

Application of Conductive Polymers to Thermoelectric Materials

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We need materials and devices for reducing the environmental burden through their life cycles. Thermoelectric materials, which convert directly from heat to electricity, can generate power from waste heat. Thermoelectric energy conversion is an important technique to save heat energy and provide power. All of thermoelectric materials, however, are inorganic and most of them have many problems such as that 1) main elements are heavy metals, 2) fabrication energy of materials is high, 3) manufacturing energy of thermo-modules is very high, 4) separate and recovery is difficult, and so on. Polymers are characterized by light element system, abundant resources, low fabrication and production energy and possible recovery. They are superior to inorganic materials concerning to environmental burden. The problem is very low Seebeck coefficient as well as low electrical conductivity. We must resolve the low properties of Seebeck coefficient and electrical conductivity. In this paper, we show some results on the experimental relationships between Seebeck coefficient and electrical conductivity of typical conductive polymers.

Key words: conductive polymers, thermoelectric materials, Seebeck coefficient, electrical conductivity, eco-devices

1. INTRODUCTION

Now we meet with worsening global environment. Our prompt action to stop the worsening is demanded for posterity. New materials and devices are no exception. We need materials and devices to reduce the environmental burden through their life cycles of mining ore, refining raw material, material synthesis, product manufacturing, product use, separate and recovery, recycling and disposition. Eco-devices, as shown in Fig.1, should be realized for our future. Thermoelectric materials, which convert directly from heat to electricity, can generate power from waste heat. Thermoelectric energy conversion is an important technique to save heat energy in our lives. Only inorganic thermoelectric materials such as Bi_2Te_3 have been researched and developed. Most of them are, however, suffering from environmental problems such as that 1) main elements are heavy metals, 2) synthesis energy of materials is high, 3) manufacturing energy of thermo-modules is high, 4) separate and recovery is difficult, and so on.

Polymers are characterized by light element system, abundant resources, low synthesis and production energy, possible separate and recovery, which are superior to inorganic materials concerning to environmental burden. Polymer thermoelectric materials are likely to realize the

Fig.1 Eco-device

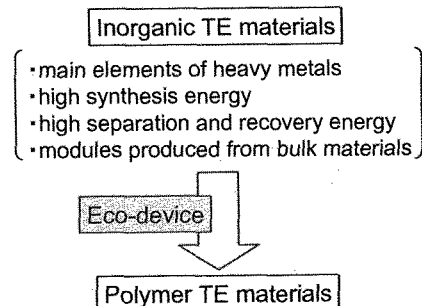
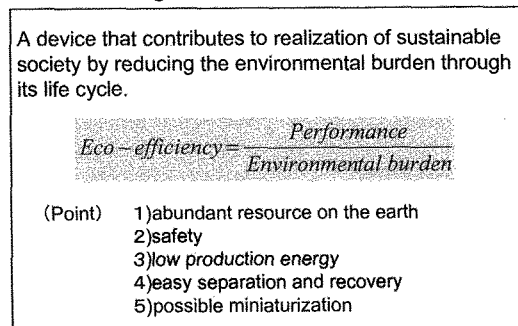


Fig.2 Flow chart to polymer TE materials

eco-devices, as summarized in Fig.2. The problem is very low Seebeck coefficient as well as low electrical conductivity. We must resolve the problem of low thermoelectric properties to apply polymers to thermoelectric materials. There are few reports on thermoelectric study of conductive polymers.[1,2]

In the present paper, we have evaluated thermoelectric properties of typical conductive polymers and presented the experimental relationships between the Seebeck coefficient and electrical conductivity.

