

## 1

## Backgrounds and Principles of Low-Grade Heat Harvesting

Developing sustainable energy is one of the most promising ways to mitigate the energy crisis caused by fossil fuels and greenhouse gas emissions. Low-grade heat ( $<100\text{ }^{\circ}\text{C}$ ), as a typical wasted energy, exhibits widely in nature, industry, and daily life. Except for geothermal energy, almost all generated heat resources (solar heat, machine heat, body heat, etc.) depend on some factors and cannot meet the continuous energy demand of the modern Internet of Things (IoTs) [1]. In particular, partial solar energy can be converted into electricity by solar cells based on the photovoltaic effect. However, the enormous amount of thermal energy is still not harvested efficiently. Therefore, the development of devices to convert heat into electricity should be the top priority at present.

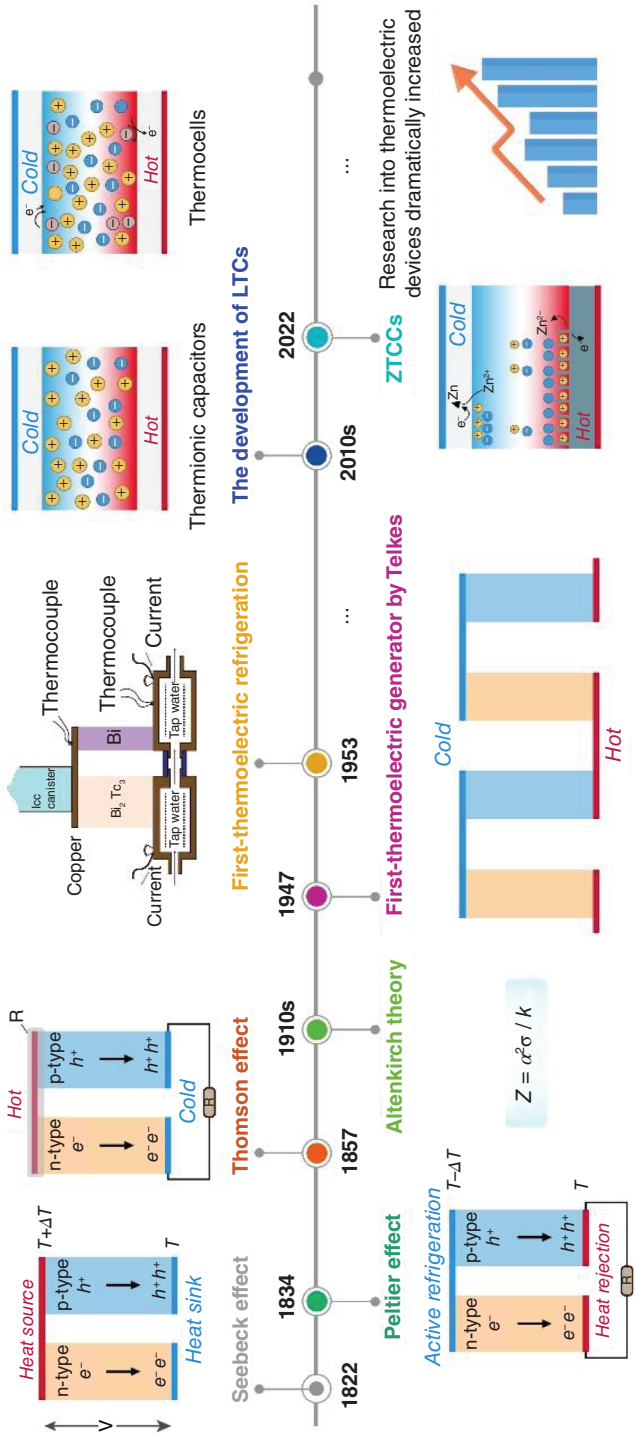
Among the various technologies, solid-state thermoelectric (s-TE) and liquid thermocell (LTC) are the two dominant energy conversion technologies for high-value-added utilization of low-grade heat [2]. It is worth noting that all thermodiffusion-based cells (TDCs), thermogalvanic effect-based cells (TGCs), and thermoextraction-based cells (TECs) using liquid electrolytes fall into the category of LTCs. With the rapid development of sustainable energy, high power, and energy electronics, new and urgent demands have been placed on energy conversion technologies, such as the integration of TE conversion and storage. Unfortunately, most of the reported devices can only realize the energy conversion from heat to electricity, and external energy storage devices (i.e. capacitors and batteries) are required to store the charge generated from thermoelectrical processes, which increases the cost and complexity of the developed systems. In general, both capacitors and batteries are the leading energy storage technologies. Especially, Li-ion batteries as one of commercial devices are widely used in consumer products due to their high energy supply. In addition, Li-ion batteries have recently been developed to further improve the energy density of batteries and meet certain requirements. However, the sluggish kinetics of electron and ion during the charging and discharging processes may lead to partial energy loss, which increases heat generation and dendrite formation. In addition, some reported failures in electric cars, airplanes, and energy storage power plants prompt us to pay attention to battery thermal management. Electrochemical capacitors, also known as

supercapacitors, can output a high power density and complement batteries in some areas due to their low cost, long cycle life, and satisfactory safety. However, many efforts are being made to improve the relatively low energy density of capacitors to meet the growing interest in high energy and power. Therefore, the development of thermoelectrochemical devices with integrated energy conversion and storage, which have fast response, long durability, and high energy/power density, is of great importance [3]. To our knowledge, TE devices can be classified into three different forms, including organic Rankine cycles, traditional TEs, and thermocells. TEs can be further divided into two types based on the electrode materials used: inorganic TEs and organic TEs. Thermocells can be identified as devices based on electric double-layer capacitive (EDLC) mechanism and pseudocapacitive behavior.

## 1.1 Backgrounds and History

The development history of thermoelectrical devices is a story of discovering energy conversion mechanisms. The demonstration of direct conversion from heat to electricity can date back to 1822. The first physical effect, named “Seebeck effect,” was found by German scientist, Thomas Johann Seebeck. As displayed by the timeline in Figure 1.1, two different metal wires were connected to form a current loop in this experiment. When heating one of the junctions while the other junction was maintained cold, there was a magnetic field exhibiting around the circuit. Although Seebeck did not provide a correct explanation for this interesting phenomenon, it did not prevent him from conducting comparative works on many materials, which laid the foundation for later thermoelectrical studies. On the basis of this design, J. C. A. Peltier found that the temperature near the junction can be changed when current flowed through two different metals in 1834, which is also called as “Peltier effect”, confirming the TE effect. Until 1838, the feature of the Peltier effect was rationally explained by Heinrich Friedrich Emil Lenz: whether the junction of two different conductors absorbs or releases heat depends on the direction of current flowing through the circuit, and the amount of heating (cooling) is proportional to the magnitude of the current. As a proof of concept, the preformed ice on the junction can be melted into water only by changing the direction of the current.

