^{4+/3-} (x = 0 M m/n = 0.42/0.25 M) compared with the pristine FeCN^{4+/3-} solution (fig. S1). The pure gelatin had a reference thermopower of 1.3 mV K⁻¹ caused by the thermodiffusion of H⁺ from the ionization of carboxyl groups (36), whereas the
Gelatin-0.42 M FeCN$^{4+}$ and Gelatin-0.25 M FeCN$^{3+}$ had a thermopower of 1.2 and 1.0 mV K$^{-1}$ (fig. S2A), respectively.

We investigated the thermodiffusion effect of ion providers by comparing three series of gelatin-based i-TE materials: Gelatin-x KCl, Gelatin-x KNO$_3$, and Gelatin-x NaCl with x = 0, 0.1, 0.3, 0.5, 0.8, and 1 M, respectively (Fig. 1C and fig. S3). Gelatin-x KCl had an increased thermopower from 4.3 mV K$^{-1}$ to a peak value of 6.7 mV K$^{-1}$ as the concentration of KCl increased from x = 0.3 to 0.8 M, and then a decline when the concentration of KCl increased further. The Gelatin-x NaCl also had a similar peak thermopower of ~6.7 mV K$^{-1}$ but at the concentration of x = 0.3 M. The Gelatin-x KNO$_3$ had a lower peak thermopower of ~3 to 4 mV K$^{-1}$ in the range of x = 0.5 to 0.8 M.

Theoretically, the contribution to the thermopower of mobile cations and anions in i-TE materials could be analogous to the multiband transport in e-TE materials. The temperature gradient drove both cations and anions to migrate across the device from the hot side to the cold side, resulting in a net charge accumulation and an internal electric field that generated voltage. We derived the total thermodiffusive thermopower of a symmetrical electrolyte, such as Gelatin-x KCl, based on the Onsager transport theory as follows (33):

$$S_{\text{di}} = \frac{D_+ \dot{S}_+ - D_- \dot{S}^-}{e(D_+ + D_-)}$$

where the subscript “+” or “−” denotes the ion species, e is the elementary charge, D and S are the mass diffusion and the Eastman entropy of transfer, respectively, and $\dot{S}$ is essentially the temperature dependence of the free energy $\Delta G/\partial T$, which is related to the interaction between solutes and the surrounding media (37). Cations and anions in i-TE materials are equal so that the ionic thermodiffusion is ambipolar, a difference from e-TE materials. Analogous to the Einstein relation for diffusion driven by a concentration gradient, thermal mobility can also be defined as $D/S/k_B T$ (33). The positive thermopower suggested that the thermal mobility $(D_+/k_BT)$ of cation K$^+$ was larger than that of $(D_-/k_BT)$ of anion Cl$^-$. The ionic interactions induced by negatively charged gelatin network could generate a larger Eastman entropy of transfer $S_+$, which might be responsible for the large p-type thermodiffusive thermopower. Alternatively, the complicated relation between the diffusion coefficient and the concentration in the matrix with a charged polymer network may also be responsible. Experiments (38) and computational analysis (39, 40) have shown that in a negatively charged polymer network, the cations have a higher diffusion coefficient. A small fraction of cations tend to “condensate” along negatively charged polymer chains. This “counterion condensation” was proposed by Manning (41). These immobilized K$^+$ condensed near the polymer could further impose frictional drags on Cl$^-$, which would reduce the mobility of Cl$^-$. However, the rest of K$^+$ not condensed around the polymer backbones remains more mobile compared with the Cl$^-$ that was dragged by the condensed immobile K$^+$. We observed that the thermopower is concentration dependent. As the concentration increases, the fraction of mobile cations increases compared with the condensed cations (39). Further increasing the concentration could decrease the Debye length of the electrical double layer and induced a screening effect of the ionic coupling between the ions and gelatin, and the thermal mobility of ions tends to converge to pure KCl solution, which has a negligibly small thermopower measured to be ~40 μV K$^{-1}$ (34). This tradeoff could explain the existence of maximum thermopower in Gelatin-x KCl and Gelatin-x KNO$_3$. The lower thermopower of Gelatin-x KNO$_3$ compared with Gelatin-x KCl can also be attributed to the smaller difference between the thermal mobility of K$^+$ and NO$_3^-$, which is a stronger water-structure breaker compared with Cl$^-$, resulting in a higher mass diffusion coefficient $D$ (42), which is consistent with the ionic conductivity measurement (fig. S4). Thus, the NO$_3^-$ cancels more thermopower than Cl$^-$ in the as-fabricated i-TE materials. Moreover, we found that the pH values affected the thermopower of the i-TE material, i.e., Gelatin-x KCl (x = 0.8 M) (Fig. 1D and fig. S5, A and B), because of the ionization of gelatin functional groups (−COOH), which could affect the ion-gelatin interaction and the surrounding media (39,40). Additionally, we investigated the Gelatin-x K$_2$SO$_4$ (x = 0.25, 0.40, and 0.50 M) with divalent anions (fig. S5C). Among the investigated concentrations, the Gelatin-x K$_2$SO$_4$ (x = 0.40 M) showed the highest thermopower at 4.9 mV K$^{-1}$, which is much less than the 6.7 mV K$^{-1}$ of Gelatin-x KCl (x = 0.8 M).

