THE TEMPERATURE DEPENDENCE OF THE
ELECTRICAL CONDUCTIVITY OF POLYPYRROLE FILMS
DOPED WITH DIFFERENT COUNTERIONS

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Abstract. The temperature dependence of the electrical conductivity of the polypyrrole films
doped with different counterions was investigated. The results show that the electrical conductivity
is strongly dependent both on the nature of the doping ions and the preparation conditions of the
samples. Measurements have been compared with predictions both of the fluctuation-induced tun-
nelling model (Sheng) and the hopping model (Zuppiroli) applied to these disordered materials.

Key words: conducting polymers, polypyrrole, electrical conductivity.

1. INTRODUCTION

One of most challenged matter concerning conducting polymers is that of
transport mechanisms which could explain the high values of electrical conduc-
tivity obtained for some conducting polymers such as polyacetylene and its tem-
perature dependence. Because of the complicated morphology of conducting
polymers due essentially to the preparation conditions and the nature of counte-
rions it is quite difficult to use a unique model to fit all the experimental data
over a large temperature range. As has been shown by different authors the
charge transport mechanisms predominantly found in conducting polymers
(polyacetylene, polypyrrole, polyaniline) are those related to the isotopic three-
dimensional hopping among localised states along and between the polymeric
chains, thermally activated tunnelling between extended conducting regions and
fluctuation-induced tunnelling between fibrils or grains [1–5].

Among the conducting polymers that are largely used for technological ap-
lications, polypyrrole (Ppy) is one of the best candidates because of its high
conductivity and stability as well as its good mechanical properties. The free-
standing films obtained by electrochemical method are quite proper to be inves-

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tigated easily by many experiments. As for other conducting polymers, the structure of polypyrrole is very dependent on the preparation conditions and the nature of the doping ions. For instance, using toluene-sulfonate an anisotropic structure is determined rather than an isotropic one that appears for isotropic counterions [6].

The temperature dependence of the electrical conductivity on PPy shows a positive temperature coefficient of conductivity but a metallic behaviour for PPy ($PF_6^-$) below 20 K was observed [7]. Charge transport in PPy is explained mostly by hopping or tunnelling models found as acceptable for fitting many experimental data. The exponent value associated to the hopping mechanisms (interchain or intrachain charge transport) is $1/4$ for a variable-range hopping model and varies from $1/4$ to 1 if Coulomb correlations are taken into account [8]. The high degree of disorder in PPy also suggests a complicated nature of the carriers involved in the hopping mechanism. Recently, Zuppiroli et al. have demonstrated the formation of polaronic and bipolarons clusters in high disordered conducting polymers [2]. Besides the longitudinal polaron and bipolaron, they consider that transverse polaron and bipolaron are created due to fluctuations in the ion concentration as metallic grains in the granular-metal hopping model [9].

Another model that describes well the conductivity behaviour over a large temperature range is the Sheng model. This is related to the fluctuation-induced tunnelling between metallic islands separated by small insulating barriers [1, 10].

On the other hand, the thermal dependence of the electrical conductivity of composites chemically prepared was mainly interpreted by the percolation theory [11, 12]. This predicts a dependence of conductivity on the volume fraction of the conducting species. The differences in the structures are explained by different percolation thresholds below which conductivity falls to a very low value [13,14]. Above room temperature, the changes in conductivity are determined by formation and interruption of percolation paths which are very dependent on the polypyrrole concentration.

In this paper we analyse the temperature dependence of the electrical conductivity carried out on polypyrrole films (PPy films) electrochemically prepared with different ions. We have tried to identify which conduction mechanism might account for the data by comparing the fluctuation-induced tunnelling mechanism (Sheng model) with the hopping model as stated by Zuppiroli [2].

2. EXPERIMENTAL

The doped polypyrrole was electrochemically prepared by standard method. A steel stainless plate electrode was used as a counter-electrode which was inserted in a solution containing acetonitrile as solvent and lithium perchlorate ($ClO_4^-$ doping ion), tetrabutyl-ammonium-tetrafluoroborate ($BF_4^-$ doping
ion), p-toluenesulfonic acid (HTSO) and sodium toluenesulfonic (NaTSO) as electrolytes at concentrations which varied from 0.005 to 0.1 mole per litre (M/L). The polymerization was carried out at room temperature in a nitrogen atmosphere under galvanostatic conditions at a constant current density of 0.625 mA/cm². The as-prepared films were peeled off from the electrode washed with water and then dried under vacuum. The film thickness were in the range 8–40 μm.

