Review on advances in thermoelectric conversion using ion-conducting polymers

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Abstract

The ionic Seebeck effect has been extensively investigated in thermoelectric conversion due to the substantial Seebeck coefficient it promotes. In this context, polymer-based electrolytes have been reported as one of the good ionic Seebeck material categories, demonstrating extraordinary potentials in heat collection for wearable and adaptable hardware. In this review, we make a summary of the latest progress in the ponder for ionic thermoelectric systems based on organic polymer electrolytes and mixed ionic-electronic conductors. Moreover, the investigation on the electrodes utilise in ionic thermoelectric devices is discussed. Finally, the recent progress in novel applications of ionic thermoelectric systems, including ionic thermoelectric supercapacitors, transistors, and sensors, which utilise the materials mentioned above’ aggregate vital properties, is also discussed.

1. Introduction

Low-level heat energy (e.g., lower than 140 °C) from human bodies and combustion engines has attracted ever-growing attention because of imminent global environmental and energy challenges. As a result, the utilisation of thermoelectrics (TEs) is an efficient approach to recycling these power sources to generate electricity and provide the power supply for wearable electronic devices based on the Seebeck effect [1–4]. Conventional thermoelectrics based on both inorganic and organic materials [3, 5–9] includes electron diffusion under a temperature gradient (namely, the electronic Seebeck effect), which has been comprehensively investigated exhibits considerable progress in device performance. However, the inherently tiny Seebeck coefficients (generally on the order of 10–100 μVK−1) have hindered their practical utilization since the thermovoltage only originates from the electrons near the Femi level [10].

Recently, a novel perception called ‘ionic Seebeck coefficients’ discovered in the electrolytes to convert heat into electricity has been proposed, which are several hundred times larger than the electronic Seebeck coefficients in traditional thermoelectric materials [7]. The giant thermopower, reaching several mV K−1, was proved to result from the ionic Seebeck effect [8] primarily. When a temperature gradient is applied to an electrolyte, the internal ions will experience a thermal diffusion process until it reaches equilibrium. Finally, an ion concentration gradient is formed after the ions are reorganized (namely, the Soret effect). Such ionic Seebeck effect can be observed not only in ionic solids [11, 12], liquids [13–19] but also in gel electrolytes [20, 21] and inorganic solid electrolytes [22].

Among various ionic TE materials, polymer-based electrolytes have drawn tremendous attention because they exist as solids (solid solutions of electrolyte salts in polymers) or gels (‘ion gels’ of electrolytes trapped in polymers) [23] rather than liquids. The benefits offer great ease for device manufacturing, especially the attachment of devices or on curved surfaces. The ionic thermovoltage can originate from mainly two effects: thermogalvanic effect, typically in a thermogalvanic cell (TGC) [24–28]. This effect is due to the temperature-dependent entropy changes, which originates from the electron transfer between the electrode and redox molecules. The other is the Soret effect [24, 29, 30], which occurs in a redox-free electrolyte. This effect functions mainly through the electric double layer (EDL) [31], formed after the ions have accumulated at the electrodes. It
is noteworthy that both effects involve two key components: (i) electrodes to conduct currents and provide potentials and (ii) a polymer electrolyte to facilitate the ion movement. Electrodes coordinating with polymer electrolytes is another significant issue to address in ionic thermoelectric systems. Such electrodes include carbon nanotubes and graphene, which have greatly promoted the power output [24, 32–34]. Polymer electrolyte systems that have been intensively studied include poly(ethylene oxide) (PEO) [35], poly(vinyl chloride) (PVC) [26], and (vinyl alcohol) (PVA) [26, 36].

In this review, we make a summary of the latest progress in the ionic thermoelectric systems of organic polymer electrolytes and mixed ionic–electronic conductors based on organic polymers. Furthermore, we discuss the various novel electrodes that are indispensable components of ionic thermoelectric systems for energy conversion. The recent progress in novel applications of these electrodes is also summarized. Finally, a perspective on the future development of ionic thermoelectric systems based on polymer electrolytes is demonstrated.

2. Electrolyte materials

Apart from utilizing the traditional Seebeck effect [1–4], thermal-to-electrical energy conversion can also be achieved by the temperature-dependent electrochemical redox potential [13, 24, 37, 38], thermally driven ion diffusion [5, 7, 39, 40], or mixed ion/electron diffusion [8, 9]. In order to explore the potential of those physical processes to convert heat to electricity, numerous materials have been investigated to improve the thermoelectric performance, such as inorganic ionic solids [12] and liquid electrolytes [13, 18, 41–45], however, poor flexibility and leakage problems that impede their applications. The emergence of polymer-based electrolytes, as an alternative with unique properties of flexibility, lightweight, and superior processability, enables the development of novel ionic TE based facilities such as electrochromic displays [46], ion pumps [47], and ionic bipolar diodes [48]. This section will review the progress of the polymer materials developed for ionic thermoelectrics based on those as mentioned above three physical processes.

