The High Thermoelectric Properties of Conducting Polyaniline with Special Submicron-fibre Structure

Qin Yao, Lidong Chen,* Xiaochuan Xu, and Chunfen Wang
State Key Laboratory of High Performance Ceramics and Surperfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

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Thermoelectric properties of camphorsulfonic acid (CSA) doped conducting polyaniline with different structures have been studied. The sample with special submicron-fibre structure exhibited 20 times higher thermoelectric power factor at 300 K than the sample with general grain structure, which could be ascribed to its higher carrier mobility caused by its higher order of chain packing.

Conducting polymers possess several attractive features for use as thermoelectric materials because of their potential low cost due to rich resources, easy synthesis, and easy processing into versatile form. Some researches have been carried out on the thermoelectric properties of polyaniline films.[1–3] The main disadvantage of conducting polymers is their low electrical conductivity and Seebeck coefficient compared with inorganic thermoelectric material.

Nowadays, nanowires and nanotubes of conducting polymers have attracted considerable attention because of their unique properties and potential applications in a variety of areas.[4,5] In this article, we got the camphorsulfonic acid (CSA) doped conducting polyaniline with different structures and studied their thermoelectric properties. The sample with special submicron-fibre structure has higher conductivity and Seebeck coefficient than the sample with general grain structure, which could provide a new way to improve the thermoelectric properties of conducting polymer.

High molecular weight emeraldine base polyaniline (PANI) was synthesized at 0 °C following the method reported by Adams et al.[6] CSA doped Polyaniline was synthesized by solid-state protonation.[7] The dopant camphorsulfonic acid (CSA) was dried at 60 °C in a vacuum oven for 24 h. The PANI was mixed with CSA in a mole ratio of 0.5:1 (CSA to phenyl-N (PhN) repeat unit of PANI) for more than 15 min, using an agate mortar and pestle. The obtained doped polyanline solid powders was denoted as PANI(CSA)$_{0.5}$. The solvent *m*-cresol was first dried with magnesium sulfate then decanted and filter. 0.5 g PANI(CSA)$_{0.5}$ powder was mixed with 5 mL *m*-cresol to prepare solutions. Magnetic stirring was carried out for 24 h at room temperature, during which time the complex dissolved to yield viscous, dark-green solutions. The solution was slowly dried at about 30 °C for 4 days and then was dried under vacuum at 60 °C for 12 h and most of the *m*-cresol was removed. The powder treated with *m*-cresol was denoted as PANI(CSA)$_{0.5}$/*m*-cresol.

PANI(CSA)$_{0.5}$ and PANI(CSA)$_{0.5}$/*m*-cresol powder were pressed into a pellet under 22 Mpa with the diameter 10 mm and thickness 0.5 mm. The morphology of the resulting samples was confirmed by scanning electron microscopy (JSM-6360LV). X-ray diffraction was performed on a diffractometer (Rigaku RINT2000). The chemical compositions of the samples were measured by IR spectrum (Nicolet 670) and electron probe microanalysis (EPMA, 8704QH$_2$). The conductivity, carrier density and carrier mobility were measured by the Van der Paw method with disk sample using the Hall effect measurement system (Accent-5500). The Seebeck coefficient was measured using a 10-K temperature difference between two ends of the bar–cut samples. Pt and Pt/Pt–Rh 13% wires were used as thermocouples.

The SEM of PANI(CSA)$_{0.5}$ and PANI(CSA)$_{0.5}$/*m*-cresol are shown in Figure 1. The PANI(CSA)$_{0.5}$ sample shows the obvious grain structure with diameter about 100–200 nm (see Figure 1a). But for the sample PANI(CSA)$_{0.5}$/*m*-cresol, great quantity of submicron fibres with typical size of 200–500 nm in diameter and 5–10 µm in length are formed (see Figure 1b). The element analysis of PANI(CSA)$_{0.5}$/*m*-cresol by EPMA and the IR spectrum indicate both of the submicron fibres and the matrix are CSA doped polyaniline.

