Assessment of Mass Transport through Polymeric Electrolyte Membrane by Means of Potentiometric Measures

M. S. S. Gonçalves, A. S. Gomes*

Summary: This work aims to present a simple methodology to evaluate the proton transport of polymeric electrolyte membranes for fuel cells (PEMFC). The device consists of two 'L' tubes with a flanged edge, jointed by a metallic union that allows changing the different membranes to be analyzed. Through Ficḱs equations, the matter that flows through the membrane can be assessed. For instance, a composite membrane made of SPSU containing TPA and modified with bis-benzimidazole derivatives as cross-linker showed flux and diffusion coefficient of $2.27.10^{-12}$ $gm^{-2}s^{-1}$ and $2.18.10^{-7}$ m^2s^{-1}, respectively. These results are 65% larger than the SPSU membranes. The device also allows visualizing, for instance, that the difference between the water columns under atmospheric pressure is not levelled; which means that the pore diameters are sufficiently small to hinder the water molecules crosses them. The conductance values have been found 10^{-3} S and 10^{-4} S to composite membrane and sulfonated membrane, respectively, while the Nafion® membrane presented value at same order of composite membrane.

Keywords: Fick's law; mass transport measurements; PEMFC; polysulfone (PSU); polysulfone sulfonated (SPSU); polysulfone sulfonated ionically cross-linked doped with TPA

Introduction

It is well known the race for development of new technologies as well as researches to find out other alternatives to energy supply. Needless to say about the importance of fuel cells in current world scenery, as well as the strong environmental appeal exhibited by this modal of energy production. The use of this device has been getting attention to produce energy continually, by means of feeding with fuel and oxidizer agent, and continuous conversion of chemical energy in electric power. Moreover, it can be used as stationary source; they can propitiate the provisioning of small groups' consumers. A special attention has been given to those that can be used in feeding of mobile devices, such as, desktops, laptops, cell phones and other apparatus that use batteries, including automobiles.

Thus, it is important to emphasize the fundamental role exercised by the polymeric electrolyte membranes for fuel cells (PEMFC), they should avoid that the electrodes touch each other, therefore there is not short circuit, allow only protonic crossing, supporting temperatures of order of 120 °C at least, and should have good mechanical resistance.

Induced for previously published articles,[1–5] we notice the simplification possibility of methodology used in that works, as well as robustness contained in this proposal, assessment of mass transport through potentiometric measurements, once this measure type is reliable. This way, with a glass blower's aid, we could construct the apparatus (Figure 1). The device presented in this work is consequence of countless readings about pertinent papers related to

Universidade Federal do Rio de Janeiro – IMA – Instituto de Macromoléculas Professora Eloisa Mano P.O Box 68525, Zip Code: 21945-970 Cidade Universitária, Rio de Janeiro, Brazil
Fax: +552125627210; E-mail: gaughin@gmail.com

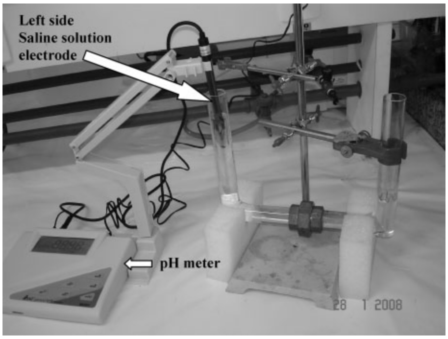

Figure 1.
Device totally prepared to make measurements, pH meter in position to register changes.

mass transport and diffusion.[6,7] In the majority of reported works, impedance spectrometry has been used for proton transport measurement. This method has as answer the resistivity that can be converted in electric conductivity. Logically, materials prevailing resistive do not allow the hydronium ion cross. This way, in case some electronic conductivity; is probable that such system also allows that, the hydronium ion across through the membrane. However, the mathematical correlation between two amounts is not very accurate.

Searching for alternatives to Electrochemical Impedance Spectrometry (EIS) method, aiming quantify protons that crosses the membrane, another approach was tried, incorporating several concepts, such as, osmotic pressure, chemical potential (Equation 1) and potentiometric measures (pH meter), it is worth to emphasize that the simplicity and low cost can turn it more accessible. It is important to mention, that this model must be not confused with cell proposed by Hittorf, where it is used electric potential application on both sides of device.

