Flexible thermoelectric materials and devices

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ARTICLE INFO

Article history:
Received 5 June 2018
Received in revised form 9 July 2018
Accepted 9 July 2018

Keywords:
Energy harvesting
Wearable
Flexible
Thermoelectric
Power generators

ABSTRACT

Thermoelectric generators (TEGs) can directly convert waste heat into electrical power. In the last few decades, most research on thermoelectrics has focused on inorganic bulk thermoelectric materials and corresponding devices, and their thermoelectric properties have been significantly improved. An emerging topic is flexible devices, where the use of bulk inorganic materials is precluded by their inherent rigidity. The purpose of this paper is to review the research progress on flexible thermoelectric materials and generators, including theoretical principles for TEGs, conducting polymer TE materials, nanostructures comprised of inorganic nanostructures in polymer matrices and fully inorganic flexible TE materials in nanostuctured thin films. Approaches for flexible TEGs and components are reviewed, and remaining challenges discussed.

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Abbreviations: TE, thermoelectric; TEG, thermoelectric power generator; σ, electrical conductivity; T, absolute temperature; κ, thermal conductivity; k e, electron thermal conductivity; k l, lattice thermal conductivity; S, Seebeck coefficient; ZT, figure of merit; PF, power factor; n, carrier concentration; q, charge; μ, carrier mobility; I, Lorenz number; m∗, the effective mass; k B, Boltzmann constant; h, Planck constant; N, number of p-n thermocouples; κ TEG, thermal resistance of TEG; κ hot, thermal contact resistances of the hot side of the TEG; κ cool, thermal contact resistances of the cold side of the TEG; R TEG, internal electrical resistance of TEG; R L, external loading of TEG; V TEG, voltage generated by TEG; T max, maximum power TEG; E, output power density; A, geometric cros-sectional areas of the p-type leg; A, geometric cros-sectional areas of the n-type leg; η, maximum efficiency of a TEG; θ, Carnot efficiency; T hot, hot side temperature; T cool, cold side temperature; OCV, open circuit voltage; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate); RT, room temperature; CNT, carbon nanotube; DMSO, dimethyl sulfoxide; DMF, N,N-dimethylformamide.

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https://doi.org/10.1016/j.apmt.2018.07.004
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1. Introduction

In fossil fuel combustion, typically only \( \sim 34\% \) of the resulting energy is used efficiently, while the remainder is lost to the environment as waste heat [1]. Taking petrol-driven vehicles as an example, only \( \sim 25\% \) of the energy from the fuel combustion process is utilized for vehicle mobility and accessories [2]. Thermoelectric (TE) materials offer a way to convert this low-grade waste heat into electrical power, based on the Seebeck effect (Fig. 1a). This effect was discovered in 1821 by German scientist Thomas Johann Seebeck, and can be used in a wide range of energy conversion applications [3,4]. The TE energy-harvesting mechanism of a material is that when a temperature gradient (\( \Delta T \)) is applied, the charge carriers (electrons for n-type materials or holes for p-type materials) from the hot side diffuse to the cold side. As a result, an electrostatic potential (\( \Delta V \)) is induced [5,6]. The electrostatic potential generated by a single n or p-type TE leg is very low (from several \( \mu V \) to \( mV \) depending on context). Therefore, to achieve high output voltage and power, TE generators are typically made of dozens, or even hundreds, of TE couples. TE materials can also convert electrical power into thermal energy (i.e., cooling or heating) based on the Peltier effect (Fig. 1b), discovered in 1834 by French scientist Jean Charles Athanase Peltier. The Peltier effect is essentially the inverse of the Seebeck effect. TE devices exhibit many advantages, such as having no moving parts, no moving fluids, no noise, easy (or no) maintenance, and high reliability.

Traditional thermoelectric materials [7], especially tellurides like Bi$_2$Te$_3$ and PbTe, have been established since the 1950s and were used in radioisotope TEGs already on the Apollo missions. Space applications have remained an important area for thermoelectrics ever since. Since the mid-1990s, research in the TE area has largely focused on enhancing the TE properties of inorganic materials, such as Bi-Te [8,9] and Pb-Te [10] based alloys, by reducing their physical dimensionality, so as to enhance the Seebeck coefficient and increase scattering of phonons, which leads to reduction of the thermal conductivity. Enhancing the efficiency of TEGs made from inorganic materials by optimizing their geometry has been technologically important. Although the TE properties of inorganic materials and the efficiency of their corresponding TEG have been significantly improved, the thermal to electrical conversion efficiencies is still much lower than that of the maximum possible Carnot efficiency [11]. Furthermore, the traditional inorganic TE materials mentioned above are expensive and based on rare and/or toxic elements and have issues with processability. In particular, tellurium is prohibitively scarce for use of tellurides outside niche application [12].

A major emerging trend is the development of flexible thermoelectrics. This is partly motivated by the need for wearable and autonomous devices. Personal electronic devices are common in our daily lives and often rely on batteries. However, supplying power is an issue for personal electronic devices, since they are still operated on battery power, with its limitations on lifetime and requirement for periodic recharging [13]. This is a restriction, in particular, in applications such as unobtrusive low cost self-powered sensors and integrated devices for biometric monitoring. TE power generators can convert waste heat dissipated from the human body into electrical power. The output power is induced by the temperature difference between the human body (normally \( 37 \, ^\circ C \)) and the ambient temperature [6].

For flexible thermoelectrics, the most common approaches are to use either fully organic thermoelectrics or inorganic/organic hybrids. Some conducting polymers exhibit relatively good thermoelectric properties, such as poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) [14–17], polyaniline (PANI) [18], polypyrrole (PPy) [19,20] and their derivatives, by doping, or de-doping, or molecular structure optimization [21]. Nevertheless, higher thermoelectric performance (in terms of output power and/or efficiency) may be achieved in inorganic/polymer hybrid materials. For example, in inorganic/organic composite materials, the high electrical conductivity and Seebeck coefficient of the inorganic constituent can be integrated with the low thermal conductivity of the polymers, and thus achieve high thermoelectric efficiency [22–24]. More complex approaches to inorganic/organic hybrid materials include organic/inorganic laminates, and intercalation of organic molecules in layered inorganic compounds [25,26].

Finally, flexible TE legs can be made from inorganic thermoelectric materials. An alternative here is to deposit thin legs of inorganic material on a flexible polymer substrate, where good thermoelectric performance of the inorganic material can be integrated with the flexibility of the substrate. However, this is subject to the inherent limitation of thermal stability of the polymeric substrate. Therefore, to enable high-temperature use of flexible thermoelectrics, the development of fully inorganic, and high-temperature-stable, materials for flexible thermoelectrics is an outstanding issue.

There are reviews covering specific subtopics on flexible thermoelectrics, notably several excellent reviews on organic/wearable thermoelectrics [17,27–29] and carbon-nanotube-based materials and devices [30]. The purpose of the present paper is to provide a more complete overview the research progress on flexible (inorganic, organic, and hybrid) thermoelectric materials and devices. We highlight the current state-of-art strategies to optimize the TE properties of conducting polymers and their corresponding composites, and discuss approaches to achieve flexible inorganic materials. We review the preparation, characterization, and application of flexible TEGs, and assess outstanding research and technological challenges on flexible thermoelectric materials and devices. The paper is organized as follows. First, the theoretical basis is summarized (Section 2). Conducting polymer TE materials are reviewed in Section 3, and Section 4 covers inorganic materials.
nanostructure/polymer TE nanocomposites. The emerging topic of fully inorganic flexible TE materials (thin films) is covered in Section 5. Section 6 reviews flexible thermoelectric devices, and Section 7 offers some final perspectives, outlook and challenges.

2. Theoretical principle for TEGs

TEGs can be put to use in various energy conversion applications, from wrist watches to vehicles, since their output power can be in the range from several μW to kW [31]. In particular, thermoelectrics benefit from low- to medium-power and -size applications, while other conversion systems (including power plants) become less efficient as they are scaled down in size and power. They are therefore of interest for use in low- to medium-power applications, notably those used in large numbers. Taking the human body as an example, it is also a thermal source losing heat by convection, conduction, and radiation [32]. The energy expenditures of the body vary depending on activities. When a person is sitting, ~116 W power is dissipated [33]. Assuming that the temperature of the human body is 310 K (37 °C), and the ambient temperature is 263 K, the theoretical maximum of the recoverable power is 17.6 W, assuming the Carnot efficiency (see Section 2.3) which is the theoretical maximum for the efficiency of a thermodynamic process (heat engine). If the ambient temperature increases to 308 K, the maximum recoverable power correspondingly decreases to 0.75 W [6,34]. Evaporative heat, such as water-saturated air expelled from the lung and water diffusing through skin, etc., normally accounts for ~25% of the total heat dissipation [6,33]. As a result, the highest power that could theoretically be harvested from the human body is in the range from ~0.5 W to ~13 W depending on the temperature difference [6], which is still more than sufficient to power low-power personal electronics, since they normally require power supplies in the μW-to-mW-range [31].

2.1. Thermoelectric figure of merit (ZT)

The thermoelectric efficiency of a TEG depends on the thermoelectric figure of merit (ZT) of its constituent leg materials, which is expressed as Eq. (1):

\[ ZT = \frac{S^2 \sigma T}{k} \]  

where \( S \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, \( k \) is the thermal conductivity, and \( T \) is the absolute temperature. For high ZT material should have high \( \sigma \), and \( S \), and low \( k \). Design of such materials is challenging, as \( \sigma, S, \) and \( k \) are interdependent, since they are mainly determined by scattering of charge carriers, and electronic structure [35]. For example, with increasing carrier concentration, \( \sigma \) and \( k_e \) will be enhanced. As a result, \( k \) will also be increased as per Eqs. (2) and (3):

\[ \sigma = n q \mu_{\text{H}} \]  
\[ k = k_e + k_l \]  

where \( n \) is the carrier concentration, \( q \) is the charge, \( \mu_{\text{H}} \) is the carrier mobility, \( k_e \) is the electronic contribution to thermal conductivity, and \( k_l \) is the lattice thermal conductivity.

For degenerate semiconductors and metals, \( S \) can be calculated by Eq. (4) [36]:

\[ S = \frac{1}{k} \frac{8 \pi^2 k_l^2}{3 e h^2} \left( \frac{\pi}{3 n} \right)^{2/3} \]  

where \( m^* \) is the carrier effective mass, \( k_B \) and \( h \) are the Boltzmann constant and Planck’s constant, respectively.