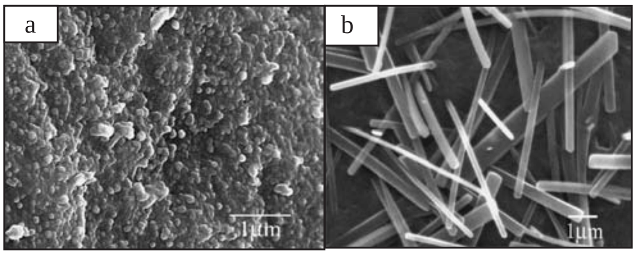

Figure 1. SEM images of the pallet samples for (a) PANI(CSA)$_{0.5}$ and (b) PANI(CSA)$_{0.5}$/*m*-cresol.

The temperature dependence of electrical conductivity and Seebeck coefficient for the two samples from 180 K to 300 K are shown in Figures 2 and 3, respectively. Surprisingly, both the electrical conductivity and Seebeck coefficient of PANI(CSA)$_{0.5}$/*m*-cresol are much higher than PANI(CSA)$_{0.5}$ over the measured temperature range. The electrical conductivity of PANI(CSA)$_{0.5}$/*m*-cresol is up to 66.7 S cm^{-1} at 300 K, about 8 times of PANI(CSA)$_{0.5}$(8.3 S cm^{-1}); the Seebeck coefficient is 12.8 µV/K, 50% higher than that of PANI(CSA)$_{0.5}$(8.6 µV/K). Consequently, the thermoelectric power factor ($S^2\sigma$)for PANI(CSA)$_{0.5}$/*m*-cresol is about 20 times of the PANI(CSA)$_{0.5}$ at 300 K. The electrical conductivity and Seebeck coefficient of PANI(CSA)$_{0.5}$/*m*-cresol could be compared with the oriented conducting polyaniline film.[8]

Conducting polyaniline is a rigid macromolecule due to conjugated phenyl and can be easily oriented in appropriate solution. The *m*-cresol is a good solvent for polyaniline.[9] CSA doped polyaniline was found to form liquid-crystalline solutions in *m*-cresol,[10] indicating its extraordinary order of chain packing

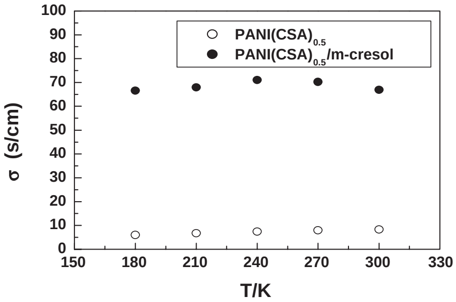

Figure 2. The temperature dependence of electrical conductivity for PANI(CSA)$_{0.5}$ and PANI(CSA)$_{0.5}$/*m*-cresol.

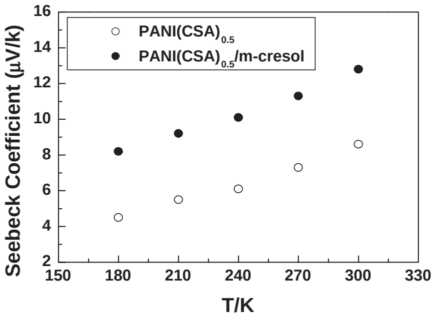

Figure 3. The temperature dependence of Seebeck coefficient for PANI(CSA)$_{0.5}$ and PANI(CSA)$_{0.5}$/*m*-cresol.

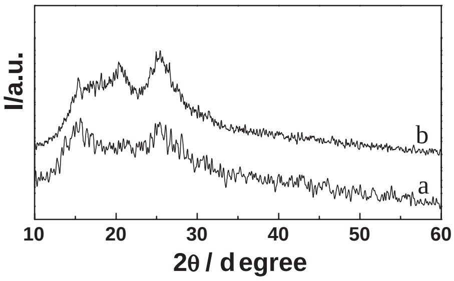

Figure 4. X-ray diffraction patterns (XRD) of (a) PANI-(CSA)$_{0.5}$ and (b) PANI(CSA)$_{0.5}$/*m*-cresol.

in the solvent. When the PANI(CSA)$_{0.5}$ was solved in *m*-cresol, the polyaniline main chains could be oriented. When the *m*-cresol was removed, the oriented polyanline chains clustered. Then the submicron-fibre structure was obtained.

