Modification of polysulfone membranes with polyethylene glycol and lignosulfate: electrical characterization by impedance spectroscopy measurements

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Abstract

Two sets of composite membranes having an asymmetric sulfonated polysulfone membrane as support layer have been obtained and electrically characterized (membranes SPS–PEG and PA–LIGS). The skin layer of the membrane SPS–PEG contains different percentages of polyethylene glycol in the casting solution (5, 25, 40, and 60 wt%), while lignosulfonate was used for manufacturing PA–LIGS membranes (5, 10, 20, and 40 wt%). Membrane electrical characterization was done by means of impedance spectroscopy (IS) measurements, which were carried out with the membranes in contact with NaCl solutions at different concentrations ($10^{-3} \leq c(M) \leq 5 \times 10^{-2}$). Electrical resistance and equivalent capacitance of the different membrane samples were determined from IS plots by using equivalent circuits as models. Results show a clear decrease in the membrane electrical resistance as a result of both polysulfone sulfonation and the increase of the concentration of modifying substances, although a kind of limit concentration was obtained for both polyethylene glycol and lignosulfonate (40 and 20%, respectively). Results also show a decrease of around 90% in electrical resistance due to polysulfone sulfonation, while the value of the dielectric constant (hydrated state) clearly increases.

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1. Introduction

Membrane separation systems are currently employed in different industrial fields, mainly those related to the use of pressure and concentration gradients (ultrafiltration, nanofiltration, or reverse osmosis and dialysis or hemodialysis, respectively), but those associated with an electrical potential gradient (electrodialysis) are also well established nowadays [1–3]. Moreover, new membrane applications such as fuel cells must be considered, due to their industrial interest importance [4]. It is clear that the structure of membranes and the materials used in such diverse kinds of separation processes, as well as the characterization techniques, have to be rather different. In fact, to predict the membrane performance under pressure differences, it is often necessary to know the mean pore size and pore size distribution, or membrane (active layer) thickness and salt rejection [5–9]. However, for processes directly related to the transport of charged species, membrane electrical parameters such as ion transport numbers, bulk and surface charge concentration, and membrane resistance (or conductivity) are parameters of major interest [10–13]. On the other hand, with respect to membrane materials, polyamide, polysulfone, and regenerated cellulose are polymers commonly used in separation under pressure and concentration gradients [1,2,7, 11], while sulfonated polymers are used as cation-exchange membranes in electrolysis and electrodialysis cells [14,15].
As a result of the need for new membranes for emerging applications, the synthesis of new materials (or the modification of some of the known polymer) must be considered, in order to improve the membrane behavior for a specific use. Sulfonated polymers have also recently gained importance as materials for fuel cell membranes, where a strong demand has arisen for polymer electrolytes [16].

The purpose of this work is the evaluation of changes in the electrical resistance of two sets of modified sulfonated polysulfone membranes. Membrane modification consists in the addition of different percentages of polyethylene glycol (PEG) or lignosulfonate (LIGS), respectively. The reasons to choose these polymers are related to the possibility of facilitating the transport of ions (particularly protons) across the membranes, which could be of interest in the application of the membranes in fuel cell systems. In this context, it should be mentioned that lignosulfonate is a highly anionic polymer consisting of a complex mixture of small to moderate-sized polymeric compounds with sulfonate groups attached to the molecule, which can affect the proton transport across lignosulfonated–polysulfone membranes, while polyethylene glycol is a polymer widely used in many fields, since it is compatible with many organic materials; it presents as a hydrogel and can be used as a proton-selective layer [17,18]. Membrane electrical resistance was determined from impedance spectroscopy (IS) measurements, which were carried out with the membranes in contact with NaCl solutions at different concentrations. IS measurements enable us to obtain information about the different sublayers of heterogeneous systems (such as those formed by membrane/electrolyte solutions) by means of the impedance plots, using equivalent circuits as models, in order to correlate the different circuit elements with the structural/transport properties of the system [19–22].

2. Theory

Impedance spectroscopy is an ac technique for electrical characterization of materials and interfaces based on impedance measurements carried out over a wide range of frequency (10^−6–10^9 Hz). In fact, one of the most important features of IS comes with the development of a direct correlation between the response of a real system and an idealized model circuit composed of discrete electrical components [23].

