Polymeric Proton Conducting Systems Based on Commercial Polymers: Crossover Analysis and Single Cell Testing

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ABSTRACT: Continuing with the work published previously (Escribano et al., J Appl Polym Sci 2004, 93, 2394; Escribano et al., J Appl Polym Sci 2006, 102, 13) this article shows the final part of the characterization of the films object of our study, containing hydrogenated poly(butadiene-styrene) block copolymer, ethylene-propylene terpolymer, and a third component, polypropylene, polystyrene or silica, crosslinked with peroxides and heterogeneously sulfonated. Water uptake and methanol crossover were determined, and the results were compared with those of Nafion prepared by casting. A complete Membrane electrode Assembly was tested in a single cell obtaining the polarization and power curves at different temperatures and pressures, and modeling it by an electrical equivalent circuit in the symmetrical mode configuration using the electrochemical impedance spectroscopy technique. This study offers a physical interpretation relating physical parameters to several processes occurring in the system. Methanol crossover is lower than in Nafion, and power density values are in some cases higher than in Nafion. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2386–2392, 2011

Key words: block copolymer; ionomers; swelling; power density; impedance spectroscopy

INTRODUCTION

Ion conducting polymers have attracted a great deal of interest because of their numerous electrochemical applications, such as batteries, sensors, or low temperature fuel cells such as direct methanol fuel cells (DMFC) and hydrogen polymer fuel cells (PEMFC). Both, PEMFC and DMFC are attractive, energy efficient, and environmentally friendly power sources, concretely they are promising candidates for transportation, distributed power, and portable power applications. Hydrated perfluorosulfonic acid membranes, such as Nafion®, are typically used as the electrolyte in fuel cells because of their excellent chemical, mechanical, and thermal stability in addition to their high conductivities, but it has mainly two disadvantages, high cost and high methanol crossover.[1–3] Current research is focused on the development of new polymer membranes to make these fuel cells an economical and practical option.[4,5]

Our group has been working on the synthesis and characterization of ionomers based on block copolymers like an alternative to Nafion.[6,7] When one of these blocks contains ionic groups attached to its structure, these types of materials are very interesting. In the presence of water they swell, due to the strong hydrophilic character of the ionic aggregates or clusters. The hydrophilic dominions carry water and protons whereas the hydrophobic dominions confer stability to the material and can act as a barrier for methanol crossover.

In this work we have carried out the synthesis (via heterogeneous sulfonation), the water uptake, and methanol crossover analysis and electrochemical characterization of three families of ionomers based on a mixture of block copolymer ionomers (hydrogenated styrene butadiene block copolymer (HSBS) and ethylene-propylene-norbornene terpolymer (EPDM)) and a third component: polypropylene (PP), polystyrene (PS) and silica, respectively. HSBS possesses a two phase microstructure consisting of polystyrene (PS) domains where sulfonation ocurrs, dispersed in a rubbery continuous phase of hydrogenated polybutadiene. EPDM permits the crosslinking for obtaining better mechanical properties. And the third component will provide different characteristics to the mixture: PP improves mechanical properties, PS provides additional reactive groups for the sulfonation reaction, and silica improves the absorption water capacity of the samples.

EXPERIMENTAL

Materials

The following initial materials were used: hydrogenated butadiene-styrene block copolymer (HSBS) containing 30 wt % of styrene ($Mn = 55,000$) supplied

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TABLE I
Sulphur content, Ion-Exchanges Capacities, and Percent Water Absorption