As discussed above, the interdependency of \( \sigma, k, \) and \( S, \) constitutes a major challenge for ZT enhancement of any material system. For example, increase in carrier concentration will enhance \( \sigma \) and \( k \), but deteriorate \( S \). The carrier concentration of high TE performance materials depends on materials system. However, it is typically between 10^{15} and 10^{23} carriers per cm^3 [36].

2.2. Output voltage, power, and power density

The voltage (\( V_{\text{TEG}} \)) generated by a TEG can be estimated by Eq. (5):

\[ V_{\text{TEG}} = N(S_p - S_n) \cdot \Delta T_{\text{TEG}} = N(S_p - S_n) \frac{K_{\text{TEG}}}{K_{\text{hot}} + K_{\text{TEG}} + K_{\text{cold}}} \]  

where \( S_p \) (positive value) and \( S_n \) (negative value) are the Seebeck coefficients of the p-type and n-type semiconductors, respectively. \( N \) is the number of p–n thermocouples. \( K_{\text{TEG}}, K_{\text{hot}}, \) and \( K_{\text{cold}} \) are the thermal resistance of TEG, thermal contact resistances of hot side and cold side, respectively. Normally, the temperature drop across the TEG (\( \Delta T_{\text{TEG}} \)) is lower than that of temperature difference to the ambient (\( \Delta T \)). This is mainly attributed to the thermal resistances \( K_{\text{hot}} \) and \( K_{\text{cold}} \). This is especially important for thin devices [37].

The output power (\( P \)) can be estimated from Eq. (6):

\[ P = \frac{V_{\text{TEG}}^2}{(R_{\text{TEG}} + R_{\text{EL}})^2} R_{\text{EL}} \]  

where \( R_{\text{TEG}} \) and \( R_{\text{EL}} \) are the internal electrical resistance and the external resistive load, respectively. The power maximum (\( P_{\text{max}} \))
of the TEG is achieved, when the value of $R_{\text{TEG}}$ is equal to $R_{\text{EL}}$. This maximum power can be expressed by Eq. (7):

$$P_{\text{max}} = \frac{V_{\text{TEG}}^2}{4R_{\text{TEG}}} = \frac{[N(S_p - S_n) \cdot \Delta T_{\text{TEG}}]^2}{4R_{\text{TEG}}}$$

The output power density ($E$) can be calculated by Eq. (8):

$$E = \frac{\mathcal{P}}{S} = \frac{P}{L \times W}$$

where $S$, $W$, and $L$ are the surface area, width and length of the TEG, respectively.

### 2.3. Maximum efficiency

There are many parameters that affect the conversion efficiency of a TEG, such as the TE properties and geometric cross-sectional areas of the p and n-type legs. The optimal ratio of the geometric cross-sectional areas of the p-type ($A_p$) and n-type ($A_n$) legs can be estimated by Eq. (9) [38]:

$$\frac{A_n}{A_p} = \sqrt{\frac{\sigma_{p,kT}}{\sigma_{n,kT}}}$$

The maximum efficiency of a TE generator $\eta_{\text{TE}}$ is given by Eq. (10):

$$\eta_{\text{TE}} = \eta_c \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \left( T_{\text{cold}}/T_{\text{hot}} \right)}$$

where $\eta_c$ is the Carnot efficiency, which is an upper limit on using the waste heat for thermoelectric power generation. Again, the Carnot efficiency is the theoretical maximum for the efficiency of a thermodynamic process (heat engine), and is expressed as:

$$\eta_c = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$

where $T_{\text{hot}}$ and $T_{\text{cold}}$ are the hot side and cold side temperature, respectively.

The output voltage and power are very important for the TEGs, since they are the premise for operating normal practical electronics.

### 3. Conducting polymer TE materials

Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa first discovered conducting polyacetylene (PA) in 1970s. They were jointly awarded with the Nobel Prize in 2000 for this discovery. After that several kinds of conducting polymers were discovered, such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH), poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), polyphenylenevinylene (PPV), polycarbazoles (PC), and their corresponding derivatives [21]. Like traditional polymers, conducting polymers have a low thermal conductivity when compared to inorganic TE materials, which is beneficial for high ZT. Furthermore, conducting polymers also have low density, low cost and easy synthesis and processing into versatile forms [21]; therefore, much attention has recently been paid to conducting polymers for TE applications.

#### 3.1. P-type conducting polymer TE materials

PEDOT is one of the most successful conducting polymers [39], due to its high conductivity when doped with suitable dopants, low-density, good environmental stability, and easy synthesis [40]. One of the biggest issues restricting the application of PEDOT is its insolubility in water and common solvents, which can be addressed by emulsifying with PSS, and then forming aqueous solution, e.g., PEDOT:PSS aqueous solution (PH1000) has been commercially produced on a large scale [41]. There are mainly three methods used for enhancing the TE performance of conducting polymers: doping and de-doping, post-treatment, and crystallinity and alignment.

#### 3.1.1. Doping and de-doping

Normally, doping and de-doping strongly affect carrier mobility, carrier density, and oxidation level, which in turn influence the electrical conductivity and Seebeck coefficient of conducting polymers [15,42,43]. A range of chemicals can be used as dopants, e.g., dimethyl sulfoxide (DMSO) [44], tetrahydrofuran (THF) [45], and KOH [46]. After doping with suitable dopants, the electrical conductivity for the conducting polymers can sometimes be enhanced by several orders of magnitude, mainly because dopants help reorienting the chains of conducting polymers and enhance carrier transport [47]. For instance, Bubnova et al. [16] achieved a ZT of 0.25 in PEDOT-tosylate. The electrical conductivity of PEDOT:PSS can also be enhanced to above 1000 S/cm by doping with various organic solvents. After KOH de-doping, the Seebeck coefficient of PEDOT:PSS can increase from 15 μV/K to 90 μV/K due to the reduction of charge carriers [46].

#### 3.1.2. Post-treatment

Post-treatment can change the conformation and oxidation level of PEDOT, so as to optimize its ZT value [48]. Different kinds of solvents [48], organic solutions of inorganic salts [49], post-treatment methods [50,51], and temperatures [52] all affect the ZT value of PEDOT. For instance, Kim et al. [15] immersed spin-coated PEDOT:PSS films in ethylene glycol (EG) solvent to induce different level of de-doping of PSS by adjusting the EG treatment times, and a highest ZT value of 0.42 was achieved at RT (Fig. 2), which indicates that reducing dopant volume was an effective strategy for enhancing the ZT value of the PEDOT:PSS films. Kim et al. [53] reported that the electrical conductivity of PEDOT:PSS can reach to 4380 S/cm through H2SO4 post-treatment. The high value of the electrical conductivity mainly because the structural rearrangement of the PEDOT:PSS when treated by H2SO4. For the H2SO4 vapor treated PEDOT:PSS film, a power factor of 17 μW m⁻¹ K⁻² was achieved. This value is much higher than that of pristine PEDOT:PSS film (0.006 μW m⁻¹ K⁻²), due to the increased Seebeck coefficient and electrical conductivity, resulting from the reduction of Coulomb interaction between PSS and PEDOT, as well as the structural rearrangement of PEDOT:PSS [54]. When the PEDOT:PSS film was treated by H2SO4 three times, and then treated with NaOH, a highest power factor of 334 μW m⁻¹ K⁻² was obtained [51]. The function of acid and base treatment is to increase the electrical conductivity and adjust the oxidation level of the PEDOT, respectively [55]. In addition, the TE performance of PEDOT:PSS can also be enhanced by treatment with organic solutions of inorganic salts (e.g., ZnCl₂, CuCl₂, InCl₃, LiCl, NaCl), due to the segregation of PSS and the conformation change of PEDOT chains. After treatment with N,N-dimethylformamide (DMF) solution of ZnCl₂, an electrical conductivity of 1400 S/cm, Seebeck coefficient of 26.1 μV/K, and power factor of 98.2 μW m⁻¹ K⁻² was achieved for the PEDOT:PSS film, respectively [49].

#### 3.1.3. Crystallinity and alignment

Carriers can move both along the conducting polymer chain and interchain, however the mobility of the carriers along the chain is higher than for hopping events [43]. Therefore, the electrical conductivity and TE properties of conducting polymers can also be improved by enhancing the crystallinity and chain alignment. For example, single-crystal PEDOT nanowires with high crystallinity and high electrical conductivity (~8000 S/cm)
were fabricated via a direct printing combined with vapor phase polymerization process by Cho et al. [56]. The reason for this high electrical conductivity is mainly because of good crystalline structures, which results in enhancement of the charge-carrier mobility in PEDOT nanowires. Tsukamoto et al. [57] reported that the electrical conductivity of iodine doped polyacetylene was 10-fold enhanced (up to 10^5 S/cm) by 5-fold stretching, which indicates that high orientation resulting from stretching can enhance the electrical conductivity of PA.

3.2. N-type conducting polymer TE materials

So far, most reported conducting polymers are p-type materials, and the corresponding ZT values have been significantly enhanced (up to 0.42 at RT [15]). For TE devices, both p-type and n-type conducting polymers are required. However, most of the n-type conducting polymers are not stable in air, which limits the application of conducting polymers in TEGs. The reason why n-type doped π-conjugated conducting polymers are not stable in air is mainly because of reduced polymer chain and counterions (e.g., alkaline metal ions) undergo oxidation by O_2 [58]. Therefore, most research has been focused on p-type conducting polymers.