The electrical conductivity of the dried films was measured by using the four-point contacts method at room temperature. All samples were measured three months after preparation. Conductivity values are in the range 5–50 S/cm for PPy films.

The temperature dependence of conductivity was measured in the temperature range 150–400 K for some of the films but in the temperature domain 5–300 K for the PPy(TSO⁻) films derived from NaTSO. The cold finger was interfaced to a PC computer to allow automatic data collection; generally 800 readings were made over the temperature range. The value of the sampling current was of 0.1 mA for PPy films. The data analysed are extracted from the first heating process after cooling from room temperature. Although the cooling rate was faster than the heating rate, no hysteresis was observed at low temperature.

3. RESULTS AND DISCUSSION

In Fig. 1 the temperature dependence of the electrical conductivity for PPy films doped with different counterions and prepared with different electrolyte concentrations \(c_e\) is shown. Conductivity exhibits several trends when cooling down from 400 K to room temperature. There has been observed that conductivity either increases as in a previous study [15] or decreases (in most cases) and quite a good reversibility for other samples appears. The increasing is due to the reduction of structural defects during thermal annealing for the stable samples at chemical changes (such as PPy/TSO⁻ films). On the other hand, the falling of conductivity at above 400 K is due mainly to the loss of solvent [16].

Another feature of these curves is the inflexion around 270 K which is observed in the heating process. Because this inflexion also appears in the second heating cycle as shown in Fig. 2, we have considered that it cannot be due to the weight loss partially attributable to the loss of water incorporated in samples [17]. A better explanation is based on the conformational changes which could appear in the polymer structure and lead to the temperature relaxation of conductivity. This relaxation process is influenced by the rate of the cooling and heating [18]. In the cooling cycle the rate is quite much higher than the heating one and this inflexion is not observed. This is because the equilibrium of lattice dynamics is not established and the polymer chains are being frozen in the high temperature state. On the other hand, the inflexion could also have a connection...
Fig. 1. – The temperature dependence of the electrical conductivity for PPy films doped with different counterions and prepared with different electrolyte concentrations. Data are collected during the first heating process and the second cooling process.

Fig. 2. – Electrical conductivity versus temperature for PPy(TSO⁻) (c_e = 0.15 M/l) film during two cycles starting from the room temperature. The arrows indicate the sequence of cooling and heating processes.
The temperature dependence of the electrical conductivity

with the maximum observed in polyacetylene or polyaniline as determined by increasing the number of thermally excited lattice vibrations (phonons) that scatter the electrons [3, 4].

Moreover, the gradual process of thermal decomposition of the dopant is accelerated at sufficiently high temperatures [17] and this is suggested by curve inflexions and the rough falling in conductivity. In addition, the reaction with oxygen increases this decomposition especially in the case of inorganic counte-
rions and polymer backbone [19].

In order to analyse the transport mechanisms for PPy films, we have con-
sidered a temperature domain ranging from 4 to 300 K for PPy (TSO ) films (de-
\textit{rived from NaTSO}) and from 150 to 300 K for the other PPy films. The temperature dependence of conductivity for the PPy (TSO ) films by using Na-
TSO, prepared in different conditions as expressed below is shown in Fig. 3.

While the electrical conductivity for $N_1$ ($c_e = 0.01 \text{ M/l}; j = 0.25 \text{ mA/cm}^2$) and $N_2$
\left($c_e = 0.005 \text{ M/l}; j = 0.25 \text{ mA/cm}^2$\right) tends abruptly toward zero at low tempera-
tures, the electrical conductivity for the $N_3$ ($c_e = 0.005 \text{ M/l}; j = 0.625 \text{ mA/cm}^2$)
has a finite value.

The only difference between these samples seems to be the current density
used in preparation which determines different conduction paths. The electrical
conductivity values at room temperature is $\sigma_{RT} = 5.08 \text{ S/cm}$ for $N_3$ sample and
$\sigma_{RT} = 3.12$ S/cm for $N_2$ sample. By using the ratio $\rho_r = \rho(4\,\text{K})/\rho(300\,\text{K})$ as an indication of conduction regime [8], we have obtained the values of 85 and 75 for $N_1$ and $N_2$ respectively, which suggest that these materials are situated in the region characteristic to the metal-insulator transition. Anyway, the metallic behaviour at low temperatures for samples with low conductivities ($\sigma < 10$ S/cm at room temperature) is rather surprising and additional measurements must be performed to confirm it.