2.1. Polymer electrolytes with redox couples

In terms of thermal energy conversion based on polymer electrolytes, thermochemical cells (or thermocells, TECs) [13, 37] have been developed to build thermodynamic cycles through the thermoelectric effect. For a TEC, its redox electrolyte is usually filled in an aqueous or nonaqueous solution. Besides, for the current relatively novel TEC, the electrolyte has been filled in a solid-state membrane. Therefore, when a temperature gradient is applied to the electrolyte, a voltage proportional to the redox reaction entropy will be generated [49]. Regarding TECs, the initial investigations were centred on the thermal diffusion potentials, which were induced by the Soret effect under non-isothermal conditions [50–52].

To date, the redox couples of Fe(CN)$_6^{3−/4−}$ and Cu$^{2+}/$Cu dissolving in aqueous solutions has become the focus in the study of TEC [53–56]. Compared to aqueous solutions, TECs with novel polymer electrolytes, which provide high dielectric strength and good mechanical stability, have successfully triggered a new round of research. Figure 1(a) shows the operating mechanisms of a thermally chargeable supercapacitor [57], in which polystyrene sulfonic acid (PSSH) was employed as a solid electrolyte as well as a voltage generator. The change in H$^+$ concentration under a temperature gradient (Soret effect) electrochemically generates a potential between the two electrodes. Upon external connection, the PANI at the hot (emeraldine salt) electrode was oxidized while being reduced at the cold (emeraldine salt) electrode due to electron flow induced by the potential difference. At 70% relative humidity (RH), this solid electrolyte achieves the highest thermopower and electrical conductivity (approximately 7.9 mV K$^{-1}$ and 9 Sm$^{-1}$, respectively). Another kind of quasi-solid-state electrolyte is also of interest due to its achievement of an optimum balance of mechanical properties, Seebeck coefficient, diffusion coefficients and decent power output. Compared with liquid electrolyte systems, it consists of cellulose (5 wt%) matrix and infiltrated Ferr/ferrocyanide redox couple and shows a balance between $S_c (−1.38$ mV K$^{-1}$) and the optimal mechanical properties. Therefore, a power output of 14 mW m$^{-2}$ is reached (figure 1(b)) [58]. Inspired by the possible use of gel electrolytes in elasticionic devices [59–62], Zhou et al [63] used Poly(vinyl alcohol) (PVA) as the gel matrix to prepare wearable thermocells (figure 1(c)). After adding ferric/ferrous chloride (PFC) or potassium ferricyanide/ferrocyanide (PFP) couples, the integrated gel electrolytes for converting low-grade thermal energy exhibited positive or negative thermochemical Seebeck coefficients of 1.02 and $−1.21$ mV K$^{-1}$, respectively. Moreover, a 0.7 V open-circuit voltage and 2 mA short-circuit current can be generated from body heat through this stretchable ionic device, reaching a maximum output power (0.3 mW). Similarly, the common thermochemical electrolyte potassium ferricyanide and potassium ferrocyanide also can be made into an effectively gelled electrolyte by adding poly(sodium acrylate) beads as a gelling agent [64]. The gelled electrolyte possesses two advantages in heat conversion: a more stable power output. The other benefit is that heat transfer can be hindered effectively, which promotes thermoelectric conversion efficiency.
Therefore, the Seebeck coefficient improved to $-1.09 \pm 0.04$ mV K$^{-1}$ (figure 1(d)). Apart from the conventional electrolyte (K$_2$Fe(CN)$_6$/K$_3$Fe(CN)$_6$), for example, ionic liquid electrolytes have played an increasingly significant role in the field of ionic thermoelectric conversion. In this context, one practical approach is to add the polymers into nonvolatile redox-active ionic liquid electrolytes. By mixing polyvinylidene difluoride (PVDF) or its derivatives (PVDF-HFP) with an ionic liquid, Jennifer et al. [65] prepared soft gels and free-standing films based on the polymer content. (figure 1(e)). The Seebeck coefficients of the obtained quasi-solid-state electrolytes range from 1.50 to 1.56 mV K$^{-1}$, while the power output reduces because of the decrease of mass transport. Recently, Chen et al. [66] exploited polyacrylamide (PAAm) to fabricate an intelligent thermogalvanic (TG) hydrogel. The PAAm polymer chains provided a solid-state framework to contain the mixture of ions (Li$^{+}$, Br$^{-}$, Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$) and water. Notably, through the reuse of the redox couple (Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$), low-level heat can be converted into electrical energy under a temperature gradient. Meanwhile, considering the hydrogels’ regeneration, Li$^{+}$ and Br$^{-}$ ions were adopted to absorb water from the air to control the moisture equilibrium. Therefore, two separate thermodynamic cycles were built in the hydrogel. The heat-to-electricity conversion was achieved through thermogalvanic reaction, while the extra heat also promoted the evaporation of water to cool the solid framework. Finally, a Seebeck coefficient of 1.2 mV K$^{-1}$ and the corresponding optimal energy output (6 to 12 $\mu$W m$^{-2}$ K$^{-2}$) under 20 °C–60 °C were achieved from the intelligent thermogalvanic (TG) hydrogel (figure 1(f)). To date, Liu et al. [67] introduced a flexible, quasi-solid-state ionic thermoelectric gel with a maximum positive thermopower of up to 17.0 mV K$^{-1}$, which was