Sample	Composition (wt %)					S (%)	IEC (mmol g^{-1})	Water uptake (%)
	HSBS	EPDM	PP	PS	SILICA			
Nafion®	–	–	–	–	–	–	0.91	20.6
BG-01Vs	45	45	10	–	–	6.24	1.95	56.2
BG-02Vs	40	40	20	–	–	5.54	1.73	55.6
BG-11Vs	45	45	–	10	–	7.51	2.35	109.1
BG-12Vs	40	40	–	20	–	8.70	2.72	149.2
BG-21Vs	45	45	–	–	10	5.95	1.86	55.3
BG-22Vs	40	40	–	–	20	5.15	1.61	70.3

by Repsol-YPF Química under the trade name Calprene CH-6110; ethylene-propylene-norbornene terpolymer (EPDM) BUNA G 3850 containing 60% ethylene, 29% propylene, and 11% norbornene, supplied by Exxon Chemical; polypropylene (PP) 099 ISPLEN supplied by Repsol ($T_m = 164.97°C$ and $T_g = 123.13°C$); polystyrene (PS) POLYSTYROL 143 E supplied by BASF ($T_g = 88.52°C$) and commercial silica ULTRASIL VN3 with a specific surface area of 175 m²/g supplied by Degussa. Table I compiles the blend compositions under study. The crosslinking agent used was dicumyl peroxide (Aldrich).

The membrane of Nafion® used to compare results (thickness = 85 μm) has been prepared by casting a 5% Nafion® solution in a mixture of water and low aliphatic alcohol supplied by Aldrich.

Sulfonation reaction and membrane preparation

An open two-roll mill was used to blend the samples. The crosslinking agent was added during mixing in a ratio of 2 g of peroxide by each 100 g of blend.

Membranes with thicknesses between 60–100 μm were obtained by compression molding using a hydraulic press Collin. The temperature of plates was 160°C and the applied pressure 200 bar.

The heterogeneous sulfonation reaction was achieved by immersing the membranes in a solution of chlorosulfonic acid in 1,2-dichloroetane 0.2 M during 6 h. Then they were washed with water and vacuum dried.

Ion-exchange capacity, methanol crossover, and water uptake

The ion-exchange capacity (IEC) (mmol of sulfonic acid/g of polymer) of each polymer was determined by elemental analysis (EA) in a LECO CHNS-932.

Methanol crossover through the membranes was determined using a hand made device that consists of two glass containers (one contains water and the other 2 M methanol solution under mechanical stirring) with double shirt for water circulation and temperature control ($T = 40$ and 60°C). Both contain-

ers are interconnected through the membrane. The aliquot samples from water container are extracted at different times (30 min, 1, 2, 4, 6 and 24 h) to be analyzed by means of gas chromatography in a Hewlett Packard M5890 series II.

Methanol permeability coefficient P, expressed in cm²/s, is determined by applying the continuity equation[8] for diffusion on a plane sheet geometry, an approach which is valid for short test times: $[(C_B(t)V_B L)/(C_A A)] = P(t - (L^2/6D))$ (1), where C_A is the methanol concentration in the donor compartment (2 M) and C_B (t) stands for the methanol portion that has crossed over to the receptor or water compartment, which is determined after each test interval t by means of gas chromatography. V_B (t) is the volume in the receptor compartment. Initially this volume amounts to 23 mL water, from which, after each test interval, 0.8 mL are extracted, which have to be deducted at each point. L stands for membrane thickness (cm), and A for the membrane surface area (0.7223 cm²). D is the methanol crossover coefficient, and t the time at which each aliquot is extracted (30 min, 1, 2, 4, 6, and 24 h).

From the slope of the plot of methanol concentration against time, we can obtain the methanol permeability in each case.

Water uptake was determined as follows: the membranes were immersed in deionized water for a week. They had been weighed prior to immersion (w_{dry}) and weighed again at the end of the week, after removing the excess of water (w_{wet}). Water uptake was defined as the percentage in weight gain due to water absorption and calculated according to this expression: Water uptake (%) = $[(w_{wet} - w_{dry})/w_{dry}] \times 100$ (2)

