Current rectification and electrical parameters of NH₄UO₂PO₄·3H₂O (NUP) films in contact with the generating electrolytes

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The electrical behaviour of the ammonium uranylphosphate film, NH₄UO₂PO₄·3H₂O (NUP), when it is in contact with two different electrolyte solutions which contain the precipitate generating ions (UO₂(NO₃)₂/NUP/H₃PO₄ and UO₂(NO₃)₂/NUP/NH₄H₂PO₄), have been studied using both direct and alternating current. The dc measurements show the asymmetry of the current-voltage curves depending on the polarity of the external electric field. From impedance spectroscopy measurements some characteristic parameters for the NUP film have been obtained.

1. Introduction

The electrical behaviour of different inorganic films, when they are in contact with electrolyte media and as solid phases, is being studied by means of direct current as well as the impedance spectroscopy technique [1-4]. In this paper, the ammonium uranylphosphate film, NH₄UO₂PO₄·3H₂O (NUP), placed between two different electrolyte solutions which contain the precipitate generating ions (UO₂(NO₃)₂, NH₄H₂PO₄ and H₃PO₄) is studied. Two systems: (i) UO₂(NO₃)₂/NUP/H₃PO₄; (ii) UO₂(NO₃)₂/NUP/NH₄H₂PO₄ are considered.

From the direct current measurements the asymmetry of the current-voltage curves, depending on the polarity of the external electric field applied to the system, is determined. This asymmetry is related to the different ions responsible for the driving current in each case, and it can be taken as a measure of the film efficiency for electric current rectification. From impedance spectroscopy measurements some characteristic electrical parameters of the NUP self-supported films are determined. A comparison of these results with those found when the film is placed between two solutions of the same electrolyte [4] is also made.

2. Experimental

2.1. Material

The NH₄UO₂PO₄·3H₂O (NUP) film was obtained by immersion for three days in a 10⁻² M solution of ammonium phosphate of a H₃O₂UO₂PO₄·3H₂O (HUP) film previously prepared, which was obtained following a procedure similar to that indicated by Alberti [3,5]. Aqueous solutions of H₃PO₄, NH₄H₂PO₄ and UO₂(NO₃)₂ at three different concentrations were used (C= 10⁻³, 5X10⁻³ and 10⁻² M). Measurements were carried out at room temperature (t=25°C).

2.2. Experimental setup

The experimental device used is similar to that described in ref. [3]. It is basically composed of two glass half-cells separated by the membrane holder, which consists of two methacrylate rings. The film was placed separating two diluted solutions, at the same concentration, of the different generating electrolytes (depending on the system considered).

For direct current measurements two kinds of
electrodes were used: gold electrodes for injecting current and platinum electrodes to measure the potential difference at both sides of the film. Three series of current–voltage measurements were made at each concentration and, due to the film asymmetry, different values of the electrical resistance were obtained for each current polarity. The final resistance values for each direction was obtained as the average of the three corresponding ones.

Impedance measurements were carried out using a frequency response analyzer FRA (Solartron 1255) with frequency ranging between 100 Hz and 15 MHz. The experimental data were corrected by software, as well as by other parasite capacitances [6]. In this case only two electrodes were used (gold electrodes) and, in order to insure a linear response, the maximum voltage applied to the system only exceeded in 20 mV to the corresponding membrane potential.

3. Results and discussion

Fig. 1 shows the experimental current–voltage curves (dc), when the NUP film is separating two solutions of H₃PO₄ and UO₂(NO₃)₂ at three different concentrations (the same for both electrolytes). For comparison, the values obtained with a HUP film, and the same electrolytes, are also drawn (C=0.005 M). From this picture two different zones, h and d, depending on the polarity of the external electric field, can be see. Zone h corresponds to the hyperpolarization field, which drives to the film the ions generating the precipitate and they are stopped there, forming two oppositely charged layers at the film/solution interfaces; zone d corresponds to the depolarizing field (opposite polarity), in this case no restriction to the ions' movement exists and the system behaves as an ohmic conductor. The other NUP-film system (UO₂(NO₃)₂/NUP/NH₄H₂PO₄), which corresponds to the UO₂⁺, NH₄⁺ and H₂PO₄⁻ precipitate generating ions, was also studied and the results are shown in fig. 2, where I–V curves similar to those indicated above can be seen.