Both the Seebeck effect and the Peltier effect are discovered on the junction of two different conductors; however, those are still not interface effects. The relationship between the TE effect was not well recognized until the nineteenth century. In 1857, William Thomson (Lord Kelvin) made a comprehensive analysis of the Seebeck effect and the Peltier effect using the thermodynamic principle established by himself. Thomson believed that there was a simple multiple relationship between the Peltier coefficient and the Seebeck coefficient at absolute zero. On this basis, he theoretically predicted a new TE effect, that is, when a current flows through a conductor with uneven temperature, the conductor will not only generate irreversible Joule heat but also absorb or release a certain amount of heat. This new TE effect is also known as the Thomson effect.



**Figure 1.1** Historic timeline for the development of thermoelectric devices.

In the 1910s, Edmund Altenkirch proposed a satisfactory theory for TE refrigeration and power generation. In detail, a promising TE material must have the following merits including a large Seebeck coefficient ( $S$ , ensure relatively obvious TE effect), high electrical conductivity ( $\sigma$ , reduce the generated Joule heat), and low thermal conductivity ( $\kappa$ , retain heat near the junction). It is worth mentioning that the relationship among such parameters can be described as:  $Z = S^2\sigma/\kappa$ , which can be used to evaluate the thermoelectrical performances in practical applications. Since only metals and their compounds were considered important conductors at the time, researchers focused their attention on metals and corresponding alloys, ignoring semiconductor materials. Nevertheless, most metals exhibit a very low Seebeck coefficient ( $\sim 10 \mu\text{V K}^{-1}$ ), which not only results in a low conversion efficiency but also limits the development of thermoelectrical devices.

With the rapid development of semiconductor materials in the middle of the twentieth century, researchers found that the Seebeck coefficient of semiconductors was 10 times higher than that of metals. In 1947, the first semiconductor-based TE generator was invented by Telkes, which can deliver a heat-to-current efficiency of 5%. Meanwhile, the first TE refrigeration prototype was fabricated in 1953 by  $\text{Bi}_2\text{Te}_3$  and Bi as working electrodes. However, the advantages of semiconductor as TE material are not fully manifested due to the significant difference in conductivity between semiconductors and metals in the time. In the following time, a lot of works are focused on the properties optimization of semiconductors to obtain a high energy conversion efficiency.

In the 2010s, a new class of thermoelectrochemical system, termed LTCs, which includes thermionic capacitors and pseudocapacitive thermocells, was proposed. Typically, the thermoelectrochemical performances of LTCs can be greatly improved by electrode development and electrolyte optimization. For example, Crispin et al. constructed an ionic TE supercapacitor through a remarkably strong ionic Soret effect (thermal diffusivity) using polymeric electrolyte and carbon nanotube (CNT) electrode, which can realize the conversion of heat into stored charge [4]. On the other hand, Liu and Chen et al. have proposed a new ionic TE material based on the synergistic TD and TG effects, demonstrating significant promise for heat-to-current conversion using ions as energy carriers and opening up a new research field for high-performance thermoelectrochemical devices [5]. In 2022, Zhang and co-workers demonstrated a zinc ion thermal charging cell (ZTCC) based on the TD and TE of electrolyte ions. Because of the unique feature of a multivalent charge carrier and the relatively low potential of zinc anode, a high output voltage and large ionic Seebeck coefficient/thermopower can be achieved [6].

Since the 2020s, the amount of research related to TE devices has continuously and dramatically increased in line with the emerging increased demand for sustainable, flexible, high performance, and safe energy conversion-storage devices. Moreover, many advanced materials and devices have been discovered for high-value-added conversion of low-grade heat into stored energy, along with the development of nanoscience and characterization techniques.

## 1.2 Working Principles of Current Systems

Typically, the emerging technologies for low-grade heat harvesting include TEs and thermoelectrochemical devices. For TEs, the involved mechanisms can be divided as: (i) Seebeck effect, (ii) Peltier effect, and (iii) Thomson effect.

