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Conductive Polymers as a New Type of Thermoelectric Material

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Summary: Thermoelectric properties were investigated for the films of electrically conductive doped polyanilines. The thermoelectric performance, evaluated by thermoelectric figure-of-merit ($ZT = T\ (S^2\sigma)\ /\ \kappa$), of various protonic acid-doped polyaniline bulk films was found to depend on the electrical conductivity σ of the film. Thus, the higher the electrical conductivity, the higher the figure-of-merit is, because the thermal conductivity κ of polyaniline films does not depend on the electrical conductivity. Among the conductive bulk films of polyaniline, the highest figure-of-merit ($ZT = 1 \times 10^{-4}$) was observed for (±)-10-camphorsulfonic acid (CSA)-doped polyaniline in an emeraldine form (σ = 188 S cm^{-1}) at room temperature. The multilayered film, composed of electrically insulating emeraldine base layers and electrically conducting CSA-doped emeraldine salt layers, exhibited 6 times higher ZT at 300 K than that of a bulk film of CAS-doped polyaniline, showing the highest ZT value of 1.1×10^{-2} at 423 K. Stretching of the CAS-doped polyaniline film also increased the figure-of-merit of doped polyaniline films along the direction of the stretching.

Introduction

Conductive polymers are one of the most attractive functional polymers. Since the first discovery of I_2-doped polyacetylene as an electrical conductive organic materials by H. Shirakawa, A. G. MacDiarmid, A. J. Heeger et al. in 1977,[1] a number of conductive polymers have been synthesized and are being used for many application such as secondary butteries, condensers, light-emitting diodes, etc. because of their processing advantages and mechanical properties of plastics with electronic and optical properties of metals and inorganic semiconductors. The thermoelectric performance will be one of such interesting properties specific for electroconductive polymers.

Thermoelectric properties are only discussed for inorganic semiconductors such as Bi_2Te_3, ZnSb, PbTe, $CoSb_3$, SiGe, $FeSi_2$, $Ca_2Co_2O_5$, etc.[2] Such thermoelctric materials are going to be applied to the generation of electricity from exhausted heat with low quality according to Seebeck effect, and to the precise cooling of advanced electronic

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chips by using electricity according to Peltier effect. Thus, the thermoelectric materials is one of the promising advanced materials, effective for saving energy and for developing frontier electronic devices. However, the high cost and poor processability of the inorganic semiconductors besides their efficiency are limiting their wide applications to thermoelectric systems.

In contrast, organic polymers are considered to be suitable for wide applications because of potentially low cost due to plenty of carbon resources, easy synthesis in general, and easy processing into verstile forms. However, few researches have been reported on thermoelectric application of organic materials.

Here we present the first experimental results in improvement of thermoelectric performance of doped polyaniline at wide range of temperature above room temperature.

Electroconductivity and Thermoelectrc Propertes of Polyaniline

Polyaniline, one of interesting electrically conductive organic polymers, is promising for wide thermoelectric applications because of their several attractive properties such as easy preparation, easy processing, and low cast if it has good thermoelectric properties. The thermoelectric properties are usually evaluated by so-called thermoelectric figure-of-merit $ZT = T(S^2 \sigma)/\kappa$, where T, S, σ , and κ are absolute temperature (K), Seebech coefficient (V K^{-1}), electrical conductivity (10^{-2} S cm^{-1}), and thermal conductivity (W m^{-1} K^{-1}), respectively.

As for the thermoelectric properties of polyaniline, Mateeva et al.[3] measured Seebech coefficient S and electrical conductivity σ of polyaniline below room temperature, and estimated the figure-of-merit ZT. They observed that the temperature dependence of S varies inversely as that of σ , and evaluated ZT as 10^{-5} by using estimated κ . Their conclusion is pesmistic because this value is about three to four order of magnitude lower than that of usual inorganic semiconductors. However, this paper did not report the data of S and σ above room temperature, and used only the estimated value of κ .