Inspiringly, more and more researchers are focusing on n-type conducting polymers, and therefore several kinds of n-type conducting polymers have been reported [59–67]. E.g., in 2012, Sun et al. [59] synthesized n-type poly[Na_{3}(Ni-ett)], poly[K_{2}(Ni-ett)], and p-type poly[Cu_{x}(Cu-ett)], (1,1,2,2-ethenetetrathiolate (ett)) materials. The electrical conductivity, Seebeck coefficient, and ZT value at 440 K are ~60 S/cm, ~151.7 μV/K, and 0.2 for the poly[K_{2}(Ni-ett)], respectively. Although poly[K_{2}(Ni-ett)] exhibited a high TE performance, it is insoluble in nature, limiting its application [43]. Subsequently, many solution-processed n-type conducting polymers were reported. Russ et al. [60] reported a solution-processed self-dopable polyethylene dimides (PDI), and found that as the alkyl spacer length was modified from two to six methylene groups, the Seebeck coefficient changed marginally (~200 μV/K), while the electrical conductivity increased ~100 times (up to 0.5 S/cm). A power factor of 1.4 μW m⁻¹ K⁻² was obtained. Schlitz et al. [61] prepared dihydro-1H-benzimidazol-2-yl (N-DBI) derivatives doped poly[N,N'-bis(2-octyl-dodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)] (P[NDBI]) films, with the electrical conductivity, Seebeck coefficient, and power factor of 8 × 10⁻³ S/cm, −850 μV/K, and 0.6 μW m⁻¹ K⁻², respectively. Wang et al. [62] reported a solution-processed n-type polybenzimidazobenzenanthonene (BBL) conducting polymer doped with tetrakis(dimethylamino)ethylene (TDAE), after modulating the doping level, a highest power factor ~0.43 μW m⁻¹ K⁻² was achieved. Shi et al. [63] doped FBDDPPV using [(4-(1,3-dimethyl-2,3-dihydro-1Hbenzoimidazol-2-yl)phenyl)dimethylamine] (N-DMBI). A highest electrical conductivity and power factor of 14.5 S/cm and 28 μW m⁻¹ K⁻² was achieved. Zhao et al. [64] prepared a tetrabutylammonium fluoride (TBAF) doped conjugated polymer CIDBPPV film. This material exhibit n-type conductance mainly because of electron transfer from anions F⁻ to the electron deficient polymer CIDBPPV through anion–π electronic interactions. As the TBAF doping content increased from 0 to 25 mol%, the electrical conductivity of CIDBPPV film enhanced from 1.7 × 10⁻⁶ S/cm to 0.62 S/cm, while the Seebeck coefficient decreased from −1250 μV/K to −99.2 μV/K, and a highest power factor of 0.63 μW m⁻¹ K⁻² was obtained. More recently, Zuo et al. [65] spin-coated a layer of [6,6]-phenyl-C₆₁-butryc acid methyl ester on the previously spin-coated dopant 4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)]-N,N-diphenylalanine film, and a power factor of 35 μW m⁻¹ K⁻² was obtained using this inverse-sequential doping method. Zuo et al. [66] also prepared a F4TCNQ doped P3HT multilayer film, and a power factor of 5 μW m⁻¹ K⁻² was achieved.

These examples from the literature illustrate the challenges for obtaining a sufficiently high power factor in n-type conducting polymers. The principal way to improve the power factor and ZT value of n-type conducting polymers is to enhance their electrical conductivity by doping with suitable dopants.
Most of the solution-processed conducting polymers have a low electrical conductivity, when compared to p-type conducting polymer, e.g., PEDOT:PSS. Nonetheless, Sun et al. [68] also reported a poly(Ni-ett) thin film by an electrochemical deposition method. This film shows anisotropy of the thermal transport, and a ZT value as high as 0.32 at 400 K was obtained (Fig. 3). Furthermore, this film can be deposited on flexible substrates, such as poly(ethylene terephthalate) (PET), Teflon, and polyimide, or quartz slide, or formed self-supported thin film.

Despite substantial improvement of ZT values in n-type conducting polymers (0.32 at 440 K [68]), their applicability has limiting factors, such as instability in air, poor processability, and low electrical conductivity. Developing air-stable, solution-processable, and high TE-performance n-type conducting polymers is therefore a critically important challenge.

4. Inorganic-nanostructure/polymer TE nanocomposites

4.1. Inorganic-nanostructure/conducting-polymer TE nanocomposites

Preparation of composites with inorganic nanostructure fillers in a conducting polymer matrix may be an effective route to fabricate relatively low cost, low density, and high performance TE materials, by taking advantages of the properties of conducting polymers (low thermal conductivity and tunable high electrical conductivity with dopants) and inorganic nanostructures (high electrical conductivity and Seebeck coefficient). Based on this concept, attention has been paid to inorganic-nanostructure/conducting-polymer TE composites using inorganic materials such as Te nanorods [69–71], Bi-Te- [24,72–75], and Sn-Se-based alloys [76,77], as well as carbon nanotubes [22,23,78–82], and graphene [83–85] as the fillers, and conducting polymer as matrix. Some striking experimental results have been reported. For example, the power factor of the inorganic-nanostructure/conducting-polymer composites can be greatly enhanced when using carbon nanotube or graphene as the fillers. This is mainly due to the size-dependent energy-filtering effect resulting from the surface of carbon nanotubes or graphene when coated by a layer of nanostructured conducting polymer [23], while the thermal conductivity of the composites increased marginally because of the phonon scattering effect of nanointerfaces [22]. Wang et al. [79] reported a n-type CNT/PEDOT composites treated by tetrakis(dimethylamino)ethylene (TDAE), which shows a high power factor of 1050 μW m⁻¹ K⁻², and a low thermal conductivity of 0.67 W m⁻¹ K⁻¹ mainly due to the thermally resistive CNT junctions with PEDOT. As a result, a ZT value ~0.5 was achieved.

As we discussed in an earlier review [21], using traditional methods, like physical mixing and solution mixing to prepare the inorganic semiconducting alloys/conducting-polymer composites tends to have issues of oxidation and uneven dispersion of inorganic semiconducting alloy nanostructures in the conducting polymer matrices, which significantly decreased the ZT value of the composites. To address this problem, in-situ polymerization [69], exfoliation combining spin coating or drop casting process [24,76,77] appear to be good methods to prepare inorganic semiconducting nano-layer/conducting polymer composites. For example, See et al. [69] prepared Te-nanorod/PEDOT:PSS nanocomposites, which shows a synergistic effect by taking advantages of Te nanorods with high Seebeck coefficient (408 μV/K at RT), and PEDOT:PSS with low thermal conductivity (0.24–0.29 W m⁻¹ K⁻¹ at RT). A ZT value of 0.1 at RT was achieved. In 2014, we [24] exfoliated Bi₂Te₃ based alloy particles into Bi₂Te₃ based alloy nanosheets (NSs), and then exfoliated Bi₂Te₃ based alloy NSs that can be evenly dispersed in ethanol. After that Bi₂Te₃ based alloy NS/PEDOT:PSS composite films were prepared by spin coating and drop casting the mixed solution which containing Bi₂Te₃ based alloy NSs and PEDOT:PSS, respectively. For the drop casted nanocomposite film containing 4.10 wt% Bi₂Te₃ based alloy NSs has an electrical conductivity of 1295.215 S/cm, and a ZT value of ~0.05 at RT [24]. Subsequently, Kim et al. [76,77] adopted the same method to prepare SnSe NS/PEDOT:PSS composite films, and found that as the contents of SnSe NSs filler increased from 0 to 20 wt%, the power factor of the composites dramatically increased, while the thermal conductivity of the composite increased slowly, as a result, a highest ZT value of 0.32 at RT was obtained (Fig. 4).
In addition, some layered inorganic materials, such as Bi₂Te₃, SnSe, TaS₂, MoS₂, Na₂CoO₂, and TiS₂, can be used for the preparation of layered hybrid materials. For example, Wan et al. [25] prepared a n-type hybrid superlattice of TiS₂[(hexylammonium)x(H₂O)y(DMSO)z] by an electrochemical intercalation process (Fig. 5). This compound shows an electrical conductivity of 790 S/cm, Seebeck coefficient of −78 μV/K, and thermal conductivity of 0.12 W m⁻¹ K⁻¹ at ~300 K, and a ZT value of 0.28 was obtained at 373 K. Recently, Tian et al. [26] prepared n-type TiS₂/organic hybrid superlattice films...
via an exfoliation-and-reassembly method. After annealed under vacuum, a highest power factor of 210 μWm⁻¹K⁻² was achieved at RT. Numerous other examples of this type of inorganic/organic hybrid superlattices exist [86–90]. Karttunen et al. [91] also prepared flexible thermoelectric ZnO–organic superlattices using hydroquinone as organic precursor on cotton textile though an atomic layer deposition/molecular layer deposition procedure. Preparation of inorganic-nanostructure/conducting-polymer layered hybrid structures is therefore a viable approach to fabricate high TE performance materials.

4.2. Inorganic-nanostructure/non-conducting polymer TE nanocomposites

In addition to conducting polymers, non-conducting polymer, such as poly(vinyl acetate) (PVAc) [92], polyvinylidene fluoride (PVDF) [93], and polyactic acid (PLA) [94] can be suitable matrices for the preparation of inorganic-nanostructure/polymer TE nanocomposites. This is mainly because of their low thermal conductivities and the fact that their electronic properties can be manipulated by adding inorganic fillers. For example, the electrical conductivity of the segregated-network carbon nanotube (CNT)/PVAc composites can be significantly enhanced up to 48 S/cm with 20 wt% CNT content [92], while the Seebeck coefficient (−40–50 μV/K) and thermal conductivity (0.18–0.34 Wm⁻¹K⁻¹) remain insensitive with CNT content, since they are electrically connected, but thermally disconnected. This corresponds to a ZT of 0.006 at 300 K [92]. Chen et al. [93] reported that for Ni nanowire/PVDF composites as the contents of Ni nanowires increased, an abnormal decoupling phenomenon of the electrical conductivity and Seebeck coefficient of the Ni nanowire/PVDF composites was observed. The electrical conductivity and power factor reached −4700 S/cm and 200 μWm⁻¹K⁻² at RT for the composites with 80 wt% Ni nanowires, and a maximum ZT value of 0.15 at 380 K was obtained. Zhou et al. [95] prepared a freestanding flexible Cu1.75Te nanowires/PVDF composite thin films, which showed an electrical conductivity of 2490 S/cm, Seebeck coefficient of 9.6 μV/K, and power factor of 23 μWm⁻¹K⁻² at RT. These works indicated that non-conducting polymer can also be used as a matrix to prepare inorganic-nanostructure/polymer composites, once the suitable inorganic filler was chosen, such as inorganic nanowires with high electrical conductivities. Another example is that Ju et al. [96] reported a power factor of 118 μWm⁻¹K⁻² at 400 K for camphorsulfonic acid (CSA)-doped-PANI-coated SnSe₀.₅S₀.₂ nanosheet/PVDF composite film, and after an appropriate amount of CNT was added, the power factor of the CSA-doped-PANI-coated SnSe₀.₅S₀.₂ nanosheet/PVD/CNT composite film was enhanced to 297 μWm⁻¹K⁻² at 400 K.