Starting from a simple model of control, the cation's permeation through the membrane, impelled by chemical potential difference originated from equilibrium between a strong acid, with a derived salt of reaction of that one with a strong base (Equation 3) has as consequence, the pH fall on the side of saline solution. It can be followed by pH variation and changes in the hydronium concentration, which allows to evaluate the hydroniun ion amount that crosses membrane for unit of time and area; being taken into account the Fick's laws, by means of calculations to estimate the hydronium ion flow that traverses the membrane (Equations 4 and 5).

In relation to used polymeric material, it seems which PSU has been an appropriated choice to application, due to low cost, wide availability, or easiness to synthesise, and chemo-physical characteristics, but when that polymer is sulfonated become soluble in water, therefore, is necessary to overcome this constraint. By means of molecular design proposed by Gomes et al.,[8] which developed a system whose alternative was apply another approach, i.e., totally ionic cross-linked system to join the polymer backbone, through ionic bonds, having as primary result, the inner salt's formation, outcome from acid moieties contained in main chain with basic ends of cross-link agent. The PEMFC based on SPSU composite containing tungstophosphoric acid (TPA) and modified with bis-benzimidazole derivatives (BBIz), as cross-link spacers were prepared. The cross-linkers provided a better retention of TPA particles embedded within composite membranes. In other hand, similar projects used covalent bonds that are directional, i.e., the membranes produced in this manner become very brittle, while ionic interactions are not directional, allowing materials more flexible (see Figure 2).

Thus, the main objective of this work is to show a simple way to measure the protonic mass transport accomplished by the membranes. As far as we are concerned, similar device to measure proton transport through polymeric membranes was not previously reported.

Experimental Part

Materials

Sulphuric acid 98 wt% and lithium sulphate monohydrated (Vetec, Brazil). The water

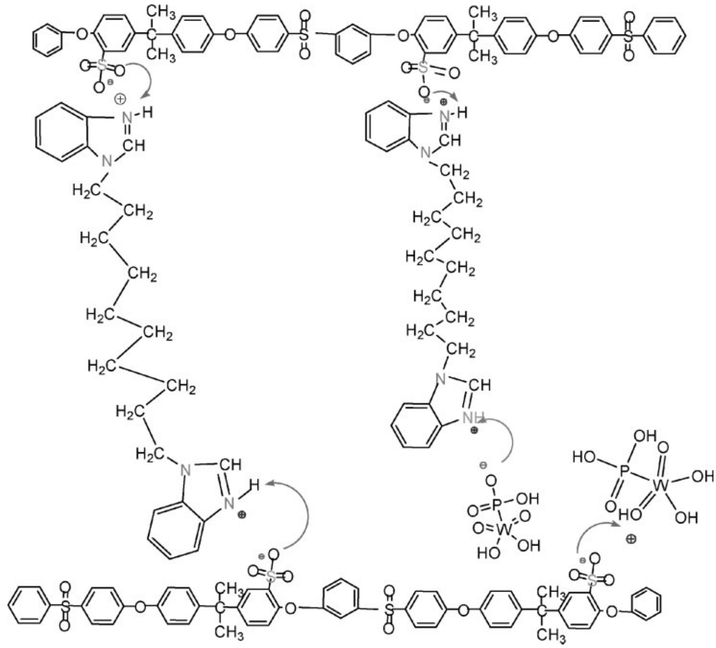

Figure 2.
Sketch of composite membrane (SPSU - BBIz - TPA).

used for solutions preparation was deionized in Millipore deionizer equipment. A pH meter Akso, model AK 122 with accuracy of ± 0.2 mA was used for pH measurements. Basf gently supplied the PSU (molar mass 40,000 Da). The dopant agent, tungstophosphoric acid hydrate (TPA); benzimidazole; 1, 10 dibromodecane and trimethylsilyl chlorosulfonate (TMSiClS) were purchased in Aldrich Co. All materials were used as received.

Device Assembly Description

The device assembly is quite simple. It is sufficient to put the membrane between the flanges and rubber O-ring's between the flanges and the metallic union, in way to avoid wear and tear between the glass parts and the metallic union. In Figure 3, the device details can be seen before assembly.