Figure 1. (a) Schematic diagrams of the operating mechanisms of a thermally chargeable supercapacitor. Reprinted with permission from [57]. Copyright (2016) Wiley-VCH. (b) Schematic illustration of a quasi-solid-state TEC with a cellulose-based electrolyte and its power output compared with liquid electrolyte systems. Reprinted with permission from [38]. Copyright (2016) American Chemical Society. (c) Schematic illustration of the integrated gel-based thermocell and its operating mechanism. Reprinted with permission from [65]. Copyright (2013) Wiley-VCH. (d) Photographs of the quasi-solid-state TEC with a cellulose-based electrolyte and its power output compared with liquid electrolyte systems. Reprinted with permission from [65]. Copyright (2016) Elsevier. (e) Photographs of the quasi-solid-state electrolyte [Co(bpy)$_3$Fe$^{2+/3+}$]$^{[NTf_2]$^2_2}$ in [C$_{6}$mim][NTf$_2$] with different contents of PVDF and PVDF-HFP, and the corresponding mechanical properties. All panels Reprinted with permission from [65]. Copyright (2018) Royal Society of Chemistry. (f) Schematic diagram of the structure and working principle of the smart thermogalvanic hydrogel. Reprinted with permission from [66]. Copyright (2020) American Chemical Society.
promoted by the combination of synergistic thermodiffusion and thermogalvanic effects. In their study, KCl was used as ion providers to modulate the gelatin matrix to promote the thermodiffusion effect. Meanwhile, Fe(CN)_4^{3-}/Fe(CN)_6^{4-} was selected as a redox couple for the thermogalvanic effect. Hence, these two effects’ synergy has demonstrated that the utilisation of ions as energy carriers has great potential in heat-to-electricity conversion.

2.2. Polymer electrolytes without redox couples

Unlike thermoelectric cells based on electrolytes with redox couples, ionic charge carriers’ utilisation in a redox-free electrolyte for the Soret effect has turned into a novel approach for energy harvesting, especially for polymer electrolyte systems. In this ionic thermoelectric material system without redox couples, ionic thermal diffusion (Soret effect) is the vital process for generating thermal voltage. Furthermore, at the electrolyte/electrode interfaces, the surface potential is dependent on the temperature, which also leads to the thermal voltage.

Polyethene oxide (PEO) has been extensively studied as a solid polymer electrolyte [68]. Herbert et al [69] investigated undoped PEO and detected its thermoelectric potential under a temperature gradient. A pair of aluminium electrodes were used to sandwich the samples, thus inducing the formation of oxide, which functioned as a blocking layer. When a temperature difference is applied, the electrolyte’s thermally activated ionic carriers diffuse from the hot end to the cold side (positive ions are migratory species). Furthermore, during the thermal diffusion of ions, the height of the energy barrier in the multiwell potential is the main factor determining the absolute value of the thermoelectric potential. To fully understand and utilise the ionic Seebeck voltage (similar to Seebeck potentials in conventional electronic thermoelectric materials), Xavier et al [70] investigated the ionic thermodiffusion behaviours of the polyelectrolyte polystyrene sulfonate sodium (PSS: Na) under different relative humidity and evaluated the charging efficiency of an ionic thermoelectric supercapacitor (ITESC) fabricated from it. The potential graph and a mechanism description of a complete charging and discharging circulation of the ITESC are depicted in figure 2(a). A positive ionic Seebeck coefficient of +4 mV K^{-1} was measured from PSS: Na (100% RH), which suggests that the entire thermal diffusion process is cation-dominated. Therefore, the experimental results remain consistent with expectations that the anions are almost immovable due to the large volume size.

