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Study of the Transport of Multivalent Metal Cations through Cation-Exchange Membranes by Electrochemical Impedance Spectroscopy

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Abstract**—**In the present work, Electrochemical Impedance Spectrocopy (EIS) is applied to study the transport of different metal cations through a cation-exchange membrane. This technique enables the identification of the ionic-transport characteristics and to distinguish between different transport mechanisms occurring at different current density ranges. The impedance spectra are dependent on the applied dc current density, on the type of cation and on the concentration.

When the applied dc current density increases, the diameter of the impedance spectra loops increases because all the components of membrane system resistance increase. The diameter of the impedance plots decreases in the order of Na(I), Ni(II) and Cr(III) due to the increased interactions between the negatively charged sulfonic groups of the membrane and the cations with greater charge. Nyquist plots are shifted towards lower values of the real impedance, and its diameter decreases with the increase of concentration due to the decrease of the solution resistance.

Keywords**—**Ion-exchange Membranes, Electrochemical Impedance Espectroscopy, Multivalent Metal Cations.

I. INTRODUCTION

THE metal finishing industry is known for its intensive consumption of water [1], [2]. Recently, electrodialytic techniques have arisen as promising procedures for the regeneration of the waste waters discharged from these industries [3]. Thus, the transport of different monovalent cations involved in those processes such as Na^+ or K^+ through cation-exchange membranes (CEMs) has been intensively studied. However, electrochemical operations in which ion-exchange membranes are used to remove multivalent ions arise as a promising and clean alternative to other technologies, since they could be potentially applied to treat waste effluents with undesirable effects on the environment. Among the target effluents containing ionic contaminants, those with transition metal cations in their composition deserve special interest principally because of the great value of the recovered metals and due to the necessity of reducing their discharge to the environment.

Transition metals have special characteristics owing to the fact that their most common oxidation states are multivalent cationic forms and due to the larger size of their ions in comparison with that of monovalent ones. Besides the size and charge effects of cations on their transport through conducting membranes, they may also affect the electrolyte characteristics thus involving possible changes in the pattern of the ionic transport near the membrane when concentration polarization takes part in the process. Finally, it should be stressed that the type of co-ion and the different chemical equilibria involving multivalent cations may imply the concurrence of different complex species of varying charge, shape and transport properties. This induces significant alterations in the transport through conducting membranes as a result of the change in the predominant species present in the solution layers next to the membrane and in the membrane phase, which is determined by the pH and the chemical equilibria involved [4]-[6].

For these reasons, the study of the transport of multivalent ions through CEMs is important in order to gain a better knowledge on the process.

The transport phenomena of the ion-exchange membrane (IEM) systems have mainly been studied using current–membrane potential curves. However, unknown transport phenomena such as electroconvection, water dissociation or fraction of conducting region of IEMs are out of the field that can be investigated using current–membrane potential curves. Then, new methods are required to understand such complex transport phenomena.

Electrochemical impedance spectroscopy (EIS) has been proven to be a valuable tool for the characterization of polymer membranes. In this way, EIS has been used to characterize the surface porous structure and pore size distribution of ultrafiltration membranes [7], to characterize the sub-layers structure of composite membranes [8], [9], to evaluate the kinetic parameters of water dissociation reaction and the structure of bipolar junction [10], [11]. In addition, EIS also provides valuable information on ion transport process through membranes [12] and fouling phenomena of electrodialysis processes [13]-[15].

In this work, in order to achieve a better understanding of the transport mechanisms which take place in IEMs, electrochemical impedance spectroscopy is applied to study the transport of various metal cations through a cation-exchange membrane.

II. EXPERIMENTAL

A. Experimental Test Rig

The experimental test rig was composed of an

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electrodialytic cell, which consisted of three different compartments made of PVC separated by the AEM and the CEM as shown in Fig. 1. Each compartment has a volume of 130 ml and the effective area of the membranes used for the electrochemical characterization tests was 1 cm^2. Experiments were carried out at room temperature (25ºC) and without stirring. The three compartments were filled with the same solution, so as to reduce the effect of diffusive transport between different compartments. Two Ag/AgCl reference electrodes immersed in Luggin capillaries were installed next to the membrane surface to measure the voltage drop across the CEM. Two graphite electrodes were used as anode and cathode respectively.

B. Membranes

The CEM employed in the experiments was a Nafion® 117 (Du Pont) membrane. The Nafion membrane was a homogeneous membrane made of tetrafluoroethylene in which the fixed ion-exchanging sites are sulphonic ionizable groups covalently attached to the side chains. On the other hand, the anion exchange membrane (AEM) used in the experimental tests was a heterogeneous Ionics AR-204-SZRA-412 membrane (from Ionics Inc.). The transport of cations through the CEM will be the main issue of the present work while the utilization of the AEM will serve to minimize alterations during the electrochemical measurements due to the H$^+$ ions generated at the anode. Prior to performing each experiment, membranes were equilibrated during 24 h under stirring immersed in the solutions of the same concentration as those required in the experiments. After this period, the fixed charges are supposed to be in equilibrium with the counter-ions present in the solution and membranes are ready to be used in the experiments.