2. EXPERIMENTAL PROCEDURE

Polyaniline and polythiophene specimens were prepared in the present work. Doped polyaniline powders supplied by Aldrich Chem. Co. were used as starting material. The polyaniline compact specimens of 3mm ϕ x0.4mm were fabricated using hand press. The polyaniline film specimens about 1 μ m thick were prepared by casting the powers dissolved in a solvent of hexafluoro-2-propanol on the quartz substrate. The polythiophene film specimen was synthesized by electrolytic polymerization. Thiophene was mixed with an electrolyte solution of tetra-n-butyl ammonium and nitrobenzene. ITO was used as an anode and Ni was as a cathode. The applied voltage between the electrodes was 12V. The synthesized film was about 15 μ m thick.

Seebeck coefficient and electrical conductivity were measured at room temperature (RT). Low temperature at 80K~RT was also applied for electrical resistivity measurement. Polymers are, generally, easy to absorb water in air. The measurement of Seebeck coefficient and electrical conductivity was performed under humidity conditions of 20 and 70% at RT to clarify the effect of humidity on them.

Seebeck coefficient: The compact specimens were sandwiched by Au films attached with R-thermocouples of 50 μ m ϕ . The film specimens were set as shown in Fig.3. The R-thermocouples were glued with the films by Ag paste. To both types of specimens, temperature difference ΔT of ~2K was given using the Peltier module. We measured Seebeck coefficient of Pt to check accuracy of the measured value. The result is shown in Fig.4 in comparison with the reference data.[3] The measured value of 5.18 μ V/K agrees well with the reference value of 5.11 μ V/K. The measuring system of Seebeck coefficient is demonstrated to be accurate and quantitative.

Electrical resistivity: The 4-probe method was used for all the specimens. The applied current was as small as 10 μ A to prevent from the Joule heat.

3. RESULTS AND DISCUSSION

3.1 Reproducibility of thermoelectric properties

The Peltier module was switched on for 20min at the start of measuring Seebeck coefficient and

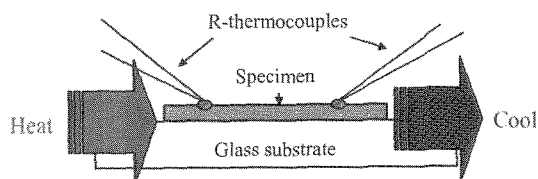


Fig.3 Schematic view of Seebeck coefficient measurement

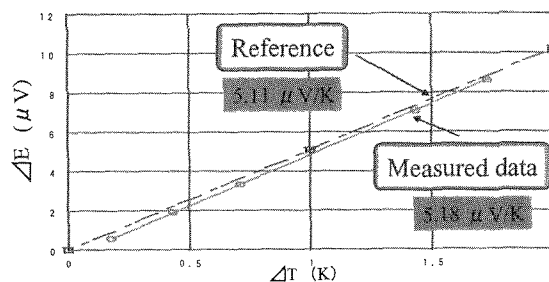


Fig.4 Seebeck coefficient of Pt

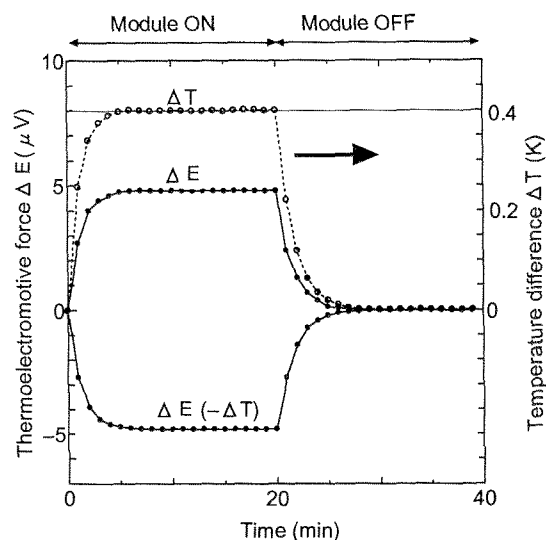


Fig.5 The variations of thermoelectromotive force of polyaniline film as a function of time

then switched off to confirm reproducibility of thermoelectromotive force ΔE . The variations of ΔE of the polyaniline film specimen are shown in Fig.5 as a function of time. The ΔE responds quickly to the ΔT given to the specimen. Even if heating and cooling was opposite against the specimen ($-\Delta T$), the absolute value of ΔE was not changed. Thermal cycle test of $\Delta T=0.4K\sim 0.4K$ was performed for 5 times. Thermal hysteresis of ΔE was not observed. The polyaniline film specimen indicated the stable ΔE response to ΔT .

