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# Research Progress of Ionic Thermoelectric Materials for Energy Harvesting

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## Abstract

Thermoelectric material is a kind of functional material that can mutually convert heat energy and electric energy. It can convert low-grade heat energy (less than 130°C) into electric energy. Compared with traditional electronic thermoelectric materials, ionic thermoelectric materials have higher performance. The Seebeck coefficient can generate 2–3 orders of magnitude higher ionic thermoelectric potential than electronic thermoelectric materials, so it has good application prospects in small thermoelectric generators and solar power generation. According to the thermoelectric conversion mechanism, ionic thermoelectric materials can be divided into ionic thermoelectric materials based on the Soret effect and thermocouple effect. They are widely used in pyrogen batteries and ionic thermoelectric capacitors. The latest two types of ionic thermoelectric materials are in this article. The research progress is explained, and the problems and challenges of ionic thermoelectric materials and the future development direction are also put forward.

**Keywords:** thermoelectric materials, pyrogen batteries, ionic thermoelectric capacitors

## 1. Introduction

Thermoelectric material is a kind of functional material that can mutually convert heat energy and electric energy. It can convert low-grade heat energy below 130°C into electric energy, so it has good application prospects in small thermoelectric generators and solar power generation. Traditional electronic thermoelectric materials are divided into inorganic thermoelectric materials and organic thermoelectric materials: inorganic thermoelectric materials include Bi<sub>2</sub>Te<sub>3</sub> [1], PbTe [2], SiGe [3], etc. and their alloys, due to their high thermal conductivity, mechanical strength, and thermoelectric conversion efficiency, they have been widely used in thermoelectric coolers, thermoelectric generators, etc., but there are problems such as high price, complicated processing technology and easy to produce heavy metal pollution; organic thermoelectric materials is a kind of conductive polymer with conjugate structure polymers, mainly polyaniline, polypyrrole, polythiophene and its derivatives [4], etc., this kind of conductive high molecular polymer has good flexibility, low price, safety and pollution-free, and gradually replaces inorganic thermoelectric materials into people's field of vision. However, the Seebeck

coefficient of organic thermoelectric materials is very low, there are problems such as low conductivity and power factor, low thermoelectric conversion efficiency, etc., usually need doping modification, composite with carbon materials [5], inorganic thermoelectric materials [6] and other methods to improve their thermoelectric performance.

With the development of materials science, a new type of thermoelectric material-ionic thermoelectric material has gradually entered people's field of vision. Compared with traditional electronic thermoelectric materials, ionic thermoelectric materials have a higher Seebeck coefficient (usually several hundred times higher than traditional thermoelectric materials) and can generate 2–3 orders of magnitude higher ion thermoelectric potential than electronic thermoelectric materials, such materials have a wide range of applications in pyrogen batteries and ion thermoelectric capacitors.

The evaluation of the thermoelectric performance of thermoelectric materials is usually expressed by the dimensionless thermoelectric figure of merit  $ZT$ :

$$ZT = \frac{\sigma S^2}{\kappa} \quad (1)$$

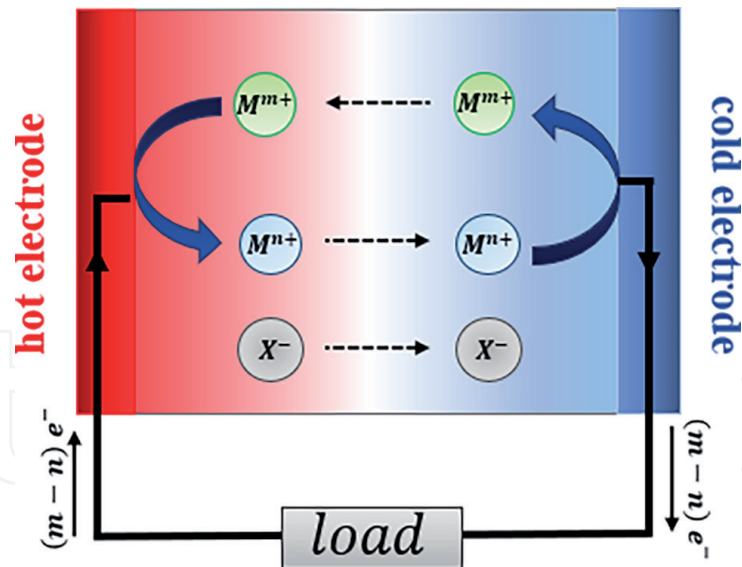
Among them,  $T$  is the absolute temperature,  $S$  is the Seebeck coefficient, which represents the inherent electron transport performance of thermoelectric materials, and is also the most basic parameter that determines the thermoelectric effect of the material;  $\sigma$  is the electrical conductivity, which represents the current transport capacity of the thermoelectric material;  $\kappa$  is the thermal conductivity, which is a performance parameter to measure the heat transfer of materials. Thermoelectric materials with excellent performance should have high electrical conductivity and Seebeck coefficient, as well as low thermal conductivity. In addition, when investigating the conversion efficiency of thermoelectric generators, the power factor  $PF = \sigma S^2$  will also be used.

The thermoelectric power of traditional electronic thermoelectric conversion materials comes from the migration of internal electrons under a temperature gradient, while the thermoelectric power of ionic thermoelectric materials comes from ion migration under temperature differences. This effect is also called the ion Seebeck effect, or Soret effect, the made thermoelectric device is called an ion thermoelectric capacitor. In addition to this way of generating thermoelectric potential, ionic thermoelectric materials have another source of thermoelectric potential: when a redox pair is used in the material, redox reactions occur on both sides of the material electrode, and the entropy change in the reaction is used to achieve heat energy to electrical energy. This effect is called the thermocouple effect, and the thermoelectric conversion device made is called pyrogen cell.

This article reviews the research progress of ionic thermoelectric materials based on the Soret effect and thermocouple effect, combs the thermoelectric conversion mechanism of such ionic thermoelectric materials used in energy conversion systems, and summarizes the research of various new electrolytes and electrode materials. Progress. Finally, the future development direction of ionic thermoelectric materials is prospected.

## 2. Ionic thermoelectric materials for pyrogen batteries

Ionic thermoelectric materials with added redox couples mainly use the temperature effect between the redox pairs, which is the thermocouple effect. The



**Figure 1.**  
 Working mechanism of TGC device.

redox reaction occurs between the redox couple and the electrode in the material electrolyte, and the temperature gradient promotes the two types of electrons. The migration and diffusion of the opposite electrodes use the entropy change of the reaction to realize the conversion from thermal energy to electrical energy. The thermoelectric conversion device made based on this redox pair is called a thermogenic cell (TGC).

## 2.1 Thermogenic battery (TGC)

The redox-active electrolyte in the pyrogen cell undergoes oxidation/reduction reactions on the electrodes on both sides to produce aggregation, and spontaneously moves to the other electrode under the concentration and temperature gradient, while the electrons generated by the reaction can enter and exit the electrodes to achieve current flow continuous output, the pyrogen battery has the advantages of low maintenance cost and long-term stable operation.

The thermogenic battery consists of two identical electrodes and an electrolyte containing a redox pair, and its operating mechanism is shown in the **Figure 1** below. When the temperature of the electrodes on both sides is inconsistent, the redox pair (such as  $M^{m+}$ ,  $M^{n+}$ ) moves to both sides of the electrode under the action of the temperature gradient, and oxidation/reduction reactions occur respectively at the electrode/electrolyte interface, and the electrons lost or gained in the reaction. The directional migration occurs through the external circuit to form a current. At the same time, the ions gathered around the electrode after the reaction will migrate to the other electrode under the action of the concentration gradient through the electrolyte solution and continue to undergo the reduction/oxidation reaction, thereby maintaining the continuity of the current output in the entire battery, and the two ends of the electrode are maintained stable and constant potential difference, the magnitude of the potential difference depends on the entropy value of the redox pair.