Polarization curve test and symmetrical electrode mode EIS analysis

The single cell of 5 cm² active area consists on the experimental membrane, two identical electrodes (Toray carbon paper 40 wt % wet proofing as the gas diffusion layer; catalyst layer 0.78 ± 0.07 mgPt/cm² using 40% platinum on Vulcan XC-72 (E-TEK))
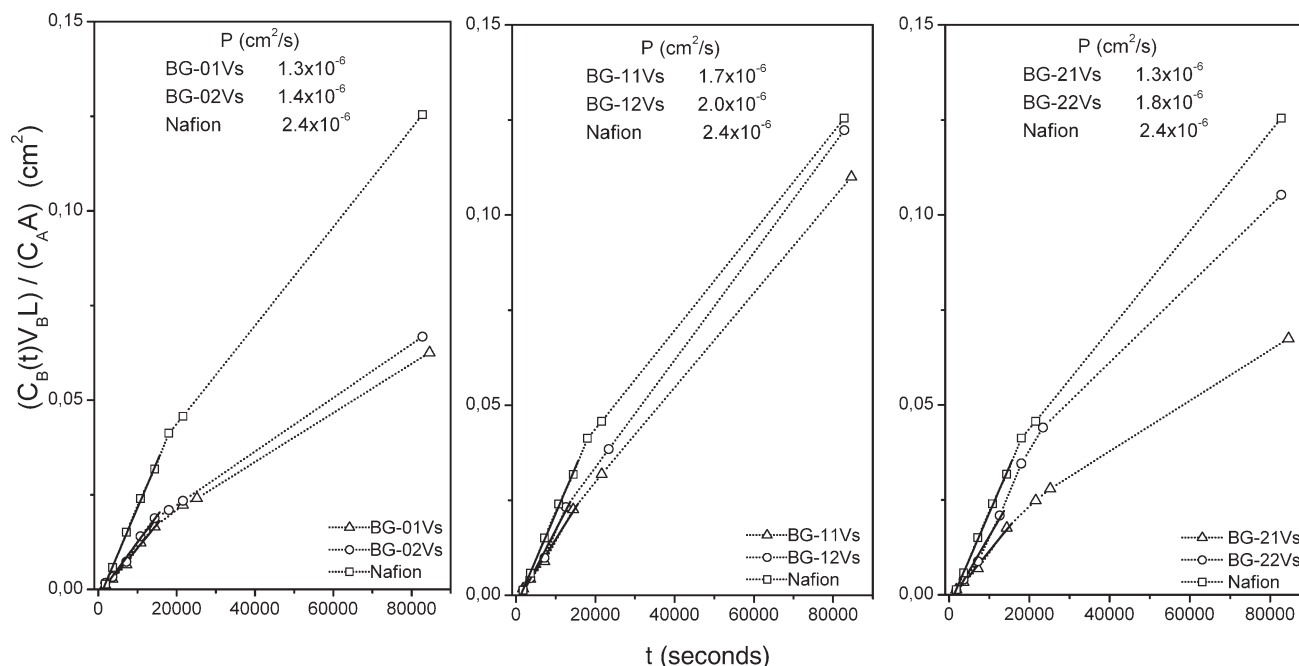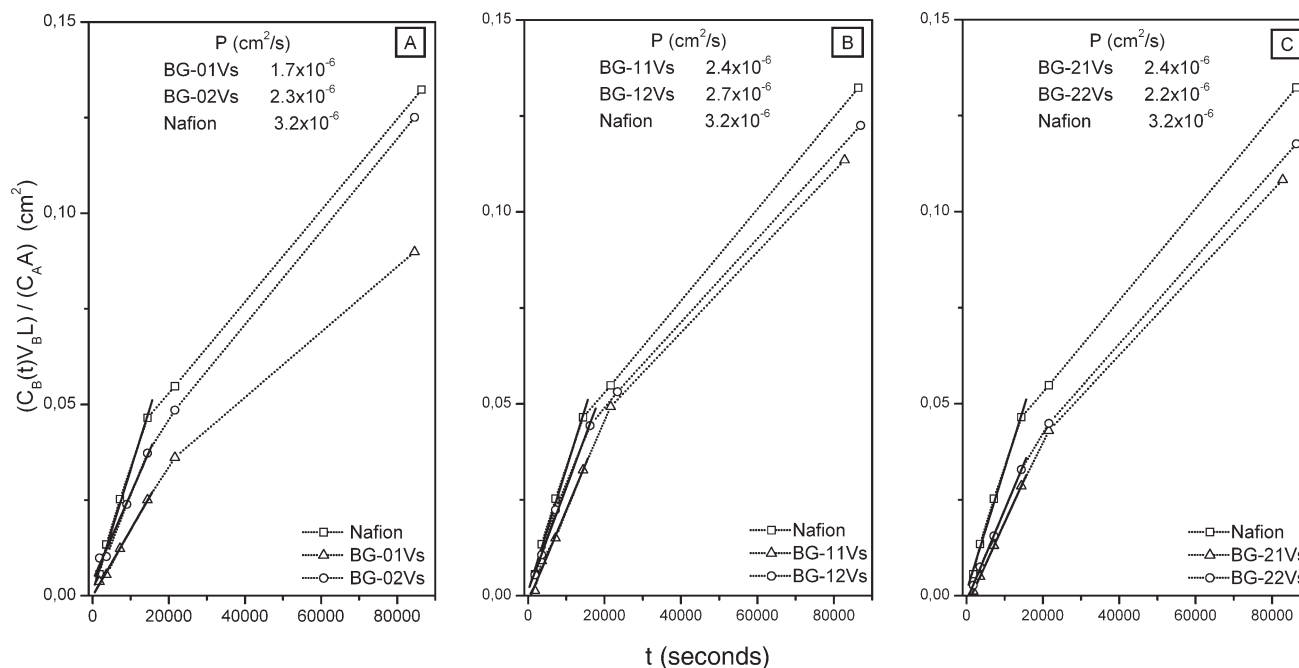
Figure 1 Methanol difusion at 40°C through the different membranes: (A) containing PP, (B) containing PS, and (C) containing silica.