Adding FeCN$^{4+}$/− into the Gelatin-x KCl i-TE system makes the thermopower sensitive to the concentration of the FeCN$^{4+}$/− redox couple. The thermopower varied from 6.7 mV K$^{-1}$ to 8.3, 10.4, 12.7, and 7.7 mV K$^{-1}$ as x = 0.8 M, whereas m/n changed from 0/0 M to 0.08/0.05, 0.25/0.15, 0.42/0.25, and 0.50/0.30 M, respectively (Fig. 1E and fig. S2B). We repeatedly observed the highest thermopower of 12.7 mV K$^{-1}$ in the as-fabricated i-TE material of Gelatin-0.8 M KCl-m/n FeCN$^{4+}$/− (fig. S6). We measured a lower thermopower of Gelatin-0.8 M KCl-m/n FeCN$^{4+}$/− with m/n = 0.25/0.25 M (11.0 mV K$^{-1}$) and 0.42/0.42 M (7.3 mV K$^{-1}$) compared with m/n = 0.42/0.25 M (fig. S2C).

We attribute the high thermopower to the synergy of the thermogalvanic effect of redox couple FeCN$^{4+}$/− and the thermodiffusion effect of the mobile ions. Additionally, the thermal conductivity of the i-TE material Gelatin-0.8 M KCl-0.42/0.25 M FeCN$^{4+}$/− is low (0.15 W m$^{-1}$ K$^{-1}$ at 293 K), allowing it to maintain a temperature difference for power generation (fig. S7) (33). We observed excellent reversibility of the redox reaction evidenced by the overlapped peaks scanned for three cycles in CV curves (fig. S8). We observed the anodic and cathodic peaks from 0.05 to 0.28 V and -0.05 to -0.28 V (versus Pt), respectively, in the CV curves of the Gelatin-0.8 M KCl-m/n FeCN$^{4+}$/− (fig. S9A). We found increasing redox peak potential ($E_p$) and current density with increasing m/n values (fig. S9B). Additionally, the oxidized species (FeCN$^{3+}$) generated at the hot side and the reduced species (FeCN$^{4+}$) generated at the cold side migrated to the other electrode under a concentration gradient, making continuous current output possible (9, 43).

The water/gelatin volume ratio ($r_w$) also boosted the thermopower of the as-fabricated Gelatin-0.8 M KCl-0.42/0.25 M FeCN$^{4+}$/− system. The water in the gelatin matrix provides the diffusion channel for ions in the quasi-solid-state i-TE material, affecting the thermopower (Fig. 1F and fig. S10). We varied $r_w$ values and observed a continuous increase from 12.7 to 17.0 mV K$^{-1}$ as $r_w$ increased from 2.0 to 3.0. Increasing $r_w$ further to 3.3 decreased the thermopower to 14.1 mV K$^{-1}$ (fig. 1F). Higher $r_w$ also reduced the fracture strain and stretchability. We fixed $r_w$ at 2.0 for device demonstration.