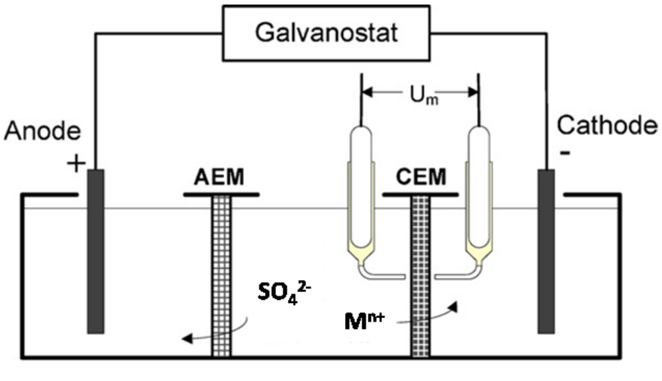

Fig. 1 Experimental test-rig used during the electrochemical measurements

C. Materials and Reagents

Different solutions of Na(I), Ni(II) and Cr(III) with concentrations of 0.001 M and 0.01 M were prepared from their respective sulfate salts. All the reagents employed in the experiments were of analytical grade. For the preparation of solutions, distilled water was employed.

D. Electrochemical Measurements

Firstly, current-membrane potential curves for each solution composition were obtained. For this, different values of current were imposed between the two graphite electrodes by a potentiostat/galvanostat (Autolab, PGSTAT 20) and the membrane potential (U_m) was measured through the Ag/AgCl reference electrodes.

EIS measurements were performed after obtaining the current-membrane potential curves at different values of the applied dc current density. The values of applied current density were selected differently depending on the aim of each experiment and were calculated in relation to the limiting current density values (i_{lim}) of the membrane-solution system obtained from the current-membrane potential curves: 0 mA/cm^2, 0.5 i_{lim}, 0.8 i_{lim}, i_{lim} and 1.2 i_{lim}. The measurements were made in the frequency range from 10 kHz to 3 mHz. Ten frequencies per decade were scanned using a sinusoidal signal of 1 mA peak-to-peak. For the measurement of the membrane voltage drop in the EIS experiments two Ag/AgCl reference electrodes immersed in Luggin capillaries were installed next to the membrane surface, as shown in Fig. 1.

III. RESULTS

Fig. 2 shows the current-membrane potential curves of the CEM for the solutions of the three cations at the same concentration of 0.01 M. These curves have been obtained by plotting the current density against the U_m. As found in the literature, three different regions characterize the current-membrane potential curves [16]. A quasi-ohmic variation of the current–membrane potential curves in the lower voltage range (region 1), followed by a plateau, from which the value of the limiting current density (i_{lim}) is defined (region 2), and then, an increase of the current density (region 3).

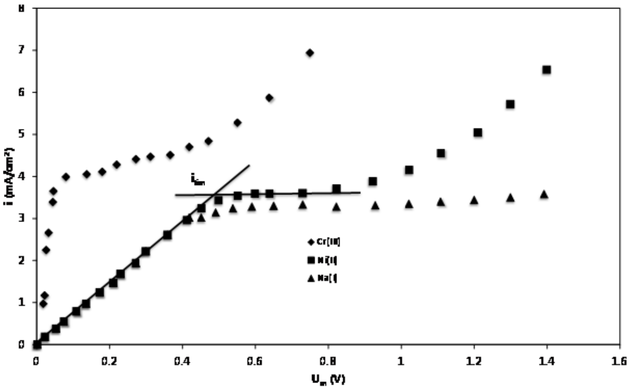

Fig. 2 Current-membrane potential curves obtained for solutions 0.01 M of Na_2SO_4, $NiSO_4$ and $Cr_2(SO_4)_3$

The formation of the plateau region in the current-membrane potential curve is a consequence of the ion depletion, mass transfer is limited by concentration polarization phenomena and the resistance of the membrane system increases, which leads to the formation of a plateau region in the current-membrane potential curve. The i_{lim} value can be experimentally calculated from the cross-point of the tangents drawn from the first and the second region of the curves. The latter region is known as the overlimiting region, which is originated due to different concurring mechanisms, such as water splitting, electroconvection or gravitational convection. Some aspects of these overlimiting mechanisms of mass transfer still remain unclear and constitute the subject of several publications in the recent time [17], [18].

