Research Article

Modification of Nafion Membranes by IL-Cation Exchange: Chemical Surface, Electrical and Interfacial Study

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Bulk and surface changes in two proton-exchange membranes (Nafion-112 and Nafion-117) as a result of the incorporation of the IL-cation *n*-dodecyltriethylammonium (or DTA$^+$) by a proton/cation exchange mechanism after immersion in a DTA$^+$ aqueous solution were analysed by impedance spectroscopy (IS), differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS), and contact angle measurements performed with dry samples of the original Nafion and Nafion-DTA$^+$-modified membranes. Only slight differences were obtained in the incorporation degree and surface chemical nature depending on the membrane thickness, and DTA$^+$ incorporation modified both the hydrophobic character of the original Nafion membranes and their thermal stability. Electrical characterization of the dry Nafion-112 membrane was performed by impedance spectroscopy while different HCl solutions were used for membrane potential measurements. A study of time evolution of the impedance curves measured in the system "IL aqueous solution/Nafion-112 membrane/IL aqueous solution" was also performed. This study allows us monitoring the electrical changes associated to the IL-cation incorporation in both the membrane and the membrane/IL solution interface, and it provides supplementary information on the characteristic of the Nafion/DTA$^+$ hybrid material. Moreover, the results also show the significant effect of water on the electrical resistance of the Nafion-112/IL-cation-modified membrane.

1. Introduction

As it is well known, ionic liquids are room temperature molten salts (RTILs) with very low vapour pressure and composed only of ions. These salts are characterized by weak interactions owing to the combination of a large cation and a charge-delocalized anion. Ionic liquids exhibit very interesting properties such as the solubilization of a large range of organic molecules and transition metal complexes or the possibility of their repeated use due to reduced environmental loss, while their good thermal stability tolerates reactive processes at high temperatures favouring a faster kinetic [1–4]. Various kinds of salts can be used to design an ionic liquid with tailoring properties for a given application, but typical IL-cations are imidazolium and quaternary ammonium salts, while hexafluorophosphate is a common anion. Due to their particular characteristics, the use of ILs in many areas of technology and science has increased lately

and they can be used as solvents for organic reactions and catalysis, CO_2 capture devices, selective separation of chemical species, dissolution of natural biomaterials, energy conversion, bioscience, and so forth [5–7]. Miscibility of ionic liquids with water is also a point of interest and it seems to be mostly determined by the associated anion. RTILs with anions such as halides, BF_4^-, nitrate, and perchlorate, are water miscible, while those with PF_6^- AsF_6^-, and so forth are immiscible. The activity of water seems to be higher in the hydrophilic ionic liquid than in the hydrophilic one and thus water will partition to the gas-liquid interface of the immiscible ionic liquid more than in the miscible one [8].

The conductivity of ionic liquids is also being studied for their application in batteries and fuel cells. As it is well known a fuel cell basically consists of two electrodes sandwiching a proton-conducting membrane (or MEA). Nafion is the polymeric material widely used as a reference in proton fuel cell (PEMFCs) due to its high ionic conductivity as well as its

mechanical and chemical stability at room temperature, and it consists of a backbone of polytetrafluoroethylene (PTFE) with sidechains of perfluorovinylether (PFAE) with a sulfonic group end. Nafion combines the high hydrophobicity of the PTFE with the great hydrophilicity of the sulfonic groups at intervals along the chain, which facilitate the transport of ions and give it the character of a polymer electrolyte structure [9, 10]. The mechanism of transport across the Nafion membranes seems to be associated to both the presence of water and its state within the membrane structure [11, 12], which is a point of significant importance for its application in PEMFCs due to the conductivity decrease found in Nafion membranes at temperature above 80°C, which is associated to the Nafion membrane water loss. For this reason some authors have proposed the modification of Nafion membranes by incorporation of ILs as a way to reduce the Nafion limitation at temperature higher than 120°C as a result of water loss and/or to minimize other kinds of electrode/membrane surface interactions due to electrode or catalyst changes [13–16].

In this context, it should be pointed out the significant number of papers published in recent years dealing with original and modified proton-exchange membranes conductivity and permeability, which are considered key parameters for their applications in proton and methanol (DMFCs) fuel cells, respectively [16–22]; particularly, a reduction of around two orders of magnitude in the methanol permeability across Nafion/IL-modified membranes attributed to the decrease of the methanol crossover associated to the presence of the IL-cation has already been reported [23]. However, a more reduced number of papers on surface study of both original and modified membranes are published, although membrane surface represents the interface between two different transport media, which can be solid/solid in the case of fuel cells or solid/liquid when supported liquid membranes (SLMs) or other electrochemical devices proposed for selective solute separation are considered [15, 24, 25].

