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The flexible hydrogel ion thermoelectric devices for wearable applications

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Abstract: Thermoelectric devices have garnered significant attention in the field of thermal energy conversion due to their unique ability to utilize low-grade heat. However, most devices are limited in terms of application scope and stability due to the specific characteristics of the materials used. In contrast, hydrogels, with their excellent physicochemical properties such as stretchability, high thermal sensitivity, and portability, offer great potential in the field of flexible thermoelectric devices. In this study, we have developed a hydrogel-based thermoelectric device using the I^-/I_3^- redox couple. This device demonstrates excellent stretchability, bendability, and a maximum thermal power of up to 0.65 mV/K. Additionally, it shows good sensitivity to human body signals, with excellent repeatability, making it a promising candidate for use as a comfortable electronic skin for human monitoring. Its potential applications are vast, including medical body monitoring and respiratory monitoring.

1. Introduction

The efficient utilization of energy has always been a hot topic of interest. Low-grade heat (0-100 ℃), as a rich and sustainable energy source, is often difficult to utilize. Low-grade heat is widely distributed in urban residential buildings, transportation industries, manufacturing, biological systems, solar energy, and geothermal energy[1]. Thermoelectric (TE) technology has significant potential in providing sustainable power by harvesting energy from the environment, the human body, and industrial waste heat[2]. Traditional TE devices based on semiconductor materials convert heat into electrical energy through the Seebeck effect (based on electron or hole transport)[3]. However, the traditional electronic thermoelectric (e-TE) effect produces much lower thermal power compared to the ionic thermoelectric (i-TE) effect (based on ion or hole transport), which hinders the effective utilization of low-grade heat[4]. In typical thermoelectric chemical cells, the Seebeck coefficient is enhanced by the thermoelectric effect of redox potentials that change with temperature[5]. However, the instability and leakage risks of liquid electrolytes also limit the development of their applications[6]. Therefore, hydrogel-based ionic thermoelectric materials have gained widespread attention, as hydrogel materials offer higher thermal power, excellent stability, and good mechanical properties[7]. Compared to liquid ionic thermoelectric cells, hydrogel systems provide more stability and a broader range of applications[8].

In this study, we introduce a redox-type ionic thermoelectric cell based on PVA hydrogel as the main framework, aimed at improving the stability and mechanical properties of ionic thermoelectric cells. The iodine/iodine redox system used here exhibits higher thermoelectric performance and greater ionic conductivity and mobility compared to the traditional $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ system. Furthermore, iodine/triiodide is non-toxic and more environmentally friendly. At a NaI:I_2 ratio of 2.5:1, the Seebeck coefficient reaches 0.65 mV/K, with a conductivity of 1.14 S/m. Subsequently, continuous charge-discharge tests were conducted on the thermoelectric gel at a temperature difference of about 2K. The results indicate that the thermoelectric gel in this study has good reusability, providing important reference for future applications of flexible thermoelectric materials.

2. Sample Preparation

The PVA/NaI/I_2 redox-type thermoelectric hydrogel is abbreviated as RTEG, and its preparation process is shown in Figure 1.