In the thermogenic battery, the Seebeck coefficient is determined by the partial molar entropy difference of the redox pair [7]:

$$S_e = \frac{\Delta V}{\Delta T} = \frac{S_B - S_A}{nF} \quad (2)$$

Among them,  $S_A$  and  $S_B$  are the partial molar entropy of the redox pair,  $\Delta V$  is the open-circuit voltage on both sides of the electrode,  $\Delta T$  is the temperature difference between the hot and cold ends of the electrode, and  $n$  is the number of electrons transferred in a unit reaction. The entropy change includes the entropy change caused by the electrode reaction, various transfer entropies, and the transmission entropy of electrons. This entropy change will change significantly with the properties of the redox couple. At the same time, the solvent environment also affects the entropy change.

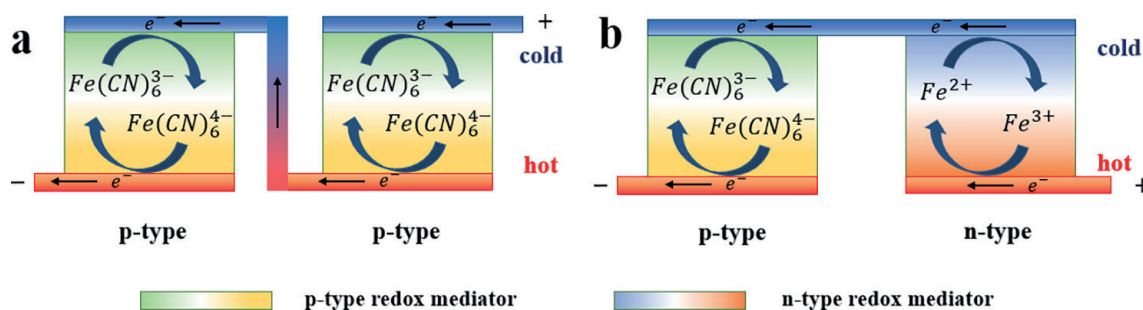
## 2.2 Electrolyte materials

At present, the most widely used electrolyte material in thermogenic batteries is gel electrolyte, which has high ionic conductivity and flexibility and can also hinder the overall heat conduction of the battery and prevent electrolyte leakage. Gel electrolyte is usually composed of polymer matrix and electrolyte added with redox pair. The cross-linking of the polymer provides mechanical strength and a certain network support space, in which redox ions migrate freely and move to the electrodes on both sides for redox reaction. Ionic thermoelectric materials are classified into p-type and n-type thermoelectric materials according to the positive and negative of the ion Seebeck coefficient, and the redox pairs contained therein are also called p-type and n-type redox pairs, respectively.

In order to effectively collect waste heat, stacking individual thermocouples together to form a battery-like series structure can increase the potential output of the thermogenic battery exponentially. However, if only a single type of redox couple is used, a hot-cold-hot short circuit between adjacent units will occur (as shown in **Figure 2**). Take the p-type redox couple  $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$  as an example, If the same type of thermocouple is used, the hot end of the thermocouple must be connected to the cold end of the next thermocouple by wire, which will cause unnecessary heat transfer between the hot end and the cold end. Therefore, the TEC device is made by connecting n-type thermocouples and p-type thermocouples in series, and the polarity of the battery can be replaced by using alternating n-type thermocouples and p-type thermocouples, so as to reduce unnecessary heat transfer, simplify the manufacturing process of the device and realize the effective utilization of heat energy.

### 2.2.1 n-type redox couple

Commonly used n-type redox pairs include  $\text{Co}(\text{bpy})_3^{2+}/^{3+}$ ,  $\text{Fe}^{2+}/^{3+}$ ,  $\text{I}^-/\text{I}_3^-$ , etc., and their Seebeck coefficients are negative.  $\text{Co}(\text{bpy})_3^{2+}/^{3+}$  is a more commonly used



**Figure 2.**

*Hot-cold-hot short-circuit phenomenon of TGC. a) Illustration of two in-series-connected p-type half-cells that both use aqueous  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  as the redox mediator. b) Illustration of a p-type half-cell (using aqueous  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  as the redox mediator) and an n-type half-cell (using aqueous  $\text{Fe}^{2+}/\text{Fe}^{3+}$  as the redox mediator) that are connected in series.*

n-type redox pair. In the redox reaction, electron transfer will cause changes in the spin state of the central ion  $\text{Co}^{2+/3+}$ , causing additional entropy effects. This redox pair has low solubility in water and is often used in organic solvents or ionic liquid electrolytes.  $\text{Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  has a higher Seebeck coefficient in organic solvents. Jiao et al. first tried to use  $\text{Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  as a redox couple, and it has been applied to five different ionic liquid systems [8], and found that it has lower thermal conductivity in the  $[\text{C}_{2\text{mim}}][\text{NTf}_2]$  system, which is  $0.16 \text{ W}/(\text{m}\cdot\text{K})$ . When using  $0.1 \text{ M Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  pairs, the maximum output power of TEC reaches  $77 \text{ mW}/\text{m}^2$ .

In addition to ionic liquids, gelling agents can also be used to prepare quasi-solid gel electrolytes to prevent electrolyte leakage. Pringle et al. used polyvinylidene fluoride (PVDF) and polyvinylidene fluoride co-fluoropentene (PVDF-HFP) as gelling agents [9], using a hybrid gel method to prepare gel electrolytes. By optimizing the concentration of redox pairs and the interval between cold and hot electrodes, the performance of the thermoelectric battery was further improved. On this basis, Pringle et al. added 5% biphasic cellulose and used a solvent exchange method to prepare an electrolyte gel containing  $\text{Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  redox couple [10]. The use of this cellulose structure as the transmission network of redox couples avoids the toxicity of organic solvents and the risk of flammability and leakage. Cellulose also provides mechanical flexibility for gel electrolytes and provides new ideas for the development of human wearable devices. In addition, Laux et al. combined the  $\text{Co}^{2+/3+}(\text{bpy})_3(\text{TFSI}_2)_{2/3}$  redox pair with choline lactate, and its Seebeck coefficient was increased to  $-3.63 \text{ mV}/\text{K}$  [11].

Another type of n-type redox couple is  $\text{Fe}^{2+/3+}$ , which has good chemical stability in water and is also used as a redox couple for thermogenic battery electrolytes. Polyvinyl alcohol (PVA) has good mechanical tensile properties, non-toxic and environmentally friendly, hydrophilic and high-temperature resistant, and has low production cost.  $\text{Fe}^{3+}$  makes the solution strongly acidic under the action of hydrolysis, which can just maintain the acidic gel environment required by PVA, so PVA is often added to  $\text{Fe}^{2+/3+}$  to prepare gel electrolyte. Zhou et al. prepared a PVA- $\text{FeCl}_2$  film [12], the power density of which exceeds the Co redox couple. On this basis, he also added HCl solution [13], which significantly improved the mechanical tensile properties of the gel and synergistically reduced the charge transfer resistance. This type of gel has good thermoelectrochemical properties. In addition, phosphoric acid ( $\text{H}_3\text{PO}_4$ ) can also significantly increase the ionic conductivity of PVA-based polymer electrolytes. This type of gel electrolyte has broad application prospects in supercapacitors, fuel cells, and lithium batteries.