This work studies both surface and bulk phase changes caused in two polytetrafluoroethylene sulfonate Nafion membranes (both in protonated form but different thickness) as a result of the incorporation of a IL-cation (n-dodecyltriethylammonium or DTA$^+$) by cation-exchange mechanism after their immersion in a water DTA$^+$ (Nafion/DTA$^+$ samples). Surface changes associated to IL-cation incorporation in the Nafion membranes were studied by X-ray photoelectron spectroscopy (XPS) analysis and contact angle measurements, while its effect on the thermal stability of the Nafion membranes was determined by analyzing the DSC curves. Electrical modifications in dry Nafion/IL-cation samples were determined by impedance spectroscopy (IS) measurements, but proton transport numbers across the membrane were obtained from membrane potential measurements carried out with the membranes in contact with HCl aqueous solutions. Moreover, IS technique was also used for the electrical characterization of the *IL solution/Nafion 112 membrane/IL solution* system, which was performed at different times ($0 \leq t(h) \leq 40$) as a way of monitoring kinetic changes in the membrane and the membrane/IL-solution interface and to estimate of interfacial effects.

2. Experimental

2.1. Materials. A protonated Nafion membrane from Dupont (USA), Nafion-112, was modified by incorporation of the IL-cation n-dodecyltrimethylammonium (DTA$^+$) through H$^+$/cation exchange mechanism [15]. The membrane has the following characteristics given by the manufacturer: nominal thickness of 51 μm, density 2000 kg/m^3, ionic conductivity 8.3 S/m, acid capacity 0.89 meq/g, and initial water content 5 wt%. To see the effect of membrane thickness on the IL-cation incorporation degree and membrane surface characteristics another similar membrane with a thickness of 180 μm (Nafion-117 sample) was also studied. The DTA$^+$ (C$_{12}$H$_{25}$N(CH$_3$)$_3$$^+$) IL-cation characteristics are molecular weight of 228 g/mol and molar volume (estimated by Schroeder' method [26]) of 350 cm^3/mol and it was supplied by TCI Instrument (England). Although DTA$^+$Cl$^-$ is not an ionic liquid but a quaternary amine, the DTA$^+$ cation is typical of common ILs.

Samples of Nafion-112 and Nafion-117 membranes without any previous pretreatment were immersed in a 60% DTA$^+$Cl$^-$ aqueous solution and variations in the liquid of pH and conductivity were measured using a pH conductivity meter (model 720 A, Orion) and a conductivity meter (model 960, Schott Instruments), respectively. Both the pH and the conductivity were measured before and after DTA$^+$ incorporation to determine the concentration of ions inside the membranes. The incorporation degree, ID (mol/m^3), was determined by the following expression: ID = $(K_t - K_0)/\lambda_{H}{}^+$, where K_0 and K_t represent the conductivity of the IL-aqueous solution at times 0 and t, respectively, while $\lambda_{H}{}^+$ is the proton conductivity; taking into account the solution volume and the ion-exchange capacity of a given membrane the percentage of cation incorporation (mol/membrane mass) was determined. All these measurements were performed at the laboratory of Professor J. Crespo, REQUIMTE/CQFB, FCT, Universidade Nova de Lisboa (Portugal).

2.2. XPS Measurements. The chemical characterisation of the surface of the studied modified membranes and the Nafion-112 was performed by XPS. A Physical electronics spectrometer (PHI 5700) was used, with X-ray Mg Kα radiation (300 W, 15 kV, 1253.6 eV) as the excitation source. High-resolution spectra were recorded at a given take-off angle of 45° by a concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Under these conditions, the Au 4$f_{7/2}$ line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu 2$p_{3/2}$, Ag 3$d_{5/2}$, and Au 4$f_{7/2}$ photoelectron lines at 932.7, 368.3, and 84.0 eV, respectively. Charge referencing was done against –CF$_2$-carbon of Nafion (C 1s, 292.0 eV).

Membranes were mounted on a sample holder without adhesive tape and kept overnight at high vacuum in the preparation chamber before being transferred to the analysis chamber of the spectrometer for testing. Each spectral region was scanned for several sweeps until a good signal-to-noise ratio was observed. The pressure in the analysis chamber was maintained lower than 5×10^{-6} Pa. PHI ACCESS

ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves and following the methodology described in detail elsewhere [24], in order to determinate more accurately the binding energy (BE) of the different element core levels. Atomic concentration percentages of the characteristic elements of the surfaces were determined taking into account the corresponding area sensitivity factor [25] for the different measured spectral regions. Membrane samples were irradiated for a maximum time of 20 min to minimize possible X-ray damage.

2.3. Contact Angle Measurements.

The hydrophobic/hydrophilic character of the membrane surfaces was determined from contact angles measurements, and they were performed with a Teclis T2010 instrument equipped with a video system. Membrane samples were mounted on glass slides to provide a flat surface for analysis. The drop method was used to measure the contact angle of deionized water on the surface of the membranes at ambient temperature. Dry samples of Nafion-112, Nafion-117, Naf-112/DTA$^+$, and Naf-117/DTA$^+$ membranes with any pretreatment were analyzed.

2.4. Thermal Analysis.

TG/DSC analysis was performed with a thermobalance TGA/DSC1 of Mettler. A working air flow of 50 cm^3/min was used for measurements carried out under most similar atmospheric conditions. The TG profile was collected in the $30 < T$ ($^\circ$C) < 750 temperature range with a heating rate of 10°C/min, using an open platinum pan of 70 μL. The thermal analysis was performed with dry samples of all the membranes with any pretreatment.