From the slopes of these straight lines Rₑ(h) and Rₑ(d) values were determined, for each system and concentration, and the ratio Rₑ(h)/Rₑ(d), which is a measure of the film current rectification efficiency [2], is indicated in table 1. Due to the electrolyte layer between the end of the platinum electrodes and the film surface, the resistance value Rₑ(d) does not correspond exactly to the membrane resistance, but it is assumed that the electrolyte presents a similar contribution for both current directions. Another parameter related to the current rectification is the limit intensity, Iₒ, which is determined by the interception of the slopes corresponding to the two opposite current polarities. This limit current is mainly attributed to the H⁺ and OH⁻ ions present in the aqueous solutions [7]. The Iₒ values, for the different systems studied, are also shown in table 1. It can be observed that the limit intensity values are almost
Table 1
Variation with concentration of the resistance ratio, \(R(h)/R(d)\), and limit current, \(I_0\), for the systems \(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{H}_3\text{PO}_4\), \(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{NH}_4(\text{H}_2\text{PO}_4)\), and \(\text{UO}_2(\text{NO}_3)_2/\text{HUP}/\text{H}_3\text{PO}_4\), measured with direct current.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{H}_3\text{PO}_4)</th>
<th>(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{NH}_4(\text{H}_2\text{PO}_4))</th>
<th>(\text{UO}_2(\text{NO}_3)_2/\text{HUP}/\text{H}_3\text{PO}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (M)</td>
<td>(R(h)/R(d)) (I_0) (mA)</td>
<td>(R(h)/R(d)) (I_0) (mA)</td>
<td>(R(h)/R(d)) (I_0) (mA)</td>
</tr>
<tr>
<td>0.001</td>
<td>7.6 0.075</td>
<td>2.6 0.12</td>
<td>2.6 0.51</td>
</tr>
<tr>
<td>0.005</td>
<td>18.6 0.075</td>
<td>3.9 0.16</td>
<td>4.4 1.30</td>
</tr>
<tr>
<td>0.01</td>
<td>24.5 0.081</td>
<td>5.7 0.13</td>
<td>5.6 2.85</td>
</tr>
</tbody>
</table>

Independent of the concentration, but they slightly depend on the electrolyte considered and the nature of the film. These results show that the highest rectification, which means higher resistance ratio and lower limit intensity values, is obtained when \(\text{UO}_2(\text{NO}_3)_2\) and \(\text{H}_3\text{PO}_4\) solutions are involved, and the lowest rectification appears when the HUP film is considered, which agrees with the high proton mobility presented by the precipitate.

Impedance measurements with the systems \(\text{UO}_2(\text{NO}_3)_2(C)/\text{NUP}/\text{H}_3\text{PO}_4(C)\), \(\text{UO}_2(\text{NO}_3)_2(C)/\text{NUP}/\text{NH}_4\text{H}_2\text{PO}_4(C)\) were also made, and the corresponding Nyquist plots are drawn in fig. 3. Two different circles, for each system, can be seen in this picture: the circle at low frequencies corresponds to the film and the other one, at high frequencies, is due to the electrolyte solution. The experimental points were fitted to a circuit formed by two parallel elements connected in series: \(R_cC_s-W\), where \(R_c\) and \(R_f\) represent the electrolyte and film resistance, \(C_s\) is the electrolyte and measuring cell capacity, and \(W\) is a Warburg impedance related to the diffusion effect in the film. The experimental data were analysed using a NLLS program [8], and the circuit parameter values, as well as the corresponding error coefficient, are indicated in table 2.

As can be seen from this table, good concordance between experimental and calculated values is obtained in all cases, since differences between both kinds of values are always lower than 10%. The \(\text{UO}_2(\text{NO}_3)_2/\text{NUP-film}/\text{NH}_4\text{H}_2\text{PO}_4\) system presents higher resistance and Warburg impedance values, which agrees with the higher \(R_f\) values previously found with direct current.