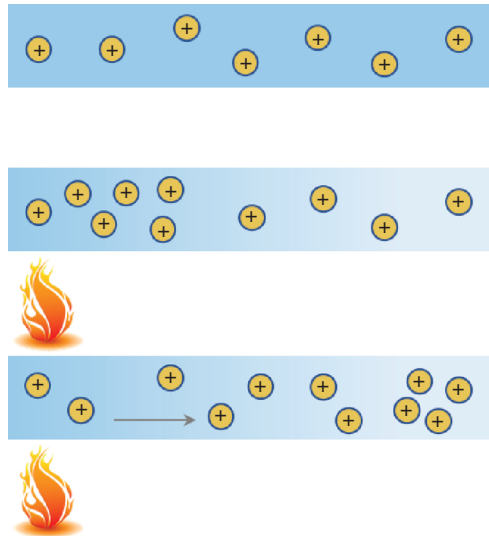
### 1.2.1 Seebeck Effect

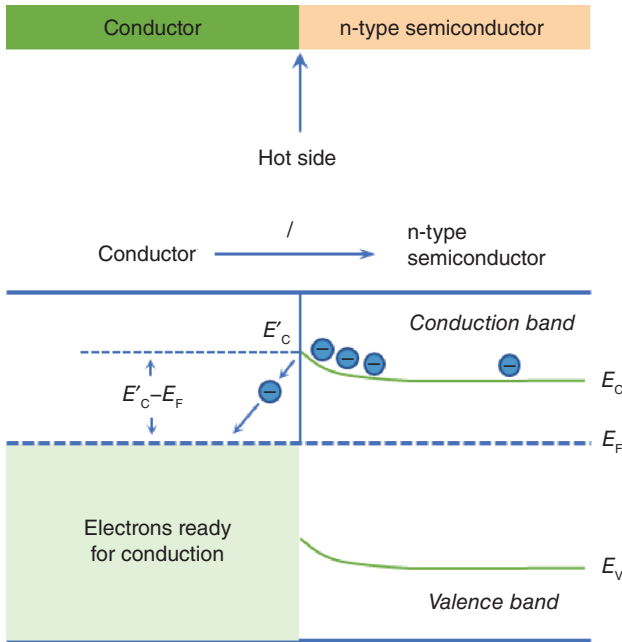
The characteristic of the Seebeck effect can be simply explained by the change of charge distribution in the conductor under temperature gradient. For p-type semiconductors, the material is electrically neutral due to the even distribution of internal carriers under a uniform temperature field. As shown in Figure 1.2, with adopting temperature difference on both ends of the conductor, a large amount of holes can be aggregated on the hot side due to the continuous energy input. Consequently, the uneven distribution of internal charge concentration leads to an electrical field or potential difference in materials. Meanwhile, under the action of the potential difference, a reverse drift charge flow could be generated. When the charge diffusion flow of thermal motion is equal to the drift charge flow generated by the internal electric field, a dynamic equilibrium is reached, and a stable thermal-induced potential ( $V$ ) can be formed at both ends of the semiconductor. Accordingly, the Seebeck coefficient ( $S$ ) of material at a specific temperature ( $T$ ) can be defined as:

$$S = \lim_{\Delta T \rightarrow 0} \frac{V}{\Delta T} \quad (1.1)$$

Similarly, the direction of thermal-induced potential for n-type semiconductors is opposite to that of p-type materials.

**Figure 1.2** Illustration of Seebeck effect using p-type materials.





**Figure 1.3** Illustration of the Peltier effect.

### 1.2.2 Peltier Effect

As displayed in Figure 1.3, when electrons flow from n-type semiconductor with high energy level to a conductor with low energy level under the action of an electric field, the electrons transition is downward at the interface barrier, resulting in a macroscopic exothermic process. When electrons flow from a conductor with low energy level to a conductor with a high energy level, they will absorb a certain amount of heat and jump upward, which is manifested as an endothermic effect. Moreover, the heat absorbed or released per unit time is proportional to the current intensity, as described by the following equation:

$$\frac{dQ}{dt} = \pi I \quad (1.2)$$

where  $\pi$  is the differential Peltier coefficient,  $t$  is the operation time, and  $I$  is the adopted current. Notably, when the current flows from the metal conductor to the p-type material, the system shows heat absorption, and the differential Peltier coefficient is negative. If the current is reversed, the Peltier coefficient also reverses positive and negative accordingly and has directionality.

### 1.2.3 Thomson Effect

The discovery of the Seebeck effect and the Peltier effect both involve a loop composed of two metals and both occur at the junction of different conductors, but neither of them is an interfacial reaction. Based on our current knowledge, we find

that they both originate from the intrinsic properties of two conductors that make up the junction.

In fact, the current regarded Thomson effect was verified experimentally in 1876. When the temperature difference of the conductor along the current direction is  $\Delta T$ , the heat released (or absorbed) per unit time on this conductor can be expressed as:

$$\frac{dQ}{dt} = \beta \Delta T I \quad (1.3)$$

where  $\beta$  represents the Thomson coefficient. When the current direction is consistent with the temperature gradient, if the conductor absorbs heat, the Thomson coefficient is positive; otherwise, it is negative. Compared with the Seebeck effect and Peltier effect, the Thomson effect contributes very little to the energy conversion in the TE conversion process, so it is often ignored in the design of TE devices and energy conversion analysis.

Thermoelectrochemical devices are another category of energy conversion systems based on the diffusion of electrolyte ions or Faradaic redox processes. Generally, the electricity is generated from the concentration difference between cation and anion caused by their different thermal mobility as well as the entropy change. Moreover, the standard electrode potential can be improved at the isothermal condition with the introduction of redox species. According to the background integrated transport property and thermodynamic behavior, various electrode materials and electrolyte systems have been developed to construct promising thermoelectrochemical devices. Although the combination of the TD and TG effects can achieve a high thermopower (or Seebeck coefficient), the relatively low output voltage and complex packaging still limit the practical applications of common thermoelectrochemical devices. Therefore, the proposal of satisfying thermoelectrochemical devices with large Seebeck coefficient, high efficiency, and low cost shows great promise to solve the bottleneck of current technology for high-value-added low-grade heat harvesting near room temperature.

Different from the traditional s-TEs, the LTCs mainly involve the electrochemical processes such as electrostatic adsorption/desorption and near-surface redox reactions, whereas TEs display the physical process dominated by directional transport of electrons and holes. It is necessary to clarify that the direct introduction of concepts about TEs into the LTCs is inappropriate. For the TD effect, the thermopower derived from ions can be defined as:

$$S_{td} = -\frac{V(T_H) - V(T_C)}{T_H - T_C} \quad (1.4)$$

where  $V(T_H)$  and  $V(T_C)$  represent the output voltage of electrode at hot temperature ( $T_H$ ) and cold temperature ( $T_C$ ), respectively. Notably, this concept is similar to conventional TEs because of their similar nature of carrier ions mobility. The essential driving force of LTCs depends on the transport of entropy from the hot end to the cold end, which is mainly contributed by the TG effect. Specifically, the redox couples in electrolyte are typically oxidized at the electrode on hot side ( $O + ne^- \rightleftharpoons R$ ), while reduction reaction occurs on cold side. The reaction products are brought to the original place by the convection in electrolyte, and thus generate thermo-voltage under

a certain temperature gradient ( $\Delta T$ ), which is defined as temperature coefficient ( $\alpha$ ), expressed as:

$$\alpha = \frac{\partial V}{\partial T} = -\frac{1}{nF} \frac{\partial \Delta G}{\partial T} = \frac{\Delta S}{nF} \quad (1.5)$$

where  $\Delta G$ ,  $\Delta S$ ,  $F$ , and  $n$  are the Gibbs free energy, entropy change, Faraday's constant, and the number of electrons transferred in the reaction, respectively. Accordingly, the increase in concentration difference and the entropy change under low-temperature gradient is an efficient way to enhance the performance of the TD-dominated device and TG effect-governed cells, respectively.