In addition to the above material system, an ionic liquid (IL) mixed with a polymer electrolyte matrix has become a popular choice. In the ionic liquid-based electrolytes, both the anions and cations are migratory. When the interaction between the polymer matrix and ions changes, it leads to a complete change in the dominating thermodiffused ionic current from anions to cations. Normally, if the thermodiffusion of cations is easier than anions, the Seebeck coefficients in these electrolytes will show a positive value. (in analogy to solid-state semiconductors, which are defined as ‘p-type’). While for ‘n-type’ ionic thermoelectric materials with liquid-based electrolytes, negative Seebeck coefficients of about −1 to −2 mV K^{-1} due to the electrochemical reactions (i.e., thermogalvanic effect) at the electrodes have been reported [63, 74]. Notably, no ‘n-type’ ionic thermoelectric materials based on the pure Soret effect have been reported to date. Xavier et al [71] found that a vast negative ionic Seebeck coefficient also can be generated by an ‘ambipolar’ ionic gel. The gel consists of a water-free polymer matrix (PVDF-HFP) and the electrolyte ionic liquid ([EMIM][TFSI]). Notably, the conductive and thermodiffusion properties (−4 mV K^{-1} to +14 mV K^{-1}) of the polymer electrolytes will change as the liquid ionic content in the composite is adjusted (figure 2(b)). Similarly, Ouyang et al [72] fabricated eco-friendly flexible quasi-solid-state ionogels which were made of PVDF-HFP (figure 2(c)) and three different ionic liquids: 1-ethyl-3-methylimidazolium dicyanamide (EMIM: DCA), EMIM: TFSI and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM: BF4). Among them, the Seebeck coefficient of ionogels made of EMIM: DCA and PVDF-HFP can reach an impressive value of 26.1 mV K^{-1}, which is by far the highest reported value for electronic and ionic conductors. Finally, a ZT of 0.75 was achieved with the high ionic conductivity while low thermal conductivity (6.7 S cm^{-1} and 0.176 W m^{-1} K^{-1}, respectively). Similar material systems were also reported by Sabri et al [78].

Through in situ thermally initiated free-radical polymerisation, the IL N, N, N triethyl octyl ammonium bromide ([N2228] Br), water and 1 wt% of the azobisisobutyronitrile (AIBN) were confined in a polyethylene glycol dimethacrylate (PEGDMA) matrix to prepare a gel electrolyte. Eventually, the ionic conductivity of 74 mS cm^{-1} at 70 °C and a Seebeck coefficient of 1.38 mV K^{-1} was achieved. Then, they changed the type of IL from [N2228] Br to BMIMBF4, the concentration of which in the IGs (figure 2(d)) varied from 60 to 90 wt%. The ionic conductivity of the resulting IGs with 90 wt% BMIMBF4 reached 49.41 mS cm^{-1}, while the maximum Seebeck coefficient reached 2.35 mV K^{-1} at 60 wt% BMIMBF4 content [73].

To study single-ion conductors and their thermoelectric effect, Rachel et al [74] explored silver Nafion (Ag-Nafion) and silver polystyrene-sulfonate (Ag-PSS) with high ionic conductivity (figure 2(e)). Under a temperature gradient, a voltage was generated (Soret effect) through the diffusion of silver ions between the electrodes [79–82]. At RH > 50%, a positive/negative Seebeck coefficient of 5 mV K^{-1}/−2 mV K^{-1} for Ag-PSS.
were obtained. The maximum ZT of 0.006 and 0.003 were achieved for Ag-Nafion and Ag-PSS, respectively. To better understand the thermoelectric effects in recently developed polyelectrolytes, Choongho et al [75] performed comparative experimental studies on the RH (relative humidity)-dependent thermoelectric performance of three polyelectrolytes-cation conductors (figure 2(f)). The thermopower of the proton conductors (Nafion and S-PEEK) reached ~5.5 mV K\(^{-1}\), which increased remarkably with RH for S-PEEK but slightly decreased with RH for Nafion. For PVA-NaOH and PVA-H\(_3\)PO\(_4\), in which both cations and anions thermally diffuse, the thermopower is relatively small in absolute terms (1–1.5 mV K\(^{-1}\)) and unaffected by humidity. For PDDAC (anion conductor), the thermopower increased significantly to 19 mV K\(^{-1}\) because of the intense dissociation of Cl\(^-\) and immobilization of cations.

A new class of ionic thermoelectric materials containing cellulose has recently aroused much interest because of the simple, scalable and economical preparation method. Xavier et al [76] fabricated a polymer nanocomposite with nanofibrillated cellulose (NFC) and the polyelectrolyte PSSNa (figure 2(g)). The flexible and mechanically robust NFC-PSSNa thermoelectric film exhibited a high ionic conductivity/ionic Seebeck coefficient of 9 mS cm\(^{-1}\)/8.4 mV K\(^{-1}\), respectively. Hu et al [83] also demonstrated a cellulosic paper infiltrated with electrolytes. Under a temperature difference, the ions were constrained by neatly arranged molecular chains of cellulose, thus promoting the selective ion diffusion processes. The cellulosic film was firstly oxidized by TEMPO, followed by infiltration with a gel-like polymer electrolyte containing NaOH and PEO. In the cellulosic film with NaOH-based electrolyte, Na\(^+\) ions were well absorbed while the OH\(^-\) ions are expelled, leading to a 24 mV K\(^{-1}\) thermovoltage of the ionic conductor.

Very recently, Fang et al [77] reported TE ionogels prepared with WPU and EMIM: DCA (figure 2(h)). As the ionic liquid content increases, the ionic gel’s mechanical tensile strain also changes, which is up to 156% (40 wt% EMIM: DCA). Notably, at RH of 90%, the thermopower/ionic conductivity are 34.5 mV K\(^{-1}\)/8.4 mS cm\(^{-1}\),
respectively. Therefore, after testing the thermal conductivity \((0.23 \text{ W m}^{-1} \text{ K}^{-1}\)), ZT (ionic figure of merit) is calculated to be as high as \(1.3 \pm 0.2\).

