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Introduction of Organic Thermoelectrics

Yingqiao Ma, Ye Zou, Chong-an Di, and Daoben Zhu

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun North First Street 2, Haidian District, Beijing 100190, China

1.1 Brief Introduction and Historical Overview

In the past two decades, energy and environmental issues have become major challenges for human society. The development of a new category of green energy is then becoming an important direction to deal with these challenges. From the viewpoint of energy conversion, the efficiency is less than 40% in average, whereas the remaining energy is mainly lost in heat. Taking into consideration of energy resources, solar is an abundant energy resource, which can be converted into electricity by photovoltaic technology. Although the state-of-the-art efficiency of photovoltaic cells has exceeded 30% [1], of the rest more than 60% cannot be converted into electricity in a simple way. From the perspective of new applications, the scientists began to pay attention to the distributed energy supply mode featured by portability to satisfy the growing requirements of wearable electronics. The utilization of environmental and even body heat is considered as a promising solution to satisfy such requirements. These joint demands indicate that the highly efficient application of ubiquitous heat energy is extremely important in the next 10–30 years, which may breed a new energy industry.

Thermoelectric (TE) materials can directly convert the heat into electricity or vice versa and provide a straightforward way to exploit the waste and natural heat energy. The so-called thermoelectric conversion is resulting from the interference of electric current and heat flow in various materials. Basically, there are two kinds of TE devices (Figure 1.1), including thermoelectric power generator and thermoelectric cooler, which have no moving parts and require no maintenance. The power generator possesses a great potential for natural and waste heat recovery from solar, industrial facilities and various engines, thus providing reliable power in distributed and even remote areas, such as in deep space and mountaintop telecommunication sites. In addition, TE cooler offers a reverse route to enable refrigeration and temperature control in electronic packages and medical instruments.

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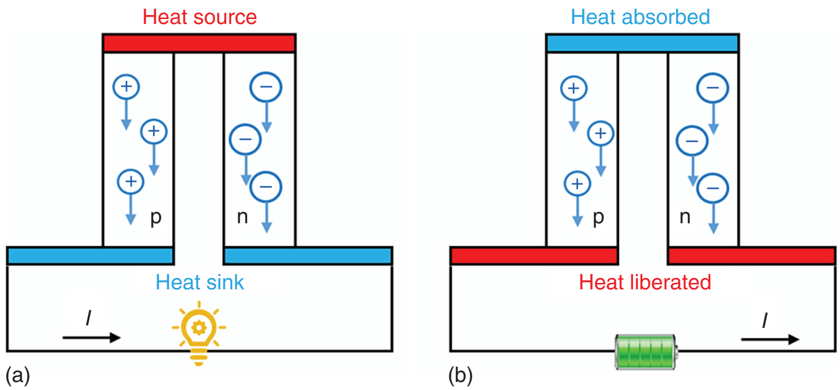

Figure 1.1 Schematic diagrams of thermoelectric (a) power generator and (b) cooling device. Source: Ye Zou.

To have a clear map of thermoelectric behavior, we start with a brief history of TE effects. In 1821, Thomas Johann Seebeck found that the temperature difference between two different metals led to the deflection of the magnetic needle [2]. Subsequent studies showed that the phenomenon was due to the potential difference caused by the temperature difference, which led to the change in current and magnetic field. The basic connotation of this experimental phenomenon constitutes the Seebeck effect. Thirteen years later, in 1834, Jean Charles Athanase Peltier discovered a reverse process – that the passage of electric current through a thermocouple produces heating or cooling effect depending on its direction [3]. This led to another TE effect, the Peltier effect, which can realize electric heating and cooling in a direct way. In 1854, William Thomson (Lord Kelvin) discovered that if a temperature difference exists in a current-carrying conductor, heat is either liberated or absorbed depending on the direction of current and materials [4], which is supplementary to the Peltier heating. This is called the Thomson effect. Moreover, he analyzed the relationship between Seebeck effect and Peltier effect from a theoretical point of view. These three kinds of TE effects and the Joule heat effect constitute the physical basis of the TE conversion process.

In the first 100 years after the discovery of Seebeck effect, TE materials suffer from a slow development. The material category was limited to metals and are mainly used for temperature measurement thermocouples. In the mid-twentieth century, with the emergence and rapid development of quantum mechanics and semiconductor theory, narrow-band gap semiconductors represented by Bi_2Te_3 and PbTe have been developed. The TE performance began to improve rapidly, and the figure-of-merit ZT was close to 1.0 [5]. Although TE materials-based power generator and solid-state refrigerator begin to be applied, the theoretical model is not perfect, and the performance needs to be further optimized. Since the 1990s, the theoretical model of "phonon glass and electronic crystal" [6], the design strategy of low-dimensional thermoelectric materials, and the cross-scale control method of material structure have been put forward one after another, which promote the rapid development of the fundamental theories and material categories. The ZT value has broken 1.0 and enabled a variety of functional applications.

In the past decade, with the prospects of flexible devices in artificial intelligence, health monitoring, and Internet of things (IoTs), TE materials begin to show a variety of new development trends. The first trend is to continuously develop new generation of model materials and drive new breakthroughs in ZT; the second is to develop high-performance low-temperature flexible TE materials to expand the TE application in micro-temperature difference power generator; the third is to give full play to the advantages of reversible energy conversion of TE materials and focus on solid-state refrigeration with TE materials.