**Mechanism of synergistic effect**

This section explains the synergy between the thermodiffusion and thermogalvanic effects (Fig. 2, A to C). The thermodiﬀusion of KCl accumulated positive net charges near the cold electrode, generating an electric field pointing from the cold electrode to the hot electrode (Fig. 2A). This generated a thermodiﬀusive voltage $\Delta V_{\text{td}} = -\frac{m-n}{C_0} \Delta \phi$ = $V(T_h) - V(T_c) < 0$. The higher solvation entropy generates more FeCN$^{3+}$ than FeCN$^{4+}$ at higher T (33) through oxidation. This transfers electrons to the hot electrode increases the electrochemical potential (61). FeCN$^{4+}$ generation was promoted and extracted electrons from the cold electrode. The T gradient drives thermodiﬀusion and balances the redox reaction. Consequently, the thermogalvanic effect shifts the $\mu$ of both electrodes in the same direction as the thermodiﬀusion effect. The thermogalvanic voltage that we measured was the difference in standard electrode potential $\Delta E_0^* = -\frac{m-n}{C_0} \Delta \phi < 0$, which has the same sign as the thermodiﬀusive voltage. The FeCN$^{4+}$/− also participated in thermodiﬀusion and contributed to the final thermopower.

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From the Onsager transport formulation, we see how a large, positive thermopower comes from the coupling of the thermodiffusion and thermogalvanic effects \((33)\). We observed that the total thermopower \(S_i\) could be written as a summation:

\[
S_i = -\alpha_R + S_{td}(K^+ - FeCN^{4+/3-}) + S_{td}(KCl) + S_{td}(gelatin) \tag{2}
\]

where \(-\alpha_R\) is the contribution to thermopower from the redox reaction \(FeCN^{5-} + e \leftrightarrow FeCN^{4+}\), \(S_{td}\) is the thermopower from the thermodiffusion of mobile ions, and \(S_{td}(gelatin)\) is the intrinsic thermopower of the gelatin. We used an isothermal three-electrode system (Fig. 2D) to effectively eliminate the \(T\) gradient and determine the temperature coefficient \((33)\). The contribution from the redox
couple was finally determined to be $\alpha_R = 2.27$ mV K$^{-1}$ (Fig. 2E and fig. S11) by compensating the temperature coefficient of the saturated calomel electrode (SCE) (33). Figure 2F shows a schematic illustration of partial contribution thermopower in a complex system containing K$^+$, Cl$^-$, FeCN$^{4+/3-}$, and water, as well as a gelatin molecule structure. Relative contribution to the total thermopower in Gelatin-0.8 M KCl-0.25 M FeCN$^{4+/3-}$ ($r_v = 2.0$) is determined as follows (see Fig. 2G): 10.2% contribution of Gelatin, 17.9% of redox entropy of FeCN$^{4+/3-}$, 9.7% contribution of thermodiffusion of K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$, and 62.2% contribution of thermodiffusion effect of KCl (33). We conducted additional experiments by switching the direction of the temperature differences between two electrodes, and observed a hysteresis showing the dynamical response of the device to the transient temperature field (figs. S12 and S13) (33).

**Working modes of an i-TE cell**

A thermodiffusion effect–based i-TE cell is essentially capacitive (10, 30) because the discharge current is nonfaradaic and no electrons transport across the electrode–electrolyte interfaces. A thermogalvanic cell works in a continuous manner, with redox couples reacting in opposite directions on the hot and cold electrodes and ionic diffusion supplying the reactants to electrode surfaces, thus ensuring continuous operation (9). We demonstrate a quasicontinuous working mode by using the i-TE material of Gelatin-0.8 M KCl-0.25 M FeCN$^{4+/3-}$ ($r_v = 2.0$). We assembled the i-TE cell in a laminar structure of Cu | Au | i-TE | Au | Cu (15 × 15 × 1.8 mm). We maintained the cold side at 283 K and the hot side at 301.5 K ($\Delta T = 8.5$ K). The as-fabricated i-TE cell was charged in ~55 min to reach a high (near-saturation) voltage. We then stepped it into the quasicontinuous working mode. The cell discharged to 0 V in 10 s by connecting to an external circuit with a current linearly ramped up from 0 to maximum, and then recovered back to the high voltage in 3 min in open circuit under the same applied temperature difference. In the discharge process, the electrons flowed from the hot side to the cold side through the external circuit, resulting in a decreased internal electrostatic field and hence the cell voltage. The discharging current is also a synergistic result of redox couples and ion providers, contributed partially by the faradaic process caused by the redox couple FeCN$^{4+/3-}$ and the capacitive desorption of K$^+$ and Cl$^-$. Once the external circuit is disconnected, the diffusion of the redox couple resupplies the consumed species to the electrode and the concentration profile of ion providers reestablishes, so the cell voltage recovers, allowing for the next discharge cycle (fig. S14). We completed 100 of these charge-discharge cycles (Fig. 3A) over a time span of 5 hours. The corresponding power curve of the fifth cycle displayed parabolic behavior with the maximum at 8 µW (Fig. 3B). We expect that such quasicontinuous operation can last much longer until the electrodes are fully polarized (33). Output power decreased as the quasicontinuous cycle number increased (Fig. 3C, inset), which was probably caused by the polarization of the electrodes. To solve this issue, we reactivated the i-TE cell by removing the temperature difference and totally cooling down the cell while short-circuiting the electrodes. The reactivated cell recovered the voltage and current (fig. S15). The concentrations of all ionic species redistributed and the electrodes were depolarized after this process (33). We reproducibly achieved high thermally charged voltage over several consecutive days (fig. S16). This demonstrates that the cell can be used repetitively rather than being a one-time energy source. We reduced the thermal charge time from 3 min to ~20 s by increasing number of the layers of the i-TE cell from one to three (Cu | i-TE | Cu | i-TE | Cu | i-TE | Cu, 15 × 15 × 1.8 mm). The internal electrode shortened the time for ions to diffuse across the shortened distance, and hence shortened the thermal charging process (fig. S17).