In summary, considering the interactions between the polymer matrix and ions, the polymer electrolytes can be classified into three types: polyelectrolytes, ionic liquid-based electrolytes and composite electrolytes (table 1). For polyelectrolytes, the small charge carriers (cation or anion) are more mobile than the negative or positive charge attached covalently to the polymer chain. The varied mobility of these ions leads to the unbalanced concentration difference, thus inducing the generation of a potential difference between the cold and hot side. For ionic liquid-based electrolytes, both the cations and anions are mobile. Hence, when the interaction between the polymer matrix and ions changes, it leads to a complete change in the dominating thermodiffusion of ionic current from anions to cations, thus triggering a thermal voltage under temperature difference. Compared with polyelectrolytes and ionic liquid-based electrolytes, composite electrolytes are prepared from the composite of polyelectrolytes with ‘water-soluble’ ions (i.e., NaOH treated polyethene oxide (PEO)) or with polymers matrix (i.e., PSSNa-nanofibrillated cellulose (NFC)). They are more complex than the first two polymer electrolytes because many factors might have a giant impact on the thermodiffusion in those complex systems, which are hydrogen bond capability of a solute [84], interface effect and nanoporosity [83]. Therefore, the mechanism of interaction between ions and electrolytes in composite electrolytes has not been fully understood to date.

### 2.3. Mixed organic ionic-electronic conductor materials

This section presents a brief review of a unique material system, mixed organic ionic-electronic conductor materials, which can transfer not only electronic charge carriers but also ionic carriers. First, poly(3,4-ethylene dioxythiophene) (PEDOT), as the most explored conjugated polymer, has a distinguished property of transporting electronic as well as ionic carriers. Nevertheless, to date, it is mainly the electronic thermoelectric (TE) effect in PEDOT that has been extensively studied, while the ionic TE effect has barely been reported. Recently, Xavier et al [8] investigated five PEDOT derivatives (where PEDOT: PSS is used as a comparison group) and illustrated ions’ function in the thermoelectric effect. Compared to the potential (several or dozens of \(\mu\)V/K) generated by the pure electronic TE effect, the voltages triggered by the ionic Seebeck effect under temperature difference can increase to hundreds of \(\mu\V/K\) at high humidity (figure 3(a)). Two parts contribute to the voltage: nonconstant and constant parts prompted by ions and electronic carriers. Therefore, under intermittent heat, significant improvements in the thermoelectric conversion efficiency can be achieved with ionic-electronic conductor materials. To further explore the internal mechanism of the ionic Seebeck effect, Xavier et al [85] further investigated the open-circuit voltage \(V_{oc}\) (time curves of three ionic-electronic conductor materials (PEDOT-PPS, PEDOT-Tos and PSSNa) (figure 3(b)). The results suggest that the ionic thermoelectric effect leads to electrochemical reactions within the conductive polymer layer. Hence, based on the above research, Magnus and Xavier et al [86] summarized the recently built views of two characteristics of PEDOT [87] that are closely related to the ionic thermoelectric properties: the mixed ion-electron charge transfer properties and the bulk capacitance. Furthermore, they also describe the phenomenon of ion-electron coupling, which occurs during the accumulation of charge in conducting polymers and in the compensation of ionic charges provided by electrolytes.

Apart from the above mixed organic ionic-electronic conductor materials, another proton-doped mixed ionic conductive (PMIC) membrane for robust thermoelectric harvesting was explored by Kim et al [88]. In the composite films with highly doped PEDOT: PSS, a metal–organic framework (MOF) is used to harvest airborne

| Types                    | Polymer electrolytes | References |
|--------------------------|----------------------|------------|
| Polyelectrolytes         | PEO                  | [69]       |
|                          | PSS: Na              | [70]       |
|                          | Ag-Nafion            | [74]       |
|                          | Ag-PSS               | [74]       |
|                          | Naion                | [75]       |
|                          | S-PEEK               | [75]       |
|                          | PDDAC                | [75]       |
| Ionic liquid-based electrolytes | PVDF-HFP/IL          | [71]       |
|                          | PVDF-HFP/IL          | [72]       |
|                          | PEGDMA/IL            | [73]       |
|                          | WPU/IL               | [77]       |
| Composite electrolytes   | NFC-PSSNa            | [76]       |
|                          | cellulosic film/     | [83]       |
|                          | NaOH/PEO             |            |
moisture, while the hydrogel layer is used for the storage of water and doping agents. Thus, the Seebeck coefficient of the composite film is above 16.2 mV K\(^{-1}\) when 30 wt% poly(styrene sulfonic acid) (PSSH) is added to dope the PEDOT: PSS (figure 3(c)). Additionally, with the assistance of a self-humidifying layer (MOF/HG), a constant RH of 90% and a stable Voc at ambient conditions were provided to achieve sustainable, robust TE harvesting. Based on the distinguished properties of mixed ionic-electronic conductors (MIECs), Xavier et al [89] fabricated aerogels of polymeric MIECs with four components (figure 3(d)) by freeze-drying their blended water emulsion. In the aerogel, electronic/ionic thermoelectric potentials generate through the ionic-electronic conductor material (PEDOT: PSS). Simultaneously, the superior strength and elasticity originate from nanofibrillated cellulose (NFC) and glycidoxypropyl trimethoxysilane (GOPS) [90]. The fabricated aerogels can sense pressure, temperature, and humidity independently, thus greatly facilitating the design and manufacture of low-cost, versatile thermoelectric devices.