Figs. 3 and 4 show the impedance spectra when the stationary current density flowing across the membrane increases, for solutions of Cr(III) 0.001 M and Na(I) 0.001M respectively. In these figures the real part of the impedance, Z', is plotted against the imaginary part of the impedance, Z'', with the angular frequency, ω, as a parameter increasing from the right to the left of the plot (Nyquist plots).

As can be seen in these figures, the typical intersection point of the Nyquist plot with the real axis, Z', at high frequencies, which is related to the ohmic resistance of the system polarized by stationary current is not shown for these membrane/solution systems. This can be due to the higher water (or solution) uptake presented by the CEM used in this work. Similar results have been obtained for other membranes [19]. On the other hand, at high frequencies, the Niquist plot depends rather slightly on the current density, at least at current densities below 0.5 i_{lim}.

At i=0 mA/cm^2 in the case of the solutions of Ni(II) and Cr(III), and i < 0.5 i_{lim} in the case of Na(I) solutions, an inductive loop is observed in the low frequency range. This inductive loop is related with the adsorption of metallic ions on the surface. However, when the applied dc current density increases three overlapped capacitive loops can be observed. The diameter of these loops increases with the de current density, because with increasing dc current density, all the components of membrane system resistance increase.

IEM systems dominantly comprised three sublayers, the ion-exchange membrane immersed in the solution, the electrical double layers (i.e., heterogeneous transport effect), and the diffusion boundary layers. As a consequence of Donnan exclusion, when a current passes through an IEM, charge is transported through the membrane by counter ions, while in the bulk solution current is carried by both positive and negative ions. The difference in ion transport number between the bulk solution and the membrane results in the building up of diffusion boundary layers at the membrane surface. The concentration decreases at one side of the membrane and increases at the other side of the membrane.

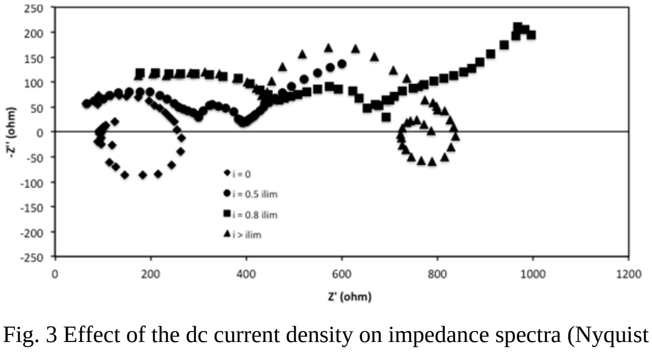

Fig. 3 Effect of the dc current density on impedance spectra (Nyquist plots) of the CEM in 0.001 M $Cr_2(SO_4)_3$

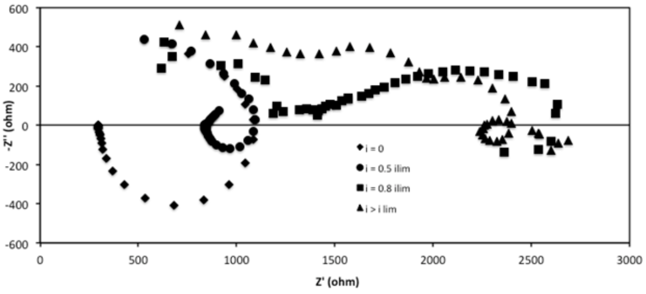

Fig. 4 Effect of the dc current density on impedance spectra (Nyquist plots) of the CEM in 0.001 M Na_2SO_4

EIS allows distinguishing between these different layers because the different layers respond differently to the applied current at different frequencies. At the high frequency range when there is no phase shift between voltage and current and the Ohmic relation holds, the ohmic resistance of the polarized membrane system can be obtained [20]. When the frequency is decreased the contribution of the interfacial ionic charge transfer from the solution phase through the electric double layer to the membrane can be extracted. Ions start to migrate through the interfacial double layers. The resistance and capacitance of ionic transport through these double layers become visible.

When a very low frequency current is applied, in addition to the membrane and the ionic transfer through the electrical double layer, also concentration gradients in the diffusion boundary layers adjacent to the membrane become visible. The electrolyte concentration decreases at the dilution compartment interface and increases at the concentration compartment. The resistance of the dilution compartment diffusion boundary layer (DBL) increases while that of the concentration compartment decreases. This results in an increase of the total ohmic resistance: the diameter of the first semicircle increases with increasing dc current density, as it can be seen in Figs. 3 and 4. The distortion of the semicircle is due to the combination of generally three different geometric arcs associated with ion transfer in the membrane and two adjoining DBLs.

