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Review

Recent progress of organic and hybrid thermoelectric materials

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ABSTRACT

Organic and hybrid thermoelectric materials have been very rapidly developed in the past decade, because the requirement for new energy and energy savings has increased due to the rapid economic development of developing countries and environmental crisis resulting in global warming. Thermoelectric technology has been considered to create electricity from a temperature difference, and be effective for energy harvesting. Organic and hybrid thermoelectric materials cannot be used at high temperature. In the practical world, most of the waste heat energy comes from temperatures below 150 °C. Thus, organic materials could be applied to recover electricity from waste heat energy below 150 °C. In this review, after an introduction of the advantages of organic and hybrid thermoelectric materials, their brief history over two decades and the recent progress to improve the thermoelectric performance will be described by focusing on the researches of the author's group.

Contents

1. Introduction

Energy is a key issue for human beings. The increasing world population, food shortages, and economic differences are also big issues, but these problems could be solved if we would have enough sustainable energy. Presently, the developed countries as well as developing countries obtain most of their energy from fossil fuels like coal, petroleum and natural gas, as shown in Fig. 1 [1]. In 2014, Japan obtained 95% of its energy from fossil fuels, the USA 83%, Germany 81%, China 88%, etc. Only one exception was France, who obtained only 48% of its energy from fossil fuels

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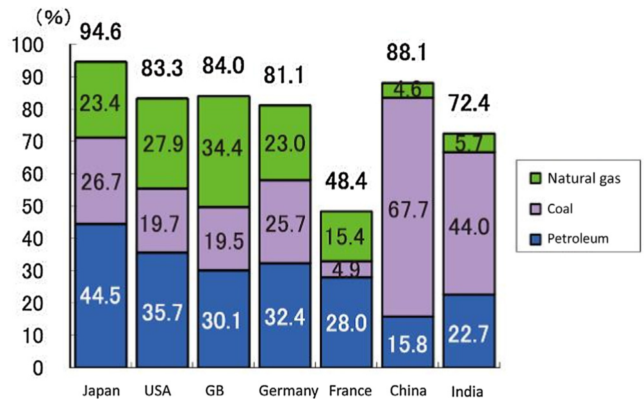

Fig. 1. Ratio of Fossil Fuels in Energy Resources of Various Countries [1].

because France obtains a lot of energy from nuclear power stations. When we use these energy sources, more than half of the energy is lost without utilizing them in the planned form, which results in waste heat. For example, we use most of our energy in the form of electricity. The percent of electricity in the total energy was 25.3% in Japan in 2014 [1]. However, the conversion efficiency to get electricity from fossil fuels was 42.2% in Japan in 2014, meaning that 57.8% of the energy from fossil fuels was lost as heat energy without its use. If we could acquire some electricity from these lost heat energies, we could save the consuming of fossil fuels and reduce the increasing worldwide temperature. This is the reason why the thermoelectric (TE) technology has become interesting in recent years.

I have to emphasize that these lost heat energies are mostly at temperatures below 150 °C as shown in Fig. 2 [2]. This is one of the reasons why organic and hybrid TE materials have received much attention in recent years, because organic materials can easily decompose at high temperature, where most of power generation by TE materials has been applied [3,4]. Another factor for the increased interest in organic TE materials is the stimulated growth of organic electronics. Although most researchers of organic electronics are focusing on organic solar cells and semiconducting devices, some innovators could find organic TEs as a new field.

Fig. 3 reveals the number of publications per year about organic hybrid TEs cited from SciFinder®, indicating that the publications rapidly increased after 2007. This is the year we published a paper on the organic TE materials having the high TE figure-of-merit of 0.1 near room temperature by using the stretched polyphenylenevinylene derivative [5]. This figure-of-merit was a world record at that time for organic TE materials, and comparable to those of inorganic TE materials near room temperature.

