Thermoelectric Properties of Alternatively Layered Films of Polyaniline and (±)-10-Camphorsulfonic Acid-Doped Polyaniline

Hu Yan and Naoki Toshima*

Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, Onoda-shi, Yamaguchi 756-0884

(Received August 6, 1999; CL-990688)

Thermoelectric performance of polyaniline can be improved by formation of multilayered film structure. The alternatively layered films are composed of electrically insulating emeraldine base layers and electrically conducting (±)-10-camphorsulfonic acid (CSA)-doped emeraldine salt layers. The multilayered film exhibited 3.5 times higher thermoelectric power factor at ca. 300 K than a bulk film of polyaniline doped by CSA.

Exhaustion of fossil fuel and effect of green house are crucial global problems for the twenty-first century. Recently, thermoelectric materials have attracted considerable attention from a viewpoint of recovery of energy source and reduction of carbon dioxide, a global warming gas.[1] On the other hand, since semiconductor electronic devices become smaller and smaller, the thermal management of their exhausted heat becomes increasingly challenging. Therefore, incorporating the thermal management of the electronic devices at the design stage is expected by using thermoelectric devices.[2] Currently, almost all R&D studies for thermoelectric applications were carried out on inorganic materials.[3] The high cost and poor processability of the inorganic materials, however, would limit their wide thermoelectric applications.

Usually, organic compounds are considered to be suitable materials for wide applications because of potentially low cost due to plenty of material resource and ease of synthesis. Especially, organic polymers are most widely utilized since they could be processed into versatile forms. Nevertheless, few researches on organic materials for thermoelectric applications have been reported probably because of their unattractive electronic transporting characters. Recently electrically conducting organic polymers with aromatic structures have attracted a great attention because of electronic transporting properties and considerable thermal stability. Among them, polyaniline is well studied due to its feasible background for wide application to electronic devices.[4]

In our opinion, polyaniline, one of electrically conducting organic polymers, is promising for wide thermoelectric applications because of their several attractive properties, such as easy preparation, easy proecssability, low cost,[5,6] and low thermal conductivity,[7] if it has considerably high thermoelectric power factor. However, phosphoric acid and 2-naphthalenesulfonic acid-doped polyanilines showed low thermoelectric performance, mainly because of its very low electric conductivities.

In this article we first present experimental results on improvement of thermoelectric power factor of polyaniline through inducing high electric conductivity by CSA-doping, and further more through constructing multilayered films.

High molecular-weight and less defect polyaniline was chemically prepared at -6 ~ -8 °C according to the procedure previously reported by Adams *et al.*[8] Electrically insulating polyaniline film was prepared from an *N*-methyl-2-pyrrolidone (NMP) solution of emeraldine base. On the other hand, highly electrically conducting polyaniline film was prepared from an *m*-cresol solution of CSA-doped emeraldine salt,[9] which also provided highly electrically conducting bulk film. Multilayered polyaniline film was prepared by alternatively casting of the above two different solutions of polyaniline.

Thermoelectric properties such as Seebeck coefficient and electrical conductivity, and their temperature-dependence were determined by a four-point measurement unit of thermoelectric property coupled with electrical oven for rectangular shape of films. Pt and Pt/Pt-Rh 13% wires were used as electrodes and thermocouples, respectively.

Infrared (IR), ultraviolet-visible (UV-Vis) spectra and elemental analytic data of the polyaniline prepared at -6 ~ -8 °C were well consistent with those of the well-defined emeraldine structure of polyaniline.[10,11] The gel permeatation chromatographic (GPC) weight-average molecular weight (M_w) was as high as 10^5 Da with relatively narrow polydispersity ($M_w / M_n = 3.2$). The IR spectrum of the electrically insulating polyaniline film (corresponding to insulating layers in the multilayered film) clearly showed fingerprint peaks of the emeraldine structure of polyaniline.[12] The data and elemental analysis[12] have revealed that the polyaniline in the film maintains an initial chemical structure of emeraldine even after several dissolving and casting processes. In thermogravimtric (TG) and differential scanning calorimetric (DSC) analyses, the present films have exhibited higher T_d (395 °C) and T_g (230 °C) than the previously reported value.[13] This correlates with high M_w and less defect structure of the present polyaniline. The X-ray diffraction (XRD) pattern of the film showed only broad and weak band centered at 18° of 2θ, which indicates the amorphous character of the film. On the other hand, elemental analysis data of polyaniline in the CSA-doped film (corresponding to the electrically conducting layers in the multilayered film) are principally consistent with the composition of the film doped with 0.5 mole CSA per aniline unit,[14] which is the best stoichiometric doping of emeraldine from the viewpoint of the highest electrical conductivity. The doped film is thermally stable until 150 °C under nitrogen in TG analysis. However, the film is considerably brittle.

