CHARGE TRANSPORT IN PRUSSIAN BLUE FILMS DEPOSITED ON ITO ELECTRODES

J. J. GARCIA-JARENO, J. NAVARRO-LABOULAS and F. VICENTE*

Dept de Quimica-Fisica, Universidad de Valencia C/Dr Moliner 50, 46100 Burjassot, Valencia, Spain

(Received 5 June 1995; in revised form 11 September 1995)

Abstract—Charge transport processes that can occur in Prussian Blue films deposited on ITO (indium-tin oxide) electrodes in contact with aqueous solutions have been studied. The concentration in the solution of some ions such as the proton or the potassium influence the films conductivity as well as the degree of hydration of the film. This points to the fact that Prussian Blue films act as ionic conductors when they are immersed in aqueous solutions. Furthermore, the apparent diffusion coefficient calculated from impedance spectra of PB films increases with the temperature which confirms the idea of an ionic conductor. The impedance spectra for the Everitt’s Salt films, however, differ from the PB films and is much less sensitive to temperature.

Key words: charge transport, Prussian Blue films, degree of hydration, potassium ion, hydrogen ion, electronic and ionic conductor.

INTRODUCTION

Prussian Blue (PB, ferric ferrocyanide) has been described in two different formulas: the insoluble PB Fe\textsuperscript{III}([Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsubscript{3}), and the soluble PB KFe\textsuperscript{III}([Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsubscript{3}). Films of PB have been obtained by electrodeposition on electrodes[2-10]. Films of PB present electrochromic properties and have been used to build electrochromic devices by the coating of transparent electrodes[6,12].

By reduction in a KCl solution the PB films give a colorless compound called Everitt’s Salt (ES) that corresponds to the formula K\textsubscript{2}Fe\textsuperscript{III}([Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsubscript{3}) and K\textsubscript{2}Fe\textsuperscript{III}([Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsubscript{3}) for the insoluble and soluble forms respectively.

As initially formed, the films are in the insoluble form[6], but during cyclic voltammetric experiments in a KCl solution around the PB $\rightarrow$ ES system, the film loses part of the Fe\textsuperscript{III} (high spin iron) that is substituted by potassium ions and the film is converted into the soluble forms[10, 13].

Investigations of the crystal structure of the PB films show that there are between 14 and 16 water molecules per unit cell[14, 15]. In PB films, two kinds of water molecules have been described. About 6 molecules of water are part of the coordination shell of high spin iron and the remaining occupy interstitial positions and represent uncoordinated water[14, 15]. Ganguli et al.[16, 17] have studied the de-hydration process in Prussian Blue by means of thermal gravimetric analysis and they identified three different stages of hydration and the anhydrous form. The Prussian Blue decomposition takes place at temperatures above 150°C. The degree of hydration of the films depends on the temperature and ambient humidity[14-17]. It has been observed that by heating at 150°C about 90% of the water is removed and re-exposure of the solid to ambient conditions reversibly restores the original degree of hydration[14-15]. The semiconductivity behavior of PB in solid state and the influence of the degree of hydration and temperature on the films have been studied[15, 18, 19]. However, the film conductivity behavior in contact with an aqueous solution could be totally different due to the possibility of ion exchange between film and the outer solution medium. Feldman et al.[20, 21] have studied the role of some counterions and water during the electrochemical processes that occur in Prussian Blue films. Since the proton and water play an important role in the electrochemical reduction and re-oxidation of PB films[20], it could be expected that the degree of hydration of the films strongly influences the electrochemical behavior of those films and on the films conductivity.

Charge transport through PB films can be described as an electron hopping between neighboring iron sites accompanied by the motion of several counterions within the film to maintain the electroneutrality[20, 21] and the rate of charge transport can be expressed by means of an apparent diffusion coefficient of electrons.

In the last few years, Electrochemical Impedance Spectroscopy (EIS) has become one of the most powerful techniques in the study of charge transport processes that take place through conducting films deposited on electrodes[22-35]. The impedance spectrum of these films could be interpreted in several ways. It could be considered that the films behavior is similar to a porous solid[31-32] and to interpret the results obtained in terms of resistances to transport of charged species through the film.

* Author to whom correspondence should addressed.
pores. On the other hand, an interesting interpretation to this kind of impedance spectra is given by Albery et al.[23-25] who consider that charge motion through the film takes place by means of a redox polymer mechanism.