Sulfonation of Polymer in a Glove Bag

Previously dried PSU (50 g) was dissolved in dichloroethane (DCE) - 410 mL under magnetic stirring and N_2 atmosphere. After that a solution of TMSiClS (25 mL) in 80 mL of DCE was added in drops for 30 minutes within PSU solution, the reactional system has been stirred for an additional 5 hours. The system was heated in a water bath at 50 °C. Afterwards, the solution has been poured into a large amount of freeze propanol-2. It is important to mention that we cannot get results with methanol, because the product was soluble in that one. A viscous mass was produced, after filtration; the material was dried into oven under 130 °C for 6 hours.

Membrane Preparation

After dissolution of PSU in dichlorethane, the membrane's material was cast and poured on a flat glass plate; originating a film after having evaporated the solvent. Starting from film, we have prepared membranes. The other SPSU and SPSU ionically cross-linked membranes were produced in a similar way. The difference lies in the starting material; SPSU was used as polymeric backbone, in both cases, dissolved in N-methyl pirrolydone. In the membranes ionically cross-linked and

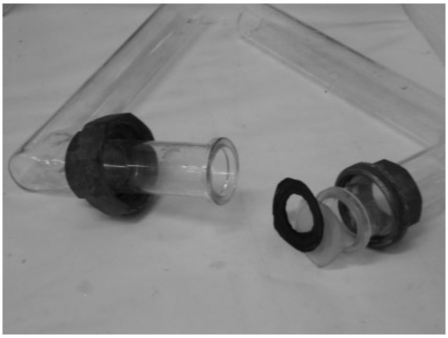

Figure 3.
Construction details of the device.

doped with TPA, these other components were dissolved in same solvent and added to SPSU solution. Such solutions were cast and poured and the produced membranes obtained in a similar way of that one used to produce the PSU membrane.

Proton Transport Measurements

It is worth emphasizing that the saline solutions pH varied between 6 and 9,[9] the deionized water presented pH of order of 6.64 on average. During the experiments were recorded only pH below 7, as we know, only below this value hydronium ion activity begins to present relevance. After solution preparation, the pH was measured; the saline solution was added first within column of left side, followed by electrode introduction, waiting until pH stabilization. Once stabilised the pH, the acid solution was added within right side column, to preventing that chemical potential could promote cations displacement before the effective measurement, although the pH fall took long to happen, about 15 minutes to begin, considering as initial pH that measured before additions.

It was also put a narrow tube, where gaseous nitrogen was injected, to producing some turbulence and avoid stagnation points into solution. The experiments were carried out under environmental conditions (temperature and pressure). The pH was measured from time to time, being the registered values converted in concentration, all results were summarised in Table 1. The pH values were converted in hydronium concentrations (gram per cubic centimetre), through Equation 7 and then plotted against time in Figure 4. In opposition to illustration 4, Figure 5 displays the pH falling against time. All membranes

Table 1.
pH values and hydronium ion concentration increasing with time.

SPSU ionically cross-linked			Pure SPSU 65%		
Time (s)	pH ± 0.02	$[H^+]$ g.cm^{-3}	Time (s)	pH ± 0.02	$[H^+]$ g.cm^{-3}
0	6.72	1.91E-10	0	7.00	1.00E-10
22	6.56	2.75E-10	32	6.84	1.45E-10
44	6.38	4.17E-10	98	6.57	2.69E-10
83	6.04	9.12E-10	169	6.33	4.68E-10
90	5.97	1.07E-09	321	6.00	1.00E-09
121	5.60	2.51E-09	373	5.80	1.58E-09
162	5.13	7.41E-09	447	5.57	2.69E-09
184	4.88	1.32E-08	532	5.25	5.62E-09
225	4.50	3.16E-08	592	4.98	1.05E-08
276	4.09	8.13E-08	612	4.60	2.51E-08
311	3.87	1.35E-07	693	4.24	5.75E-08
368	3.57	2.69E-07	768	3.93	1.17E-07
413	3.38	4.17E-07	843	3.61	2.45E-07
451	3.26	5.50E-07	967	3.29	5.13E-07
492	3.14	7.24E-07	1105	3.05	8.91E-07
553	3.00	1.00E-06	1235	2.92	1.20E-06
640	2.89	1.29E-06	1909	2.62	2.40E-06
714	2.82	1.51E-06	2271	2.54	2.88E-06
1364	2.59	2.57E-06	3207	2.46	3.47E-06