When a linear system is perturbed by a small $v(t)$ voltage, its response, the electric current $i(t)$, is determined by a differential equation of $n$th order in $i(t)$, or a set of $n$ differential equations of the first order. If $v(t)$ is a sine-wave input, the current intensity $i(t)$ is also a sine wave,

$$v(t) = V_0 \sin \omega t,$$

$$i(t) = I_0 \sin(\omega t + \phi),$$

where $V_0$ and $I_0$ are the maximum voltage and intensity; $\omega$ and $\phi$ are the angular frequency and the phase angle, respectively. Thus, a transfer function, the admittance function, can be defined: $Y^*(\omega) = |Y(\omega)| \exp(j\phi)$. The inverse of the admittance is the impedance function: $Z^*(\omega) = Y^*(\omega)^{-1}$. Since both the amplitude and phase angle of the output may change with respect to the input values, the impedance is expressed as a complex number.

Phenomenologically, a resistance ($R$) represents the dissipative component of the dielectric response, while a capacitance ($C$) describes the storage component of the material. The overall admittance of a parallel ($RC$) circuit is given by the sum of conductance and capacitance contributions,

$$(1/Z^*) = (1/R) + (j\omega C).$$

(1)

The complex impedance can be separated into real and imaginary parts by algebraic rules:

$$Z_{\text{real}} = \left(\frac{R}{[1 + (\omega RC)^2]}\right),$$

$$Z_{\text{img}} = -(\omega R^2 C / [1 + (\omega RC)^2]).$$

(2)

Analysis of the impedance data is often carried out by the complex plane $Z^*(\omega)$ method using the Nyquist plot ($-Z_{\text{img}}$ vs $Z_{\text{real}}$). The equation for the parallel ($RC$) circuit gives rise to a semicircle in the $Z^*(\omega)$ plane such as that shown in Fig. 1a for an electrolyte solution (NaCl); the semicircle has intercepts on the $Z_{\text{real}}$ axis at $R_{\infty}$ ($\omega \to \infty$) and
$R_0\ (\omega \to 0),\ (R_0 - R_{\infty})$ being the resistance of the system. The maximum of the semicircle equals $0.5(R_0 - R_{\infty})$ and occurs at such a frequency that $\omega RC = 1,\ RC = \tau$ being the relaxation time [24]. The Bode plot ($-Z_{\text{imag}}\ vs\ f$) allows the determination of the frequency interval associated with each relaxation process. As can be seen in Fig. 1b, for an electrolyte solution a unique relaxation process at frequencies ranging between $10^5$ and $10^7$ Hz (with the maximum frequency around $10^6$ Hz) can be observed, while at low frequencies ($10 \leq f\ (\text{Hz}) \leq 10^3$) electrode/electrolyte interaction is observed.

Membranes in contact with electrolyte solutions are heterogeneous systems consisting of two subsystems with different dielectric properties. In such cases, two or more different semicircles can exist, which are associated with the different relaxation processes taking place in the system [24]. Moreover, complex systems present a distribution of relaxation times, and the resulting plot is a depressed semicircle; thus, a nonideal capacitor or constant phase element (CPE), which is related to bulk and interfacial inhomogeneities of the system, must be considered [25,26]. The impedance for the CPE is expressed by

$$Q(\omega) = Y_0(j\omega)^{-n},$$

where the admittance $Y_0 = R_0\epsilon_0^{-n}$ is a real parameter ($0 \leq n \leq 1$); in these cases, an equivalent capacitance ($C^{eq}$) can be determined [27]:

$$C^{eq} = (R_0\epsilon_0(1/n)/R.$$ When $n = 0.5$, the circuit element is called a Warburg impedance, $W$, and is associated with a diffusion process according to Fick’s first law.

Impedance spectroscopy data allow the determination of the membrane electrical resistance and capacitance, and from these results membrane geometrical parameters can also be determined [20,28,29]. Symmetric dense membranes (or the dense active sublayers of composite membranes) can be considered as plane capacitors [20,30].

$$C = \varepsilon_0\varepsilon_S/\Delta x_m,$$

where $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon_S$ the relative dielectric constant of the membrane; $S$ and $\Delta x_m$ are the membrane surface and thickness, respectively. The dielectric constant of a dense symmetric membrane can be estimated from the capacitance value if the membrane thickness is known [29,30]. In the case of composite membranes (two-layer systems), formed by a dense active layer and a porous and thick support, Eq. (4) allows the estimation of its thickness from capacitance results if a certain value for the dielectric constant is assumed [30].

3. Material and methods

3.1. Materials

Two sets of asymmetric composite membranes having a sulfonated polysulfone membrane as support layer have been obtained and characterized (membranes SPS–PEG and PA–LIGS). The skin or active layer of SPS–PEG membranes contain different percentages of polyethylene glycol (PEG), while lignosulfonate was used for the manufacturing of asymmetric polyamide PA–LIGS samples. Membrane preparation and thermal sulfonation process for the polysulfone support are briefly indicated in the following paragraphs, but it is extensively developed in Ref. [31].

