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Impedance spectroscopy study with H-doped ammonium uranylphosphate self supported membranes

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Equivalent circuit and electrical parameters for H-doped $NH_4UO_2PO_4.3H_2O$ self supported membranes have been determined by impedance spectroscopy. The measurements were carried out with a dry membrane, at different temperatures, and a wet membrane in contact with different electrolyte solutions. Resistance values for the dry membrane decrease with temperature increase, which agrees with the weak protonic character of the H-doped ammonium uranylphosphate. On the other hand, differences in the electrical parameters, depending on the electrolyte considered were also obtained and are attributed to different conduction mechanisms.

1. Introduction

Hydrogen uranyl phosphate, $H_3OUO_2PO_4.3H_2O$ (HUP) and its derivatives are lamellar solids which present intercalation and ion exchange reactions [1, 2]. The HUP is a very well known proton conductor and is being employed in some microelectronics devices [3]. Recently, we studied the electrical behaviour of some of these materials as membranes or thin films by means of direct current measurements, and their properties as current rectifiers in electrolyte media were considered [4, 5].

A study of the HUP derivative ammonium uranyl phosphate, $NH_4UO_2PO_4.3H_2O$, is presented in this paper. It is an insoluble compound ($K_{sp} = 10^{-6.85}$) and it precipitates rapidly from its generating electrolytes ($NH_4H_2PO_4$ and $UO_2(NO_3)_2$). For this reason, it is an optimal material to be used as a current rectifier when in contact with two of the generating electrolytes (d.c. measurements).

In this work ammonium uranylphosphate membranes are examined by impedance spectroscopy in two different ways: viz (i) as a dry membrane (solid phase) and (ii) as a wet membrane in contact with an electrolyte solution.

The analysis of the impedance spectroscopy measurements permit determination of the equivalent circuit associated with each system. For the dry membranes, measurements at different temperatures were carried out, while, for the wet membranes, different concentrations of the electrolytes containing the generating ions ($NH_4H_2PO_4$, H_3PO_4 and $UO_2(NO_3)_2$) were considered, at a given temperature.

2. Experimental details

2.1. *Materials*

The ammonium saturated uranyl phosphate membrane (NUP) was obtained from a $H_3OUO_2PO_4.3H_2O$ (HUP) film previously prepared which was obtained from the HUP solid following a procedure described in [5]: the HUP solid (1 g) was suspended in N,N′-dimethylacetamide (10 ml) and stirred in an ultrasonic bath for 2 h, then polyvinylidene fluoride (0.5 g) was added. The slurry so obtained was maintained under stirring for 2 h. The mixture was spread on a glass plate and the solvent was removed in an oven at 85° C. The removal of the solvent was accomplished in a water vapour saturated atmosphere. Finally, a flexible membrane, or thin film, easily detached from the plate, was obtained.

By immersion of the HUP membrane in a 10^{-2} M solution of $NH_4H_2PO_4$ for three days, the ammonium uranylphosphate (NUP) membrane was obtained. The characterization and identification of active phases in the NUP membrane was carried out by X-ray diffraction in a Siemens D-501 automated diffractometer, and i.r. spectroscopy (Perkin–Elmer 883). This ammonium-saturated membrane (NUP) contains $NH_4UO_2PO_4.3H_2O$ as the main active phase, although about 20% of the exchange sites have still not been saturated by NH_4^+ cations, remaining as H^+ sites (HUP). For this reason, this membrane is termed as H-doped ammonium uranylphosphate.

Aqueous solutions of $NH_4H_2PO_4$, H_3PO_4 and $UO_2(NO_3)_2$, the electrolytes containing some of the NUP precipitate ions, were used at different concentrations ($10^{-4} \leqslant C(M) \leqslant 10^{-2}$).

