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ELECTRIC CONDUCTIVITY AND THERMOELECTRIC POWER OF VARIOUS POLYPYRROLES

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ABSTRACT

The dc-conductivity and thermoelectric power of electrochemically prepared polypyrroles have been investigated in the temperature range between 300 K and 1.3 K on unaged, aged (24-120 days at 80°C in air) and chemically modified samples. The linear temperature dependence of the thermopower of unaged polypyrroles demonstrates clearly the contribution of metallic regions to the electronic transport properties. The temperature dependence of the conductivity of the polypyrroles investigated corresponds to that predicted by the variable range hopping model.

INTRODUCTION

Electrochemically polymerized polypyrrole films are relatively stable against oxygen attack and thermally induced aging as compared to other conducting polymers like polyacetylene, for example [1]. The stoichiometric ratio of pyrrole moieties and the anions (ClO_4^-, benzenesulfonate$^-$) was measured as about 3:1 for the polypyrroles (PPy) investigated. The influence of aging , caused by storing the samples for a limited time (24-120 days) at a temperature of 80°C, on the electronic transport properties as well as the change in conductivity (σ) and thermopower (S) after a chemical treatment of the samples with aqueous H_2SO_4 (4 min.,1o%) or NaOH (4 min.,0.1%,2%) was measured. The complexe morphology of PPy (polymer chains, small crystalline regions, fibrils, disturbances effected by the anions), makes it impossible to describe the transport properties by a consistent model within a larger temperature range. The question whether the charge carrier transport is determined by bipolarons on the polymer chain [2], transitions between the chains, hopping between localized sites associated with the anions [3] or whether there exist metallic regions [4] is decisive for the interpretation of the results of measurements taken. However the answer to this question cannot be given by measuring the transport properties alone and this is the reason for the differing theoretical approaches to explain the behaviour of the conductivity and thermopower of PPy .

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From all measurements on conductive polypyrroles it is evident that the conductivity can not be described by a simple activated electron transport process,but it corresponds in its temperature (T) dependence below 300 K to Mott's law for variable range hopping conduction [5] given in eq. 1.

$$\sigma(T) = \sigma_o' \, T^b \exp-(T_o/T)^p \qquad (1)$$

Here it is expected that b=-1/2 and p=1/4. The constants σ_o' and T_o are determined by the densitity and extension of the localized states and a phonon frequency, although for conducting PPy it was impossible to get reasonable values [6].A numerical fit to the data using this equation is difficult because of the weak temperature dependence in highly conductive polypyrroles and the uncertainty of b and p. The deviation from p=1/4 may have various reasons. In PPy these can be, for example, spatial inhomogeneities, variations of the density of states with energy, or lower dimensionality. Although the conductivity is nonmetallic, the existence of metallic regions in PPy is indicated by the linear temperature dependence of the thermopower and optical measurements [4]. For this hypothesis of a mixture of different electronic transport mechanisms in highly conducting PPy it is of interest to analyze systematically the resulting changes of the thermopower and conductivity effected by controlled aging and chemical treatment.

RESULTS AND DISCUSSION

Dc-conductivity

The temperature dependence of the dc-conductivity of PPy/benzenesulfonate$^-$ and the influence of aging is shown in Fig. 1 . Room temperature values of 120 S/cm for the unaged samples have been measured. The results of similar measurements on PPy/ClO_4^- are given in Fig.2 . The temperature dependence is shown in a log(σ) versus $(1/T)^{1/4}$ plot. Fig.3 shows the influence of chemical treatment on the conductivity. The local activation energy ΔE is the gradient of the conductivity in the Arrhenius plot. Hill proposed the analysis of the dependence of log(ΔE) versus log(1/kT) [7,8].

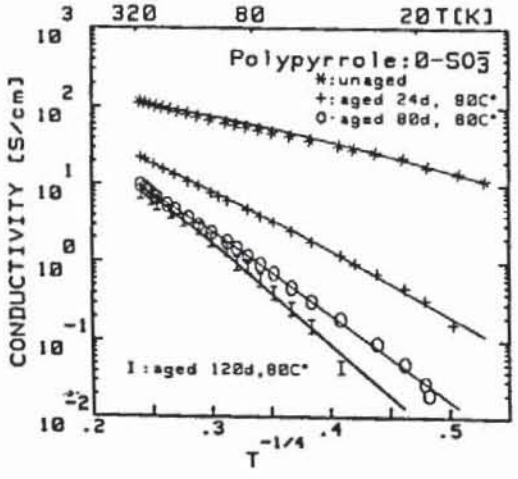


Fig. 1. Aging of PPy/benzenesulfonate.