3. Electrode materials

Electrodes have rapidly become a research hotspot as crucial components of novel ionic thermoelectric devices prepared from the above material systems. The electrolytes commonly used in thermoelectric devices are mainly liquid electrolytes and the material systems (solid or quasi-solid-state electrolytes) mentioned above. Furthermore, it is worth noting that the electrode materials used in these devices are essentially similar. Therefore, in this section, we mainly introduce the representative electrodes used in ionic thermoelectric units such as ionic thermoelectric supercapacitors and thermogalvanic cells that contain liquid electrolytes or the

Figure 3. (a) Performance testing for five different PEDOT derivatives. Reprinted with permission from [8]. Copyright (2015) WILEY-VCH. (b) Electrical conductivity-humidity curve and Voc-time curve for PEDOT-Tos, PEDOT-PSS and PSSNa. Reprinted with permission from [85]. Copyright (2016) WILEY-VCH. (c) Thermoelectric properties of films with different doping levels (left) and the charging process of thermal supercapacitor (right). Reprinted with permission from [88]. Copyright (2018) WILEY-VCH. (d) Chemical structures of the components (left) and optical images of MIEC aerogel used in a pressure-temperature-humidity sensor (right). Reproduced from [89]. CC BY 4.0.
above three material systems. The electrodes can be classified mainly into three types: (i) metal electrodes, (ii) carbon material electrodes, and (iii) conductive polymer electrodes.

Metal, as the most common electrode material, was first used in thermogalvanic cells. Among metals, platinum (Pt) has been investigated as an electrode in TGCs for decades due to its superior conductivity and chemical inertness, making it the most widely applied electrode material for TGCs [56, 91, 92]. Recently, Jiao et al. [14] reported a 0.5 mm thick platinum wire electrode for a thermoelectrochemical device in which ILs containing cobalt redox couples were used as electrolytes. Similarly, Jennifer et al. [93] employed platinum disk electrodes deposited from Pt black to improve the power generation of the thermoelectrochemical system. The cobalt redox couples were dissolved in a dispersion system containing an IL and a molecular solvent, resulting in a liquid electrolyte. Hence, when the mass ratio of redox couples in the electrolyte is optimal, the electrochemical device’s power density is up to 880 mW m$^{-2}$ at a temperature difference of 70 K. In addition to liquid electrolytes with metal electrodes, Jennifer et al. [94] also demonstrated platinum disk electrodes corporated with gelled electrolytes in thermocells. For gel electrolytes, the addition of PVDF and PVDF-HFP is required to gel the electrolyte after the redox couples were added to the organic solvent. Therefore, at a temperature gradient of 40 K, the optimal thermocell power density is up to 23 mW m$^{-2}$.

In addition to metals, carbon materials have also been chosen as electrode materials in recent years. Carbon materials like carbon nanotubes possess continuous electrical and thermal conductivity networks and, more importantly, an intrinsically high specific surface area, thus accelerating the redox reactions on their surfaces [95]. In the electrochemical energy system [49], the desired carbon electrode materials can provide the electrolytes with a sufficient mass transport channel and efficient charge transport network, which are indispensable for the high power density and conversion efficiency. Therefore, the carbon nanotubes array has demonstrated unprecedented advantages as electrode material in an electrochemical energy system. Its high specific surface area leads to a higher exchange current density between the electrode and electrolyte [96]. Meanwhile, the low tortuosity of the pore structure promotes efficient ion accessibility, which ensures sufficient redox molecules needed for electron generation or consumption, thus promoting the continuous generation of power in a thermocell.

Hu et al. [24] reported multiwalled carbon nanotube (MWNT) buckypaper electrodes, which lead to a 1.4% Carnot cycle efficiency. Furthermore, a hybrid electrode made of single-walled carbon nanotube (SWNT) and reduced graphene oxide (rGO) was introduced to the thermocell by Chen et al. [34]. Notably, the Carnot cycle efficiency rose to 2.63% by optimizing the electrode composition and thickness. Moreover, the Carnot cycle efficiency was further raised to 3.95% by Kim et al. through the fabrication of carbon nanotube aerogel-based thermoelectrochemical cells (figure 4(a)) [19].

