A comparative study of the electrical behaviour of different uranyl phosphate-based membranes by a.c. and d.c. measurements*

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Abstract

A comparative study of the electrical response of three uranyl phosphate-based membranes, when they are separating solutions of the generating electrolytes, is carried out by means of direct and alternating current measurements. The rectifier behaviour (d.c.) as well as the circuit associated with each membrane (a.c.) was obtained. The variation of the behaviour with concentration of the different circuit elements is also indicated. A comparison between the membrane matrix electrical resistances calculated from these results and those obtained by measuring dry membrane samples is also made. Good agreement between both sets of results was found.

Keywords: A.c. measurements; D.c. measurements; Membranes; Uranyl phosphate

1. Introduction

Membranes or films made from inorganic precipitates were described several decades ago [1,2], but were not commonly used because of the difficulty in handling them. In order to avoid this problem, different authors have used filter paper or porous polymeric membranes as supports for the inorganic precipitates [3-7]; self-supported membranes have also been obtained [8,9]. In a previous series of papers, we studied the electrical behaviour of porous-supported and self supported membranes made of hydrogen uranyl phosphate (HUP), which is a well-known proton conductor [10], and different derivatives such as calcium and ammonium uranyl phosphate (Ca(UO_2PO_4)·nH_2O (CaUP) and NH_4UO_2PO_4·3H_2O (NUP)), when they were in contact with electrolyte solutions (wet membranes) under different external conditions [7,9]. Different inorganic precipitates are being used in micro-electronic devices as new capacitors which make use of the electric double layer formed at the electrode/electrolyte interface [11].

In this work, a comparative study of the electrical behaviour of three different membranes (HUP, CaUP and NUP), when they are separating solutions of the precipitate-generating electrolytes (UO_2(NO_3)_2 and H_3PO_4), is carried out by means of direct and alternating current measurements, with both solutions at the same concentration. D.c. measurements show that the asymmetry of the current–voltage curves depends on the polarity of the external voltage applied to the membrane, which is related to the rectifier behaviour of the inorganic membrane/electrolyte systems [5–7].

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contrast, a.c. impedance measurements are frequently used in studies of electrochemical systems in order to obtain information about them by means of impedance plots and using equivalent circuits as models, being the different circuit elements related to the respective processes taking place in the system (ionic conductivity, Warburg diffusion, double layer capacitance, etc.) [12]. A comparison between the electrical responses obtained by impedance spectroscopy with wet and dry samples of HUP, CaUP and NUP membranes is also made.

2. Experimental

2.1. Materials

The HUP membrane was prepared from HUP solid precipitate, which was characterized by X-ray diffraction and chemical analysis, following a procedure similar to that of Alberti [8]. The other two membranes, NUP and CaUP, were obtained by immersion of the previously prepared HUP film in 10⁻⁴ M solutions of ammonium phosphate and calcium nitrate, respectively, for three days.

The characterization and identification of the active phases in these membranes was carried out by means of X-ray diffraction in an automated Siemens D-501 diffractometer, using monochromated CuKα radiation and IR spectroscopy (Perkin-Elmer 883). The CaUP membrane contains calcium uranyl phosphate hydrate [Ca[(UO₂)₂PO₄]₅.nH₂O] as the main active phase according to the X-ray diffractogram. The basal spacing increases from 8.8 Å (HUP) to 10.1 Å, but the H⁺/Ca²⁺ exchange is not complete since a small amount of the 8.8 Å phase still remains. For the NUP membrane the basal spacing is 8.9 Å, which indicates that H⁺/NH₄⁺ exchange does not produce structural changes in the precipitate; it contains NH₄[UO₂PO₄]₃H₂O as the main active phase, although about 20% of the exchange sites have still not been saturated by NH₄⁺ cations, remaining as H⁺ sites (HUP) as revealed by chemical analysis of the nitrogen.