However, both models give identical equivalent circuits and it is not possible to choose between these two interpretations. In both cases the film associated impedance could be represented by a finite transmission line element. The values obtained for the parameters of the transmission line give information about the rate of the charge transport processes through the film[22-29, 33] that can be evaluated by an apparent diffusion coefficient[34-37].

The aim of this paper is the study of the dependence of parameters obtained from experimental impedance spectroscopy on the solution conditions such as the pH, the degree of hydration of the films, the temperature or the potassium concentration in the solution in order to help to explain the influence of counterions on the charge transport processes that take place through PB films.

**EXPERIMENTAL**

FeCl₃ (chemically pure), K₃Fe(CN)₆, KCl and HCl (p.a.) (A.R. Panreac) were used for the synthesis of PB films. Water used to prepare solutions was distilled and deionized (Mili Q-plus-Milipore).

PB films were galvanostatically deposited on ITO (indium-tin oxide) electrodes (Ageo, A = 1 cm², Glasstron)[2, 4, 6]. ITO electrodes were immersed into a solution 0.02 M K₃(Fe(CN))₆, 0.02 M FeCl₃ and 0.01 M HCl and a controlled cathodic current of \(i_c = 40 \mu\text{A/cm}^2\) was applied for 150 s.

Electrochemical experiments were carried out by means of a typical three electrodes cell were the PB films deposited on ITO glass were used as the working electrode, platinum plate [4 cm²] was the counter electrode and Ag/AgCl (KCl 1 M) was the reference electrode. Potentiostat-galvanostat PAR 273 and the frequency analyzer were used with the lock-in-amplifier PAR 5210.

The impedance was measured in the range from 0.05 Hz to \(10^4\) Hz and 5 mV of signal amplitude. The stabilization potential was set to 0.6 V for the impedance spectra of PB films while for the ES films the potential was set to \(-0.2\) V against the Ag/AgCl (KCl 1 M) reference electrode.

The pH influence has been studied keeping the potassium concentration in the solution (0.75 M) constant and using Britton-Robinson buffer solutions[38]. 25 ml of a 0.4 M solution in H₂BO₃, H₃PO₄, and HAC were added to 75 ml of a mixture of KOH (1 M) and KCl (1 M). For these solutions, the concentration of potassium ion was always 0.75 M while buffer solutions of different pH were obtained by modifying the proportion between KOH and KCl.

EIS experimental data have been analyzed by means of a complex nonlinear least squares fit procedure based on Marquardt algorithm for function optimization[39]. Although simulated curves reproduce the experimental impedance spectra very well[33], these curves will not be shown in this work so as not to complicate figures in excess.

**RESULTS AND DISCUSSION**

The ac response of PB films deposited on ITO electrodes has been studied in a previous paper[33]. The Warburg type impedance observed is typically obtained for polymer films deposited on electrodes[22-30] and for porous electrodes[31-32]. This ac response could be interpreted as a migration process as well as a diffusion process. In both cases the mathematical forms of the film associated impedance can be modeled as a finite transmission line element in a Randls's modified equivalent circuit[22-30]. In the case of PB films, it has been observed that it is better represented by an equivalent circuit containing two transmission lines associated in parallel[33] (Fig. 1), each one of which corresponds to a different charge transport process[29, 33].

The mathematical form of the film associated impedance represented by a transmission line is given by:

\[
Z_F = Z_0 \cosh \left( \frac{j\omega D}{D} \right) \cosh \left( \frac{j\omega D}{D} \right) \cosh \left( \frac{j\omega D}{D} \right)
\]

or its mathematically equivalent expression when it is considered the charge transport process as a migration process:

\[
Z_F = R_F \frac{\left( j\omega R_F C_F \right)^{1/2} \left( j\omega R_F C_F \right)^{1/2}}{\left( j\omega R_F C_F \right)^{1/2} \left( j\omega R_F C_F \right)^{1/2}}
\]

In these expressions, \(j = (-1)^{1/2}\), \(\omega\) the angular frequency in rad/s, \(C_F\) and \(R_F\) the total distributed capacitance and the total distributed resistance of the transmission line, while \(D\) represents the apparent diffusion coefficient and \(l\) a characteristic length of diffusion.

