



## Electrochemical Properties of Cation-Exchange Membranes Based on Polysulfones

Ethel Parcero,<sup>a</sup> Franciso J. Fernández-Carretero,<sup>c</sup> Vicente Compañ,<sup>c</sup>  
Rafael Herrera,<sup>a</sup> Luis F. del Castillo,<sup>b</sup> and Evaristo Riande<sup>d,z</sup>

<sup>a</sup>Departamento de Ingeniería Química, Facultad de Química and <sup>b</sup>Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México DF, Mexico

<sup>c</sup>Departamento de Termodinámica, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Valencia, 46020 Valencia, Spain

<sup>d</sup>Instituto de Ciencia y Tecnología de Polímeros, CSIC, 28006 Madrid, Spain

This paper reports the electrochemical characteristics of phosphonic and sulfonic acid membranes based on commercial polyphenyl sulfone Radel. Proton membranes' permselectivity was determined from the electromotive force of concentration cells measured with silver/silver chloride electrodes reversible to the anions of the electrolyte solutions. Apparent proton transport numbers in most membranes are close to the unit, even at moderately high electrolyte concentrations. The water uptake of polyphenyl sulfone phosphonic acid membranes is lower than that of membranes containing sulfonic acid groups anchored to their structure and, as a result, the former membranes have a lower conductivity than the latter ones with a similar cation-exchange capacity. For example, the conductivity of the sulfonic acid membrane with an ion-exchange capacity of 2.06 meq/g dry membrane, equilibrated with water, is  $3.56 \times 10^{-4}$  S/cm at 25°C, about one order of magnitude higher than that of the phosphonic acid membrane with an ion-exchange capacity of 1.90 meq/g dry membrane, measured in the same conditions. The diffusion coefficient of protons in the membranes equilibrated with distilled water was calculated and compared with that found for Nafion 117 in the same conditions.

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There has been considerable interest in the development of ion-exchange membranes since the application of these materials in ionic separation processes was recognized a long time ago.<sup>1-3</sup> The interest increased even more when cation-exchange membranes showed their potential capability to be used as a polymer electrolyte for lithium batteries<sup>4-6</sup> and low-temperature fuel cells.<sup>7,8</sup> Anions are bound to polymer chains in cation-exchange membranes, and the inherent cation transport number is 1 in dry membranes. This property deters salt buildup in lithium-ion batteries. It has been established that dry polymer electrolytes can produce room-temperature conductivities nearly two decades below the target conductivity, about  $10^{-3}$  S/cm, for commercially available lithium batteries.<sup>9</sup> Nowadays proton-exchange membranes are available which equilibrated with distilled water may exhibit proton conductivities larger than  $10^{-2}$  S/cm, at room temperature. Owing to electro-osmotic transport and evaporation processes that decrease the conductivity of protons in membranes at the working temperatures of low-temperature fuel cells, the development of low water uptake membranes with high conductivity is imperative.<sup>10</sup> Good performance membranes should exhibit low conductivity, low electro-osmosis, good chemical stability and high mechanical resistance, high flexibility, and good dimensional stability under different wetting conditions.

Aside from low conductivity and good mechanical properties, ion-exchange membranes used for ionic separation processes in electro dialysis should exhibit a high permselectivity. This property is determined by the counterion transport number, which should be close to the unit. Nevertheless some properties required for good membrane performance are incompatible. Thus, a high mechanical resistance requires thick membranes which negatively affect the conductance. Moreover, a high concentration of fixed ions positively affects the permselectivity and conductivity of membranes, but decreases the mechanical properties and increases free ionic diffusion. From a practical point of view, a balance must be reached among these incompatible properties to accomplish good performance membranes for separation processes.<sup>1,2</sup>

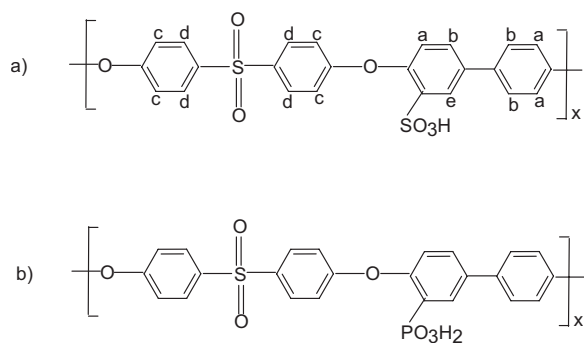
Owing to their chemical stability, sulfonated perfluorocarbon polymers are promising electrolytes for low-temperature fuel cells.<sup>7</sup> However, the still-high cost and negative environmental effects of

these polymers have promoted the search for alternative materials. At first glance, polymers with a high chemical stability and good mechanical properties, such as polysulfones, polyamides, polyether ketenes, etc., could be suitable materials to prepare proton-exchange membranes, with a potential capability also to be used for ionic separation processes. Several reviews of polymer-based proton conductors have been published.<sup>11-16</sup> The synthesis of acid membranes of sulfonated polyether sulfones,<sup>17</sup> sulfonated poly(arylene-co-arylene sulfone)s,<sup>18</sup> phosphonic acid functionalized poly(aryloxyphosphazenes),<sup>19</sup> acidic blends of sulfonated poly(ether-ketone) and sulfonated polysulfone,<sup>20</sup> sulfonated polyimides,<sup>21-23</sup> etc., has been reported.

Polysulfones are relatively cheap materials with a high chemical stability in aqueous solutions of acids, bases, and salts. Some commercial polysulfones such as UDEL and Victrex have been sulfonated and applied in several processes.<sup>24-29</sup> However, commercial polyphenylsulfone Radel has been studied little in spite of offering an exceptional hydrolytic stability, and a toughness superior to other commercially available, high-temperature engineering resins. This material offers a high deflection temperature, outstanding resistance to environmental stress cracking, excellent thermal stability, and good electrical properties. Therefore, it is important to investigate the electrochemical characteristics of functionalized polyphenyl sulfones.<sup>30</sup> It has been argued<sup>31-33</sup> that phosphonic acid functionalized membranes may combine a satisfactory proton conductivity even in the water-free state at an intermediate temperature (<200°C), and a comparatively high thermo-oxidative and electrochemical stability.

