

# Transport Properties in Polypyrrole–PVA Composites: Evidence for Hopping Conduction

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## SYNOPSIS

Experimental results on electrical conductivity and thermoelectric power for FeCl<sub>3</sub>-doped polyvinyl alcohol–polypyrrole composites, with polypyrrole content exceeding the percolation threshold, are presented. The electrical conductivity is analyzed in terms of the hopping theory, whereas the thermoelectric power displays a metallic-like dependence. A model involving both the intrinsic resistance of the fibrils (V.R.H. hopping mechanisms) and the resistance of the junctions between fibrils (fluctuations-induced tunneling conduction) has been retained.

## INTRODUCTION

Polypyrrole can be easily prepared by electro-chemical or chemical polymerization. However, the latter method leads to insoluble powders that are difficult to process, which significantly impedes their application. Several attempts have been undertaken to prepare composites or blends of conducting polymers with classical ones in order to improve their properties and processability. Recently, a simple method for a preparation of the PPy–PVA composite has been proposed.<sup>1–3</sup> This method is based on the oxidation of pyrrole by PVA-transition metal salt complexes. The result in products exhibits both good mechanical properties (high transparency for lower content of polypyrrole) and good conductivity. Therefore, these prepared film composites are excellent candidates for technological application in electronics.

The prepared film composites' electrical properties obviously depend upon the dopant species, but also upon the band structure of the oxidized poly-

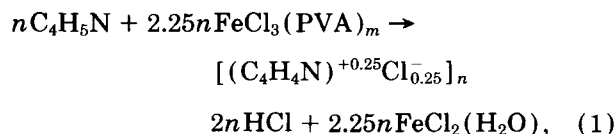
pyrrole and the energy values involved in the electronic transfers. A possible approach is to study the behavior of the transport phenomena of the film composites in a wide temperature range. Then, details on the band structure of the material near the Fermi level can be deduced from this study. Measurements of the electrical conductivity  $\sigma$  and thermoelectric power  $S$  have been recently performed on several PVA–PPy film composites with different dopant concentrations in the temperature range 80–300 K. Classical models have been tested in order to interpret the conduction mechanisms that take place in these film composites. A general feature of nearly all these models is hopping of charge carriers between localized states.

## PREPARATION

PVA films containing molecularly dispersed transition metal halides were prepared by dissolving PVA powders and FeCl<sub>3</sub> in water. The films were cast by water evaporation at 323 K. Free standing films so formed were then suspended over 50% v/v solution of pyrrole in ethanol and were kept in a static vacuum for periods ranging from 1 to 7 days.

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Under these conditions, polymerization of pyrrole occurred on the PVA-transition metal salt film. After polymerization, the sample was degassed under a dynamic vacuum. Since, for the preparation of polypyrrole in the oxidized state, 2.25 molecules of  $\text{FeCl}_3$  are needed per one pyrrole ring according to the equation:

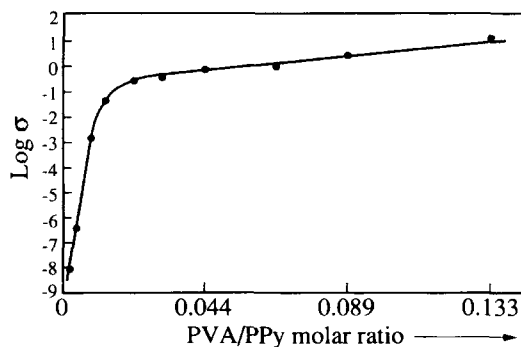


the content of the polypyrrole in the composite can be very easily calculated knowing the concentration of the oxidant in the PVA matrix. In addition, Mossbauer spectroscopic studies have been performed after the reaction in order to verify whether traces of  $\text{Fe}^{+3}$  exist or not and therefore whether the oxidant has been consumed completely or not. In all samples studied, only  $\text{Fe}^{2+}$  species were detected, that is, the PPy content could be determined from eq. (1).

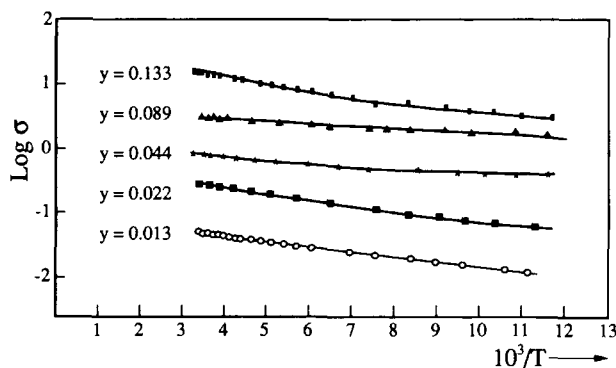
## EXPERIMENTAL

Electrode contacts were applied and electrical conductivity measurements were carried out on free standing films using the method of Van der Pauw. Temperature dependence of the conductivity was tested in the temperature range of 77–300 K. Special care was taken to ensure good temperature stability for each experimental point. The above described experimental conditions enabled us to measure the conductivity within  $\pm 2\%$  accuracy.

