Short communication

Preparation, characterization and single cell testing of new ionic conducting polymers for fuel cell applications☆

P.G. Escribano*, C. del Río y, J.L. Acosta

Instituto de Ciencia y Tecnología de Polímeros (CSIC), C/Juan de la Cierva, 3, 28006 Madrid, Spain

ABSTRACT

In this work, heterogeneous sulfonation and both, structural and electrical characterization of a mixture composed on block copolymer ionomers (HSBS and EPDM) and commercial silica, are studied. The incorporation of sulfonic groups was checked by infrared spectroscopy (FTIR-ATR). Microstructure was studied by means of dynamic mechanical analysis (DMA). Also, water uptake and methanol crossover were determined, and the results were compared with those of Nafion® 117. Electrical behavior was recorded by means of electrochemical impedance spectroscopy (EIS) at different hydration times. Results show that sulfonation of the styrene rings has effectively occurred. Conductivity values are similar to Nafion and they improve with hydration time. Methanol crossover is lower than in Nafion.

Finally, a single complete proton exchange membrane fuel cell (PEMFC) as a whole was tested obtaining the polarization and power curves at different temperatures and pressures, and modeling it by an electrical equivalent circuit (EC) in the symmetrical mode (SM) configuration using the EIS technique. This study offers a physical interpretation relating physical parameters to several processes occurring in the system. Power density values are higher than in Nafion.

© 2008 Elsevier B.V. All rights reserved.

1. 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 use a polymer membrane as proton exchanger. For this application, Nafion® (Dupont) is still the most frequently used membrane although it has mainly two disadvantages, high cost and high methanol crossover [1,2]. Current research is focused on the development of new polymer membranes to make these fuel cells an economical and practical option [3,4].

In this sense, our group has been working on the synthesis and characterization of ionomers based on block copolymers like an alternative to the commercial membrane Nafion [5–8]. When one of these blocks contains ionic groups attached to its structure, this type of materials are very interesting due to, 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 the proton charge, whereas the hydrophobic dominions confer stability to the material and can act as a barrier for methanol crossover. Because of that, hydration is the principal condition for these polymers to show their conductive properties.

Thus, in this work we have carried out the synthesis (via heterogeneous sulfonation), the structural, electrical and electrochemical characterization of two ionomers based on a mixture composed on block copolymer ionomers (hydrogenated styrene butadiene block copolymer (HSBS) and ethylene–propylene–norbornene terpolymer (EPDM)) and commercial silica. HSBS possesses a two-phase microstructure consisting of polystyrene (PS) domains where sulfonation occurs, dispersed in a rubbery continuous phase of polybutadiene. EPDM permits the crosslinking for obtaining better mechanical properties. And silica that also improves properties and absorption water capacity of the samples.

2. Experimental

2.1. Materials

The following initial materials were used: a hydrogenated styrene butadiene block copolymer (HSBS) containing 30 wt.% of styrene (Mn = 55,000) supplied by Repsol-YPF Química under the trade name Calprene CH-6110; an EPDM BUNA G 3850 contain-

ing 60% ethylene, 29% propylene and 11% norbornene, supplied by Exxon Chemical; and a commercial silica ULTRASIL VN3 with a specific surface area of $175\,m^2\,g^{-1}$ supplied by Degussa. The crosslinking agent used was dicumyl peroxide (Aldrich).

The commercial membrane Nafion® 117 (thickness = 183 μm), supplied by Dupont, was used to compare results.

2.2. Sulfonation reaction and membrane preparation

An open two-roll mill was used to blend two samples: one with concentration HSBS/EPDM/silica (45/45/10) named BG-21Vs and another with concentration HSBS/EPDM/silica (40/40/20) named BG-22Vs. 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 80 and 100 μm were obtained by compression moulding 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 placing membranes in a solution of chlorosulfonic acid in 1,2-dichloroetane 0.2 M during 6 h. Then they were washed and vacuum dried.

2.3. Structural and electrical characterization

Dynamic mechanical analysis (DMA) was carried out on a Mettler Toledo DMA 861 analyzer operating in the tension mode. Spectra were recorded at a frequency of 1, 5 and 10 Hz within a temperature range from −100 to 130 °C for the cured samples, and from −100 to 300 °C for the sulfonated samples, and at a heating rate of 2 °C min^{-1}.