This article reports the permselectivity performance and conductivity of cation-exchange membranes based on commercial polyphenyl sulfone Radel with either sulfonic or phosphonic acid fixed groups bound to the polymer chains. The structural unit of the membranes is shown in Fig. 1. A thorough study on the synthesis and conductivity properties of different membranes based on the polyphenyl sulfone Radel has been reported recently.<sup>34</sup> It is the aim of this work to extend this study to the analysis of the permselectivity of the membranes to protons over a wide hydrochloric acid concentration window lying in the range  $10^{-3}$  to 1 M. Moreover, the conductivity of the cation-exchange membranes equilibrated with distilled water is also reported and compared with that obtained for sulfonated Nafion in the same conditions. Attention is paid to the effect of the chemical nature of fixed anionic groups on proton dif-

<sup>z</sup> E-mail: riande@ictp.csic.es



**Figure 1.** Repeating unit of the polyphenylsulfone Radel chains functionalized with (a) sulfonic and (b) phosphonic acid groups. The functionalization degree in the scheme is 1. Letters a, b, c, d and e denote different types of protons associated with the NMR peaks of sulfonated chains (see Ref. 34).

fusion in the membranes, an issue theoretically studied earlier in perfluorosulfonic acid membranes.<sup>35</sup> With a single exception, the conductivity of the membranes is only studied at 25°C. Further work is in progress to investigate the conductivity of phosphonic acid membranes at higher temperatures, even beyond 100°C.

### Experimental

**Preparation of sulfonated and phosphonated membranes.**— Polyphenylsulfone Radel R-5000 dissolved in dichloromethane was sulfonated with trimethylsilylchlorosulfonic under argon. Then the cool solution was poured into methanol, and the functionalized polymer was separated by filtration, washed with methanol, then with water, and finally dried at 45°C in vacuum. Full details of the sulfonation process are reported elsewhere.<sup>34,36</sup> Phosphonated polyphenylsulfone was obtained by a homogeneous catalytic reaction involving previously brominated polyphenylsulfone, diethyl phosphate, and Pd<sub>2</sub>(dba)<sub>3</sub>CHCl<sub>3</sub>. Under the action of the catalyst, the bromine of the chains is replaced by diethyl phosphate and the phosphonic acid ester is thus anchored to the polyphenylsulfone chains. The polymer was isolated from the solution by precipitation in methanol, redissolved in chloroform, reprecipitated with methanol, and dried at 50°C in vacuum. Finally, by reaction of the phosphonated polymer with concentrated hydrobromic acid, polyphenylsulfone chains with phosphonic acid groups anchored to their structure were obtained. The synthesis process is described in detail elsewhere.<sup>34,36</sup> By varying the reaction time, polymers with different degrees of sulfonation and phosphonation were obtained. The membranes were prepared by casting of the functionalized polyphenylsulfones in methyl pyrrolidone solutions.

**Water uptake and proton exchange capacity.**— Membranes in the acidic form (R-SO<sub>3</sub>H or R-PO<sub>3</sub>H<sub>2</sub>) were immersed in distilled water, removed from water at different time spans, superficially dried by gently blotting them between filter paper, and again weighed. Each experiment was repeated three times. From the weights of the dried and wet membranes, the values of the average water uptake shown in the second column of Table I were obtained.

To measure the ion-exchange capacity (IEC) of the membranes, these materials were equilibrated in a 1 M HCl solution overnight. The acidic membranes were further washed several times with distilled water to remove the soaked hydrochloric acid and then equilibrated with a 1 M sodium chloride solution. The protons exchanged in the ion-exchange reaction  $R-SO_3H + Na^+ \rightarrow R-SO_3Na + H^+$  were determined with a pH meter, and the pertinent values obtained for the IEC of the membranes are collected in the third column of Table I.

**Electromotive forces of concentration cells.**— The electromotive force (emf) of concentration cells made up of two compartments filled with electrolytes of the same chemical nature but different

**Table I.** Water uptake and ion-exchange capacity for polyphenylsulfone membranes containing phosphonic (P1, P3, and P5) and sulfonic (S7 and S9) acid groups in their structure.

Membrane	Water uptake, %	Ion-exchange capacity, $10^3 \times [H^+]/g$ dry membrane	$\lambda$ , moles of water/equiv. fixed anions in the wet membrane
P1	9.2	1.31	3.9
P3	6.7	0.77	4.8
P5	8.8	1.90	2.6
S7	3.1	0.28	6.0
S9	24.3	2.06	6.6
Nafion 117	36.6	1.03	13.74

concentration, separated by the ion-exchange membrane of interest, were measured at 25°C with Ag/AgCl electrodes using a high-impedance pH meter ( $Z > 10^{14} \Omega$ ), model Crison 2002. The emf was recorded with a PC taking measurements every 10 s. During the measurements, the cell solutions were stirred to minimize concentration polarization effects.

**Impedance spectroscopy.**— Complex impedance spectroscopy measurements were carried out in the frequency range  $10^{-2} < f < 10^7$  Hz, at 25°C. The membranes previously equilibrated with distilled water were placed between two gold electrodes coupled to a Novocontrol broadband dielectric spectrometer. The equivalent electric circuit consisted of a resistance  $R_0$  accounting for the conductivity protons in the membrane, in series with an ideal  $R_p$ - $C$  parallel circuit modeling the electrode-membrane polarization processes. The complex impedance  $Z^*$  of the system, at the angular frequency,  $\omega$ , is given by

$$Z^* = R_0 + \frac{R_p}{1 + j\omega R_p C} \quad [1]$$

Equation 1 leads to the following expressions for the real,  $Z'$ , and loss,  $Z''$ , components of the complex impedance,  $Z^*$

$$Z' = R_0 + \frac{R_p}{1 + (\omega R_p C)^2} \quad [2]$$

$$Z'' = -\frac{\omega R_p^2 C}{1 + (\omega R_p C)^2} \quad [3]$$

The complex  $Z''$  vs  $Z'$  plot, called a Nyquist diagram,<sup>37</sup> is a semi-circle intersecting the abscissa axis at  $Z' = R_0$  ( $\omega \rightarrow \infty$ ) and  $Z' = R_0 + R_p$  ( $\omega \rightarrow 0$ ). The frequency dependence of the modulus of the impedance,  $|Z^*|$ , also called a Bode plot,<sup>38</sup> is an alternative method to obtain the resistance of protons in the membranes. As in the Nyquist representation,  $|Z^*| = R_0$  ( $\omega \rightarrow \infty$ ) and  $|Z^*| = R_0 + R_p$  ( $\omega \rightarrow 0$ ). Note that  $\phi = \tan^{-1}(Z''/Z') = 0$  ( $\omega \rightarrow \infty$ ).

