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# Study on the electrical conductivity and morphology of porous polypyrrole layers prepared electrochemically in the presence of pyridinium chlorochromate

S. KOŠINA, S. BALÚCH, J. ANNUS
*Department of Chemical Physics, Faculty of Chemical Technology, STU, Radlinského 9, CS-812 37, Bratislava, Slovak Republic*
M. OMASTOVÁ
*Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, CS-842 36, Bratislava, Slovak Republic*
J. KRIŠTÍN
*Central Laboratory of Electron Optics Methods, Faculty of Natural Sciences, Mlynská Dolina, CS-842 15, Bratislava, Slovak Republic*

The electrical conductivity and morphology of thick (up to 3 mm) porous polypyrrole (PPy) layers produced electrochemically from pyrrole in acetonitrile (ACN) solutions have been studied. The electrical conductivity of pressed porous layers ranges from 1 to 10 S cm$^{-1}$, which is about one order of magnitude less than that in films which were prepared under similar conditions but without PnClCr. Analysis of the temperature dependence of conductivity has confirmed the major role of hopping in relation to tunnelling in charge transport inside the PPy layers even at lower temperatures. Scanning electron microscopy (SEM) showed a globular structure, which is different from the usual cauliflower-like structure of PPy films prepared without any oxidizing agent. Globular particles of about 1–3 μm diameter have been found under a thin smooth crust on the electrode side of the sample. Globular particles form linked chain-like or larger round formations poorly filling the space. Closely packed fibrils of about 20 nm diameter and over 100 nm in length were found inside the aggregates.

## 1. Introduction

Electrical conductivity of PPy films strongly depends on preparation conditions (solvent, temperature, current density, etc) and on the kind of dopant (ion size and dopant concentration); and varies within a wide range, with top values up to 300 S cm$^{-1}$. It has been found that dopants not only strongly influence conductivity values [1], but also the mechanism of charge transport [2, 3]. Similarly, film morphology remarkably depends on preparation conditions as well as upon the kind of dopant, as mentioned above. Many authors have studied the influence of preparation conditions and the kind of dopant on the bulk morphology of PPy films and most of them confirmed the close relation between film conductivity and the morphology and chain structure of the film. Salmon *et al.* [4] compared the surface morphology of PPy films prepared under similar conditions, but using eight different counter ions. The surface morphology of films which contained $BF_4^-$ and $SF_6^-$, $NO_3^-$, $F^-$ was very alike. The most different surface was found in the film which was doped with $PF_6^-$. The increase of current density and the rate of polymerization has led to less compact and less smooth films [5]. Bi *et al.* [6] have described the morphology of PPy films, PPy–$BF_4$, PPy–$PF_6$ and PPy–$ClO_4$, prepared electrochemically from an acetonitrile solution, which consisted of particles of about 1 μm diameter, and which aggregated forming hollow bowls varying from 20 to 30 μm in diameter. Maddison and Unsworth [7] optimized the conditions of PPy film preparation from a water solution containing p-toluene sulphonate salt. From SEM studies they confirmed that smooth surface of the PPy films, without any artifacts, grew at an optimal current density of about 2.8 mA cm$^{-2}$ for 0.1 M anion concentration between 0–20 °C.

Previous work [8] found that the addition of pyridinium chlorochromate (PnClCr) into the electrolyte solution caused a considerable increase in the reaction rate and enabled the preparation of PPy layers of several millimeter thickness. The layers prepared in this way are porous; however, they are quite compact. Their surface morphology is very different from that of the thin films which were prepared under similar conditions but without any PnClCr. The conductivity

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of pressed porous layers is about one order of magnitude less than that of the films.

The surprisingly higher polymerization rate and considerably different appearance of PPy layers led to a more detailed study of the influence of PnClCr concentration on d.c. and a.c. conductivity of porous layers and its temperature dependence, and to a more detailed study of morphology and chain structure by SEM at very high magnification in order to find out any relation between morphology, microstructure and conductivity in porous layers.