IR analysis, attenuated total reflection (ATR) technique was carried out on a PerkinElmer spectrum one spectrometer. Infrared spectra were recorded using four scans at 4 cm^{-1} resolution.

Analysis of the electrical properties of the sulfonated samples was made by means of electrochemical impedance spectroscopy (EIS) using a Hewlett Packard 4192A analyzer. Frequency range was 10^{-2} to 10^4 kHz and the amplitude of the oscillation applied was 0.1 V. The tests were carried out on hydrated samples at two working temperatures, 60 and 80 °C, during different hydration times (30 min, 1–6 h). A first measurement was taken immediately after taking the membrane out of a deionized water bath, where it had been immersed for 10 min ($t = 0$), for achieving optimum hydration conditions. Subsequently, the membranes were placed in a glass container filled with water at working temperature under a N_2 current, thus forming a water steam-saturated atmosphere, in order to maintain the hydration level.

2.4. Ion-exchange capacity (IEC), methanol crossover and water uptake

The IEC (mmol of sulfonic acid g^{-1} 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 containers 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 cm^2 s^{-1}, is determined by applying the continuity equation [9] for diffusion on a plane sheet geometry, an approach which is valid for short test times:

$$\left[\frac{C_B(t)V_B L}{C_A A} \right] = P \left(t - \left(\frac{L^2}{6D} \right) \right) \tag{1}$$

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:

$$\text{water uptake (\%)} = \left[\frac{w_{wet} - w_{dry}}{w_{dry}} \right] \times 100 \tag{2}$$

2.5. Polarization curve test and electrode symmetrical mode (SM) EIS analysis

A single cell of 5 cm^2 consisting on the experimental membrane previously immersed in a deionized water bath for a few minutes, two identical electrodes made of the catalytic layer (0.7 mg Pt cm^{-2}) and carbon Vulcan dust, and two metallic bipolar plates was assembled for the MEA testing using a experimental bank for PEMFC. 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 in order to maintain the hydration level, and three different pressures (1, 1.5 and 2 bar) were applied in anode and cathode. 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 EIS technique [10]. Impedance was measured directly in the frequency domain by applying a single-frequency voltage to the cell and 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 was the software chosen for the data analysis [11]. Measurements were carried out with the single fuel cell working in an electrode "symmetrical mode", 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.

3. Results and discussion

Fig. 1 shows the dynamic mechanical spectra recorded for the samples before and after sulfonation. Two glass transitions are observed in the non-sulfonated samples spectrum, corresponding to the hydrogenated polybutadiene (HPB) units (~ -35 °C) and PS domains (~ 95 °C). This is due to a HPB–PS phase separation. Furthermore another relaxation is observed at about −90 °C, corresponding to movements in the aliphatic chains.

DMA analysis of the samples indicates that the HPB glass transition slightly shifts towards higher temperatures due to the appearance of restrictions in the movements of the polymer because of the presence of ionic aggregates or clusters (Fig. 1 B). Relaxations due to the presence of clusters are also observed in the spectrum. They appear between 50 and 150 °C and could be assigned to ionic associations of minor or greater size (quadruplets, sextuplets, multiplets, or finally clusters [12]).

The infrared spectroscopy was used to verify the sulfonation of membranes. Fig. 2 compares the samples spectra before and after sulfonation. The broad band over 3000 cm^{-1} is associated to the O–H groups and to the associated water. The band that appears about 1700 cm^{-1} is associated with the O–H stretching
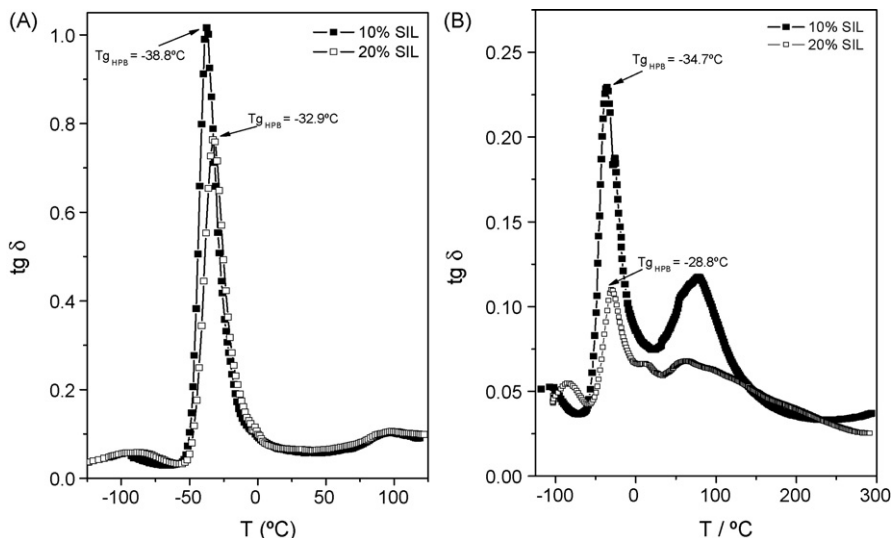
Fig. 1. DMA spectra for the non-sulfonated (A) and sulfonated (B) samples: 10% SIL, 20% SIL.