### Concentration Potentials Revisited

The configuration used to determine the emf of concentration cells is Ag|AgCl aqueous ionic solution ( $c_L$ )|membrane|aqueous ionic solution ( $c_R$ ) AgCl|Ag. Let us assume that the electrolyte dissociates as  $C_{v_+}A_{v_-} = v_+C^{z_+} + v_-A^{z_-}$ . In the approach used, the two adjacent boundary layers flanking the membrane are included in the system. The local dissipation function at every point of the membrane system is given by<sup>39</sup>

$$-Ts = j_w^0 \nabla \mu_w + j_+^0 \nabla \tilde{\mu}_+ + j_-^0 \nabla \tilde{\mu}_- \quad [4]$$

where  $\tilde{\mu}_i$  ( $i = +, -$ ) are, respectively, the electrochemical potential of the cations and anions in the electrolyte solution,  $\mu_w$  the chemical potential of water, and  $j_i^0$   $i = +, -, w$  is the flux density of the ionic species and water in the membrane-fixed reference frame, in mol/m<sup>2</sup> s units. Using reversible electrodes to one of the ions, i.e.,

to the anion, the local dissipation under the driving force acting on the  $x$  direction perpendicular to the surface of the membrane can be written as

$$-T\dot{s} = j_w^0 \frac{d\mu_w}{dx} + \frac{1}{v_+} j_+^0 \frac{d\mu_2}{dx} + j \frac{d\psi}{dx} \quad [5]$$

where  $j = F(z_+ j_+^0 + z_- j_-^0)$  is the electric current density in A/m<sup>2</sup> and  $\mu_2 = v_+ \tilde{\mu}_+ + v_- \tilde{\mu}_-$  is the chemical potential of the electrolyte in J/mol. In the development of Eq. 5, the gradient of the electrical potential at equilibrium measured by the electrodes at the electrodes/solution interfaces,  $d\psi/dx$ , was considered to be related to the electrochemical potential gradient of the anion by<sup>40,41</sup>

$$\frac{d\mu_-}{dx} = z_- F \frac{d\psi}{dx} \quad [6]$$

where  $F$  is Faraday's constant. By combining Eq. 5 with the Gibbs–Duhem's equation,  $c_2 d\mu_2 + c_w d\mu_w = 0$ , where  $c_w$  and  $c_2$  are, respectively, the concentration of solvent and solute, and taking into account the electroneutrality principle  $v_+ z_+ + v_- z_- = 0$ , the following expression for the dissipation function is obtained

$$-T\dot{s} = \frac{1}{v_+} j_+ \frac{d\mu_2}{dx} + j \frac{d\psi}{dx} \quad [7]$$

where  $j_+ = j_+^0 - (v_+ c_2 / c_w) j_w^0$  is the flux of cations taking the center of gravity of the moving liquid as reference frame.

By considering that fluxes  $[(1/v_+) j_+, j]$  are linear functions of forces  $(d\mu_2/dx, d\psi/dx)$ , the following transport equations can be postulated<sup>40,41</sup>

$$\frac{1}{v_+} j_+ = -\lambda_{11} \frac{d\mu_2}{dx} - \lambda_{12} \frac{d\psi}{dx} \quad [8]$$

$$j = -\lambda_{21} \frac{d\mu_2}{dx} - \lambda_{22} \frac{d\psi}{dx} \quad [9]$$

If  $\psi = \text{constant}$ , Eq. 8 becomes Fick's first law and  $\lambda_{11}$  is related to the solute diffusion coefficient. However, if  $\mu_2 = \text{constant}$ , Eq. 8 yields

$$\frac{1}{v_+} j_+ = -\lambda_{12} \frac{d\psi}{dx} \quad [10]$$

Equation 10 is related to the density of current  $j$  flowing across the membrane flanked by solutions of the same concentration, under the electric potential gradient  $-d\psi/dx$ . Actually, the current  $j$  involves the transport of  $z_+ j_+$  equivalents, hence  $(z_+ j_+ / j) = t_+ / F$ , where  $t_+$  is the so-called counterion transport number or the cation equivalents transported by Faraday current, taking as reference the center of gravity of the moving liquid across the membrane. Then

$$j_+ = \frac{t_+}{F} j \quad [11]$$

Now, let us consider Eq. 9. For  $\mu_2 = \text{constant}$ ,  $-d\psi/dx = j/\sigma$ , where  $\sigma$  is the ionic conductivity and  $-\lambda_{22} = \sigma$ . Carrying Eq. 11 into Eq. 10,  $\lambda_{12} = -(t_+ / F v_+ z_+) \sigma$  is obtained. For an open circuit ( $j = 0$ ), Eq. 9 leads to

$$\frac{d\psi}{dx} = \frac{dE}{dx} = -\frac{t_+}{F v_+ z_+} \frac{d\mu_2}{dx} \quad [12]$$

where  $E$  is the emf of the concentration cell. In the development of Eq. 12 the symmetry of the Onsager coefficients ( $\lambda_{12} = \lambda_{21}$ ) was taken into account. By integrating Eq. 12,  $E$  is obtained as

$$E = -\frac{1}{v_+ F} \int_0^l \tau_+(c_2) \frac{d\mu_2}{dx} dx \quad [13]$$

where  $\tau_+ = t_+ / z_+$  is the so-called reduced apparent transport number in moles/Faraday, and  $l$  is the membrane thickness. Notice that as

