Current rectification by H₃OUO₂PO₄·3H₂O (HUP) thin films in electrolyte media

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Factors influencing the electrical current rectification by HUP thin films in the generating electrolyte media were studied. Variations of electrolyte concentration, thickness of electrolyte layers, electrolyte nature, and chemical modification of thin films were evaluated in order to establish the optimization of electrical response. The current-voltage curves were used to obtain the limit intensity of rectification and resistances in depolarizing and hyperpolarizing field. Chemical modifications in the film also allow the current rectification even when no-generating ions are present in the electrolyte solutions.

1. Introduction

Hydrogen uranyl phosphate, H₃OUO₂PO₄·3H₂O, (HUP) is a very well known proton conductor and, consequently, it is being employed in some micro-electronic devices [1]. In many of such systems, mixtures of HUP and carbon particles are used as separators of the different parts of the systems, but mainly solid-solid interfaces are considered [2,3].

In this work, the electrical behaviour of hydrogen uranyl phosphate thin films (HUP-tf) and calcium saturated uranyl phosphate thin films (CaHUP-tf) placed between two different aqueous electrolyte solutions, at the same concentration C, are considered. The following four systems were studied:

UO₂(NO₃)₂(C)/HUP thin film/H₃PO₄(C),
UO₂(NO₃)₂(C)/CaHUP thin film/H₃PO₄(C),
UO₂(NO₃)₂ + Ca(NO₃)₂(C)/CaHUP thin film/H₃PO₄(C).

This study is focusing on the asymmetry of the current-voltage curves measured with these systems depending on the polarity of the external electric field applied and the ions responsible for driving the current in each case. The film asymmetry is indicated by the different resistances measured for the two opposite directions of the electric field [4,5]: (i) hyperpolarizing field, R(+), (H₃PO₄ as anodic electrolyte); (ii) depolarizing field, R(-), (H₃PO₄ as cathodic electrolyte). The ratio R(+)/(R)(-) can be considered as a measure of the efficiency for the electric current rectification of thin films. A comparison of the rectifier effect with HUP and CaHUP films is made.

2. Experimental

2.1. Materials

The H₃OUO₂PO₄·3H₂O (HUP) solid was prepared from aqueous solutions 1 M and 1.1 M of UO₂(NO₃)₂ and H₃PO₄ respectively. The product was characterized by X-ray diffraction and chemical analysis.

The HUP thin film (HUP-tf) was prepared using a method similar to that described by Alberti [6]. Two grams of HUP were suspended in 20 ml of N, N’-dimethylacetamide and stirred in an ultrasonic bath for two hours. Then 1 g of Kynar™ (polyvi-
nylidene fluoride) were added and the slurry so obtained was maintained under stirring for two more hours. This mixture was then spread on a glass plate and the solvent was removed in an oven at 85–90°C. The removal of the solvent was accomplished in saturated vapour water atmosphere. A flexible film is obtained, which is easily detached from the glass plate. Another film was prepared from HUP-tf by immersion for three days in a solution of calcium nitrate, 10^{-2} M and it will be thereafter called CaHUP-tf. The characterization and identification of active phases in these films was carried out by means of X-ray diffraction in a Siemens D-501 diffractometer automated, using monochromated Cu Ka radiation.

This Ca-saturated film (CaHUP-tf) contains calcium uranyl phosphate hydrate \([\text{Ca}(\text{UO}_2\text{PO}_4)_2\cdot n\text{H}_2\text{O}]\) as the main active phase according to the X-ray diffractogram. The basal spacing increases from 8.8 Å (HUP) to 10.1 Å. The H^+ / Ca^{2+} exchange is not complete since a small amount of the 8.8 Å phase still remains.

Film thickness, \(\delta\), was measured using a Digimatric-Mark II instrument and the value \(\delta = (60 \pm 5) \mu m\) was obtained, which corresponds to the average of 6 measurements covering the whole membrane area.

2.2. Current–voltage measurements

The experimental device used for current–voltage measurements is essentially like that described in ref. [7], and it is schematically shown in fig. 1. The cell was constructed of glass and made up of two half-cells, each one of approximately 120 ml volume. Each half-cell was filled with one of the above indicated electrolytes at the same concentration. The film, with 5 cm² area exposed to flow, was fixed in place by two methacrylate rings. One pair of working electrodes (gold) and another of probe (platinum) were placed at both sides of the film. The platinum electrodes were located in a moving plug, then current–voltage curves at different electrode distances were measured.

