

Study on Thermoelectric Properties of Conductive Polymers

Y. Shinohara, K. Hiraishi, H. Nakanishi, Y. Isoda*, Y. Imai*

IMARAM, Tohoku Univ., 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

Fax: 81-22-217-5645, e-mail: shinohar@tagen.tohoku.ac.jp

hiraishi@mail.tagen.tohoku.ac.jp

hnakanis@tagen.tohoku.ac.jp

*National Institute for Materials Science, 1-2-1, Sengen, Tsukuba 305-0047, Japan

Fax: 81-298-59-2601, e-mail: ISODA.Yukihiko@nims.go.jp

IMAI.Yoshio@nims.go.jp

We have synthesized conductive polythiophene films by electrolytic polymerization using nitrobenzene as solvent and tetra-n-butylammonium perchlorate as electrolyte, and evaluated the thermoelectric properties of Seebeck coefficient, electrical conductivity and Hall mobility of the films in the in-plane direction. The films showed a tendency that Seebeck coefficient decreased with an increasing electrical conductivity. The figure of merit of $\sim 1 \times 10^{-4} \text{K}^{-1}$ was achieved at the electrical conductivity of 90S cm^{-1} . High conductivity was due to smooth surfaces, high compactness, and high crystallinity of monoclinic structure. Electrical conductivity was strongly dependent on Hall mobility.

Key words: conductive polymers, polythiophene, thermoelectric properties, electrolytic polymerization

1. INTRODUCTION

Thermoelectric materials can directly convert waste heat to electricity. 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, hazardous to environment 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) difficult to separate and recover, and so on[1].

Polymers are characterized by light element system, abundant resources, low synthesis and production energy, easy to separate and recover, which are superior to inorganic materials concerning to environmental burden. Conductive polymers are likely to realize environmentally conscious thermoelectric devices. Developing technique of polymers is also useful to make multi-functional or high performance devices with designed molecular structures. The problem is very low Seebeck coefficient as well as low electrical conductivity[2]. In the present study, we have electrolytically synthesized polythiophene films as shown in Fig.1 and investigated the effect of film structure on the thermoelectric properties.

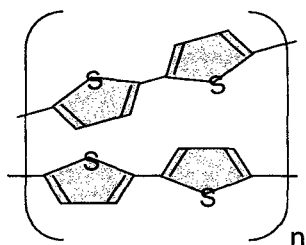


Fig.1 Structure of polythiophene films

2. EXPERIMENTAL PROCEDURE

Polythiophene films were synthesized by electrolytic polymerization using the apparatus in Fig.2. Thiophene monomer and electrolyte tetra-n-butyl ammonium were mixed with a solvent of nitrobenzene. ITO was used as an anode and Ni was as a cathode. The applied voltage between the electrodes was 12V. The reaction temperature was changed in the range of between 273 and 300K to control the electrical conductivity of the films. Reaction mechanism of the electrolytic polymerization is shown in Fig.3. The synthesized film was about 5~10 μm thick.

Thermoelectric figure of merit (Z) can be calculated using the following equation:

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

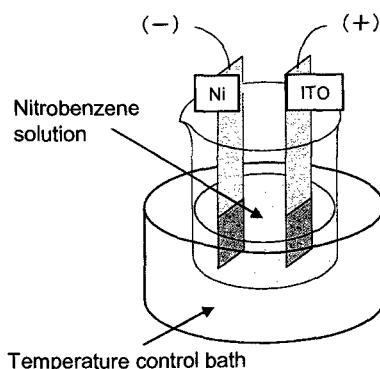


Fig.2 Apparatus of electrolytic polymerization

S , σ and κ are Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. High S and σ , and low κ are necessary for high Z . In the present study, S and σ of the films were measured in the plane direction at room temperature.

Hall mobility μ_H and apparent carrier concentration n of the films was also evaluated using permanent magnet system of 0.35T. Hall mobility and apparent carrier concentration were calculated using the following equation[3]:

$$\mu_H = \frac{d}{B} \frac{\Delta R/R}{\rho} \quad (2)$$

$$n = \frac{\sigma}{e\mu_H} \quad (3)$$

B , d , R , ΔR , and e are magnetic field intensity, thickness of the film, resistance, resistance change by magnetic field and electric charge, respectively.