**Table II. Degree of functionalization (DS) in equiv/mol repeat unit for phosphonic and sulfonic acid membranes obtained by <sup>1</sup>H NMR spectroscopy and elemental analysis (EA). (Taken from Ref. 34).**

Type of membrane	Acronym	DS from <sup>1</sup> H NMR	DS from EA
Phosphonic acid membranes	P1	0.59	0.66
	P3	0.30	0.30
	P5	0.88	1.06
Sulfonic acid membranes	S7		0.12
	S9	0.88	0.86

concentration increases, co-ions may intervene in current transport and therefore the apparent transport number for homogeneous membranes is only a function of concentration of electrolyte in the membrane phase. Because  $\mu_2 = \mu_2^0 + RT \ln(a_2^{v_+} a_2^{v_-})$ , Eq. 13 becomes

$$E = -\frac{RTv_2}{Fv_+} \int_{a_L}^{a_R} \tau_+(c_2) d \ln a_2 \quad [14]$$

where  $v_2 = v_+ + v_-$ , and  $a_L(a_R)$  denotes the electrolyte activity of the left (right) bulk solutions flanking the membrane.

## Results and Discussion

Three polyphenyl sulfone membranes with phosphonic acid groups anchored to the polymer chains, represented with the acronyms P1, P3, and P5, were used in this study. Also, two membranes containing sulfonic acid groups anchored to the polyphenyl sulfone chains, denoted with the acronyms S7 and S9, were studied. Schemes of the chemical structures of sulfonated and phosphonated chains are shown in Fig. 1a and b, respectively. According to previous studies,<sup>34</sup> functionalization of the chains preferentially occurs in the carbon atom of the aromatic ring of the phenylene moiety in the *ortho* position with respect to the ether bond (protons of type a in Fig. 1a). A thorough study on the characterization of the phosphonated and sulfonated membranes is described in Ref. 34. Briefly, the sulfonation degree was determined by comparing the intensity of the peak relative to the proton *e*, adjacent to the sulfonic group, with the peak relative to protons contiguous to the sulfone group (protons of type d in Fig. 1a). The phosphonation degree was obtained from the CH<sub>2</sub> protons of the  $-\text{PO}(\text{CH}_2-\text{CH}_3)_2$  ester group attached to the chains previous to the hydrolytic step that converts it into the phosphonic acid group. The peaks corresponding to these protons appear at 4.1 and 1 ppm, respectively, and disappear after the hydrolysis, confirming that the acid form was obtained. The phosphonation degree was estimated from the ratio between the integrated peak at 4.1 ppm before the hydrolysis and the integrated peaks of protons at the main aromatic chain between 7.6 and 8.2 ppm. Spectra of these membranes are given in Ref. 34.

Values of the functionalization degree for the membranes used in this study, estimated from elemental analysis and <sup>1</sup>H NMR spectroscopy, are collected in Table II. A fair agreement is seen between the results obtained by the two techniques.

The main characteristics of both the phosphonic and sulfonic acid membranes concerning the IEC and water uptake are given in Table I. The good agreement between the values obtained for IEC from exchange reactions and those estimated from the functionalization degrees shown in Table II is remarkable. As an example, the values of IEC estimated from <sup>1</sup>NMR are 1.87 and 1.85 meq/g dry membrane for the S9 and P5 membranes, respectively, in very good agreement with the results obtained by titration of the exchange reactions that amount to 2.06 and 1.90 meq/g dry membrane, respectively. The water uptake is lower than 10% for all membranes except for the S9 membrane which is 24%. Although the water uptake increases with the ion-exchange capacity, the number of moles of water/fixated ionic group,  $\lambda$ , given in the fourth column of

**Table III.** Values of the electromotive force  $E$  for several membranes (Nafion S9, P5, P1, P3, and S7) flanked by aqueous  $c_L$  and  $c_R$  hydrochloric acid concentrations, at 25°C.

$c_L$	$c_R$	$-E$ (mV) Nafion 117	$-E$ (mV) S9	$-E$ (mV) P5	$-E$ (mV) P1	$-E$ (mV) P3	$-E$ (mV) S7
0.0100000	0.001	-116.2	-115.8	-116.3	-115.8	-112.5	-111.5
0.0100000	0.0050000	-35.4	-34.9	-35.7	-35.3	-34.4	-33.9
0.0100000	0.0500000	81.5	80.4	79.5	76.5	75.5	74.5
0.0100000	0.1000000	113.2	112.5	110.6	109.6	108.2	105.8
0.0100000	0.5000000	194.9	192.2	190.3	187.6	186.1	181.8
0.0100000	1.0000000	226.4	224.6	227.0	226.0	221.7	220.0
0.5000000	1.0000000	38.7	38.3	38.1	37.7	37.3	37.2
0.1000000	1.0000000	115.8	115.2	115.2		113.9	112.3
0.1000000	0.5000000	79.3	78.8	78.5		76.8	75.4

Table I, does not follow a definite trend. For example, the value of  $\lambda$  for the S9 membrane with IEC = 2.06 meq/(g of dry membrane) is 6.6 moles of water/(equiv fixed groups), of the same order as that displayed by the S7 membrane with IEC = 0.28 meq/g. The values of  $\lambda$  for the P1, P3, and P5 phosphonated membranes, with IECs equal to 1.33, 0.77, and 1.90 equiv fixed groups/(g dry membrane), respectively, are 3.9, 4.8 and 2.6 moles of water/(equiv fixed groups), respectively. Surprisingly, the values of  $\lambda$  and IEC follow opposite trends for the phosphonated polyphenyl sulfone membranes. The values of  $\lambda$  are higher for the sulfonated membranes than for the phosphonated ones with similar IEC. The differences of water uptake between the sulfonated and phosphonated membranes arise from the differences of acid strength of the  $-\text{SO}_3\text{H}$  ( $\text{p}K = 1$ ) and  $-\text{PO}_3\text{H}_2$  ( $\text{p}K_1 = 2$  and  $\text{p}K_2 = 8$ ) groups.<sup>42</sup> In all cases, polyphenylsulfone cation-exchange membranes exhibit significantly lower values of  $\lambda$  than the Nafion 117 membrane used for comparative purposes in this study.