Organic material is assembled by weak intermolecular interactions, which endows them with unique optoelectronic functionalities. As far as TE conversion is concerned, organic thermoelectric (OTE) materials have many advantages, such as good flexibility, low intrinsic thermal conductivity, and excellent performance at room temperature [7–9]. They are expected to complement traditional inorganic TE materials and become a key element for the next-generation flexible devices. Although OTE materials have attracted great attention in the past decade, it is not a new research direction. Several decades ago, scientists began to use Seebeck effect to investigate the charge transport property in molecular crystals. For one example, Prof. D. Zhu from Institute of Chemistry, Chinese Academy of Sciences, and Prof. D. Schweitzer in Germany studied the electrical properties of two-dimensional organic conductor β-$(BEDT\text{-}TTF)_2BrI_2$ in 1986 [10]. They accurately measured the Seebeck coefficient at different temperatures and discovered the sign change behavior of Seebeck coefficient around 110 K, which revealed its excellent bipolar charge transport behavior (Figure 1.2). It is worth noting that the p-type and

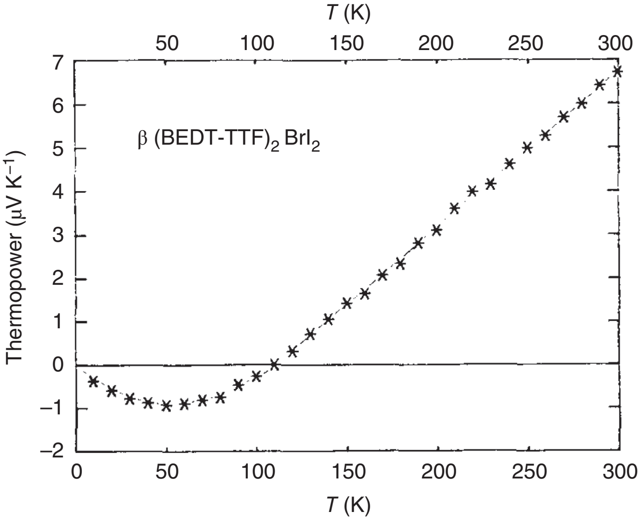

Figure 1.2 Temperature-dependent thermopower curve of β-$(BEDT\text{-}TTF)_2BrI_2$. Source: [10]. Reproduced with permission of Elsevier.

n-type power factors of this material at different temperatures reach 2.2 and 0.05 μW m^{-1} k^{-2}, respectively. These early research progress laid the foundation for the rapid development of OTE materials in the past decade.

The recent rapid developments of OTE materials are inspired by the breakthrough in PEDOT and poly[Ni-ett] [11–14]. For p-type materials, PEDOT is the most widely studied conductive polymer, which shows a broad application potential in organic solar cells, transparent electrodes, and so on. Based on the previous research on conductive molecular system, Joo et al. in Korea University studied the influence of solvents on the electrical conductivity and Seebeck coefficient of PEDOT:PSS thin films, which was the early work to investigate the TE properties of the system [15]. Thereafter, Xu et al. investigated the TE properties of PEDOT:PSS films doped with DMSO and glycol, and reported a ZT value of 0.00175 [16]. In 2011, Crispin et al. studied the influence of doping levels to the TE properties of PEDOT:Tos. By precisely adjusting the oxidation level, the figure-of-merit of the film reached 0.25 [11]. Compared with p-type materials, the development of n-type OTE materials is more challenging. After several years of systematic research, Zhu et al. reported n-type metal–organic complex OTE materials, namely, poly(Ni-ett), in 2012. By using ion coordination to control the performance and polarity of the materials, the ZT value over 0.2 was obtained [12]. After that, polycrystalline thin films were prepared by electrochemical method, and the ZT value was further increased to 0.3 [14]. These breakthroughs in high-performance p-type and n-type OTE materials have attracted increasing attention and directly promoted the rapid development of OTE materials and devices. More recently, increasing attention has been paid to design novel OTE molecules and combine conventional TE theory with organic materials, leading to tremendous progress in composite/hybrid OTE materials, chemical doping of OTE semiconductors, and multi-functional OTE devices. These remarkable progresses constitute the current status of OTE field.

1.2 Thermoelectric Effect

The TE conversion is based on the diffusion transport of carriers. It includes three basic physical phenomena, namely, the Seebeck effect, the Peltier effect, and the Thomson effect. The three effects are called by a joint name the TE effect.

1.2.1 Seebeck Effect

The Seebeck effect, which is also known as the first TE effect, was firstly discovered in 1821 by the German scientist Thomas Johann Seebeck. As shown in Figure 1.3a, when two different wires “a” and “b” are connected at both ends to form a circuit loop, if a temperature difference is created between the two junctions W and X by heating one of the junction W, the carriers in both wires will move from the high-temperature junction W to low-temperature junction X, resulting in a potential difference ΔV between the two junctions and an electric current in the loop. Through the Seebeck effect, the temperature difference in environment

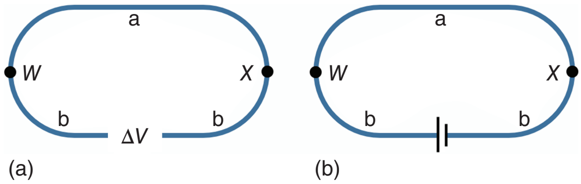

Figure 1.3 Basic principle of (a) Seebeck effect and (b) Peltier effect. Source: Ye Zou.

