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Perspective and advances on ionic thermoelectric energy conversion

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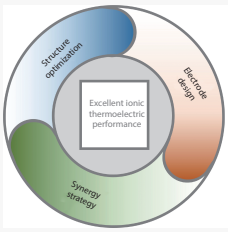
Ionic thermoelectric energy conversion uses ions as carriers to convert heat into electricity. The high temperature-induced voltage of several millivolts per degree Kelvin has attracted more attention to the application of self-powered sensors in IoTs. In this perspective, the thermogalvanic and thermodiffusion effects are illustrated, together with the research advances on ionic thermoelectric gels. However, the status in recent 3 years is high temperature-induced voltage but low output power. The authors propose that the synergy of two effects, electrode design and structure optimization are believed to be effective ways to improve ionic thermoelectric properties.



Utilizing the ubiquitous heat effectively to realize the energy supply is an effective route to achieve the "carbon dioxide emission and carbon neutrality". Low-grade heat (<100 °C) is widely distributed in the environment, which arises from solar-thermal and geothermal energy, industrial waste heat by-product, and dissipation from the human body and electronic equipment.[1,2] Thermoelectric technology is believed to be a straightforward way to convert heat into electricity. Semiconductor thermoelectric materials, as the typical representative, employ electrons and/or holes to generate currents. Great advances and achievements have been realized in thermoelectric semiconductors with a high *ZT* value of 2.8~3.1 up to now.[3,4] And many scenarios, including self-powered sensors in the Internet of Things (IoTs)[1,5], could be found in the use of thermoelectric semiconductors based on their highly produced current and output power.

On the other hand, employing ions as carriers can also convert heat into electricity, which was classified as "ionic thermoelectric" originally for the thermogalvanic effect of a thermocell containing a redox couple.[6] The ionic thermocell usually possesses the high temperature-induced voltage (uniformly called "ionic thermopower") in the order of ~mV K^{-1}, showing the potential application with the high voltage requirement. In addition, the ion concentration gradient in a redox couple-free system via the thermodiffusion effect (i.e., Soret effect) can also create a temperature-induced voltage, which could also be labeled "ionic thermoelectric".[7] The ionic thermoelectric gels exhibit superior flexible and mechanical properties as well as a higher ionic thermopower than the liquid-based ones, receiving more research interest. It consists of an organic matrix, redox couple and/or thermodiffusive ions, and electrodes. Depending on the thermogalvanic effect, an oxidation/reduction reaction occurs at the hot/cold electrode, releasing electrons through the external circuit to form a current. The reaction products migrate to the opposite direction under diffusion and convection, ensuring the continuous redox reaction and electron release. The ionic thermopower of gel-based thermocells contained the redox entropy changes and diffusion parts of ions. The ionic thermoelectric gels of poly(vinyl alcohol) (PVA)-Fe^{2+}/Fe^{3+}[8], poly (N-isopropylacrylamide) (PNIPAM)-I^-/I-3[9], Gelatin-$FeCN^{4-/3-}$ ($Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$)[10] and bacterial cellulose-$FeCN^{4-/3-}$[11] were fabricated, displaying an ionic thermopower of −1.0, −1.9, 4.8 and 4.5 mV K^{-1}, respectively. Under the thermodiffusion effect, a large number of organic polymer chain groups in a gel system can capture certain cations or anions of thermodiffusive ions, amplifying the ion concentration profile and resulting in a high ionic thermopower.[12] The ionic thermoelectric gels of PEO-NaOH[13], cellulose-based PEO-NaOH[12] and (PVDF-HFP)-EMIM:DCA (1-ethyl-3-methylimidazolium dicyanamide)[14], showed an ionic thermopower of 10, 24, and 26 mV K^{-1}, respectively. The high temperature-induced voltage at a small temperature gradient exhibits the merits of self-powering the sensors in IoTs, which the commercialized sensors (Texas Instruments) such as temperature sensors, humidity sensors, magnetic sensors, and so on usually require a minimum voltage of more than 1.6 V. Furthermore, a flexible wearable device assembled by ionic thermoelectric gels can harvest the human body heat due to the constant body temperature of 37 °C, generating the electricity to drive the intelligent headphones, eye masks, smartwatches, and so on.