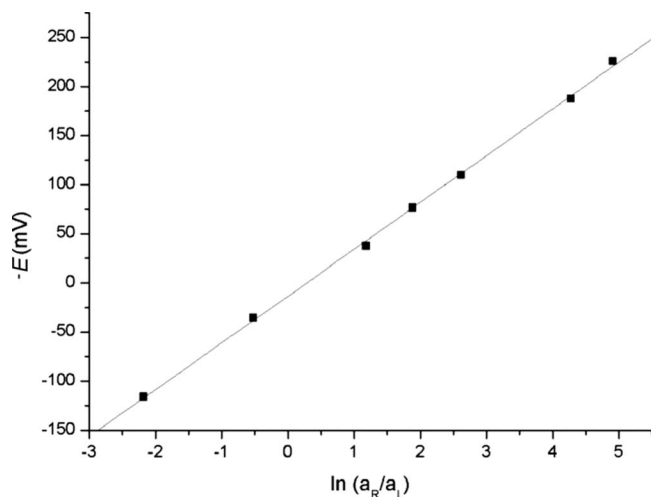
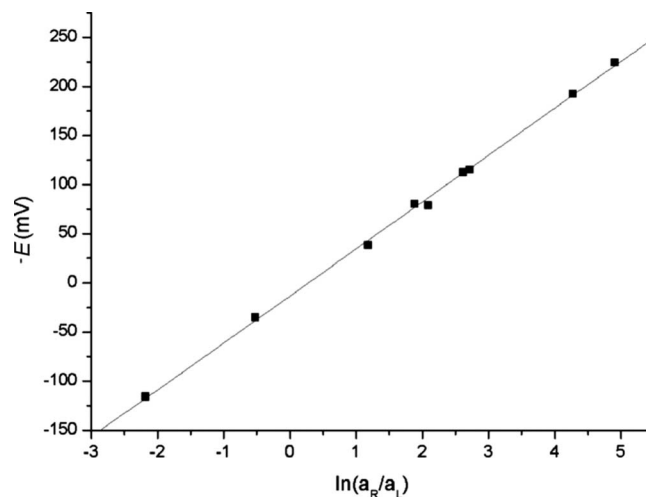
Electric concentration potentials are an alternative and easier way than the Hirthof method<sup>43</sup> for determining apparent proton transport numbers.<sup>1,2</sup> Table III presents the variation of the emf of the membranes for different concentration ratios  $c_R/c_L$ . In the same table, the emf for the concentration cell with Nafion 117 is also shown. The symmetry of the membranes was checked by interchanging the solution concentrations in the semicells, and the changes observed in the absolute values of the electric concentration potentials are negligible. This fact guarantees the symmetry of the membranes. Assuming an average value  $\bar{\tau}_+$  for the apparent proton transport number in the range of concentration used in each experi-

ment, integration of Eq. 14 for HCl ( $\nu_+ = \nu_- = 1$ ) yields the following expression for the emf of the concentration cell

$$E = - \frac{2RT}{F} \bar{\tau}_+ \ln \frac{a_R}{a_L} \quad [15]$$

Values of  $-E$  for different ranges of  $a_R/a_L$  corresponding to membranes P1 and S9 are plotted as a function of  $\ln(a_R/a_L)$  in Fig. 2 and 3, respectively. The plots obtained show that the emf is roughly a linear function of the logarithm of the concentrations ratio. This behavior suggests only a slight dependence of the apparent proton transport number on the concentration profile of electrolyte inside the membrane, even though this profile covers a wide range of concentrations.

In qualitative terms, one can visualize wet cation-exchange membranes as made up of pores filled of water, the walls of which are fluctuating polymer chains with fixed negative ions. Counterions come close to the fixed ions, forming a double layer, the potential of which, called potential zeta, undergoes a sharp decrease as the distance from the pores' walls increases. Co-ions are repelled in pores of small diameter with a high concentration of fixed ions, and only counterions take place in transport processes. As the pores' diameter increases by the effect of the water uptake, repulsion between fixed ions and co-ions diminishes so that co-ions can be present in the pores of the membranes. Then, the electric current flowing across the membranes under an electrical potential driving force depends on the concentration of electrolyte flanking the membrane. An increase in the external electrolyte concentration increases the amount of free electrolyte entering into the pores, and co-ions take part in

**Figure 2.** Dependence of the emf on the ratio of the activities of the solutions flanking the membrane P1.**Figure 3.** Variation of the emf of the cell with the ratio of the activities of the solutions flanking the membrane S9.

**Table IV.** Values of the apparent transport number for several membranes (Nafion S9, P5, P1, P3, and S7) flanked by different flanked by aqueous  $c_L$  and  $c_R$  hydrochloric acid concentrations, at 25°C.

$c_L$	$c_R$	$\bar{\tau}_+$ , Nafion 117	$\bar{\tau}_+$ , S9	$\bar{\tau}_+$ , P5	$\bar{\tau}_+$ , P1	$\bar{\tau}_+$ , P3	$\bar{\tau}_+$ , S7
0.0100000	0.001	1.01	1.00	1.01	1.00	0.97	0.96
0.0100000	0.0050000	1.00	0.99	1.01	1.00	0.97	0.96
0.0100000	0.0500000	1.05	1.03	1.02	0.98	0.97	0.96
0.0100000	0.1000000	1.02	1.01	1.00	0.99	0.97	0.95
0.0100000	0.5000000	1.02	1.01	1.00	0.98	0.97	0.95
0.0100000	1.0000000	0.98	0.98	0.98	0.98	0.96	0.95
0.5000000	1.0000000	0.99	0.98	0.98	0.96	0.95	0.95
0.1000000	1.0000000	0.98	0.98	0.98	0.96	0.97	0.95
0.1000000	0.5000000	1.01	1.00	0.99	0.97	0.97	0.95