To obtain enough strong and flexible as well highly electrically conductive polyaniline film to measure thermoelectric properties, the multilayered structure was prepared by alternatively casting of the above-mentioned two solutions of polyaniline. The electrically insulating 3 layers and conducting 4 layers have similar chemical compositions to the corresponding bulk electrically insulating and conducting films, respectively, because the alternative casting of a new layer is carried out on the well-dried preceding layer by the same procedures as the fully analyzed bulk films. Mechanical strength is considerably improved by the mutilayered structure. The total thickness of the multilayered film was adequate for measurement of thermoelectric properties. The thickness of electrically conducting bulk film and the total thickness of the multilayered film were calculated to be 165 and 191 μm, respectively, from scanning electron microscopic (SEM) observation. Thus average thickness of the individual layers is 27

Copyright © 1999 The Chemical Society of Japan

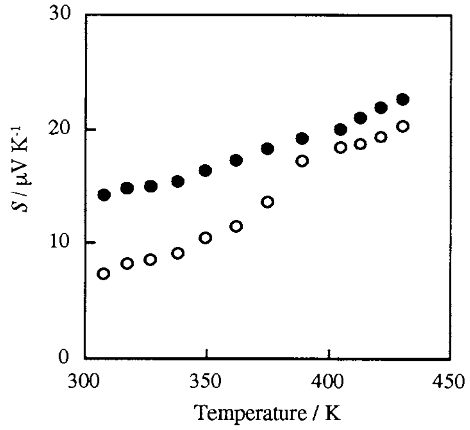

Figure 1. Seebeck coefficient (S) of bulk film (○) and multilayered film (●) of CSA-doped polyaniline at various temperature.

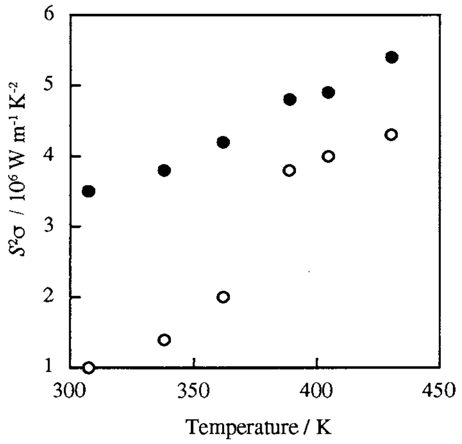

Figure 2. Thermoelectric power ($S^2\sigma$) of bulk film (○) and multilayered film (●) of CSA-doped polyaniline at various temperature.

μm. The methodology for thickness measurement of individual electrically conducting and insulating layers is under investigation.

The thermoelectric properties have been investigated for the multilayered film, consisting of the two kinds of well-defined polyanilines, on comparison with the bulk film. The electrical conductivity (σ) of the multilayered film at 300 K is 173 S cm^{-1}, a little less than 188 S cm^{-1} for the bulk counterpart. Both films showed very high electric conductivities which provide larger thermoelectric power if without decrease in Seebeck coefficient. Seebeck effect is due to electric carriers. Thus, undoped insulating polyaniline does not show any thermoelectric phenonena, while doped one does due to the carriers. Figure 1 shows plot of Seebeck coefficient *vs*. temperature. The bulk film exhibited low Seebeck coefficient but comparable with that of phosphoric and 2-naphthalenesulfonic acid-doped ones which showed very low electric conductivities. However, surprisingly the Seebeck coefficient (S) of the multilayered film (14 μV K^{-1}) is doubly larger than that of the bulk one (7 μV K^{-1}) at ca. 300 K. Consequently, the thermoelectric power factor ($S^2\sigma$) of the multilayered film, as shown in Figure 2, is 3.5 times higher than that of the bulk one at ca. 300 K. To elucidate whether the increment of Seebeck coefficient is due to the multilayered structure, phosphoric acid-doped polyaniline multilayered film (electrically conducting 6 layers and insulating 5 layers) was investigated as well. Similar increment was observed for the film. However, the film showed very low electric conductivity. According to the experimental results we consider that the increment of Seebeck coefficient originates from the multilayered structure. The increment of the thermoelectric power factor, however, decreases with increasing in temperature of the sample. Mechanism of the improvement of the thermoelectric properties is not clear yet. Conduction of electric carriers in polyaniline occurs by Mott's variable-range hopping (VRH).[15] However, few studies on correlative relationship between Seebeck coefficient and transporting mechanism were carried out for such amorphous organic material. The exact mechanism of the improvement is under investigation.