## 2. Experimental procedure

### 2.1. Preparation of PPy layers

PPy layers were potentiostatically prepared in a three electrode cell. The polymerization solution typically contained 0.1 M pyrrole, 0.07 M dopant (either $Et_4NBF_4$ or $Me_4NBF_4$) and from 0.0 to 0.8 M PnClCr in acetonitrile. Two Pt plates of about $3 \times 5$ cm$^2$ were used as working and counter electrodes. An $Ag/Ag^+$ electrode was used as a reference electrode. The typical current density was about 3 mA cm$^{-2}$. Current and voltage were scanned by a PC. Moreover, bubbles of released gas were detected and counted by the same PC in the course of synthesis. Porous layers up to several millimeters in thickness arose on the electrode within typical reaction duration times of 30–60 min. Layers were washed with acetonitrile, dried in a vacuum drier and lastly peeled off the electrode. Further details about the electrochemical synthesis of porous PPy layers and their characterization are published in References 8 and 9.

### 2.2. Measurement of electrical conductivity

D.c. electrical conductivity was measured using a standard four probe method. A.c. conductivity was measured by an RLC bridge at several frequencies, ranging from 100 Hz to 20 kHz. In all cases the data on current, voltage and temperature were scanned by a PC. Sample layers consisted of strips about 5 mm wide and 25 mm long. To improve electrical contacts, samples were pressed at pressure, about $10^7$ N m$^{-2}$, and contacts were painted with a conducting silver paint before measurement. Measurements were performed either under vacuum or in an inert atmosphere (Ar, $N_2$), mostly within a temperature range of 95–320 K. Fitting procedures for the analysis of temperature dependent conductivity were performed by a PC using standard evaluation software.

### 2.3. Electron microscopy study

Observation of both sides of the layer were performed using a Jeol electron scanning microscope JXA 840 A and JEM 2000 FX. The surface of samples was coated with a thin gold layer (about 5–10 nm) in order to achieve a higher secondary electron yield, which facilitated better image resolution in the secondary electron mode at very high magnifications.

## 3. Results and discussion

### 3.1. Conductivity of PPy layers

The d.c. conductivity of PPy layers depended on the PnClCr concentration in the polymerized solution. Conductivity data for the layers prepared from the ACN solution, containing 0.1 M pyrrole and 0.07 M $Et_4NBF_4$ at various PnClCr concentration, are presented in Table I.

PPy films prepared under similar conditions, but without any PnClCr, showed conductivity values about one order of magnitude higher than the porous layers, i.e. up to 100 S cm$^{-1}$. Conductivity, measured in a direction perpendicular to the plane of the layer, was slightly lower, but still within the same order of magnitude. This might be due to pressing of samples, which caused the preferential deviation of chain-like aggregates to the plane direction.

A.c. conductivity was measured in a relatively narrow frequency range, from 100 Hz to 20 kHz. A.c. values were very close to the d.c. values.

To explain the lower conductivity values in the pressed layers in relation to the films which were prepared without any PnClCr dependencies of conductivity in a wider temperature range were investigated. Measured data were fitted in two separate temperature intervals. First in a range of 10 to 95 K following the Sheng model [10], which takes into consideration hopping and tunnelling mechanisms; and then in a range from 95 to 300 K following Mott's three-dimensional VRH (variable range hopping) model [11]. Evaluating the parameters, $K_0$ and $T_0$ in Mott's equation

$$\sigma = K_0 T^{-1/2} \exp[-(T_0/T)^{1/4}]$$

$$T_0 = 16\, a^3/[k_B N(E_F)]$$

$$K_0 = 0.39\, [N(E_F)/a\, k_B]^{1/2} f_0\, e^2$$

where $a^{-1}$ is the decay length of the localized state, $f_0$ is a hopping attempt frequency, $N(E_F)$ is the density of states at the Fermi energy level, $k_B$ is the Boltzmann constant, as well as the parameters $T_1$ and $T_2$ in the Sheng model, which takes into consideration both tunnelling and hopping mechanisms and is described by the following equation

$$\sigma = \sigma_1 \exp[T_2/(T + T_1)]$$

Here, $\sigma_1$ is a constant, $T_2$ is a parameter related to hopping and $T_1$ is a parameter related to tunnelling. Evaluated parameters are presented in the first row of Table II. The lower rows in Table II have been taken from Reference 2, where Sato *et al.* analysed the same parameters with respect to the size of various counter ions. They found that larger counter ions caused