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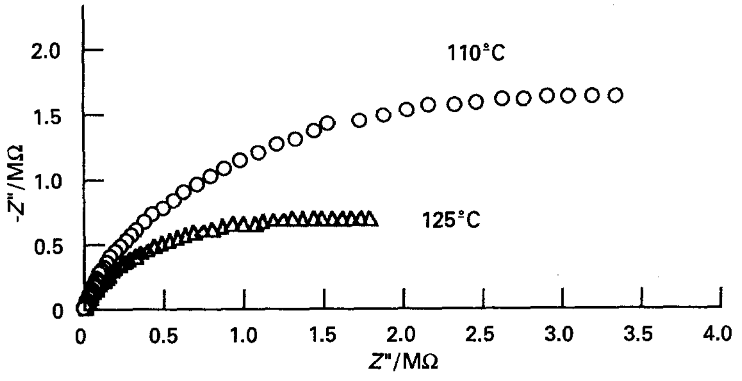

Fig. 1. Nyquist plot for the NUP dry membrane. (○) $t = 110°$ C; (△) $t = 125°$ C.

2.2. *Impedance measurements*

The electrical impedance of the NUP membrane was measured for both dry and wet membranes. For both systems, a frequency response analyser FRA (Solartron 1255) was used for frequency ranging between 100 Hz and 10 MHz. 100 different frequencies were considered The experimental data were corrected for the influence of connecting cables and other parasite capacitance [6].

The dry membrane was placed between two gold electrodes of 1.3 cm^2 area, which were clamped together by two steel screws. Measurements were carried out at different temperatures between 25° C and 125° C.

The experimental device used for the system membrane/electrolyte solution is similar to that described in [5]. It was constructed of glass and consisted of two half-cells of 125 cm^3 volume. The film, with 1 cm^2 of area exposed to flow, was placed between both half-cells with the aid of two methacrylate rings Gold electrodes were used. Both half-cells were filled with salt solutions of $NH_4H_2PO_4$, H_3PO_4 and $UO_2(NO_3)_2$ at the same concentration. Measurements were carried out at room temperature ($t \approx 25°C$) with the membrane between the half-cells and without the membrane (electrolyte impedance).

3. Results and discussion

3.1. *Dry membranes*

Figure 1 shows the impedance values corresponding to the complex impedance plot ($-Z_{im}$ against Z_{re}) for the NUP dry membrane at two different temperatures. A.c. impedance data are frequently used in the study of electrochemical systems using equivalent circuits as models.

The experimental points shown in Fig. 1, for each temperature, correspond to part of a depressed semicircle, and can be represented by a parallel combination of a resistance, R_S, and a constant phase element (CPE). The impedance of the CPE is expressed by [8]:

$$Q_s(\omega) = A_0(i\omega)^{-n} \qquad (1)$$

where the impedance $A_0(\Omega s^n)$ and n are experimental parameters ($0 < n < 1$), and ω is the angular frequency. Resistance and impedance values, for each temperature, were determined by means of a NLLS program [9]. The variation of R_s with temperature is presented in Fig. 2. It can be seen that, in general, R_s values decrease slightly with temperature increase, which is due to the partial protonic character of the precipitate; however, for the interval $70° C \leqslant t \leqslant 80° C$ a large increase in R_s values was

