

THERMAL TRANSPORTING PROPERTIES OF ELECTRICALLY CONDUCTIVE POLYANILINE FILMS AS ORGANIC THERMOELECTRIC MATERIALS

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Abstract

Thermal transporting properties of electrically conductive polyaniline films were first investigated in wide range of temperatures above room temperature as organic thermoelectric materials. Thermal conductivities of various protonic acid-doped polyaniline films were measured by combination of a laser flash method and a differential scanning calorimeter in relation with electrical conductivity and a kind of dopant. The thermal conductivities thus measured are in the range of conventional organic polymers, indicating that the doped polyaniline films have extremely low thermal conductivities among electrically conductive materials, and have correlation with neither electrical conductivity, nor a kind of dopant. Consequently the polyaniline film, which shows very high electrical conductivity, has comparable thermoelectric figure-of-merit (ZT) with feasible inorganic thermoelectric materials such as iron silicide.

Keywords: cast film, conductive polymer, polyaniline, specific heat capacity, thermal conductivity, thermal diffusivity, thermoelectric materials

Introduction

Conductive polymers have attracted a great attention because of their electron transporting property [1]. Among them, polyaniline is well studied due to its feasible background for wide applications to electronic devices. Such applications of polyaniline have been performed mainly in a processed form, especially in a film [2]. On the other hand, thermal properties, such as thermal diffusivities, specific heat capacities and thermal conductivities, of polyaniline films are crucially important not only from fundamental aspect of academia but also for various applications of the polymer processing, especially for the thermoelectric application [3]. Therefore, systematic investigations on thermal conductivities of polyaniline films at wide range of temperatures above room temperature are of scientific significance.

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Increase of electrical conductivity in inorganic thermoelectric materials usually results in increase of thermal conductivity [4], which is a disadvantage in terms of improvement in thermoelectric performance of materials. A few researches on polyaniline powders have been reported to elucidate the correlation between thermal conductivity and electrical conductivity. To the best of our knowledge no systematic researches on thermal conductivities of polyaniline films have been reported yet in a wide range of temperatures above room temperature. Here we present thermal diffusivities, specific heat capacities, and thermal conductivities of polyaniline films in a wide range of temperatures above room temperature with respect to electrical conductivity and a kind of dopant.

Experimental

Preparation of electrically insulating and conductive polyaniline films

High molecular mass and less structure-defect polyaniline was chemically prepared at $-6\sim -8^{\circ}\text{C}$ according to the procedure previously reported [5]. Electrically insulating polyaniline film was prepared from an *N*-methyl-2-pyrrolidone (NMP) solution of emeraldine base of polyaniline. On the other hand, electrically conductive polyaniline films were prepared by two different methods. First the electrically conductive films were prepared by doping insulating polyaniline films in solutions of various protonic acids such as (\pm)-10-camphorsulfonic acid, 2-naphthalenesulfonic acid, phosphoric acid, and *p*-toluenesulfonic acid. Such films showed moderate electrical conductivity. Secondly highly electrically conductive films were prepared by direct casting from an *m*-cresol solution of (\pm)-10-camphorsulfonic acid-doped emeraldine salt [2]. The surface and cross-section of films were observed by a scanning electron microscope (SEM), from which the thickness of films was calculated.

Measurements of thermal properties of the polyaniline films

Thermal diffusivities were measured by a laser flash method [6]. Disk samples (ca 10 mm in diameter and ca 40 μm in thickness) were set in an electric furnace, and kept a temperature at 300 K under reduced pressure ($4.5\cdot 10^{-2}$ Torr). The front surface of disk samples was irradiated with a laser pulse. Temperature-change at the rear surface was monitored with an infrared detector.