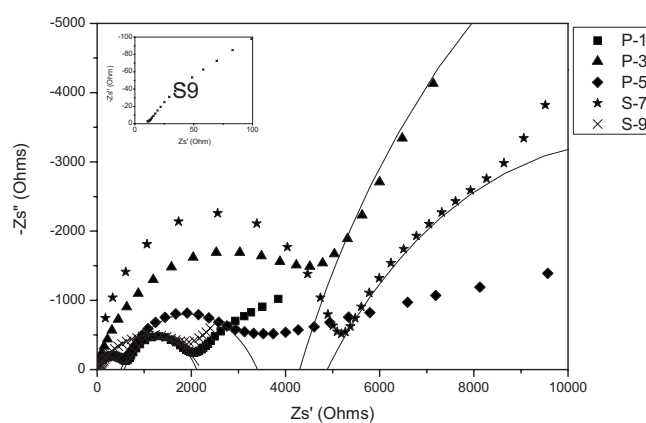
electric current transport. As a result, the value of the proton transport number decreases. Values of the mean proton transport number for polyphenyl polysulfones with sulfonic and phosphonic acid groups over a wide range of electrolyte concentrations obey this scheme (see Table IV). The membranes with a higher ion-exchange capacity exhibit the higher values of  $\bar{\tau}_+$ , independently of the ionic groups (sulfonic or phosphonic) anchored to the polyphenylsulfone chains. As a consequence of the rather low water uptake, co-ions are mostly excluded in the pores of the membranes with high IEC, at low concentrations. For example, the values of  $\bar{\tau}_+$  in S9, P1, and P5 membranes are nearly the unit, and the membranes behave as ideally permselective. However, as the concentration increases, the presence of co-ions in the membrane augments, and  $\bar{\tau}_+$  decreases, reaching a value of 0.95 at relatively high concentrations. The values of proton transport numbers are similar to those obtained for Nafion 117 in the same concentration range. For the membranes with a lower IEC (P3 and S7), co-ions are not totally excluded at low concentrations and  $\bar{\tau}_+$  is somewhat lower than the unit. The relatively high permselectivity exhibited by most membranes used in this study relies on the low diameter of the pores that excludes free electrolyte from the surroundings of the anionic groups anchored to the pores' wall.

Proton conductivity was measured by impedance spectroscopy by sandwiching the membranes between gold electrodes. Usually, acidic membranes are considered ohmic resistors in series with a black-box circuit accounting for electrode properties and electrode-polymer electrolyte interfaces. The black box may be assumed to consist of resistances, capacitances, and inductances in such a way that the circuit becomes short-circuited at high frequency, and the phase comes close to zero. In this situation only the ohmic resistance contributes to the impedance. Nyquist diagrams for the phosphonic and sulfonic acid membranes are shown in Fig. 4 and 5. The curves for the phosphonic acid membranes (P1, P3, and P5) as well as the diagram for the sulfonic acid membrane with a low IEC (S7) present an arc intersecting with the abscissa axis at the high-frequency side at  $Z' = R_0 = 605, 4450, 504, \text{ and } 4900 \Omega$ , respectively, followed by a semicircle that intersects the abscissa axis at the origin. The equivalent circuit that reflects this behavior is shown in Fig. 6. In the case that the geometrical capacitance  $C_g$  is much lower than  $C$ , the impedance of the equivalent circuit is given by Eq. 1. The behavior displayed by these membranes was also found for the conductivity of poly(ethylene oxide)-LiSCN and 2,5-diphenyloxazole-LiClO<sub>4</sub> electrolytes.<sup>44</sup> However, the diagram for the sulfonic acid membrane S9 intersects with the abscissa axis at  $R_0 = 90 \Omega$ . The semicircle intersecting the origin of coordinates at high frequency, detected in the other membranes, is not found in membrane S9.

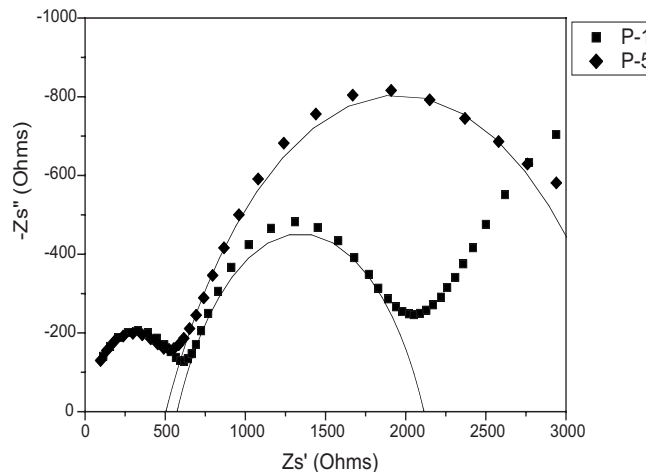
Bode diagrams for the membrane phosphonic and sulfonic acid membranes are shown in Fig. 7 and 8, respectively. By taking as proton resistance the value of the modulus of the impedance corresponding to the maximum of the phase angle in the Bode diagram, we find  $R_0$ , the values collected in the fifth column of Table V. The results obtained are in good agreement with those obtained from the alternative Nyquist diagrams. Values of the geometric parameters,

and conductivities for the P1, P3, P5, S7, and S9 membranes, obtained at 25°C from the Bode plots, are also given in Table V. Within each group of membranes (phosphonic or sulfonic), the proton conductivity follows the same trends as the ion-exchange capacity. However, the conductivity of the membranes functionalized with phosphonic acid groups is lower than that of sulfonated membranes with a similar conductivity.

As will be discussed below, the number of moles of water per



**Figure 4.** Nyquist diagrams for membranes P1 (■), P3 (▲), P5 (◆), S7 (★), and S9 (×), at 25°C. Inset: Nyquist diagram for the membrane S9 at high frequency. Continuous lines correspond to the results for the equivalent circuit.