To increase the power density of thermocells, Li and co-workers [97] designed and fabricated the anisotropic holey graphene aerogel (AHGA) electrodes. Firstly, they reduced porous graphene oxide liquid crystals into graphene sheets through an in situ reduction technique and then assembled them into aerogel electrodes (figure 4(b)). Hence, a 3.6 W m$^{-2}$ power density and a 1.3 mV K$^{-1}$ Seebeck coefficient were achieved by the single thermocell of 1.3 mV K$^{-1}$.

To improve the charge transfer at the interface between the electrolyte and electrodes, Kang et al. [100] developed an activated carbon textile (ACT) electrode. After coating with CNTs, the ACT electrodes were used in a thermocell, exhibiting a 0.46 mW m$^{-2}$ power density. Kang et al. [98] also employed a CNT / Pt mixed electrode, in which porous CNT sheets wrapped a Pt wire, thus leading to the fabrication of a tubing-shaped, flexible thermocell (figure 4(c)). Therefore, compared with pure Pt wire, the CNT / Pt mixed electrodes exhibited higher power density and short-circuited current density. Kang’s group [101] has recently reported a double-walled carbon nanotube (DWCNT) composite sheets electrodes. The ion transfer efficiency improved because of the aligned sheet structure. Therefore, the output power is up to 200 mW m$^{-2}$ with 3-layer DWCNT sheets, indicating an impressive enhancement in the electrodes’ performance. Ray et al. [18] used activated carbon cloth (A-CC) as thermocell electrodes to take advantage of its high specific surface area. Besides, multiwalled carbon nanotube (MWNT) foam and carbonized cork were also adopted as electrodes for further investigation. Overall, the highest power density of 1.2 W m$^{-2}$ was obtained with activated carbon cloth electrodes.

Another type of electrode material for TGCs is conductive polymers. To improve the thermogalvanic device efficiency, Jennifer et al. [102] introduced a range of novel electrode materials to TECs, including PEDOT–Pt and PEDOT–Stainless steel, which demonstrated high maximum output powers of 233 mW m$^{-2}$ and 179 mW m$^{-2}$, respectively. Moreover, a novel conductive polymer-based electrode using PEDOT–Tos without a supportive metal (figure 4(d)) was investigated by Xavier’s group [99]. The results show that TGCs with PEDOT–Tos as electrodes produce essentially the same power as TGCs with platinum as electrodes.
4. Applications

At present, almost all industrial thermoelectric devices’ main functional components in practical applications are made of inorganic material systems. Correspondingly, from the perspective of organic material systems, mature device manufacturing and industrialization processes have not been implemented. Their application prospects tend to be more dependent on researchers’ conceptual ideas. However, with the in-depth exploration of researchers, organic material systems’ thermoelectric performance has been dramatically improved, thus spawning their vast application potential. Therefore, in this section, we review the representative potential applications (or devices) of organic ion thermoelectric material systems, such as thermally chargeable supercapacitors, organic electrochemical transistors, and sensors.

First, an ITESC is a novel thermoelectric concept with great potential for applications in boosting thermal potential. Recently, for the first time, Xavier et al [7] demonstrated the ionic Soret effect in a polymer electrolyte (PEO-NaOH) under a temperature difference (figure 5(a)). The thermal voltage generated by electrolytes through the Soret effect was employed to charge a supercapacitor. Therefore, when the external circuit is switched on with removing the temperature difference, a conversion from temperature difference to electrical energy is completed. Furthermore, Xavier’s et al [70] also investigated the polyelectrolyte PSS, another pure ionic thermoelectric material, which can be charged by temperature gradient at different humidities. Therefore, PSS was used as the electrolyte of an ITESC, and the equivalent expression for the charging efficiency can be expressed by the figure of merit \(Z_{T1} = \sigma \alpha_i 2T / \lambda\) (figure 5(b)). Similarly, a polystyrene sulfonic acid (PSSH) film was reported by Choongho’s group [57]. The output voltage is up to 8 mV K\(^{-1}\) due to the efficient thermally driven ion diffusion. Voltage-enabled electrochemical reactions were thermally induced in the PSSH film sandwiched by polyaniline-coated electrodes, resulting in charging behaviour. Therefore, the thermally
chargeable supercapacitor produced a voltage of 38 mV and a large areal capacitance of 1200 F m$^{-2}$ under a small temperature gradient of 5 K.

He and co-workers [103] recently reported quasi-solid state ionogels made of ionic liquids (1-ethyl-3-methylimidazolium dicyanamide, EMIM-DCA) and SiO$_2$ nanoparticles, exhibiting high thermovoltage and ionic conductivity. At room temperature, a 4.75 $\times$ 10$^{-2}$ S cm$^{-1}$ ionic conductivity and 14.8 mV K$^{-1}$ ionic Seebeck coefficient were achieved, resulting in an equivalent ionic ZT$_1$ value of 1.47, proven the ionogels a superior candidate in the application of ITESCs for efficient thermal harvesting (figure 5(c)).