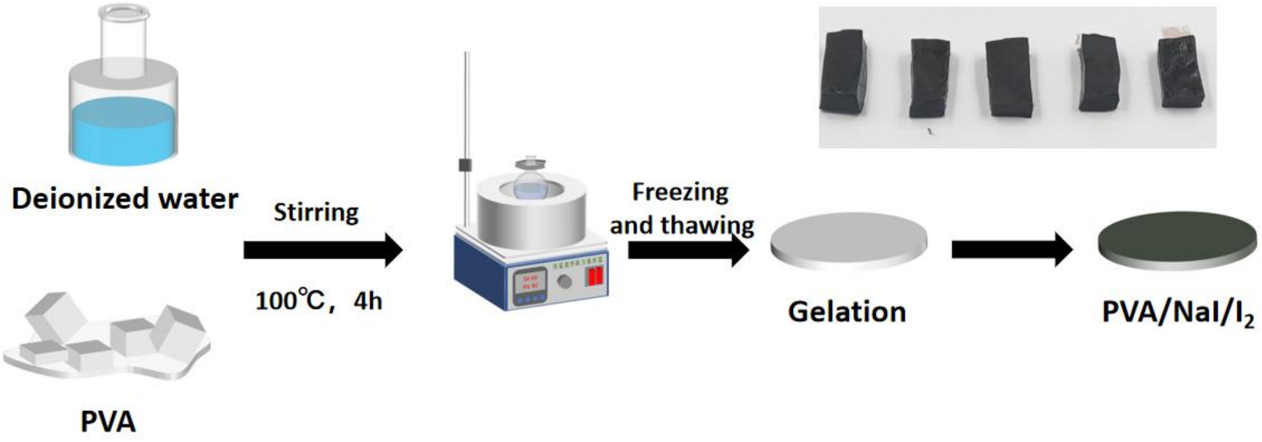

Figure 1 The preparation process of RTEG

Preparation of PVA aqueous solution: Weigh 2 g of PVA powder and add it to 18 g of deionized water. Then, place the mixture in a 100 ℃ water bath and stir for 4 hours to fully dissolve the PVA. Afterward, seal the solution and allow it to sit for 12 hours to let any air bubbles rise and escape from the surface, thereby reducing or eliminating any potential impact on the gel quality during the gelation process. This ensures the uniformity and consistency of the gel. Finally, a 10 wt% PVA solution is obtained.Preparation of RTEG ionic thermoelectric hydrogel: Pour the obtained PVA solution into a PVDF mold with dimensions of 10 mm in length, 5 mm in width, and 4 mm in thickness. Then, perform freeze-thaw cycling between -10 ℃ and room temperature for 3 days. This process strengthens the hydrogen bonds between PVA and H2O, leading to further crosslinking within the hydrogel and resulting in a more stable PVA hydrogel. Next, add varying mass fractions of NaI, I_2, and H_2O to prepare RTEG solutions with different concentrations (molar mass ratio NaI: I_2 = 2.5:2, 2:1.5, 3:1, 2:1, and 2.5:1). Subsequently, pour the RTEG solutions with different concentration ratios into the prepared hydrogel. Once the hydrogel has fully integrated with the TIG solution, a complete RTEG hydrogel is obtained.

3. Experimental Methods

3.1 Seebeck Coefficient Testing

The glass substrate (75×25 mm) was cleaned for 10 minutes with detergent, deionized water, and anhydrous ethanol, and then exposed to ultraviolet light (365 nm, 7.5 mW cm-2) for 3 hours. Two copper electrodes (20 mm × 2 mm) with a 5 mm spacing were connected to the glass substrate, and the RTEG hydrogel (10 × 5 × 4 mm) was carefully adhered to the electrodes on the glass substrate. Additionally, two 20×20 mm Peltier semiconductor chips were connected to the ends of the glass substrate using a DC power supply (DP832), with one end for heating and the other for cooling. The lower ends of the Peltier chips were equipped with two heat sinks for real-time heat dissipation. In this study, the Seebeck coefficients of all samples were measured inside a constant temperature and humidity incubator set to 298 K and 30% ambient humidity (Figure2).