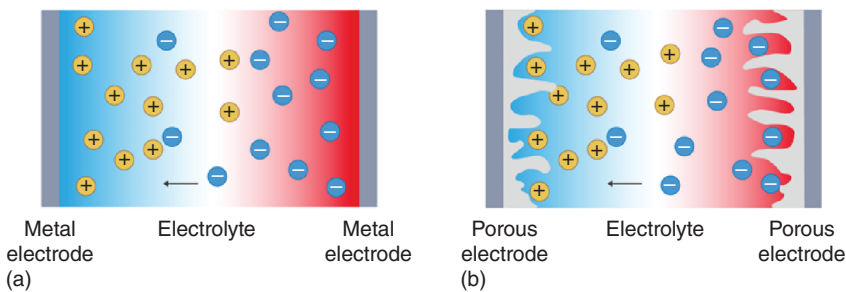
Nowadays, several works about LTCs have been contributed with the aim of achieving high-performance conversion of low-grade heat together with the design of functional electrolytes. It should point out that the development of electrode with high electrical conductivity, large surface area, and catalytic properties also can boost the output performances of LTCs. Under this consideration, well understanding of the energy conversion modes and the mechanisms between functional electrodes and electrolytes is critical to build satisfactory LTCs.

In detail, the energy conversion mechanism of thermoelectrochemical devices can mainly be classified into three types: (i) TD effect, (ii) TG effect, and (iii) TE effect.

#### 1.2.4 Thermodiffusion Effect

Generally, the mobility of electrolyte ions is the most important property of TD processes. As shown in Figure 1.4a, the cations with relatively small size can diffuse from hot side to cold side under a temperature gradient. It is worth mentioning that the anions with relatively large size would also move with the continuous input of heat. For convenience, we regraded that only cation will move and the anion will be accumulated on the hot side during the TD process. Consequently, a reasonable concentration difference of cations can be formed by the separation of electrolyte ions, which can lead to a voltage output. The potential generated from TD can be typically estimated according to the following equation [7]:

$$E_{TD} = E_{TD}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{Cation}]_H}{[\text{Cation}]_C} \quad (1.6)$$



**Figure 1.4** Illustration of thermodiffusion effect based on (a) metal electrode and (b) porous electrode.



where  $E_{TD}$  and  $E_{TD}^{\ominus}$  represent the potential difference and the standard potential between two electrodes,  $[Cation]_H$  and  $[Cation]_C$  are the concentration of cations near the hot and cold side,  $R$ ,  $T$ , and  $F$  refer to the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), temperature, and Faraday constant ( $96485.338 \text{ C mol}^{-1}$ ), respectively. Inspired by this principle, the size of electrolyte ions should be seriously considered to obtain a high cation concentration difference between the two sides. In addition, the TD processes only involve the adsorption and desorption of ions on hot/cold side. Thus, the performances (i.e. Seebeck coefficient, output voltage) of TD-dominated cells (TDCs) with metal electrodes are always at a low level.

As an efficient strategy, the TDCs can achieve attractive heat-to-current performances by replacing the metal electrodes with porous electrodes (i.e. active carbon, carbon nanotubes, and graphene) [8]. Benefitting from the structural advantages of porous electrodes including large surface area, abundant porosity, high electrical conductivity, and good stability, more electrolyte ions can be stored in porous electrodes than in plane metal electrodes, significantly enhancing the thermoelectrochemical behaviors of TDCs (Figure 1.4b). In fact, the TD procedure can belong to the category of EDLC behaviors. The open-circuit voltage (OCV) for TDC shows a linear relationship with the change of time, further confirming the EDLC processes. Therefore, the interaction between electrolyte and electrode should be well understood for further construction of TDCs.

### 1.2.5 Thermogalvanic Effect

For TGCs, the electrolyte containing redox species is sandwiched between two electrodes with different temperatures (Figure 1.5a). Due to the reversible reactions of redox couples, the entropy change can be found in TGCs during reduction and oxidation, therefore generating a thermovoltage. Notably, the electron associated with the redox reactions can move from the oxidized side to the reduced side through the external circuit. According to the Nernst equation, the equilibrium potential ( $E_{TG}$ ) of TGC can be determined by the following equation [9]:

$$E_{TG} = E_{TG}^{\ominus} - \frac{RT}{nF} \ln \frac{[\alpha_R]_H}{[\alpha_O]_C} \quad (1.7)$$

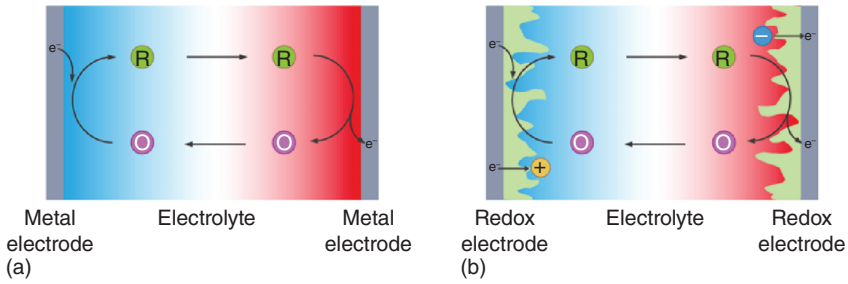
where  $E_{TG}^{\ominus}$  is the standard potential, and  $\alpha_R$  and  $\alpha_O$  represent the activities of reduced species and oxidized species, respectively. Moreover, the activity can be defined as the product of activity coefficient ( $\gamma_i$ ) and concentration ( $C_i$ ):

$$\alpha_i = \gamma_i \times C_i \quad (1.8)$$

Thus, Eq. (1.5) can be described as:

$$E_{TG} = E_{TG}^{\ominus} - \frac{RT}{nF} \left[ \ln \frac{[\gamma_R]_H}{[\gamma_O]_C} + \ln \frac{[C_R]_H}{[C_O]_C} \right] \quad (1.9)$$

In typical TGCs with metal electrodes, both concentrations of reduced species and oxidized species at hot side and cold side are same, that is, the output potential only depends on the activity coefficient of both redox couples.

