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Thermopower sign reversal versus temperature and DC conductivity in polyaniline derivatives

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Abstract. The DC conductivity and thermopower of polyaniline derivatives were measured for temperatures ranging from 80 to 345 K. The samples were oxidized to different degrees, fully protonated and further doped with $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phosphorylated polystyrene additives to concentrations varying from 0 to 100 mol% of functional group per mole of aniline. The DC conductivity $\sigma(300\text{ K})$ ranges from 0.01 to 16 S cm^{-1} , depending on the degree of oxidation and dopant concentration, while $\sigma(T) = \sigma_0 \exp[-(T_0/T)^{0.5}]$, where T_0 is mainly determined by the degree of oxidation. The thermopower, which is of the order of $-15\ \mu\text{V K}^{-1}$ at 300 K, changes sign from *n* to *p* with increasing temperature at T_1 , which varies between 290 and 325 K. This change in sign, which is reversed during cooling, is attributed to the existence of a half-filled polaronic band situated deep in the energy gap of polyaniline.

1. Introduction

Protonated polyaniline, with its high conductivity and excellent stability under environmental conditions, is one of the most promising polymers for technological applications. Moreover, polyaniline has been extensively studied because it is the only known conjugated polymer with a chain in which nitrogen, instead of carbon atoms, bridges the benzoid and quinoid rings, playing an important role to the π -bond formation and the electrical intrachain conduction (McManus *et al* 1987).

Protonation, i.e. addition of protons in the $-\text{N}=\text{}$ sites by a protonic acid such as HCl, causes a great increase in conductivity σ from 10^{-10} to $100\ \text{S cm}^{-1}$ at room temperature (Geniès *et al* 1990), although the number of electrons in the chain remains unaltered. Band-structure calculations for protonated polyaniline revealed very asymmetric valence and conduction bands with only a half-occupied polaron band deep into the gap, instead of the usual two bands as in other conducting polymers (Stafström *et al* 1987). This half-filled polaron band gives to the protonated polyaniline metallic properties such as Pauli magnetic susceptibility, a small value of the thermopower linearly decreasing with decreasing T , and a free-carrier absorption typical of a metal (Zuo *et al* 1987, Park *et al* 1987).

The DC conductivity of polyaniline is thermally activated and follows the expression

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^n] \quad (1)$$

where $n = \frac{1}{4}$ or $n = \frac{1}{2}$, the second value being common in pressed powder samples (Park

et al 1987). The exponent $n = \frac{1}{4}$ is predicted by Mott's model of variable-range hopping in three dimensions, although the value $n = \frac{1}{2}$ is implied by more than one model.

The fact that in polyaniline a Pauli susceptibility appears with protonation and increases linearly with it suggests phase segregation into fully protonated metallic 'islands' embedded in an unprotonated insulating matrix (Ray *et al* 1989, Nechtschein *et al* 1989, Monkman *et al* 1989). In this 'granular metal' model the DC conductivity follows equation (1) with $n = \frac{1}{2}$ (Sheng *et al* 1973, Sheng and Klafter 1983).

The granular metal model, however, does not agree with the momentum dependence of the electron energy loss spectra. Spin dynamics, concluded from the frequency dependence of proton NMR T_1 and ESR linewidth, suggested the existence of fully protonated conducting and paramagnetic domains, each consisting of only one single polyaniline chain embedded in an unprotonated insulating matrix (Mizoguchi *et al* 1989). In such a quasi-one-dimensional system, the conductivity is due to variable-range hopping between the localized states and equation (1) holds with $n = \frac{1}{2}$ (Wang *et al* 1990).

In a recent paper (Epstein *et al* 1990) an alternative explanation was given to the results of Mizoguchi *et al*. The protonated emeraldine was considered to form three-dimensional metallic islands consisting exclusively of crystalline material embedded in an amorphous polymer (Jozefowicz *et al* 1989).

Another suggestion which allows the exponent of equation (1) to have not only the values $n = \frac{1}{4}$ and $n = \frac{1}{2}$ but also any other value less than unity, was recently proposed (Cowan *et al* 1990). An equation of the form

$$\sigma = (A/T) \exp[-E_b/kT] \quad (2)$$

is considered for the conductivity and the conduction involves three-dimensional electron hopping between amine nitrogen atoms which is not of the variable-range type. In this model a distribution of barrier heights between allowed carrier states shifts the effective E_b to smaller values as the temperature falls, leading approximately to equation (1) with $n < 1$.

Generally, protonated polyaniline is characterized by a metallic intrachain conduction in a partially filled polaron band and a much smaller interchain charge transfer which leads to a conduction governed by equation (1) with $n = \frac{1}{2}$. On the other hand, the thermopower is almost exclusively determined by intrachain charge conduction. So, the DC conductivity and thermopower give information about first the interchain charge transfer and secondly the intrachain conduction.