can be directly converted into electricity, thus achieving the power generation by temperature difference. It is found that the magnitude of the thermoelectric potential difference is proportional to the temperature difference at the junctions. Assuming that the temperature at the hot junction W is T_h and at the cold junction X is T_c, the potential difference ΔV between the two junctions can be expressed as:

$$\Delta V = S_\mathrm{ab}(T_\mathrm{h} - T_\mathrm{c}) \tag{1.1}$$

where S_ab is the differential Seebeck coefficient of the two materials. The direction of the potential difference ΔV is dependent on the properties of the two materials forming the loop and the direction of temperature difference. For instance, suppose the temperature at junction W is higher than junction X (Figure 1.3a), if the current generated by the Seebeck effect is in the clockwise direction from “a” to “b,” then the loop a-b has a positive differential Seebeck coefficient. The Seebeck coefficient is usually measured in $\mu\mathrm{V\,K^{-1}}$. It should be noted that the Seebeck coefficient has also been called the thermoelectric power or the thermal electromotive force (EMF) coefficient.

The Seebeck effect introduced above is based on two different wires forming a current loop. For a homogeneous material, the absolute Seebeck coefficient at temperature T is defined as:

$$S = \lim_{\Delta T \to 0} (\Delta V/\Delta T) \tag{1.2}$$

The relationship between the differential Seebeck coefficient S_ab in the loop and the absolute Seebeck coefficients (S_a and S_b) of the two materials can be illustrated as: $S_\mathrm{ab} = S_\mathrm{a} - S_\mathrm{b}$.

The absolute Seebeck coefficient is independent of the direction of temperature difference but is only determined by the property of the thermoelectric material itself. For any TE materials, the carriers (both the holes and electrons) move from hot end to cold end under the temperature difference. However, due to the different sign of carriers, the direction of thermal EMF of p-type materials (holes are majority carriers) is from the hot end to the cold end, resulting in a positive absolute Seebeck coefficient. On the contrary, the direction of thermal EMF of n-type materials (electrons are majority carriers) is from the cold end to the hot end, resulting in a negative absolute Seebeck coefficient. The absolute Seebeck coefficient is more commonly used than the differential Seebeck coefficient in assessing TE material property. In the following part of this book, the Seebeck coefficient is referred to the absolute Seebeck coefficient unless otherwise specified.

1.2.2 Peltier Effect

The Peltier effect, also known as the second thermoelectric effect, is physically an opposite process of the Seebeck effect and was first discovered by French scientist Jean Charles Athanase Peltier in 1834. The Peltier effect can basically convert electricity directly into temperature difference, which therefore has great application in thermoelectric cooling or heating (heat pumping). As shown in Figure 1.3b, when an electrical current passes through a loop composed of two different wires “a” and “b,” a small change in heat arises at both the two junctions W and X in addition to the Joule heating by resistance. Thereby, the two junctions appear to absorb or liberate heat creating a cooling or heating effect, respectively, related to the direction of current flow. The Joule heating is irreversible, while Peltier heating or cooling is reversible between heat and electricity without a loss of energy. The magnitude of the heat absorbed or liberated is proportional to the current flow. Assuming that the current I clockwise flows from “a” to “b,” the heat absorbed or liberated per unit time at junction X is:

$$\mathrm{d}Q/\mathrm{d}t = \Pi_{\mathrm{ab}} I \tag{1.3}$$

where Π_{ab} is the differential Peltier coefficient and the sign of Π_{ab} is negative if the clockwise current I leads to a heat liberation at junction W and a heat absorption at junction X. Therefore, the way in which heat is exchanged, either heat absorption or liberation, at the junctions is related to the properties of the two materials and the current direction. The Peltier coefficient is usually measured in volts (V).

The Peltier effect stems from the different potential of electrical charge carriers in different materials. In detail, when current flows across a junction between two different wires, energy exchange occurs due to different potential energy of carriers, leading to cooling or heating effect at the junction. For instance, if electrons move from the high-energy level material to low-energy level material, they will release energy and the junction will exhibit the heat liberation effect on the macroscopic level. On the contrary, if electrons move from the low-energy level material to high-energy level material, they will absorb energy and the junction will show the heat absorption effect.

Similar with the case of the Seebeck coefficient, the relationship between the differential Peltier coefficient Π_{ab} at the junction and the absolute Peltier coefficients (Π_{a} and Π_{b}) of the two materials forming the loop follows: $\Pi_{\mathrm{ab}} = \Pi_{\mathrm{a}} - \Pi_{\mathrm{b}}$. The absolute Peltier coefficient is independent of the current direction and is only determined by the properties of the material itself. The reported Peltier coefficient of organic material is in the order of tens of mV [17].

1.2.3 Thomson Effect

In 1855, the British scientist William Thomson (later Lord Kelvin) established the relationship between the Seebeck coefficient and Peltier coefficient by analyzing the thermoelectric effect in a homogeneous material with thermodynamic theory. His research also indicated that a third thermoelectric effect existed in the homogeneous material, which is later known as the Thomson effect. In detail, when current I flows through a homogeneous conductor with a temperature gradient (ΔT), in addition to produce Joule heat, the conductor needs to absorb or release heat in order to maintain the original temperature gradient ΔT. This effect was later successfully and experimentally verified by other scientists in 1867. The rate of Thomson heat absorption or release ($\mathrm{d}Q/\mathrm{d}t$) across the homogeneous conductor is:

$$\mathrm{d}Q/\mathrm{d}t = \beta I \Delta T \tag{1.4}$$

where β is the Thomson coefficient with a unit in $\mathrm{V\,K^{-1}}$. If the direction of current coincides with the temperature gradient and the conductor absorbs heat, then the Thomson coefficient is positive.