and two metallic bipolar plates. The membrane electrode assembly (MEA) was assembled using a hydraulic press, applying heat and pressure. The polarization curves were recorded at three cell temperatures, 60, 70, and 80°C, with H_2 in the anode and O_2 in the cathode. Both gases were previously hydrated by passing across two containers with water warmed up to 60°C to maintain the hydration

level, and three different pressures (1, 1.5, and 2 bar). Each experiment lasted between 7 and 8 h.

Single cells modeling was carried out by an electrical equivalent circuit (EC) in the symmetrical mode configuration using the electrochemical impedance spectroscopy (EIS) technique.[9] Impedance was measured directly in the frequency domain by applying a single-frequency voltage to the cell and

Figure 2 Methanol difusion at 60°C through the different membranes: (A) containing PP, (B) containing PS, and (C) containing silica.

TABLE II
Maximum Power Density Values for the Experimental Samples and Nafion[®]

Sample	Thickness (μm)	Power density$_{max}$ (mW cm^{-2}) $T = 60°C$			Power density$_{max}$ (mW cm^{-2}) $P = 2$ bar		
		$P = 1$ bar	$P = 1.5$ bar	$P = 2$ bar	$T = 60°C$	$T = 70°C$	$T = 80°C$
Nafion[®]	85	117	123	137	137	141	119
BG-01Vs	62	106	134	160	160	145	90
BG-02Vs	83	52	57	76	76	70	65
BG-11Vs	91	102	129	141	141	100	54
BG-12Vs	82	50	74	90	90	51	41
BG-21Vs	71	115	129	166	166	173	162
BG-22Vs	99	64	81	92	92	100	87

recording the real and the imaginary parts of the resulting current at that frequency. An impedance analyzer (HP 4192 A LF) was used to measure complex impedance data. Equivalent circuit Boukamp was the software chosen for the data analysis.[10] Measurements were carried out with the single fuel cell working in an electrode "symmetrical mode" (SM), that is, with the same gas injected in both electrodes (O_2/O_2 and H_2/H_2). The working temperatures of the cell were 60, 70, and 80°C, and the applied pressure 2 bar.