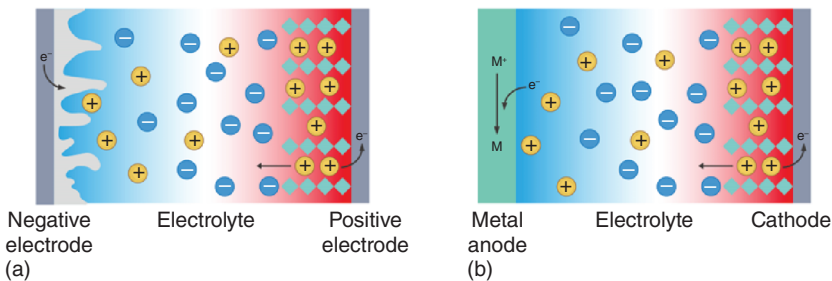


**Figure 1.5** Illustration of thermogalvanic effect based on (a) metal electrode and (b) redox electrode.

In contrast to traditional TGCs, the thermoelectrochemical performances can be further improved by changing the metal electrodes with pseudocapacitive electrodes. As known, the charge transfer (Faradaic process) at the surface or near the surface of pseudocapacitive materials exhibits fast and reversible features. As displayed in Figure 1.5b, the redox reactions that occurred between the ion carriers and active electrode materials would greatly enhance the output voltage and the thermopower of modified TGCs, owing to the integration of typical TG effect, redox-free ions concentration gradient, and contribution from redox electrode materials. Accordingly, the OCV curves for TGCs display visible platform attributed to the related redox reactions.

### 1.2.6 Thermoextraction Effect

As one attractive device among the most low-grade heat harvesting systems, TECs combine the advanced properties of both electrode and electrolyte. Most importantly, as-constructed TECs can realize the integration of energy conversion and storage. As illustrated in Figure 1.6a, the TECs are assembled by the insert-type materials (i.e.  $\text{LiMn}_2\text{O}_4$ ), EDLC materials (i.e. porous carbon), and functional electrolytes [10]. Typically, the cations inserted in positive electrodes can be extracted and transported to negative electrodes under temperature gradient. During this process, the electron produced from the redox reaction of cations extraction can move from hot side to cold side through the external circuit. After the



**Figure 1.6** Illustration of TE effect based on (a) capacitor and (b) battery mechanism.

charge accumulates on the surface of negative electrode, a plenty of cations can be adsorbed, which leads to a high concentration difference of ions between electrodes as well as the thermovoltage. Thus, the TE processes still belong to the category of pseudocapacitive behavior-induced thermoelectrochemical conversion. Similar to the above-mentioned strategies for the development of high-performance devices, both porous electrodes and insert-type electrodes should possess abundant electroactive sites, good conductivity, and high capacity, providing enough capability for ions storage and charge transfer.

Electrochemical metal anodes have recently emerged as the most promising electrode to build batteries or capacitors for energy storage due to the unique properties of metal anodes. When integrating the facile metal anode like zinc, a water-compatible device can be proposed for energy conversion and storage [6]. As shown in Figure 1.6b, the cations inserted in cathode materials can be gradually extracted with the heat input. After moving to anode side, such cations get deposited on the surface of metal anode. The formed electrons transfer from hot side to cold side during the whole thermoelectrochemical process through the external circuit. Thanks to the multivalent feature of  $Zn^{2+}$ , a high energy density and heat conversion efficiency can be obtained by TECs. Notably, attractive OCV curves can be obtained for TECs, and obvious redox feature together with relatively high kinetics can greatly enhance the output voltage. Excitingly, the metal anode can be replaced with other promising candidates, such as lithium, sodium, potassium, and some pre-metalized anodes. Worthily, the compatible electrolyte engineering and device integration should be well considered for the development of nonaqueous TECs to avoid potential safety problems.

Besides, the use of redox-free porous materials as electrodes for TGCs can also improve the output performances of devices by the combination of TD and TG effects. When employing redox-free materials as anode and redox materials as cathode, another TGC can be developed similar to “asymmetric capacitor.” We believe that more ideal mechanisms and devices will be proposed with the development of technology for energy conversion and storage.

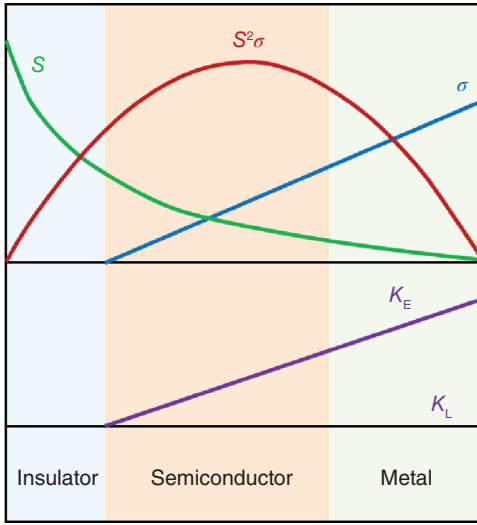
### 1.3 Parameters for Low-Grade Heat Harvesting

The unitless TE figure of merit ( $ZT$ ) of materials is an important criterion for judging the TE properties of materials. When taking n-type semiconductor as an example, the electrons and holes can be regarded as their major and minor carriers. Therefore, the relationship of  $S$ ,  $\sigma$ , and  $\kappa$  can be expressed as follows [11]:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} \quad (1.10)$$

where  $k_B$ ,  $e$ ,  $h$ , and  $m^*$  represent the Boltzmann constant, the electrical charge, the Planck constant, and the carrier effective mass, respectively.

$$\sigma = ne\mu \quad (1.11)$$



**Figure 1.7** The relationship among  $S$ ,  $\sigma$ , and  $\kappa$  for different materials.

where  $\mu$  represents the carrier mobility.

$$\kappa = D_T C_p \rho = \kappa_e + \kappa_l \quad (1.12)$$

$$\kappa_e = L\sigma T = ne\mu LT \quad (1.13)$$

where  $D_T$ ,  $C_p$ ,  $\rho$ , and  $L$  represent the thermal diffusivity, the specific heat, density, and the Lorenz number, respectively.