The relationship between the humidity and ΔE of the polyaniline film specimen is shown in Fig.6. The Seebeck coefficient calculated from the slopes in the figure is 11.6 μ V/K at 20% humidity and 10.7 μ V/K at 70%. The electrical

conductivity also changed with humidity. The values were 2.1S/cm at 20% humidity and 2.33S/cm at 70%. When the humidity is high, the polyaniline film specimen seems to form carriers from the chemical dopants, resulting in high electrical conductivity and low Seebeck coefficient. The conductive polymers tend to change the thermoelectric properties with humidity. We should take care of humidity in measuring the thermoelectric properties.

Temperature dependence of the electrical conductivity of the polyaniline film specimen below RT is shown in Fig.7. The electrical conductivity increased with an increasing temperature. The apparent activation energy E_0 of conductivity is calculated to be approximately 400J/mol. It is not sure whether the E_0 is derived from carrier generation from the dopants or carrier activation from the trapped sites. The electrical conductivity is easy to change with temperature as well as that of the degenerated β -FeSi₂. We should take care of temperature in measuring the thermoelectric properties.

3.2 Relationship between Seebeck coefficient and electrical resistivity

The measured data of the polyaniline compact and film specimens and polythiophene electrolytic polymerization film specimen are summarized in Fig.8. The reference data of p-type polyacetylene, polyaniline, polythiophene and inorganic thermoelectric materials are also plotted in the figure. The conductive polymers present the tendency that the Seebeck coefficient is low when the electrical conductivity is high. This tendency is same as that of inorganic thermoelectric materials.

Performance of thermoelectric materials is judged from thermoelectric figure-of-merit Z . Z is calculated by the following equation:

$$Z = \frac{S^2 \sigma}{\kappa} \quad (1)$$

, where S is Seebeck coefficient, σ is electrical conductivity and κ is thermal conductivity. High Z indicates high energy conversion efficiency.

The conductive polymers indicate about 2 digits lower Seebeck coefficient and ~1 digits lower electrical conductivity than Bi_{0.5}Sb_{1.5}Te₃. From the low thermal conductivity (1 digit lower), the Z is almost 1/10000 of Bi_{0.5}Sb_{1.5}Te₃. The conductive polymers are just at the starting line of research of thermoelectric application. The biggest problem of the conductive polymers is low Seebeck coefficient with respect to decent electrical conductivity.

The champion data of electrical conductivity of typical conductive polymers are listed in Table I [4]. Some conductive polymers have achieved a superior conductivity to the practical Bi₂Te₃. However, the mobility is very small, probably due to hopping conduction. High electrical conductivity of some conductive polymer is attributed to by very high carrier

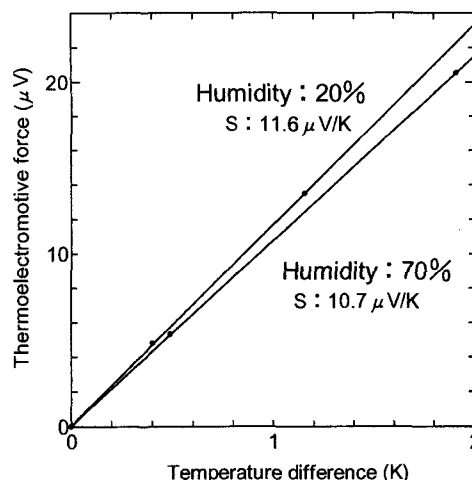


Fig.6 Relationship between thermoelectromotive force and humidity of polyaniline film