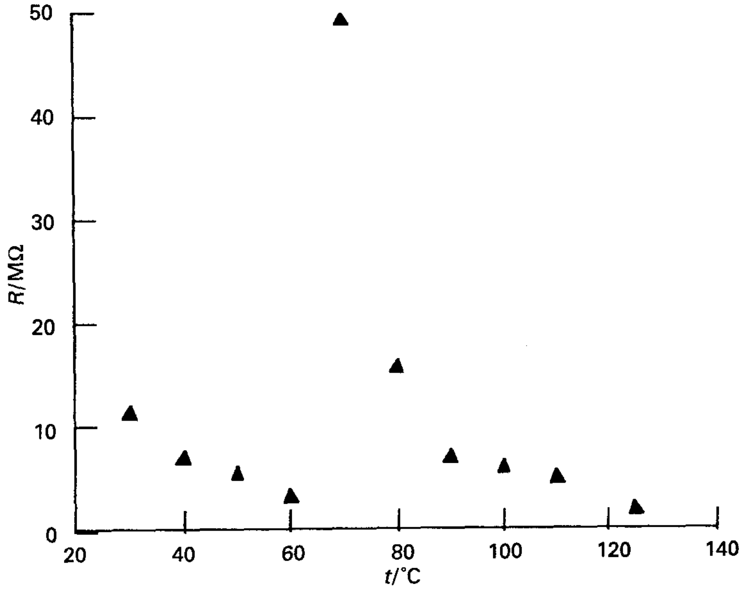

Fig. 2. Variation of the resistance, R, with temperature for the NUP dry membrane.

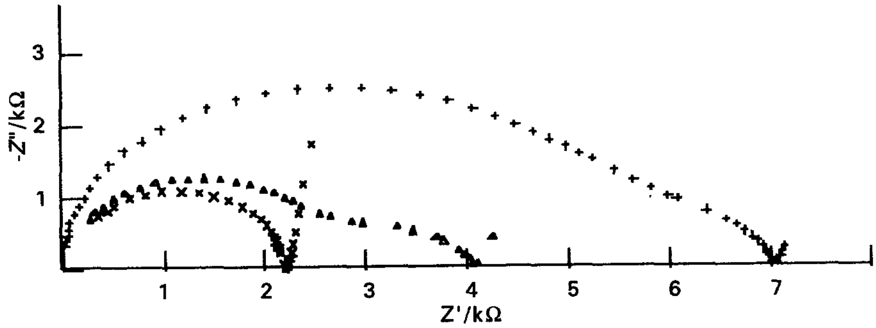

Fig. 3. Nyquist plot for the NUP wet membrane with different electrolytes ($C = 5 \times 10^{-3}$): (△) $UO_2(NO_3)_2$; (+) $NH_4H_2PO_4$; (×) H_3PO_4.

found. This may be attributed to the loss of hydration water in the solid which causes a structural rearrangement in the ammonium uranylphosphate phase; the new phase is called 'meta-autunite'. Water loss is detected by an endothermic effect, associated with the loss of mass from DTA–TG measurements. Conductivity values for temperatures ranging between 80° C and 125° C were calculated and an activation energy of 0.22 eV was obtained by means of the Arrhenius plot.

For the other two parameters indicated above, A_s and n_s, the following average values were obtained depending on the temperature interval:

For 25° C < t < 70° C:

$\langle A_s \rangle = (2.8 \pm 0.2)10^8(\Omega\, s^n s)$ $\langle n_s \rangle = 0.976 \pm 0.008$

For 80° C < t < 125° C:

$\langle A_s \rangle = (2.2 \pm 0.6)10^8(\Omega\, s^n s) \ldots$ $\langle n_s \rangle = 0.964 \pm 0.015$

For temperatures lower than 70° C both parameters, A_s and n_s, have almost constant values; however, for temperatures between 80° C and 125° C a slight linear decrease of n_s (from 0.9794 and 80° C to 0.94 at 125° C), and a more significant decrease for A_s (from 2.8×10^8 at 70° C to 1.65×10^8 at 125° C) were found.

3.2. *Wet membranes*

The electrical behaviour of the NUP wet membrane when the generating ions were involved in the system was also studied at 25° C. In this case two different media (membrane and electrolyte solution) exist, each having different dielectric properties. The influence on the electrical response of the NUP membrane of both precipitate generating ions and electrolyte concentration was considered.