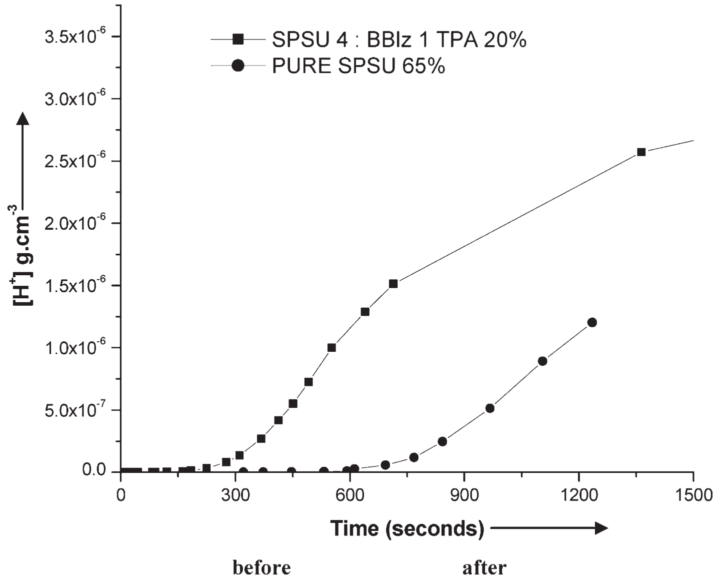

Figure 4.
Hydronium concentrations increasing against time.

had diameters of 2,10 cm and thickness of 170 μm, approximately. The expectation was that the sulfonated ionically cross-linked and doped membranes have better permeability than sulfonated polysulfone membrane.

Scanning Electron Microscopy

Samples were fractured under cryogenic conditions and vacuum. They were sputtered with a thin layer of gold before imaging by scanning electron microscopy (SEM) JEOL model JSM-5610LV.

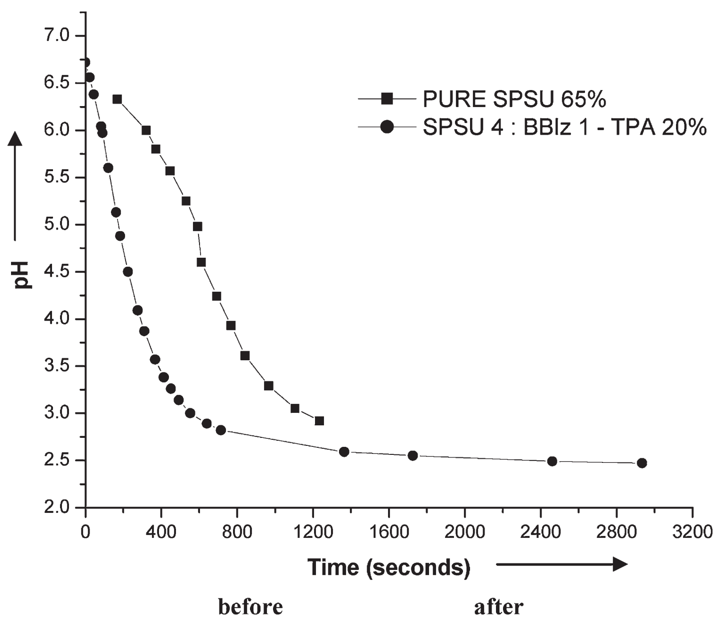

Figure 5.
pH fall against time.

Electrical Characterizations

Proton conductivities were measured in transverse direction. The membranes were sandwiched within stainless steel electrodes. When submitted to temperatures around 80 °C, membranes were under full hydration conditions. Measurements were performed using Autolab PGSTAT-30, over a frequency range of 10 Hz–1 MHz, using voltage amplitude of 0,1V.

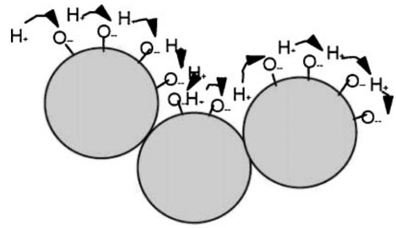

Figure 6.
Protonic jumps forecast by Grotthuss.[10]

Results and Discussion

Chemical Potential

Using the equation (1) for both cations and making the difference between the equations and rearranging, we obtain equation (2):

$$\mu = \mathrm{RT}\ \ln\gamma \tag{1}$$

$$\frac{\mu_{\mathrm{H}}^{+} - \mu_{\mathrm{Li}}^{+}}{\mathrm{RT}} = \ln\gamma_{\mathrm{H}}^{+} / \ln\gamma_{\mathrm{Li}}^{+} \tag{2}$$