Specific heat capacities were measured with a differential scanning calorimeter (DSC, Mac Science DSC-3200S) [7]. Four steps of temperature program were used: from 203 to 263 K by 5 K min^{-1} ; first thermostat at 263 K for 20 min; from 263 to 453 K by 10 K min^{-1} ; second thermostat at 453 K for 20 min. 12.9 mg $\alpha\text{-Al}_2\text{O}_3$ was used as a standard and the sample sizes were chosen between 7.1 and 13.4 mg. Mass-differences between sample- and reference-pans used for the measurements were less than 0.1 mg.

Bulk apparent densities were calculated from masses and volumes of the disk samples. Finally, thermal conductivities (κ) at 300 K were calculated from thermal

diffusivities (α), specific heat capacities (C_p) and densities (ρ) of the films at 300 K using the following Eq. (1):

$$\kappa = \rho \alpha C_p \quad (1)$$

Measurement of thermoelectric properties of the polyaniline films

Thermoelectric properties such as Seebeck coefficient and electrical conductivity, depending on temperature, were determined by a four-point measurement unit of thermoelectric property coupled with an electric oven for a rectangular shape of films. Pt and Pt/Pt-Rh 13% wires were used as electrodes and thermocouples, respectively. The thermoelectric figure-of-merit ($ZT = (S^2 \sigma / \kappa) T$) was calculated from the corresponding Seebeck coefficient S and electrical conductivity σ as well as thermal conductivity κ at a certain temperature T [3], in which κ above 300 K was estimated from values of ρ , α and C_p at 300 K.

Results and discussion

Polyaniline films with various electrical conductivities

IR, UV-Vis spectra and elemental analytic data indicate that the polyaniline prepared at $-6 \sim -8^\circ\text{C}$ has a well-defined emeraldine structure with high molecular mass ($M_w = 10^4$ Da, $M_w/M_n = 3.2$) which is determined by gel permeation chromatography

Table 1 Electrical conductivity, bulk density and thermophysical properties of polyaniline films doped with various dopants

Dopant ^a	$\log \sigma / S \text{ cm}^{-1}$	$\rho / \text{g cm}^{-3}$	$\alpha / 10^{-3} \text{ cm}^2 \text{ s}^{-1}$	$C_p / \text{J g}^{-1} \text{ K}^{-1}$	$\kappa / \text{W m}^{-1} \text{ K}^{-1}$
Non	-7.0	1.26	2.9	0.43	0.16
NSA ^b	-4.2	1.39	1.2	0.43	0.08
TSA ^b	-2.9	0.88	3.1	0.44	0.12
NSA ^b	-2.4	0.54	4.7	0.61	0.16
CSA ^b	-1.4	1.15	1.7	0.47	0.09
PA ^b	-1.4	1.36	2.1	0.35	0.10
PA ^b	-0.9	1.45	2.2	0.59	0.19
TSA ^b	-0.9	0.91	3.5	0.33	0.11
PA ^b	0.1	1.80	1.5	0.92	0.24
CSA ^c	1.8	1.51	1.4	0.66	0.14
CSA ^c	2.2	1.25	2.6	0.46	0.15
CSA ^c	2.4	2.03	0.7	0.13	0.02

^aNSA: 2-naphthalenesulfonic acid; TSA: *p*-toluenesulfonic acid; CSA: (\pm)-10-camphorsulfonic acid; PA: phosphoric acid

^bPrepared by the first method mentioned in Experimental section

^cPrepared by the second method

(GPC; using NMP/0.1% LiCl and monodispersed polystyrenes as an eluent and standards of molecular mass, respectively, at 60°C). IR spectrum and elemental analytic data of the electrically insulating polyaniline film showed that the polyaniline in the film maintains an initial chemical structure of emeraldine even after several dissolving and casting processes. In thermogravimetry (TG) and DSC, the present films had T_d (395°C) and T_g (230°C), both of which were higher than the corresponding values previously reported [8]. This is a considerable advantage as organic thermoelectric materials. The doped polyaniline films showed considerably different electrical conductivities according to the preparation method and a kind of protonic acid (dopant). Films prepared by the first method written in Experimental section showed moderate electrical conductivity in the range of 10^{-3} ~ 10^0 S cm⁻¹. Films prepared by the second method showed high electrical conductivity in the range of 10^1 ~ 10^2 S cm⁻¹. The bulk densities were considerably low, which were in the range of 0.5~1.8 g cm⁻³. The electrical conductivity and bulk density of the polyaniline films doped with various dopants were summarized in Table 1.