Figure 3 shows the impedance plot for the system NUP-membrane/electrolyte solution, at a constant concentration ($C = 5 \times 10^{-3}$ M), and for the three different electrolytes containing one of the ions forming the NUP precipitate. Two relaxation effects, one corresponding to the membrane and other to the electrolyte, can be seen for $UO_2(NO_3)_2$ and $NH_4H_2PO_4$ solutions (two circles), while for H_3PO_4 only one circle was found. These results indicate that in this last case, a clear differentiation of the relaxation processes (electrolyte and membrane) is not possible, this is mainly attributed to the content of the HUP phase in the NUP membrane previously indicated. The HUP presents a high proton mobility and, for H_3PO_4 solutions, the membrane behaves as a 'proton reservoir' and hardly affects the H^+ movement; when H_3PO_4 solutions are in contact with the NUP membrane the NH_4^+/H^+ ionic exchange is favoured, increasing the content of the HUP phase in the membrane. This agrees with the impedance results obtained for a self-supported HUP membrane and H_3PO_4 solutions [10].

In Fig. 4 the influence of $UO_2(NO_3)_2$ concentration on the impedance values is shown. The equivalent circuit associated with the whole membrane/electrolyte system is also indicated. The experimental values were fitted to a series association of two parallel $R_i Q_i$ elements, one of them corresponding to the NUP membrane ($R_m Q_m$) and the other to the electrolyte solution ($R_e Q_e$), as indicated in Fig. 4.

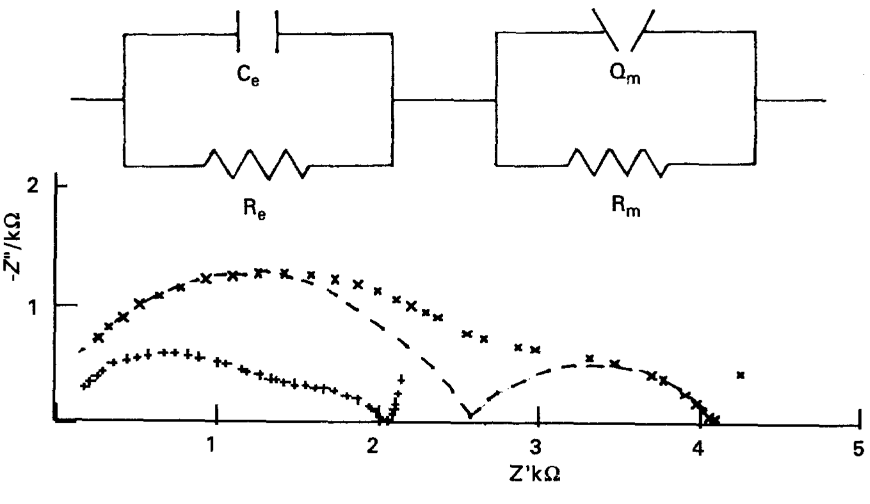

Fig. 4. Nyquist plot for the NUP membrane and two $UO_2(NO_3)_2$ solutions: (+) $C = 10^{-2}$ M; (×) $C = 5 \times 10^{-3}$ M.

Table 1. Variation with concentration of calculated values for the impedance, A_m, and the constant phase parameter, n_m, for a wet NUP membrane in contact with $UO_2(NO_3)_2$ and $NH_4H_2PO_4$ solutions

$UO_2(NO_3)_2$					$NH_4H_2PO_4$			
C /M	$A_m \times 10^6$ Ωs^n	ϵ_A* /%	n_m	ϵ_n* /%	$A_m \times 10^6$ $/\Omega s^n$	ϵ_n* /%	n_a	ϵ_n* /%
10^{-4}	1140	9.00	0.99	2.50				
2×10^{-4}					19700	9.00	0.99	1.80
5×10^{-4}	33.9	7.80	0.87	1.70	590	6.70	0.96	2.00
10^{-3}	28.1	7.00	0.75	1.90	50	5.50	0.89	1.50
5×10^{-3}	9.4	5.00	0.67	1.30	40	3.00	0.75	1.80
10^{-2}	8.5	6.15	0.66	1.53	13	4.67	0.68	1.38

* Percentage error between experimental and calculated values.