The parameter \(l^2/D\) could be related to the transmission line resistance and capacitance by means of[26]:

\[
\text{Fig. 1. Equivalent circuit used to reproduce impedance spectra of PB films deposited on ITO electrodes. } R_u \text{ represents the uncompensated resistance, } C_{d1} \text{ the double layer capacitance at the ITO/PB interface and } R_{ct} \text{ the charge transport resistance at the ITO/PB interface. } Z_{F1} \text{ and } Z_{F2} \text{ are the film associated impedances.}
\]
Before the EIS experiments, the freshly prepared PB films were cycled for 15 times around the PB-ES system until a stable voltammogram was obtained[10, 13]. Films were dehydrated by heating to 120°C for 7 days[14, 16]. In such conditions it is expected that films lose most of the inner water, but it is not expected that the decomposition of the films could occur[16]. It has been observed that films do not immediately recover their electrochemical properties after immersion in an aqueous solution. Nevertheless, it has been observed that the film gradually recovers its electrochemical properties during a cyclic voltammetric experiment. This behavior could be explained considering that the film re-hydration does not take place immediately and if it is considered that the film re-oxidation from ES to PB is accompanied by water incorporation within the film[20, 21]. Thus, the study of how the ac response depends on the number of cycles could show how the impedance spectrum varies with the degree of hydration of the film. Figure 2 shows that the semi-infinite diffusion region[26], which corresponds to the intermediate frequencies in the impedance spectrum, becomes narrower as the film is cycled which implies a decrease in the film associated resistance and the consequent increase in the apparent diffusion coefficient. Table 1 shows the results obtained for the fitting of experimental data to the equivalent circuit of Fig. 1. The apparent diffusion coefficient is calculated from equation (4), assuming the characteristic length of diffusion is the thickness. This film thickness is estimated from the electrogeneration electrical charge as[40]:

$$l = \frac{Q}{4FA}$$

where $Q$ represents the electrical charge, $l_0$ the unit cell length (~10μA)[14], $N_A$ the Avogadro's number, $F$ the Faraday's constant and $A$ the electrode area.

Both the dependence on the number of cycles of the resistance of the film as well as of the apparent diffusion coefficients show that the film recovers its electrochemical properties while the water incorporation is taking place and the conductivity of the film also increases. According to these results, it can be concluded that in effect, the electrochemical behavior and charge transport through the PB film are strongly influenced by the degree of hydration of the film.

The second part of this work corresponds to the study of the dependence of impedance spectra on the concentration in the solution of some ions that can act as counterions during electrochemical processes such as the hydrogen or the potassium ion.

In Fig. 3 it can be observed that as the pH increases, the semi-infinite diffusion region in the impedance spectrum becomes wider, corresponding furthermore with an increase in the resistance associated with the film. The obtained values of parameters from the fit of impedance spectra of the equivalent circuit of Fig. 1 are collected in Table 2. The apparent diffusion coefficient decreases with the pH, while the resistance of the film increases. These results can be explained taking into account that charge transport through PB films takes place by means of electron hopping between neighboring Fe

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$R_1$</th>
<th>$C_{dl}$</th>
<th>$R_{cf}$</th>
<th>$R_{ct}$</th>
<th>$C_{F1}$</th>
<th>$D_1$</th>
<th>$R_{F2}$</th>
<th>$C_{F2}$</th>
<th>$D_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>52.6</td>
<td>0.5</td>
<td>8600</td>
<td>113000</td>
<td>0.03</td>
<td>3.0E-11</td>
<td>168000</td>
<td>0.07</td>
<td>1.0E-11</td>
</tr>
<tr>
<td>10</td>
<td>49.1</td>
<td>0.6</td>
<td>5400</td>
<td>78400</td>
<td>0.04</td>
<td>3.2E-11</td>
<td>140000</td>
<td>0.08</td>
<td>1.0E-11</td>
</tr>
<tr>
<td>20</td>
<td>42.7</td>
<td>0.8</td>
<td>1900</td>
<td>45600</td>
<td>0.06</td>
<td>3.7E-11</td>
<td>125000</td>
<td>0.08</td>
<td>1.0E-11</td>
</tr>
<tr>
<td>30</td>
<td>39.4</td>
<td>1.0</td>
<td>830</td>
<td>34200</td>
<td>0.07</td>
<td>4.2E-11</td>
<td>117000</td>
<td>0.08</td>
<td>1.1E-11</td>
</tr>
<tr>
<td>50</td>
<td>34.5</td>
<td>1.5</td>
<td>280</td>
<td>20600</td>
<td>0.08</td>
<td>6.1E-11</td>
<td>106000</td>
<td>0.08</td>
<td>1.2E-11</td>
</tr>
</tbody>
</table>