In the present paper the DC conductivity and thermopower data are presented for polyaniline samples, in which $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phosphorylated polystyrene groups were chemically introduced. From the DC conductivity data some general conclusions concerning the role played by the dopants in the charge carrier conduction can be drawn. Moreover, the thermopower data are consistent with the existence of a half-filled polaronic band and can be explained by the shift in the Fermi level with temperature.

2. Experimental details

Freshly distilled aniline was polymerized using hydrochloric acid-water solutions, either in the presence of KClO_3 and CuCl_2 between 80 and 100 °C (Langer 1978), or by ammonium persulphate in an ice bath followed by Soxhlet extraction for 36 h (Menardo *et al* 1988). The precipitates were washed with 1 N HCl and dried overnight under

vacuum. By the first method, polymers with conductivities ranging from 0.01 to 0.04 S cm⁻¹ were obtained; however, the second method gave polyaniline with much greater conductivities in a range from 3 to 16 S cm⁻¹.

It is known that the conductivity of polyaniline depends on both the oxidation state of the polymer and the degree of protonation of the nitrogen atoms (Salaneck *et al* 1987). On the other hand, protonation takes place almost exclusively at the oxidized units of the polymer (Ray *et al* 1989). As the polymerization took place in a highly acid environment (pH < 2), which ensured entire protonation of the oxidized polymer, the difference in conductivities can be attributed to the different degrees of initial oxidation. From curves of polyaniline conductivity versus oxidation and protonation level (McManus *et al* 1987, Salaneck *et al* 1987), we can conclude that polyanilines with σ in the range 3–16 S cm⁻¹ were about 50% oxidized, although polyanilines with σ in the range 0.01–0.04 S cm⁻¹ were about 45% oxidized.

The —SO₃H groups were introduced by the reaction of the —NH groups of the polyaniline with freshly distilled chlorosulphonic acid at 5 °C, the various amounts of which produced polymer with different extents of sulphonation. The —COOH groups were introduced by copolymerization of *m*-aminobenzoic acid with aniline in the proper proportion (Dalas *et al* 1991a).

All the polymeric powders were further characterized by x-ray diffraction, scanning electron microscopy, infrared spectroscopy and elemental analysis for C, H and N. The last method gave for the polymers the carbon, hydrogen and nitrogen expected theoretically (in weight per cent) within 1% (Dalas *et al* 1991b).

The DC conductivity and thermopower were measured as functions of temperature and group concentration on disc-shaped specimens, 13 mm in diameter and about 1.5 mm thick, produced by pressing powder of the conducting polymer in an IR press. The apparatuses and techniques employed have been described elsewhere (Dalas *et al* 1991b, Wieder 1979).

3. Results and discussion

The $\sigma(T)$ experimental data for each sample were fitted by the least-squares method to equation (1) for $n = 1$ to 0.1 and the sum of square errors (SSE) was determined. In all cases the SSE for T^{-1} was about 2.5 times larger than that for $T^{-1/4}$ and this in turn was 3–50 times larger than that for $T^{-1/2}$. Then, the exponent for which the SSE was minimum and its standard deviation were determined by curve-fitting techniques (Redfield 1973, Guest 1961).

In figure 1 the $\ln \sigma$ versus $T^{-1/2}$ lines are shown for samples 493a and 481a, which consist of pure, fully protonated polyaniline, with 50% and 45% oxidation, respectively. The other two lines concern samples 498a and 486a, which are polyaniline derivatives originating from sample 481a and sample 493a material after the addition of 100 mol% and 90 mol% of —SO₃H per mole of aniline, respectively. The conductivities σ_{RT} at room temperature and the best exponents n for the $\sigma(T)$ experimental data shown in figure 1 with their standard deviations and T_0 are summarized in table 1.

As shown in table 1, T_0 is determined mainly from the degree of oxidation in fully protonated polyaniline, decreasing by a factor of about 6 for only a 5% increase in oxidation. Values of T_0 starting from 6400 K for fully protonated emeraldine ($x = [H^+]/N = 0.5$) and rapidly increasing to about 28 000 K at $x = 0.1$ have been reported

Table 1. Room-temperature conductivity σ_{RT} and statistical evaluation of best values of n and T_0 to fit the data shown in figure 1.