TABLE I D.c. conductivity of PPy layers prepared from the ACN solution containing 0.1 M of pyrrole and 0.07 M of $Et_4NBF_4$ at various PnClCr concentrations

| PnClCr concentration (M) | 0.01 | 0.03 | 0.05 | 0.07 | 0.09 |
|---|---|---|---|---|---|
| Conductivity (S cm$^{-1}$) | 3.0 | 6.0 | 10.0 | 2.0 | 0.7 |

TABLE II Parameters derived from the Mott and Sheng equations for PPy layers and PPy films containing various ions [2]

| Ion | Size (nm) | $\sigma_{293}$ (S cm$^{-1}$) | $T_0$ ($10^4$ K) | $K_0$ ($10^4$ S cm K$^{-1/2}$) | $\sigma_1$ (S cm$^{-1}$) | $T_1$ (K) | $T_2$ (K) |
|---|---|---|---|---|---|---|---|
| PPy layers-$BF_4^-$ + remaining PnClCr |  | 12 | 15.2 | 2.9 | 13.2 | 21 | 99 |
| PPy film containing various ions |  |  |  |  |  |  |  |
| $BF_4^-$ | 5.3 | 188 | 5.2 | 11.8 | 457 | 177 | 403 |
| [a] t-BuBsO$^-$ | 10.7 | 68 | 11.9 | 10.0 | 179 | 108 | 401 |
| [b] β-NsO$^-$ | 11.1 | 66 | 12.8 | 10.4 | 166 | 98 | 351 |

[a] p-tert-butylbenzenesulfonate.
[b] β-naphthalenesulfonate.

shortening of the decay length, $a^{-1}$, which led to higher $T_0$ values. They also found that the larger the counter ion, the higher the $T_2:T_1$ ratio, which means that hopping rather than tunnelling dominated the charge transport.

Elemental and X-ray analyses, as well as electron spectroscopy for chemical analysis (ESCA) of porous layers, showed that layers contained, in addition to $BF_4^-$ ions, PnClCr; these were present in layers in the cation form of the original molecule, as well as in reduced $Cr^{3+}$ form. It is very difficult to express the size of such intercalated group in this relatively complex system. Admittedly, it is a very large group, which may lead to a considerably shortened decay length; it is also probable that the density states decrease at the Fermi level as well. This could explain the low value of $K_0$. The lower conductivity value of PPy layers with respect to films may be due to a higher chain disorder and, moreover, to the presence of C–O, C–OH and C = O bonds, which were found by ESCA analysis. The latter suggests overoxidation in the chain layers. The small value of $T_1$ in relation to $T_2$ indicates that hopping rather than tunnelling dominates the charge transport in the case of large ions, which is the case for these layers. From morphological studies, it follows that considerable transport among isolated chain-like aggregates is not possible. Inside globular particles, i.e. along and among fibrils, a three-dimensional variable range hopping mechanism dominates over tunnelling, even at lower temperatures. This can be understood to be the consequence of large intercalated groups, the presence of which represents a high barrier to tunnelling.

## 3.2. Morphology of PPy layers

Apart from the fact that porous PPy layers are considerably thicker than films, the different appearance of the former is visible at first sight. Porous layers are spongy and elastic. The electrode side is coated with a thin, smooth crust $\leqslant 1\ \mu m$ thickness. The electrolyte side is porous. The crust, which was partially peeled off a sample, can be seen in Fig. 1a. It covers globular particles of about 1 μm diameter, which aggregate into bigger formations, as is seen in Fig. 1b. The quality of the crust surface depends on the surface of the Pt plate electrode, and partly replicates it. The origin of the crust may be explained if the initial condition of the reaction is appreciated. The Pt plate is relatively smooth and, therefore, the reaction may have progressed homogeneously on the whole electrode surface. Moreover, the initial current, as seen in Fig. 2, was quite small. However, it then began to increase rapidly until it reached a more or less stable value. A very similar time dependence, to that shown in Fig. 2, was observed for the volume of released gas during the course of the reaction. All the above mentioned facts suggest that the reaction rate in the very beginning was small, which may lead to the formation of a smooth coat on the electrode side of porous layers. Nevertheless, surprising, no cauliflower-like structures, which are typical of PPy films and which were observed in films prepared under the same conditions