Cycle represents the number of voltammetric cycles after the dehydration process, $C_{dl}$ is the double layer capacitance and $R_{ct}$ the charge transport resistance at the PB/ITO interface, $R_{F1}$ and $R_{F2}$ are the total distributed resistances of the two transmission lines and $C_{F1}$ and $C_{F2}$ the total distributed capacitances of the two transmission lines. $R_1$ represents the uncompensated resistance. $D_1$ and $D_2$ are the apparent diffusion coefficients of electrons calculated from equation (4), considering that the film thickness is given by equation (5) ($10^{-7}$ m). The potassium concentration was 1 M and the solution pH 3.03.
sites that needs the coincident transport of some counterions to maintain the film electroneutrality[20, 21]. A decrease in the hydrogen ion concentration in the solution will cause a decrease in the concentration of the ion in the inner solution. As the hydrogen ion can also act as a counterion, a decrease in its concentration within the film will cause an increase in the resistance of charge transport through the film or its equivalent decrease in the apparent diffusion coefficient of electrons.

In contrast, the study of the dependence on the potassium ion concentration in the solution shows that the resistance of the film decreases and the diffusion coefficient increases as the concentration of KCl is lowered (Fig. 4 and Table 3). In these experiences the pH of the solution was kept constant (≈2.6) to prevent the changes in the concentration of hydrogen ions from influencing the results obtained.

This behavior seems to be in contradiction with the fact that when the concentration of a counterion in the inner solution is reduced, the films associated resistance should increase. This can be explained taking into account that the hydrogen ion as well as the potassium ion can act as counterions and that a decrease of the inner concentration of the potassium ion would be accompanied by an increase in the inner hydrogen ion concentration to maintain the electroneutrality of the film. As the mobility of the hydrogen ions is much greater than that of the potassium ions, the substitution of these ions by protons will cause an increase in the film conductivity, or which is the same, a decrease of the resistance of the

Table 2. The pH dependence on the impedance spectra of Prussian Blue films. Parameters in this table are calculated from the fit of experimental impedance spectra of Fig. 3 to the equivalent circuit of Fig. 1

<table>
<thead>
<tr>
<th>pH</th>
<th>$R_\alpha$</th>
<th>$C_{dl}$</th>
<th>$R_\eta$</th>
<th>$R_{\alpha\beta}$</th>
<th>$C_{\alpha\beta}$</th>
<th>$D_{\alpha}$</th>
<th>$R_{\eta\beta}$</th>
<th>$C_{\eta\beta}$</th>
<th>$D_{\eta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.52</td>
<td>35.6</td>
<td>10</td>
<td>1050</td>
<td>4100</td>
<td>0.16</td>
<td>1.5E-10</td>
<td>55600</td>
<td>0.09</td>
<td>1.9E-11</td>
</tr>
<tr>
<td>1.93</td>
<td>55.5</td>
<td>10</td>
<td>1780</td>
<td>5680</td>
<td>0.16</td>
<td>1.1E-10</td>
<td>68000</td>
<td>0.09</td>
<td>1.7E-11</td>
</tr>
<tr>
<td>2.88</td>
<td>34.2</td>
<td>9.6</td>
<td>3190</td>
<td>7340</td>
<td>0.14</td>
<td>9.9E-11</td>
<td>87000</td>
<td>0.08</td>
<td>1.4E-11</td>
</tr>
<tr>
<td>4.15</td>
<td>34.9</td>
<td>9.1</td>
<td>4470</td>
<td>9730</td>
<td>0.14</td>
<td>7.2E-11</td>
<td>114000</td>
<td>0.08</td>
<td>1.2E-11</td>
</tr>
<tr>
<td>4.69</td>
<td>35.5</td>
<td>8.9</td>
<td>4700</td>
<td>11450</td>
<td>0.15</td>
<td>6.0E-11</td>
<td>136000</td>
<td>0.07</td>
<td>1.1E-11</td>
</tr>
</tbody>
</table>

pH represents the pH in the solution of KCl, $C_{dl}$ is the double layer capacitance and $R_\alpha$ the charge transport resistance at the PB/ITO interface, $R_{\alpha\beta}$ and $R_{\eta\beta}$ are the total distributed resistances of the two transmission lines and $C_{\alpha\beta}$ and $C_{\eta\beta}$ the total distributed capacitances of the two transmission lines. $R_\eta$ represents the uncompensated resistance, $D_\alpha$ and $D_\eta$ are the apparent diffusion coefficients of electrons calculated from equation (4), considering that the film thickness is given by equation (5) ($10^{-7}$ m). After immersion into the new solution and before the impedance measurement, the film was cycled 5 times in order to establish the equilibrium between the inner and outer hydrogen ion concentration. The potassium concentration was set to 0.75 M.