2.5. Impedance Spectroscopy and Membrane Potential Measurements.

Impedance spectroscopy (IS) measurements with dry Naf-112/DTA$^+$ and Naf-117/DTA$^+$ samples at equilibrium IL-cation incorporation were performed in a cell consisting of a Teflon support on which two Pt electrodes were placed and screwed down [27]. However, an electrochemical cell similar to that described in [28], which consists in two glass half cells with the membranes placed in the middle and separating the IL-solutions was used for IS measurements with both the IL-solution and the IL-solution/membrane/IL-solution. Time evolution of the impedance curves measured in this latter system allows the monitoring of dynamical changes in both the membrane bulk phase and the membrane/IL-solution interface.

With both cell systems, IS measurements were performed using a response frequency analyzer (Solartron 1260, England) controlled by a computer. 100 different frequencies in the range 1 Hz–10^7 Hz at a maximum voltage of 0.01 V were measured, and the experimental data were corrected by software, the influence of connecting cables, and other parasite capacitances.

The electromotive force, ΔE, between two HCl solutions of concentrations c_1 and c_2 at both sides of the membranes caused by the concentration gradient was measured by two reversible Ag/AgCl electrodes connected to a digital
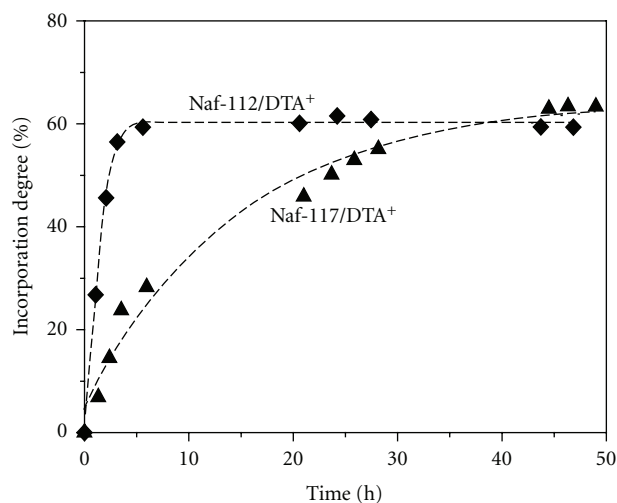

FIGURE 1: Time dependence of DTA$^+$ incorporation into the structure of ($\blacklozenge$) Nafion-112 membrane and ($\blacktriangle$) Nafion-117 membrane.

voltmeter (Yokohama 7552, 1 GΩ input resistance). Measurements were carried out by keeping the concentration of the solution at one membrane side constant ($c_1 = 0.001$ M) and gradually changing the concentration of the solution at the other side, c_2, from 2×10^{-4} M to 7.5×10^{-3} M [27].

3. Results and Discussion

3.1. Incorporation of DTA$^+$ Cation in the Nafion Membranes.

The dynamic of IL-cation inclusion into Nafion-112 and Nafion-117 membranes as a function of the contact time is shown in Figure 1, where the incorporation degree is expressed as a % of the cationic exchange capacity of Nafion samples. Differences in the kinetic of DTA$^+$ incorporation depending on the thickness of the Nafion membrane thickness were obtained, which seems to be related to the time necessary to reach an equilibrium state (around 5 h for Nafion-112 and 30 h for Nafion-117), while the equilibrium value for DTA$^+$ incorporation hardly depends on the membrane (59.6% for Naf-112/DTA$^+$ and 61.4% for Naf-117/DTA$^+$), which allows the estimation of an average value of (60.5 $\pm$ 0.5)% for Nafion-DTA$^+$ aqueous solution system.

3.2. Membrane Surface Characterization.

Surface chemical changes associated to the inclusion of the IL-cation DTA$^+$ into the structure of the Nafion membranes was studied by XPS analysis, which allows the determination of the atomic concentration percentage (A.C. %) of the elements present on the surfaces of both Nafion and Nafion/IL-modified membranes, which were obtained from high resolution spectra of the main photoelectron peaks (C 1s, O 1s, F 1s, S 2p, and N 1s). Figure 2 shows the chemical structure of Nafion, while Table 2 presents the atomic concentration percentages (A.C.) of the characteristic elements found on the surface of the Nafion-112 and Nafion-117 membranes and the Nafion/IL-cation modified samples at equilibrium state, that is, after more than 40 h in contact with the IL-cation aqueous solution; small
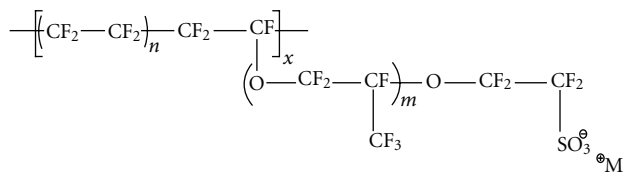
$$-\left[\!\left(CF_2-CF_2\right)_{\!n}-CF_2-CF\right]_{\!x}$$

FIGURE 2: Chemical structure of Nafion.

TABLE 1: Atomic concentration percentages of the characteristic elements found on the membranes surfaces.