The films were placed separating two diluted solutions of different electrolytes, depending on the system considered, at the same concentrations, (H₃PO₄, UO₂(NO₃)₂, Ca(NO₃)₂ and UO₂(NO₃)₂ + Ca(NO₃)₂). The current–voltage curves were measured at room temperature (20°C) and for five aqueous electrolyte concentrations (5 × 10^{-5}, 10^{-4}, 10^{-3}, 5 × 10^{-3} and 10^{-2} M).

Three series of measurements were made at each concentration and electrode distance. Due to the asymmetric behaviour of the HUP thin film, different values of the resistance were obtained depending on the polarity of the electric current. Then the film/solution resistance for each direction \((R(+)\) and \(R(-)\) was obtained as the average value of the three corresponding measurements.

Due to the values decay when high voltages were applied, all measurements were made at the same time delay.

3. Results and discussion

Fig. 2 shows the current–voltage curves measured when the HUP-tf is separating two solutions of UO₂(NO₃)₂ and H₃PO₄ at different concentrations, but the same for both electrolytes, and a constant electrode distances. From this picture the asymmetry of the \(I–V\) curves depending on the polarity of the external electric field applied to the system is seen. Similar behaviour has been reported in the literature for different systems [5,8]. In this case, the asymmetry is mainly due to the adsorption of UO₂^3+ and H₂PO₄^- ions at the film surfaces when the external
electric field drives these ions toward the film (hyperpolarizing field). Under this situation two oppositely charged layers appear, one at each electrolyte/film interface, and only a residual or limit current \((I_0)\) exists, which is driven by \(H^+\) and \(OH^-\) ions from the water.

It is worth noting that for self-supported films, which are made with a polymeric binder, the effect of the hyperpolarizing field starts when the external voltage exceeds 1.6 V (1-1.6 V depending on the concentration) while for films without any binder, only a few mV are required (about 50 mV) \([9]\). This fact can be due to the binder effect which avoids in some way the contact between the generating ions of the precipitate, and it also distresses the mobility and diffusion of the ions across the films. In this situation an extra voltage is needed in order to reach the hyperpolarizing effect.

On the other hand, when the polarity of the external electric field is reversed (depolarizing field) there is not any restriction for ions movement, and a linear current–voltage relationship is obtained. Fitting the experimental points corresponding to each zone, two different values of the electrical resistance for the hyperpolarizing, \(R(+)\), and the depolarizing, \(R(-)\), potential are obtained. The resistance ratio, \(R(+)/R(-)\), can be taken as a measure of the efficiency for the current rectification of the HUP film. At very low concentrations \((C < 10^{-5} \text{ M})\) no rectifier effect was observed, \(R(+)/R(-) = 1\), which indicates that a minimum level of generating ions in the solution and, consequently, at the solid/liquid interfaces should exist in order to obtain this effect; at high concentrations an increase of \(R(+)/R(-)\) values when the concentration increases is obtained. The limit intensity values \(I_0\) were obtained extrapolating to \(V = 0\) the slopes of the straight lines for the high values of the hyperpolarizing potential \([10]\). Variations of both parameters, \(R(+)/R(-)\) and \(I_0\), with concentration are shown in table 1.

Current–voltage curves for a given concentration but different electrode distances are drawn in fig. 3 \((C = 0.01 \text{ M})\). Variation of \(R(+)/R(-)\) with electrode distance, \(d\), is also indicated in table 1. An almost constant ratio is obtained for each concentration except at the shorter distance when the effect of the adsorbed layers at the solution/film interface can influence strongly \(R(+)\) values. Since the limit intensity values is practically independent of electrode distance, only its average value \(\langle I_0 \rangle\) is indicated in table 1.

Because under depolarizing potential condition there is no restriction to the ions movement across the HUP film, as it was indicated above, \(R(-)\) values can be considered as the resistance of the system HUP thin film/electrolyte solutions. Variation of \(R(-)\) values with electrode distance, for the different concentrations studied, are shown in fig. 4. Then, the HUP film resistance \(R(0)\) (obtained at \(d = 0\)) at each concentration is calculated from the intercept of the corresponding straight line. These values are also indicated in table 1. Variation of \(R(0)\) with concentration is attributed to the inclusion of electrolyte solution into the HUP matrix.