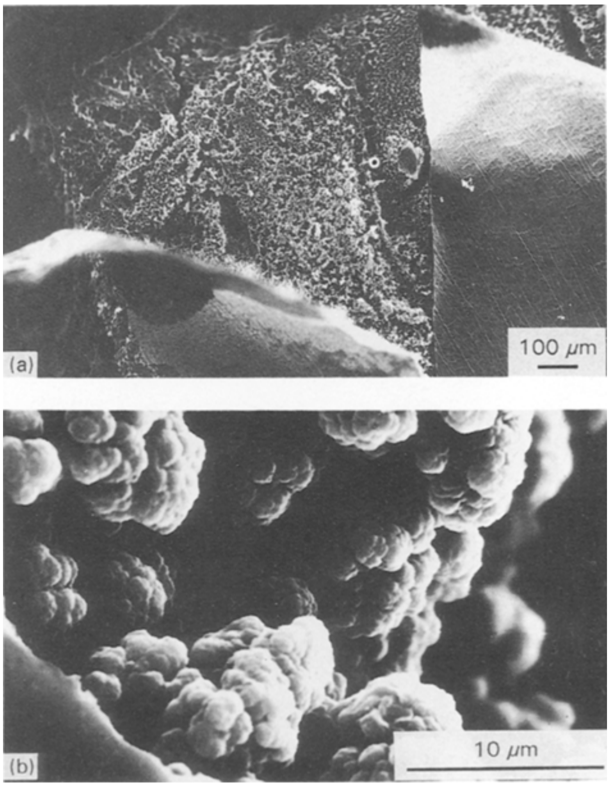

*Figure 1* SEM pictures of the electrode side of the PPy layer: (a) a partly peeled crust, and (b) globular particles partly covered by the crust.

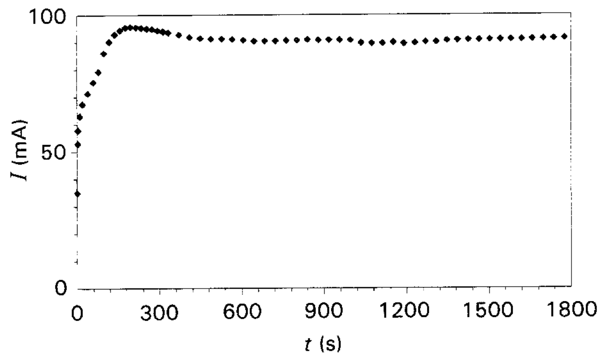

*Figure 2* The time dependence of the current during the course of the electrochemical synthesis of PPy layers.

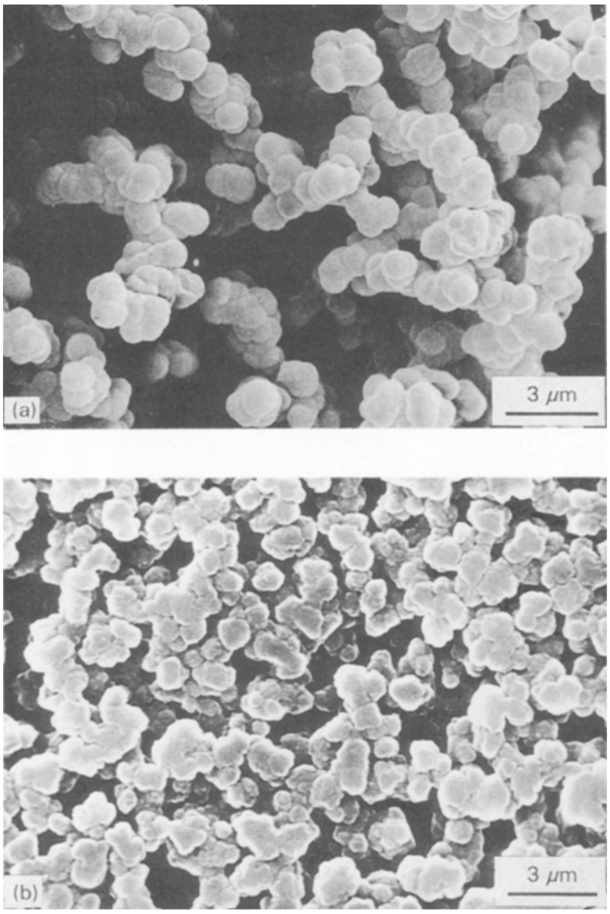

*Figure 3* SEM pictures of the electrolyte side of a PPy layer: (a) globular particles, and (b) pressed sample.