Both the Seebeck effect and the Peltier effect are discovered involving the formation of current loops in which two wires are joined together. They originated from the energy difference of carriers in different materials. Nevertheless, the Thomson effect is a phenomenon that occurs in homogeneous materials, i.e. the carriers in a homogeneous material have different energies at different temperatures, resulting in heat exchange when the carriers transport through a temperature gradient. In the design of thermoelectric devices, the Thomson effect is usually ignored because of its relatively small contribution compared with the Peltier effect to thermoelectric energy conversion.

The interrelationship between the three thermoelectric parameters, namely, the Seebeck coefficient (S), the Peltier coefficient (Π), and the Thomson coefficient (β), thermodynamically derived by Thomson is expressed as:

$$\Pi = ST \tag{1.5}$$

$$\beta = T\mathrm{d}S/\mathrm{d}T \tag{1.6}$$

These two equations later came to be known as the Kelvin relationship. Their rigorous derivation requires the use of non-reversible thermodynamic theory. The Kelvin relationship is important in understanding the basic phenomena, which indicates that the values of β and Π can be calculated directly from S. These three parameters are important for characterizing the thermoelectric properties of TE materials, where S and Π are widely used to evaluate the ability of thermoelectric power generation and thermoelectric cooling, respectively.

1.2.4 Other Related Effects

When a charge carrier is moving in the direction perpendicular to a magnetic field, the moving charge will be deflected by the Lorentz force of the magnetic field. Similar to the effect of magnetic field on charge transport property, the thermoelectric effects also become changed under perpendicular magnetic field, resulting in some new phenomena, which are called as the thermogalvanomagnetic effects or the transverse magnetothermoelectric effects. Generally speaking, the impact of magnetic field on the Seebeck effect and the Peltier effect can be obvious only when the applied magnetic field is strong and the carrier mobility of the material is high.

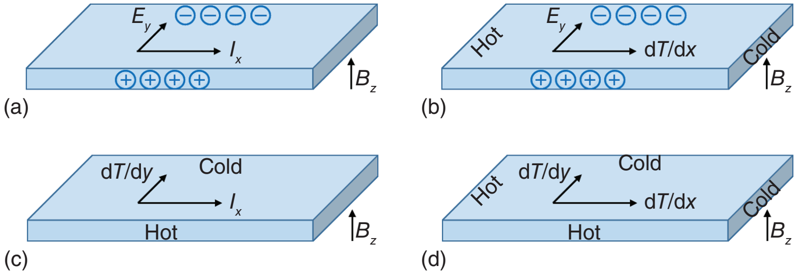

Figure 1.4 Schematic illustration of Hall effect and the other three effects of transverse magnetic field on thermoelectric properties: (a) Hall effect, (b) Nernst effect, (c) Ettingshausen effect, and (d) Righi–Leduc effect. Source: Ye Zou.

Figure 1.4 summarizes the Hall effect and the other three effects of magnetic field on thermoelectric properties, which correspond to the phenomena of generating a new electric field or a new temperature gradient under a current flow or a temperature gradient in a perpendicular magnetic field. In detail, in the spatial three-dimensional coordinate, when an isotropic sample is subjected to a uniform magnetic field B_z with direction along the longitudinal axis (z), by applying a current I_x or a temperature gradient $\mathrm{d}T/\mathrm{d}x$ to the sample along the horizontal axis (x), a new electric field E_y or a new temperature gradient $\mathrm{d}T/\mathrm{d}y$ in the vertical axis (y) direction will be generated under the transverse force of magnetic field B_z.

The charge deflection direction in a perpendicular magnetic field can be determined by Fleming's left-hand rule. For the well-known Hall effect, as illustrated in Figure 1.4a, if the longitude current density is I_x, the perpendicular magnetic field is B_z, and the transverse generated electric field strength is $E_y = \mathrm{d}V/\mathrm{d}y$, then the Hall coefficient R_H can be expressed as: $|R_\mathrm{H}| = \frac{\mathrm{d}V/\mathrm{d}y}{I_x B_z}$. The Hall effect is not directly related to the energy conversion, but it is an extremely important and effective method for investigating the charge carrier transport behavior. The Hall effect will be further introduced in Section 10.6.2.

Among different transverse magnetothermoelectric effects, the Nernst effect and the Ettingshausen effect are more directly relevant to the TE energy conversion. The Nernst effect is somewhat similar to the Hall effect in that when a perpendicular magnetic field is applied in the direction of the sample temperature gradient or heat flow, an electric field then generally appears in a direction perpendicular to both the temperature gradient ($\mathrm{d}T/\mathrm{d}x$) and the magnetic field (B_z) (Figure 1.4b). The Nernst coefficient N is determined by the relationship: $|N| = \frac{\mathrm{d}V/\mathrm{d}y}{B_z \mathrm{d}T/\mathrm{d}x}$, where $\mathrm{d}V/\mathrm{d}y$ is the generated transverse electric field. The sign of Nernst effect is illustrated in Figure 1.4b. The sign of the Hall effect is related to the polarity (sign) of the carriers, while the sign of the Nernst effect does not depend on the carrier positivity or negativity but is only related to the temperature gradient and the magnetic field direction.