Regarding applications in transistors with polymer electrolytes, electrolyte-gated transistors (EGTs) have been comprehensively summarized by Frisbie’s group [105]. However, the ionic thermoelectric properties (or ionic Seebeck effect) of the transistors’ electrolytes were not investigated or utilised in the review. To verify that the voltage generated by the ion Seebeck effect can be used for gating of organic transistors, Xavier et al [104] developed an external heat-gated organic transistor fabricated by polymer electrolytes, producing a thermopower up to 10 mV K$^{-1}$ (figure 5(d)). Under a temperature difference $\Delta T$, a large thermoelectric voltage induced by the Soret effect in the ionic thermoelectric leg was applied to gate the transistor effectively. Therefore, it is feasible to convert $\Delta T$ to a modulated signal of drain current $\Delta I$ using this organic transistor.

Under a temperature difference, two processes can occur in an ionic polymer electrolyte: the redox reactions at two electrodes through the thermogalvanic effect or thermodiffusion of ions through the Soret effect. Therefore, a novel flexible temperature sensor also sparked interest in using the thermal voltage to measure temperature or sense heat flow. Inomata et al [106] reported an organic temperature sensor with an 8.94 mK temperature resolution and a 10.6 mV K$^{-1}$ thermopower. In addition to the three electrodes and a heating stage, the essential part of the sensor is two microfluidic reservoirs, filled with a polymer electrolyte polyethylene.
glycol-NaOH (PEG-NaOH) and an aqueous iodine solution, respectively. Therefore, this sensor’s output voltage changes linearly with temperature when there is an external temperature input. Xavier et al.[71] demonstrated a nonaqueous ‘ambipolar’ temperature sensor made of electrolyte gel (figure 5(e)). Moreover, it is worth noting that an ionic thermoelectric module can be constructed by connecting ionic thermocouples prepared from polymer electrolytes, which exhibits an adjustable Seebeck coefficient and an optimum value of $0.333 \text{ V K}^{-1}$.

5. Summary and perspectives

To conclude, polymer electrolytes and electrodes are critical and indispensable components in developing novel ionic thermoelectric devices converting thermal energy into electrical energy. Compared with organic TE materials subjected to low Seebeck coefficients and the limitation of high-temperature applications, ionic thermoelectric materials have higher Seebeck coefficients by several orders of magnitude, demonstrating greater potential in thermal harvesting. First, there are two distinctly different mechanisms for direct thermal harvesting for pure ionic systems: the thermogalvanic effect and the Soret effect. Under a temperature gradient, the thermogalvanic effect triggers a redox reaction between the electrolyte and the electrodes, resulting in an output voltage or current to the external load. Therefore, devices that perform thermoelectric conversion primarily with this effect are called thermogalvanic cells[107, 108]. Compared with the thermogravimetric effect, the Soret effect[20, 29] mainly promotes the thermodiffusion process of ions in the electrolyte at a temperature difference without redox reactions. These two mechanisms have extensively promoted thermopower by working individually or simultaneously. Second, for polymer mixed conductors (e.g., PEDOT: Tos) at temperature difference, current and voltage is induced mainly from two parts: the electronics contribute a regular part while the ions contribute a nonconstant part. Moreover, in mixed ionic-electronic conductors, the maximum power factor can be enhanced by the ion Seebeck effect by two to four orders of magnitude. Therefore, by combining quasi-solid polymer electrolytes involving the above-mentioned ionic thermoelectric mechanisms with suitable electrodes, the outstanding benefits of nonvolatility, stretchability, reduced thermal convection, and zero solvent leakage can be achieved.

However, there are still some existing disadvantages in polymer electrolyte-based ionic thermoelectric systems and polymeric mixed conductors. First, although high Seebeck coefficients and low thermal conductivities are achieved by ionic thermoelectric systems and polymeric mixed conductors, the ZT values are typically below 0.1, mainly because of the low ionic conductivities ($\sigma$) and electronic conductivities ($\sigma_e$) (for mixed ionic-electronic conductors). Then, for hydrogel electrolyte ionic systems, issues such as water loss, volume shrinkage and ageing caused by oxygen have yet to be resolved, which will lead to poor durability. Besides, the electrodes, as integral components of the above material systems, need to be designed in their structure and chemistry to fully incorporate the physical and chemical contributions of the electrolyte, thus converting heat into electricity efficiently. Therefore, the electrodes’ optimisation, including stability, specific surface area and current density, for their continuous operation is still a challenge. Finally, the low energy conversion efficiencies and low areal output power have restricted their industrial applications, partly due to the difficulties in manufacturing and scalability.

Despite the considerable challenges encountered thus far, tremendous opportunities still coexist with this field’s inspiring progress. It is foreseeable that with the advent of the era of soft energy supply devices, the integration of polymer electrolytes and stretchable electrodes into innovative ionic thermoelectric systems consisting of multiple flexible components will become a trend. These ionic thermoelectric systems contain sustainable power harvesting, energy storage, actuation and sensing units and will become an increasingly crucial interdisciplinary topic shortly.

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Conflicts of Interest

The authors declare no conflict of interest.

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