The electrolyte CPE element consists of a capacitor ($n = 1$) [10], and both resistance and capacitance values agree with those obtained with the electrolyte alone, without a membrane in the membrane holder (electrolyte impedance).

Membrane resistance and impedance values, for $UO_2(NO_3)_2$ and $NH_4H_2PO_4$ solutions, were determined using the NLLS data analysis program indicated above. Variation of both CPE parameters, A_m and n_m, with the concentration of $UO_2(NO_3)_2$ and $NH_4H_2PO_4$ solutions are given in Table 1, and the corresponding error interval, $\epsilon(\%)$. For both electrolytes, A_m and n_m values decrease with concentration increase. It is worth noting the change in n_m values when the concentration increases, from 0.99 (similar to a capacitor, where $n = 1$, as previously indicated) to values more similar to a Warburg impedance (in this case, $n = 0.5$), which corresponds to a diffusion process according to Fick's law. These results may be interpreted assuming that at low concentration the capacitive effects are predominant, but at higher concentrations diffusion may occur.

The experimental values corresponding to the whole NUP membrane/H_3PO_4 solution system were fitted to a parallel resistance–capacitor association ($R_{em}C_{em}$) where R_{em} and C_{em} values include both the membrane and the electrolyte contribution. R_m values were obtained by subtracting those corresponding to the electrolyte solution: $R_m = R_{em} - R_e$.

Variation of R_m with concentration for both electrolytes is shown in Fig. 5. The exponential decrease of the NUP membrane resistance with concentration increase is similar to that reported in the literature for different inorganic and polymeric membranes [11, 12], and is attributed to electrolyte invasion into the membrane matrix. The resistance values obtained for the HUP membrane in contact with H_3PO_4 solution are also indicated (data from [10]), and a comparison of these values with those obtained for the system NUP membrane/H_3PO_4 solutions, indicates that, at high concentrations, resistance values for both membranes are very similar, corresponding to the high HUP content in the NUP membrane indicated above.

Because of the concentration dependence of resistance values shown in Fig. 5 and, in order to determine the resistance of the membrane alone, no contribution from the electrolyte solution in the membrane matrix, R_m values were fitted to the following expression [13]:

$$R_m(C) = R_0 - AC^b \quad (2)$$

where A and b are empirical parameters.

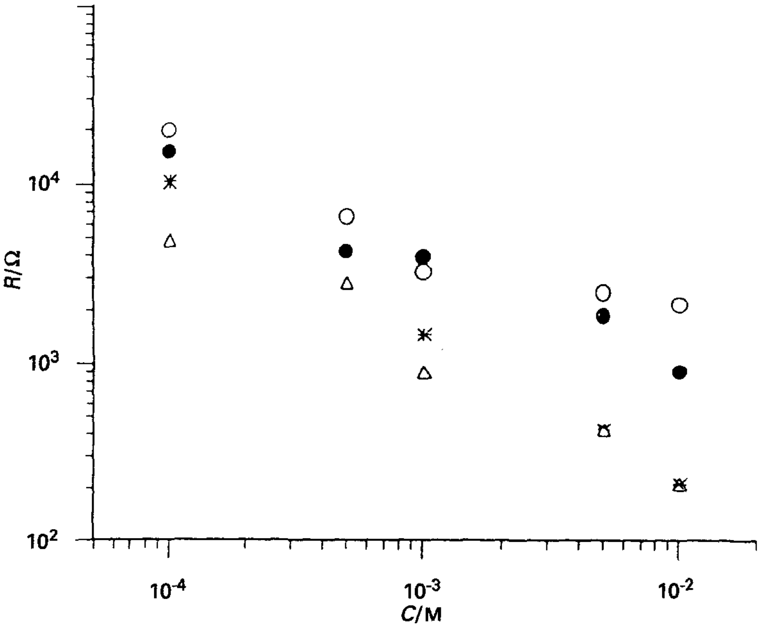

Fig. 5. Variation of the resistance, R_m, with concentration: (●) $UO_2(NO_3)_2$; (○) $NH_4H_2PO_4$, (∗) H_3PO_4. HUP membrane and H_3PO_4: (△).