Membrane thickness was measured using a Digimatrix-Mark II instrument and the following \( \langle \delta \rangle \) values, which correspond to the average of five measurements covering the whole membrane area, were obtained:

- HUP \( \langle \delta \rangle = (51 \pm 4) \mu m \)
- NUP \( \langle \delta \rangle = (55 \pm 5) \mu m \)
- CaUP \( \langle \delta \rangle = (60 \pm 5) \mu m \)

Aqueous solutions of H₃PO₄ and UO₂(NO₃)₂ at three different concentrations were used (C = 10⁻³, 5 x 10⁻³ and 10⁻² M). All measurements were carried out at room temperature (t = 25°C). No changes in the pH of the solutions in contact with the membranes before and after the experiments were detected.

2.2. Experimental setup

The experimental device used for both d.c. and a.c. measurements is similar to that described in Ref. [9]. It basically consists of two half-cells separated by the membrane holder, which consists of two methacrylate rings with a free area of 1 cm². The membranes were placed separating H₃PO₄ and UO₂(NO₃)₂ solutions, at the same concentration.

For d.c. 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 membrane. Three series of current–voltage measurements for each membrane and concentration were made and, due to the membrane asymmetry, different values of the electrical resistance, depending on the direction of the current, were measured. The final resistance values for each direction and concentration \( R(+) \) and \( R(-) \) were obtained as the average of the three corresponding values.

Impedance spectroscopy measurements (a.c.) for the three membrane/electrolyte systems were carried out in the same measuring cell, but in this case only gold electrodes were used. A frequency response analyzer (Solartron 1255), with frequency ranging between 100 and 10 MHz, was used. The experimental data were corrected by software as well as by other parasite capacitances [13]. In order to ensure a linear response, the maximum voltage applied to the system only exceeded the corresponding membrane potential by 20 mV.

Impedance measurements with dry samples of
these membranes (without any electrolyte solution) were also carried out in the test-cell indicated in Ref. [13]. These membranes will thereafter be called HUPI(d), CaUP(d) and NUP(d).

3. Results and discussion

3.1. d.c. results

Fig. 1 shows the experimental current–voltage curves (d.c.) for the HUP membrane at different concentrations of the generating electrolytes. The asymmetry of the curves, which is a characteristic of the precipitation membranes [5], is clearly shown in this Figure. Hirch-Ayalon [5] indicates that a minimum level of ions generated in the solution and, consequently, at the membrane/electrolyte interfaces should exist in order to obtain asymmetric behaviour with precipitation membranes, as can be seen from the results indicated in Fig. 1, since at \( C = 10^{-4} \text{ M} \) (the lowest concentration) a straight line was obtained over the whole voltage range. For this reason, \( 10^{-3} \text{ M} \) was the lowest concentration measured with NUP and CaUP membranes.

In Fig. 1, two different zones (h and d) can be seen, depending on the polarity of the external applied voltage:

— Zone \( h \) corresponds to the hyperpolarizing (or positive) voltage, which drives the ions forming the precipitate (\( \text{UO}_2^{2+} \) and \( \text{H}_3\text{PO}_4 \)) to the membrane. In this situation two oppositely charged layers appear, one at each membrane/electrolyte interface, and only a residual or limit current \( (I_o) \) exists, most of which is driven by \( \text{H}^+ \) and \( \text{OH}^- \) ions from the water [14].

— Zone \( d \) corresponds to the depolarizing (or negative) voltage; in this case no restriction to the movement of the ions exists and the system behaves as an ohmic conductor.

A comparison between the rectifier effects found for the three membranes is shown in Fig. 2, for the same external conditions \( (C = 5 \times 10^{-3} \text{ M} \) for \( \text{H}_3\text{PO}_4 \) and \( \text{UO}_2(\text{NO}_3)_2 \) solutions). From this Figure, it can be observed that for the depolarizing

![Fig. 1. Current–voltage curves for the HUP membrane at different concentrations. (+) \( C = 10^{-4} \text{ M} \); (▲) \( C = 10^{-3} \text{ M} \); (○) \( C = 5 \times 10^{-3} \text{ M} \); (●) \( C = 10^{-3} \text{ M} \).](image-url)
potential zone the resistance values obtained for the three membranes are very similar, but significant differences exist in the hyperpolarizing potential zone. The highest rectifier effect is found for the NUP membrane, while the lowest is found for the HUP membrane. This result is attributed to the different transport mechanisms of ions in the membranes: an almost free exchange of H⁺, mainly for the HUP membrane [10], in contrast with a diffusion for the CaUP and NUP membranes. In this case the higher rectification presented by the NUP membrane with respect to the CaUP membrane is related to differences in their matrix structures. Thus, the CaUP membrane has a more open structure ($d_{CaUP} = 10.1 \text{ Å}$ and $d_{NUP} = 8.9 \text{ Å}$) with more water molecules in the interlayer space, which facilitates ionic diffusion.