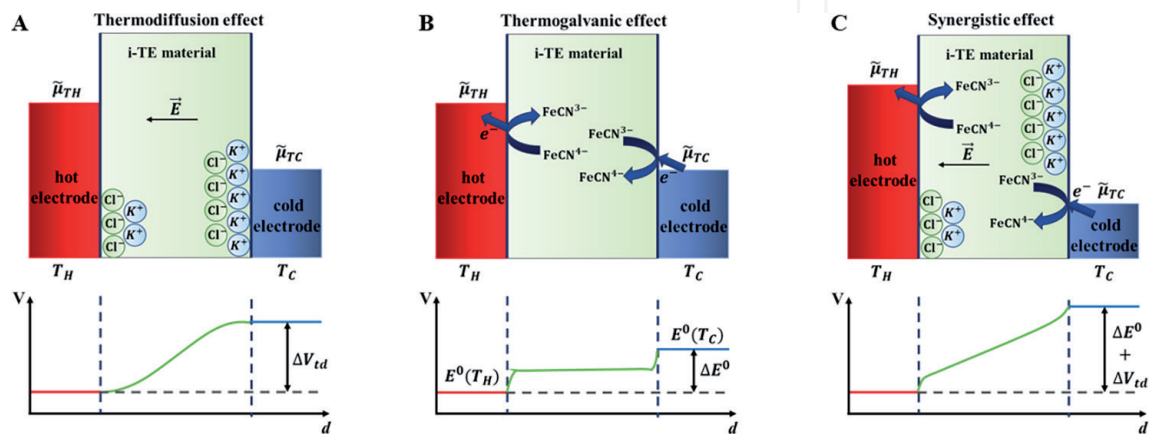
### 2.2.2 p-type redox pair

Zhou et al. used PVA as a gel solution and added  $\text{FeCl}_3/\text{FeCl}_2$  or potassium ferricyanide/potassium ferrocyanide as two redox pairs to obtain a quasi-solid ion gel with positive (PFC) or negative (PPF) Seebeck coefficients. Glue [12], and fabricated an integrated wearable thermal battery, this thermal battery has excellent mechanical properties and thermoelectric properties can be used for low-level thermal energy conversion. The mechanism of PFC and PPF gel generating thermoelectric voltage is similar to the transfer mechanism of pure  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  in an aqueous solution. The charge is not through the migration of electrons or holes in the conductor, but it is the migration of ions under the action of temperature difference. This integrated wearable device can use body heat to generate an open circuit voltage of about  $0.7 \text{ V}$  and a short circuit current of  $2 \text{ mA}$  and achieve a maximum output power of about  $0.3 \text{ mW}$ .

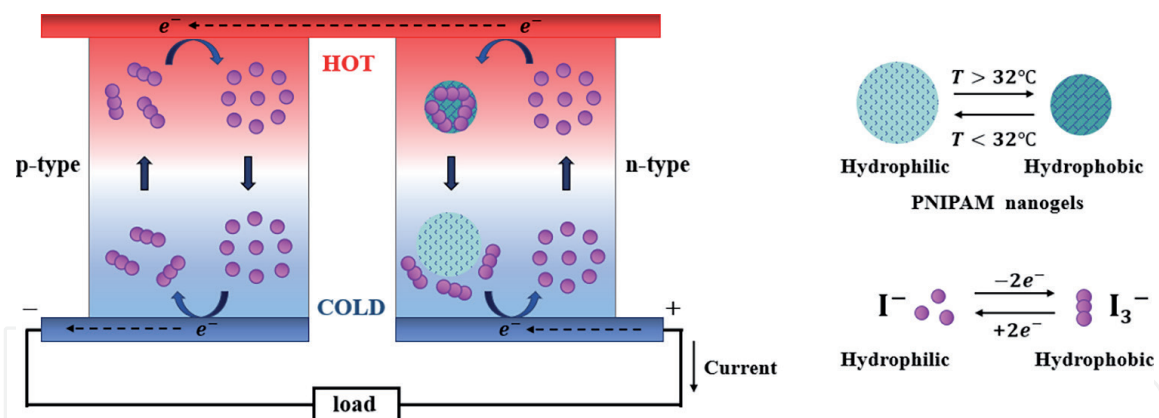
The above-mentioned  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  is the most typical p-type redox pair. Aldous et al. studied the water-based thermal battery containing  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  as gel electrolyte and compared the interaction between traditional gels such as  $\text{SiO}_2$  nanoparticles and agar, and new gelling materials of sodium polyacrylate beads, and the aqueous solution system [14]. This kind of three-dimensional network crosslinked polymer is self-assembled by hydrogen bonding and hydrophobic interaction, which can fix electrolyte solution in situ. Experiments show that fumed silica cannot form an effective gel in a neutral solution and is mainly used in a strongly acidic gel electrolyte. The effective, uniform, and transparent gel electrolyte can be formed by mixing 5.5 wt% sodium polyacrylate beads in 0.1 M  $\text{Fe}(\text{CN})_6^{3-/4-}$  solution and the maximum efficiency of thermocouple is twice higher than that of the liquid thermocouple.

Cellulose is an environmentally friendly biomaterial, and it can also be used as the curing matrix of liquid electrolytes. Cellulose is insoluble in water, and the porous structure of its fiber network provides additional heat transfer paths and tortuous ion diffusion channels. Pringle et al. soaked cellulose membrane in 0.4 M  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox electrolyte, and measured that the power density of TEC can reach  $168 \text{ mW/m}^2$ , and increasing the concentration of ionic liquid can further improve the current density [10]. Using this kind of cellulose-based electrolyte can improve the safety of equipment and significantly reduce the amount of electrolyte.

Gelatin can also be used as an electrolyte matrix for fixing redox couple because of its low cost, good biocompatibility, and good mechanical flexibility. Han et al. prepared Gelatin-KCl- $\text{Fe}(\text{CN})_6^{3-/4-}$  ionic gel electrolyte in gelatin matrix with KCl, NaCl, and  $\text{KNO}_3$  as ion donors [15], and showed a high thermal potential of 17.0 mv/k. 25 components were made into wearable equipment, which could generate a high output voltage of 2.2 V by using the temperature difference between the human body and environment. This kind of ionic thermoelectric material has a synergistic effect, and the ion provider realizes the thermal diffusion effect. KCl accumulates positive charges near the cold end of the electrode through thermal diffusion and generates an electric field from the cold end to the hot end, which is called thermal diffusion voltage. The reduction pair realizes the thermocurrent effect.  $\text{FeCN}^{3-}$  is more likely to undergo oxidation reaction than  $\text{FeCN}^{4-}$  under high-temperature electrode, and produces higher solvation entropy, and electrons migrate to the hot end electrode, thus improving the electrochemical potential.  $\text{FeCN}^{3-}$  gets electrons at the cold end to generate  $\text{FeCN}^{4-}$ , which drives thermal diffusion and balances oxidation–reduction reaction under the temperature gradient. The thermoelectric current effect makes the potential of electrodes at both ends move in the same direction as the thermal diffusion effect.  $\text{FeCN}^{4-/3-}$  also participates in thermal diffusion and contributes to the final thermoelectric energy (Figure 3).