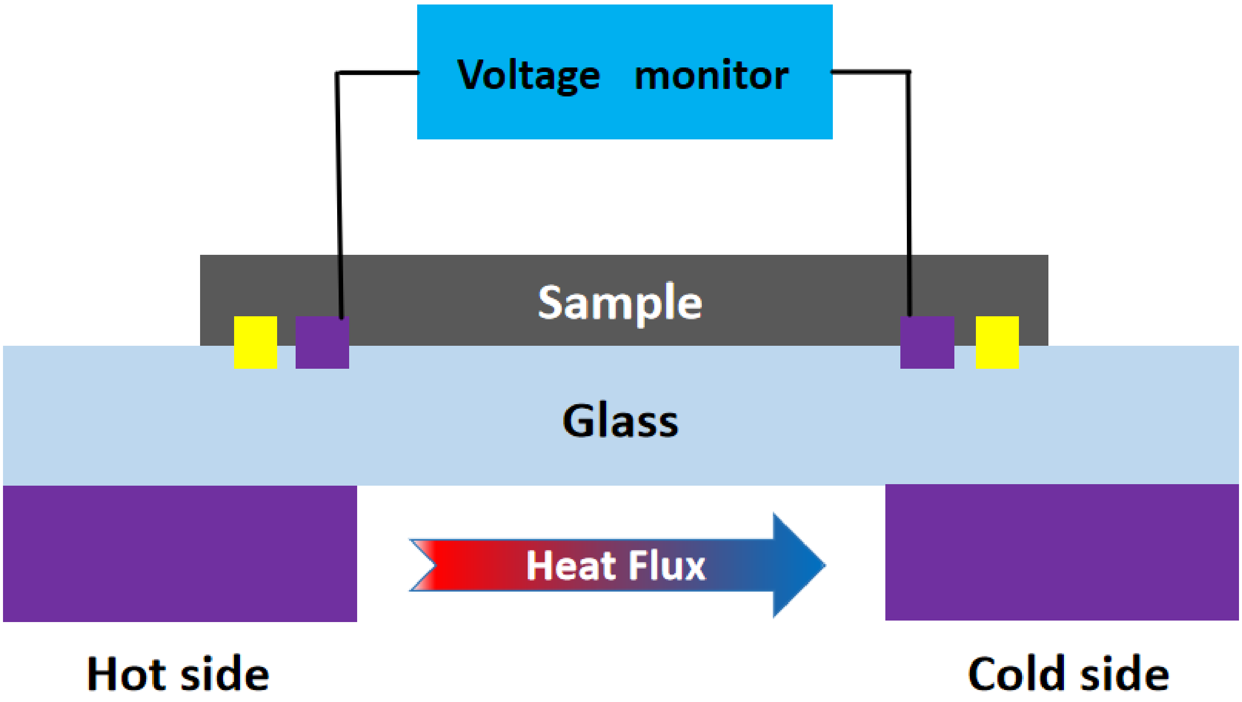

Figure 2 The schematic diagram of the thermoelectric performance testing principle of RTEG

The open-circuit voltage was monitored by a Keithley 2450, which detected the electrical signal between two wires. The temperature was automatically recorded by a USP-R200T wireless data logger, with both devices reading data once per second to ensure synchronization. The Seebeck coefficient was calculated using the following formula. A K-type thermocouple was fixed to the lower surface of the sample to reduce thermal resistance and monitor the temperature in real-time. The Seebeck coefficient of the ionic gel was tested using a self-made device and system as follows:

$$\mathrm{Se}=\frac{\Delta \mathrm{V}}{\Delta \mathrm{T}} \tag{1}$$

Where:
ΔV is the potential difference across the two ends of the gel,
ΔT is the temperature difference across the two ends of the gel.

3.2 Conductivity Testing

The ion conductivity was measured using an SP-200 impedance/frequency response analyzer. The alternating voltage had a frequency range of 1 Hz to 100 kHz, with an amplitude of 0.1 V. Two 304 stainless steel round button cells were used to hold the hydrogel. The impedance's negative imaginary component was taken from the Nyquist plot, and its minimum value relative to the real component was used as the sampling resistance. The ion conductivity was then calculated using the following formula:

$$\sigma=\frac{L}{RA} \tag{2}$$

Where:
L is the thickness of the ionic thermoelectric gel,
R is the resistance,
A is the cross-sectional area of the ionic thermoelectric gel.

4. Ionic Thermoelectric Seebeck Coefficient Testing and Analysis

For thermoelectric cells based on the iodine redox couple, the reversible redox reaction occurs between the hot and cold ends under a temperature gradient[9]. At the hot end, the reduction reaction $I_3^-+2e^-\longrightarrow I^-$ is predominant, where electrons are attracted to the hot electrode, lowering the electrochemical potential of the electrode, which causes the electrode potential to increase. At the cold end, the oxidation reaction $3I^--2e^-\longrightarrow I_3^-$ dominates, where electrons are injected into the cold electrode, raising its electrochemical potential and causing the electrode potential to decrease. The oxidized iodine ions are transferred to the low-temperature electrode via convection, diffusion, and migration, while the reduced iodine ions return to the high-temperature electrode, thus achieving continuous cyclic reactions. Therefore, under an uninterrupted temperature gradient, the voltage generated between the two electrodes is also continuous and uninterrupted.