From the slopes of straight lines similar to those shown in Fig. 1, $R(+) / R(-)$ values were determined for each membrane and concentration. The $R(+) / R(-)$ ratio represents a measure of the membrane current rectification efficiency, and its values for each membrane and concentration are indicated in Table 1. The other parameter related to the current rectification is the limit intensity, $I_o$, which was determined by the interception of the straight lines obtained for each current polarity [14]. $I_o$ values for each membrane and concentration are also indicated in Table 1. From this Table, some differences in the $I_o$ values depending

<table>
<thead>
<tr>
<th>Electrolyte concentration (M)</th>
<th>$UO_2(NO_3)_2$/HUP/H₃PO₄</th>
<th>$UO_2(NO_3)_2$/NUP/H₃PO₄</th>
<th>$UO_2(NO_3)_2$/CaUP/H₃PO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R(+) / R(-)$</td>
<td>$I_o$(mA)</td>
<td>$R(+) / R(-)$</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>0.001</td>
<td>2.6</td>
<td>0.51</td>
<td>7.6</td>
</tr>
<tr>
<td>0.005</td>
<td>4.4</td>
<td>1.30</td>
<td>18.6</td>
</tr>
<tr>
<td>0.01</td>
<td>5.6</td>
<td>2.85</td>
<td>24.5</td>
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</table>
on the membrane considered can be observed. While for the NUP membrane the limiting current values are almost independent of concentration, for the two other membranes, HUP and CaUP, the limiting current increases with the concentration of the external solution, particularly for the HUP membrane. These results indicate that the highest rectification is obtained with the NUP membrane and the lowest corresponds to the HUP membrane, which is due to the high proton conductivity of the HUP precipitate as indicated above. This fact demonstrates the importance of protonic diffusion through the HUP membrane, being ionic for the CaUP membrane, whereas transport across the NUP membrane is almost completely blocked.

3.2. a.c. results

Analysis of the a.c. data is carried out by a complex plane method, which involves plotting the impedance imaginary part ($Z''$) against the real part ($Z'$). When plotted on a linear scale, the equation for a parallel resistance-capacitor circuit gives rise to a semi-circle in the complex impedance plane ($Z^*$ plane), which has intercepts on the $Z' = Z_{\text{real}}$ axis at $R_m (\omega = \infty)$ and $R_0 (\omega = 0)$, where $(R_0 - R_m)$ is the resistance of the system and $\omega$ is the angular frequency. The maximum of the semi-circle is $0.5 (R_m - R_0)$ and occurs at a frequency such that $\omega R C = 1$ ($RC$ is the relaxation time) [15]. Complex systems may present different relaxation times and the resulting plot is a depressed semi-circle [16]. In such cases, a non-ideal capacitor, which is called a constant phase element (CPE), is considered. The impedance for the CPE, $Q(\omega)$, is expressed by

$$Q(\omega) = Y_0(\omega)^{-n}$$  \hspace{1cm} (1)

where $Y_0(\Omega s^{-n})$ and $n$ are two empirical parameters. Two special cases depending on the $n$ parameter value can be considered: if $n = 1$, it corresponds to an ideal capacitor; if $n = 0.5$, the element circuit is called a Warburg impedance, $W_m$, which is associated with a diffusion processes according to Fick’s first law [16].

Figs. 3(a)–3(c) show the impedance plot for the three $\text{H}_3\text{PO}_4$/membrane/$\text{UO}_2(\text{NO}_3)_2$ systems at $C = 5 \times 10^{-3} \text{ M}$ (HUP, NUP and CaUP, respectively). From this Figure two relaxation effects can be clearly observed: one at low frequencies, which corresponds to the membrane, and the other at high frequencies, which is due to the electrolyte solution. In the following analysis only the membrane effect will be considered. Similar results were obtained at the other concentration studied.