RESULTS AND DISCUSSION

Table I shows sulphur content and ion-exchange capacity (IEC) as determined by EA, and percent water absorption (wt %) of the membranes. Proton conductivity depends on the concentration of ion conducting units (sulfonic acid) in the polymer membrane and on the water absorption as water is needed like the mobile phase. The ion content is characterized by the molar equivalents of ion conductor per mass of dry membrane and is expressed as IEC.

In experimental samples, both IEC determined from EA and water content are higher than that observed for Nafion. Concretely, IEC and water uptake values for experimental membranes with 10 and 20 wt % of polystyrene, respectively are the highest because these samples have additional reactive groups where sulfonation occurs.

Figures 1 and 2 show the plot of methanol concentration against time and the methanol permeability values at 40 and 60°C, respectively calculated from the slope of the plot for the experimental membranes and Nafion for comparing results. As it can be seen the methanol crossover in experimental membranes is minor than in Nafion, due to the barrier effect exerted by the nonsulfonated blocks of HSBS. It is important to consider that the cured polymers are insoluble materials. This can be an advantage to reduce methanol crossover as it can be seen from the results.[11]

The good state and correct operation of the fuel cell were proved by determining the polarization and power curves operating with H_2/O_2 at different cell temperatures and gases pressures. Table II lists the maximum power density values for the experimental membranes and Nafion. As it can be seen, higher gas pressures cause an increase of the maximum power density in all cases. It is important to emphasize that those samples with 10 wt % of the third component (BG-01Vs, BG-11Vs and BG-21Vs) reach values of power density higher than Nafion in some cases. However, the membrane with 10 wt % PP suffers dehydration at 80°C and the sample with 10 wt % PS at 70°C, being power density significantly lower from these temperatures, just like Nafion. However, the membrane with 10 wt % silica shows higher power density values at all temperatures, although power density decays slightly at 80°C, perhaps due to a worse water or thermal