The TE performance of both p-type and n-type inorganic-nanostructure/polymer TE nanocomposites has been greatly improved by homogeneous and uniform dispersion of inorganic nanostructures in the polymer matrices. However, many factors affect the ZT value of polymer-based nanocomposites and therefore need to be optimized. These factors include (1) Fermi levels of inorganic nanostructures and conducting polymer must be matched, so as to minimize the energy barrier for carriers (holes or electrons) traveling between the inorganic and organic phases [97]; (2) the morphology and aspect ratios of inorganic nanostructures, e.g., nanowires, nanorods, and nanosheets need to be selected; (3) new materials and advanced preparation process also need to be developed.

5. Inorganic flexible thermoelectric thin-film materials

As discussed in the previous sections, the thermoelectric properties of conducting polymers and their corresponding nanocomposites have been significantly improved, however, they are still much lower than those of inorganic thermoelectric materials. However, for flexible thermoelectric devices, the use of inorganic materials is in general hampered by their inherent rigidity. Overcoming this issue by preparing inorganic materials as thin films, combined with micro- or nanostructural tailoring to allow flexibility, is therefore an emerging topic, and shows promise for flexible TEGs.

The most obvious manner to construct a flexible thermoelectric inorganic thin film is to deposit a thin film device onto a flexible organic substrate. However, this does not overcome the inherent limits of organic materials on application at higher temperature. Even temperature-resistant polymers such as polyimide (e.g., Kapton®) are typically restricted in use to not much above 200 °C. This leads to emerging approaches for fully inorganic thin films, which to date are mainly divided into three types: thin films based on carbon nanotubes (CNTs) or other carbon nanostructures, layered-structure or complex hexagonal-structured inorganic thin films, and thin films based on inorganic two-dimensional materials. In particular, the last approach may allow large improvements, since the ZT value of a material can be enhanced by reducing their physical dimensionality, which leads to increased density of states (DOS) for electrons (or holes) near the band edge [98,99].

5.1. Inorganic thin films deposited on flexible organic substrates

The methods for preparation of thin film thermoelectrics on organic substrates include magnetron sputtering [100–102], co-evaporation [103–105], spin-coating [106], and screen printing [107]. The idea is generally to deposit an active thermoelectric material onto an organic flexible substrate. Often, however, temperature is an issue. For example, zinc antimonide thin films deposited at low temperature on polyimide substrate required an annealing step to reach improved thermoelectric properties. A thin film annealed at 325 °C exhibited a power factor of 2350 μWm⁻¹K⁻² at 260 °C [102]. However, the annealing step must then be very rapid, as polyimide degrades if exposed to such temperatures longer-term.

Physical vapor deposition techniques such as sputter-deposition or evaporation are atomistic techniques. In contrast, spin coating, some spray-coating techniques, or screen printing directly deposit the final material from solution or powder, which may eliminate the need for high temperature deposition or annealing. For example, Yang et al. [106] fabricated flexible γ-Ag₂Te thin film by spin coated γ-Ag₂Te solution on the polyethersulphone (PES) substrate. The Seebeck coefficient of the as-prepared thin film is 1330 μV/K at RT in air and the variation is <6.7% even after 1000 bending cycles, however, the electrical conductivity is only 3.7 × 10⁻⁴ S/cm.

Generally, however, the limited tolerance temperature of the flexible organic substrates has a significant effect on the TE properties of inorganic thin films. As a result, the TE performance of the as-deposited flexible thin films is typically much lower than that of the bulk TE materials [108]. Furthermore, the use of such devices is restricted to a temperature range near room temperature.

5.2. Carbon-nanotube (CNT)-based thin films

Among the first examples of fully inorganic thin films for flexible thermoelectrics were doped fullerene-based films. In 1993, Wang
et al. [109] prepared potassium-doped fullerene ($K_5C_{70}$) thin films, which exhibited n-type conduction, with electrical conductivity, Seebeck coefficient, and power factor of 550 S/cm, $-22.5 \mu V/K$, and 2.8 $\mu W m^{-1} K^{-2}$, respectively. However, most research has focused on carbon nanotubes rather than fullerenes. This was reviewed in-depth very recently by Blackburn et al. [30]. CNTs have many advantages, such as high electrical conductivity, stable chemical properties, and strong mechanical properties. However, the reported experimental ZT value of CNTs ($10^{-3}$–$10^{-2}$) are several orders of magnitude lower than that of theoretical calculations ($>2$) [110]. To enhance the ZT value of flexible CNTs an effective method is to treat CNTs by Ar plasma. For example, the Seebeck coefficient of Ar-plasma-irradiated single-wall carbon nanotube (SCWNT) bucky ‘paper’ can reach $>300 \mu V/K$. Moreover, the thermal conductivity of the treated samples also decreased to $\sim 0.3 W m^{-1} K^{-1}$ [110]. As a result, a ZT value of 0.4 was obtained at 673 K for Ar-plasma-treated SCWNT bucky paper, which is $\sim 40$ times higher than that of the untreated pristine material, mainly because the structural order and carrier concentration change after plasma treatment [110]. A second method is to prepare composites of CNTs and inorganic materials with high Seebeck values. For instance, flexible SWCNT/Te nanowire films was prepared by a vacuum filtration [111]. The high Seebeck coefficient of Te nanowires was maintained after 2 wt% SWCNTs were added into the SWCNT/Te nanowire films, and the electrical conductivity of the composite films was significantly enhanced [111]. A third method is to design the SWCNT work function to enhance energy filtering effect at the composite interfaces. As a result, low-energy charge carriers are scattered by the energy barrier, while high-energy charge carriers can cross the energy barrier [112], leading to increased Seebeck coefficient of the composites. For instance, Choi et al. [112] adjusted the SWCNT work function by acid treatment, and then prepared flexible SWCNT/Te nanowire films by vacuum filtering. A highest power factor of $3.40 \mu W m^{-1} K^{-2}$ was obtained for the SWCNT/Te nanowire films with a lower interfacial barrier of 0.23 eV between the acid treated SWCNTs and Te nanowires, which is much higher than that of Te nanowire or the SWCNT/Te nanowire films with an interfacial barrier of 0.82 eV, mainly due to 12% enhanced energy filtering at the acid treated SWCNT and Te nanowire interfaces. The reason for decreasing energy barrier between the Te nanowires and SWCNTs from 0.82 eV to 0.23 eV is ascribed to the introduction of oxygen functional groups on SWCNT surfaces by reaction SWCNTs with nitric acid treatment for 4 h [112]. The energy filtering effect also found in the reduced graphene oxide/Te nanowires composite films [113]. In this composite system, the Te-nanowire network serves as pathway for the transport of holes from one piece of reduced graphene oxide to another one [113].

CNTs can be changed from p-type conductors to n-type conductors when doped with suitable dopants, such as polyethyleneimine (PEI), NaBH4, etc. [114–116], which provide a potential material for flexible TEGs with high TE performance. Furthermore, incorporated particles can also act as electron injectors. For example, CNT/Ag$_2$Te composite bucky papers were fabricated by a solvothermal combining drop casting process, and exhibited n-type conduction, due to electrons injected from Ag$_2$Te to CNTs [117].

5.3. Layered and other complex inorganic thin-film materials

There are approaches to grow inorganic films on thin metallic substrates to induce flexibility. For example, screen printing can be applied to deposit TE thin films on flexible substrates. For example, Lee et al. [107] fabricated ZnSb thin films on a Cu plate (200 $\mu m$ thickness) by screen printing ZnSb paste (mainly Zn and Sb powder), followed by annealing at 500 $°C$ to form ZnSb. While this temperature causes stability issues (such as Cu softening), these results indicate that screen printing can be used for flexible TEGs.

Generally, however, more complex structures are needed to synthesized free-standing inorganic flexible films. Complex layered materials, such as thermoelectric ternary cobalt oxides, show opportunities for making temperature-stable flexible fully inorganic thermoelectrics. Compared to Bi–Te based alloys, Ca$_2$Co$_4$O$_9$ has many advantages, such as abundance, nontoxicity, and inexpensive of the raw materials, which is also a promising TE material [118,119]. Paul et al. [118] fabricated flexible Ca$_2$Co$_4$O$_9$ thin films on mica substrates by sputtering/annealing using elemental targets of Ca and Co. The layered and highly anisotropic structure of Ca$_2$Co$_4$O$_9$ forms platelets in thin films. For the right composition and density, this allows the mechanical motion by gliding and rotation of the platelets, inducing mechanical flexibility in a stable thermoelectric material. The films can also be transferred onto other flexible platforms. This process is illustrated in Fig. 6 [118].

Most recently, Paul et al. [120] also prepared nanoporous Ca$_2$Co$_4$O$_9$ thin films with a power factor of $232 \mu W m^{-1} K^{-2}$ at room temperature. Another key contribution is the development of copper iodide (CuI) flexible films by Yang et al. [121], which demonstrated good room-temperature thermoelectric performance of p-type transparent CuI thin films, achieving a room-temperature ZT above 0.2, due to large Seebeck coefficients and power factors combined with low thermal conductivity attributed to a combined effect of the heavy element iodine and strong phonon scattering. Furthermore, Yang

![Fig. 6. (a) Flexible Ca$_2$Co$_4$O$_9$ films (the SEM image shows the vertical orientation of nanolaminated grains of Ca$_2$Co$_4$O$_9$). (b) Image of the thin flexible film ($T_s$: 675 $°C$). (c) Demonstration of the preparation of the thin film from the post-annealed film ($T_s$: 675 $°C$). From Paul et al. [118] (under CC-BY license).](image-url)
et al. also demonstrated a transparent and flexible CuI-based unilayer thermoelectric element [121]. These results are of major importance, since they not only show good thermoelectric performance in a p-type flexible inorganic material but are also transparent.

5.4. Thin-film thermoelectrics based on 2D materials

Layered solids, both inherently and artificially layered materials, have the fundamental limit of an atomic laminate, where each layer is an atomic or molecular layer [122]. When delaminated or exfoliated to its physical limits, the properties of the layered material are fundamentally different from its bulk counterparts, becoming a two-dimensional (2D) material. Graphene, the 2D form of carbon was demonstrated in free-standing form in 2004 [123] and awarded the Nobel Prize in Physics in 2010. Beyond graphene, there is an abundance of 2D materials stemming from layered bulk three-dimensional (3D) solids [124–129]. The term “2D material” is used not only for the single-layer free-standing form of materials (such as individual graphene sheets), but also for materials of stacked 2D layers, where the 2D properties are retained even for large total thicknesses.