The Ettingshausen effect refers to the phenomena that a transverse temperature gradient appears in the direction perpendicular to the orthogonal current flow and magnetic field (Figure 1.4c). The relationship between the Ettingshausen effect and the Nernst effect is similar to that between the Peltier effect and the Seebeck effect. They differ in that the temperature difference in the Ettingshausen effect or the Nernst effect is perpendicular to the electric field, while the temperature difference in the Peltier effect or the Seebeck effect is parallel to the electric field. The Ettingshausen coefficient P is defined by: $|P| = \frac{\mathrm{d}T/\mathrm{d}y}{I_x B_z}$, where $\mathrm{d}T/\mathrm{d}y$ is the resulting vertical transverse temperature gradient. The relationship between the Nernst coefficient and Ettingshausen coefficient is $P\kappa = NT$, where κ is the thermal conductivity.

In addition, there is another transverse magnetothermoelectric effect, namely the Righi–Leduc effect (Figure 1.4d). The Righi–Leduc effect is the phenomenon that a transverse temperature gradient ($\mathrm{d}T/\mathrm{d}y$) arises in the vertical direction when heat ($\mathrm{d}T/\mathrm{d}x$) flows across a vertical magnetic field (B_z). The Righi–Leduc coefficient M is given by: $|M| = \frac{\mathrm{d}T/\mathrm{d}y}{B_z \mathrm{d}T/\mathrm{d}x}$.

The magnetothermoelectric effect can be applied for a new type of energy conversion. Although the transverse magnetothermoelectric effect has not yet been widely applied in practice, the Ettingshausen effect has potential advantages compared with the Peltier effect for thermoelectric cooling, and the Nernst effect also has some unique advantages compared with the Seebeck effect for thermal radiation detection. For example, in cooling application, the heat source and heat sink of the Ettingshausen device are in direct contact with the side face of magnetothermoelectric material, while the heat source and heat sink of the Peltier device are in electrical contact.

1.3 Thermoelectric Parameters

1.3.1 Basic Parameters

The basic parameters associated with thermoelectric power generation (Seebeck effect) are the Seebeck coefficient, electrical conductivity, and thermal conductivity. As described in Section 1.2.1, the Seebeck coefficient is used to characterize the magnitude of Seebeck effect and is expressed as $S = \Delta V/\Delta T$, where ΔT is the temperature difference and ΔV is the corresponding potential difference under the temperature difference. The Seebeck coefficient is measured in $\mathrm{V\,K^{-1}}$ or $\mathrm{\mu V\,K^{-1}}$.

The electrical conductivity (σ), which is the reciprocal of resistivity (ρ), is used to describe the ability of electrical transport. For isotropic solid materials, the resistivity is determined by the equation $\rho = (U/I)(A/L)$, where A and L are the cross-sectional area and length of the sample, respectively; I is the current flowing through the cross-sectional area, and U is the potential difference of the sample. The electrical conductivity is then determined by $\sigma = 1/\rho = (I/U)(L/A)$ and is usually measured in $\mathrm{S\,m^{-1}}$ or $\mathrm{S\,cm^{-1}}$.

The thermal conductivity (κ) reflects a fundamental ability to transfer heat through a material by conduction. It is defined as the heat transfer per unit area of a specimen under per unit temperature difference and per unit time, and thereby is given by the formula: $\kappa = (Q/t)(L/(A\Delta T))$, where ΔT is the temperature difference, t is the time, and Q is the heat transferred. The thermal conductivity is mostly composed by the carrier contribution (carrier thermal conductivity, κ_c) and the lattice contribution (lattice thermal conductivity, κ_L), which can be described as: $\kappa = \kappa_c + \kappa_L$. The thermal conductivity is measured in $\mathrm{W\,m^{-1}\,K^{-1}}$.

The basic parameters associated with thermoelectric cooling (Peltier effect) are the Peltier coefficient, electrical conductivity, and thermal conductivity. As described in Section 1.2.2, the Peltier coefficient is used to characterize the magnitude of the Peltier effect and is expressed as $\Pi = \frac{1}{I}\frac{\mathrm{d}Q}{\mathrm{d}t}$, where $\mathrm{d}Q/\mathrm{d}t$ is the heat absorbed or liberated per unit time and I is the current. The Peltier coefficient is measured in V or mV.

1.3.2 Power Conversion Efficiency and TE Figure-of-Merit

There are two common types of thermoelectric devices based on their operational modes, namely, the power generation devices and cooling devices. They have similar structure but opposite energy conversion process. Figure 1.1 shows their operating principles. As illustrated previously, thermoelectric devices usually consist of p-type and n-type thermoelectric elements, which are connected in series to form the basic unit of a thermoelectric circuit loop. In practical application, multiple p-type and n-type units are connected alternately to form a thermoelectric module which makes heat flow in parallel and current flow in series, thereby effectively increasing the open-circuit voltage of power generator or cooling capacity of refrigerator.