The experimental values, for each membrane and concentration, were fitted to a circuit consisting of a series combination of a capacitor, $C_m$, and a Warburg impedance, $W_m$, both in parallel with a resistance, $R_m$, also shown in Fig. 3. The data were analyzed using a non-linear Program [17], and the calculated circuit parameters, $C_m$, $W_m$ and $R_m$, for each membrane and concentration, are indicated in Table 2. In all cases, the differences between the experimental and calculated values were lower than 8%. From the results shown in Table 2, it can be seen that the $W_m$ and $C_m$ values depend only slightly on the membrane and concentration considered, whereas significant differences are obtained for the resistance values with both

<table>
<thead>
<tr>
<th>C(M)</th>
<th>HUP</th>
<th>NUP</th>
<th>CaUP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_m$ (k$\Omega$)</td>
<td>$W_m$ ($\Omega^{-1}\text{Hz}^{1/2}$)</td>
<td>$C_m$ (nF)</td>
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<tr>
<td>0.001</td>
<td>1.32</td>
<td>$1.1 \times 10^{-6}$</td>
<td>2</td>
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<td>9</td>
</tr>
<tr>
<td>0.01</td>
<td>0.82</td>
<td>$4.1 \times 10^{-6}$</td>
<td>12</td>
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membrane and concentration. The dependence of the $R_m$ values on concentration is reported in the literature for inorganic and polymeric membranes, and is mainly due to the electrolyte invasion into the membrane matrix [9,18].

In order to determine the inorganic membrane matrix resistance (without any electrolyte contribution), $R_m$ values were fitted to the following expression:

$$R_m(C) = R_0 - aC^b$$  \hspace{1cm} (2)

where $R_0$ represents the membrane resistance at $C=0$ (without salt contribution), and $a$ and $b$ are two empirical parameters. The calculated $R_0$, $a$
and $b$ values for each membrane are given in Table 3.

In order to compare these calculated $R_0$ values with the experimental results, impedance spectroscopy measurements with a dry sample of each membrane, HUP(d), CaUP(d) and NUP(d), were carried out. Fig. 4 shows the impedance plots for the dry membrane samples, which correspond to part of a depressed semi-circle. The experimental values were fitted to a circuit consisting of a parallel combination of resistance, $R_d$, and constant phase element, $Q_d$. Using the non-linear program previously indicated, the electrical resistance for each dry membrane, $R_d$, was determined and their values are given in Table 3. These results show very similar resistances for CaUP(d) and NUP(d) membranes; however, for the HUP(d) membrane the resistance is almost ten times lower, corresponding to its nature as a solid state protonic conductor [10]. A comparison of the wet and dry membrane resistance values shown in Table 3 indicates very good agreement between both types of value, the small differences being attributed to the different degree of hydration of each kind of membrane sample.

4. Conclusions

Electrical parameters for three uranyl-based membranes, HUP, CaUP and NUP, when they were in contact with different solutions of the generating electrolytes, $\text{UO}_2(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4$, were determined. Although the three membranes have a similar framework, small chemical and structural modifications provoke important changes in their electrical behaviour.

The asymmetry of the current–voltage curves determined with d.c. measurements shows the rectifier behaviour of these membranes in electrolytic media, being more pronounced for the NUP membrane. Current rectification is a characteristic of precipitation membranes and may be used to detect the presence of precipitate-generating ions (in this case $\text{UO}_2^{2+}$ or $\text{H}_3\text{PO}_4^-$) among other ions in the solutions containing the membranes.

From a.c. measurements the equivalent circuits and characteristic parameters, $R_m$, $C_m$, and $W_m$, were determined for the three wet membranes. The impedance spectroscopy technique for membrane/electrolyte systems permits us to determine the contribution of both membrane and electrolyte solution separately; however, the electrolyte invasion into the membrane must be taken into account, since it affects the resistance value. For this reason, membrane resistance is strongly dependent on concentration. Extrapolated resistance values at $C=0$ are in agreement with those determined for dry membrane samples.

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References