Like graphene, if a suitable exfoliation process is used, layered materials such as Bi2Te3, SnSe, Bi2Se3, MoS2, WS2, MoSe2, MoTe2, TaSe2, NbSe2, and NiTe2 can be efficiently exfoliated and dispersed in solvents, and form flexible TE films [128,129]. For example, MoS2 can exist in both a hexagonal and a tetragonal form 2H and 1T phase, respectively [130,131]. The electrical conductivity of metallic 1T MoS2 phase is 102 times higher than that of the semiconducting 2H phase [130]. Exfoliated layers of 1T phase MoS2 films exhibited a power factor of 73.1 μW m−1 K−2 at RT [132]. Coleman et al. [129] exfoliated layered materials, primarily MoS2 and WS2, into 2D sheets, and then prepared MoS2/graphene and WS2/SWCNT composite films. The electrical conductivity of the WS2/SWCNT composite films was enhanced several orders of magnitude and up to ~200 S/cm as the content of SWCNT increased, as a result, the power factor increased more than 500 times (>100 μW m−1 K−2) when compared to the WS2 films (0.2 μW m−1 K−2).

Much theoretical research work on the TE properties of 2D materials has also been reported (see, e.g., [133–138]). For example, Chen et al. [133] investigated the TE properties of WSe2, MoSe2, WS2, and MoS2 monolayer, zigzag (10, 0), and armchair (6, 6) nanotubes by first-principles calculations. The results show that the ZT value of small nanotubes is lower than that of monolayers, due to the lower Seebeck coefficient, and a highest ZT of 0.91 was predicted for the WS2 monolayer at RT, which is much higher than that of zigzag WSe2 (10, 0) nanotube (0.47 at RT). As per density functional theory combined with Boltzmann transport theory, Wang et al. [135] calculated a ZT value of SnSe monolayer of up to 3.27 at 700 K, which is ~7 times higher than that of the SnSe bulk materials at 700 K, mainly due to the quantum confinement effect. Sharma et al. [136] predicted that a ZT value of 2.42 at 700 K can be obtained in 2D Bi2Te3 by optimizing the carrier concentration.

While these theoretical predictions are exciting, building on the same ideas as the original works by Hicks and Dresselhaus [98,99] and Mahan and Sofo [139], several words of caution are in order. From density functional theory, it is today rather straightforward – at least for many materials – to compute, for example elastic or piezoelectric properties. Electrical-transport and thermoelectric properties are much more challenging, since both electronic and thermal transport are involved, often outside equilibrium [140]. Calculations from Boltzmann transport theory [141] are performed within the relaxation-time approximation and thus a relaxation time τ, an unknown parameter. For Seebeck and Hall coefficients [142–144], τ cancels out if it is an isotropic constant, which is often not a valid assumption [140,143,145]. Electrical and (electronic) thermal conductivities, however, will necessarily require fitting to experimental data – for the specific material – to allow a numeric determination. In most of the predictions mentioned above, τ is either unknown or at least not accurately known, which can readily introduce order-of-magnitude errors in the predicted ZT or power factor.

Among emerging 2D materials, the class of 2D transition-metal carbide and nitrides known as MXenes (M = transition metal, X = carbon and/or nitrogen) stand out given the large possible variations in chemistry and surface termination, which allow for a wide range of property tuning [122,146–149]. Most MXenes are metallic, which causes unusual combinations of properties such as metallic conductivity combined with hydrophobicity [146–148] or very high specific capacitances for possible use as supercapacitors [150–153]. However, by tailoring the chemistry and surface terminations of MXenes, some can be made semiconducting, e.g., Mo2CTx (where T is a generic notation for surface termination). This has been predicted, for example, with a termination of pure oxygen [154]. There are also theoretical predictions that some MXenes can exhibit Dirac points like graphene [155–158]. The possibility to make semiconducting MXenes triggered interest in their thermoelectric properties, and there are numerous theoretical predictions about very high Seebeck coefficients and power factors in MXenes [159–162]. Generally, these predictions need to be treated with great care because of the inherent methodological limitations described above, and because of the great difficulty in modeling the termination in order to accurately describe the experimental conditions. Normally, the termination is a complex mix of species [163].

However, the thermoelectric properties of MXenes were investigated experimentally recently by Kim et al. [164], Three different Mo-based MXenes (Mo2CTx, Mo2TiC2Tx, and Mo2Ti2C2Tx) were investigated and processed into free-standing flexible sheets of stacked 2D materials, rendering a mechanically flexible thin and n-type material. For the Mo2TiC2Tx, relatively high power factors of 1–3 × 10−4 W m−1 K−2 were reached, although the stability to thermal cycling was an issue when cycled between room temperature and 800 K. Nonetheless, these results suggest that further exploration of the thermoelectric properties of flexible MXenes are warranted.

In summary, the development of fully inorganic flexible thin films for thermoelectrics remains in its infancy but is a rapidly emerging topic. In particular, the use of complex, layered or 2D solids to form flexible thermoelectrics shows great promise, and may overcome the inherent temperature limitations on organic materials.

6. Flexible TEGs

A TEG powered wristwatch was reported in 1999 by Kishi et al. [165]. This TEG was made of 104 elements of Bi-Te compound plates with element size of 80 μm × 80 μm × 600 μm. A maximum voltage was achieved in a time interval from 0.5 min to 1.5 min after first wearing the watch. The voltage then decreased until ~30 min (voltage at ~300 mV) since the temperature difference between the wrist and air was balanced. This result indicates that the waste heat dissipated from people can be used for powering wearable electronics using TEGs. Consequently, more and more research focused on wearable flexible TEGs. So far, many methods have been used to fabricate wearable flexible TEGs, such as, integrating commercial TE thermomple on textiles, using only p-type or n-type materials, using both of p-type and p-type materials, and endowing fabrics with a TE power-generating function.
6.1. Integrating commercial TE thermopile on textiles

In 2007, a prototype of wireless sensor nodes powered by a wearable TEG was reported [166]. This TEG produced an average power of ~250 μW (~20 μW/cm²) at daytime. Leonov [167] have integrated a commercial thermopile in a shirt and jeans and a power of 9 μW/cm² was obtained at an indoor temperature of 23 °C. In order to enhance the output power, several thermopiles were integrated into garments and a power of 0.5–5 mW was generated at environmental temperature of 27–15 °C [168].

When the wearable TEG is not worn, it will not generate power. In this case, a photovoltaic cell is a complementary approach to provide power for personal electronics [166]. Based on this train of thought, Leonov et al. [169] fabricated a hybrid energy harvester by combining TEG and photovoltaic cells. A TE module was integrated in the front side of a shirt (the area ratio of the TE module to shirt is less than 1.5%). When worn, an output power of ~0.8–1.0 mW was obtained in the office (23 °C) for a person’s sedentary activity. When the shirt is taken off, the photovoltaic cells can provide standby power. This shirt does not require technical service for its entire service life because the electronic module has waterproof encapsulation [169].

6.2. Using only p-type or n-type materials

PEDOT:PSS is used as a p-type material for flexible TEG, as due to its high TE properties. However, it requires device design. For example, an output power of merely ~0.24 μW and an open circuit voltage of ~50 μV was obtained at ∆T = 5 K in a flat configuration of a TEG fabricated by PEDOT:PSS/Ag (8 thermocouples) [170]. In contrast, a maximum power output of 334 nW was obtained at ∆T = 100 K for a 5-pair TEG (PEDOT:PSS leg dimensions: 5 mm × 15 mm × 10 μm), which was fabricated firstly by casted dimethyl sulfoxide (DMSO) doped PEDOT:PSS on the polyimide substrate, and then connected by Ag electrodes [171]. PEDOT:PSS SV3, which has different compositions of PEDOT:PSS, also shows p-type conduction characteristics. Stepien et al. [46] disperse-printed KOH dedoped commercial product PEDOT:PSS SV3 on a polyimide substrate, and used silver paste as interconnectors to fabricate a TEG. A highest output voltage and output power is ~25 mV and ~100 nW was obtained at a ∆T = 90 K for the flexible TEG with 61 unicouples.

So far, most conducting polymers and their corresponding TE composites are p-type materials, due to the poor stability of conventional n-type conducting polymers in air. This has a significant effect on the development of wearable TEGs. Wan et al. [172] reported a flexible free-standing TiS2/hexylamine superlattice foil through a solution-based synthesis process after grinding TiS2 and hexylamine using a mortar and pestle. The value of Seebeck coefficient of the as-prepared foil is negative, which demonstrates n-type conduction, mainly because of electronic transfer from hexylamine molecules into TiS2 via a Lewis acid-based reaction. A single-leg of the prepared foil with a size of 5 mm × 5 mm × 15 μm can generate a maximum output power of 24 nW and a power density of 32 μW/cm² at a ∆T = 20 K [172].

In summary, the output parameters (voltage/power) of these unipolar devices are generally low, stressing the need for using both p-and n-type materials.

6.3. Using p-type and n-type materials

Normally, the power required for micromotors, micropumps, wireless sensor networks, and micro electromechanical systems, etc., is in the range from milliwatt to microwatt [173,174], and the operating voltage for many practical devices is ~1.5 V [59]. Using both p-type and n-type materials to fabricate TEGs is an effective method to enhance their output power and voltage. Bi-Te based alloys are the most used active materials for flexible TEGs.

6.3.1. Bi-Te based alloys as active materials

Several kinds of materials can be used as substrates for flexible TEGs using p-type and n-type Bi-Te based alloys as active materials, such as organic films, fabrics, flexible printed circuit boards, and papers.