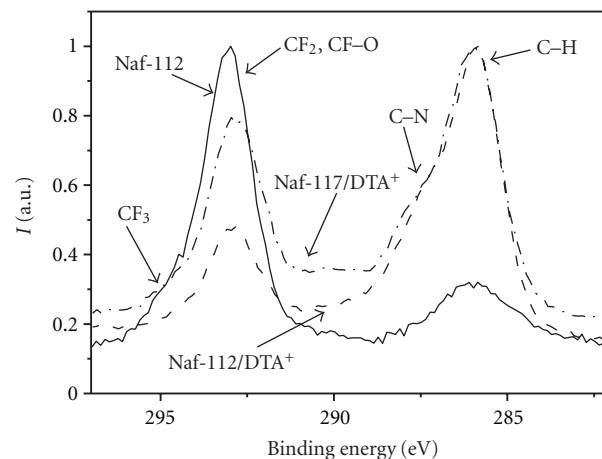| Sample	C%	O%	F%	S%	N%
Nafion (theoretical)	30.8	7.7	60.0	1.5	—
Naf-112	39.0	6.6	53.4	1.0	0.2
Naf-117	41.4	6.4	50.5	0.9	0.4
Naf-112/DTA$^+$	54.5	11.5	27.2	1.1	2.8
Naf-117/DTA$^+$	49.5	9.8	36.2	1.1	1.5

TABLE 2: Average values of the contact angles for original and IL-modified membranes.

Membrane	Average contact angle (°)
Nafion-112	91 ± 2
Nafion-117	91 ± 3
Naf-112/DTA$^+$	74 ± 6
Naf-117/DTA$^+$	85 ± 5

FIGURE 3: Comparison of the C 1s core level spectra obtained for Nafion-112, Naf-112/DTA$^+$, and Naf-117/DTA$^+$, membranes (both modified membranes after 48 h in contact with the IL-solution).

percentages <0.5% of other elements such as chlorine and silicon were also found and they are associated to surface contamination. For comparison, the theoretical values for the Nafion membrane calculated by its chemical formulae are also indicated in Table 2, and only slight differences between theoretical and experimental values for both Nafion membranes were obtained, which could be due to membranes surfaces contamination, particularly to the presence of adventitious carbon [29].

As can be observed in Table 1, the concentration of fluorine (Nafion characteristic element) in both modified membranes is significantly lower than in the original samples due to the membrane surface coverage by the IL; however, high experimental carbon percentage was obtained for both modified samples, which could be associated to DTA$^+$ component, but the result of surface contamination indicated above might affect the A.C. of this element.

This point can be discriminated by considering the XPS spectra, which give information on the chemical interactions among the different elements on the solid surface. Figure 3 shows the C 1s core level spectrum for Nafion-112 and both Nafion/IL-cation modified membranes (Naf-112/DTA$^+$ and Naf-117/DTA$^+$) and certain differences can be observed. The Nafion-112 sample shows three different photoemissions at binding energies (BE) of 291.8–292.0 eV (associated to CF$_2$ and CF–O) and at 284.8–285.0 eV (C–H bond), plus a small shoulder at 294.0 eV (CF$_3$). The C 1s spectra for both Nafion/DTA$^+$-modified membranes also present those peaks and shoulder, but another shoulder at 286.4 eV associated to C–N can also be observed [29, 30].

Surface modification of the Nafion membranes associated to the incorporation of the IL-cation might also affect its hydrophobic character, which can be determined by contact angle measurements. Figure 4 shows differences in the form of the water drops on the surface of the Nafion-112 membrane and the Naf-112/DTA$^+$ sample after 40 h of immersion in the solution, which is a clear indication of the superficial changes due to DTA$^+$ incorporation. Table 2 shows the average contact angle values obtained for the studied membranes; as can be observed practically the same values were obtained for original Nafion-112 and Nafion-117 membranes, but small differences were found between both IL-cation-modified samples presenting membrane Naf-112/DTA$^+$ a slightly more hydrophilic character, which also agrees with XPS results.

Since the results presented in this section only show slight chemical surface differences for both Nafion-IL-modified membranes related to the sample thickness, in the following section dedicated to the electrical effect of IL-cation modification only the Naf-112/DTA$^+$ membrane will be considered.

3.3. Thermal Characterization of Original and IL-Cation-Modified Membranes. The thermogravimetric profiles of the Nafion-112 and Nafion-117 pristine membranes show a weight loss of 79.76% between 320 and 470°C (for Nafion-117) and 72.8% between 310 and 480°C (for Nafion-112). The profile obtained for the Nafion-117 sample is similar to that observed by Di Noto et al. [31], although measurements were performed under different conditions (N$_2$ atmosphere in [31] and in air in this paper). Upon incorporation of DTA$^+$, the weight losses occur at higher temperatures: 85.8% between 340 and 520°C for Nafion-117/DTA$^+$ and 77.8% between 350 and 550°C for Nafion-112/DTA$^+$, which also includes the degradation of the DTA$^+$. According to DSC results the incorporation of DTA$^+$ seems to communicate higher thermal stability to the studied membranes, which is reflected by the higher finishing decomposition temperatures
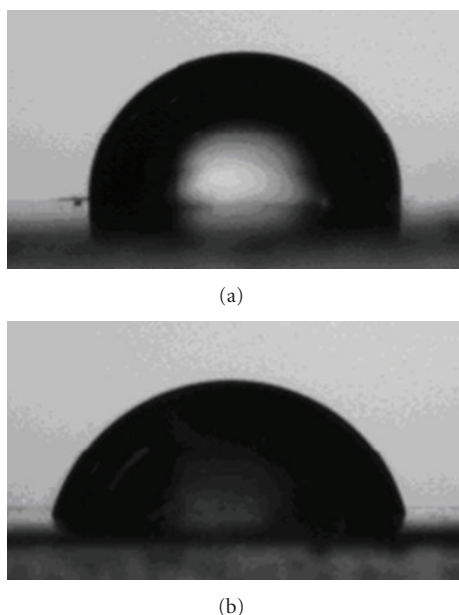
(a)