The electrical response of the NUP film when it is separating two similar solutions of the generating electrolytes was previously obtained [4], and the values of the electrical resistance determined under these external conditions, \(R_f\), are indicated in table 3. A comparison of the results shown in tables 2 and

Table 2
Variation with concentration of the circuit parameters: film resistance, \(R_f\); Warburg impedance, \(W\), and error coefficient, \(r\), for the system \(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{H}_3\text{PO}_4\) and \(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{NH}_4(\text{H}_2\text{PO}_4)\).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{H}_3\text{PO}_4)</th>
<th>(\text{UO}_2(\text{NO}_3)_2/\text{NUP}/\text{NH}_4(\text{H}_2\text{PO}_4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (M)</td>
<td>(R_f) ((\Omega)) (r) (%) (W) ((\Omega^{-1}\text{Hz}^{-0.5})) (r) (%)</td>
<td>(R_f) ((\Omega)) (r) (%) (W) ((\Omega^{-1}\text{Hz}^{-0.5})) (r) (%)</td>
</tr>
<tr>
<td>0.001</td>
<td>7620 3.6 3.9\times10^{-7} 9.7</td>
<td>12260 2.0 4.3\times10^{-7} 6.8</td>
</tr>
<tr>
<td>0.005</td>
<td>3110 1.6 6.6\times10^{-7} 5.4</td>
<td>4510 1.7 6.8\times10^{-7} 5.6</td>
</tr>
<tr>
<td>0.01</td>
<td>1734 0.9 7.3\times10^{-7} 3.2</td>
<td>2690 1.6 9.3\times10^{-7} 5.5</td>
</tr>
</tbody>
</table>
Table 3
Values of the resistance, $R^\circ$, for the NUP-film in contact with the generating electrolytes.a)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$H_3PO_4$/NUP/$H_3PO_4$</th>
<th>$UO_2(NO_3)_2$/NUP/$UO_2(NO_3)_2$</th>
<th>$NH_4H_2PO_4$/NUP/$NH_4H_2PO_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (M)</td>
<td>$R^\circ$ ((\Omega))</td>
<td>$R^\circ$ ((\Omega))</td>
<td>$R^\circ$ ((\Omega))</td>
</tr>
<tr>
<td>0.001</td>
<td>1750</td>
<td>3220</td>
<td>3890</td>
</tr>
<tr>
<td>0.005</td>
<td>3500</td>
<td>1850</td>
<td>2500</td>
</tr>
<tr>
<td>0.01</td>
<td>1700</td>
<td>910</td>
<td>2080</td>
</tr>
</tbody>
</table>

a) Values from ref. [4].

3 indicates that the resistance values when the NUP film is in contact with two of the generating electrolytes are not the sum of those obtained with the single ones, as can be also inferred by the two different kinds of electrical responses shown in figs. 4 and 5. These differences could be attributed to the effect of the adsorption of both oppositely charged layers at the film/solution interfaces when it is placed between two of the generating electrolytes.

In short, the electrical response of NUP film, when there is contact with the generating electrolytes (\(UO_2(NO_3)_2\) and \(NH_4H_2PO_4\) or \(UO_2(NO_3)_2\) and \(H_3PO_4\)), for alternating and direct current has been considered. From the ac measurements the equivalent circuit and the characteristic parameters of the systems have been determined. The asymmetry of the current–voltage curves presented by the NUP film with direct current is also indicated. This property could be used to detect the presence of the \(UO_2^3+\), \(H_2PO_4^-\) and \(NH_4^+\) ions in the solution bathing the NUP film.

Fig. 5. A comparison of the impedance plots for the NUP film with different electrolytes (\(C=5\times10^{-3}\) M): (+) \(UO_2(NO_3)_2$/NUP/$UO_2(NO_3)_2\); (O) \(NH_4H_2PO_4$/NUP/$NH_4H_2PO_4\); (▲) \(UO_2(NO_3)_2$/NUP/$NH_4H_2PO_4\).

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References