Table 3. The KCl concentration dependence on the impedance spectra of Prussian Blue films deposited on ITO electrodes. Parameters in this table are calculated from the fit of experimental impedance spectra of Fig. 4 to the equivalent circuit of Fig. 1

<table>
<thead>
<tr>
<th>[KCl]</th>
<th>$R_\alpha$</th>
<th>$C_{dl}$</th>
<th>$R_\eta$</th>
<th>$R_{\alpha\beta}$</th>
<th>$C_{\alpha\beta}$</th>
<th>$D_{\alpha}$</th>
<th>$R_{\eta\beta}$</th>
<th>$C_{\eta\beta}$</th>
<th>$D_{\eta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>36.2</td>
<td>9.6</td>
<td>2350</td>
<td>5120</td>
<td>0.18</td>
<td>1.1E-10</td>
<td>68400</td>
<td>0.10</td>
<td>1.5E-11</td>
</tr>
<tr>
<td>0.8</td>
<td>36.2</td>
<td>9.9</td>
<td>2630</td>
<td>5380</td>
<td>0.19</td>
<td>1.0E-10</td>
<td>78000</td>
<td>0.10</td>
<td>1.3E-11</td>
</tr>
<tr>
<td>0.48</td>
<td>38.6</td>
<td>9.8</td>
<td>2440</td>
<td>4200</td>
<td>0.21</td>
<td>1.1E-10</td>
<td>62900</td>
<td>0.11</td>
<td>1.5E-11</td>
</tr>
<tr>
<td>0.29</td>
<td>41.4</td>
<td>9.9</td>
<td>2160</td>
<td>3350</td>
<td>0.24</td>
<td>1.2E-10</td>
<td>55500</td>
<td>0.16</td>
<td>1.2E-11</td>
</tr>
<tr>
<td>0.17</td>
<td>47.1</td>
<td>9.7</td>
<td>2370</td>
<td>2850</td>
<td>0.26</td>
<td>1.4E-10</td>
<td>47100</td>
<td>0.17</td>
<td>1.3E-11</td>
</tr>
</tbody>
</table>

[KCl] represents the concentration in the solution of KCl, $C_{dl}$ is the double layer capacitance and $R_\alpha$ the charge transport resistance at the PB/ITO interface, $R_{\alpha\beta}$ and $R_{\eta\beta}$ are the total distributed capacitances of the two transmission lines and $C_{\alpha\beta}$ and $C_{\eta\beta}$ the total distributed resistances of the two transmission lines. $R_\eta$ represents the uncompensated resistance, $D_\alpha$ and $D_\eta$ are the apparent diffusion coefficients of electrons calculated from equation (4), considering that the film thickness is given by equation (5) ($10^{-7}$ m). After immersion into the new solution and before the impedance measurement, the film was cycled for 5 times in order to establish the equilibrium between the inner and outer potassium concentration.
Charge transport in PB films deposited on ITO electrodes

It is known that a freshly prepared film of PB does not contain potassium ions [6, 10, 13]. This ion is incorporated into the film when the film is cycled in a solution that contains this ion [10, 13] and then the film structure is changing from the insoluble to the soluble form. Therefore, in PB films in the insoluble form it is expected that the only ion which could act as a counterion would be the hydrogen ion. The Nyquist plot of Fig. 5 shows the impedance spectra for a PB film initially in the insoluble form and its variation during the substitution of hydrogen ions by potassium ions that simultaneously changes the structure of the film from the insoluble form to the soluble form by losing part of high spin iron. Table 4 shows the obtained results from the fit of these impedance spectra to the equivalent circuit of Fig. 1. It is clearly concluded that the resistance of the film increases in an important way while the film is converted into the soluble form. Although this variation could be explained by the partial substitution of hydrogen ions by potassium ions that present smaller mobility, in this case, it would also be necessary to consider another factor that could cause an influence, namely that the film is changing its structure by losing part of the high spin iron, thus a decrease in the number of electroactive sites within the film takes place. Perhaps in this case, the replacement of hydrogen ions by potassium ions could be the most important factor that causes that decrease in transmission line and an increase in the apparent diffusion coefficient of electrons.