6.3.1.1. Organic film as a substrate. Polymide films are frequently used substrates for flexible TEGs. For example, a flexible TEG was fabricated by deposited of Bi2Te3 and Sb2Te3 thin films (thickness: 500 nm) on Kapton HN polyimide foil with a total size of 70 mm × 30 mm (Fig. 7) by RF magnetron co-sputtering technique [38]. The internal resistance of the device with 100 thermocouples was 380 kΩ, which is much higher than that of the calculated internal resistance (43.5 kΩ), mainly because the contact resistance and the overlapping of gold contacts on active regions. An open circuit voltage and maximum output power of 430 mV and 32 nW,
respectively, was achieved for the as-prepared TEG at a temperature different of 40 K [38]. A flexible TEG with 4 thermocouples was prepared by screen printed Bi2Te3 and Sb2Te3 pastes on a Kapton substrate, and an output power \( \sim 195 \text{nW} \) was achieved at a \( \Delta T = 20 \text{K} \). This value decreased to \( \sim 95 \text{nW} \) after 50 days, probably due to the oxidation of Bi2Te3 powder [175]. In addition to RF magnetron co-sputtering technique and screen printing, inkjet printing is a low cost and solution-based technique to fabricate flexible TEGs. For instance, Lu et al. [176] fabricated a flexible TE film device by an inkjet printing method on polyimide film using Bi0.5Sb1.5Te3 and Bi2Te2.7Se0.3 materials as p- and n-type legs, respectively.

6.3.1.2. Fabric as a substrate. Polymer-based fabric and silk fabric, etc., can also be used as the substrates for flexible TEGs, due to their advantages, such as flexible, low-cost, and low-density. For example, a flexible TEG fabricated by dispenser printed the mixture of ceramic binder and Bi1.5Te3 powder (p-type and n-type, respectively) into the windows of the fabric was reported, and a maximum power output for the TEG with 20 thermocouples was \( 2.08 \mu \text{W} \) at \( \Delta T = 30 \text{K} \). When the flexible TEG was attached to the human body (chest), a power output of 178 nW was obtained in ambient temperature of 5 °C [177]. Kim et al. [178] fabricated a wearable TEG by dispenser printing of p-type Bi0.5Sb1.5Te3 and n-type Bi2Se0.7Te2.7 printable ink in a polymer-based fabric. A maximum power output is \( \sim 224 \text{nW} \) at \( \Delta T = 20 \text{K} \) for the as-prepared 12-couple TEG. This device can harvest energy dissipated from human body and generated an output power of 146.9 nW in an ambient temperature of 5 °C. Compared to stationary people, a higher voltage output was kept when people are walking. Lu et al. [179] prepared p-type Sb2Te3 and n-type Bi2Te3 nanostructures by a hydrothermal method and then repeatedly deposited the Bi2Te3 and Sb2Te3 corresponding pastes on both side of a silk fabric to fabricate a TEG (Fig. 8). The highest power output and voltage was \( \sim 15 \text{nW} \) and \( \sim 10 \text{mV} \) at \( \Delta T = 35 \text{K} \) for the as-prepared 12-thermocouple TEG. They also found that the resistance and voltage of the TEG were stable after 100 cycles of bending, however, the resistance increased <10% after 100 cycles twisting although the voltage was no obviously enhanced [179].

Normally, polymer-based fabric and silk fabric, etc., unable to withstand high temperature, which will affect the TE properties of the Bi-Te based alloys since they need annealing at high temperatures. To this point, using glass fabric as a substrate is one of the options. Kim et al. [180] prepared a flexible TEG by successively screen printing Bi2Te3 and Sb2Te3 pastes on the glass fabric before annealed under 530 °C or 500 °C in N2 atmosphere, respectively. An open-circuit voltage, output power per unit area, and output power per unit weight of 90 mV, 3.8 mW/cm², and 28 mW/g, at \( \Delta T = 50 \text{K} \) was achieved for the generator with 8 thermocouples, respectively. The as-prepared band-type flexible TEG (11 thermocouples) can generate an open-circuit voltage and output power of 2.9 mV and 3 \( \mu \text{W} \), respectively, at an environmental temperature of 15 °C when worn on human skin (Fig. 9) [180].

6.3.1.3. Other materials as a substrate. Other materials such as paper or flexible printed circuit boards can also be used as the substrates to fabricate flexible TEGs. A flexible and foldable TEG was fabricated by a micromachining and microfabrication method using standard paper and polyester paper as a substrate, respectively [181]. The internal resistance of the standard paper based TEG (425 kΩ) is much higher than that of the polyester paper based TEG (\( \sim 130 \text{kΩ} \)) with 20 thermoelectric pairs, mainly because the smoother surface of the polyester paper. As a result, the highest output power (\( \sim 24 \text{nW} \)) of standard paper based TEG is much lower than that of the polyester paper based TEG (80 nW) at \( \Delta T = 75 \text{K} \) [181]. A flexible TEG was prepared by welding p and n-type Bi2Te3-based TE materials on the flexible printed circuit board. An output voltage of 48 mV was obtained for the TEG with 18 thermocouples at a \( \Delta T = 12 \text{K} \). When applied on a human wrist at an ambient temperature of 25 °C, the TEG produced an open circuit output voltage of 2.8 mV and an output power of 130.6 nW, and a power density of 10.4 nW/cm² [182].

These results from the literature emphasize the need for sufficient power output in these types of devices. The ZT value of materials used and structure of the devices significantly affect the output power and voltage. For example, Hyland, et al. [183] reported the effect of heat spreader material, heat spreader size, and sandwich device structure, etc. on the output powers of the...
Fig. 9. Demonstration of band-type flexible TE generator for harvesting thermal energy from human skin: (a) photos of band-type flexible TE generator and (b) electricity generation measured on human skin at an air temperature of 15 °C. Scale bar, 1 cm.

From Kim et al. [180]. © Royal Society of Chemistry, reproduced with permission.

![Diagram of flexible TE generator](image)

6.3.2. CNT as active materials

CNTs always show p-type conduction, as due to oxygen doping when exposed to air [186], Kim et al. [186] treated CNTs using polyethylenimine, diethylenetriamine, and NaBH₄ to form n-type materials with a Seebeck coefficient and an electrical conductivity of −86 μV/K and 52 S/cm, respectively. An open-circuit voltage of 465 mV was obtained at a temperature difference of 49 K for a flexible TEG fabricated by 72 thermocouples of CNT films (Fig. 10). This TEG can operate a glucose sensor at ΔT = 32 K. Hewitt et al. [187] prepared a multilayered TE fabrics using p-type carbon nanotube (CNT)/polyvinylidene fluoride (PVDF) and n-type CNT/PVDF composite films (Fig. 11), and found that the TE voltage generated by the as-prepared fabrics is the sum of contributions from every p-type and n-type layer. A highest output power of 137 nW was achieved for the TE fabrics fabricated 72-layer film at ΔT = 50 K. Both the TEGs shown in Figs. 10 and 11 are connect as l-type, a structure that can reuse the temperature gradient parallel to the surface of the TEGs. That is the main difference between the commercial inorganic TEGs (connect as π-type structure), since the π-type inorganic TEGs can reuse the temperature gradient perpendicular to the surface of the TEGs [188]. A high power factor of n-type (1500 μW m⁻¹ K⁻² at RT) single-walled carbon nanotube (SWNT) doped by polyethylenimine (PEI) was reported. A flexible TEG fabricated by p-type and n-type SWCNT with 3 pairs of thermocouples (Fig. 12) can generate an open-circuit voltage of 11.3 mV and a maximum output power of 2.51 μW at a temperature difference of 27.5 K [189]. Furthermore, p-type poly(3-hexylthiophene) (P3HT)/CNT composites can be photoinduced switching into n-type, which simplifies the TEG fabrication process by using only a single solution (Fig. 13) [190], and this is the main difference between the procedure for fabrication of flexible TEGs used in Ref. [189] (Fig. 12). Most recently, Luo et al. [191] fabricated a flexible TEG using 3-pairs of p-type and n-type LiClO₄ doped poly(ether-b-amide 12)/CNT composite films, and a voltage of 120 mV was achieved at ΔT = 60 K.

6.3.3. Other materials as active materials

Other materials such as nickel [192], poly[Kx(Ni-ett)]/poly(vinylidene fluoride) (PVDF) [193], poly[Cux(Cu-ett)]/PVDF [193], and TiS₂/organic hybrid superlattice films [26], can also be used as active materials to fabricate flexible TEGs. For instance, a flexible TEG was fabricated by evaporating nickel and silver thin films (thickness: 120 nm) on silica fiber substrates, respectively, and a highest power output of 2 nW was obtained at ΔT = 6.6 K for 7 thermocouples [192]. Jiao et al. [193] prepared n-type poly[Kx(Ni-ett)]/poly(vinylidene
Fig. 11. (a) Layer arrangement for the multilayered fabric. CNT/PVDF conduction layers (B and D) are alternated between PVDF insulation layers (A, C, and E). Every other conduction layer contains p-type CNTs (B), while the others contain n-type CNTs (D). The shorter insulating layers allow for alternating p/n junctions when the stack is pressed and heated to the polymer melting point of 450 K to bond the layers. Layers A–D can be repeated to reach the desired number of conduction layers N. When the film is exposed to a temperature gradient $\Delta T$, charge carriers (holes h, or electrons e) migrate from $T_h$ to $T_c$ resulting in a thermoelectric current $I$. (b) The resulting thermoelectric voltage $V_{TEP}$ can be read across the ends of the first and last conduction layers. (c) The thermoelectric fabric remains flexible and lightweight.

Reprinted with permission from Ref. [187]. Copyright 2012 American Chemical Society.

Fig. 12. Photographs and performance of compact-designed TE modules. The optical photograph of (a) large-area thick CNT films prepared by superposing multilayer continuously produced CNT films and densified by ethanol, (b) a CNT stripe composed of three pairs of continuous p-n couples, (c) the as-prepared flexible and compact TE module with dimensions of 16 mm × 10 mm × 0.15 mm and (d) the flexible display of the TE module.

From Zhou et al. [189] (under CC BY 4.0 license).

Fig. 13. Proposed fabrication and applications of a device geometry that plays on the advantages of the presented material. (a) A large area is coated from a single solution, and patterned by UV irradiation. (b) If desired, additional contacts (on what will be the outer side) are deposited. (c) The flexibility of the PET substrate is employed to easily connect the couples electrically in series by depositing contacts at what will be the inner side of the torus. (d) The final toroidal device geometry. Possible application geometries in the form of (e) a single torus, (f) an extended spiral, and (g) a wristband. The width of a single leg of the pictured device is 5 mm.