vibration of the hydrated sulfonic group. And the most characteristic bands associated to the vibration of sulfonic groups (SO_3H) are the $O=S=O$ symmetric and asymmetric stretching vibrations that appear at 1150 and 1030 cm^{-1}, and the bands observed at 1005 and 1130 cm^{-1} that are associated with the vibrations of a phenyl ring *para*-substituted with a sulfonated group (indicated by the arrows in the extended spectrum zone in Fig. 2) [13]. Furthermore, a broad band appears in this same spectrum zone due to the Si–O–Si bond in all cases ($\sim$1000 cm^{-1}).

Table 1 shows sulphur content and ion exchange capacity (IEC) as determined by E.A., 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 due to water is needed as 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

Table 1
Sulphur content, ion-exchanges capacities and percent water absorption.

Sample	Composition (wt.%)			%S	IEC (mmol g^{-1})	Water uptake (%)
	HSBS	EPDM	SILICA			
Nafion 117	–	–	–	–	0.91	20.6
BG-21Vs	45	45	10	5.95	1.86	55.3
BG-22Vs	40	40	20	5.15	1.61	70.3

water uptake value for experimental membrane with 20 wt.% of silica is more than three times higher than that of Nafion.

Ionic conductivity of the membranes was determined by means of impedance spectroscopy, being the conductivity σ (S cm^{-1}) the inverse of the resistivity ρ (Ω cm) of the membrane that is obtained from the intercept of high frequency impedance curves with the real axis (ρ'). Fig. 3 represents the logarithm of conductivity as a function of hydration time for experimental membranes and Nafion 117 with the purpose of comparing results. While unhydrated, the
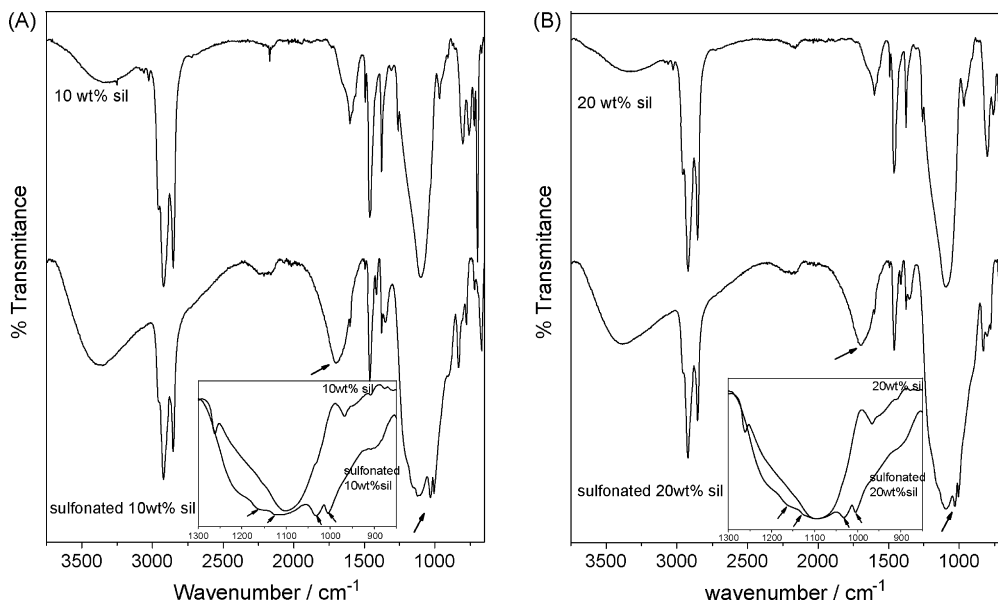