**Figure 3.** Mechanism of the synergistic effect. Electrochemical potential ( $\mu$ -) of charge carriers diagrams and the corresponding voltage (V) distribution of i-TE material of Gelatin-KCl-FeCN.



**Figure 4.** Schematic of the p-n conversion mechanism for the  $I^-/I_3^-$  system (left). The hydrophilic/hydrophobic conversion of PNIPAM nanogels and the equilibrium reaction between  $I^-$  and  $I_3^-$  (right).

### 2.2.3 p-n conversion of redox pair

Using the special properties of some solvents, the reversion of redox to N-type and P-type can also be realized.  $I^-/I_3^-$  is a redox couple with a positive Seebeck coefficient, but Zhou et al. induced the redox couple of  $I^-/I_3^-$  to undergo p-n conversion by using the heat-sensitive polymer of n-isopropylacrylamide (PNIPAM), and prepared gel electrolyte with negative Seebeck coefficient [16]. The mechanism of p-n conversion is that the transition temperature of PNIPAM nanogels synthesized by emulsion polymerization is about 32°C, and above this temperature, the gel changes from hydrophilic state to hydrophobic state. In these PNIPAM nanogels, relatively hydrophobic  $I^-$  can be captured by dehydrated nanogels at the hot end by hydrophobic action, and electrons are released at the hot end, resulting in free  $I_3^-$  passing through the battery with a concentration gradient, resulting in Seebeck coefficient changing from 0.71 to  $-1.91$  mV/K. The transition temperature of 32°C is very suitable for human body temperature, which is especially suitable for human body heat collection. Zhou et al. prepared a wearable device composed of alternating  $I^-/I_3^-$  (p-type) and PNIPAM- $I^-/I_3^-$  gel (n-type) units connected in series. The open-circuit voltage of about 1 V was generated by human body heat energy, and the maximum output power reached  $9 \mu\text{W}$ , which can meet the power consumption requirements of small wearable devices. This work opens a new perspective for controlling the Seebeck coefficient of redox pairs in a gel electrolyte (Figure 4).

## 2.3 Electrode materials

Metal electrode material is the earliest electrode type used in the thermal cell, and the platinum electrode is a typical non-reactive catalytic material, which is widely used because it does not participate in electrode reaction and has high conductivity. However, platinum, as a precious metal, has a high production cost, so developing electrode materials with low price and higher conductivity is a thinking direction of thermoelectric chemical batteries at present.

The porous structure of nano-carbon materials makes the electrode have a higher active surface area and can generate higher thermal voltage under thermal gradient. Among them, carbon nanotubes (CNTs) and reduced graphene oxide (r-GO) are ideal candidate materials for thermoelectric battery electrodes. CNTs have fast carrier migration, excellent chemical stability, and catalytic activity. Kim et al. deposited CNTs on activated carbon textiles by dip-coating method [18] to obtain higher specific surface area and flexibility. The thermocouple manufactured can generate



the maximum power density of  $0.46 \text{ mW/m}^2$  by bulk heat. Chen et al. vacuum filtered the r-GO dispersion to obtain an electrode with a thickness of about  $1.8 \text{ }\mu\text{m}$ , which was applied in an electrolyte solution of  $0.4 \text{ M K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6$ . when the temperature difference was  $60^\circ\text{C}$ , the maximum mass power density of the r-GO electrode reached  $25.51 \text{ W/kg}$ , which was three orders of magnitude higher than that of the platinum electrode [17].

Pure CNTs have tortuous transmission channels, while pure r-GO is easy to form sheet-like accumulation, which is unfavorable to electron transmission. Chen et al. prepared SWNT-rGO composite electrode material by combining SWNT with reduced graphene oxide dispersed in 1- cyclohexyl –2- pyrrolidone (CHP) [19], and designed porosity for thermocouple electrode by controlling electrode composition and thickness. Increasing the amount of reduced graphene oxide will lead to the sheet stacking again, while decreasing the amount of r-GO will also lead to a more tortuous structure and hinder ion movement, thus reducing the performance of thermocouples. By optimizing the composition and thickness of the electrode, the balance between porosity and curvature is obtained, which is beneficial to the rapid diffusion of electrolytes. When 90% SWNT and 10% r-GO are added, the electrode thermocouple has the best performance, and when the temperature difference is  $t = 31^\circ\text{C}$ , the power density is  $0.327 \text{ W/m}^2$ .

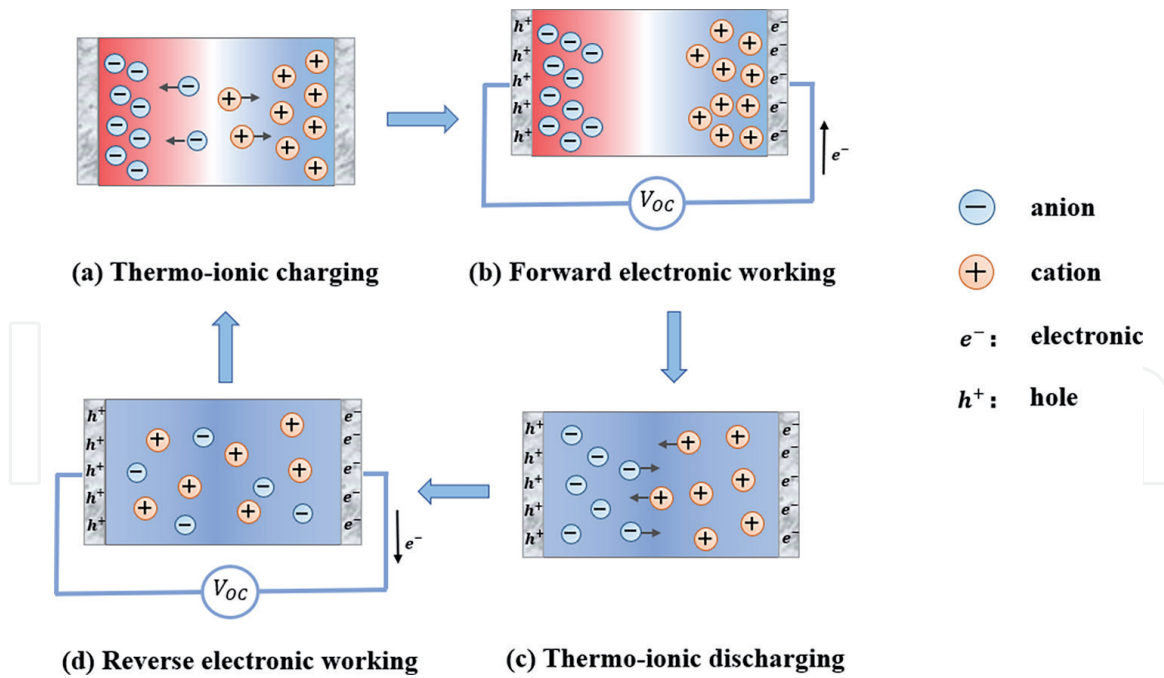
Apart from pure carbon-based materials, the conductive polymer is another promising flexible electrode active material, which not only has high polymer porosity and high active surface area but also shows good flexibility and stretchability. Poly (3,4-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT: PSS) is a promising conductive polymer. When it is added to graphene or carbon nanotube films, it can alleviate the bending of carbon nanotubes and mass transfer problems caused by graphene sheet stacking. Chen et al. prepared a composite thin film electrode composed of PEDOT: PSS, edge functionalized graphene (EFG), and carbon nanotubes by a simple drop-casting method [20]. PEDOT: PSS can not only provide an ion transport pathway and increase the porosity of EFG/ CNT, but also be used as a dispersant and film-forming agent in the manufacturing process to promote the uniform dispersion of EFG/CNT in the electrode, which in turn provides a more catalytic surface in the composite membrane.