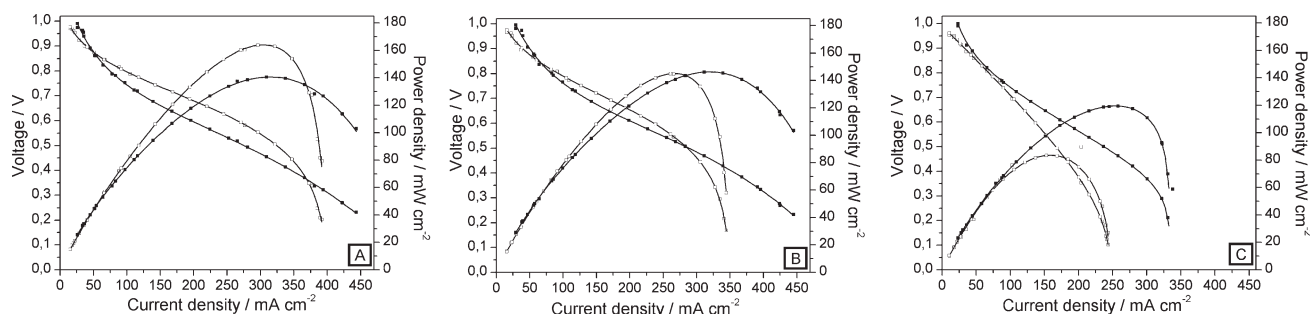
Figure 3 Polarization and power curves for the sample with 10 wt % of PP (BG-01Vs), at 2 bar of pressure and temperatures of: (A) 60°C, (B) 70°C, and (C) 80°C (—□— experimental sample, ---■--- Nafion).
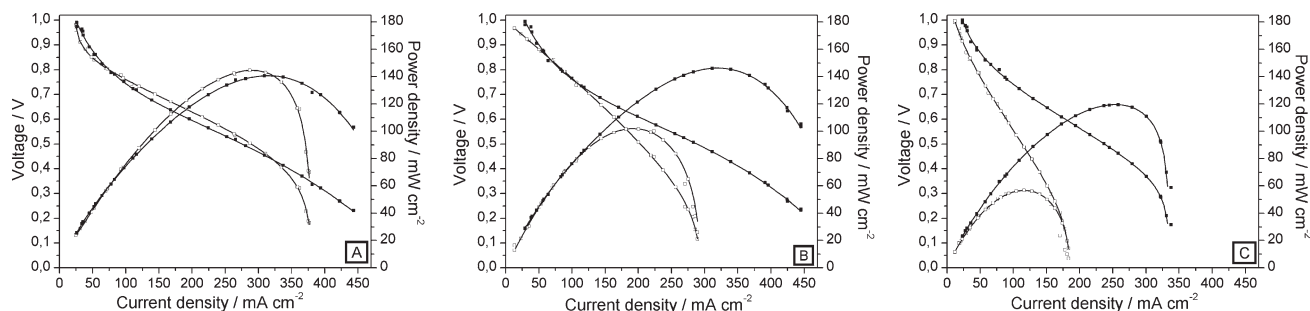
Figure 4 Polarization and power curves for the sample with 10 wt % of PS (BG-11Vs), at 2 bar of pressure and temperatures of: (A) 60°C, (B) 70°C, and (C) 80°C (—□— experimental sample, ---■--- Nafion).
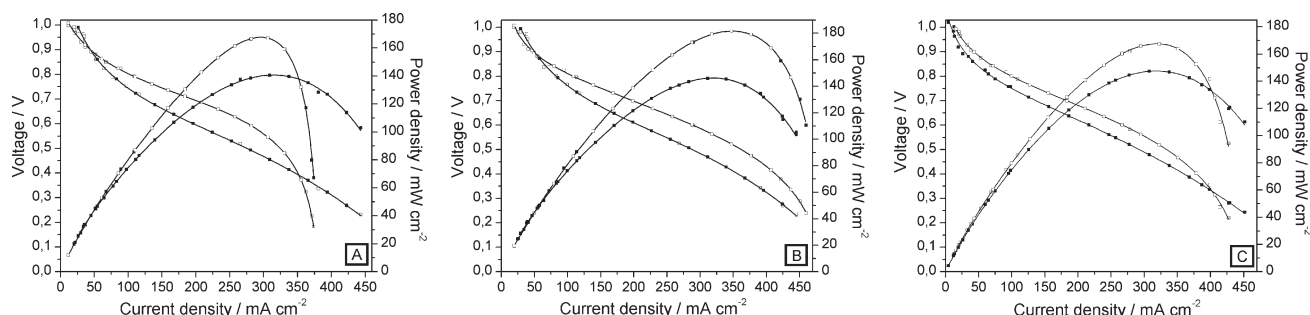

Figure 5 Polarization and power curves for the sample with 10 wt % of silica (BG-21Vs), at 2 bar of pressure and temperatures of: (A) 60°C, (B) 70°C, and (C) 80°C (—□— experimental sample, ---■--- Nafion).

management at this temperature. Nevertheless, power density continues being higher than Nafion and stable after several load cycles. This fact is indicating a greater capacity of hydration and water retention in the case of this hybrid membrane, at least during the time that each experiment lasted (7–8 h). In all cases and when the test finished and cell was opened, the membranes presented a good state maintaining their dimensional stability. Figures 3, 4, and 5 show the polarization and power density curves for these membranes and for Nafion with the purpose of comparing results.

In spite of the promising results obtained previously in the IEC and water-up-take measurements, the experimental membranes BG-02Vs, BG-12Vs, and BG-22Vs, show lower performance than Nafion at all temperatures. This fact can be due to other parameters that directly affect the power density values obtained, like the MEA preparation or the membrane hydration. These aspects will be commented in more detail when the charge transfer resistance (R_1) in the electrode-membrane interface be studied by EIS.