Independently we had started the research of polyaniline as thermoelectric materials. The thermoelectric properties of polaniline were investigated above room temperature. First we prepared thermostable polyanilines doped with phosphoric acid and naphthalene-solfonic acid. Although they have lower thermal conductivity than that estimated by Mateeve et al., they still have low ZT values as 2×10^{-5}. During this investigation we found that the thermal conductivity κ of polyaniline does not doped on the kind of dopant.[4] This means that ZT can be improved by increasing σ.

Thus, we used the polyaniline with high electrical conductivity, which was chemically prepared at low temperature according to the procedure previously reported by Adams et al.[5] Then, the ZT value increased to 10^{-4} as shown in Table 1.[6] In inorganic semiconductors, thermal conductivity κ generally increases with increasing electrical conductivity σ, which results in the conclusion that the ZT value is kept constant even though σ increases. In organic conductive polymers, however, it is concluded that the ZT value can be improved by increasing σ.[7]

Table 1. Electrical Conductivity and Thermoelectric Figure-of-merit ZT of Various Polyaniline Bulk Films.[6]

Polyaniline film	σ / S cm^{-1}	ZT (at rt)
Polyaniline film in lit. [3]	10	1×10^{-5}
Polyaniline film initially investigated	6	2×10^{-4}
Polyaniline film with high electrical conductivity	188	1×10^{-3}

Multilayered Films of Polyaniline

It is known in inorganic semiconductors that the multilayered structure can improve the thermoelectirc performance by so-called quantum effect.[8] On the other hand, polyaniline is known to have several structures, as shown in Fig. 1, and that the electrical conductivity depends on such structures. Thus, we prepared a multilayered film of polyaniline, composed of electrically conducting (±)-10-camphorsulfonic acid (CSA)-doped emeraldine salt layers and electrically insulating emeraldine base layers, as shown in Fig. 2. The multilayered film exhibited 6 times higher ZT than that of a bulk film of CSA-doped polyaniline at room temperature. At a little higher temperature, the ZT value of this multilayerd film was about 10^{-2}.[9] Among inorganic semiconductors, $FeSi_2$, which is investigated as one of practical thermoelectric materials because of low cost and plenty of raw materials, has the ZT value of 10^{-2}. Thus, the present multilayered film shows the same order of figure-of-merit as that of $FeSi_2$, being worth further investigation.

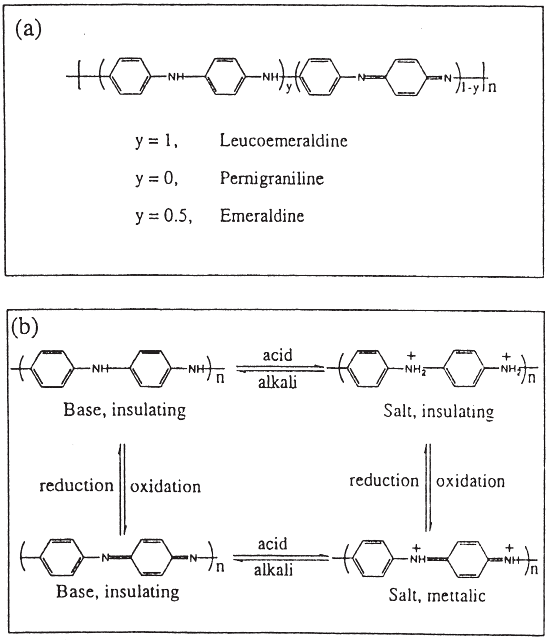

Figure 1. (a) Chemical structure of polyaniline at various oxidative states, and (b) reversible structural changes of polyaniline by oxidation-reduction, and by treatment with acid and base.