**Figure 5.** Details of the Nyquist diagram at 25°C for membranes P1 (■) and P5 (◆) at high frequency.

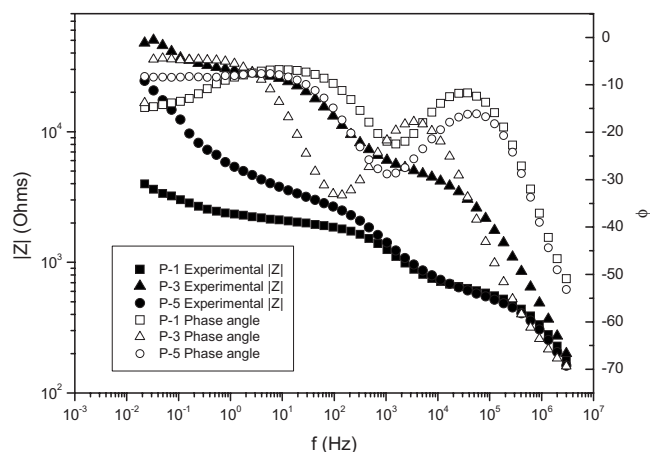


Figure 7. Bode diagrams for membranes P1, P3, and P5, at 25°C.

functionalized acid group,  $\lambda$ , plays a fundamental role in the diffusive process of protons in acidic membranes. Though a clear correlation between the experimental values of the conductivity and  $\lambda$  is not found, the results suggest that the strong acid character of the sulfonic acid groups, which allows a higher membrane swelling accompanied by a higher water uptake, is responsible for the higher conductivity of the sulfonated polysulfone membranes. Actually, dry ion-exchange membranes behave as isolators and about 2–3 molecules of water<sup>14,45</sup> per acid fixed group seem to be necessary for the dissociation of the proton from the acid site. Proton conduction is a complex process that involves dissociation of the acidic group, subsequent transfer of the proton to the first hydration shell water molecules, separation of hydrated proton from the conjugate base or fixed anion, and diffusion of the proton in the confined water in the polymeric matrix.<sup>14</sup> In view of the important role play by water in proton transport, the rather low conductivities of the phosphonic acid membranes may be the result of the small number of molecules of water per fixed anionic group.

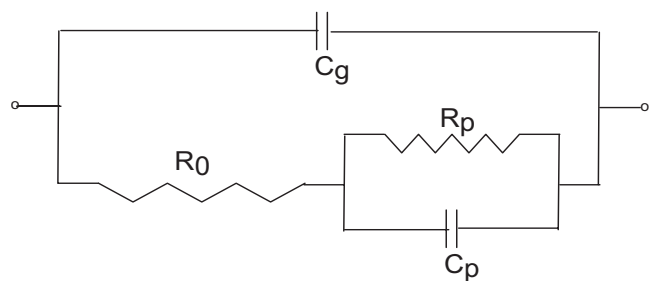


Figure 6. Equivalent electric circuit for membranes P1, P3, P5, and S7.

Table V. Characteristics of the membranes involving geometric dimensions used in conductivity measurements, conductivity,  $\sigma$ , and proton diffusion coefficient,  $D_+$ , at 25°C.

Membrane	Surface (cm <sup>2</sup> )	Thickness (cm)	Ion exchange capacity, equiv/g dry membrane	Proton resistance, $\Omega$	$\sigma$ , S/cm	$109 \times D_+$ , cm <sup>2</sup> /s
P1	0.7854	0.0066	1.31	625	$1.35 \times 10^{-05}$	3.29
P3	0.7854	0.0098	0.77	5000	$2.26 \times 10^{-06}$	0.94
P5	0.7854	0.0079	1.90	550	$1.69 \times 10^{-05}$	2.83
S7	0.7854	0.0045	0.28	4980	$1.14 \times 10^{-06}$	1.29
S9	0.7854	0.0112	2.15	90	$3.56 \times 10^{-04}$	52.8
Nafion 117	0.7854	0.0244	1.03	1.80	$1.73 \times 10^{-02}$	4700

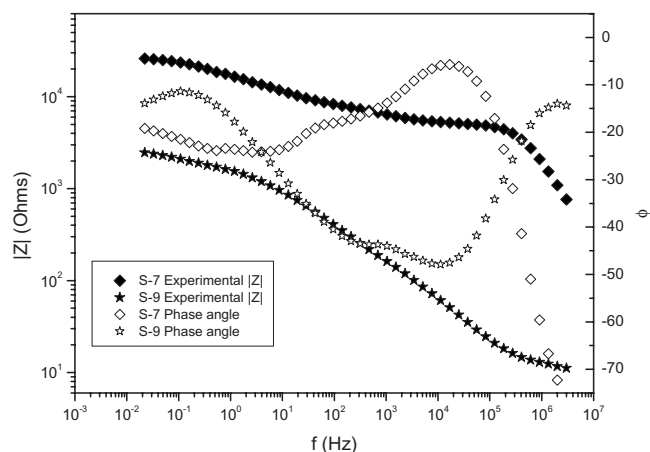


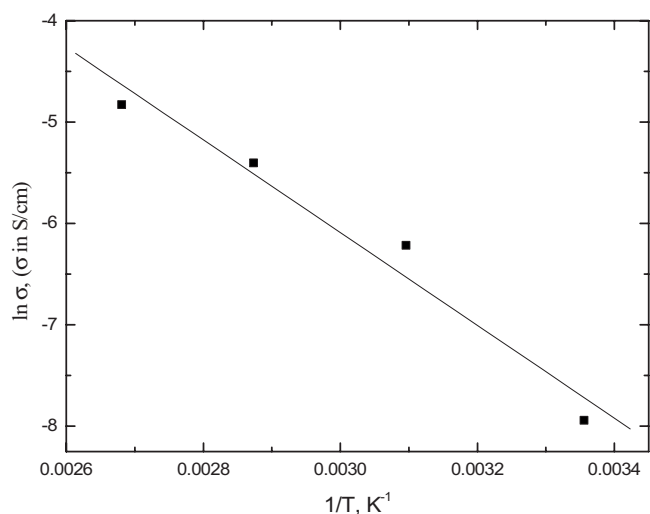
Figure 8. Bode diagrams for membranes S7 and S9, at 25°C.