Thermoelectric power (TEP) measurement was performed using a method described previously.<sup>4</sup> The



**Figure 1** Experimental variations of  $\log \sigma$  vs. PVA-PPy molar ratio  $y$ . The percolation threshold is reached for  $y_c = 5.3 \times 10^{-3}$ .



**Figure 2** Experimental variations of  $\log \sigma$  versus  $10^3/T$  obtained on conducting PVA-PPy composites with different dopant concentrations. The theoretical variations are drawn in full line.

samples were placed between two microheaters made of constantan wire wrapped around an aluminium oxide tube ( $\phi = 1$  mm). The thermal emfs between the two copper and the two constantan wires were measured simultaneously using two digital nanovoltmeters. In the experiment, the help of a data acquisition system monitored by computer was required. All numerical values were computer controlled.

The electrical conductivity or polyvinyl alcohol-polypyrrole chloride composites is strongly dependent on the polypyrrole content and reaches ca.  $15 \Omega^{-1} \text{cm}^{-1}$  for the composition of PVA-PPy 0.13 at room temperature. The conductivity vs. PPy/PVA molar ratio ( $y$ ) curve exhibits features characteristic of percolating systems (Fig. 1). For low and high contents of polypyrrole, the obtained curve can be approximated by two straight lines with drastically different slopes. The abscissa of the intersection of these two lines gives the value of the percolation threshold. It should be noted that the percolation threshold is reached for a very low polypyrrole content ( $y_c = 5.3 \times 10^{-3}$ ), which may reflect peculiar morphology of the conducting phase.

The temperature dependence of the conductivity was studied for samples with polypyrrole content exceeding the percolation threshold. The results are presented in Figure 2 ( $\log \sigma$  vs.  $10^3/T$ ).

In order to interpret the obtained results, we tried to fit the experimental curves in the frame of a classical hopping mechanism, obeying the law  $\sigma = \sigma_0 \exp - \left( \frac{T_0}{T} \right)^{1/n}$ , in which the power coefficient may be 1, 2, 3, or 4.

The first question to be answered is: Which of the possible coefficients gives the best fit to the ex-

perimental data? A curve-fitting technique, based upon the Marquardt algorithm,<sup>5</sup> was therefore applied. The good agreement between the experimental ( $y_i$ ) and theoretical ( $f(T_i)$ ) data is estimated by calculating the classical standard deviation:

$$e = \left[ \frac{1}{N} \sum_i \left( \frac{y_i - f(T_i)}{y_i} \right)^2 \right]^{1/2}$$

The results of this analysis can be summarized as follows:

1. In the case of lower polypyrrole contents ( $y = 0.013$  and  $0.022$ ), the best fit is clearly obtained for  $n = 2$  on the whole temperature range investigated.
2. For higher polypyrrole contents ( $y = 0.044$  and  $0.089$ ), the data are well fitted with  $n = 4$  ( $T^{-1/4}$  Mott's law<sup>6</sup>). However, the experimental differentiation of a  $T^{-1/4}$  from a  $T^{-1/2}$  law is less significant for PVA-PPy 0.089.
3. For the highest doped compound, it appears that two main contributions to the transport properties are needed to obtain the best fit. The first one is described by Mott's law whereas the second one obeys at  $T^{-1}$  law.

It should be stressed that in all cases the calculated standard deviation  $e$  of the experimental data from the theoretical model is lower than the experimental accuracy of  $\pm 2\%$ .

All results obtained from the fits are collected in Table I.

Such behavior becomes understandable if one takes into account the composite nature of the material. The macroscopic conductivity requires not only the hopping of carriers between the different

chains with a conducting fibril, but also the hops between the fibrils.

On one hand, interchain hopping of carriers is well interpreted in the framework of the variable range hopping. Above the percolation threshold, a pure  $T^{-1/4}$  law is in most cases observed at low dopant concentration in conducting polymers, which presents a good uniformity of the dopant concentration into the polymer structure.<sup>7,8</sup> As has been suggested by several authors,<sup>9,10</sup> the occurrence of the  $T^{-1/2}$  law could be associated with some inhomogeneity in the dopant: molecules cluster together and form conducting islands.