(b)

FIGURE 4: Differences in the hydrophobic character of (a) Nafion-112 and (b) Naf-112/DTA$^+$ membranes by the comparison of water-membrane surfaces contact angles.
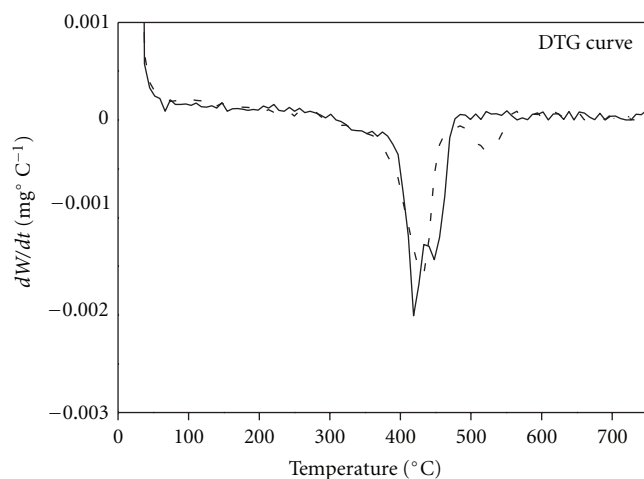

FIGURE 5: DTG profiles for Nafion-117 (solid line) and Nafion-117/DTA$^+$ (dashed line) membranes.

for membranes containing DTA. The DTG profiles also confirm this point as can be observed in Figure 5, where a comparison between Nafion-117 and Nafion-117/DTA$^+$ membranes is presented. The minima of the DTG curve for Nafion-117/DTA$^+$ membrane are shifted to higher temperatures in comparison to those observed in the DTG curve for the pristine Nafion-117.

3.4. Electrical Characterization of the Naf-112/DTA$^+$ Membrane. The evaluation of the electric modification of Nafion-112 membrane by IL-cation incorporation was performed by
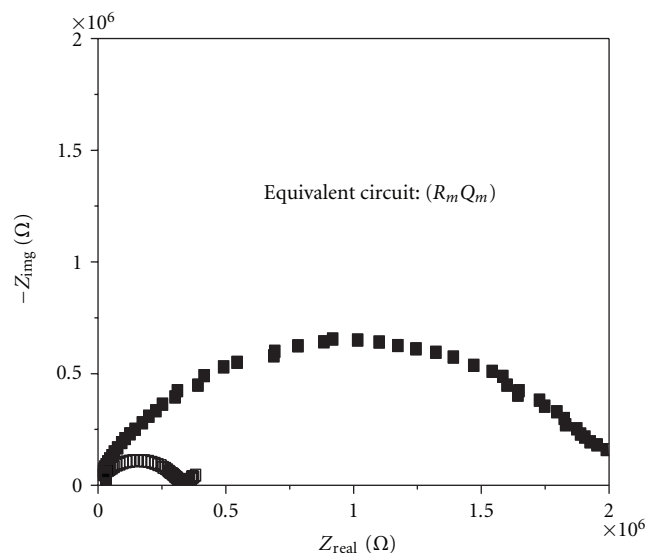

FIGURE 6: Nyquist plot ($-Z_{img}$ versus Z_{real}) and equivalent circuit for Naf-112/DTA$^+$ dry sample (■) and Naf-112/DTA$^+$(w) hydrated sample (□), that means, after 24 h submerged in distilled water.

impedance spectroscopy and membrane potential measurements. Since these latter measurements are carried with HCl-aqueous solutions, the effect of water on membrane electrical parameters is also considered by comparing impedance curves for Naf-112/DTA$^+$ and after 24 h submerged in distilled water (Naf-112/DTA$^+$(w)) samples. Figure 6 shows a comparison of the Nyquist ($-Z_{imag}$ versus Z_{real}) plot obtained for both samples, where significant differences can be observed, although in both cases the equivalent circuit corresponds to a parallel association of a resistance (R_m) and a constant phase element (Q_m) or nonideal capacitor [32, 33]. The fitting of the impedance date by a nonlinear program allows the estimation of R_m [34] and the following values were obtained: $R_m(\text{Naf-112/DTA}^+) = 2 \times 10^6$ ohm and $R_m(\text{Naf-112/DTA}^+(w)) = 2.8 \times 10^5$ ohm, this represents practically one order of magnitude lower for the hydrated membrane. However, no indication of membrane conductivity (σ) can be determined from these results since the well-known and commonly used relationship between electrical resistance and conductivity, $R = L/\sigma \cdot S$, is only valid for homogeneous conductors, and it is not applicable to the modified membranes since no evidence of homogeneous distribution of the IL-cation throughout the Nafion structure exists. In any case, the obtained values show the significant increase of electrical resistance caused in the Nafion membrane by the inclusion of the IL-cation but membrane rehydration clearly reduce this effect.