By the theoretical calculations, it was concluded that the chemical potential is enough to promote the balance between the cationic species, that is, exchange between H^+ and Li^+ originated from the acid and the salt, respectively. It was confirmed by fall of pH during time that the experiment was carried out. It was observed that solutions more concentrated propitiated a larger pH fall, for instance, with a concentration of 2 M or 0.5 M, was obtained a pH in order of 1, although the concentration 0.1 M promotes a rapid cationic exchange, but the final pH was of order of 2.

Protonic Transport Mechanism

This way, among the possible transport mechanisms, we believed in that mechanism attributed to Grotthuss (see Figure 6[10]), which forecast the H^+ ions jumps through water molecules or sites that contains pairs of available electrons, is the most plausible, because water molecules do not permeate the membrane. According to equation (3) below:

$$\mathrm{Li_2SO_{4(aq.)}}||\mathrm{H_2SO_{4(aq.)}} \xrightarrow{\text{time}} \mathrm{LiHSO_{4(aq.)}}||\mathrm{LiHSO_{4(aq.)}} \tag{3}$$

Water Permeation

As mentioned before, the water permeation did not take place through membranes. In other words, the membranes made with PSU, SPSU and SPSU ionically cross-linked and doped with TPA, it possess such properties that do not allow water molecules to cross them under atmospheric pressure, it was expected that the columns of separate water by the membrane were balanced, but it was not observed, even after 30 days of observation.

Sulfonation Degree Versus Ionic Cross-Link

In reference to PSU membranes, besides it does not allow the water molecules crossing by them, it did not also make possible the balance between the cations. In other words, the H^+ and Li^+ did not traverse the membrane, which is in agreement with the article of W. Richard Bowen et al., and Juana Benavente et al.[11,12] Although in his papers, the PSU membranes have been submitted to pressure, and that the focus of his work was in polymeric blends and their effects on permeation and dielectrical properties, respectively. This way, we can infer that sulfonic groups contained in SPSU contribute to cation flow through membrane. In relation to SPSU membranes, has been verified that a high sulfonation degree, as 65%, produced a protonic flux in the order of 1.64 10^{-12} g.m^{-2}.s^{-1} in a process of facilitated diffusion, as well as the membrane that possesses ionic cross-links presented a protonic flux in the order of 65% larger than that just sulfonated. Such result seems to be coherent with that one anticipated, after all, the cross-link agent, besides having a larger volume, when interacting with sulfonic groups, it forms salts and this improves the hydrophilic characteristic of the system. Additionally, the imidazole groups have nitrogen atoms with pair of free electrons to aiding in protonic jumps. There is also the possibility of sulfonic groups promote, or even accelerate the cation exchange process, where they could be used as platform for the jumps.

Flux

By equations, (4) and (6) it can be evaluated theoretical values of measure of membranes mass flow and diffusion constant. The obtained values are 1.64 10^{-12} g m^{-2} s^{-1} and 1.73 10^{-7} m^2 s^{-1} for the SPSU membrane and 2.27 10^{-12} g m^{-2} s^{-1} and 2.18 10^{-7} m^2 s^{-1} for the ionically cross-linked membrane, respectively.

$$J = \mathcal{D}\,\partial C/\partial x \tag{4}$$

$$\mathcal{D}\,\nabla^2 C = \partial C/\partial t \tag{5}$$

Done due readjustments and considering a unidirectional flow (1-D), in X for instance, we have:

$$\mathcal{D}\,\partial^2 C/\partial x^2 = \partial C/\partial t \tag{6}$$

It is worthwhile to mention that the found values are relative, because it is a simplification and imposition of boundary conditions. For example, the diffusion coefficient is considered as being constant, unidirectional flow, no reaction occurrence, no turbulence, constant density. Although, it is a good approach of what happens in fact.

Concentration Measurements

In agreement with pH measures through equation 6, we can calculate the hydroniun concentration, as follow:

$$[H^+] = 10^{-pH} \tag{7}$$

Membrane Porosity

Considering the fact of SPSU and SPSU ionic cross-linked and doped membranes do not allow the water crossing, but let the ions Li^+ and H^+ cross the membrane, in agreement with the pH measures, we could also foresee about membranes porosity, that lies between 240 pm < pore diameter < 280 pm.[11] It is empiric estimate; taking into account neither tortuousity nor connectivity among the pores, considering the pores that does not allow cations crossing.