### **3. Ionic thermoelectric materials for ionic thermoelectric capacitors**

Due to the temperature gradient, the anions and cations in the thermoelectric electrolyte migrate directionally to both sides of the electrode to form a potential difference, which is then connected with an external circuit to generate a thermal voltage, thus realizing the conversion from thermal energy to electrical energy. This thermoelectric conversion device based on the Soret effect is called an ion thermoelectric capacitor (TEC).

#### **3.1 Ion thermoelectric capacitor (TEC)**

Ion thermoelectric capacitor is composed of two identical electrodes and a solid electrolyte containing positive and negative ions. Driven by the temperature difference between the two ends, the directional migration of internal ions is realized due to the Soret effect. When the ions gather around the electrodes, the continuous generation of current in the circuit is realized because the ions cannot enter the electrodes. Similar to a capacitor, after the temperature difference is generated, with the continuous accumulation of ions at both ends of the electrodes, the current will gradually decrease to reach equilibrium, and the maximum thermal potential will be generated at both ends of the electrodes at this time. This working mode is discontinuous, and the current



**Figure 5.**  
 Working mechanism of TEC device.

output mode belongs to transient output, which requires human intervention to realize the storage of thermal energy into electrical energy. This device is mainly used for intermittent heat sources, such as solar cells and supercapacitors. The working mechanism of TEC is shown in the **Figure 5** [21], which is mainly divided into four stages.

1. Thermionic charging stage: One end of the electrode is heated, resulting in a temperature difference between the two electrodes. The anion and cation migrate to both ends of the electrode due to the Soret effect, and the final gathering produces a voltage difference between the two electrodes, which is called ion thermoelectric potential.
2. Forward electronic working stage: When the electrodes on both sides are connected with the external load, the electrons in the circuit migrate through the external load, and finally, the holes and electrons are collected on the electrodes on both sides to achieve charge balance. The current generated at this stage can do work for the external load.
3. Thermionic discharge stage: When the external load is disconnected and the heating end of the ion thermoelectric capacitor is cooled, the disappearance of the temperature gradient will drive the ions back to their original state, but the electrons remain on the electrodes on both sides, and there is still a voltage difference between the two ends of the electrodes.
4. Reverse electronic working stage: When the external load is connected again, electrons flow out of the capacitor electrode through the external circuit, thus doing work for the external load.

In ion thermoelectric capacitors, the Seebeck coefficient is related to the Soret effect. Different types of particles have different thermal diffusion in the mixture, and the electrode produced when particles migrate from the hot end to the cold end is called the positive electrode. On the contrary, the electrode produced when particles migrate from the cold end to the hot end is called the negative electrode.

Under the influence of the Soret effect, positive and negative ions diffuse to the electrodes on both sides in opposite directions, and then a voltage gradient, that is, thermal voltage, will be generated. Its contribution to  $S_e$  is expressed as [22]:

$$S_e = \frac{F}{\sigma T} zcD_T \quad (3)$$

In the formula,  $z$  is the number of ion charges,  $F$  is the Faraday constant,  $c$  is the ion concentration,  $\text{mol/m}^3$ ;  $\sigma$  is the conductivity,  $\text{S/m}$ ;  $D_T$  is the Soret thermal diffusion coefficient of the ion.

### 3.2 Electrolyte material

The electrolyte in the ionic thermoelectric capacitor is mainly composed of an organic polymer and a salt electrolyte that can be electrolyzed into ions and has ionic conductivity. The polymer molecular chains are entangled with each other to form a certain network space structure. Anions and cations are connected with the functional groups of the polymer by coordination bonds and are distributed in the gaps of the polymer structure. When there is a temperature gradient, the anions and cations Due to the directional migration of the Soret effect, an uneven charge distribution is generated inside and a thermal voltage is generated. Common electrolytes can be divided into conductive polymers, single-ion conductors, ionic liquid quasi-solid gels, and chemically cross-linked ionic gels according to their structure and composition.

#### 3.2.1 Conductive polymer

The most widely used electrolyte materials for thermionic capacitors are conductive polymer electrolytes. Among them, PEDOT: PSS has become the most in-depth researched type of conductive polymer material due to its excellent conductivity, good solution processing performance, and low price. Crispin researched PEDOT: PSS for the first time, and synthesized various PEDOT derivatives (PEDOT: PSS, PEDOT: PSS: PSSNa, etc.), which provided the basis for the electrolyte materials of thermionic capacitors [23]. PEDOT: PSS is a kind of mixed ion electronic conductor. Both electrons and ions can be used as charge carriers in electrolyte materials. It is the basic material of many emerging ionic thermoelectric materials. This type of conductive polymer has two types of thermoelectric current and thermovoltage. Contribution: The constant contribution of electrons and the non-constant contribution of ions. The total thermoelectric energy is expressed as the sum of the electron Seebeck coefficient and the ion Seebeck coefficient. For PEDOT: PSS polymer mixed conductors, the ion Seebeck effect accounts for the main part. The maximum power factor is increased by 2 to 4 orders of magnitude. Therefore, Crispin added PSSNa to PEDOT: PSS to enhance ionic conductivity and increase the mobility of cations. Relative humidity also has a significant effect on ion transmission. The results show that the Seebeck coefficient suddenly rises when the relative humidity is about 40%, and finally reaches  $215 \mu\text{V/K}$  at a relative humidity of 80%.

In addition, Kim et al. used PSSH as an additive, doped it into PEDOT: PSS polymer to make an ion hybrid thermoelectric capacitor [24], and realized ion thermally driven diffusion through polystyrene sulfonic acid (PSSH) film, which greatly improved the output voltage ( $8 \text{ mV/K}$ ). If a polyaniline coating containing graphene and carbon nanotubes is used as an electrode, a large area capacitance

(1200 F/m<sup>2</sup>) of 38 mV can be generated at a small temperature difference (5 K). The exploration of this thermal drive ion diffusion behavior provides a new research direction for the collection of low-grade heat energy.

### 3.2.2 Single ion conductor

In addition to the self-contained cations in the conductive polymer, it is also possible to add an electrolyte solution containing free cations to the PEDOT:PSS to prepare a single-ion conductor thermoelectric material, which can further improve the conductivity of the electrolyte material, thereby increasing the thermoelectricity of the ion thermoelectric capacitor Figure of merit and power factor, in which Ag ions and Na ions are the most used ion transport carriers.

Segalman et al. prepared Ag:PSS by ion exchange, and then incorporated it into PEDOT:PSS to form a conductive mixture enriched with Ag:PSS along PEDOT [22], in which PEDOT:PSS was used as an electronic conductor and Ag<sup>+</sup> was used as a carrier carrying out ion transport, but also participating in the electrochemical reaction of the silver electrode. This mixed ion-electronic conductive polymer combines the redox reaction on the electrode and the thermoelectric transport of ions in the system. It is an electrochemically active material that enhances the Seebeck coefficient of ions. However, this material requires anions to pass from an electrode in one direction. Transmitted to the other electrode, if all the silver at one end of the system is consumed, the ion Seebeck enhancement will disappear.