We coated the Cu foils (10 µm thickness) with Au (40 nm) because electrode corrosion is a performance concern and found a
comparable thermopower (fig. S18). However, the total energy density of initial 50 cycles was much higher (7.4 J m$^{-2}$) than for Cu foil electrodes (1.5 J m$^{-2}$) (Fig. 3C and fig. S19). The Au (40 nm)-coated Cu foil electrode has an enlarged surface area (fig. S20) (21, 44). We also measured a slightly (8%) higher thermopower using a Pt electrode compared with the Cu foil electrode (fig. S21). Electrode optimization may boost the output power density of a gelatin-based i-TE cell. We calculated the specific pulsed power density, $P_{\text{max}}/(\Delta T)^2 = V_{\text{oc}}I_{\text{sc}}/(2\Delta T)^2$, where $V_{\text{oc}}$ and $I_{\text{sc}}$ are the open-circuit voltage and short-circuit current, respectively. We measured the maximum output power density at 0.66 mW m$^{-2}$ K$^{-2}$, which is one or two orders higher than previously reported in a gel-based i-TE cell (Fig. 3C).

**Proof-of-concept wearable i-TE device**

An ionic liquid in a polymer gel i-TE cell based on thermodiffusion was demonstrated by Zhao *et al.* and achieved a device thermopower of 0.33 V K$^{-1}$. This device combined 18 pairs of n- and p-type elements (29). Using 25 p-type unipolar elements allowed us to reach a comparable device thermopower. Our i-TE materials are highly flexible and suitable for wearable electronics applications (fig. S22). After bending the Gelatin-0.8 M KCl-0.42/0.25 M FeCN$_{4}^{-}$/3$^{-}$ ($r_v = 2.0$), it remained intact after stretching from 3 to 7.2 cm and recovered after release (Fig. 4A).

The giant thermopower of the as-fabricated ionic gelatin i-TE materials (Gelatin-x KCl-m/n FeCN$_{4}^{-}/3$) provides a promising solution for the voltage needed for IoT sensors in a near-room temperature environment. We constructed a flexible and wearable i-TE device assembled by serially connecting 25 i-TE elements using copper-only electrodes (Fig. 4B). This device can be worn at the back of hand (Fig. 4B, inset). We obtained a voltage of 2.2 V in a cold environment ($\Delta T$ of ~10 K). The voltage generated by our device is enough to drive different sensors without additional DC-DC
work in a quasicontinuous thermal charge/electrical discharge mode for long-time usage, but can also work in continuous mode, delivering a maximum energy density of 12.8 J m⁻².

This work provides a promising approach to realizing cable- and battery-free energy supplies for IoT sensors, demonstrating the promise of using ions as the energy carriers in thermo-electric energy conversion.

REFERENCES AND NOTES

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33. Materials and methods are available in the supplementary materials.
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Improving ionic thermoelectrics
Using ions as charge carriers in thermoelectric devices usually requires using either thermal diffusion or redox reactions at two electrodes with different temperatures. Han et al. leveraged both of these strategies to develop a gelatin-based ionic thermoelectric device that uses alkali salts and an iron-based redox couple to generate a large thermopower. This device is capable of generating useful amounts of energy from body heat.
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