From Dörling et al. [190] (under CC BY-NC 4.0 license).
Fig. 14. Typical fabrication process for the rolled modules using PEDOT:PSS as p-type and CPE/CNT nanocomposite as n-type legs, respectively. First, long strips of p and n legs are deposited on a flexible Kapton film using a three-dimensional-printed mask. Second, silver contacts are deposited on the p and n legs and the films are then encapsulated using one-sided Kapton tape. Then, the Kapton film with all the thermoelectric elements is cut into several bands with p and n legs connected electrically in series. Finally, the bands are electrically connected with copper tape and rolled into cylinders.

From Fang et al. [195]. © John Wiley and Sons, reproduced with permission.

Fig. 15. (a) Chemical structure of PEDOT:PSS, (b) SEM image and (c) digital photo of polyester fabric after coating treatment.

From Du et al. [6] (under CC BY-NC-SA 4.0 license).

Fig. 16. (a) Schematic illustration of the fabric-based TE generators (I-type connection). Positive (b) and negative face (c) of the 5-strip fabric-based TE generators connected with Constantan wires. (d) TE voltage generated versus $\Delta T$, (e) the experimental results and calculated results, for the TE voltage generated per $1K\cdot\Delta T$ ($V/\Delta T$), and (f) the output voltage and power as a function of current (by adjusting the load resistance with different values) for the prepared 5-strip fabric-based devices connected by Constantan wires. (g) The thermal stability of the TE voltage generated by the 5-strip devices connected by Constantan wires under different time at a $\Delta T$ up to 78 K. (h) is the magnified results marked by a pink dotted line area in Fig. 3(d).

From Du et al. [188] (under CC BY-NC 3.0 license).
fluoride) (PVDF) and p-type poly(Cu₂O(Cu-ett))/PVDF composites using ball-milling method, and then fabricated a flexible TEG using a inkjet-printed process. The electrical conductivity and Seebeck coefficient of the as-prepared n-type and p-type composites are 2.12 S/cm and \(-44.9 \mu V/K\), and 5.14 S/cm and 41.0 \( \mu V/K \) at 300 K, respectively. The maximum output voltage 15 mV and output power 45 nW were obtained at a \( \Delta T=25 K \) for the flexible device with six thermocouples. Tian et al. [26] used TiS₂/organic hybrid superlattice films as n-type legs, and then combined PEDOT:PSS films as p-type legs to fabricate a TEG (5 pairs). An open circuit voltage, maximum output power and power density of the TEG at a temperature difference of 70 K are \( \sim 33 \) mV, \( \sim 0.9 \mu W \), and 2.5 W/m², respectively. Wang et al. [194] fabricated a 2-pair flexible TEG using C₆₀/TiS₂ hybrid films and SWNT/PEDOT:PSS films as n-type and p-type materials, respectively, and a output power of 335 nW was obtained at \( \Delta T=20 K \).

Recently, a rolled flexible TEG was fabricated by a screen printing method using PEDOT:PSS and CPE/CNT nanocomposite as p-type and n-type materials, respectively (Fig. 14) [195]. A maximum output power and open circuit voltage of the TE modules with 288 legs is 46 \( \mu W \) and 260 mV at \( \Delta T=65 K \). The as-prepared rolled generator can light up the light emitting diodes (LEDs) after boosting the output voltage. They also prepared a corrugated generator using PEDOT:PSS and Constantan as p-type and n-type materials, respectively, which is more easy to be used in a nonplanar heat sources [195].

### 6.4. Endowing fabrics with a TE power-generating function

In 2015, one of us (Du et al. [6]) first reported a flexible, air-permeable TEG by connecting the PEDOT:PSS coated commercial polyester fabric (Fig. 15) using silver wires. After PEDOT:PSS coating, the air permeability of the polyester fabric increased from 30.70 \( \pm 1.10 \) cm³/cm²/s to 47.67 \( \pm 1.73 \) cm³/cm²/s, indicating that the PEDOT:PSS coating has no negative effect on the breathable feature of the fabric. ATE voltage output and maximum output electrical power of 4.3 mV and 12.29 nW at a \( \Delta T=75.2 K \) was obtained for the flexible TE device which contain 5-stripe of PEDOT:PSS coated polyester fabric [6]. In order to further enhance the output voltage and output power, most recently we fabricated a flexible, air-permeable TEG by connecting the PEDOT:PSS coated cotton fabric using Constantan wires [188]. A voltage output of 18.7 mV and maximum output electrical power of 212.6 nW at \( \Delta T=74.3 K \) was obtained for the 5-stripe TEG, respectively (Fig. 16). The maximum output electrical power is 17.5 times higher than that of 5-stripe PEDOT:PSS coated cotton fabric TEG connected by silver wires. The reason for the multifold enhancement of the output power of the flexible TEG was mainly because both the PEDOT:PSS coated polyester and cotton fabric are p-type materials, while the silver wire and the Constantan wire function like a p-type and n-type TE material with Seebeck coefficient of 3.07 \( \mu V/K \) and \(-34.97 \mu V/K \) \( \sim 300 K \), respectively. When the PEDOT:PSS coated fabrics were connected by silver in series, hole conduction occurred in the silver wires and coated fabrics from the hot side to the cold side. As a result, the silver wires have a deleterious effect on power generation. Furthermore, this flexible TEG can be rolled up and remain operational after being bent at different bending radii and in different directions [188].

Integrating commercial TE thermopile on textiles, using only p-type or n-type materials, using both of p-type and n-type materials, and endowing fabrics with a TE power-generating function are the main methods to fabricate wearable flexible TEGs. However, the devices fabricated by the above-mentioned methods might have one or more of the following issues: containing toxic heavy metals, being difficult to process and rigid, etc. [188]. To this point, a suitable technology and process for flexible TEGs is still required.

### 7. Challenges, summary and conclusions

In summary, this review provides a number of key findings to guide and focus future research on TEGs for flexible applications. Table 1 presents a summary of the fabrication methods, materials, TE properties, size etc. of the flexible TEGs covered in this review for reference purpose.

The ZT value of conducting polymers, inorganic/conducting polymer nanocomposites, and the TE performance (output voltage, output power, output power density, flexibility, etc.) of wearable TEGs have been significantly improved in the last decade. However, flexible TEGs still have many challenges in future before they can be widely used.

The TE properties of conducting polymers depend on their chemical structure and microstructure. Doping and de-doping, post-treatment, and crystallinity and alignment are the effective methods to enhance their ZT value, however the technological conditions and process are still required to be optimized. In order to enhance the ZT value of the inorganic/conducting polymer nanocomposites, the Fermi levels of inorganic nanostructures and conducting polymer must be matched. Furthermore, the enhanced energy filtering at the interfaces should be enhanced.

Up to now, most of the conducting polymers and their corresponding TE composites are p-type materials, because of the poor stability of n-type conducting polymers in air, which significantly affect the development of wearable TEGs. Although poly[A80(Ni-ett)] exhibited the best performance in all the n-type conducting polymers, its insoluble nature severely limited its application. Therefore, research and development for stabilizing n-type conducting polymers and their corresponding TE composites are urgently needed.

For wearable applications, due to the thermal resistances of human skin and air, the temperature drop across the generator is lower than that of temperature difference to the ambient. This will significantly decrease the output voltage, power, and conversion efficiency of wearable TEGs. Therefore, enhancing the thermal resistance of TEGs and decreasing the contact thermal resistances, so as to keep a higher temperature gradient in the TEGs is important. Furthermore, many flexible TEGs are not really wearable due to their impermeability to air and moisture, which will reduce the wearing comfort. Keeping the fabric permeability unchanged and endowing fabrics with a TE power-generating function is the research direction for flexible TEGs in the future.

Due to the ZT value of p-type legs and n-type legs used for wearable TEGs are typically not equal, therefore the geometric cross-sectional areas of the p-type and n-type legs should be optimized. In addition, the skin is not smooth, which is a challenge to enhance the conversion efficiency of TEGs. Therefore, more work on optimizing wearable TEGs structure, such as the device geometry, dimension, structure, arrangement, etc. is required.

For applications in higher temperature regime, inorganic materials are required. One of the main issues for commercial devices fabricated using bulk inorganic materials is their poor mechanical flexibility. To this point, preparation of inorganic materials into thin film form, such as inorganic thin films deposited on flexible organic substrates, CNT-based thin films, layered and other complex inorganic thin-film materials, thin-film thermoelectric based on 2D materials, are promising options for flexible TEGs. However, at present, this direction of research is at an early stage, as reviewed here.