1.3.2.1 Power Conversion Efficiency

In Figure 1.1a, when the p-type and n-type thermoelectric legs are connected to form a unit thermocouple for a power generator and a temperature difference ΔT is created between the hot and cold ends, then a thermopower will be generated between the p-type and n-type legs at the two cold ends and a current will appear in the circuit loop. In this way, the thermoelectric materials can realize the TE energy conversion. Power conversion efficiency is the most important index to evaluate the performance of thermoelectric devices. For thermoelectric power generation devices, the power conversion efficiency η or the thermal efficiency is the ratio of the power output over the heat absorbed at the hot end. For power generation device with homogeneous legs shown in Figure 1.1a, assuming that the thermocouple legs transport coefficients σ, S, and κ are temperature independent, the thermoelectric power conversion efficiency can be expressed as:

$$\eta = P/Q_\mathrm{h} \tag{1.7}$$

where P is the power output to the load R_L and Q_h is the absorbed heat at the source. If the current in the loop is I, then the power output in Figure 1.1a can be defined by the external load resistance as:

$$P = I^2 R_\mathrm{L} \tag{1.8}$$

Since the Seebeck voltage V in the loop is $V = S\Delta T = S(T_\mathrm{h} - T_\mathrm{c})$, the electrical current flow through the load, and the power output can then be described as:

$$I = \frac{S(T_\mathrm{h} - T_\mathrm{c})}{R + R_\mathrm{L}} \tag{1.9}$$

$$P = \left[\frac{S(T_\mathrm{h} - T_\mathrm{c})}{R + R_\mathrm{L}}\right]^2 R_\mathrm{L} = \frac{S^2(T_\mathrm{h} - T_\mathrm{c})^2}{R} \frac{R_\mathrm{L}/R}{(1 + R_\mathrm{L}/R)^2} \tag{1.10}$$

In the power generation device, assuming there is no heat transport at the heat sink other than through the two thermocouple legs and neglecting the Thomson effect and the lateral heat loss, then the total heat transfer from heat source to sink, which is composed of absorbed heat at the hot end Q_h and half the overall Joule heating travels to each of the ends, is balanced to the thermal conduction along the thermocouple legs and the Peltier cooling associated with the current flow. Therefore, the heat absorbed at the hot end with temperature $\mathrm{T_h}$ can be expressed as:

$$Q_\mathrm{h} = ST_\mathrm{h}I - \frac{1}{2}I^2R + K\Delta T \tag{1.11}$$

where S is the total Seebeck coefficient (absolute value) of the p-type and n-type thermoelectric elements, T_h and T_c are the temperatures at the ends of heat source and heat sink, respectively, R is the internal total electrical resistance, and K is the internal total thermal conductance of the p-type and n-type thermocouple legs of the device, and $\Delta T = T_\mathrm{h} - T_\mathrm{c}$ is the temperature difference between the hot and cold ends. R and K can be expressed as:

$$R = \frac{L_\mathrm{p}}{A_\mathrm{p}}\rho_\mathrm{p} + \frac{L_\mathrm{n}}{A_\mathrm{n}}\rho_\mathrm{n} \tag{1.12}$$

and

$$K = \frac{L_\mathrm{p}}{A_\mathrm{p}}\kappa_\mathrm{p} + \frac{L_\mathrm{n}}{A_\mathrm{n}}\kappa_\mathrm{n} \tag{1.13}$$

Here, ρ and κ are the resistivity and thermal conductivity of the thermocouple elemental material, and A and L are the cross-sectional area and length of the thermocouple legs. The subscripts p and n represent the p-type or n-type thermocouple legs. The first, second, and third terms on the right side of Eq. (1.11) are the Peltier cooling associated with the current flow, half the overall Joule heating travels to each of the ends, and thermal conduction along the thermocouple legs, respectively. Therefore, the power conversion efficiency η can be expressed as:

$$\eta = \frac{P}{Q_\mathrm{h}} = \frac{I^2R_\mathrm{L}}{ST_\mathrm{h}I - \frac{1}{2}I^2R + K\Delta T} = \frac{S^2(T_\mathrm{h} - T_\mathrm{c})R_\mathrm{L}}{\frac{1}{2}S^2R(T_\mathrm{h} + T_\mathrm{c}) + S^2T_\mathrm{h}R_\mathrm{L} + K(R + R_\mathrm{L})^2} \tag{1.14}$$

Defining the value of Z as $Z = S^2/KR$, the above Eq. (1.14) can be expressed as:

$$\eta = \frac{T_\mathrm{h} - T_\mathrm{c}}{T_\mathrm{h}} \frac{R_\mathrm{L}/R}{(1 + R_\mathrm{L}/R) - \frac{T_\mathrm{h} - T_\mathrm{c}}{2T_\mathrm{h}} + \frac{(1 + R_\mathrm{L}/R)^2}{ZT_\mathrm{h}}} \tag{1.15}$$

Formula 1.15 indicates that the power conversion efficiency η varies with the ratio of R_L/R in addition to the properties of the TE materials themselves and the temperature difference. The maximum power conversion efficiency $\eta_{\max}$ can be obtained by differentiating the power conversion efficiency η in Eq. (1.15) with respect to the ratio of the load resistance to the internal resistance and setting it to zero. The result yields a relationship of $R_L/R = \sqrt{1 + Z\overline{T}}$. Then, the maximum power conversion efficiency $\eta_{\max}$ is:

$$\eta_{\max} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + Z\overline{T}} - 1}{\sqrt{1 + Z\overline{T}} + T_c/T_h} \tag{1.16}$$

here, $\overline{T} = \frac{T_h + T_c}{2}$ is the average temperature. The first term on the right side of Eq. (1.16) is the Carnot cycle efficiency, and the second term is related to the temperature at both ends of the thermoelectric device. When the temperature is fixed, the power conversion efficiency is only determined by Z value of the material, and η increases monotonically with the Z value.