For a long time, research on TE materials focused mainly on improving the  $ZT$  value. According to  $ZT = S^2\sigma/\kappa$ , high-performance TE materials must have a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. Based on these relationships, the values of  $S$ ,  $\sigma$ , and  $\kappa$  for electrical materials should be balanced to optimize a high  $ZT$  value. In Figure 1.7, the relationship between the three parameters affecting the TE properties of materials and the carrier concentration is shown qualitatively. The Seebeck coefficient and the conductivity of the material are related to the charge carrier concentration of the material. As the carrier concentration increases, the conductivity increases and the Seebeck coefficient decreases, with the changes in the two parameters showing an opposite trend. For most semiconductor materials, the magnitude of the optimum carrier concentration with the best TE properties is usually  $10^{19}$ – $10^{20}$   $\text{cm}^{-3}$ , which corresponds to a heavily doped state (or degenerate state). The thermal conductivity can usually be divided into the thermal conductivity of the charge carriers and the thermal conductivity of the lattice. The thermal conductivity of the charge carriers is proportional to the electrical conductivity. Therefore, too high electrical conductivity directly leads to high thermal conductivity, which is not conducive to improving the  $ZT$  value of the material. The thermal conductivity of the lattice is relatively independent. However, since the scattering mechanisms of electrons and thermal conduction phonons are usually interconnected and interact, a decrease in lattice thermal conductivity due to scattering phonons often affects the electrical conductivity and Seebeck

coefficient. Therefore, the three important parameters,  $S$ ,  $\sigma$ , and  $\kappa$ , are closely related to each other and significantly determine the TE properties of materials. Increasing or decreasing one of the parameters alone often leads to non-synergistic changes in the other parameters. For this reason, it is difficult to continuously improve the TE performance  $ZT$ . Therefore, realizing independent or coordinated control of current and heat transport is a goal that TE materials science has long pursued.

$S$ ,  $\sigma$ , and  $\kappa$  are the main parameters that determine the TE properties of materials, and the accurate measurement of these three parameters is the core content of the performance characterization of TE materials. The Seebeck effect and the Peltier effect often interfere with the accurate measurement of the electrical and thermal properties of TE materials. After many years of technical improvements, the measurement technique for TE transport properties of bulk materials is relatively mature, but the complexity of measurement error sources and incomplete uniformity of measurement standards are still difficult problems for TE materials researchers. Here, we will focus on the measurement principles and methods of Seebeck coefficient, electrical conductivity and thermal conductivity, analyze the causes of measurement errors, and search for solutions.

### 1.3.1 Seebeck Coefficient

In the s-TE field, the Seebeck coefficient is the key instinct parameter of materials. As defined in Eq. (1.1), the  $S$  value highly depends on the adopted temperature difference ( $\Delta T$ ) and as-generated potential difference ( $\Delta V$ ). In a typical run, a temperature gradient can be established on the sample for test through the heating plate and cooling plate at the upper and lower ends. Meanwhile, the potential difference between two sides can be determined by the voltage probe. Accordingly, some conditions should be considered, including (i) stable and uniform temperature and voltage, (ii) temperature and voltage tests at the same position, and (iii) only temperature-induced case. Based on these principles, a series of  $\Delta T$  and corresponding  $\Delta V$  values can be obtained. When the  $\Delta T$  is small enough, the Seebeck coefficient can be fitted as the slope of the function of  $\Delta V$  and  $\Delta T$ . It is worth mentioning that such a proposed method is the most used way for measuring the Seebeck coefficient of TE materials.

### 1.3.2 Electrical Conductivity

Electrical conductivity is one of the basic electrochemical properties of functional materials. Compared with the measurement of the Seebeck coefficient, the testing method of electrical conductivity is relatively simple and mature. For a material with a uniform composition, the electric field inside the material is evenly distributed when a constant current is applied.

At this time, the electric field strength inside the material can be described as:

$$E = V/l \quad (1.14)$$

and the current density flowing through the material can be written as:

$$J = I/A \quad (1.15)$$

where  $l$  and  $V$  are the distance of two sides and corresponding potential differences, and  $A$  and  $I$  are the cross-sectional area and current.

Thus, the electrical conductivity ( $\sigma$ ) of materials can be determined by:

$$\sigma = \frac{J}{E} = \frac{Il}{VA} \quad (1.16)$$

Typically, the measurement methods of material conductivity mainly include the two-probe method and the four-probe method. Taking the four-probe method as an example, the sample for measurement should have a uniform composition, and the probes and the surface of sample should be kept in contact as much as possible. Besides, some other factors also need to be considered in actual measurement. To our knowledge, the thermoelectrical materials like semiconductors exhibit low resistivity, which would lead to a non-negligible error. As the self-oxidation of most materials such as alloy in atmosphere, as-formed oxide layer on the surface of materials causes a relatively large contact resistance between sample and metal probe, which will generate additional nonohmic voltage and cause test errors. To eliminate the influence of contact resistance, the slope of  $I$ - $V$  curve recorded by various voltage signals under different currents is generally employed to measure the real resistance of testing sample. Notably, TE material always has a large Seebeck coefficient and Peltier coefficient, which may inevitably form a temperature difference  $\Delta T$  at both ends of the testing sample. This process further generates additional Seebeck potential during actual test, affecting the accuracy of obtained results. Besides, the applied current should not be too high to reduce the temperature fluctuation of the sample caused by self-generated Joule heat.

### 1.3.3 Thermal Conductivity

Thermal conductivity reflects the heat conduction ability of testing materials. According to Fourier's law, thermal conductivity can be defined as the heat transferred by a unit temperature gradient (the temperature drops by 1 K within a length of 1 m) through a unit heat transfer surface in a unit time. However, due to the existence of various forms of heat exchange such as radiation, conduction, and convection, the key to accurately measuring thermal conductivity is to solve the problem of heat exchange between the testing sample and environment. It is one of the most important goals to achieve thermal insulation.

In general, the methods used for measuring thermal conductivity of samples mainly include steady-state method and nonsteady-state method. The steady-state method is the earliest method used in thermal conductivity measurement. The sample to be tested is placed between the heater and the radiator, and a stable heat source is applied at one end to keep it in a steady state. By measuring the temperature difference between the two ends of samples and the corresponding heat flux flowing, the thermal conductivity of materials can be calculated by the

following equation:

$$J_T = -\kappa \frac{dT}{dx} \quad (1.17)$$

where  $\kappa$  represents the thermal conductivity.  $dT/dx$  and  $J_T$  are temperature gradient and heat flux density, respectively.

It should be pointed out that the  $J_T$  can be directly obtained by the power of heater applied during test. However, the thermal resistance and heat exchange will cause large errors. Some great efforts have been contributed to solve this problem.

Nonsteady-state method is a rapid measurement method developed to solve the problems of long measurement time and great influence of heat loss on measurement accuracy in the steady-state heat flow method. According to the different ways of applying heat source, nonsteady-state methods mainly include periodic heat flow method and transient heat flow method. The basic principle is to apply periodic heat flow or transient (pulse) heat flow on the sample, and then measure the temperature change of sample to calculate thermal conductivity. The laser pulse method is a transient heat flow method developed in the 1960s and has become one of the most commonly used and mature thermal conductivity measurement methods [12]. In this way, the thermal conductivity of the sample can be calculated by applying a pulsed laser to heat one side, and then measuring the temperature change on the other side caused by heat conduction.