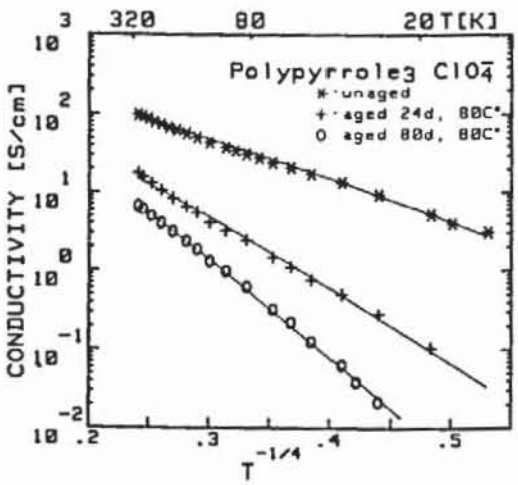


Fig. 2. Aging of PPy/ClO_4^-.

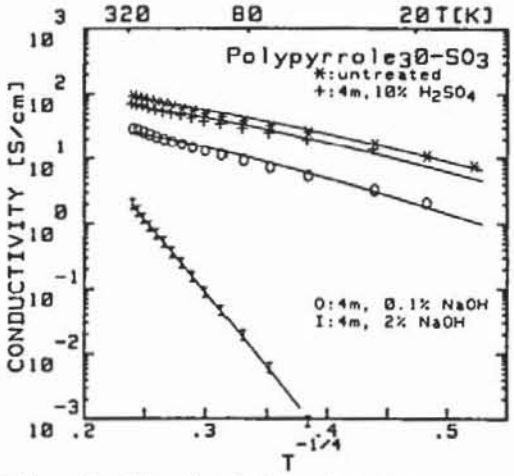


Fig. 3. Chemical treatment of PPy/benzenesulfonate$^-$.

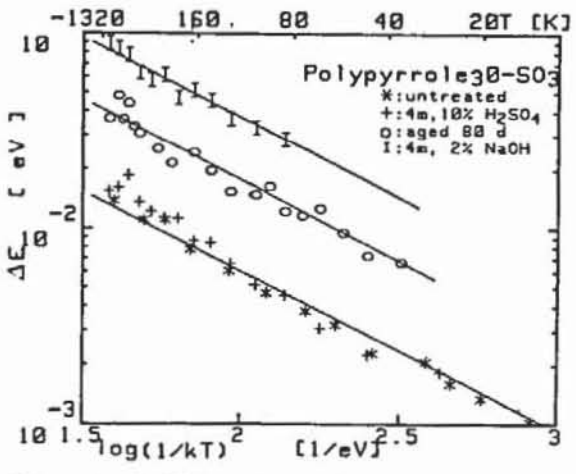


Fig. 4. Hill's plot of the data.

Hill's plot is presented in Fig. 4, which shows the effect of the different treatments on the conductivity data more clearly. Using Eq. (1) for $\sigma(T)$, one obtains

$$\Delta E = -\,d(\ln\sigma)/d(1/kT) = b\,k\,T + p\,k\,(T_0/T)^{(p-1)} \qquad (2)$$

The small value of ΔE in Fig. 4 indicates that the unaged samples are in the region of a metal-insulator transition and that a fit of the data is very sensitive to the temperature dependence of the pre-exponential factor. Aging or treatment with NaOH increases the local activation energy, in contrast to the treatment with H_2SO_4 which has no significant effect. From Fig. 4 for all PPys a value of $p=0.2$ ($\pm 10\%$) is obtained (even down to 1.3 K as measured for unaged PPy).

Thermoelectric power

Figures 5 and 6 show the effect of aging on the thermopower of PPy/benzenesulfonate$^-$ and PPy/ClO_4^-. For the unaged samples room temperature values of 5μV/K respectively 10μV/K were measured.

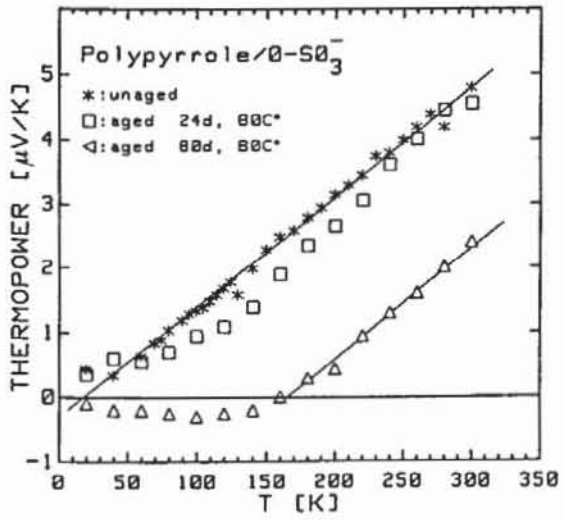


Fig. 5. Thermopower of PPy/benzenesulfonate$^-$.