For the thermoelectric cooling device with the p-type and n-type thermoelectric legs connected together to form a unit thermocouple as shown in Figure 1.1b, the majority carriers (holes) in p-type thermocouple leg move in the same direction as the current, while the majority carriers (electrons) in n-type thermocouple leg move in the opposite direction of the current. Therefore, when an electrical current is applied, the carriers will move in a directional manner and carry heat, thus achieving refrigeration. In thermoelectric refrigeration device, the power conversion efficiency η is the ratio of the absorbed heat to the input electrical power. Using the same derivation method of the maximum power conversion efficiency of thermoelectric power generation device, the maximum cooling efficiency $\eta_{\max}$ of thermoelectric cooling device can be expressed as:

$$\eta_{\max} = \frac{T_c}{T_h - T_c} \frac{\sqrt{1 + Z\overline{T}} - T_h/T_c}{\sqrt{1 + Z\overline{T}} + 1} \tag{1.17}$$

The first term on the right side of Eq. (1.17) is the Carnot cycle efficiency, and the second term reflects that when temperatures of the heat absorbed and heat liberated ends are fixed, the thermoelectric cooling efficiency of the device is only determined by the Z value and increases monotonically with the Z value.

1.3.2.2 Thermoelectric Figure-of-Merit and Power Factor

In order to characterize the thermoelectric performance of a given material, the Soviet physicist Abram F. Ioffe developed a comprehensive theory from both macroscopic and microscopic aspects of thermoelectric energy conversion and proposed the quality factor, which is also known as the celebrated figure-of-merit (ZT), to explicitly describe the power conversion efficiency. The figure-of-merit is given by:

$$\mathrm{ZT} = S^2 \sigma T/\kappa \tag{1.18}$$

From the derivation of power conversion efficiency of thermoelectric device, it is clear that the dimension of Z is K^{-1} and the product of Z and T is a

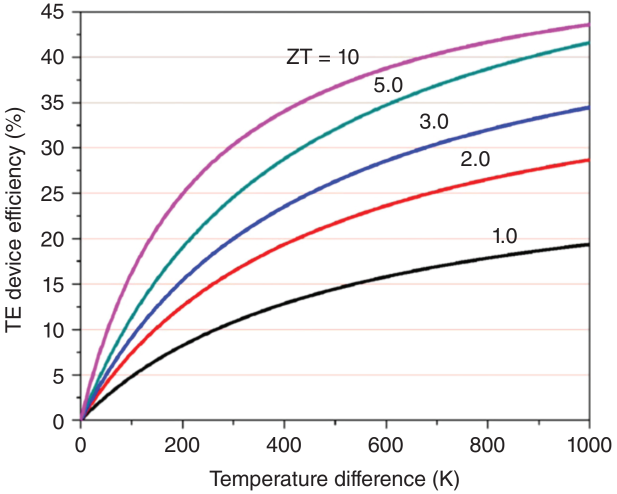

Figure 1.5 Thermoelectric power conversion efficiency as a function of ZT at $T_c = 300\,K$. Source: [18]. Reproduced with permission of Elsevier.

dimensionless value. Therefore, ZT is usually called the dimensionless thermoelectric figure-of-merit, which is determined by the property of thermoelectric materials. A higher ZT value leads to better thermoelectric performance of the thermoelectric material and a higher power conversion efficiency of the thermoelectric device. Figure 1.5 shows the variation of the power conversion efficiency as a function of ZT at $T_c = 300\,K$ for a thermoelectric generator [18]. It can be seen that the TE device efficiency increases with increasing the ZT value.

It can be known from Eq. (1.18) that an ideal TE material is expected to possess a large Seebeck coefficient to improve energy conversion, a high electrical conductivity to minimize Joule heating, and a low thermal conductivity to maintain a temperature gradient. Compared with conventional inorganic thermoelectric materials, the thermal conductivity of OTE materials is usually relatively low [9, 19–23], and the difference in thermal conductivity between different OTE materials is usually relatively small. In addition, the characterization of thermal conductivity of organic materials is complicated and difficult for precise measurements. Therefore, power factor (PF) is frequently utilized to simplify the evaluation of TE properties of OTE materials. The PF is given by the following equation:

$$\mathrm{PF} = S^2\sigma \tag{1.19}$$

The unit of PF is $\mu W\,m^{-1}\,K^{-2}$. However, ZT is still the most comprehensive evaluation index for OTE materials.

1.4 Challenges and Perspectives

Despite the rapid development of OTEs in the past decade, it is still in its infancy and facing many challenges, including: (i) the rational design and synthesis of OTE materials cannot be achieved owing to the lack of fundamental concepts and strategies; (ii) the physical images of TE conversion in conjugated molecules and structure–property relationship are not clear; (iii) the construction and integration of multifunctional OTE devices are far from satisfactory; (iv) there is no unified standard for the measurement of key TE parameters of organic thin films.

To overcome these challenges, future OTE studies should focus on the development of high-performance model systems with ZT values over 1.0, highly controllable doping method, the fundamental understanding of the mechanism of charge transport and electron–phonon coupling, multi-stage and spin-involved TE conversion, low-temperature generator, and ultrathin cooling device. In terms of application, OTE materials should focus on developing self-powered systems at room temperature by integrating portable OTE devices with low-power consumption sensors. Another opportunity relies on the integration of OTE devices and organic photovoltaic devices to improve the conversion efficiency of solar power and promote a new research topic.