Finally, there is no established standard to measure the TE properties of flexible TEGs, although different systems have been
<table>
<thead>
<tr>
<th>Year and authors</th>
<th>Devices name, methods, and substrates</th>
<th>Materials</th>
<th>Numbers</th>
<th>P-type</th>
<th>N-type</th>
<th>$R$</th>
<th>$\Delta T$</th>
<th>OCV</th>
<th>$P_{\text{max}}$</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>2017, Beretta et al. [170]</td>
<td>Flexible TEG (inkjet printing method, 25 µm thick polyimide substrate)</td>
<td>PEDOT:PSS/Ag</td>
<td>8 thermocouples</td>
<td>5 K</td>
<td>OCV ∼ 50 µV</td>
<td>∼ 0.24 pW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014, Hokazono et al. [171]</td>
<td>Flexible TEG (casting solution method, polyimide substrate)</td>
<td>PEDOT:PSS film (Ag electrodes)</td>
<td>5 pairs</td>
<td>31.3 Ω</td>
<td>100 K</td>
<td>OCV: 7.07 mV</td>
<td>334 nW (56.8 µW/cm²)</td>
<td></td>
<td>Leg dimensions: 5 mm × 15 mm × 10 µm</td>
<td></td>
</tr>
<tr>
<td>2016 Stepien et al. [46]</td>
<td>Flexible TEG (dispense-printing, polyimide substrate)</td>
<td>PEDOT:PSS</td>
<td>61 unicouples</td>
<td>∼ 7.7 kΩ</td>
<td>90 K</td>
<td>Output voltage: ∼ 25 mV</td>
<td>∼ 100 nW</td>
<td></td>
<td>Length: 253 mm</td>
<td></td>
</tr>
<tr>
<td>2016, Wan et al. [172]</td>
<td>Free-standing flexible TE foil (solution-based synthesis process)</td>
<td>TiS$<em>2$HA$</em>{0.01}$NMF$_{0.001}$</td>
<td>Single-leg</td>
<td>20 K</td>
<td>OCV: ∼ 1.3 mV</td>
<td>24 nW (32 µW/cm²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011, Francioso et al. [38]</td>
<td>Flexible TEG (RF magnetron sputtering technique, 50 µm thick Kapton substrate)</td>
<td>Sb$_2$Te$_3$ Bi$_2$Te$_3$</td>
<td>100 thermocouples</td>
<td>380 kΩ</td>
<td>40 K</td>
<td>OCV: 430 mV</td>
<td>32 nW</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2013 Cao et al. [175]</td>
<td>Flexible TEG (screen printing method, Kapton substrate)</td>
<td>Sb$_2$Te$_3$ Bi$_2$Te$_3$</td>
<td>4 thermocouples</td>
<td>20 K</td>
<td>∼ 195 nW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kim et al. [177]</td>
<td>Fabric-based TEG (dispenser printing, polyester substrate)</td>
<td>Bi$_2$Te$_3$</td>
<td>20 thermocouples</td>
<td>300 Ω</td>
<td>30 K</td>
<td>OCV: ∼ 25 mV</td>
<td>2080 nW</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014, Kim et al. [178]</td>
<td>Fabric based TEG (dispenser printing)</td>
<td>Bi$<em>{1.5}$Sb$</em>{1.5}$Te$_3$ printable ink</td>
<td>12 thermocouples</td>
<td>∼ 900 Ω</td>
<td>20 K</td>
<td>OCV: ∼ 25 mV</td>
<td>224 nW</td>
<td></td>
<td>Area: 6 mm × 25 mm</td>
<td></td>
</tr>
<tr>
<td>2016, Lu et al. [179]</td>
<td>Silk fabric-based TEG (repeatedly depositing)</td>
<td>Bi$<em>{2.5}$Se$</em>{0.5}$Te$_{2.2}$ printable ink</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014, Kim et al. [180]</td>
<td>Glass fabric-based TEG (screen printing method)</td>
<td>Sb$_2$Te$_3$ Bi$_2$Te$_3$</td>
<td>8 thermocouples</td>
<td>∼ 0.35 Ω</td>
<td>50 K</td>
<td>OCV: 90 mV</td>
<td></td>
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</tbody>
</table>

Table 1
The TE performance of the wearable flexible TEGs covered in this review.
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<table>
<thead>
<tr>
<th>Year and authors</th>
<th>Devices name, methods, and substrates</th>
<th>Materials</th>
<th>Numbers</th>
<th>R</th>
<th>ΔT</th>
<th>OCV</th>
<th>$P_{\text{max}}$</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>2017, Rojas et al. [181]</td>
<td>Flexible and foldable standard paper based TE generator (micromachining and microfabrication method)</td>
<td>$\text{Sb}_2\text{Te}_3$</td>
<td>20 pairs</td>
<td>$425 \text{ k}\Omega$</td>
<td>$75 \text{ K}$</td>
<td>OCV: $190.7 \text{ mV}$</td>
<td>$\sim 24 \text{ nW}$</td>
<td></td>
</tr>
<tr>
<td>2017, Rojas et al. [181]</td>
<td>Flexible and foldable polyester fabric based TE generator (micromachining and microfabrication method)</td>
<td>$\text{Sb}_2\text{Te}_3$</td>
<td>20 pairs</td>
<td>$\sim 130 \text{ k}\Omega$</td>
<td>$75 \text{ K}$</td>
<td>80 nW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2017, Liu et al. [182]</td>
<td>Wearable TEG (Welded method, flexible printed circuit board substrate)</td>
<td>$\text{Bi}_2\text{Te}_3$-based TE materials</td>
<td>18 thermocouples</td>
<td>60 $\Omega$</td>
<td>12 K</td>
<td>Output voltage: 48 mV</td>
<td>8.3 $\mu$W (0.67 $\mu$W/cm$^2$) at $\Delta T = 11 \text{ K}$</td>
<td>Device size: 40 mm x 30 mm</td>
</tr>
<tr>
<td>2016, Hyland et al. [183]</td>
<td>Wearable TEG</td>
<td>$\text{Bi}_2\text{Te}_3$-based tellurium</td>
<td>25 pairs</td>
<td>Optimum load resistance: 1.8 $\Omega$</td>
<td>25.6 K</td>
<td>OCV: 693 mV</td>
<td>6.32 mW/cm$^2$</td>
<td></td>
</tr>
<tr>
<td>2017, Kim et al. [184]</td>
<td>Flexible TEG (screen printing method)</td>
<td>$\text{Bi}_2\text{Te}_3$</td>
<td>72 pairs</td>
<td>11.5 $\text{ K}\Omega$</td>
<td>49 K</td>
<td>OCV: 465 mV</td>
<td>2.28 $\mu$W/cm$^2$</td>
<td></td>
</tr>
<tr>
<td>2018, Kim et al. [185]</td>
<td>Flexible TEG</td>
<td>$\text{Bi}_2\text{Te}_3$</td>
<td>72 couples</td>
<td>2.14 $\Omega$</td>
<td>25 K</td>
<td>OCV: 693 mV</td>
<td>6.32 mW/cm$^2$</td>
<td></td>
</tr>
<tr>
<td>2014, Kim et al. [186]</td>
<td>Flexible TEG (vacuum-filtered method, polytetrafluoroethylene membrane substrate)</td>
<td>CNTs</td>
<td>72 pairs</td>
<td>11.5 K $\Omega$</td>
<td>49 K</td>
<td>OCV: 465 mV</td>
<td>2.28 $\mu$W/cm$^2$</td>
<td></td>
</tr>
<tr>
<td>2012, Hewitt et al. [187]</td>
<td>Multi layered CNT/polymer composite based TE fabrics</td>
<td>$\text{CNT/PVDF}$</td>
<td>72 layers</td>
<td>1270 $\Omega$</td>
<td>50 K</td>
<td>OCV: 26 mV</td>
<td>137 nW</td>
<td></td>
</tr>
<tr>
<td>2017, Zhou et al. [189]</td>
<td>Flexible TEG (drop casting method, 2 $\mu$m thick polyethylene terephthalate substrate)</td>
<td>$\text{SWCNTs}$</td>
<td>3 pairs</td>
<td>12.5 $\Omega$</td>
<td>27.5 K</td>
<td>OCV: 11.3 mV</td>
<td>2.51 $\mu$W (167 $\mu$W/cm$^2$)</td>
<td>Size: 16 mm x 10 mm long x 0.15 mm wide</td>
</tr>
<tr>
<td>2018, Luo et al. [191]</td>
<td>Flexible TEG (solution casting method, polyimide substrate)</td>
<td>$\text{LiClO}_4$ doped poly(ether-b- amide 12)/CNT</td>
<td>3 pairs</td>
<td>60 K</td>
<td>OCV: 120 mV</td>
<td>2.51 $\mu$W (167 $\mu$W/cm$^2$)</td>
<td>Leg size: (80 mm long x 10 mm wide)</td>
<td></td>
</tr>
</tbody>
</table>
The TE performance of the wearable flexible TEGs covered in this review.

<table>
<thead>
<tr>
<th>Year and authors, Devices name, methods, and substrates</th>
<th>Materials</th>
<th>Numbers</th>
<th>R</th>
<th>ΔT</th>
<th>OCV</th>
<th>$P_{\text{max}}$</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008, Yadav et al. [192] Fiber-based TEG (thermal evaporation method, on Silica fiber of diameter 710 μm)</td>
<td>Silver</td>
<td>7 thermocouples</td>
<td>123 Ω</td>
<td>6.6 K</td>
<td>OCV: ∼1 mV</td>
<td>2 nW</td>
<td>Nickel layer thickness: 120 nm; Silver layer thickness: 120 nm</td>
</tr>
<tr>
<td>2014, Jiao et al. [193] Flexible TEG (inkjet printing method, polyethylene terephthalate (PET) substrate)</td>
<td>poly[Cu0.75(Cu- ett)]/PVDF/DMSO</td>
<td>6 thermocouples</td>
<td>Load resistance: 5000 Ω</td>
<td>25 K</td>
<td>Maximum output voltage: 15 nV</td>
<td>45 nW</td>
<td></td>
</tr>
<tr>
<td>2017, Tian et al. [26] Flexible TEG (deposited on PET substrate)</td>
<td>PEDOT:PSS/TiS2/organic hybrid superlattice films</td>
<td>5 pairs</td>
<td>250 Ω</td>
<td>70 K</td>
<td>OCV: ∼33 mV</td>
<td>∼0.9 μW (2.5 W/m²)</td>
<td>Leg size: 5 mm × 20 mm</td>
</tr>
<tr>
<td>2018, Wang et al. [194] Flexible TEG (flexible plastic substrate)</td>
<td>SWNT/PEDOT:PSS</td>
<td>2 pairs</td>
<td>16.6 Ω</td>
<td>20 K</td>
<td>335 nW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2017, Fang et al. [195] Flexible rolled TEG (screen printing method, Kapton substrate)</td>
<td>PEDOT:PSS</td>
<td>288 legs</td>
<td>350 Ω</td>
<td>65 K</td>
<td>OCV: 260 mV</td>
<td>46 μW</td>
<td></td>
</tr>
<tr>
<td>2017, Du et al. [188] Cotton-based fabric TEG (solution coating, cotton fabric substrate)</td>
<td>PEDOT:PSS coated polyester fabric strips connected with Constantan wire</td>
<td>5</td>
<td>74.3 K</td>
<td>OCV: 18.7 mV</td>
<td>212.6 nW</td>
<td></td>
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Years and authors...
proposed for the characterization of the TE properties of commercial bulk TEGs. In this scenario, a standard technology for characterization of flexible materials and wearable TEGs need to be developed.

Acknowledgments

This work has been supported by the National Natural Science Foundation of China (61504081, 61611530550), the Program for Professor of Special Appointment (Young Eastern Scholar Program) at Shanghai Institutions of Higher Learning (Q20150309), and the Shanghai Innovation action plan project (17090503600). We also acknowledge support from the European Research Council under the European Community’s Seventh Framework Program (FP/2007–2013)/ERC grant agreement No. 335383, the Swedish Research Council (VR) under project No. 2016-3365, the Eurostars project E18892 T-to-Power, the Swedish Foundation for Strategic Research (SSF) through the Future Research Leaders 5 program, and the Knut and Alice Wallenberg Foundation under the Wallenberg Academy Fellows program.

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