3.1.1. Preparation of asymmetric polysulfone support membrane

Polysulfone casting solution was prepared by dissolving 15 wt% PS ($M_n \ 16,000$) purchased from Aldrich in $N,N$-dimethylformamide (DMF) with vigorous agitation for 12 h at room temperature. The solutions were cast onto a glass plate using a casting knife of thickness 200 mm followed by precipitation in 15 wt% DMF solution. Then the polysulfone membranes were taken from the bath and rinsed with distilled water (membrane PS). The thickness of the different samples was determined by a digital micrometer (Digimatrix Marck II) and the following average value can be taken: $\Delta x_m = (75 \pm 10) \mu m$.

3.1.2. Thermal sulfonation process

The obtained PS membranes were kept in a 0.25 M H$_2$SO$_4$ aqueous solution for 3 h at $80^\circ$C. Excess acid on the surface was removed by a short water rinse. Afterwards the membranes were put into an oven at $80^\circ$C for 1 h. The thermally treated samples were soaked in distilled water and rinsed daily until the rinsed water reached neutral pH; this type of membrane is labeled as SPS.

Fig. 2 shows the molecular structure of sulfonated polysulfone. The presence of sulfonic acid groups (–SO$_3$H) improved the polysulfone hydrophilicity, which increases the solution taken-up by the membrane matrix [32], which should affect the membrane electrical resistance.

3.2. Synthesis of polyethylene glycol (PEG) membrane

Wax-like PEG (MW 1000, from Aldrich) was dissolved in methanol with different concentration of 5, 25, 40, and 60 wt%. The solution was deposited coherently onto the top surfaces of different samples of the sulfonated polysulfone support membrane. The PEG-covered asymmetric SPS composite membranes obtained were put into an oven to cross link at $80^\circ$C for 30 min, and they were stored in water before use. These membranes will hereafter be named SPS–PEG-5, SPS–PEG-25, SPS–PEG-40, and SPS–PEG-60, respectively. A SEM micrograph of the cross

![Fig. 2. Molecular structure of sulfonated polysulfone.](image-url)
3.3. Synthesis of polyamide containing lignosulfonate (LIGS) membrane

The skin layer of polyamide containing lignosulfonate at different concentrations (5, 10, 20, and 40 wt%) were obtained by interfacial polymerization. Thermally treated sulfonated polysulfone membranes were immersed in a 3 wt% 1,3-phenylenediamine solution, which contains water-soluble lignosulfonate (MW 7000 g/mol, acid groups 8.4 wt%). A solution of 0.15 wt% 1,3,5-trichlorotrichlorobenzyl benzene in hexane was continuously dropped onto the membrane surface, where the interfacial polymerization happened immediately. The formed polyamide composite membrane was cured at 60 °C for 30 min, followed by a complete water rinse. All the obtained polysulfone–polyamide–lignosulfonate membranes were also stored in distilled water before use. These membranes will hereafter be named PA–LIGS-5, PA–LIGS-10, PA–LIGS-20, and PA–LIGS-40, respectively. Fig. 3b shows a SEM micrograph of the membrane cross section, where the asymmetric structure with degradation in the pore size can be observed.

3.4. Impedance spectroscopy measurements

Impedance spectroscopy (IS) measurements were carried out in a test cell similar to that described elsewhere [33] and using an impedance analyzer (Solartron 1260) controlled by a computer. The membrane was tightly clamped between two glass half cells by using silicone rubber rings. In order to minimize concentration-polarization at the membrane surfaces, a magnetic stirrer was placed at the bottom of each half cell, which allows an external control of its speed rate. IS data were corrected by software as well as the influence of connecting cables and other parasite capacitances. One hundred different frequencies in the range 10–10^6 Hz, at a maximum voltage of 0.01 V, were used. Measurements were carried out at a stirring rate of 525 rpm, at six different NaCl solutions (10^{-3} \leq c(M) \leq 5 \times 10^{-2} M), at room temperature t = (25.0 \pm 0.3) °C and standard pH (5.8 \pm 0.3); the solutions on both sides of the membrane having the same concentration. Before use, the membranes were immersed for at least 10 h in a solution of the appropriate concentration.