Abovementioned methods are typically employed in block thermoelectrical materials. Moreover, the accuracy of test is greatly affected by the shape and size of samples. Thus, some advanced methods should be developed for the characterization of other systems.

#### 1.3.4 Conversion Efficiency

Among the state-of-the-art techniques, TDCs and thermocells are regarded as potential devices besides s-TEs for the direct conversion of low-grade heat into electricity. When evaluating the thermoelectrochemical performances of such devices, the ratio of device voltage output to temperature difference input ( $\Delta V/\Delta T$ ) is always used as a key numeric performance index to characterize the energy conversion ability of devices. However, some differences still should be claimed.

Typically, the thermoelectrochemical performances can be evaluated by some parameters including ionic Seebeck coefficient ( $S$ ), power density ( $P$ ), normalized power density ( $P/(A \Delta T^2)$ ), and conversion efficiency ( $\eta$ ). From previous reports, various methods were used to calculate these values. However, the applicable conditions of different methods should be carefully considered to accurately report the results of developed systems [13]. Establishing the standardized principle for as-obtained performance is very helpful for researchers in thermoelectrochemical areas to avoid the confusion.

For as-assembled thermoelectrochemical devices, the energy conversion efficiency ( $\eta$ ) can be defined as the ratio of the maximum electrical power output ( $P_{\max}$ )

to the total heat power input ( $P_{\text{heat}}$ ) [14]:

$$\eta = \frac{P_{\text{max}}}{P_{\text{heat}}} \quad (1.18)$$

In a typical run,  $P_{\text{heat}}$  represents the heat flux through the cell, which can be obtained by the following equation:

$$P_{\text{heat}} = \kappa_{\text{eff}} A \frac{\Delta T}{d} \quad (1.19)$$

where  $\kappa_{\text{eff}}$  is the effective thermal conductivity,  $A$  is the cross-sectional area,  $\Delta T$  is the temperature difference between hot side and cold side, and  $d$  is the distance of both electrodes.

Under this case, the energy conversion efficiency can be written as:

$$\eta = \frac{P_{\text{max}}}{P_{\text{heat}}} = \frac{P_{\text{max}}}{\kappa_{\text{eff}} A (\Delta T / d)} \quad (1.20)$$

When considering the limitation of Carnot efficiency ( $\eta_c = \Delta T / T_{\text{hot}}$ ) for a heat engine, the Carnot-related efficiency ( $\eta_r$ ) is employed as one important criterion to evaluate the practicability of as-constructed devices, which can be further defined as:

$$\eta_r = \frac{\eta}{\eta_c} = \frac{P_{\text{max}} / \left( \kappa_{\text{eff}} A \frac{\Delta T}{d} \right)}{\frac{\Delta T}{T_{\text{hot}}}} = \frac{P_{\text{max}} d T_{\text{hot}}}{\kappa_{\text{eff}} A \Delta T^2} \quad (1.21)$$

Here, it is worth mentioning that the  $P_{\text{max}}$  can be obtained from the relationship between OCV ( $V_{\text{oc}}$ ) and short-circuit current ( $I_{\text{sc}}$ ):

$$P_{\text{max}} = \frac{V_{\text{oc}} I_{\text{sc}}}{4} \quad (1.22)$$

Thus, the Carnot-related efficiency can be expressed as:

$$\eta_r = \frac{V_{\text{oc}} I_{\text{sc}} d T_{\text{hot}}}{4 \kappa_{\text{eff}} A \Delta T^2} \quad (1.23)$$

For most reported thermoelectrochemical systems, the relationship between  $V_{\text{oc}}$ ,  $I_{\text{sc}}$ , and ionic Seebeck coefficient can be defined as  $V_{\text{oc}} = \alpha \Delta T$  and  $I_{\text{sc}} = \alpha \Delta T / R_{\text{cell}}$ , where  $R_{\text{cell}}$  is the internal resistance of systems. Thus, the following equations are obtained:

$$\eta = \frac{\alpha^2 d \Delta T}{4 \kappa_{\text{eff}} A R_{\text{cell}}} \quad (1.24)$$

$$\eta_r = \frac{\alpha^2 d T_{\text{hot}}}{4 \kappa_{\text{eff}} A R_{\text{cell}}} \quad (1.25)$$

Here, the measurement of thermal conductivity should be seriously emphasized. Due to the high mobility of liquid, the thermal conductivity could change in a large range when applying a temperature or force disturbance. Generally, the thermal conductivity of liquid can be derived from thermal conduction and thermal convection. Typical methods like hot-wire method and laser flash method are performed to measure the intrinsic thermal conductivity of materials under an isothermal and



non-flow state, in which the thermal convection can be negligible. However, these methods are not applicable for measuring the effective thermal conductivity of liquid in thermocells under a non-isothermal state. Because of the existence of large temperature difference in thermocells, the considerable convection formed in system can significantly enhance the thermal conductivity of applied liquid. Alternatively, the steady-state method based on the heat flux conservation law can directly measure the effective thermal conductivity from both thermal conduction and convection. As discussed above, the energy conversion efficiency of thermoelectrochemical devices is highly dependent on their effective thermal conductivity. Thus, the measurement of thermal conductivity for LTCs should be well considered to avoid the overevaluation of thermoelectrochemical performances.

Besides, another method for the calculation of energy conversion efficiency is established in heat recuperation. As described, the heat-to-current efficiency can be determined by the quotient of output electrical energy ( $W$ ) and input heat energy ( $Q$ ). Such general expression can be written as [15]:

$$\eta = \frac{W}{Q} = \frac{W}{Q_H + Q_{\text{dis}}} \quad (1.26)$$

where  $Q_H$  and  $Q_{\text{dis}}$  are the adsorbed heat and the continuous energy input at  $T_H$ , respectively.

Owing to the heating from  $T_C$  to  $T_H$ , the heat consumption involved in this process can be calculated by using this equation:

$$Q_H = (1 - \eta_{\text{HX}}) \sum m_i c_{p,i} \Delta T \quad (1.27)$$

where  $m_i$  and  $c_{p,i}$  represent the mass loading and specific heat capacity of the component  $i$  (such as anode, cathode, electrolyte, and current collector).  $\eta_{\text{HX}}$  is the efficiency of heat recuperation.  $\Delta T$  is the temperature difference applied, which can be determined by  $T_H - T_C$ .