Figure 4 is the X-ray diffraction (XRD) patterns of the two samples. For PANI(CSA)$_{0.5}$, only two broad weak peaks near $2\theta = 20^\circ$ and 25° was observed (see Figure 4a). For PANI-(CSA)$_{0.5}$/*m*-cresol, three peaks are visible, centred at $2\theta = 15$, 20 and 25° (see Figure 4b). Their XRD profiles are agreement with that already reported by J. P. Pouget et al.[11] and D. Djurado et al.[12] and are due to the scattering of interchain packing. The peaks of PANI(CSA)$_{0.5}$/*m*-cresol are more sharpen than that of PANI (CSA)$_{0.5}$, indicating its higher order of chains packing than that of PANI(CSA)$_{0.5}$. The increase of order of polyaniline chains packing reduces π-conjugation defects in polymer backbone and improve the carrier mobility, so the electrical conductivity increases. The carrier density and carrier mobility were measured at room temperature. They have similar carrier density, about 1.1×10^{19}/cm^3 for PANI(CSA)$_{0.5}$ and 1.21×10^{19}/cm^3 for PANI(CSA)$_{0.5}$/*m*-cresol, which could be due to their same dopant content. But the carrier mobility of PANI(CSA)$_{0.5}$/*m*-cresol is 32.8 cm^2/Vs, about 8 times of that of PANI(CSA)$_{0.5}$ (4.2 cm^2/Vs). The results also prove that the higher electrical conductivity of PANI(CSA)$_{0.5}$/*m*-cresol should be ascribed to its higher carrier mobility. The carrier mobility of PANI-(CSA)$_{0.5}$/*m*-cresol also is much larger than the CSA doped unoriented polyaniline film,[13] but the carrier density of the former is lower than that of the latter, which could be ascribed to the different chain packing state and different synthetic method.

Usually an increase of electrical conductivity, if induced by increasing carrier concentration, results in a decrease of the Seebeck coefficient.[14] Mateeva et al. investigated the Seebeck coefficient and electrical conductivity of polyaniline film at different doping levels.[1] In their report, the Seebeck coefficient decreased with increasing electrical conductivity because of increasing concentration of carriers. However, Hu Yan et al. found that both the electrical conductivity and Seebeck coefficient increased for stretched polyaniline films.[3] They attributed the improvement of the thermoelectric properties to the increment of carrier mobility, which is proposed to be induced by the extended coil-like conformation of polyaniline caused by stretching. In our experiment, the submicron-fibre structure was formed owing to extraordinary order of chain packing in the *m*-cresol. The increasing order of arrangement of the polyaniline main chains increased the carrier mobility, so both the electrical conductivity and Seebeck coefficient increased. The result could give us a new way to improve the thermoelectric properties of conducting polymer.

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References

1 N. Mateeva, H. Niculelsue, J. Schlenoff, and L. R. Testard, *J. Appl. Phys.*, **83**, 3111 (1998).
2 H. Yan and N. Toshima, *Chem. Lett.*, **28**, 1217 (1999).
3 H. Yan, T. Ohta, and N. Toshima, *Macromol. Mater. Eng.*, **286**, 139 (2001).
4 R. C. Smith, W. M. Fisher, and D. L. Gin, *J. Am. Chem. Soc.*, **119**, 4092 (1197).
5 M. N. Ralph and M. P. Reginald, *J. Phys. Chem.*, **100**, 17041 (1996).
6 P. N. Adams, P. J. Laughlin, and A. P. Monkman, *Polymer*, **37**, 3411 (1996).
7 J. Stejskal, I. Sapurina, and M. Trchov, *Macromolecules*, **31**, 2218 (1998).
8 E. R. Holland and A. P. Monkman, *Synth. Met.*, **74**, 75 (1995).
9 Y. Cao, P. Smith, and A. J. Heeger, *Synth. Met.*, **48**, 91 (1991).
10 Y. Cao and P. Smith, *Polymer*, **34**, 3140 (1993).
11 J. P. Pouget, G. H. Hsu, and A. G. Mac Diarmid, *Synth. Met.*, **69**, 119 (1995).
12 D. Jurado, Y. F. Nicolau, I. Dalsegg, and E. J. Samuelsen, *Synth. Met.*, **84**, 121 (1997).
13 E. R. Holland and A. P. Monkman, *J. Phys.: Condens. Matter*, **8**, 2991 (1996).
14 A. F. Ioffe, "Semiconductors and Thermoelements and Thermoelectric Cooling," Infoserch Limited, London (1957).

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