In conclusion, we have first investigated highly electrically conductive polyaniline film and its multilayered film as a thermoelectric materials. The multilayered film of polyaniline has exhibited 3.5 times improvement in thermoelectric power factor at ca. 300 K. The value of power factor is not comparable with that of traditional inorganic thermoelectric materials.[3] However, the experimental results of the increment by multilayered structure indicate that organic polyaniline could be a candidate of thermoelectric materials for wide thermoelectric application, such as recovery of waste low-temperature thermal energy and cooling of semiconductor electronic devices.

This study was supported in part by the Proposal-Based New Industry Creative Type Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References and Notes

1 D. M. Rowe, Proceedings, 17th International Conference on Thermoelectrics, Nagoya, May 1998, pp. 18-23.
2 M. S. Dresselhaus, Proceedings, 17th International Conference on Thermoelectrics, Nagoya, May, 1998, pp.29-32.
3 T. M. Tritt, M. G. Kanatzidis, H. B. Lyon, Jr., and G. D. Mahan, Ed, "Thermoelectric Materials—New Direction and Approaches," Materials Research Society, Warrendale, Pennsylvania (1997).
4 A. G. MacDiarmid, *Synth. Met.*, **84**, 27 (1997).
5 N. Toshima and S. Hara, *Prog. Polym. Sci.*, **20**, 1551 (1995).
6 N. Toshima, *Makromol. Symp.*, **59**, 123 (1992).
7 N. Toshima, H. Yan, and N. Ohno, *Polymer Preprints, Japan*, **48**, 422 (1999).
8 P. N. Adams, P. J. Laughlin, and A. P. Monkman, *Polymer*, **37**, 3411 (1996).
9 Y. Cao, P. Smith, and A. J. Heeger, *Synth. Met.*, **55-57**, 3514 (1993).
10 IR: 1587 cm^{-1} (quinoid); 1494 cm^{-1} (benzoid); 825 cm^{-1} (1,4-disubs.). UV-Vis: 642 nm (quinoid); 330 nm (benzoid). Elemental analysis: Found: C, 75.63; H, 5.03; N, 14.29%. Calcd for $C_{12}H_9N_2$: C, 79.56; H, 4.97; N, 15.47%.
11 A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, *Synth. Met.*, **18**, 285 (1987).
12 IR: 811 cm^{-1} (1.4-disubs.); 1488 cm^{-1} (benzoid); 1587 cm^{-1} (quinoid); 1660 cm^{-1} (carbonyl). Elemental analysis: Found: C, 74.25; H, 5.76; N, 14.20%. Calcd for $C_{12}H_9N_2$: C, 79.56; H, 4.97; N, 15.47%.
13 Y. Wei, G. W. Jang, K. F. Hsueh, E. M. Scherr, A. G. MacDiarmid, and A. J. Epstein, *Polymer*, **33**, 314 (1992).
14 Elemental analysis: Found: C, 64.88; H, 6.60; N, 4.98; O, 12.74% (by difference); S, 5.80. Calcd for $C_{22}H_{25}N_2O_4S$: C, 63.92; H, 6.05; N, 6.78; O, 15.50%; S, 7.75. The doping ratio (S/N, atom/atom), calculated from the result of elemental analysis, is 0.51.
15 F. Zhou, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B*, **36**, 3475 (1987).