4. Results and discussion

Nyquist plots obtained with PS and SPS membranes in contact with a NaCl solution (c = 0.01 M) are shown in Figs. 4a and 4b, while Fig. 4c shows a comparison of the Bode plots obtained for both membranes. Two relaxation processes for the whole membrane/solution system were obtained, as can be clearly observed in Fig. 4c, which correspond to the membrane (100 \leq f_{\text{max}} \leq 1000 Hz) and the electrolyte layers between the membrane and the electrodes (f_{\text{max}} \approx 3 \times 10^6 Hz). The shift of the maximum frequency to lower values is associated to closer membrane structure [32].

The impedance plots for two SPS–PEG samples with different concentration of polyethylene glycol (5 and 25 wt%, respectively) are shown in Fig. 5, while Fig. 6 shows the experimental values obtained for two PA–LIGS samples containing 10 and 40 wt% of lignosulfate; all these data correspond to measurements carried out with the membranes in contact with a 0.002 M NaCl solution. For both sets of membrane/electrolyte solution systems two different relaxation processes were also obtained, and a similar maximum frequency was determined in all cases (f_{\text{max}} \approx 4000 Hz).

The equivalent circuits for the different membrane/solution systems consists in series associations of two subcircuits: (i) a resistance in parallel with a constant-phase element for the membrane (circuit: R_m Q_m); (ii) a parallel association of a resistance and a capacitor for the contribution of the electrolyte solution placed between the membrane and the electrodes (circuit: R_e C_e). The fitting of the experimental points was carried out by means of a nonlinear program [34], which allows the determination of the different circuit parameters (electrical resistance and equivalent capacitance). It
should be pointed out the clear difference in the subcircuit assigned to the membrane \((m)\) for the samples containing different percentages of modifying substance (see Figs. 5 and 6), while in all cases similar values were obtained for the impedance part associated with the electrolyte solution \((e)\). It can be considered as a test of the reliability and reproducibility of the impedance spectroscopy measurements.

The variation of PS and SPS membranes electrical resistance with NaCl concentration is shown in Fig. 7a. The decrease in the values of membrane resistance when the salt concentration increases is attributed to the concentration dependence of the electrolyte solution embedded in the membrane network [21,22]. As can be observed, significant differences in the values of the electrical resistance for both samples were obtained; in fact, \(R_m\) values for the sulfonated membrane are around 15 times lower than that for the nonsulfonated polysulfone one, and the average resistance ratio for the whole range of concentration is \((R_m^{PS})/(R_m^{SPS}) = 16 \pm 4\). As was previously indicated, the sulfonic groups incorporated into the sulfonated sample greatly enhance the uptake of aqueous solutions by the membrane matrix, reducing its electrical resistance. Variation of equivalent capacitance with NaCl concentration for PS and SPS membranes is shown in Fig. 7b; differences in \(C_{eq}\) values were also obtained, the values for the sulfonated sample being approximately 10 times higher than those for the nonsulfonated membrane. As can be observed, the equivalent capacitance
Fig. 6. Impedance plots and equivalent circuits for two PA–LIGS membranes in contact with a 0.002 M NaCl solution, (\(\%\)) 10 wt% and (+) 40 wt%: (a) Nyquist plot; (b) Bode plot.

Table 1
Average values for the equivalent capacitance, \(C_{eq}\), and the empirical parameter, \(n\), of the different membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>(C_{eq}) (F)</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>((6.1 \pm 1.1) \times 10^{-11})</td>
<td>0.92 \pm 0.02</td>
</tr>
<tr>
<td>SPS</td>
<td>((2.0 \pm 0.4) \times 10^{-10})</td>
<td>0.87 \pm 0.04</td>
</tr>
<tr>
<td>SPS–PEG</td>
<td>((5.1 \pm 1.3) \times 10^{-9})</td>
<td>0.75 \pm 0.08</td>
</tr>
<tr>
<td>PA–LIGS</td>
<td>((3.2 \pm 1.2) \times 10^{-9})</td>
<td>0.70 \pm 0.06</td>
</tr>
</tbody>
</table>

of both membranes slightly decreases when the salt concentration increases, but an average value for the whole range of concentrations for \(C_{eq}\) as well as for the empirical parameter \(n\) can be determined, and the values are indicated in Table 1. According to these results, the nonsulfonated membrane practically behaves as an ideal capacitor.

Taking into account Eq. (4), the membrane dielectric constant can be estimated from capacitance values, and the following average values were obtained, \(\varepsilon (PS) = (10 \pm 2)\) and \(\varepsilon (SPS) = (30 \pm 6),\) which correspond to both materials in hydrate state. The higher dielectric constant obtained for the sulfonated polysulfone membrane support the improve of hydrophilicity assumed for this sample. In fact, the differences obtained in the electrical parameters for PS and SPS samples clearly show the effect of sulfonation process in the membrane electrical parameters, and they are in agreement with those previously obtained for sulfonated poly(ether sulfones) with different sulfonation degrees [30].