On the other hand, it is also interesting to note that, as shown in Table 3, the uncompensated resistance does not vary significantly with the outer solution concentration in potassium ions between the limits 0.5 and 1 M, staying about 36 Ω, while for the most diluted solutions the value of this resistance increases as the potassium concentration decreases. This shows that the value of the uncompensated resistance obtained for the most concentrated solutions should be attributed to the uncompensated resistances due to the electrodes, since the resistance of the solution begins to rise to a significant value only for concentrations smaller than 0.5 M. Furthermore, this value of the uncompensated resistance about 36 Ω could be firstly attributed to the ITO electrode resistance (30Ω/cm).

Table 4. The Prussian Blue film’s form dependence on the impedance spectra. Parameters in this table are calculated from the fit of experimental impedance spectra of Fig. 5 to the equivalent circuit of Fig. 1. The Prussian Blue film used was freshly prepared.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$R_n$ Ω</th>
<th>$C_{dl}$ μF</th>
<th>$R_{C1}$ Ω</th>
<th>$R_{F1}$ Ω</th>
<th>$C_{F1}$ mF</th>
<th>$D_1$ cm² s⁻¹</th>
<th>$R_{F2}$ Ω</th>
<th>$C_{F2}$ mF</th>
<th>$D_2$ cm² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.0</td>
<td>7.7</td>
<td>300</td>
<td>2340</td>
<td>0.17</td>
<td>2.5E-10</td>
<td>42600</td>
<td>0.11</td>
<td>2.1E-11</td>
</tr>
<tr>
<td>1</td>
<td>33.0</td>
<td>7.7</td>
<td>300</td>
<td>2740</td>
<td>0.17</td>
<td>2.1E-10</td>
<td>58960</td>
<td>0.10</td>
<td>1.7E-11</td>
</tr>
<tr>
<td>2</td>
<td>33.0</td>
<td>7.7</td>
<td>300</td>
<td>2850</td>
<td>0.17</td>
<td>2.1E-10</td>
<td>64800</td>
<td>0.09</td>
<td>1.7E-11</td>
</tr>
<tr>
<td>5</td>
<td>33.0</td>
<td>7.7</td>
<td>300</td>
<td>3170</td>
<td>0.17</td>
<td>1.9E-10</td>
<td>67200</td>
<td>0.09</td>
<td>1.7E-11</td>
</tr>
<tr>
<td>10</td>
<td>33.0</td>
<td>7.7</td>
<td>300</td>
<td>3550</td>
<td>0.17</td>
<td>1.7E-10</td>
<td>77800</td>
<td>0.08</td>
<td>1.6E-11</td>
</tr>
<tr>
<td>28</td>
<td>33.0</td>
<td>7.7</td>
<td>300</td>
<td>5630</td>
<td>0.17</td>
<td>1.0E-10</td>
<td>130000</td>
<td>0.07</td>
<td>1.1E-11</td>
</tr>
</tbody>
</table>

Cycle $N$ represents the number of voltammetric cycles, $C_{dl}$ is the double layer capacitance and $R_n$ the charge transport resistance at the PB/ITO interface, $R_{F1}$ and $R_{F2}$ are the total distributed resistances of the two transmission lines and $C_{F1}$ and $C_{F2}$ the total distributed capacitances of the two transmission lines. $R_n$ represents the uncompensated resistance. $D_1$ and $D_2$ are the apparent diffusion coefficients of electrons calculated from equation (4), considering that the film thickness is given by equation (5) (10⁻⁷ m).
Table 5. The temperature dependence on the impedance spectra of Prussian Blue films. Parameters in this table are calculated from the fit of experimental impedance spectra of Fig. 6 to the equivalent circuit of Fig. 1