In order to see the influence of electrolyte solutions without any of the HUP generating ions, a piece of the film was immersed in a \(Ca^{2+}\) solution and a
Table 1
Variation of $R(+) / R(-)$ ratio at different electrode distances, $<I_0>$ and $R(0)$ values with electrolyte concentration for HUP-tf.

<table>
<thead>
<tr>
<th>Electrolyte conc. (M)</th>
<th>$R(+) / R(-)$ 0.75 cm</th>
<th>$R(+) / R(+)$ 1.15 cm</th>
<th>$R(+) / R(-)$ 1.75 cm</th>
<th>$R(+) / R(-)$ 2.00 cm</th>
<th>$I_0$ (mA)</th>
<th>$R(0)$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-3}$</td>
<td>2.60</td>
<td>2.37</td>
<td>1.93</td>
<td>1.73</td>
<td>0.026</td>
<td>6000</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>2.77</td>
<td>2.57</td>
<td>2.44</td>
<td>2.25</td>
<td>0.065</td>
<td>3360</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>3.97</td>
<td>2.87</td>
<td>2.52</td>
<td>2.84</td>
<td>0.510</td>
<td>360</td>
</tr>
<tr>
<td>$5 \times 10^{-3}$</td>
<td>7.42</td>
<td>4.35</td>
<td>5.14</td>
<td>4.83</td>
<td>1.300</td>
<td>92</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>9.74</td>
<td>5.43</td>
<td>6.23</td>
<td>6.20</td>
<td>2.854</td>
<td>61</td>
</tr>
</tbody>
</table>

CaHUP-tf was obtained, as previously described. Fig. 5 shows the $I$-$V$ curves when this CaHUP-tf is placed between different electrolytes at $C=0.005$ M:

$\text{UO}_2^{2+}/\text{CaHUP-tf}/\text{H}_2\text{PO}_4^-$,
$\text{Ca}^{2+}/\text{CaHUP-tf}/\text{H}_2\text{PO}_4^-$,
$\text{UO}_2^{2+}, \text{Ca}^{2+}/\text{CaHUP-tf}/\text{H}_2\text{PO}_4^-$.

For comparison the $I$-$V$ curve for the system $\text{UO}_2^{2+}/\text{HUP-tf}/\text{H}_2\text{PO}_4^-$ is also indicated. From this picture it can be seen that the highest current rectification appears when at one side of the CaHUP film there is a mixture of calcium and uranyl nitrates with a molar ratio Ca/U = 0.2; this rectifier effect is even slightly higher than that found with the

CaHUP-tf. It is worth noticing that the system $\text{Ca}^{2+}/\text{HUP-tf}/\text{H}_2\text{PO}_4^-$ presents the lowest rectification. These results may be explained as follows: when the polarizing electric field is acting on the system $\text{UO}_2^{2+}, \text{Ca}^{2+}/\text{CaHUP-tf}/\text{H}_2\text{PO}_4^-$, the $\text{UO}_2^{2+}, \text{Ca}^{2+}$ and $\text{H}_2\text{PO}_4^-$ ions are driven towards the film and they are stopped at the interfaces because $\text{Ca}(\text{UO}_2\text{PO}_4)_2$ and/or $\text{H}_3\text{O}\text{UO}_2\text{PO}_4$ precipitate is forming. These solids and the film active phase have the same crystal structure and, consequently, they act as a barrier to the ions movement and, at the same time, they are removed from the solution to a solid phase. However, when the cathodic electrolyte is calcium nitrate, the only new solid material will be calcium hydrogenphosphate, which is much more soluble than

Fig. 3. $I$-$V$ curves for the system $\text{UO}_2^{2+}/\text{HUP-tf}/\text{H}_2\text{PO}_4^-$; $C=0.01$ M at different electrode-film distances: (△) 2 cm; (+) 1.75 cm; (○) 1.15 cm.

Fig. 4. $R(-)$ values versus electrolyte-film distances at different concentrations: (△) $C=5 \times 10^{-3}$ M; (+) $C=10^{-4}$ M; (○) $C=10^{-3}$ M; (●) $C=5 \times 10^{-3}$ M.
(ii) a minimum level of ions in the solutions is necessary to have current rectification;
(iii) the nature of the electrolytes separated by the film. This work shows that it is not strictly necessary for all the film-generating ions to be present in the solutions in order to obtain a rectifier response.

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References