Fig. 2. Infrared spectra for the samples with 10 wt.% silica (A) and 20 wt.% silica (B), before and after sulfonation.
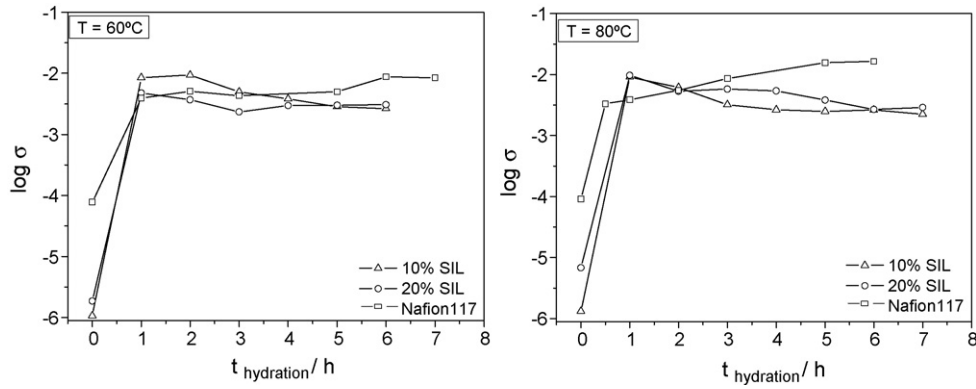
Fig. 3. Lograrithm of conductivity as a function of hydration time for the experimental membranes and Nafion® 117.

Table 2
Methanol permeability results for the experimental samples and Nafion® 117.

Sample	Composition (wt.%)			$P_{Methanol}$ (cm^2 s^{-1})	
	HSBS	EPDM	SILICA	40 °C	60 °C
Nafion 117	–	–	–	1.8×10^{-6}	2.3×10^{-6}
BG-21Vs	45	45	10	0.8×10^{-6}	1.2×10^{-6}
BG-22Vs	40	40	20	1.3×10^{-6}	1.7×10^{-6}

films are practically insulators, a rapid increase in conductivity can be observed with hydration, similar to Nafion at 60 °C and lightly lower than that of Nafion at 80 °C. Both experimental samples show analogous values, which remain stable during the measuring time. The highest values obtained are in the order of 9×10^{-3} S cm^{-1}.

Table 2 compiles the methanol permeability values at 40 and 60 °C respectively for the experimental samples 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 non-sulfonated 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 [14].

The good state and correct operation of the fuel cell were proved by working it with H$_2$/O$_2$ at different temperatures and pressures and determining the polarization and power curves. Table 3 com-

piles the maximum power density values for the experimental samples and Nafion. As it can be seen a pressure increase causes a maximum power density increase in all cases. It is important to emphasize that sample with 10 wt.% of silica (BG-21Vs) shows values of power density higher than Nafion and these values are similar at all temperatures, although power density decays slightly to 80 °C, perhaps due to a worse water or thermal management at this temperature, but power density continues being higher than Nafion and stable after several 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). When the test finished and cell was opened, the membranes presented a good state. Fig. 4 shows the polarization and power curves for this membrane (BG-21Vs) and for Nafion with the purpose of comparing results.

Nevertheless, BG-22Vs sample shows values of power density lower than Nafion in all the studied temperatures, despite the promising results obtained previously in the IEC and water uptake measurements. This fact can be due to other parameters that directly affect the power density values obtained, like can be the MEA structure. This aspect is commented next when studying the resistance of the charge transfer (R_1) in the electrode–membrane interface.

From the impedance plots for the cells with experimental membranes and Nafion measured by means of EIS, impedance data are

Table 3
Maximum power density values for the experimental samples and Nafion® 117.