From the perspective of TE performance, increasing ZT value is the core task. According to the definition of ZT, high-performance TE materials should have a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. What is more complicated is that these parameters are highly correlated. Figure 1.6 shows the dependence of three parameters of thermoelectric materials on carrier concentration. For instance, even though the increase of carrier concentration benefits high electrical conductivity, it will lead to the decrease of Seebeck coefficient and enhance thermal conductivity, simultaneously. Under this circumstance of extremely complex trade-off relationship, the TE material shows a maximum performance only at a specific carrier concentration. As a result, it is very important to realize the precise regulation of carrier concentration toward a balanced electrical and thermal transport, which is the key to enable new breakthrough in optimization of ZT value.

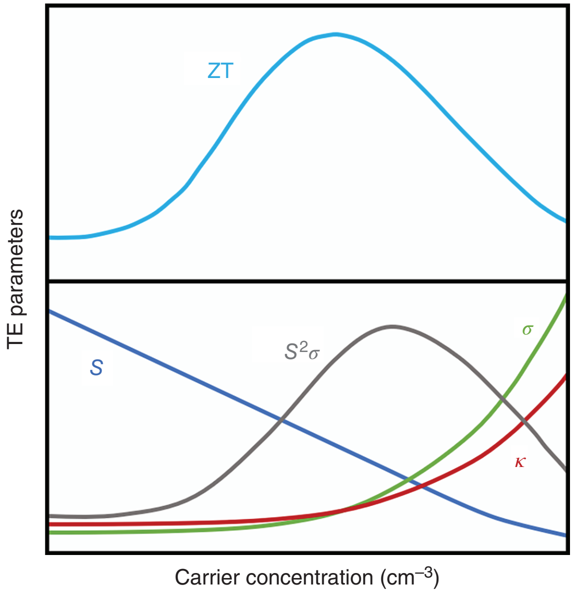

Figure 1.6 Carrier concentration dependence of electrical conductivity, Seebeck coefficient, thermal conductivity, power factor, and the ZT value. Source: Ye Zou.

Most conventional TE materials are inorganic semiconductors, and the related theory is based on the band charge transport model. In contrast, OTE materials rely on weak intermolecular interactions, and the charge transport mainly follows the hopping model. In this case, the design strategies of traditional materials cannot be fully applied to OTE candidates. At present, the molecular design and performance modulation of OTE materials are limited in three aspects: (i) the physical properties of organic materials are closely related to the conjugated and electronic structure of molecules. However, the reported excellent OTE materials are very scarce, resulting in limited experience in molecular design. Meanwhile, the existing TE theory can be hardly utilized to guide molecular design. Therefore, the design and synthesis of OTE materials are in the initial stage of exploratory attempts. (ii) Considering the multiple charge and phonon transport and scattering mechanisms, the development of low-dimensional nanostructures and superlattice-like molecular assemblies with long-range orderings is an important direction to improve TE performance. However, the assembly of such kind of specific structures is of great challenge; (iii) The enhancement of charge transport mobility is an important strategy to break the trade-off relationship of the key TE parameters. Unfortunately, current high mobility organic semiconductors usually possess low carrier concentration, which cannot meet the TE requirements. Although chemical doping can solve this problem, the introduction of dopants could easily destroy the ordered molecular packing. Keeping this in mind, universal, efficient, stable, and highly controllable doping is particularly desired for developing high-performance OTE materials based on high mobility organic semiconductors.

The lack of understanding on TE conversion mechanism is another issue for OTEs. TE conversion involves many physical processes, including charge transport, phonon transport, and scattering. Taking charge transport as an example, there are many open questions in conjugated molecules, such as complicated structures and low-ordered molecular packing. After half a century of research, the theoretical model of charge transport is still not perfect. On the other hand, the study of phonon transport and scattering in conjugated molecules is far from satisfactory. It is difficult to exploit the size effect, dimension effect, and boundary effect of traditional TE materials to introduce phonon scattering and reduce the thermal conductivity. In conclusion, a deep understanding of charge/phonon transport mechanism and the induced trade-off relationship will facilitate the rational design of OTE materials in an unexpected manner.

Devices are the key to enable the functional application of OTE materials. Currently, the studies of OTE materials mainly focus on the expansion of material categories and the improvement of performance. In contrast, the device research is still in the stage of preliminary demonstration of TE-related functionality. The future research on OTE devices mainly includes: (i) investigating the key factors affecting the power output and cooling performance of OTE devices from the aspects of interface properties, condensed structure, and device geometry; (ii) developing fabrication and integration technology of wearable OTE devices by taking advantage of the good flexibility and printability of organic candidates; (iii) systematic study of novel OTE devices, such as photo-thermoelectric device and spin thermoelectric device, will bring unprecedented opportunities for OTE device applications beyond typical power generators, refrigerators, and multifunctional sensors.

The investigation of TE performance is not only affected by aforementioned aspects, but also limited by the accurate measurement of TE parameters. For organic systems, the TE studies mainly focus on thin films with thickness of several tens to hundreds of nanometers. Compared with bulk materials, the measurement of Seebeck coefficient of thin films can be easily affected by the device structure and temperature differences. In addition, the measurement of thermal conductivity is more challenging. The 3ω method has strict requirements on the thickness and uniformity of the thin films, device structures, and test methods. Owing to this limitation, the thermal conductivity of most OTE films cannot be measured. On the other hand, carrier concentration and carrier mobility are key to study the relationship between TE process and performance. Although Hall effect is a general method to evaluate carrier concentration and carrier mobility of inorganic materials, the same measurement can be hardly utilized in many OTE materials. In Chapter 10 of this book, the topic of parameter characterization in OTE materials is discussed in detail.

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