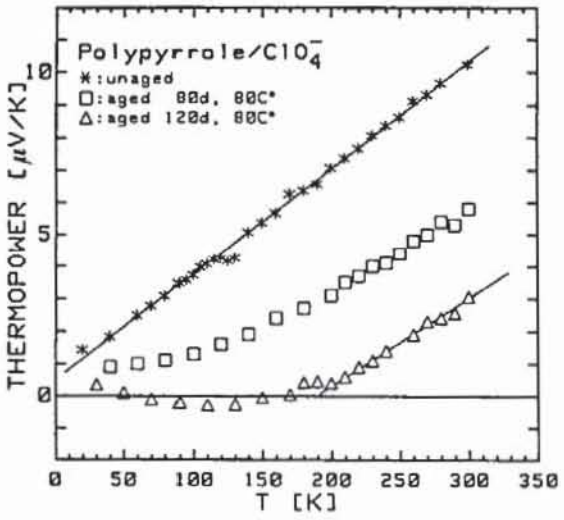
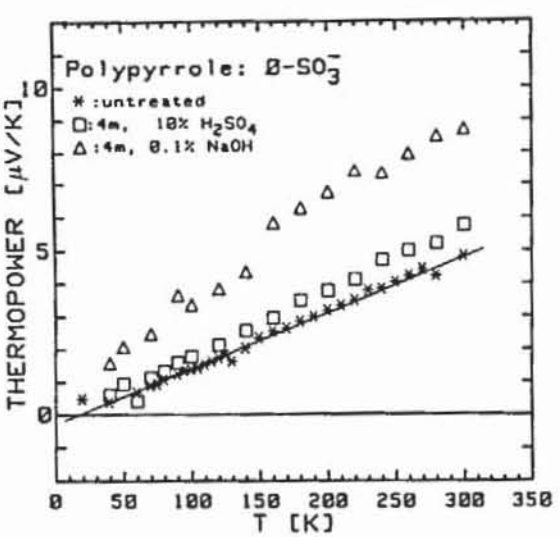


Fig. 6. Thermopower of PPy/ClO_4^-.



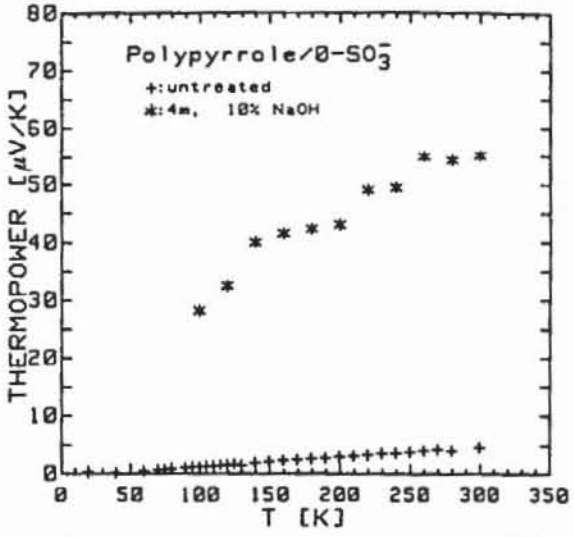


Fig. 7. (left) Thermopower of PPy/benzenesulfonate⁻ and Fig. 8. (right) after chemical treatment.

The thermoelectric power decreases linearly by lowering the temperature, which is typical for a metal.For the aged samples the thermopower is smaller, reaching the value of zero at higher temperatures (up to 200 K), but the slope in the linear range changes less. Chemical treatment has the effect of changing the slope from a linear to a sublinear T dependence (Fig. 7) and increasing the value drastically after a treatment with 10% NaOH (Fig.8). Calculations on this subject can be found in reference [9].

CONCLUSIONS

Aging as well as chemical treatment destroys the metallic strands, decreases the conjugation length of the PPy-chains and therefore the contribution of the variable range hopping conduction becomes stronger. The thermopower is influenced by this type of charge transport, too, losing its metallic character.

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