From the impedance spectra (Fig. 6 shows an example of the type of obtained spectra) recorded by means of EIS for the single cells with experimental membranes and Nafion, the corresponding equivalent circuit (EC) model was determined. The circuit diagram was similar for all the tested membranes and is shown in Figure 7.

This EC describes the electrical behavior of the single cell like a series combination of a pseudo-inductance (L) associated with the effects produced by all the metallic components of the single cell, the ohmic resistance associated with the membrane (R_m) and two sub circuits, one describing the charge transport in the electrode-membrane interface (sub circuit 1) and the other related to the mass transport processes (sub circuit 2). Each sub circuits are composed in his turn of a resistance in parallel with a
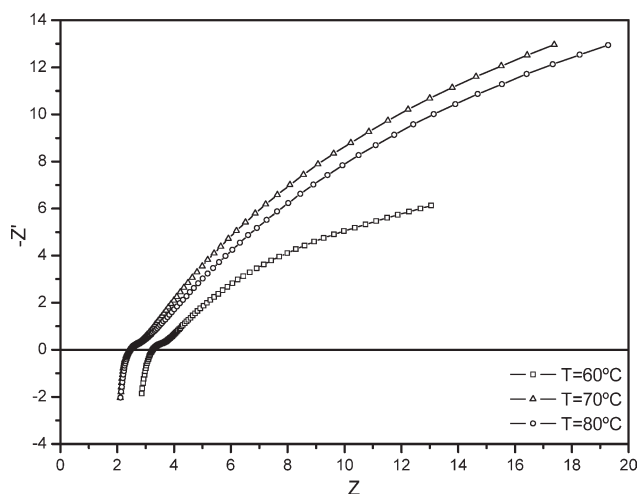
Figure 6 Impedance spectrum obtained by EIS for BG-11Vs sample, injecting O_2 in both electrodes, at 60, 70, and 80°C, and 2 bar of pressure.
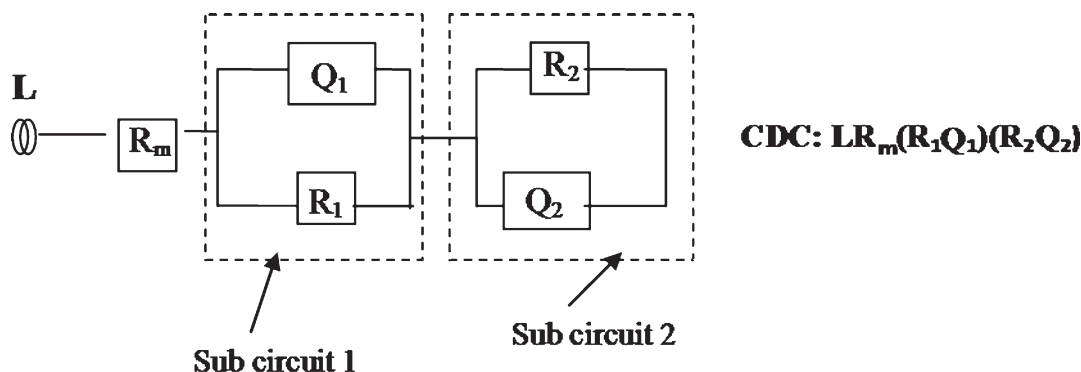
Figure 7 Equivalent circuit fitted for a complete single cell using each experimental membrane and Nafion, in SM, with electrode gases H_2/H_2 and O_2/O_2, at 2 bar and 60, 70, and 80°C.

pseudo-capacitance. Sub circuit 2 shows that mass transport occur by a combined process of adsorption and diffusion.

The ionic resistance of the membrane (R_m) and the resistance of the charge transfer in the electrode-membrane interface (R_1) which is associated with the presence of mixed conduction (protonic-electronic) at this interface will be are analyzed subsequently.