Meanwhile, the energy consumption associated with chemical reactions requires continuous heat input to maintain isothermal conditions during discharge states, which can be defined as:

$$Q_{\text{dis}} = T_H \Delta S_H \quad (1.28)$$

where  $\Delta S_H$  is the total entropy change, which equals to the entropy change at cathode ( $\Delta S_{\text{H}+}$ ) and anode ( $\Delta S_{\text{H}-}$ ).

Based on the partial molar entropy change ( $\Delta s_i$ ) and the amount of component ( $i$ ), the  $\Delta S_H$  can be expressed as:

$$\Delta S_H = \int \Delta s_i dn_i \quad (1.29)$$

For electrochemical reactions involved during heat recuperation,

$$\frac{d\Delta G}{dT} = -\Delta S \quad (1.30)$$

$$\Delta G = -nFE \quad (1.31)$$

Therefore,

$$\Delta S_H = \int nF \frac{\Delta E}{\Delta T} dn_i = \alpha \int nF dn_i = \alpha q_{\text{dis}} \quad (1.32)$$

where  $q_{\text{dis}}$  is the charge transferred during discharge.

When applying Eq. (1.32) to (1.28),

$$Q_{\text{dis}} = T_H \alpha q_{\text{dis}} \quad (1.33)$$

It is worth mentioning that the specific capacitance  $C$  ( $\text{F g}^{-1}$ ) according to the report from F. Béguin's group for GCD process [16]:

$$C = \frac{2 \times I \times S}{m \times \Delta V^2} = \frac{2 \times I \int_{t_0}^{t_1} V(t) dt}{m \times \Delta V^2} \quad (1.34)$$

where  $S$  (Vs) is the integral area of discharge curve.  $I$  (A),  $m$  (g),  $\Delta V$  (V), and  $t$  (s) represent the current, the mass of active materials, the voltage range operated, and discharging time. After unit conversion and normalization of the active mass loading, the  $q_{\text{dis}}$  can be calculated.

Besides, the total network output in this experiment is measured by galvanostatic discharge technique and can be calculated from:

$$W = \int_{t_0}^{t_1} (V_1 - V_0) I_{\text{dis}} dt \quad (1.35)$$

Under above equations, we can obtain the heat-to-current efficiency of as-designed heat recuperation setup.

$$\eta = \frac{\int_{t_0}^{t_1} (V_1 - V_0) I_{\text{dis}} dt}{(1 - \eta_{\text{HX}}) \sum m_i c_{p,i} \Delta T + T_H \alpha q_{\text{dis}}} \quad (1.36)$$

However, the calculation accuracy of this method still requires attention. As found, the specific heat capacity is typically measured by differential scanning calorimetry (DSC), which cannot rule out the existence of measurement errors. Thus, the performance evaluation for thermoelectrochemical devices should be considered comprehensively with other parameters.

### 1.3.5 Power Density

Power density, as another key index, is always reported to highlight the breakthrough of as-fabricated devices. However, the units used are relatively different including W,  $\text{W g}^{-1}$ , and  $\text{W m}^{-2}$ . This phenomenon not only makes comparisons between different works difficult but also makes it difficult to determine whether there is a real breakthrough. Thus, the normalized power density ( $P/(A \cdot \Delta T^2)$ ) should be provided for reported findings. To date, the value of  $P/(A \cdot \Delta T^2)$  is still relatively low (below  $3 \text{ mW m}^{-2} \text{ K}^{-2}$ ), implying relatively sluggish conversion kinetics from heat to electricity using reported thermoelectrochemical techniques [5, 9, 14, 17–20]. In this case, new materials and devices should be further developed with high energy conversion efficiency and satisfying normalized power density.

## References

- 1 Forman, C., Muritala, I.K., Pardemann, R., and Meyer, B. (2016). *Renewable Sustainable Energy Rev.* 57: 1568.
- 2 Shi, X.L., Zou, J., and Chen, Z.G. (2020). *Chem. Rev.* 120: 7399.
- 3 Massetti, M., Jiao, F., Ferguson, A.J. et al. (2021). *Chem. Rev.* 121: 12465.
- 4 Zhao, D., Wang, H., Khan, Z.U. et al. (2016). *Energy Environ. Sci.* 9: 1450.
- 5 Han, C.G., Qian, X., Li, Q. et al. (2020). *Science* 368: 1091.
- 6 Li, Z., Xu, Y., Wu, L. et al. (2022). *Nat. Commun.* 13: 132.
- 7 Chen, D., Li, Z., Jiang, J. et al. (2020). *J. Power Sources* 465: 228263.
- 8 Kang, T.J., Fang, S., Kozlov, M.E. et al. (2012). *Adv. Funct. Mater.* 22: 477.
- 9 Yu, B., Duan, J., Cong, H. et al. (2020). *Science* 370: 342.
- 10 Meng, T., Xuan, Y., Zhang, X., and Appl, A.C.S. (2021). *Energy Mater.* 4: 6055.
- 11 Cho, J.Y., Lim, Y.S., Choi, S.-M. et al. (2011). *J. Electron. Mater.* 40: 1024.
- 12 Parker, W., Jenkins, R., Butler, C., and Abbott, G. (1961). *J. Appl. Phys.* 32: 1679.
- 13 Buckingham, M.A. and Aldous, L. (2020). *J. Electroanal. Chem.* 872: 114280.
- 14 Im, H., Kim, T., Song, H. et al. (2016). *Nat. Commun.* 7: 10600.
- 15 Lee, S.W., Yang, Y., Lee, H.W. et al. (2014). *Nat. Commun.* 5: 3942.
- 16 Laheäär, A., Przygocki, P., Abbas, Q., and Béguin, F. (2015). *Electrochem. Commun.* 60: 21.
- 17 Duan, J., Feng, G., Yu, B. et al. (2018). *Nat. Commun.* 9: 5146.
- 18 Zhang, L., Kim, T., Li, N. et al. (2017). *Adv. Mater.* 29: 1605652.
- 19 Hu, R., Cola, B.A., Haram, N. et al. (2010). *Nano Lett.* 10: 838.
- 20 Han, Y., Zhang, J., Hu, R., and Xu, D. (2022). *Sci. Adv.* 8: eabl5318.