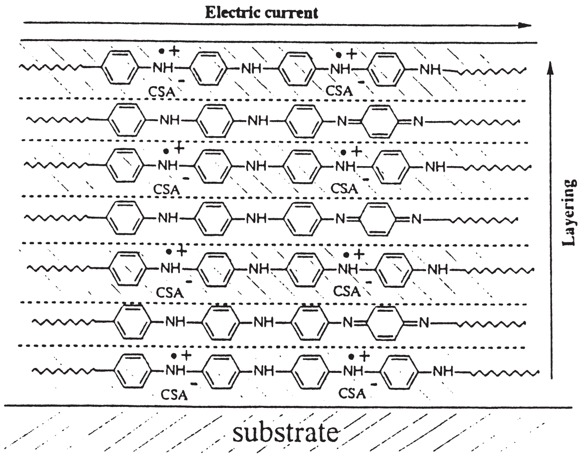

Figure 2. Schematic model of multilayered polyaniline film composed of conductive emeraldine salt layers and insulating emeraldine base layers.[6]

Stretched Films of Polyaniline

Electrical conductivity of conductive polymers is known to increase by stretching. Thus the stretched films of CAS-doped polyaniline weresubjected to measurement of σ along the direction of stretching, based on which their thermoelectric power factors (S^2 σ) and figure-of meant (*ZT*) were calculated. The results are shown in Fig. 3, indicating that the stretching can increase the *ZT* value as high as about 10^{-2} along the direction of the stretching.[10] The *ZT* value increased with increasing drawing ratio. The increment of *ZT* by the stretching process is attributable to the increment of carrier mobility induced by the extended coil-like conformation of polyaniline, which is suggested by x-ray diffraction patterns of CSA-doped stretched poyaniline films and UV-Vis-near IR spectra of a CSA-doped polyaniline films of 480 nm thickness measured in transmission and reflection modes.

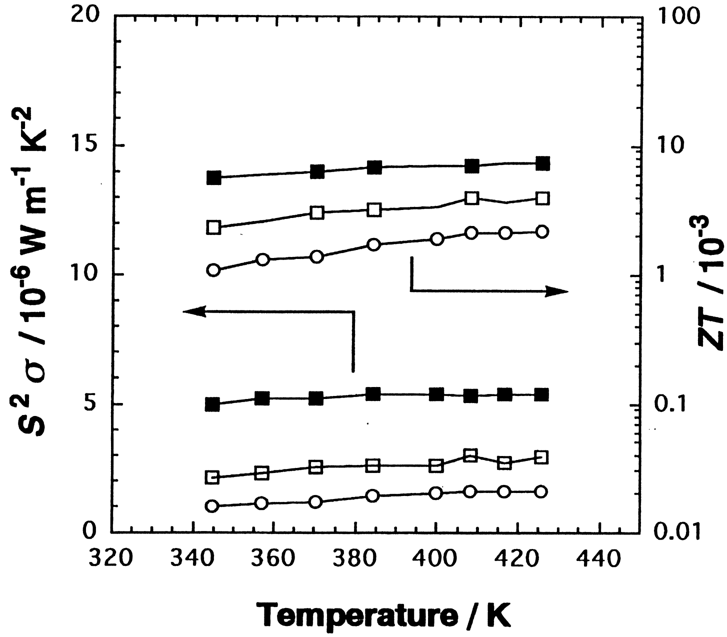

Figure 3. Thermoelectric power factor (TPF, S^2 σ) and thermoelectric figure-of-merit (*ZT*) of CSA-doped stretched polyaniline films at various temperatures. Unstretched film (○); stretched film perpendicular (□) and parallel (■) to the stretching direction.[10]

Conclusion

Development of thermoelectric materials with high performance is one of the most important research themes from the viewpoint of both saving energy and new technology for power generation. Here, polyaniline, one of organic electroconductive polymers, was used for the first time as the thermoelectric materials. The thermoelectric figure-of-merit *ZT* of polyaniline films can be improved by using polyaniline with high electrical conductivity, by using multilayered films composed of insulating and conductive polyaniline, and by using stretched polyaniline films. Since polyaniline has advantages of easy preparation and easy processing, its application for thermoelectric materials could provide a new technology for human being. The author wishes that the present science could create a new industry in the near future.

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