Thermal properties of the polyaniline films

Thermal diffusivities of polyaniline films have been reproducibly measured by a laser flash method. The polyaniline films previously exhibited extremely low thermal diffusivities at a wide range of temperatures [9]. In comparison of the polyaniline films having different electrical conductivity but doped by the same protonic acid, there are no correlation between the thermal diffusivity and the electrical conductivity, as shown in Fig. 1. It is also true for the films doped by different kind of dopants. It is worth to note that a highly electrically conductive semiconductor usually shows high thermal diffusivity in the case of inorganic thermoelectric materials because of the high order of atoms or a large amount of mobile electrical carriers. Thermal diffusivity of semiconductors usually increases with increasing electrical conductivity [4]. Therefore, the extremely low thermal diffusivity and the absence of any correlation of the thermal diffusivity with electrical conductivity of polyaniline films in the present results are con-

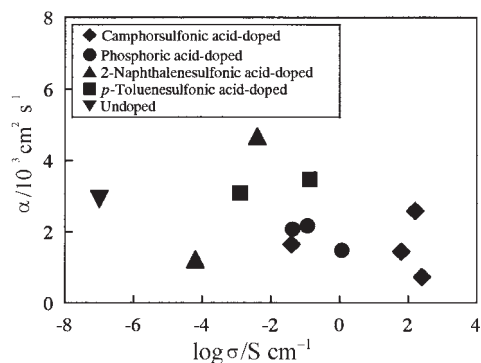


Fig. 1 Thermal diffusivities (α) of various protonic acid-doped polyaniline films with respect to the corresponding electrical conductivities at 300 K

sidered to be originated from their amorphous characters [10]. XRD data indicated that the films are principally amorphous, which also supports the present consideration.

DSC is a reasonable tool for determination of specific heat capacities. However, there have been few reports on specific heat capacity of conductive polymers determined by DSC. Therefore, the optimal conditions were investigated for the measurement of the specific heat at first. The measurement under present conditions has provided reasonable values of specific heat capacities and temperature-dependence for poly(4-bromostyrene), for which these have been well studied [7]. Similarly in comparison of the polyaniline films having various electrical conductivities but doped by the same protonic acid, there are no correlation between the specific heat and the electrical conductivity, as shown in Fig. 2. The values of the specific heat basically are in a range of those of organic polymers [11]. Our previous study also showed that the specific heat capacities of polyaniline films are higher than those of inorganic materials and still keep themselves in the range of those of organic polymers [9]. Furthermore, the temperature-dependence of the specific heat capacity is positive for all the polyaniline films investigated here, which is consistent with those of poly(4-bromostyrene) and most organic polymers [7].

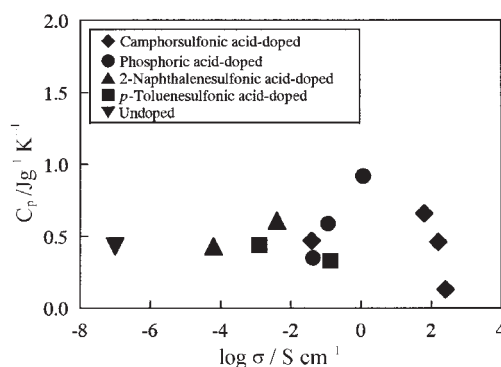


Fig. 2 Specific heat capacities (C_p) of various protonic acid-doped polyaniline films with respect to the corresponding electrical conductivities at 300 K

The thermal conductivities of polyaniline films, calculated according to Eq. (1), are shown in Fig. 3 with respect to the corresponding electrical conductivity for the cases of various dopants. All polyaniline films exhibit lower thermal conductivities at least in one order of magnitude than conventional inorganic thermoelectric materials regardless of the electrical conductivity and the kind of dopant. As previously mentioned, because the polyaniline films are dominantly amorphous, strong phonon scattering in amorphous materials usually results in low thermal conductivity [10]. Meanwhile the contribution of electrical carriers to the thermal conductivity becomes negligible.