This point can be more clearly observed in Figures 7(a) and 7(b) where a comparison of the Bode diagrams (Z_{real} versus frequency and $-Z_{imag}$ versus frequency, resp.) for Nafion-112, Naf-112/DTA$^+$, and Naf-112/DTA$^+$(w) samples is presented. As can be observed, significantly lower values for the real part of the impedance (directly related to electrical resistance) were obtained for the original Nafion-112 membrane in comparison with Naf-112/DTA$^+$(w) and
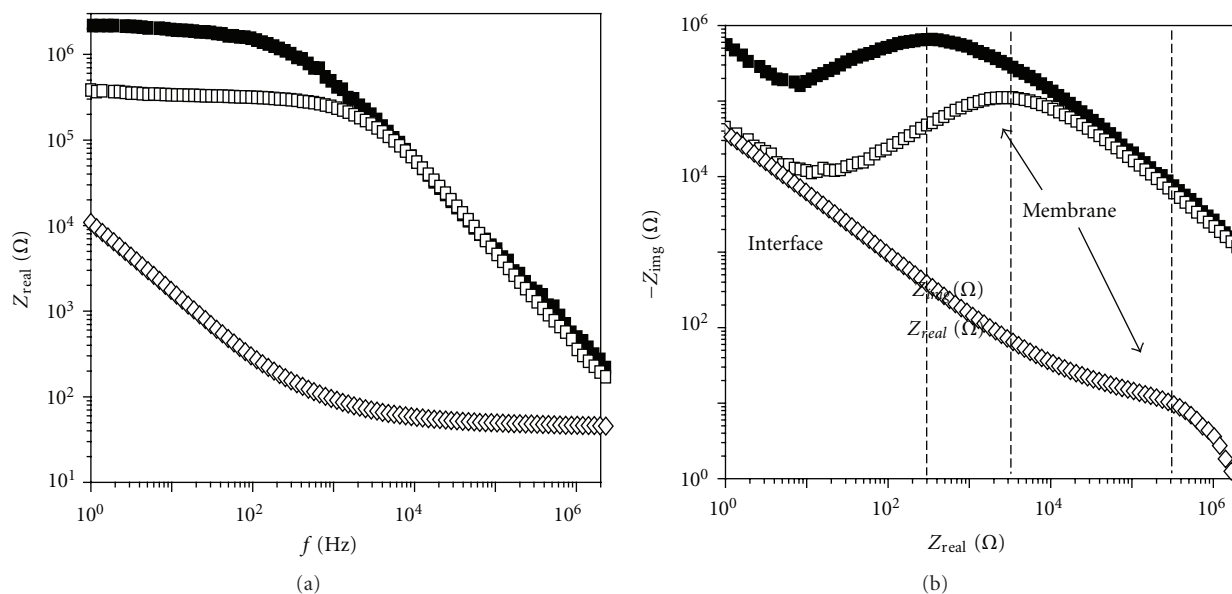
(a)

(b)

FIGURE 7: Bode plots, (a) Z_{real} versus frequency and (b) Z_{img} versus frequency, for Nafion-112 ($\lozenge$), Naf-112/DTA$^+$ dry ($\blacksquare$) and Naf-112/DTA$^+$(w) ($\square$) membranes.
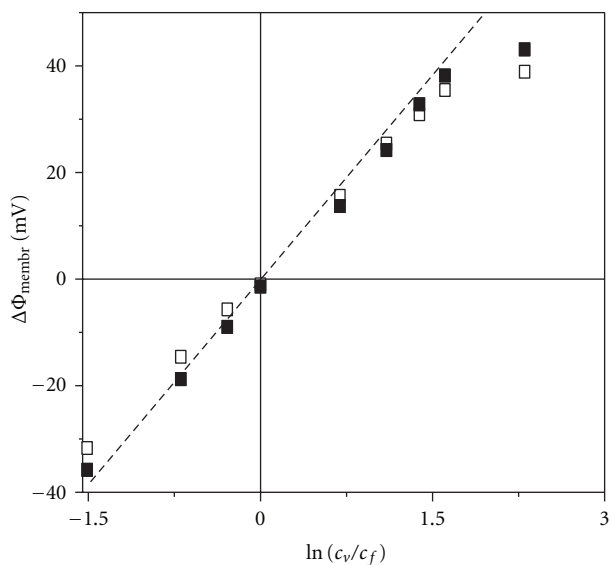

FIGURE 8: Membrane potentials versus solution concentrations ratio for Nafion-112 ($\square$) and Naf-112/DTA$^+$ ($\blacksquare$) in contact with HCl solutions.

Naf-112/DTA$^+$ samples (3 or 4 orders of magnitude, resp.), while the shift to lower values of the maximum relaxation frequency obtained for the IL-modified samples might be related to a more compact charge packing.