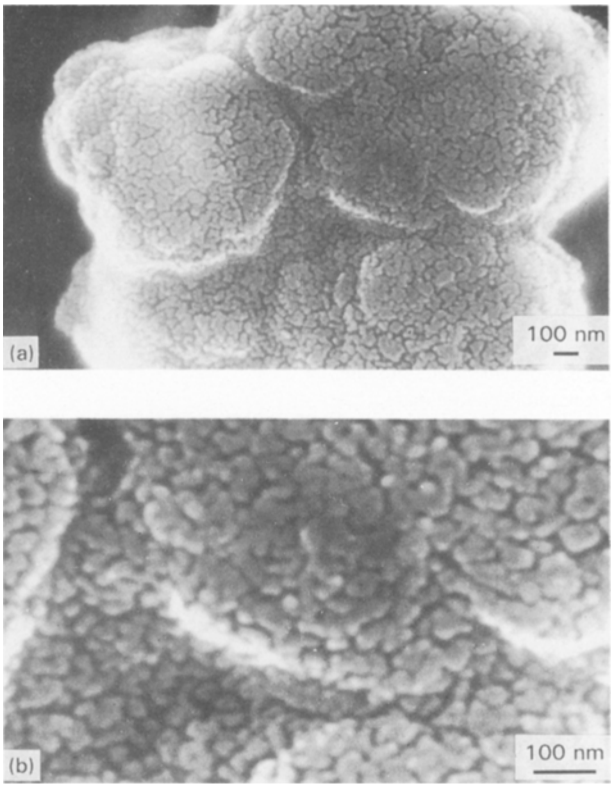

*Figure 4* SEM pictures of the structure inside globular particles in a porous layer at high magnifications: (a) × 40 000, and (b) × 100 000.

(dopant, concentrations, current density, etc) but without any PnClCr, were found.

Further microscope investigation showed that instead of the usual cauliflower-like morphology, globular particles forming irregular chain-like aggregates on the electrolyte side were typical for PPy porous layers. Similar chain-like aggregates were also found more deeply under the crust, close to the electrode side of samples. The described aggregates can be seen in Fig. 3a. Fig. 3b shows aggregates in a pressed layer, which were used for conductivity measurements. As seen in Fig. 3, aggregates do not fill the space densely. This fact might be explained by a considerably high reaction rate which (due to the presence of PnClCr in the solution) was more than 10 times higher than in the case of films prepared under similar conditions but without any PnClCr. It seems that there is a slight preferential growth direction of chain-like aggregates perpendicular to the plate electrode. Considering theoretical calculations, some authors suppose [12] a preferential growth direction in PPy films; however, if there is some preferential direction in layer growth, this may have been caused by growth of matter along moving bubbles of released gas. Densely packed fibrils of about 20 nm diameter × 150 nm or more in length can be seen in Fig. 4a, b. The dense, almost parallel growth of fibrils is probably due to template polymerization of pyrrole on polypyrrole macromolecules.

## 4. Conclusions

1. The d.c. conductivity in PPy porous layers is about one order of magnitude lower than that of the films prepared without any PnClCr. Conductivity depends on the PnClCr concentration in the solution. The large size of intercalated groups, i.e. counter ions and the remaining PnClCr, caused the hopping charge transport mechanism to dominate over tunnelling, even at lower temperatures.

2. The porous polypyrrole layers prepared electrochemically from acetonitrile solution of pyrrole in the presence of dopants, tetraethylammonium or tetramethylammonium tetrafluoroborate ($Et_4NBF_4$, $Me_4NBF_4$) and pyridinium chlorochromate (PnClCr), show considerably different morphology with respect

to the polypyrrole films prepared under similar conditions but without any PnClCr. While films mostly show dense cauliflower-like morphological structures, porous layers show globular structures, with the diameter of globular particles being about 1 μm. The particles poorly fill the space inside the layers. These particles aggregate into chain-like or larger globular formations. Particles contain fibrils of about 20 nm diameter and 150 nm length, which densely fill the space.

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