On the other hand, hopping mechanisms between fibrils can be easily described on the basis of a model involving a fluctuation-induced tunneling conduction between large metallic segments separated by an insulator.<sup>11</sup>

The tunnel barriers are probably made of junctions between fibrils and are already present in the composite structure. As a consequence, the overall resistance of the film is, on the average, made up of a sum of two resistances in series which exhibit a different temperature dependence:

$$R(T) = R_1(T) + R_2(T)$$

where  $R_1(T)$  is the intrinsic resistance due to the fibrils and reflects the main contribution of interchain hops and  $R_2(T)$  is the resistance of the junction between the fibrils:

$$R_1(T) \sim \exp\left(\frac{T_1}{T}\right)^{1/4}$$

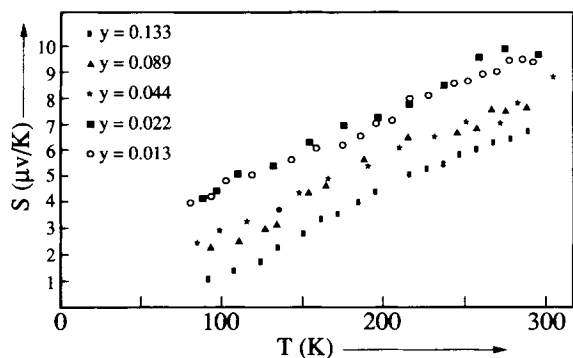
$R_2(T) \sim \exp\left(\frac{T_2}{T} + A(T)\right)$ , which depends approximately upon  $\exp\frac{T_2}{T}$  in the high temperature range limit.

Consequently, the result of the analysis can be summarized as follows:

1. For the four less doped samples, the intrinsic resistance is much larger than the overall junction resistance. Moreover, the distribution of the dopant species seems to be more heterogeneous for low polypyrrole content ( $y = 0.013$  and  $0.022$ ).
2. On the contrary, the two contributions, which have been described above, are found to be similar on PVA-PPy 0.13: this behavior clearly shows a decrease of the resistance of the fibrils with increasing PPy content.

**Table I** Parameters of  $\sigma = \sigma_0 \exp - \left(\frac{T_0}{T}\right)^{1/n}$   
Equation Obtained via Best Fitting Procedure  
for Polyvinyl Alcohol-Polypyrrole Composite  
with Varying Polypyrrole Content

Sample Composition	Temperature Dependence of Conductivity $\Omega^{-1} \text{ cm}^{-1}$
PVA-PPy 0.013	$\sigma = 0.27 \exp - (825/T)^{1/2}$
PVA-PPy 0.022	$\sigma = 1.9 \exp - (1038/T)^{1/2}$
PVA-PPy 0.044	$\sigma = 6.3 \exp - (5462/T)^{1/4}$
PVA-PPy 0.089	$\sigma = 17.5 \exp - (2785/T)^{1/4}$
PVA-PPy 0.133	$\sigma_1 \sim \exp - (18760/T)^{1/4}$ $\sigma_2 \sim \exp - (117/T)$



**Figure 3** Experimental variations of the T.E.P.  $S$  vs.  $T$  obtained on conducting PVA-PPy composites with different dopant concentrations. PVA-PPy molar ratio  $y$ : (■) 0.133, (▲) 0.089, (\*) 0.044, (■) 0.022, and (○) 0.013.

It must be recalled that for all the samples that have been studied in this article, polypyrrole content exceeds the percolation threshold. It appears that the thermoelectric power is positive, very low, and varies quasi-linearly with temperature (Fig. 3). This "metallic type" behavior of the Seebeck coefficient is not unexpected. Polypyrrole present in the composite is in its oxidized state, for which an overlap between the empty bipolaronic band and  $p$  band occurs, giving rise to empty states in the valence band. This leads, in turn, to a  $p$ -type metallic conductivity. For such systems, low and positive value of thermoelectric power is expected as observed experimentally. Consequently, thermoelectric power reflects intrinsic properties of the conducting network. Therefore, it may exhibit its metallic properties even for the samples whose macroscopic conductivity is not metallic in behavior. On the other hand, the macroscopic conductivity embraces transport mechanisms along the chain, but also the interchain and interfibrillar mechanism. Therefore, in conducting polymers, one frequently observes the  $\exp\left(-\frac{T_0}{T}\right)^n$  law in conductivity and linear dependence of the thermoelectric power.<sup>12,13</sup>

To summarize, we have studied the electrical transport properties of polyvinyl alcohol-polypyrrole composite. The obtained result allows one to draw the following conclusions:

1. The PVA-PPy composite exhibits a very low percolation threshold at a PVA/PPy ratio of

$5.3 \times 10^{-3}$ . This low value enables fabrication of highly conducting composites with only a small fraction of electron active component.

2. In all samples above the percolation threshold, a temperature dependence of the conductivity characteristic of variable range hopping (VRH) is observed.
3. For  $y < 0.013$ , the contribution of interfibrillar carrier transfer is similar to that of interchain carrier transfer. This behavior can be interpreted on the basis of a decreasing contribution of interchain carrier transfer to the overall resistance from high PPy content.
4. Measurements at temperatures below 77 K should allow improvement in the reliability of the  $1/n$ -tests on experimental data.

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