To obtain the best parameters from the experimental data and to establish mathematically which equation gives the best fit, we have used the difference between the $\ln\sigma_f - \ln\sigma_m$ as a measure of the quality of the fit [20, 21], with $\sigma_m$ the experimentally measured conductivity and $\sigma_f$ the fitted conductivity value. Although a good fit can be obtained for many given dependencies this is not sufficient to apply a model as the only one especially for a limited range of temperature. Also, the parameters obtained by fitting must be at least in a qualitative agreement and in the limits of the model.

The equations used to be compared describe the following processes characteristic to the transport mechanisms in the conducting polymers:

a) the hopping of charge carriers for different dimensions of the considered system given by Equation 1:

$$\sigma = C_1 \exp[-(C_2 / T)\gamma]$$

with: $C_1, C_2$ are constants, $\gamma = (d + 1)^{-1}$ for $d = 1$, $d = 2$ and $d = 3$, respectively;

b) the fluctuation-induced tunnelling (Sheng model) between metallic islands given by Equation 2:

$$\sigma = \sigma_0 \exp\left(-\frac{T_1}{T + T_0}\right).$$

These equations with their derived forms were the most used in literature for interpretation of the experimental data for the conducting polymers.

As shown in Figs. 4 and 5, we have suggested that the best fitting for PPy films doped with $\text{TSO}^-$ and $\text{BF}_4^-$ is obtained by using Equation 2 which describes the fluctuation-induced tunnelling as stated by Sheng [1]. The appropriate parameters obtained by fitting with the two parameters $T_0$ and $T_1$ are listed in Table 1. Moreover, we have also considered the hopping mechanism as an additional and possibly dominant process during the charge transport. The electrical conductivity depends strongly on the nature of the doping ion, varying as $T^{-1/2}$ for PPy($\text{TSO}^-$) and as $T^{-1/4}$ for PPy($\text{BF}_4^-$) and PPy($\text{ClO}_4^-$) as suggested by Figs. 4 and 5 above. After this first step, the physical interpretation of the obtained parameters is required.
The temperature dependence of the electrical conductivity

Fig. 4. – The temperature dependence of the logarithm difference (\(\ln \sigma_f - \ln \sigma_m\)) between the fitted conductivity value \(\sigma_f\) and the experimentally measured conductivity \(\sigma_m\) for PPy(TSO\textsuperscript{-}) film (\(c_e = 0.01 \, \text{M/l}\)).

Fig. 5. – The temperature dependence of the logarithm difference \(\ln \sigma_f - \ln \sigma_m\) between the fitted conductivity value \(\sigma_f\) and the experimentally measured conductivity \(\sigma_m\) for PPy(BF\textsubscript{4}\textsuperscript{-}) film (\(c_e = 0.05 \, \text{M/l}\)).
THE FLUCTUATION-INDUCED TUNNELLING MODEL (SHENG)

In order to evaluate the parameters of the tunnelling barrier between conducting regions, we have adopted a more recent model presented by Paasch et al. [22] for polypyrrole. The authors have considered a two-dimensional (2D) model structure where there is a connection between 2D metallic island through one-dimensional (1D) PPy chains. The tunnel junctions are characterised by an effective area \((A)\) and an effective width \((w)\). The image-force correction of the rectangular barrier is characterised by the constant \(\lambda\) that describes the barrier shape.

We have supposed the existence of highly conductive regions for PPy(TSO\(^{-}\)) films (derived from the NaTSO electrolyte) as suggested by the slope modification at low temperatures and by the values of \(\rho_r\) also found in other samples [8].

We have used the limit of medium barrier \(0 \leq \lambda \leq 0.25\) and considered \(V_0\) as the position of conduction band relative to the Fermi energy of the metallic phase; it is considered that the 1D chains are undoped and therefore will not contain polaronic midgap states. The expressions used to determine barrier parameters are given below [22]:

\[
\lambda = \frac{0.795e^2}{16\pi\varepsilon_0\varepsilon_r wV_0} \tag{3}
\]

\[
\frac{T_i}{T} = 2w \left(\frac{2m^*V_0}{\hbar^2}\right)^{1/2} \left[1 - (8 - \pi)\lambda + 4(4 - \pi)\lambda^2\right] \tag{4}
\]

\[
k_BT_i = \frac{1}{2} e_0\varepsilon_r \frac{1}{w} A^2 \frac{V_0^2}{e^2} \left[\frac{0.795 + 1.64\lambda - 19.28\lambda^2}{4\lambda}\right] \tag{5}
\]

The values of parameters \(\lambda\) and \(w\) barrier width are shown in Table 1 and we have used constants values of \(V_0 = 1.25\) eV, \(m^* = 0.56m_e\) [23] and \(\varepsilon_r \approx 2.5\).