Membrane Swelling

The ionic cross-linked membranes are resistant to hot water (90 °C – 24 hours), acid and the salt used in the experiments; they did not present solubility, but some samples swelled around 20% on average.

Topological Characterization

In Figure 7 is presented a micrograph obtained from SEM (scanning electronic microscope) of transversal section morphology for composite membrane, where can be seen a surface dispersed homogeneously. The arrows indicates voids and some heterogeneous dispersion, probably is the cross-linker poor dispersed, albeit,

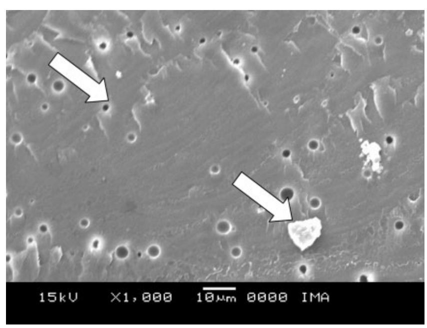

Figure 7.
SEM micrograph of composite membrane in transverse section.

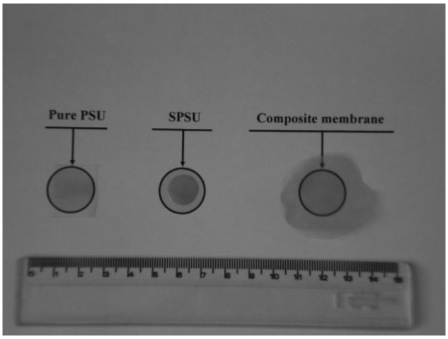

Figure 8.
Different kinds of membranes made from PSU as precursor.

the general aspect of membrane be homogeneous. In other sample, previously prepared, that is, with 20% addition of cross-link agent, these effects were more intense. Figure 8 shows all materials mentioned in this work, from pure PSU until composite membrane. Can be observed that membrane made with PSU is transparent, after sulfonation becomes brownish (SPSU), when it is mixed with cross-link agent and dopant, the material's colour stays less intense.

Electrical Characterization

The conductance was measured at room temperature (RT) and 80 °C after 60 minutes of equilibration in each temperature and was quite to reach a constant value of conductance. The conductance data were evaluated using FRA® (frequency response analyzer) from AUTOLAB and the conductance values were determined from spectra on the intercepts with X-axis. In Figure 9, we can get resistance values approximately 3020 and 450 Ω to SPSU and SPSU ionically cross-linked and doped with TPA, respectively. While the Nafion®117 membrane exhibited resistance around 185 Ω, enough to isolate the electrodes in a real cell. Translating these results in conductance can be found the following values: 10^{-4}, 10^{-3} and 10^{-3} S, respectively. Recalling that, the pure SPSU is not resistant in hot water. Therefore, although SPSU membrane presents a conductance value appropriated, it should not be used in FC. Whilst in Figure 10 we can see characteristic spectra of PSU, representative of resistive material, with resistance value in the order of MΩ.

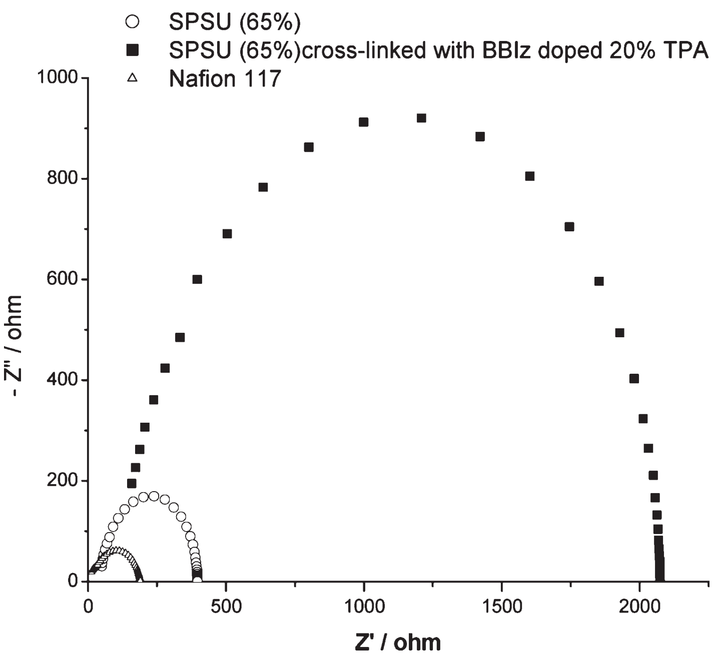

Figure 9.
Impedance spectra of different membranes.