Nafion is an ion exchanger composed of perfluorinated sulfonate. There are hydrophobic fluorocarbon framework domains and hydrophilic domains dominated by ionized sulfonic acid groups in its molecules. It has good cation selectivity and excellent ionic conductivity; it is often used as a cation exchange membrane. At the same time, it also has strong resistance to chemical corrosion. The working temperature is higher, which can reach about 190°C. Therefore, this perfluorosulfonic acid polymer is widely regarded as the best polymer ion conductor.

Segalman et al. added Ag ions to Nafion and PSS membranes to prepare two new material systems: Ag-Nafion and Ag-PSS. Both of these systems are water-processable solid electrolytes [25], which exhibit high ionic conductivity due to their sulfonate groups. The silver ions combined in Ag-Nafion and Ag-PSS undergo directional migration under the action of the temperature gradient and form an ion concentration gradient through the generalized Soret effect, and then generate a thermoelectric voltage. The silver ions also undergo electrochemical reactions on the electrodes, causing silver to enter the system from the anode and deposit on the cathode. Since the sulfonate ions are on the polymer backbone, only the silver ions are movable under the applied temperature gradient, so the Seebeck coefficient is completely the result of the movement of the silver ions. Segalman et al. also analyzed the ion transport under temperature gradient from the chemical reaction entropy and Soret effect, and finally demonstrated a flexible, water-treated solid polymer thermocurrent device. The results show that at 26°C and 50% relative humidity, the maximum ZT of 33%AgNO<sub>3</sub>-PSS is 0.006, and the maximum ZT of 33%AgOH-Nafion is 0.003. Although its ion mobility is extremely low compared with electrons, this is the first solid polymer thermocurrent device using a single ion conductor, which has good solution processability, flexibility, and air stability.

Liquid polyethylene oxide (PEO) can also be used as an electrolyte for single-ion conductor thermoelectric materials. Crispin et al. added NaOH to PEO [26] to convert the hydroxyl group (-C-OH) at the end of PEO into anionic alkoxide end groups (-CO-Na), where free Na ions are used as charge carriers. This ionic polymer electrolyte can provide a very strong ion Soret effect, with a Seebeck coefficient of up to 10 mV/K and a relatively low thermal conductivity of 0.216 W/(m•K).

In addition to the above-mentioned organic solutions as electrolytes, natural green pollution-free is the development prospect of new thermoelectric materials. Nano cellulose (NFC) is extracted from natural cellulose, fibers, or crystals with a diameter of less than 100 nm and a length of several microns. It has high mechanical strength, flexibility, biodegradability, etc. If the soft nano cellulose is used as the substrate and the conductive polymer with conductive properties to form a composite material, it can be used to prepare a biocompatible energy harvesting device. Crispin et al. added nano cellulose (NFC) flexible additives to PSSNa electrolyte to prepare NFC-PSSNa solid electrolyte [27]. The introduction of nano cellulose makes this solid electrolyte mechanically stronger than pure electrolyte, and its ion Seebeck coefficient is significantly higher than that of pure PSSNa. The preparation of this ionic thermoelectric paper provides new possibilities for the large-scale preparation of ionic thermoelectric materials. Hu Bingliang and others also used natural fibers as ionic thermoelectric electrolytes. They performed a simple chemical treatment on natural wood to make a sub-nano structured cellulose membrane, which was immersed in NaOH solution to make a cellulose-Na mixed electrolyte [28]. The cellulose-Na mixed electrolyte uses Na ions as carriers, and cellulose uses molecular chain arrays to limit ion migration. It has a high selective diffusion ability under thermal gradients. The electrolyte penetrates the cellulose membrane and applies axial temperature gradient, the thermal gradient ratio of the ion conductor (similar to the Seebeck coefficient of thermoelectric) reaches 24 mV/K. This material can be made into a flexible and biocompatible thermoelectric conversion device, which is expected to realize the scale of the thermoelectric conversion device Chemical production.

### 3.2.3 Ionic liquid quasi-solid ionic gel

Ionic liquid is a kind of salt that consists of only anions and cations and is liquid at room temperature. It has the advantages of low volatility and good thermal stability. Compared with water or common organic electrolyte solutions, ionic liquids have a higher electrochemical window (4 ~ 6 V) can be used to prepare energy storage devices, and is the most promising electrolyte material for thermoelectric capacitors. Ionic liquid electrolyte is mainly composed of ionic liquid with better performance and resin matrix, etc., to make a quasi-solid ionic gel. This gel not only has excellent electrical conductivity and ion transport properties, but the solid gel-like structure also avoids ionic liquids. The loss and environmental pollution problems.

Ouyang's team has made outstanding contributions to the preparation of thermoelectric capacitors based on ionic liquids. Cheng et al. It is mixed into a quasi-solid ionic gel [21], which exhibits ultra-high Seebeck coefficient (up to 26.1 mV/K), high ionic conductivity (6.7 mS/cm), and low thermal conductivity (0.176 W/(m K)), which is the highest Seebeck coefficient detected in electronic and ion thermoelectric materials so far. Water-based polyurethane (WPU) is also a good solid gelling agent. Fang et al. used drop-casting method to mix EMIM: DCA and WPU to prepare a stretchable transparent ionic gel with high thermoelectric properties [29]. The ionic gel exhibits extremely high flexibility and mechanical tensile properties. The tensile performance of the ionic gel containing 40 wt% EMIM: DCA is as high as 156%. It also has good ionic thermoelectric properties. When the relative humidity is 90% With high ionic thermal voltage (34.5 mV/K), high ionic conductivity (8.4mS/cm), and low thermal conductivity (0.23 W/(m K)), the ZT value can reach  $1.3 \pm 0.2$ . The advantage of ionic stretchable gel is that it has good transparency and stretchability, which provides a good research idea for the energy supply of flexible wearable devices.

Compared with organic resin gelling agents, the doping of inorganic materials can not only play a good gel effect but also greatly enhance the conductivity of the electrolyte material and further improve its thermoelectric performance. Commonly used inorganic materials are SiO<sub>2</sub> Carbon nanotubes, etc. The Lewis acid group on the surface of SiO<sub>2</sub> nanoparticles interacts with the ionic liquid, which promotes the dissociation of anions and cations, and promotes the formation of more free vacancies, and establishes rapid ion migration channels. Therefore, a small amount of SiO<sub>2</sub> nanoparticles can significantly increase ions. The ionic conductivity of the gel, but the excessive SiO<sub>2</sub> nanoparticles easily form agglomerations to hinder ion migration and transmission, thereby reducing the ionic conductivity. He et al. prepared a quasi-solid ionic gel composed of a variety of ionic liquids and SiO<sub>2</sub> nanoparticles, in which EMIM with 20 wt.% SiO<sub>2</sub> nanoparticles added: DCA ionic gel has a high ion Seebeck coefficient (14.8 mV/K), the excellent ion conductivity ( $4.75 \times 10^{-2}$  S/cm) and high power factor (1.04 mW/(m K<sup>2</sup>)), the room temperature ion ZT value is as high as 1.47 [30]. In addition, carbon nanotubes also contribute to the improvement of electrical conductivity. Salazar et al. studied ionic liquid electrolytes mixed with multi-walled carbon nanotubes (MWCNT) as an alternative electrolyte for thermoelectrochemical cells [31].

