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Research progress on polymer–inorganic thermoelectric nanocomposite materials

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ABSTRACT

A thermoelectric (TE) material is a material where a potential difference is generated as a result of a temperature difference or the corollary of this where a temperature difference is generated when a voltage is applied. These phenomena can be used to generate electricity and/or control temperature. Traditionally, thermoelectric materials are inorganic semiconductors which have been limited in their application by low efficiency and high cost. Since the 1990s, both theoretical and experimental studies have shown that low-dimensional TE materials, such as superlattices and nanowires, can enhance the value of the TE figure of merit (*ZT*) which is an indicator of TE thermodynamic efficiency. To date it has not been feasible to apply these materials in large-scale energy-conversion processes because of limitations in both their heat transfer efficiency and cost. When compared to inorganic materials, organic conducting polymers possess some unique features, such as low density, low cost, low thermal conductivity, easy synthesis and versatile processability and their use in preparing polymer-inorganic TE nanocomposites appears to have great potential for producing relatively low cost and high-performance TE materials. Recently, an increasing number of studies have reported on polymeric and polymer-inorganic TE nanocomposite materials. The purpose of this paper is to review the research progress on the conducting polymers and their corresponding TE nanocomposites. Its main focus is the TE nanocomposites based on conducting polymers such as polyaniline (PANI), polythiophene (PTH), poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS), as well as other polymers such as polyacetylene (PA), polypyrrole (PPY), polycarbazoles (PC) and polyphenylenevinylene (PPV). Typically, polymer-inorganic TE nanocomposites are produced by physical mixing, solution mixing and *in situ* polymerization. The key factors that limit the use of these polymers and their polymer-inorganic TE nanocomposites

Abbreviations: TE, thermoelectric; *ZT*, figure of merit; PF, power factor; α, Seebeck coefficient; σ, electrical conductivity; κ, thermal conductivity; *T*, absolute temperature; RT, room temperature; DOS, density of states; PANI, polyaniline; PTH, polythiophene; PEDOT, PSS poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate); PA, polyacetylene; PPY, polypyrrole; PC, polycarbazole; PIC, polyindolocarbazole; P(2Cz-D), poly(1,12-bis(carbazolyl)dodecane; PPV, polyphenylenevinylene; PMMA, poly(methyl methacrylate); PTT, polythieno[3,2-b]thiophene; PMet, poly(3-methylthiophene); P3HT, poly(3-hexylthiophene); P3HTT, poly(3-hexylthiothiophene; P3OT, poly(3-octylthiophene); PP, polypropylene; PVAc, poly(vinyl acetate); PCVH, poly(*N*-octyl-3,6-dihexyl-2,7-carbazolenevinylene); PMeOPV, poly(2,5-dimethoxyphenylenevinylene); EtO, ethoxy; BuO, butoxy; CSA, (±)-10-camphorsulfonic acid; CNT, carbon nanotube; SWNT, single-walled nanotube; BFEE, boron trifluoride diethyl etherate; DMSO, dimethyl sulfoxide; EG, ethylene glycol; DMF, N,*N*-dimethylformamide; THF, tetrahydrofuran; Tos, tosylate; PF6, hexafluorophosphate; TTF-TCNQ, tetrathiofulvalene–tetracyanoquinodimethane; VRH, variable range hopping; NDH, nearest-neighbour distance hopping.

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as TE materials are their low ZT values. More recent developments designed to overcome the limitation including, for example, the use of carbon nanotubes and graphenes and the use of computational modelling to accelerate the selection of suitable pairs of conductive polymer and inorganic TE materials to achieve best possible nanocomposites are reviewed.

Contents

1. Introduction

TE energy-conversion is an all-solid-state technology used in heat pumps and electrical power generators [1,2]. Fig. 1 illustrates the principal effects governing TE performance including: (A) the Peltier effect where power is converted to a heating and cooling and (B) the Seebeck effect where temperature differences are converted to electricity. TE devices are typically an assembly of both n- and p-type semi-conductors which may simplistically be described as electron rich (donor) and electron poor (acceptor) respectively. TE devices have many attractive features such as long operating lifetime, no moving parts, no noise, easy maintenance and high reliability [1,3]. However, their use is currently limited to only niche applications because of limited efficiency which is determined by the TE materials used [4,5]. Thermoelectric efficiency is measured by

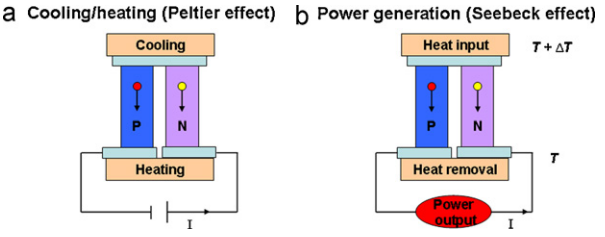

Fig. 1. TE heat engines. (A) When current is run across a TE junction, it heats or cools through the Peltier effect, depending on the direction of the current flow. (B) When heat flows across the junction, electrical current is generated through the Seebeck effect.

the dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature [6]. In polymer and polymer-inorganic TE nanocomposites the value of the Seebeck coefficient typically ranges from −4088 to 1283 μV/K, electrical conductivity from 10^{-7} to 10^4 S/cm and thermal conductivity from 0.02 to 1.2 W/mK. The best materials available today for devices that operate near room temperature have a ZT of about 1, and TE coolers with a ZT of 1 operate at only ~10% of Carnot efficiency. A domestic refrigerator operates at about 30% of Carnot efficiency and this efficiency could be achieved by a TE device having a ZT of about 4 [4]. To improve TE performance, a combination of high electrical conductivity and low thermal conductivity is necessary and which are interdependent and determined by the electronic structure (band gap, band shape, and band degeneracy near the Fermi level) and the scattering of charge carriers (electrons or holes) [7]. For example, the effect of a local increase in density of states (DOS) on α is given by the Mott expression as Eq. (1) [1]:

$$\alpha = \frac{\pi^2(\kappa_B)^2 T}{3q}\left\{\frac{d[\ln(\sigma(E))]}{dE}\right\}_{E=E_F}. \quad (1)$$

Here, α depends on the energy derivative of the energy-dependent σ taken at the Fermi energy E_F as in Eq.(2):

$$\sigma(E) = n(E)q\mu(E),\ n(E) = g(E)f(E), \quad (2)$$

where $g(E)$ is the density of states, $f(E)$ is the Fermi function, q is the carrier charge, and $\mu(E)$ is the mobility.