Neglecting convection flow, the flux of protons in an acidic membrane equilibrated with distilled water under an electric potential gradient  $d\psi/dx$  can be obtained.<sup>46</sup> Actually, the driving force moving one equivalent of protons is  $F(d\psi/dx)$ . To this force, the friction force  $\chi u$  opposes where  $\chi$  and  $u$  are, respectively, the velocity of the particles and the friction coefficient. In steady-state conditions, both forces are equal and  $u = -(F/\chi)(d\psi/dx)$ . Hence, the flux of protons is  $j_+ = -(c_+F/\chi)(d\psi/dx) = -c_+\bar{u}_+(d\psi/dx)$ , where  $\bar{u}_+ = D_+F/RT$ , called ionic mobility, was obtained taking into account the Einstein's relationship  $\chi = RT/D_+$ ,  $D_+$  being the coefficient diffusion of the particle. Because  $j = Fj_+$ , the protons' conductivity is related to the diffusion coefficient of the particles by

$$\sigma = -\frac{j}{d\psi/dx} = \frac{c_+F^2D_+}{RT} \quad [16]$$

For cation-exchange membranes in the acid form equilibrated with water, the concentration of protons in the membrane may be considered equal to the ion-exchange capacity.

Values of the diffusion coefficient of protons in the membranes are given in Table V. The results show that  $D_+$  changes relatively little with the ion-exchange capacity for polyphenyl sulfone membranes containing phosphonic acid groups in their structure, though it undergoes a significant increase for membranes with sulfonic acid fixed groups. However, even for sulfonated polyphenyl sulfone membranes with a high ion-exchange capacity, the value of the proton diffusion coefficient is nearly two orders of magnitude lower than that found for Nafion 117. This may be caused by the rigidity of the polysulfone chains that hinders the formation of hydrophilic percolation path domains through which protons may diffuse. The number of molecules of water per fixed group,  $\lambda$ , is lower than 6 for the



**Figure 9.** Arrhenius plot for the conductance of the S9 membrane equilibrated with distilled water.

polysulfone membranes functionalized with phosphonic fixed groups and lies in the vicinity of this quantity for the polysulfone sulfonic acid membranes. Pulsed gradient spin-echo NMR measurements carried out in Nafion membranes for  $\lambda = 2$ –22 show that the proton diffusion coefficient estimated by this technique,  $D_{H^+}$ , is similar to that calculated from conductivity measurements,  $D_{\sigma}$ , for low values of  $\lambda$  ( $< 5$ ).<sup>47</sup> This means that in the extreme of low water content, water and protons diffuse by an identical mechanism. However, for  $\lambda > 5$ ,  $D_{\sigma} \gg D_{H^+}$  and the difference  $D_{\sigma} - D_{H^+}$  increases as  $\lambda$  increases. From this behavior one can infer that the transport of protons by the Grotthus hopping mechanism probably becomes increasingly important as  $\lambda$  increases in the flexible polyfluorocarbon chains, but it plays a minor role at low values of  $\lambda$ .<sup>47</sup> In the modeling of proton transport in perfluorinated ionomers, Elliott and Paddison<sup>48</sup> have shown that both the vehicular and Grotthus shuttling mechanisms contribute to the mobility of protons, though they are not always correlated, resulting in a lower overall diffusion coefficient. As indicated above, the rigidity of the polyphenyl sulfone chains limits to rather low values the membrane swelling by the effect of water. As a result, the water uptake of polysulfone acidic membranes is rather low and the transport mechanism in this type of membrane is mostly of the vehicular type at room temperature. This reasoning explains that the diffusion coefficient of protons in the polyphenylsulfone functionalized with sulfonic acid groups, having  $\lambda = 6.6$  molecules of water/sulfonic acid group, is nearly two orders of magnitude lower than that of Nafion 117 with  $\lambda = 13.7$ .

The temperature dependence of membrane S9 equilibrated with water was investigated and the pertinent Arrhenius plot is shown in Fig. 9. The plot shows that the activation energy associated with protons transported in the membrane is  $9.2 \pm 0.6$  kcal mol<sup>-1</sup>. This quantity is significantly higher than the activation energy reported for the conductivity of flexible polyelectrolytes, such as perfluoro-sulfonic acid membranes, which amounts to 2.4–3.6 kcal/mol.<sup>49</sup> However, this quantity may be somewhat overestimated. Actually, the curvature of the Arrhenius plot of Fig. 6 suggests that the ionic conductance for this type of membrane may be governed by the volume. This could be a characteristic behavior of membranes made up of rigid chains, such as polymethyl sulfones. The improvement of the percolation path by effect of the increase of temperature in rigid membranes presumably involves segmental motions of the chains associated with relaxation times whose temperature dependence is governed by Vogel-type equations. Work currently being carried out in our laboratories concerning the effect of temperature on the conductivity of rigid acidic membranes will be published in forthcoming papers.

## Conclusions

Phosphonic acid membranes based on polyphenyl sulfone have a lower water uptake than sulfonic acid membranes with similar ion-exchange capacity, presumably as a consequence of the lower acidity of the phosphonic acid groups. However, both types of membranes are characterized for their low water uptake. We can structurally visualize the membranes as containing a high concentration of fixed ions in hypothetical pores filled with water through which proton transport occurs. As a result, the membranes exhibit a high proton permselectivity, even at moderately high concentrations. The effect of the sulfonic and phosphonic acid groups in proton permselectivity seems to be similar. The rather low conductivity of polyphenylsulfone membranes is a consequence of the high rigidity of polysulfone chains that hinders the segregation of hydrophilic segments from hydrophobic ones to form percolation paths through which proton transport takes place. Swelling of the phosphonated membranes is lower than that of the sulfonated membranes owing to the stronger acid character of the  $-\text{SO}_3\text{H}$  groups. As a result, phosphonated polysulfone membranes exhibit proton conductivities at room temperature roughly one order of magnitude lower than sulfonated polysulfone membranes with a similar ion-exchange capacity.

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