The surface structures of the films were observed by SEM, and the crystal structures were measured by XRD using $\text{CuK}\alpha$.

3. RESULTS AND DISCUSSION

3.1 Thermoelectric properties

The measured data on S and σ of the films are plotted in Fig.4 with the reference data of polyacetylene and polyaniline[4,5]. The polythiophene films showed higher thermoelectric performance than the other conductive polymers. The S decreased with an increasing σ , which is a same tendency as the other polymers. The Z was calculated using Eq.(1) by applying a typical κ value of polymers of $0.1 \text{ WK}^{-1} \text{ m}^{-1}$. The Z increased with an increasing σ and reached the value of $\sim 1 \times 10^{-4} \text{ K}^{-1}$ at σ of 90 Scm^{-1} . The value is only 1/30 of that of the practical Bi-Te system, but it is noted that polymers have some potential as thermoelectric materials. Now we are developing the high σ films to improve the Z .

Figure 5 shows the dependence of the σ of the films on the μ_H and n . The μ_H increased with an increasing σ , whereas the n was almost constant, independent of the σ .

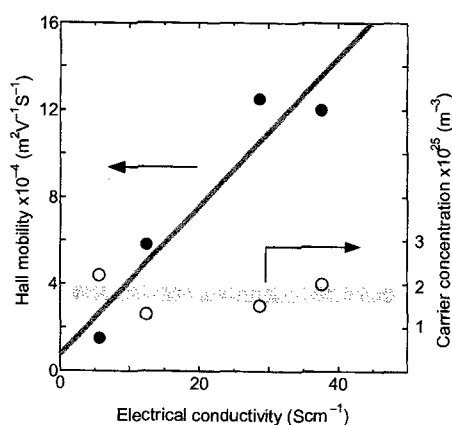


Fig.5 Dependence of electrical conductivity on Hall mobility of polythiophene films

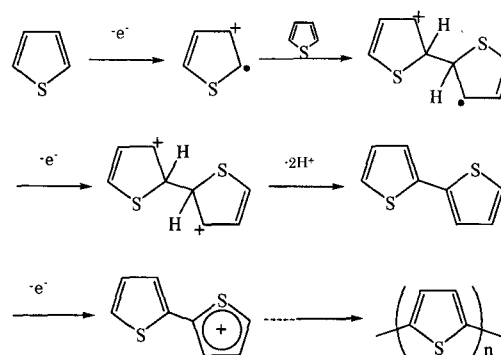


Fig.3 Reaction mechanism of electrolytic polymerization of polythiophene

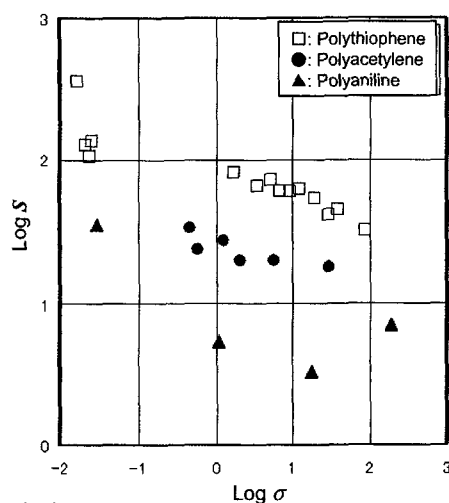


Fig.4 Relationship between Seebeck coefficient α and electrical conductivity σ for conductive polymers of polythiophene (this study), polyacetylene and polyaniline

It is clear that the μ_H is predominant to the σ . The higher Z can be realized by the higher μ_H . The high σ films are realized by low reaction temperatures near 273K. The film structure and/or crystal structure is likely to a key point to realize the high σ films.

3.2 Structures

SEM images of the surfaces of the films are shown in Fig.6. (a) and (b) are for low and high σ films, respectively. The surface changed with the σ . The surface (a) is much rougher than that (b). The compactness of (a) seems to be also lower than that of (b). The higher σ film indicated a tendency of the smoother and more compact surface. Smoothness and compactness of the films makes it easy for carriers to move in the films.

