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Current progress and future challenges in thermoelectric power generation: From materials to devices

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Abstract—Thermoelectric power generation (TEG) represents one of the cleanest methods of energy conversion available today. It can be used in applications ranging from the harvesting of waste heat to conversion of solar energy into useful electricity. Remarkable advances have been achieved in recent years for various thermoelectric (TE) material systems. The introduction of nanostructures is used to tune the transport of phonons, while band structure engineering allows for the tailoring of electron transport. In this overview, top-down approaches to phonon engineering, such as atomic construction of new materials, will be reviewed. Bottom-up approaches to electron engineering, such as the formation of ordered nanostructures, will also be discussed. The assembly of TEG devices is still particularly challenging, and consequently, thermal-to-electric conversion utilizing these devices has been realized only in niche applications. In this review paper, we will discuss some of the challenges that must be overcome to enable widespread use of TE devices. These include thermal stability at the material level, and reliable contact at the device level.

Keywords: Thermoelectric materials; Thermoelectric devices; Phonon scattering; Electron transport; Reliable contact

1. Introduction

Thermoelectric power generation (TEG) has been widely investigated as a clean energy conversion technology for the harvesting of waste heat as well as for converting solar energy into useful electricity. The energy conversion efficiency is determined by the Carnot efficiency and the dimensionless figure of merit (ZT), in which ZT is defined as $ZT = (S^2\sigma/\kappa)T$, where S, σ, κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. The utilization of waste heat, such as from ground/aerial vehicles, industrial boilers, power plants, cement plants, etc., has garnered significant interest. During the past 15 years there has been tremendous growth in thermoelectric (TE) research, in which the number of annual publications increased from 500 to 2000 according to the Web of Science database [1]. Furthermore, significant boosts in the peak ZT over the benchmark value of 1 for many conventional materials have been reported, including for Bi_2Te_3-based alloys [2–4], PbTe [5–8], PbSe [9,10], SiGe [11,12], Mg_2X ($X = Si$, Ge, Sn) [13,14], skutterudite [15–17], clathrate [18], Zintl [19] and half-Heusler alloys [20,21]. These increases have been achieved through nanostructural approaches to phonon transport tuning, and band structure engineering to tailor electron transport. Recently, Kanatzidis and coworkers have claimed a ZT of >2 in the PbTe system, in which they attributed the performance enhancement to a hierarchical length-scale phonon scattering scheme. They combined melting/casting (to incorporate nanoinclusions) and ball milling/hot pressing (to achieve fine grain size) [22,23]. Recently, a SnSe single crystal has been shown to have a new, record ZT value of 2.6 [24]. It seems that practical applications utilizing TE power generation techniques might just be within reach.

However, there is still a significant need for improvement when we consider the requirements for TEG in real applications. The University of Karlsruhe made the first attempt in 1988 [25], using a TEG device with $FeSi_2$ legs in an automobile application. Subsequently, other prototype TEG devices for cars were developed and tested by both industry and academia [26,27]. However, the maximum output power of most reported prototype TEG devices was limited to 100 W, preventing any real adoption of this new technique for commercial automobiles. In 2008, IAV (a German automotive engineering company) developed a prototype TEG device for the Volkswagen Golf exhaust pipe. It generated an output power of 600 W at highway speeds [28]. Recently, a Gentherm-led team, including BMW and Ford, launched a prototype TEG device that was integrated into two different passenger vehicles: the BMW X6 and the Lincoln MKT. This TEG device with skutterudite legs generated 700 W of power in bench testing and over 600 W in on-vehicle testing [29]. Even though the power generated provided ~30% of the electricity required for a car's operation, this was still well below

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the target of 5% fuel efficiency improvement. Similar projects to improve the fuel efficiency of automobiles by harvesting waste heat were also launched by other manufacturers, including Toyota, Honda, Nissan and GM. However, as yet there are no commercially available automobiles with integrated TEG devices on the market. The challenge of bringing this technology to the market has two main causes: (i) inadequate mechanical properties and insufficient thermal stability of TE materials; and (ii) unreliable contact between the TE leg and the electrode. As an example, PbTe is well known as a traditional TE material for intermediate temperatures. However, because of its poor mechanical properties it has not been considered favorably as a practical material for TEG in commercial applications. In contrast, skutterudites have attracted much more attention from the industry, such as from Gentherm [29], GM [30] and Furukawa [31]. However, the thermal stability of skutterudite at temperatures close to 600 °C remains a concern. Even with its lower ZT value, half-Heusler alloys have much better mechanical properties and thermal stability than PbTe and skutterudite, and hence have attracted increasing attention as the material offering the most promise for power generation applications [32,33].