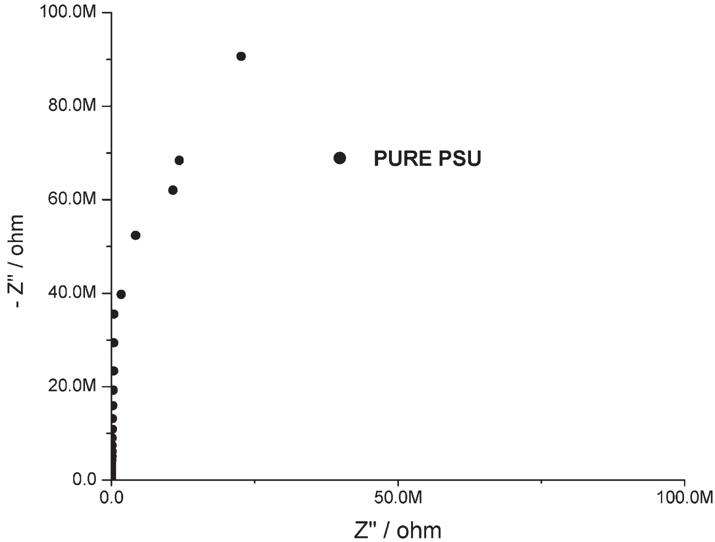

Figure 10.
Characteristic spectrum of pure PSU membrane.

Conclusion

The membranes can also work in atmospheres of low humidity, or even dry. Nevertheless, the protonic flow depends mainly of membrane porosity; in case of fuel, if the supply is done with humidified gaseous hydrogen, the water in liquid state does not aid the mass transport, since gas diffusion is necessary through the liquid. Moreover, it has been looking for an increase in the operational temperature of cell, for instance, temperatures above 100 °C. So that, the growing of work temperature in those levels also help in the conductivity, outcome of increase in molecular mobility, therefore, polymers with high temperature resistance are quite appropriate to such requirement.

In relation to the model of vehicle transport, the water can serve as carrier until the contact with membrane, but no more than this, once it does not cross membrane. On the other hand, the Grotthuss mechanism seems to be more adequate to explain this result. The membranes with sites that possess free electrons pairs help protonic jumps, facilitating the hydronium ion transport by them.

The devices, in fact, allow us to do inferences on porosity of surveyed materials, but if compared it with impedance spectrometer, can be seen that it cannot measure the electrical resistivity. Although, for didactic purposes, i.e., is possible just for the end to show those who do not have any idea of what happens in a fuel cell system, the protonic transport, and the perception that engineering polymers films through appropriated modifications can be applied in PEMFC, in opposition to initial idea, which those polymers could be highly brittle. Besides, they can keep water and serve as sophisticated filters or coating materials. Furthermore, the extremely low cost of device, allows its easy construction for everyone.

In respect of electrical measurements, we can conclude that ionic cross-link design is very successful, keeping SPSU backbone pristine and presenting conductance values acceptable to using in FC.

List of Symbols

Latin Letters

$\mathcal{D}$	diffusivity constant / $cm^2\ s^{-1}$
R	Gas Constant / $J\ mol^{-1}\ K^{-1}$

T	temperature / K
m	meter, mili
p	pico
t	time / seconds
C	concentration / g cm^{-3}
x	membrane thickness / m
pH	ionic potential of hydroniun
J	molar flux / g m^{-2} s^{-1}
M	molar concentration / g cm^{-3}
$[H^+]$	hydroniun concentration / g cm^{-3}
PSU	polysulfone
SPSU	polysulfone sulfonated

Greek Letters

μ	chemical potential, micro
∂	partial derivatives
γ	activity coefficient

Subscripts

aq. aqueous solution

Over Signs

$\rightarrow$	reaction direction
$\|\ \|$	potential junction

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