Using liquid polyethylene glycol (PEG) to dope the ionic liquid can also change the type of ionic gel electrolyte. The presence of PEG along the polymer chain hinders the interaction of PVDF/anions, and preferentially binds to cations, thereby promoting the thermal diffusion of cations. EMIM: TFSI/PVDF-HFP fluorinated polymer ion gel is an n-type thermoelectric material, which usually exhibits a negative Seebeck coefficient. After Zhao et al. doped PEG into it, the deviation of the measured value of the Seebeck coefficient changed from -4 mV to +14 mV [32]. The thermal diffusion of ion gel is extremely dependent on the polarity of the polymer matrix. This method can be used to conveniently adjust the type of polymer ion gel electrolyte (p-type or n-type) and provide sufficient energy for ion thermoelectric capacitors. Output voltage and power. Ionic liquid quasi-solid ionic gel electrolyte is newly developed and has broad development and application prospects. It is the most promising electrolyte material for thermoelectric capacitors.

#### 3.2.4 Chemical/physical cross-linking ionic gel

In addition to the method of adding a gelling agent solution, the polymer material can be electrochemically cross-linked with the ionic liquid to prepare a water ionic gel. This ionic gel also has good thermoelectric properties, and its Seebeck coefficient and electrical conductivity are significantly improved, and at the same time, it can also solve the environmental pollution problem caused by the leakage of ionic liquid. Commonly used electrochemical cross-linking methods [33] mainly include thermally initiated cross-linking, light-initiated free radical polymerization, in-situ free radical polymerization, and radiation-induced cross-linking.

Thermally initiated cross-linking is a common chemical crosslinking method. The reaction system includes reactive monomers, thermal initiators, and cross-linking agents. Thermal initiators mainly include azobisisobutyronitrile (AIBN) [34], azobisisoheptaonitrile (ABVN), dibenzoyl peroxide (BPO), etc. The cross-linking agent mainly contains two or more acrylic acid, the most widely used oligomer or monomer of ester group is polyethylene glycol dimethacrylate (PEGDMA). For the first time in the presence of ionic liquid [N2228] Br, Sajid et al. used the free radical initiator AIBN to thermally initiate polymerization/chemical cross-linking PEGDMA to prepare a new chemically cross-linked thermoelectric hydroion gel [35]. Its Seebeck coefficient is 1.38 mV/K, which is more than 10 times

higher than that of pure ionic liquid. It also has extremely high ionic conductivity, reaching 74 mS/cm, and the room temperature ZT value reaches  $1.02 \times 10^2$ . In the same year, Sajid et al. replaced the ionic liquid with 1-butyl-3-methylimidazole tetrafluoroborate (BMIM: BF<sub>4</sub>) [34], and used in-situ free radical polymerization to prepare a thermally initiated cross-linked ionic gel. The results show that the ionic conductivity of the ion gel with 90 wt.% BMIM:BF<sub>4</sub> is also 10 times that of the pure ionic liquid, reaching 49.41 mS/cm. At the same time, the ion Seebeck coefficient is significantly increased, which is 2.35 mV/K, which is a new type of p-type chemically cross-linked ionic gel.

Compared with thermally-initiated cross-linking polymerization, photo-initiated cross-linking does not use initiators and cross-linking agents. It has the advantages of high initiation efficiency, easy control of the polymerization reaction, and mild operating conditions. It is a very effective in-situ polymerization method. Therefore, it is widely used in the preparation of hydroion gel. Liu et al. studied a UV-induced photopolymerization of BMIM: Cl-based ionic gel electrolyte, and finally prepared BMIM: Cl/CS/PHEMA polymer gel electrolyte [36]. This chemically cross-linked ionic gel has Good thermoelectric performance can be used as a cheaper and more scalable way to directly convert waste heat into electrical energy.

In addition, the physical cross-linking method can also be used to prepare hydroion gels. Jang et al. A stretchable, high-performance, flexible and self-healing ternary ion thermoelectric hybrid material composed of sulfonic acid, PAAMP(SA) and physical cross-linking agent (phytic acid, PA) [37], it shows very superior ionic thermoelectric properties, Seebeck coefficient is 8.1 mV K<sup>-1</sup>, ZT<sub>i</sub> reaches 1.04. Due to the flexibility of the polymer, the ternary hybrid ion gel has good flexibility and ductility, and the dynamic interaction between the three components allows it to heal on its own without external stimulation. It is flexible and wearable. Ionic thermoelectric capacitors provide new features such as stretchability and self-repair.

### 3.3 Electrode material

Metal electrodes are one of the most widely used electrode materials for ionic thermoelectric capacitors (TEC). In addition to inert metal platinum and gold electrodes, if the carriers in the single-ion conductor electrolyte are silver ions, silver can also be used as the electrode material [25] This hybrid ion-electronic conductive polymer combines the redox reaction on the electrode and the thermoelectric transport of ions in the system, which can enhance the ionic electrochemical activity of the material. In order to make ionic thermoelectric capacitors have higher performance, TEC electrodes need to have a higher surface area and ion transport channels, thereby having higher conductivity and ion transport rate. Nano-carbon materials such as carbon nanotubes (CNT) and graphene are ideal candidate materials for TEC electrodes.

Carbon nanotubes and graphene and other nano-carbon materials have a unique two-dimensional planar structure and have good performance in ion and electron transport. Compared with silver electrodes, carbon nanotube electrodes have the higher electroactive surface area and higher capacitance than the silver electrode. Crispin et al. used the drop casting method to prepare CNT film on gold film [26]. Due to the high specific surface area of the porous network structure of the nano-electrode, the ionic thermoelectric capacitor exhibits a higher capacitance. Kim et al. deposited polyaniline on nanoporous graphene/carbon nanotube (G/CNT) films by electropolymerization to prepare sandwich electrodes [24], in which carbon nanomaterials provide high surface area, and polyaniline has good redox activity.

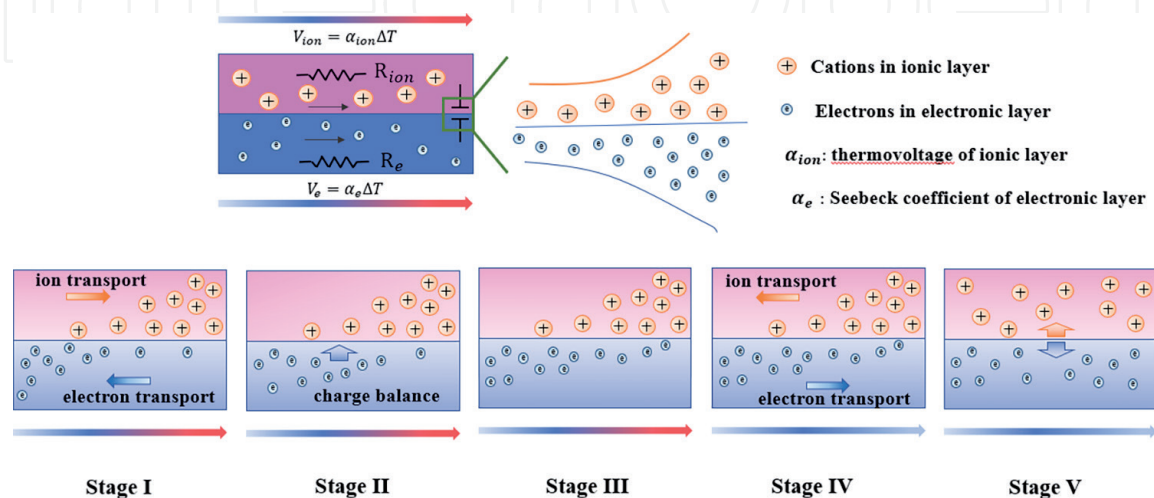
This sandwich composite electrode produces 3–7 times higher capacitance than pure CNT. Electrode materials suitable for ionic thermoelectric capacitors are still in the development stage. It is believed that future electrode materials will not only provide higher specific surface area and capacitance but will also develop in flexibility and mechanical stretchability, making them more suitable for small wearable flexible thermoelectric energy harvesting devices.