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>R1 (Ω)</th>
<th>C1 (µF)</th>
<th>R2 (Ω)</th>
<th>C2 (µF)</th>
<th>D1 (mS cm⁻²)</th>
<th>R3 (Ω)</th>
<th>C3 (µF)</th>
<th>D3 (mS cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>33.6</td>
<td>4.7</td>
<td>125</td>
<td>3400</td>
<td>0.23</td>
<td>1.5E-10</td>
<td>85 390</td>
<td>0.07</td>
</tr>
<tr>
<td>25</td>
<td>32.0</td>
<td>5.4</td>
<td>52</td>
<td>1530</td>
<td>0.25</td>
<td>3.1E-10</td>
<td>37 267</td>
<td>0.06</td>
</tr>
<tr>
<td>30</td>
<td>32.2</td>
<td>6.0</td>
<td>36</td>
<td>1010</td>
<td>0.26</td>
<td>4.6E-10</td>
<td>89 290</td>
<td>0.08</td>
</tr>
<tr>
<td>35</td>
<td>32.1</td>
<td>6.0</td>
<td>29</td>
<td>760</td>
<td>0.26</td>
<td>6.1E-10</td>
<td>79 000</td>
<td>0.09</td>
</tr>
<tr>
<td>40</td>
<td>32.3</td>
<td>6.0</td>
<td>25</td>
<td>660</td>
<td>0.25</td>
<td>7.3E-10</td>
<td>73 000</td>
<td>0.09</td>
</tr>
</tbody>
</table>

T is the temperature at which the experiment is carried out in °C, C1 is the double layer capacitance and R1 the charge transport resistance at the PB/ITO interface. R2 and R3 are the total distributed resistances of the two transmission lines and C2 and C3 the total distributed capacitances of the two transmission lines. R1 represents the uncompensated resistance. D1 and D3 are the apparent diffusion coefficients of electrons calculated from equation (4) considering that the film thickness is given by equation (5) (10⁻⁷ m).

in the film conductivity since the film electrical conductivity seems to be controlled by an ionic transport mechanism.

All the completed studies discussed so far seem to point to the fact that the PB films behave as ionic conductors, strongly influenced by the ion concentrations in the solution medium or by the degree of hydration of the film. However, a definitive test to confirm this idea would be the study of the dependence on the temperature of the impedance spectra. Although the ionic conductors increase in conductivity when the temperature is increased, the variation of conductivity observed in electronic conductors is totally different, increasing as the temperature decreases. However, it should be taken into account that this dependence is small in the range of temperatures studied (between 16 and 40°C). Impedance spectra obtained for the same film of PB at different temperatures are presented in Fig. 6. In effect, it is clearly observed that an increase in the temperature makes the resistance of the film decrease, or in other words, it makes the apparent diffusion coefficient increase (Table 5). Figure 7 represents the dependence on the temperature of this diffusion coefficient, which increases linearly with the temperature.

This linear increase corresponds to the previously expected dependence of the diffusion coefficient for ionic conductivity in solid electrolytes which corresponds to a modified Nernst–Einstein relation[41]:

\[ D_{\text{elec}} = \sigma_i kT/n_i e_i^2 \]  

where \( \sigma_i \) is defined as the contribution of species \( i \) to the ionic conductivity, \( k \) is the Boltzman constant, \( T \) the temperature, \( n_i \) the number of particles of species \( i \) per cm³ and \( e_i \) the electric charge of the ion.

These results confirm that Prussian Blue films behave as ionic conductors, at least in the range of temperatures studied. On the contrary, the study of the dependence on the temperature of the impedance spectra for the same film in the Everitt's Salt form (potential of stabilization of -0.2V against the Ag/AgCl (KCl 1 M)) clearly shows a less markedly dependence on the temperature (Fig. 8). This behavior of the film of Everitt's Salt is different from that obtained for the same film in the Prussian Blue form and suggests the control of the charge transport mechanism for this material may change depending on the applied potential[33] since the number of electroactive sites as well as the water, potassium

![Fig. 6](image_url)  
Fig. 6. The temperature dependence on the impedance spectra of PB films. \( E = 0.6 \text{V against Ag/AgCl (KCl 1 M)} \). (○) 18°C; (●) 25°C; (□) 30°C; (■) 35°C; (◇) 40°C.

![Fig. 7](image_url)  
Fig. 7. Plot of the apparent diffusion coefficient calculated from impedance spectra of Fig. 6 against the temperature.
and hydrogen ion content within the film also varies depending on the applied potential.

Acknowledgements—This work has been partially supported by CICYT (Project PETRI Mat.-66/94). J. J. Garcia-Jareño acknowledges a Fellowship from the Generalitat Valenciana, Program FPI.

REFERENCES