Membrane potential, $\Delta\Phi_{memb}$, is the electrical potential difference between both sides of a membrane separating two solutions of the same electrolyte but different concentrations (c_1 and c_2) [35]. Figure 8 shows the variation of membrane potentials with the logarithm of the solution concentrations ratio, where a practically linear relationship can be observed;

for comparison, membrane potential for an ideal cation-exchange membrane is also shown in Figure 7 (dotted line) and these values hardly differ from those corresponding to both Naf-112/DTA$^+$ and Nafion-112 membranes in agreement with the well-known electronegative character of this sample.

Ion transport number (t_i) is the parameter commonly used to characterize the effect of membrane charge on the transport of ions since it represents the fraction of the electric current transported by an ion i ($t_i = I_i/I_T$, then $\sum_i t_i = 1$; $t_+ + t_- = 1$ for single salts). For an ideal cation-exchanger membrane $t_+ = 1$, and the ΔE for the concentration cell reaches the maximum value [35]: $\Delta E_{max} = -(2RT/F)\ln(c2/c1)$; then, the value of the cation transport number for two given concentrations ($c1$ and $c2$) can be obtained as: $t_+ = \Delta E/\Delta E_{max}$. Cation transport numbers across Nafion-112 and Naf-112/DTA$^+$ membranes were calculated and the following average values were obtained: $\langle t_+ \text{ (Nafion-112)} \rangle = (0.946 \pm 0.006)$ and $\langle t_+(\text{Naf-112}/DTA^+) \rangle = (0.973 \pm 0.012)$, which hardly differentiate one from each other although they seem to indicate a slightly higher proton transport in the IL-modified membrane. Cation transport number values obtained in this paper hardly differ from those determined in [18] for a Nafion membrane and different electrolyte solutions.

3.5. Monitoring IL-Cation Inclusion Electrical Effects.

As was already established in the previous sections, the H$^+$/DTA$^+$ exchange mechanism taking place when the Nafion-112 membrane was in contact with the IL solution causes changes in the membrane and the membrane solution interface. Time evolution of the impedance spectroscopy curves can give information on such changes. Figure 9 shows the impedance diagrams (Bode plots) obtained for the system electrode//IL-solution/Nafion-112/IL-solution//electrode at different time
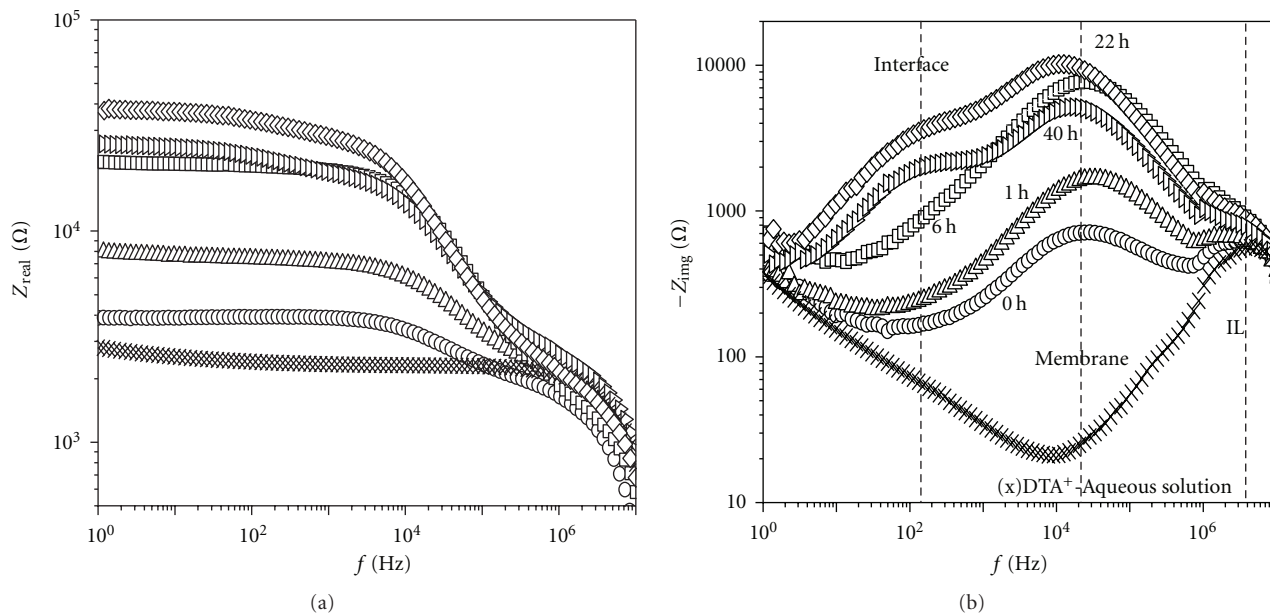
FIGURE 9: (a) Variation of the (a) real part of the impedance versus frequency and (b) imaginary part of the impedance versus frequency as a function of the Nafion-112 membrane contact time with the IL-solution. (o) $t = 0$, ($\triangle$) $t = 1$ h, ($\square$) $t = 6$ h, ($\lozenge$) $t = 22$ h, and (∇) $t = 40$ h. Impedance results for the IL-solution alone ($\times$), this means without any membrane in the measuring cell are also drawn.