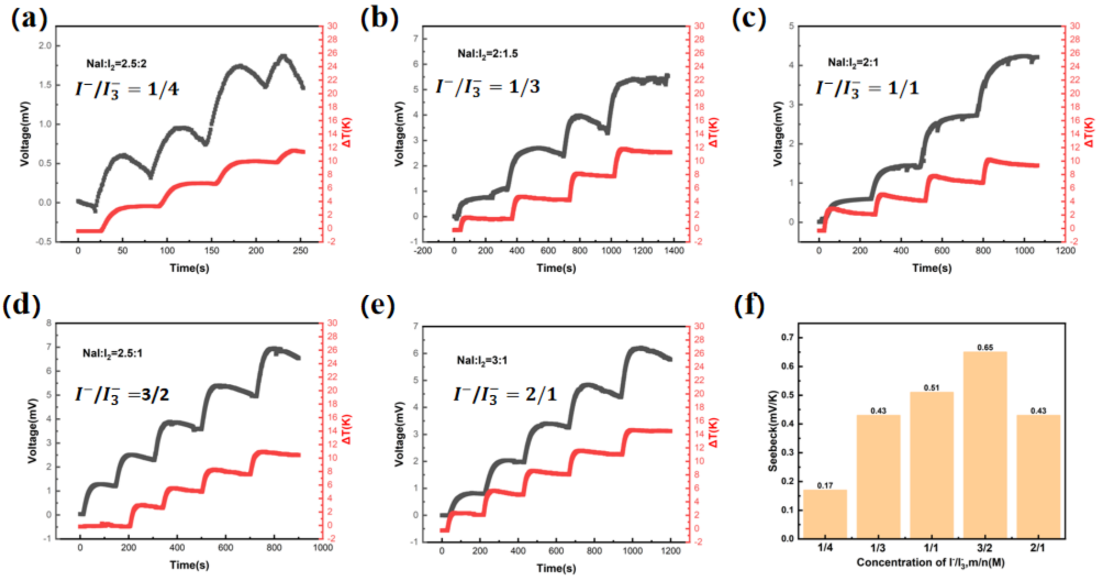

Figure 3 The Seebeck coefficient of ion thermoelectric gels at different concentrations, (a)$I^-/I_3^-=1/4$,(b)$I^-/I_3^-=1/3$, (c)$I^-/I_3^-=1/1$, (d)$I^-/I_3^-=3/2$, (e)$I^-/I_3^-=2/1$(f) the statistical Seebeck coefficient of ion thermoelectric gels at various concentrations.

The ion concentration has a significant effect on the Seebeck coefficient of ions, with different ion concentrations typically yielding different Seebeck values. Therefore, the Seebeck coefficient corresponding to five different concentration ratios of I^- /I_3^-(1:4, 1:3, 1:1, 3:2, 2:1) was tested, with the molar mass ratios of NaI to I_2 being 2.5:2, 2:1.5, 2:1, 2.5:1, and 3:1. The environment humidity was kept constant at 30 RH% in a constant temperature and humidity incubator, and the cold-end temperature was maintained at a constant 25 ℃. Specific test details are shown in Figure 3 (a-f).

From the above test results, it can be observed that the Seebeck coefficient shows an initial increase followed by a decrease as the I^- concentration increases[10]. This may be because, as the I^- concentration rises, the ionic conductivity continuously increases, which in turn causes the Seebeck coefficient to increase as well. However, when the I^- concentration becomes too high or too low, it can affect the conversion rate of I^- at the hot end, thereby influencing the overall reaction rate of the system, which results in a decrease in the Seebeck coefficient.

5. Ionic Gel Conductivity Testing and Analysis

Ion conductivity is an important parameter for evaluating ionic thermoelectric materials[11]. In this study, the ion conductivity of the ionic hydrogel was analyzed using alternating current (AC) impedance spectroscopy (Figure 4a-b). The ionic resistance was obtained by identifying the intersection point between the Nyquist plot and the real axis, and the ion conductivity was calculated using the formula (2) mentioned earlier.