The condition for the validity of this approximation is:

\[
0.1...0.15 < \lambda < 0.25 \quad \text{or} \quad 1.14 - 0.76 \geq \frac{w}{nm} \frac{V_0}{eV} \frac{\varepsilon_r}{2.5} \geq 0.46 \tag{6}
\]

and it is relatively satisfied for the samples of PPy(ClO\(_4\)) and PPy(BF\(_4\)). The values obtained for the junction area are ranged between 4–8Å\(^2\) and correspond to the cross section of the \(\pi\) electrons. The obtained values of the barrier width are in accordance with those related by other authors as well [10, 24, 25]. The higher the conductivity values, the lower the barrier width. The probability of tunnelling is increased by doping because of decreasing the distance between the metallic islands.
Table 1

The preparation conditions and the parameters obtained by using Sheng model for PPY films doped with different counterions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Doping ion</th>
<th>$\sigma_{\alpha\gamma}$ [S/cm]</th>
<th>$c_e$ [M/l]</th>
<th>$T_1$ [K]</th>
<th>$T_0$ [K]</th>
<th>$\lambda$</th>
<th>$w$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BF$_4^-$</td>
<td>8.55</td>
<td>0.05</td>
<td>561</td>
<td>133</td>
<td>0.101</td>
<td>9.04</td>
</tr>
<tr>
<td>2</td>
<td>BF$_4^-$</td>
<td>8.50</td>
<td>0.1</td>
<td>470</td>
<td>107</td>
<td>0.0987</td>
<td>9.26</td>
</tr>
<tr>
<td>3</td>
<td>ClO$_4^-$</td>
<td>21.56</td>
<td>0.05</td>
<td>365</td>
<td>113</td>
<td>0.116</td>
<td>7.84</td>
</tr>
<tr>
<td>4</td>
<td>ClO$_4^-$</td>
<td>14.54</td>
<td>0.1</td>
<td>300</td>
<td>60</td>
<td>0.0915</td>
<td>9.99</td>
</tr>
<tr>
<td>5</td>
<td>TSO$^-$ $^a$</td>
<td>18.74</td>
<td>0.05</td>
<td>337</td>
<td>16</td>
<td>0.032</td>
<td>28.92</td>
</tr>
<tr>
<td>6</td>
<td>TSO$^-$ $^a$</td>
<td>31.16</td>
<td>0.1</td>
<td>324</td>
<td>29</td>
<td>0.053</td>
<td>17.3</td>
</tr>
<tr>
<td>7</td>
<td>TSO$^-$ $^b$</td>
<td>5.08</td>
<td>0.005</td>
<td>581</td>
<td>84</td>
<td>0.075</td>
<td>12.28</td>
</tr>
</tbody>
</table>

* the electrical conductivity at room temperature
$^a$ the doping ion is derived from HTSO electrolyte
$^b$ the doping ion is derived from NaTSO electrolyte

Although there is a good correlation between the conductivity of the samples prepared in the same conditions and the $w$ values in the case of PPy(TSO$^-$) films, quite in accordance with other authors, these values do not verify relation (6). This could be due both to the relatively restrictive conditions valid especially for the highly conducting polymers and to the limited range of temperature used in fitting. For PPy(TSO$^-$) films, the morphology of samples is changed by the doping ion nature which determines an anisotropic structure [6]. The layered structure of polymer chains and counterions planes leads to a stabilisation of this anisotropic structure which could be understood in terms of a strong electrostatic interaction between the dopant and the polymer backbone. Consequently, we tried to explain the electrical conductivity for these samples in terms of granular-metal hopping model stated recently by Zuppiroli et al. [2].

THE HOPPING MODEL (ZUPPIROLI)

For the case of PPy(TSO$^-$) films though the fluctuation-induced tunnelling model conduction seems to fit well our experimental data over the temperature range, the parameters found lost their physical significance in terms of Paasch’s approximation. As has been suggested (Fig. 4), equation (1) with the exponent value $\gamma = 1/2$ is the next relation which could give us some information about the mechanism transport. This dependence of PPy films was recently explained by Zuppiroli et al. [2], who considered that besides the polaronic and bipolaronic species which contribute to the conduction process, there are also polaronic clusters originated from fluctuations in the dopant concentration which are thermally accessible. Their approach is based on the granular-metallic model [9] where the
polaronic cluster act as metallic grains where \( d \) is the diameter of the grain and \( s \) is the intergrain distance. It is considered that a disordered conducting polymer is composed of an ensemble of polaronic segments and an ensemble of dopant counterions which also control the stability of all polaronic species by their attractive potential. We have evaluated the parameter values of polaronic clusters from the following expressions [2]:

\[
T_0 = \frac{8U}{k_B} \left( \frac{\beta - 1}{2} \right)^2
\]  (7)

\[
\frac{d}{a} = \frac{1}{4(\beta - 1)} \left( \frac{T_0}{T} \right)^{1/2}
\]  (8)

\[
\frac{s}{d} = \beta - 1
\]  (9)

where \( \beta \) is a parameter given by the ratio between the average dopant separation for a uniform dopant distribution in the sample and \( \delta \) the average distance between dopants; \( d/a \) is the optimal cluster diameter, \( s \) represents the width of the gap between clusters and \( a \) is the size of monomer.

The values of \( s/a \) and \( d/a \) are listed in Table 2 and they were obtained by using \( U = 2 \) eV as one-site Coulomb interaction. The dimension of the cluster is about \( 8.5a \) which corresponds to approximately two polaron lengths [26]. It is observed that the distance between clusters is about \( 0.6a \) (\( \approx 3 \) Å) suggesting a very compact structure. A value of 3.5 Å was also found by X-ray diffraction [27] and can be referred to interchain scattering between polypyrrole chains. The higher the values of conductivity, the longer the cluster length and the shorter the distance between them. The doping ion seems to have a great importance in this process as well as the preparation conditions as in the case of PPy film doped with TSO \(^\text{-}\) derived from NaTSO.

<table>
<thead>
<tr>
<th>Doping ion</th>
<th>( \sigma_{RT} ) [S/cm]</th>
<th>( c_e ) [M/l]</th>
<th>( T_0^* ) [K]</th>
<th>( s/a )</th>
<th>( d/a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF(_4^\text{-})</td>
<td>8.5</td>
<td>0.1</td>
<td>801</td>
<td>0.43</td>
<td>8.80</td>
</tr>
<tr>
<td>ClO(_4^\text{-})</td>
<td>14.54</td>
<td>0.1</td>
<td>623</td>
<td>0.38</td>
<td>8.85</td>
</tr>
<tr>
<td>TSO(^a)</td>
<td>31.16</td>
<td>0.1</td>
<td>1148</td>
<td>0.51</td>
<td>8.72</td>
</tr>
<tr>
<td>TSO(^b)</td>
<td>5.08</td>
<td>0.005</td>
<td>1587</td>
<td>0.60</td>
<td>8.63</td>
</tr>
</tbody>
</table>

\(^a\) the electrical conductivity at room temperature  
\(^b\) the doping ion is derived from HTSO electrolyte  
\(^b\) the doping ion is derived from NaTSO electrolyte  
\(^c\) values were evaluated in the range 150–220K
It is concluded from above that the interchain or intercluster hopping could be for these samples the main transport mechanism of the charge carriers. This process is very dependent on the type of the doping ion and the preparation conditions (Table 2) which establish the morphological characteristics of the samples.

However, it is worth mentioning that it is quite difficult to distinguish between some exponent values, especially when the same temperature dependencies of the electrical conductivity could express different microscopic processes for a relatively high temperature domain. Some authors [8] have used the different parameters such as the activation energy of the process or the ratio \( \rho_r = \rho(1.4 \text{ K})/\rho(300 \text{ K}) \) as an indicator of the conducting regime and the temperature dependence of conductivity. The values obtained for the density of states at the Fermi level of \( 10^{20–21} \text{ states eV}^{-1}\text{cm}^{-3} \) and the localisation length of 1.2–15 Å suggest that a variable-range hopping could be the dominant conduction process for our samples but the condition \( T_0/T > 10^4 \) was not verified. This breaking of rule has been associated to the high delocalization of the wave functions.

4. CONCLUSIONS

The temperature variation of the electrical conductivity of the polypyrrole films is strongly dependent on the nature of the doping ion and the preparation conditions. The role of the parameters used in preparation can not be distinguished separately but they determine mainly the conductivity values.

The interpretation of conductivity data for PPy films was made using both a fluctuation-induced tunnelling model as well as a hopping mechanism recently stated by Zuppiroli. The behaviour of different samples cannot be described using only one model and is strongly dependent on the nature of the doping ion. The obtained parameters which describe a hopping or a tunneling mechanism are found in good agreement with other measurements. However, because of the temperature limitations for some of the measured samples, additional data are required for a more precise characterization of these types of samples due especially to their complicated morphology. We suggest that a more complex model which considers both tunnelling and hopping mechanism would describe better the conduction process in conducting polymers.

REFERENCES