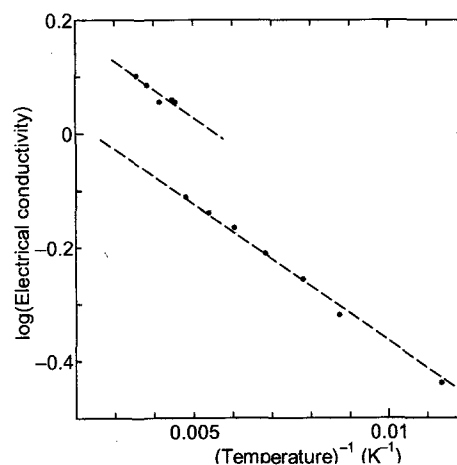


Fig.7 Temperature dependence of electrical resistivity of polyaniline film

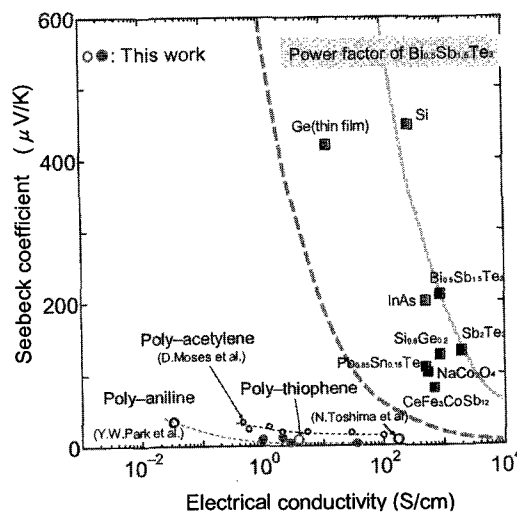


Fig.8 Relationship between Seebeck coefficient and electrical resistivity of p-type materials (RT)

concentration. Generally, materials with higher carrier concentration indicate lower Seebeck coefficient. High carrier concentration of conductive polymers is inevitable, which is a disadvantage to high Seebeck coefficient. Narrow band gap between conduction and valence bands is desirable for high Seebeck coefficient. A typical inorganic thermoelectric material for RT use is Bi_2Te_3 , which has a small band gap of 0.15eV. The band gaps of typical conductive polymers are much larger than 0.15eV. Wide band gap is also a disadvantage to high Seebeck coefficient. A way to high Seebeck coefficient is to search narrow band gap polymers. Another way may be to follow an example of high carrier thermoelectric oxides such as NaCo_2O_4 , because they show both high carrier concentration and Seebeck coefficient.

4. CONCLUSIONS

We have evaluated thermoelectric properties of typical conductive polymers. Conclusions are as follows:

- 1) The polyaniline films indicated the stable thermoelectromotive force response to temperature difference.
- 2) The polyaniline film tends to change the thermoelectric properties with humidity and temperature.
- 3) The conductive polymers present the tendency that Seebeck coefficient is low when electrical conductivity is high.
- 4) Thermoelectric figure-of-merit of conductive polymers is $\sim 1/10000$ of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, which is mainly due to low Seebeck coefficient with respect to decent electrical conductivity.

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Table I
Champion data of electrical conductivity of typical conductive polymers

	Band gap (eV)	Conductivity (S/cm)	Mobility (m^2/vs)
Polyacetylene	1.4~1.6	1.7×10^5 (I_2)	~ 1
Polyaniline	3.3	1.5×10^2 (HCl)	$\sim 10^{-2}$
Polythiophene	2.2	5.5×10^3 (I_2)	$\sim 10^{-2}$
Polypyrrol	3.2	1.5×10^3 (ClO_4^-)	$\sim 10^{-2}$
Bi_2Te_3	0.15	9×10^2	$\sim 5 \times 10^2$
FeSi_2	1	$1 \sim 3 \times 10^2$	~ 1

(Received October 10, 2003; Accepted October 31, 2003)