Table 2. Comparison of the dry membrane resistance, R_d, and the membrane matrix resistance, R_0, obtained by Equation 2, at 25° C

System	*$R/\Omega\,cm^{-2}$*
Dry NUP memb., (R_d)	1.1×10^5
NUP-memb./$UO_2(NO_3)_2$, (R_0)	1.0×10^5
NUP-memb./$NH_4H_2PO_4$, (R_0)	1.3×10^5

This kind of relationship between resistance and concentration indicates that it is possible to separate the electrical resistance measured for the wet membrane into two parts: (i) the contribution of the inorganic precipitate (R_0), which is a membrane characteristic and is independent of concentration, and (ii) the contribution of the electrolyte embedded in the inorganic material, which depends on the salt concentration. The calculated R_0 resistance value for the dry membrane, R_d, at the same temperature is also indicated. A comparison of these values show good agreement between both sets of results.

4. Conclusions

In conclusion, impedance spectroscopy (IS) is a powerful technique for studying heterogeneous systems with different dielectric properties, such as a membrane/electrolyte system. In these cases, IS measurements permit determination of the electrical contributions of both membrane phase and electrolyte solutions separately. The equivalent circuits associated with NUP membranes (dry and wet) have been determined, and the values of some characteristic electrical parameters have been obtained. For both kinds of membrane similar circuit elements were obtained (resistance and nonideal capacitor). It was also found that the ionic resistance depends on the electrolyte contacting the membrane. The different behaviour of the wet NUP membrane when H_3PO_4 solutions are involved is due to a different conduction mechanism, which is mainly protonic for H_3PO_4 solutions and ionic for the others. A comparison of the membrane matrix resistance values (without salt concentration) with that obtained with the dry sample was also made and good agreement between the results was obtained.

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References

[1] R. Pozas-Tormo, L. Moreno, S. Bruque and M. Martinez-Lara, *Can. J. Chem.* **64** (1986) 30.
[2] R. Pozas-Tormo, S. Bruque, M. Martinez-Lara and M. Moreno, *ibid.* **66** (1988) 2849.
[3] M. Pham-Thi, Rh. Adet and G. Velasco, *Appl. Phys. Lett.* **48** (1986) 1348.
[4] J. Benavente, S. Bruque and Martinez, *Colloids & Surfaces* **58** (1991) 183.
[5] A. Cabeza, M. Martinez, J. Benavente and S. Bruque, *Solid State Ionics* **51** (1992) 127.
[6] J. Benavente, A. Cabeza, M. Martinez and S. Bruque, *ibid.* **52** (1993) 175.
[7] G. Alberti, *Pontificia Academia Sci.* (Citá del Vaticano) **40** (1976) 629.
[8] C. Criado, *Doctoral thesis.* Universidad de Málaga (1991).
[9] A. R. West, 'Solid State Chemistry and its Applications', John Wiley & Sons, New York (1984).
[10] J. R. Macdonald, 'Impedance Spectroscopy', John Wiley & Sons, New York (1987).
[11] B. A. Boukamp, *Solid State Ionics* **20** (1986) 31.
[12] P. G. Bruce and M. Y. Saidi, SSI-8 International Conference, Lake Louise, Canada (1992).
[13] J. Benavente, J. R. Ramos, S. Bruque and M. Martinez, 'Solid State Ionics III', (ed. Material Research Society) (1993).
[14] J. Benavente and G. Jonsson, *J. Membrane Sci.* **80** (1993) 275.