## 4. Ionic thermoelectric materials for other energy conversion devices

### 4.1 Hybrid ion/electronic thermoelectric converter

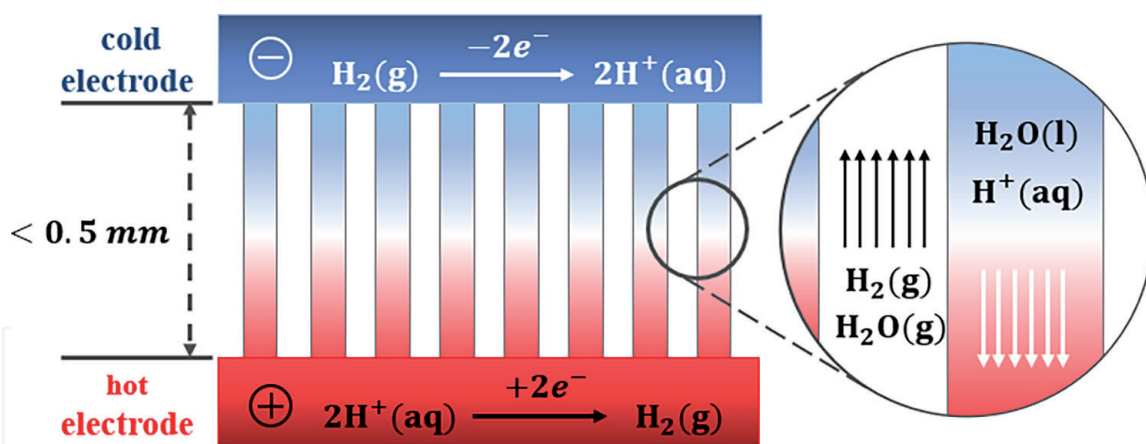
If the ionic thermoelectric capacitor is combined with an ordinary thermogenic battery, the ion conductive layer is placed on the electronic layer, the electronic unit uses the Seebeck effect under the temperature gradient to obtain heat, and the ion unit can utilize the Soret effect to convert heat into electric energy under temperature fluctuation, this thermoelectric conversion device that combines the electronic Seebeck effect and the ion Soret effect is called a hybrid ion/electronic thermoelectric converter (HTEC). Its working mechanism is shown in **Figure 6** [38]. Due to the Soret effect, the cations in the ion layer will accumulate on the hot side of the ion gel under a temperature gradient, while the additional cations induce electrons to pass through the interface between the electron layers, and neither ions nor electrons can pass through the interface between the two layers. When in equilibrium, the distribution of electrons and ions at the interface is similar to the upper electrochemical layer. The interface in the middle is called the electric double layer, and heat is the driving force for the accumulation of interface charges.

The hybrid ion/electronic thermoelectric converter combines the Seebeck effect of electrons and the Soret effect of ions, which can generate higher thermal voltage and provide new thinking directions for thermoelectric energy conversion. Ouyang et al. coated a layer of PSSH on the top surface of the acid-treated PEDOT: PSS to form a thermoelectric material with a PSSH/A-PEDOT: PSS double-layer structure. Compared with the mixture PEDOT:PSS:PSSH, this double-layer film has more high power factor, reaching  $401 \text{ mW}/(\text{m}\cdot\text{K}^2)$  [39]. In addition, similar effects were found in butylamine doped PEDOT:PSS (PSSNa/BA-PEDOT:PSS). Ionic gel can also be used as the ionic unit. Cheng et al. prepared a hybrid ion/electronic



**Figure 6.** Schematic illustration of a HTEC with the electronic and ionic layers.  $R_{ion}$  and  $R_e$  are for the ion and electron resistances under electric field, respectively..





**Figure 7.**  
Working mechanism of gas-liquid two-phase thermoelectric battery.

thermoelectric converter composed of PEDOT:PSS and ionic gel [38]. The ionic layer is composed of 80 wt% 1-ethyl-3-methylimidazolium dicyanamide (EMIM: DCA) and 20 wt% PVDF-HFP. Although the ZT value of the ionic gel is not improved, the thermal voltage is significantly increased. The stable voltage can reach  $28 \mu\text{V}$  under a temperature gradient of  $0.65 \text{ K}$ . The hybrid ion/electron thermoelectric converter not only improves the energy collection but also provides a new research direction for the future development of ionic thermoelectric conversion materials.

#### 4.2 Gas-liquid two-phase thermoelectric battery

Although the thermogenic battery can directly convert waste heat into electric energy by using the oxidation-reduction reaction under the temperature gradient, the check and balance between thermal resistance and conductance limits the improvement of its conversion efficiency. Ma et al. developed a thermoelectric battery involving gas-liquid two-phase, replacing the traditional liquid-phase redox reaction and mass transfer process with gas-liquid two-phase system. They use  $\text{H}_2\text{SO}_4$  aqueous solution as the electrolyte of the thermoelectric battery [40].  $\text{H}_2/\text{H}^+$  redox is a fast reaction involving both  $\text{H}^+$  transport and  $\text{H}_2$  gas generation. The thermogenic cell reaction process is shown in the **Figure 7**. Among them,  $\text{H}^+$  is reduced to  $\text{H}_2$  on the hot side, and  $\text{H}_2$  is oxidized to  $\text{H}^+$  on the cold side.  $\text{H}_2$  and  $\text{H}^+$  shuttle in a thin separator with ordered gas-liquid interpenetrating channels. The electrode adopts a reversible hydrogen electrode, and the electron transfer resistance is very small. Even if there is only half the volume of the acid solution in the separator, the  $\text{H}^+$  conduction is fast enough. The gas-containing electrolyte layer can also suppress the contribution of heat convection to the thermal conductivity of the thermogenic cell. Improve its thermoelectric performance, its power factor is  $12.9 \mu\text{W}/(\text{mK}^2)$ , there is still a lot of room for development.

The unique design of this gas-liquid two-phase thermoelectric battery lies in the orderly gas/liquid channel structure inside the thin separator, which provides an effective way for ion conduction/gas transport and thermal isolation, and realizes the transformation of the power characteristics of TGCs.

### 5. Summary and prospect

According to the different thermoelectric conversion mechanisms, this paper divides ionic thermoelectric materials into two types: thermoelectric materials for

thermoelectrochemical cells (thermocouple effect) and thermoelectric materials for ionic thermoelectric capacitors (Soret effect), and their latest progress in thermoelectric conversion devices is described. In recent years, small thermoelectric conversion devices have gradually developed in the direction of wearable devices, and their thermoelectric performance and conversion efficiency has been greatly improved, and more attention has been paid to the flexibility and stretchability of thermoelectric conversion materials. Compared with traditional electronic thermoelectric materials, the conversion efficiency of ionic thermoelectric materials has been improved, but there is still room for development. In order to achieve higher thermoelectrochemical performance and practical applications, it is necessary to improve the ion mobility of materials and establish ion diffusion channels. Electrode materials should also have a high specific surface area and unobstructed ion diffusion channels to achieve good electron and heat transfer. Nano-carbon materials and PEDOT/PSS and their composite materials are good candidates for ionic thermoelectric electrodes, and they still have broad Development prospects, and at the same time, single-atom doping of platinum, copper, and other metal electrodes is also a good research approach.

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