Sample	Composition	σ_{RT} (S cm ⁻¹)	Value of n for the best fit	T_0 (K)
481a	45% oxidized 0% —SO ₃ H	3.5×10^{-2}	0.54 ± 0.05	$20\,100 \pm 200$
486a	45% oxidized 90% —SO ₃ H	10.2×10^{-2}	0.54 ± 0.02	$16\,800 \pm 100$
493a	50% oxidized 0% —SO ₃ H	3.0	0.53 ± 0.02	$3\,470 \pm 20$
498a	50% oxidized 100% —SO ₃ H	5.7	0.52 ± 0.03	$2\,930 \pm 50$

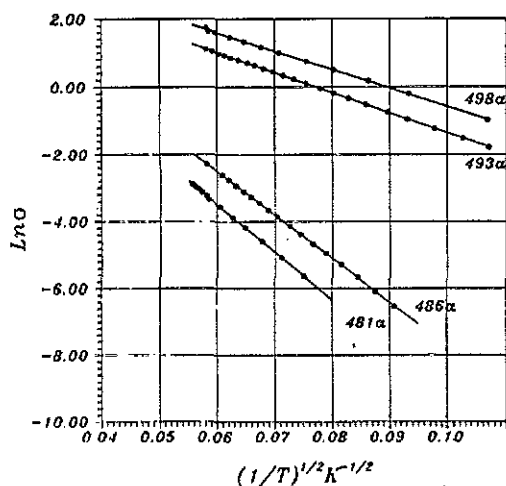


Figure 1. The $\ln \sigma = f(T^{-1/2})$ lines for pure polyaniline samples 481a and 493a with 45% and 50% oxidation, respectively. The same lines are shown for samples 486a and 498a originating from the previous polyanilines with 90% and 100% of —SO₃H, respectively.

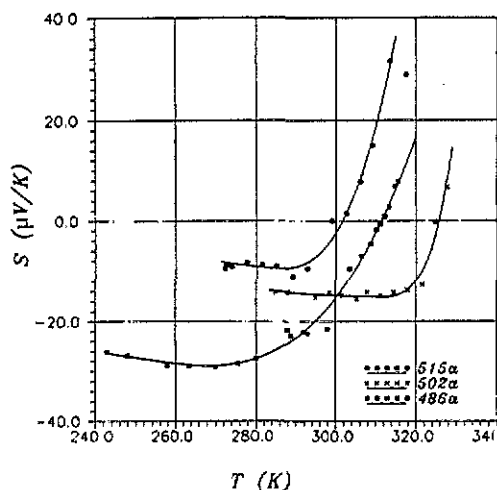


Figure 2. Temperature dependence of the thermopower for three different samples of fully protonated polyaniline: sample 486a, 45% oxidized with 90% —SO₃H; sample 515a, 50% oxidized with 50% —SO₃H; sample 502a, 50% oxidized with 30% —COOH in the carbon rings.

elsewhere (Zuo *et al* 1987, Epstein *et al* 1987, Cowan *et al* 1990). This behaviour indicates that electron localization decreases with increasing protonation.

The addition of —SO₃H improves the conductivity and simultaneously decreases T_0 and increases σ_0 . This indicates that the additive facilitates both the intrachain and interchain conduction. The exact position and role of —SO₃H groups in our samples are not known, but a recent paper refers to the fact that the introduction of such groups in the rings of emeraldine is equivalent to the protonation of imine nitrogen atoms, a process which affects the polymer conductivity in an analogous manner to the protonation by HCl (Yue and Epstein 1990). On the other hand, the introduction of —COOH groups to an extent of 30% in the rings of polyaniline reduces the conductivity from 4.43 to

1.84 S cm⁻¹ at room temperature and increases T_0 from 5600 to 7600 K. A more drastic reduction in the conductivity from 7.0 to 9.5×10^{-2} S cm⁻¹ at room temperature follows the introduction of 10% phosphorylated polystyrene in polyaniline with a parallel increase of T_0 from 4200 to 14 000 K.

In figure 2 the temperature dependence of thermopower is shown for three different samples: sample 486a, which consists of 45% oxidized, fully protonated polyaniline with 90% —SO₃H, sample 515a, which consists of 50% oxidized polyaniline with 50% —SO₃H and sample 502a, which consists of 50% oxidized polyaniline with 30% —COOH in the rings. The thermopower for $T < 290$ K is negative with values in the range between -8 and -30 $\mu\text{V K}^{-1}$ in agreement with previous measurements on fully protonated emeraldine (Park *et al* 1987, Wuld *et al* 1987, Zuo *et al* 1987).

For a metal,

$$S = -(\pi^2/3)(k_B/|e|)(k_B T) \left[\frac{d \{ \ln[\sigma(E)] \}}{dE} \right]_{E_F} \quad (3)$$

where $\sigma(E) = n(E)e\mu(E)$, with $n(E)$ the concentration of carriers and $\mu(E)$ their mobility. On the assumption that $\mu(E)$ is independent of E , equation (3) becomes

$$S = -(\pi^2/3)(k_B/|e|)(k_B T)N(E_F) \quad (4)$$

where

$$N(E_F) = (1/N)(dn(E)/dE)_{E_F}$$

is the density of states per carrier at the Fermi level.