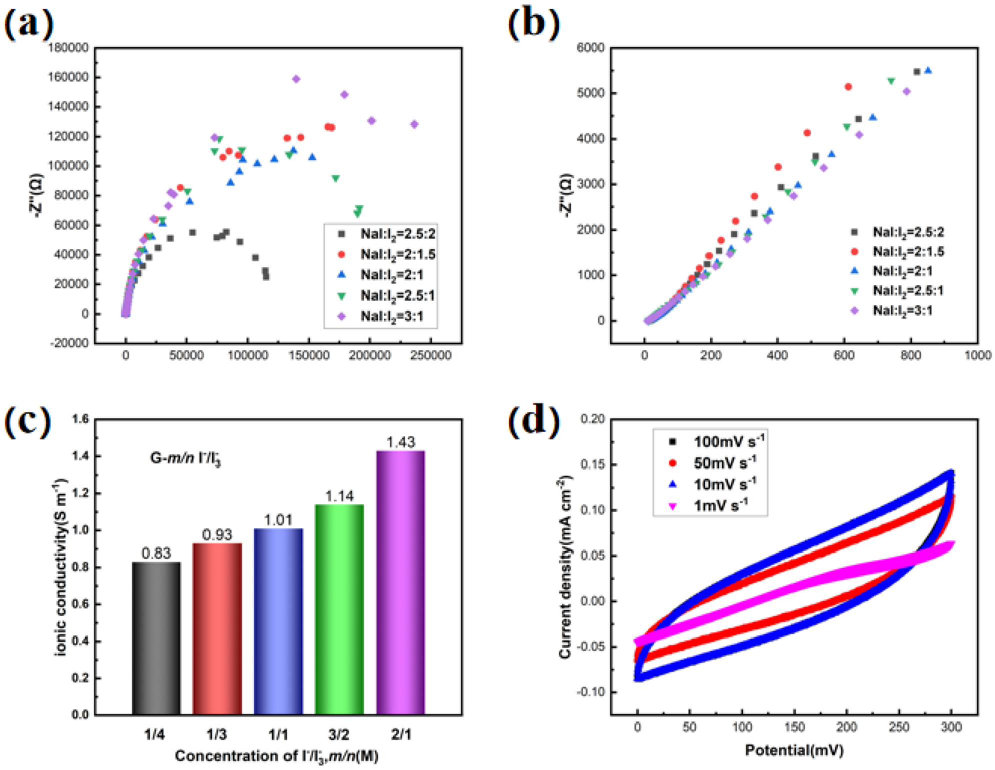

Figure 4 (a)The Nyquist plot of RTEG at different concentration ratios and (b)their zoom-in plot at high frequency region and(c)conresponding ionic conductivity(d)The CV (Cyclic Voltammetry) curve of the thermoelectric gel at I^- /I_3^-=3/2

As shown in Figure 4c, when different concentration ratios of I^- /I_3^- are added to the PVA hydrogel, the ion conductivity increases to 0.83 S/m, 0.93 S/m, 1.01 S/m, 1.14 S/m, and 1.43 S/m, respectively. It can be observed that as the I^- concentration increases, the ion conductivity continues to rise. This is because, when I^- moves within the PVA hydrogel framework, it may interact more strongly with the PVA matrix, which affects ion mobility. Since the interaction with I^- is weaker, the increase in I^- concentration leads to an overall increase in the ion mobility of the system, thereby enhancing the conductivity. Figure 4d shows the CV measurements in the range of 1 mV/s to 100 mV/s, revealing the capacitance characteristics of the material.