Tables III and IV list R_m and R_1 values obtained with O_2 and H_2 injected in both electrodes, respectively. In the most of the experimental membranes, R_m is higher than that of Nafion and values are not very steady perhaps due to problems with the water

management in the cell. The membrane with 10 wt % silica (BG-21Vs) is an exception of this behavior, because R_m values are stable enough, remaining in the same order of magnitude than Nafion, even slightly lower with increasing the cell temperature. This fact is indicating that this experimental membrane does not dehydrate when temperature increases, at least during the $\sim$ 5 or 6 h that each experiment lasted.

In the charge transfer process, also several aspects can be emphasized: R_1 values for all the samples are higher than Nafion, which indicates a worse contact membrane electrode; again the sample with 10 wt % of silica shows similar R_1 values than the commercial

TABLE III
R_m and R_1 Values Obtained in the Study with O_2 Injected in Both Electrodes

	O_2/O_2					
	R_m (Ω)			R_1 (Ω)		
	40°C	60°C	80°C	40°C	60°C	80°C
Nafion®	1.16 E-01	2.10 E-01	3.10 E-01	1.52 E-01	5.27 E-01	7.1 E-01
BG-01Vs	1.97 E-01	2.11 E-01	2.54 E-01	5.90 E+01	3.29 E-01	1.54
BG-02Vs	1.25	8.24 E-01	3.36 E-02	1.20 E+01	1.53 E-01	1.23
BG-11Vs	2.66	2.40	1.85	8.74 E-01	9.66 E-01	2.21
BG-12Vs	6.05 E-02	6.17 E-02	1.77	2.25	1.63 E+01	2.78
BG-21Vs	3.38 E-01	4.37 E-01	2.89 E-01	3.33 E-01	4.28 E-01	6.08 E-02
BG-22Vs	2.80	1.84	1.36	9.66	4.45	2.98

TABLE IV
R_m and R_1 Values Obtained in the Study with H_2 Injected in Both Electrodes

	H_2/H_2					
	R_m (Ω)			R_1 (Ω)		
	40°C	60°C	80°C	40°C	60°C	80°C
Nafion®	1.71 E-01	1.87 E-01	1.85 E-01	3.65 E-01	2.47 E-01	2.06 E-01
BG-01Vs	3.64	1.84	1.34	7.24	3.65	1.86
BG-02Vs	1.48	1.53	1.28	4.44	2.18	1.04
BG-11Vs	4.09	5.16	6.16	2.89	6.23	8.15
BG-12Vs	1.86	1.77	1.73	4.07	2.78	3.20
BG-21Vs	1.99	9.65 E-01	6.17 E-01	1.47	5.56 E-01	1.91 E-01
BG-22Vs	3.63	2.28	2.22	8.97	6.05	6.09

membrane and even smaller at 80°C, in both O_2/O_2 and H_2/H_2 testing. This fact indicates that charge transfer process in BG-21Vs membrane is very favorable, and also the performance of the cell is optimum because R_m and R_1 values are similar. However, the other membrane that reached high power densities, sample with 10 wt % PP (BG-01Vs), presents both R_1 and R_m much higher than Nafion either for O_2/O_2 and H_2/H_2 testing, so in this case, it could be essential to improve the membrane electrode assembly preparation to optimize the cell operation.

CONCLUSIONS

The results indicate that the addition of 10 wt % of a third component to the polymer mixture is a suitable way to obtain materials with the desired properties for being a possible alternative electrolyte in low temperature fuel cells.

Methanol diffusion through experimental membranes is much lower and water uptake is higher than Nafion, probably due to the block structure of HSBS whose nonionic blocks make a barrier effect to the diffusion and ionic blocks favor the water absorption and the proton transport.

The best performance results were obtained for BG-01Vs and BG-21Vs membranes. It can be emphasized that the sample with 10 wt % PP reached 160 mW/cm^2 at 2 bar and 60°C and, particularly, the membrane with 10 wt % silica behaved better than Nafion at any pressure and temperature.

Finally and furthermore, the equivalent circuit model analysis of the latter demonstrates an optimum single cell performance connected with a better MEA preparation.

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