A change in sign from n to p in S with decreasing protonation of emeraldine has been observed (Park *et al* 1987, Zuo *et al* 1987), but for each particular sample the sign remained the same through the entire temperature range from 50 to 300 K swept in the experiments. In our measurements another kind of sign change appeared. From the 19 samples in which the thermopower was measured, only seven exhibited a negative Seebeck coefficient in all the temperature range up to 345 K, where the measurements were stopped in order not to spoil the polymer. Each of the other 12 samples displayed a change in its thermopower sign from negative to positive with increasing temperature, as is shown in figure 2. The temperature T_r of the sign reversal lies in the range from 290 to 325 K.

To check whether the change in sign during heating was due to a protonation reduction, as at elevated temperatures (above 300 K) water and acid might be driven off the polymer, measurements were continued by cooling the samples until the opposite sign reversal was observed. In figure 3 the behaviour of two samples of fully protonated polyaniline, about 50% oxidized and without dopants is shown. From this, it can be concluded that the sign reversal is not due to a permanent change in the samples, such as the reduction of the protonation.

A probable explanation of the sign reversal of thermopower at T_r is that the position of the Fermi level in the half-filled polaronic band changes with temperature, affecting S in a way analogous to that of the protonation degree. At temperatures below T_r we can assume that the Fermi level lies a little below the middle of the band, in a position with positive curvature $dn(E)/dE$, which results in a negative thermopower according to equation (4). With increasing temperature the Fermi level shifts above the middle of the band, where the curvature is negative and the thermopower becomes positive. It must be mentioned that an analogous sign reversal of thermopower in amorphous Ge and Si has been explained in the same way (Stuke 1970, Grigorovici *et al* 1966, Mott and Davis 1979).

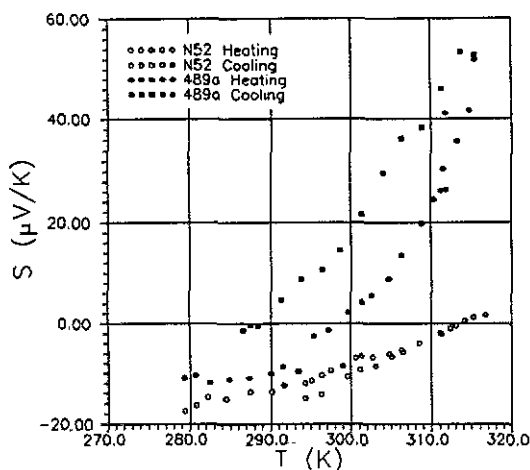


Figure 3. Sign reversal of the thermopower during heating and cooling through T_r for two samples of fully protonated polyaniline, about 50% oxidized and without dopants.

The addition of $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phosphorylated polystyrene in polyaniline results in a reduction in the absolute value of S for $T < T_r$. For example, pure polyaniline, 50% oxidized and fully protonated, has $S = -50 \mu\text{V K}^{-1}$ at $T = 290 \text{ K}$, but the addition of 10%, 30% and 100% of $-\text{SO}_3\text{H}$ reduces the thermopower to $-40 \mu\text{V K}^{-1}$, $-10 \mu\text{V K}^{-1}$ and $-7 \mu\text{V K}^{-1}$, respectively. It seems that the doping moves the Fermi level nearer to the middle of the half-filled polaronic band, in regions of progressively lower positive curvature. Moreover, this explains why the relative change in S is larger for small concentrations of dopants and why the temperature T_r , at which the change in S from negative to positive values occurs, decreases from 310 K for pure polyaniline to 305 K, 302 K and 300 K for 10%, 30% and 100%, respectively, of $-\text{SO}_3\text{H}$.

4. Conclusions

The DC conductivity experimental data of polyaniline derivatives doped with $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phosphorylated polystyrene to different concentrations from 0 to 100% follow the relation $\sigma(T) \propto \exp[-(T_0/T)^{1/2}]$. The addition of $-\text{SO}_3\text{H}$ improves the conductivity, although the other two additives reduce it.

The presence of an almost half-filled polaronic band in the energy gap of the polymer can explain the behaviour of the thermopower S versus temperature. This quantity changes sign as the Fermi level overcomes the band extremum, at each side of which $dn(E)/dE$ has opposite sign. The addition of dopants seems to move the Fermi level nearer to the band extremum, reducing the absolute value of S and decreasing T_r .

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