instances. For comparison, the impedance values measured with the IL solution (without any membrane placed in the cell) are also indicated in Figure 9. These results show the separate effect of DTA$^+$ inclusion (and H$^+$ lost) on both the real part of the impedance (related to the charge movement through the electrical resistance) and the imaginary part of the impedance (associated to charge storage by the capacitance). Figure 9 (a) shows the increase of Z_{real} values for the membrane/IL-solution system with time, where there are higher values for 22 h than for 40 h, but these results also include interfacial effects, which seem to be developed after 10 h of membrane/IL-aqueous solution contact. This point is more clearly observed in Figure 9(b), where different relaxations depending on the system and/or time period considered can be observed. As expected, the IL-solution only presents a relaxation at high frequencies ($f_{max} \approx 3 \times 10^6$ Hz) since only free or "solution" charges are involved; however, the membrane/IL-solution system exhibits different behaviours depending on the time period which is associated to the exchange kinetic: (a) at the beginning of the exchange process the main effect observed corresponds to the increase in of membrane characteristic parameters (electrical resistance and capacitance) due to the replace of the small and high conductive proton (H$^+$) by the wider and heavy DTA$^+$-cation and two relaxation processes, one associated to the membrane ($f_{max} \approx 10^4$ Hz) and another to the electrolyte solution placed between the electrodes and the membrane surfaces ($f_{max} \approx$ 2-3 $\times 10^6$ Hz) can be observed; (b) after some hours of membrane immersion in the IL-solution (around 10 h) a structured profile seems to be developed at the membrane interface and then three different relaxation processes with maximum frequencies around 200 Hz (interface), 10^4 Hz (membrane), and 2-3 $\times 10^6$ Hz

(electrolyte solution) are obtained. These latter curves are similar to those obtained with composite membranes (as those used for reverse osmosis or nanofiltration processes) in contact with common electrolytes solutions (NaCl or KCl) and are associated to the typical double layer (dense-active layer/porous-support) structure of that kind of membranes [36, 37].

The fitting of the impedance data obtained for each time allows the estimation of the electrical resistance and capacitance associated to both bulk membrane and interface and its dependence with membrane immersion time in the IL-solution is shown in Figure 10. A significant increase in the membrane electrical resistance associated to the IL-cation incorporation (similar to that shown in Figure 1) can be observed in Figure 10, but an interfacial process seems to be developed after 6–8 h, which practically corresponds to the time at which the proton/cation exchange mechanism for IL-cation incorporation reaches the plateau; this interfacial process is time decreasing probably due to counter-diffusion effect.

These results show the complexity of IL-cation incorporation into Nafion membranes associated to the kinetic of proton/IL-cation exchange as well as the possibility of using impedance spectroscopy technique to discriminate the effects associated to both the own membrane and the interface.

4. Conclusions

The modification of a typical cation-exchange polymeric membrane by inclusion of the IL-cation into the matrix structure by a proton/cation exchange mechanism and its effect on chemical, thermal, and charge transport was presented. Membrane thickness seems to affect equilibrium time
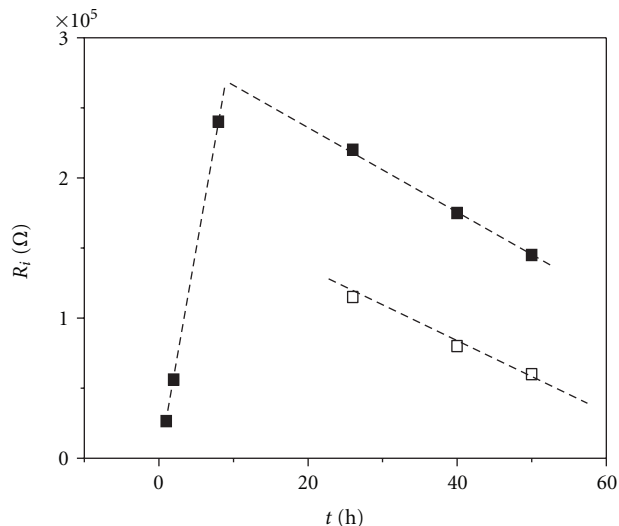
FIGURE 10: Time dependence of the electrical resistance of (■) bulk membrane, (□) interface.

but hardly modifies the incorporation degree at equilibrium, which presents an average value of $(60.5 \pm 0.5)\%$ for the Nafion-DTA$^+$ aqueous solution studied.

Electrical, thermal and surface characterizations of the studied systems were basically carried out by impedance spectroscopy, DSC, XPS, and contact angle measurements. DTA$^+$ incorporation seems to reduce the hydrophobic character of the original Nafion membranes and to increase their thermal stability. The effect of water in the electrical resistance of the modified samples was also shown, which is significant point for many electrochemical applications. Moreover, this work also presents the direct correlation between cation incorporation in the membrane and modifications in its electrical resistance but also associated interfacial effects.

The diversity of available ILs made it possible to choose that the use of IL-modified membranes' is more adequate for a specific application opening for a wide variety of applications, particularly those related to electrochemical systems.

Acknowledgments

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