Fig. 1a shows the thermogalvanic effect in a thermocell consisting of a redox couple $FeCN^{4-/3-}$, electrolyte and elec-

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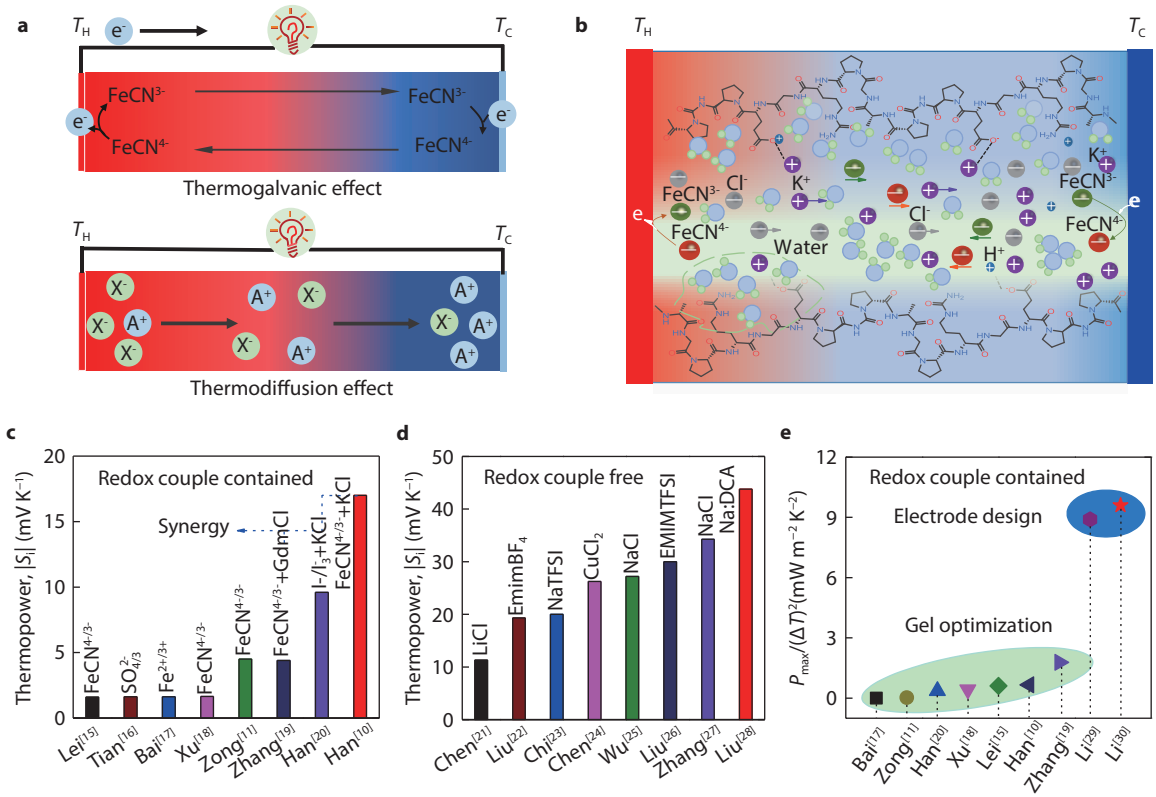

Fig. 1 **a** Schematic of the thermogalvanic effect and thermodiffusion effect; **b** Schematic of the thermodiffusion, redox reaction, and interaction between the ions in Gelatin-KCl-$FeCN^{4-/3-}$ gels.[10] Copyright 2020, American Association for the Advancement of Science; Comparison of absolute ionic thermopower for the redox couple contained gels **c** and redox couple free gels **d**; **e** Comparison of normalized maximum output power ($P_{max}/(\Delta T)^2$) for the redox couple contained gels.

trodes. For a redox reaction $FeCN^{3-} + e^- \rightleftharpoons FeCN^{4-}$, the oxidation reaction $FeCN^{4-} - e^- \rightarrow FeCN^{3-}$ occurred at the hot electrode, releasing the electrons to the electrode and forming the current across the external circuit. Meanwhile, a reduction reaction $FeCN^{3-} + e^- \rightarrow FeCN^{4-}$ happened at the cold electrode, where the electrons were received from the electrode. The $FeCN^{3-}$ and $FeCN^{4-}$ generated in the redox reaction migrated to the opposite direction under ion diffusion. The electrons released in the reaction could continue to generate the current in the external circuit. As for the thermodiffusion effect shown in Fig. 1a, free A^+ and X^- were formed in a gel electrolyte after AX dissociation and migrated from the hot side to the cold side under the temperature gradient. The concentration difference between A^+ and X^- was observed due to the different diffusion coefficient of A^+ and X^- and the effect of certain polymer chain groups on A^+ or X^-. Therefore, an electrostatic field along the temperature gradient was formed throughout the gels, inducing the voltage between the hot and cold electrodes. In our previous work[10], the thermogalvanic effect and the thermodiffusion effect were combined to obtain synergy, resulting in an improved ionic thermopower of up to 12.7 ~ 17 mV K^{-1}. The ionic thermoelectric gel consisted of the organic matrix of gelatin, redox couple $FeCN^{4-/3-}$, thermodiffusive ions KCl, and water (Fig. 1b). For the redox reaction $FeCN^{3-} + e^- \rightleftharpoons FeCN^{4-}$, the oxidation and reduction reactions happened at the hot and cold electrodes, respectively, which was contributed to the final ionic thermopower for 17.9%. The organic gelatin not only amplified the diffusive concentration difference between K^+ and $FeCN^{4-/3-}$ (redox couple), but also magnified that between K^+ and Cl^- (thermodiffusive ions) based on negatively charged chains. As a consequence, the concentration difference between cations and anions accounted for 71.9% of the total thermopower. The maximum output power of 0.66 mW m^{-2} K^{-2} and harvested energy density of 12.8 J m^{-2} were obtained in the ionic thermoelectric gel Gelatin-KCl-$FeCN^{4-/3-}$. Finally, a wearable ionic thermoelectric device was developed as the proof-of-concept. A voltage of 2.2 V and a maximum output power of 5 μW were achieved when wearing a device with 25 ionic thermoelectric gel units (5 × 5 × 1.8 mm) connected in series to harvest the human body heat.