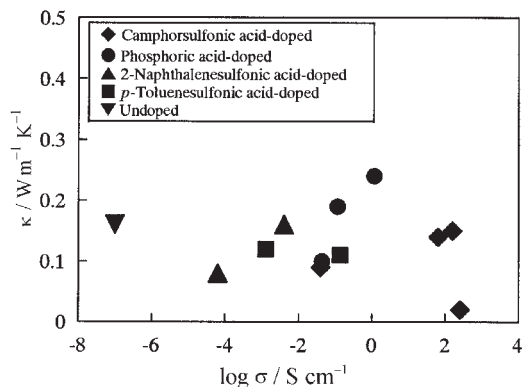


Fig. 3 Thermal conductivities (κ) of various protonic acid-doped polyaniline films with respect to the corresponding electrical conductivities at 300 K

Thermoelectric properties of the polyaniline films

The thermoelectric properties have been investigated for the polyaniline films doped by CSA (188 S cm^{-1}), phosphoric acid (6 S cm^{-1}) and 2-naphthalenesulfonic acid (1 S cm^{-1}), respectively, in a wide range of temperatures, as shown in Fig. 4. Higher electrical conductivity results in larger thermoelectric figure-of-merit (ZT) for the present polyaniline films. In our previous investigation the similar trend was found for stretched polyaniline films [12, 13]. Usually it is not true for the relation between electrical conductivity and ZT of conventional thermoelectric materials [4]. The present films exhibited a low Seebeck coefficient compared with that of conventional inorganic thermoelectric materials. However, all films showed extremely low thermal

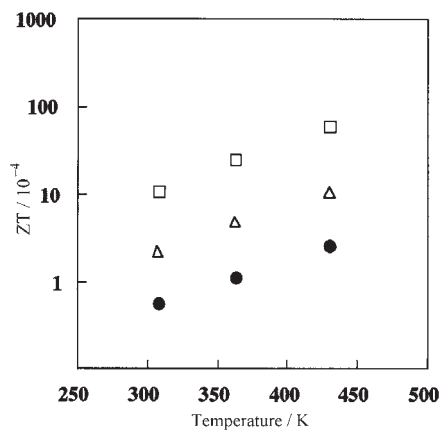


Fig. 4 Thermoelectric figure-of-merits (ZT) of polyaniline films doped by 2-naphthalenesulfonic acid (filled circle), phosphoric acid (open triangle) and (\pm)-10-camphorsulfonic acid (open square) at various temperatures

conductivity regardless of the electrical conductivity. Consequently, the thermoelectric figure-of-merits (ZT) of the films are comparable with that of inorganic thermoelectric materials such as iron silicide.

Conclusions

We have first systematically investigated on thermal conductivities of polyaniline films at a wide range of temperatures above room temperature with respect to the electrical conductivity and the kind of dopant. In comparison with the polyaniline films having different electrical conductivity but doped by the same protonic acid, there are no correlation of the thermal diffusivity, specific heat and thermal conductivity with the electrical conductivity, and the kind of dopant. The experimental results indicate that organic polyaniline could be a candidate of thermoelectric materials for wide applications for heat-electricity and/or electricity-heat conversion, such as recovery of waste low-temperature thermal energy and cooling of semiconductor electronic devices. These extremely low thermal conductivities of polyaniline films and the absence of their correlation with electrical conductivity provide a significant profit for thermoelectric figure-of-merits (ZT) when they are used as organic thermoelectric materials.

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