Finally at applied dc overlimiting current densities, an inductive loop appears in the Nyquist plots at low frequencies as can be seen in Figs. 3 and 4. This behavior could be related to hydrodynamic instabilities originated either by heterogeneities at the membrane surface or by electroconvection mechanisms occurred at high current densities, which may partially destroy the polarization layer [21]. According to the electroconvection theory, electric field lines in the solution layer adjacent to the surface of the ion-exchange membranes comprising patches of varying ion conductance are distorted. The interaction of space charges with the electric field gives rise to a spatially inhomogeneous bulk force, which is bound to set in motion the fluid in the depletion diffusion layer. As a result, an additional driving force for ion transport toward the membrane surface is created, leading to the possibility of an overlimiting current. The electroconvective forces may disturb the concentration gradient in the DBL, resulting in attenuating concentration polarization. Hence, it is expected that the electroconvective effects may decrease the resistances arising from the heterogeneous transport and DBL due to the disturbance of the formation of a space charge region and the relieved concentration gradient, respectively causing a decrease in the diameter of the impedance spectra.

Impedance spectra are also affected by the concentration of the electrolyte. The shift of the loops toward lower real impedance with the increase of concentration is due to the decrease in solution resistance. It is well known that resistance of ion-exchange membranes should be independent of solution concentration due to the electroneutrality between the counterions and the fixed exchangeable sites. It is noted in Fig. 5 that a change in the diameter of loops also occurs. The diameter decreases as the concentration of the electrolyte increases.

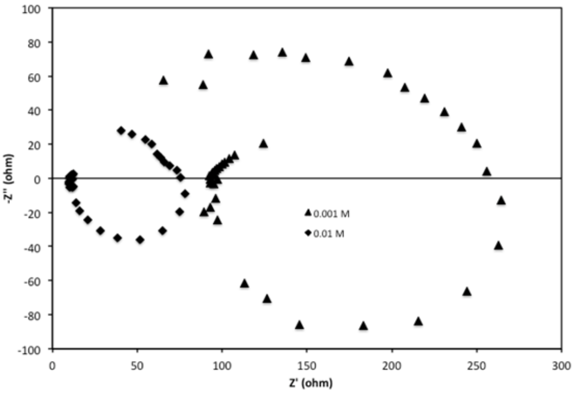

Fig. 5 Effect of the electrolyte concentration on impedance spectra (Nyquist plots) of the CEM at a dc current density of 0 mA/cm^2

Fig. 6 shows the impedance plots of the CEM in different electrolyte solutions with the same concentration (0.001 M). As can be seen in this figure, the diameter of the impedance plots decreases in the order of Na(I), Ni(II) and Cr(III). One possible explanation of this behavior can be formed according to the Donnan exclusion. Imaginably, the negatively charged membrane surface resulting from the dissociation of sulfonic acid groups and the relevant specific adsorption of ions on the membrane surface make the transport of Na^+ more difficult than that of Cr^{3+} due to their difference in electrostatic attraction.

In the active layer, the polymer chains may keep as far away as possible from each other due to the electrostatic repulsion effect due to the existence of the dissociated functional groups. Hence, the relatively big cations, such as Cr^{3+}, can also transport through the membrane relatively easily. Besides, the Donnan effect is also responsible for its easier transport through the membrane than Ni^{2+} and Na^+.

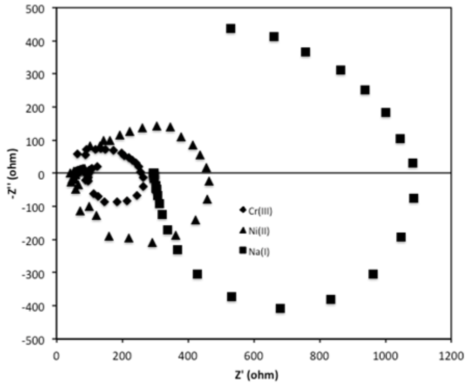

Fig. 6 Effect of the electrolyte composition on impedance spectra (Nyquist plots) of the CEM when the electrolyte concentration is 0.001M and the applied dc current density is 0 mA/cm^2

IV. CONCLUSION

In this study, the measurements of the electrochemical impedance spectra of a CEM in different electrolyte solutions (Na_2SO_4, $NiSO_4$ and $Cr_2(SO_4)_3$) with concentration of 0.001 M and 0.01 M are carried out. Different time relaxations can be observed clearly in EIS, which indicate that the membrane embraces an asymmetric structure and are corresponding to the active layer and the supporting layer, respectively.

Experimental results show that the resistance of the active layer is influenced by the concentration and ion species of electrolytes. For the different cations the corresponding resistances of the active layer take on a sequence of $Na^+ > Ni^{2+} > Cr^{3+}$.

It was confirmed that the IEM systems dominantly comprised three sublayers, the ion-exchange membrane immersed in the solution, the electrical double layers (i.e., heterogeneous transport effect), and the diffusion boundary layers, based on several impedance spectra of the IEM systems.

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