Another big challenge for TE materials is the reliability of the metallized contact layer. Direct soldering of most TE materials is problematic due to either the poor wettability of solder on TE materials or the subsequent reaction/diffusion between the materials. Metallized contact/diffusion barrier layers on the ends of the TE legs improve the wettability of TE materials by solder and prevent diffusion between the solder and TE material. However, an ohmic contact is necessary to reduce the parasitic loss arising from the extra electrical and thermal resistance at the interface. In this paper, we designate R_c as the electrical contact resistance (in ohms, Ω) as the extra electrical resistance introduced by the contact–TE interface, which can be obtained by subtracting the calculated material resistance and wiring resistance from the total measured module resistance. The contact resistance includes the effect of contact area. Because different cross-section areas were used in the modules built by different groups, contact resistance is not suitable for comparing the quality of the contacts. To compare the quality of contacts prepared with different cross-section areas, we designate the specific contact resistivity ρ_c (μΩ cm^2), which is the reciprocal of the derivative of the current density with respect to the voltage across the interface, as $\rho_c = \left(\frac{dJ}{dV}\right)^{-1}_{v=0}$. While investigating the contact for TE materials by measuring the contact resistance, the specific contact resistivity can be estimated by multiplying the contact resistance by the cross-section area, $\rho_c = R_c \times A$. Fig. 1 shows the effect of specific contact resistivity on the leg efficiency and the output power of a p-type skutterudite by using the energy balance from the one-dimensional heat flow equation. It is clearly shown that the specific contact resistivity significantly reduces the leg efficiency as well as the output power. Simply, the specific contact resistivity ρ_c between the conducting strip and TE material decreases the effective $<ZT>_{leg}$ of TE devices according to [34]:

$$\langle ZT\rangle_{leg} = \frac{L}{(L + 2\rho_c\sigma)}\langle ZT\rangle_m, \quad (1)$$

where L and σ are the length of the TE leg and the electrical conductivity of the leg, respectively. $<ZT>_m$ is the effective ZT of the TE material between T_h and T_c. For a typical device that has $L \approx 1$ mm and $\sigma \approx 10^5$ S m^{-1}, $_c$ should be much less than $L/2\sigma$ ~10^{-8} Ω m^2 (10^{-4} Ω cm^2). Ideally, the specific contact resistivity should be <1 μΩ cm^2. We are still far from this targeted low value for most materials.

Bi_2Te_3-based modules have a long history as commercially available TE solutions for silent cooling, and hence mature fabrication skills exist in industry. However, recent investigations of commercial Bi_2Te_3-based modules under thermal cycling conditions have shown significant performance degradation. Hatzikraniotis et al. have conducted a long-term performance and stability study of a commercial Bi_2Te_3-based module (Melcor HT9-3-25). The cold side was fixed at 24 °C while the hot side was subjected to thermal cycles from 30 to 200 °C [35]. A continuously decreased output power was observed due to the increased resistance and decreased open circuit voltage. The Goodson group at Stanford University conducted a similar thermal cycling test for another commercial Bi_2Te_3 module (Ferrotec 9500/127/060). After 6000 repeated thermal cycles from 30 to 160 °C, the peak output power showed an 11% reduction [36]. Mechanical damage, including voids, pores and cracks, was seen at the interface between the Cu electrode and the Bi_2Te_3 leg, as shown in Fig. 2 [37]. It seems that reliable contact is still an open challenge for TEG devices, even for conventional Bi_2Te_3 material. Recent work has shed some light on the challenge behind the contact of Bi_2Te_3 for the power generation applications [38]. The main challenge facing Bi_2Te_3-based TEG devices arises from the unstable interface between the Ni contact layer and the Bi_2Te_3, which could result in the formation of a p-type region in the n-type leg, leading to a high contact resistance.

In this review, we will summarize the latest advances in TEG materials and devices, paying special attention to new challenges that have arisen. Progress on the materials level will be considered by discussing thermomechanical properties and thermochemical reliability in addition to the TE properties. The continuous pursuit of higher ZT will be discussed from the phonon engineering and the electron engineering points of view. Phonon engineering is regarded as a top-down approach, e.g. some materials with special crystalline structure have low lattice thermal conductivity comparable to nanocomposites with hierarchical architectures. In contrast, electron engineering is considered a bottom-up approach, e.g. the self-assembly of ordered nanostructures. For device-level progress, we will first discuss challenges regarding the design of a reliable contact, and then narrow our attention to the specific contact design of several materials, including Bi_2Te_3, PbTe, $CoSb_3$ and Mg_2Si. In addition, we will examine how the contact properties play a role in maximizing the output power generation and its conversion efficiency. To conclude, we will discuss the most recent trends in TEG materials and devices.

2. Material-level progress in thermoelectric power generation

The recent improvements in ZT (from 1 to ~2) are a quite significant and welcome development. However, mechanical strength and chemical stability are equally crucial to TE applications, but these aspects have received only limited attention. Considering the working conditions encountered during TEG, the stress in most cases is induced by the large temperature difference between the hot and cold sides of the device. Mechanical problems