Figure 7 shows X-ray diffraction profiles from the films with the variations of σ in the range from 0.02 to 86 Scm^{-1} . The thick lines are detected diffraction peaks, and the dotted lines are diffraction angles from the

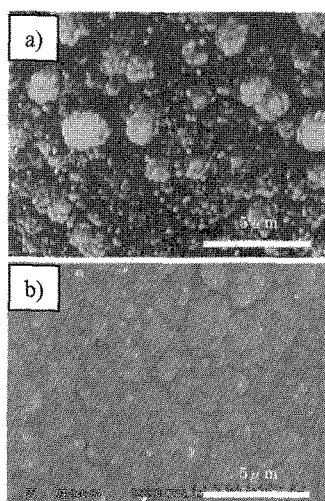


Fig.6
SEM images of the surfaces of polythiophene films
of electrical conductivity of 0.02(a) and 29 Scm⁻¹(b)

reported monoclinic structure[6]. It is not easy to determine the crystal structure of the films, but it is probable that the films are the monoclinic structure and randomly oriented. The peak positions are shifted to lower angles, which means the spacing between the neighboring thiophene rings is wider than that of the standard polythiophene. This result indicates that the electrolytically synthesized polythiophene is not always a head-to-tail structure. The electrolyte solution of tetra-n-butyl ammonium and nitrobenzene may exist between the neighboring thiophene rings.

Sharpness of the diffraction peaks was observed at the high σ film. The diffraction peak of (110) was not detected at the low σ films, while was successfully detected at a film of 86 Scm⁻¹. The crystallinity of polythiophene increased with an increasing σ . From the half-height width of the (210) peak, the crystalline size of polythiophene is calculated to be approximately

0.8 nm, corresponding to 3 layers of thiophene rings. Carrier transport is probably affected in the polythiophene molecule by the crystallinity and also affected between the molecules by the film structure.

CONCLUSION

We have electrolytically synthesized the conductive polythiophene films and evaluated the thermoelectric properties. Thermoelectric performance of the films increased with an increasing electrical conductivity, which was dominated by Hall mobility. High Hall mobility structure is essential to realize high thermoelectric performance.

REFERENCES

- [1] Y. Shinohara, K. Ohara, Y. Imai, Y. Isoda and H. Nakanishi. *Trans. MRS-J*, **29**, 5, 1921-1924 (2003).
- [2] Y. Shinohara, K. Ohara, Y. Imai, Y. Isoda and H. Nakanishi. *Proc. 22nd International Conference on Thermoelectrics*, 298-300 (2003).
- [3] A. Kinpara and H. Fujiwara, "The Thin Films", Shoukabo, Tokyo (1986) pp.255-257. (in Japanese)
- [4] D. Moses, A. Denenstein, J. Chen and A. J. Heeger, *Phys. Rev. B*, **25**, 7652-7660 (1982).
- [5] Y. W. Part, Y. S. Lee and C. Park, *Solid State Commun.*, **63**, 1063-1068 (1987).
- [6] Z. Mo, K.-B. Lee, Y. B. Moon, M. Kobayashi, A. J. Heeger and F. Wudl, *Macromol.* **1985**, 18-22 (1972).

(Received December 23, 2004; Accepted September 26, 2005)

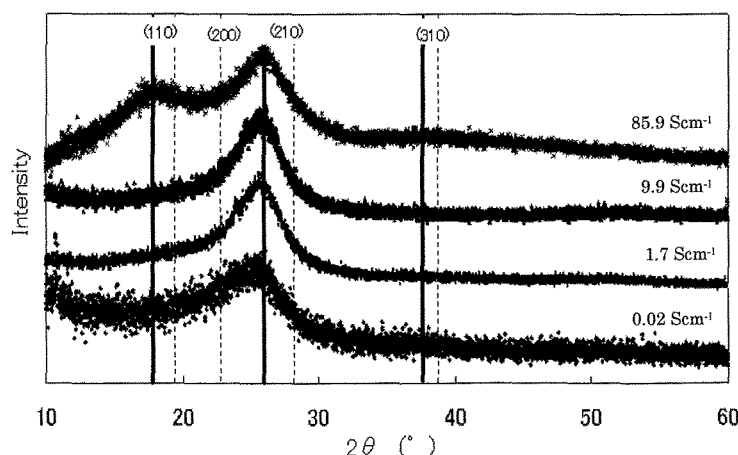


Fig.7 The variations of X-ray diffraction profiles from polythiophene films
with electrical conductivity