Variation of the electrical resistance of membranes SPS–PEG and SPS–LIGS with NaCl concentration is shown in Figs. 8a and 8b, respectively. For the samples containing the lowest amount of PEG a clear correlation between the decrease in the electrical resistance of the sample and the increase of PEG content can be observed, but small differences between SPS–PEG-40 and SPS–PEG-60 samples were obtained. According to these results, the increase of PEG concentration in the membrane up to 40% practically does not affect its electrical resistance. However, for PA–LIGS samples an optimum concentration of lignosulfate seems to exist (20 wt%) in order to obtain lower electrical resistance, as can be seen in Fig. 8b. The following sequence of values for the membrane electrical resistance of lignosulfate modified samples was obtained: PA–LIGS-5 > PA–LIGS-40 > PA–LIGS-10 > PA–LIGS-20. The increase in the electrical resistance of the samples at the higher lignosulfate content could be related to compaction of the membrane top layer.

Fig. 9 shows the variation of the equivalent capacitance of two SPS–PEG and PA–LIGS samples with different content of the modifying substances. As can be observed, \(C_{eq}\) values slightly increase when the NaCl concentration increases, and small differences depending on both the kind of sample and the concentration of modifying substance exist. However, an average value for the equivalent capacitance and the empirical parameter \(n\) for each set of membranes and the whole range of concentrations were also determined, and their val-
Fig. 8. (a) Membrane electrical resistance versus electrolyte concentration for SPS–PEG membranes: (□) 5, (○) 25, (△) 40, and (△) 60%. (b) Membrane electrical resistance versus electrolyte concentration for PS–LIGS membranes: (□) 5, (○) 10, (△) 20, and (△) 40%.

Fig. 9. Equivalent capacitance versus electrolyte concentration for two samples with different modifying substance concentration for each set of membranes: (□) SPS–PEG 5%, (△) SPS–PEG 25%, (×) PA–LIGS 10%, (△) PA–LIGS 40%.

Fig. 10. Variation of the membrane surface resistance, $r_m$, with the concentration of modifying substance. Experimental values ($c_{\text{NaCl}} = 0.01 \text{ M}$): (■) SPS–PEG, (▲) PA–LIGS; extrapolated values ($c_{\text{NaCl}} = 0.5 \text{ M}$): (□) SPS–PEG, (△) PA–LIGS.

values are also indicated in Table 1. These results show that the presence of modifying substances clearly increases the adsorption of charge by the membrane.

Finally, Fig. 10 shows a correlation between the percentage of modifying substance (polyethylene glycol or lignosulfonate) in the membrane and the surface electrical resistance, $r_m$, of the different samples at a given concentration ($c = 0.01 \text{ M NaCl}$, $r_m = R_m \times S_m$, $S_m =$ membrane area). It can be seen that the presence of polyethylene glycol produces a reduction in the membrane electrical resistance higher than that caused by lignosulfonate at similar percentages. Particularly, for PEG concentrations higher than 25 wt% the reduction in $r_m$ value is around 20% of that corresponding to the sample with the lowest PEG concentration (5 wt%), while for PA–LIGS samples that reduction is around 30%. For comparison, extrapolated values of the surface electrical resistance for the different samples at high concentration (0.5 M NaCl) are also shown in Fig. 10; these values were obtained by extrapolation of those indicated in Fig. 8 for the corresponding membranes. As was previously indicated, membranes with low electrical resistance are of great interest for their possible application in electrodialysis and fuel cell systems. In this context, the results obtained indicate that the SPS–PEG–40 membrane could be a candidate for application in low-resistance devices, since the value of its electrical resistance is only slightly higher than that presented by high-ion-exchange conducting membranes, but it could be improved by using a thinner support.

5. Summary

The electrical characterization of two different sets of composite membranes when they were in contact with NaCl solutions at different concentrations has been carried out. Different membrane samples were prepared by using a sulfonated polysulfone membrane as support layer and different percentages of a modifying substance, polyethylene glycol or lignosulfonate, respectively.

Membrane electrical resistance and equivalent capacitance were determined from impedance data using an equivalent circuit as model, which consists in parallel association of a resistance and constant phase element. A clear reduction in the membrane electrical resistance as a result of both the polysulfone sulfonation and the incorporation of modifying substance was obtained. In this later case, an optimum concentration percentage can be estimated from electrical
results (40% for PEG-containing samples and 25% for lignosulfate ones).

References