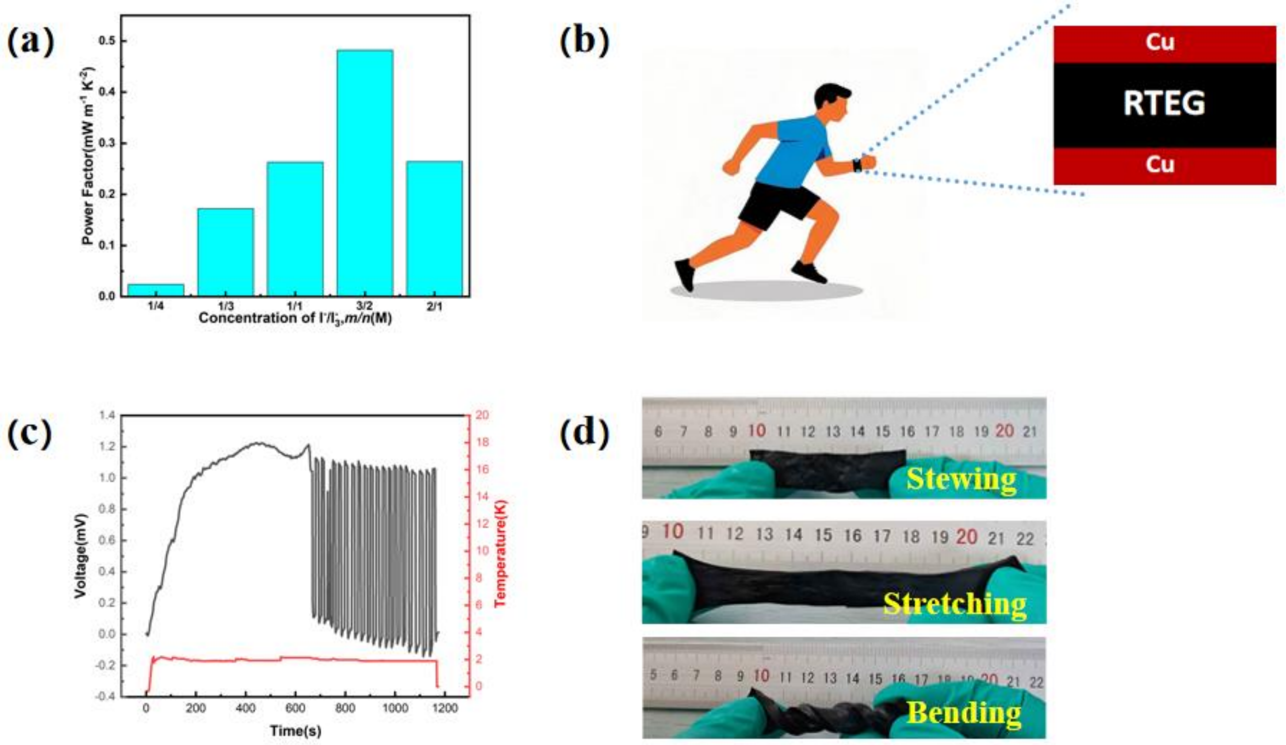

Figure 5 (a)The power factor of RETG at different concentration ratios.(b)Flexible generators for wearable applications and(c)Cyclic voltage output from human contact disconnection.(d)The normal state and the state after stretching and bending of RTEG

Figure 5a shows the power factor of RTEG at different concentrations, which is commonly used to evaluate the efficiency potential of materials in converting thermal energy into electrical energy[12]. Due to the soft and tough physical properties of hydrogels, their thermoelectric materials have great potential for applications in wearable human thermoelectric converters (Figure 5b). We also conducted output cycling tests for RTEG under human contact (Figure 5c), and after 20 continuous on-off cycles, the generated voltage remained stable within a consistent range. Finally, we performed stretching and twisting tests on RTEG (Figure 5d). The material can stretch up to 200% of its original length and can be bent freely without affecting the use of the RTEG.

6. Conclusion

In summary, we have designed an ionic thermoelectric hydrogel with strong stretchability and adaptability, utilizing the I^-/redox couple for self-powered energy generation from the human body. At an I^- concentration ratio of 3/2, the Seebeck coefficient reaches as high as 0.65 mV/K. Due to its broad range of potential applications, the hydrogel thermoelectric cell represents an important step forward in the field of ionic thermoelectrics toward self-powered monitoring.

References

[1] Nižetić S, Djilali N, Papadopoulos A, et al. Smart technologies for promotion of energy efficiency, utilization of sustainable resources and waste management[J]. Journal of cleaner production, 2019, 231: 565-591.

[2] Zheng X F, Liu C X, Yan Y Y, et al. A review of thermoelectrics research–Recent developments and potentials for

sustainable and renewable energy applications [J]. Renewable and Sustainable Energy Reviews, 2014, 32: 486-503.

[3] Wang H, Yu C. Organic thermoelectrics: materials preparation, performance optimization, and device integration [J]. Joule, 2019, 3(1): 53-80.

[4] Ji D, Liu G, Romagnoli A, et al. Low-grade thermal energy utilization: Technologies and applications[J]. Applied Thermal Engineering, 2024, 244: 122618.

[5] Jiang K, Jia J, Chen Y, et al. An ionic thermoelectric generator with a giant output power density and high energy density enabled by synergy of thermodiffusion effect and redox reaction on electrodes[J]. Advanced Energy Materials, 2023, 13(21): 2204357.

[6] Liu Y K, Zhao C Z, Du J, et al. Research Progresses of Liquid Electrolytes in Lithium-Ion Batteries[J]. Small, 2023, 19(8): 2205315.

[7] Fu M, Sun Z, Yuan Y, et al. Ionic Thermoelectric Materials Based on the Thermodiffusion Effect: Mechanism, Advancements, and Applications [J]. Macromolecular Chemistry and Physics, 2024: 2400358.

[8] Zhang C, Shi X L, Liu Q, et al. Hydrogel-Based Functional Materials for Thermoelectric Applications: Progress and Perspectives [J]. Advanced Functional Materials, 2024: 2410127.

[9] Li W, Ma J, Qiu J, et al. Thermocells-enabled low-grade heat harvesting: challenge, progress, and prospects[J]. Materials Today Energy, 2022, 27: 101032.

[10] Zuo G, Liu X, Fahlman M, et al. High Seebeck coefficient in mixtures of conjugated polymers[J]. Advanced Functional Materials, 2018, 28(15): 1703280.

[11] Zhao D, Würger A, Crispin X. Ionic thermoelectric materials and devices[J]. Journal of Energy Chemistry, 2021, 61: 88-103.

[12] Kishore R A, Priya S. A review on low-grade thermal energy harvesting: materials, methods and devices[J]. Materials, 2018, 11(8): 1433.