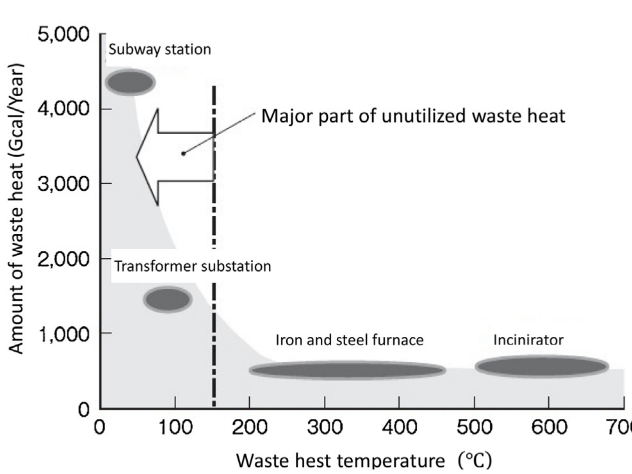

Fig. 2. Relationship between Temperature and Total Energy of Waste Heat in One Year [2].

I will now briefly mention thermoelectrics, especially the TE performance of materials. The TE performance of materials is defined by the TE figure-of-merit, *ZT*, which is expressed by the following Eq. (1);

$$ZT = (S\sigma^2/\kappa)\bullet T \quad (1)$$

where S, σ, κ, and T denote the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively [6,7]. It is usually said that the materials with a *ZT* value above 1 could be practically used. In fact, bismuth telluride (Bi_2Te_3), which is commercially used as a TE material in Peltier cooling devices, has the *ZT* value of about 1 near room temperature [8]. In order to obtain TE materials with a high *ZT* value, therefore, the materials should have a high Seebeck coefficient, high electrical conductivity and low thermal conductivity at the designed temperature.

After a brief description about the advantages of organic and hybrid thermoelectric materials, their brief history over two decades and the recent progress to improve the thermoelectric performance will be described by focusing on our studies.

2. The kinds of organic thermoelectric materials and their advantages

Regarding the TE performance of materials based on Eq. (1), the organic TE materials should be at least electroconducting. However, organic materials are usually electrically insulating, and only a few groups of organic materials are electrically conductive. The first group is the conducting polymers, which were discovered by Shirakawa et al. for doped polyacetylene [9]. Now, several kinds of conducting polymers are known. Some of them have already been practically used as parts of electrical modules. The chemical structures of typical conducting polymers are shown in Fig. 4. The second group is the charge transfer complexes, which have even longer history than the conducting polymers do [10] and there have been also many reports on their thermoelectric properties even though they are not the studies for applications. The complex of terathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ, Fig. 5**a**) is the most typical example. There are many discovered conductive complexes. The problem of the complexes as TE materials could be the rather low electrical conductivity in addition to the low duration for practical utilization. Recently, however, Daoben Zhu and coworkers in China discovered the interesting TE properties of poly(nickel 1,1,2,2-ethylenetetrathiolate) (PETT, Fig. 5**b**) [11]. The third group is carbon materials. The pressed amorphous carbon and graphite have been used for the connection of electric modules. They have a high electrical conductivity, but their thermal conductivities are also high, which is a disadvantage for the TE materials. Nanocarbon materials like fullerene, (C_{60}, Fig. 5**c**), graphene (Fig. 5**d**) and carbon nanotubes (CNTs, Fig. 5**e**) have been recently discovered [12–15]. A single CNT has a high electrical conductivity (10^4–10^5 S/cm) as well as a high thermal conductivity (more than 3000 W/m K). Thus, a single CNT could not be used as a TE material. However, the so-called buckypapers, the films made of many CNTs, have a rather high electrical conductivity and rather low thermal conductivity. In the case of a buckypaper made of commercially-available CNTs prepared by an arc plasma method (Arc-CNTs) as an example, the electrical conductivity of the buckypaper was 690 ± 16 S/cm[16] and the thermal conductivity was reported to be 0.15 [17]. Thus, the buckypapers could be one of the good candidates as an organic TE material [18].