In the last 3 years, the research on ionic thermoelectric gels has been rapidly developed and the representative advances have been made. The research fucuses on improving two objectives: ionic thermopower and output power density. Fig. 1c and d show the comparison of the absolute ionic thermopower for ionic thermoelectric gels with the redox couple contained and the redox couple free, respectively. The redox couple contained gels indicated that the gel systems included the single thermogalvanic effect or the synergy of the thermogalvanic and thermodiffusion effect. For a thermogalvanic effect, the ionic thermopower improvement could be attributed to an increase in entropy in a redox reaction, which was related to the variety of redox couples. In Fig. 1c, redox couples of $FeCN^{4-/3-}$, $Fe^{2+/3+}$, and $SO_{4/3}^{2-}$ in gels were performed, showing a value of less than 2 mV K^{-1} based on the

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single thermogalvanic effect (Lei[15], Tian[16], Bai[17], Xu[18]), expecting the ionic thermopower of 4.5 mV K^{-1} in the bacterial cellulose-$FeCN^{4-/3-}$ gels (Zong[11]). The synergy of thermogalvanic and thermodiffusion effects could improve the thermopower, e.g. 4.4 mV K^{-1} for $FeCN^{4-/3-}$-GdmCl (Zhang[19]), 9.6 mV K^{-1} for I^-/I_3^--KCl (Han[20]), and 17 mV K^{-1} for $FeCN^{4-/3-}$-KCl (Han[10]). In a redox couple free system (Fig. 1d), the gels contained the only thermodiffusive ions, which referred to as the thermodiffusion effect. Inorganic salts and ionic liquids were frequently used as the thermodiffusive ions due to their easy dissolution and high conductivity. The high ionic thermopower based on thermodiffusion effect was observed, ranging from 11 ~ 44 mV K^{-1} (Chen[21], Liu[22], Chi[23], Chen[24], Wu[25], Liu[26], Zhang[27], Liu[28]). Compared with the redox couple contained gels (Fig. 1c), the redox couple free gels possessed the higher ionic thermopower due to the easy regulation of ion concentration profile. To date, the high ionic thermopower up to tens of mV K^{-1} has been noticed in ionic thermoelectric gels. Challengingly, the low output power as a short slab should be further drastically improved to meet the market requirements. Fig. 1e shows the normalized maximum output power ($P_{max}/(\Delta T)^2$) for the redox couple contained gels. $P_{max}/(\Delta T)^2$ was only compared for redox couple contained gels due to their continuous discharge characteristics. Most $P_{max}/(\Delta T)^2$ less than 1 mW m^{-2} K^{-2} were observed, which was due to the low conductivity and slow ion migration in gels. It appeared that the strategy of simply optimizing gel compositions was difficult to dramatically improve $P_{max}/(\Delta T)^2$. Li[29,30] reported the high $P_{max}/(\Delta T)^2$ with a value of 8.9 ~ 9.6 mW m^{-2} K^{-2} in Gelatin-KCl-$FeCN^{4-/3-}$ by designing the Au@Cu 3D electrodes, which enlarged the reaction rate and catalyzation for the redox reaction. Previous works have made significant progress, but there is still a challenge to improve the output power of ionic thermoelectric gels. Other routes, including electrode design, structure optimization, etc., should be considered in the future. Designing various electrode morphologies could enlarge the contact area of redox ions for improving the reaction rate, while designing the high-conductivity electrodes could enhance the charge exchange density at the interface of ions/electrodes, thereby pushing the output power up to high values. Optimizing the interface contact of ions and electrodes could reduce contact resistance. On the other hand, more ion transport channels could be provided by optimizing the gel structure to improve the diffusion rate. Both could contribute to an increase in output power. Ionic thermoelectric energy conversion will play an important role in harvesting low grade heat to self-power sensors in IoTs and the wearable artificial intelligence field in the future, when the ionic thermopower and output power are corporately improved.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

The manuscript was written by Lijuan Yang under the conception of Cheng-Gong Han. The final version of the present paper was reviewed and edited by Cheng-Gong Han.

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