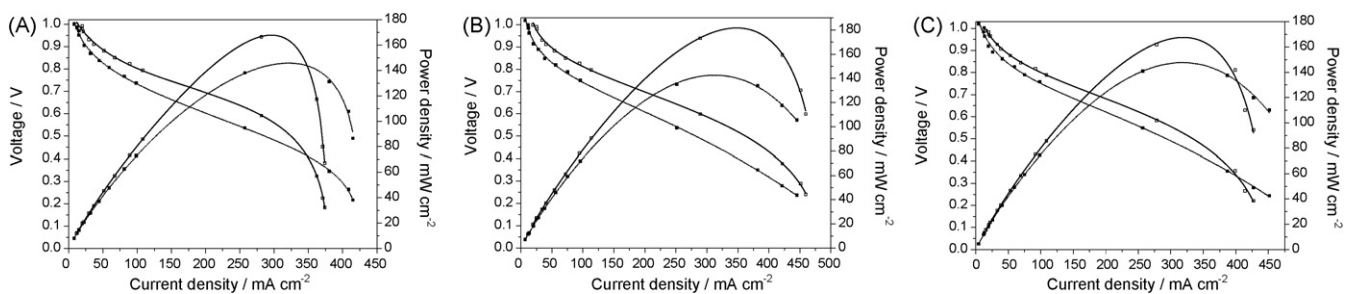| Sample	Thickness (μm)	Power density$_{max}$ (mW cm^{-2}) $T = 60$ °C			Power density$_{max}$ (mW cm^{-2}) $P = 2$ bar		
		$P = 1$ bar	$P = 1.5$ bar	$P = 2$ bar	$T = 60$ °C	$T = 70$ °C	$T = 80$ °C
Nafion 117	183	102	120	138	138	135	139
BG-21Vs	71	115	129	166	166	173	162
BG-22Vs	99	64	81	92	92	100	87

Fig. 4. 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).

Table 4
R_m and R_1 values obtained in the study with O_2 injected in both electrodes.

	O_2/O_2								
	BG-21 Vs			BG-22 Vs			Nafion 117		
	40 °C	60 °C	80 °C	40 °C	60 °C	80 °C	40 °C	60 °C	80 °C
R_m (Ω)	3.38E-01	4.37E-01	2.89E-01	2.80	1.84	1.36	1.26E-01	1.49E-01	2.06E-01
R_1 (Ω)	3.33E-01	4.28E-01	0.61E-01	9.66	4.45	2.98	1.78E-01	6.69E-01	6.12E-01

Table 5
R_m and R_1 values obtained in the study with H_2 injected in both electrodes.

	H_2/H_2								
	BG-21Vs			BG-22Vs			Nafion 117		
	40 °C	60 °C	80 °C	40 °C	60 °C	80 °C	40 °C	60 °C	80 °C
R_m (Ω)	1.99	9.65E-01	6.17E-01	3.63	2.28	2.22	1.52E-01	2.02E-01	1.48E-01
R_1 (Ω)	1.47	5.56E-01	1.91E-01	8.97	6.05	6.09	3.33E-01	1.88E-01	1.89E-01
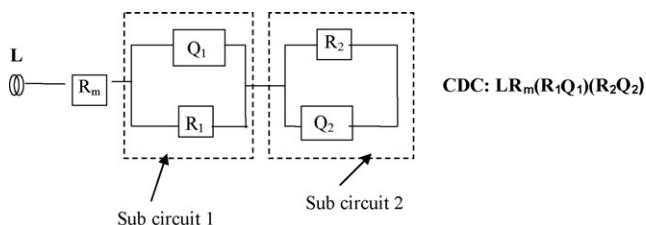
Fig. 5. Equivalent circuit fitted for a complete single cell using each experimental membrane and Nafion, in SM, with electrode gases H_2/H_2 and O_2/O_2, at 2 bar and 60, 70 and 80 °C.

represented by an EC obtained using an EC program. The structure of the EC is similar for all the membranes and is shown in Fig. 5.

This EC describes the electrical behavior of the cell like a combination in series of the pseudo-inductance (L) associated with the effects produced by all the metallic components of the single cell, the resistance associated with the membrane (R_m) and two sub-circuits, one which describes the charge transport in the electrode-membrane interface (sub-circuit 1) and another for the mass transport (sub-circuit 2). Both sub-circuits are composed of a resistance in parallel with a pseudo-capacitance. Sub-circuit 2 shows that mass transport occur by a combined process of adsorption and diffusion. R_m, and the resistance of the charge transfer (R_1) which is associated with the presence of mixed conduction (protonic–electronic) at this interface, are analyzed in this study.

Tables 4 and 5 compile R_m and R_1 values obtained in the study with O_2 and H_2 respectively injected in both electrodes. In both cases R_m of the experimental samples is lightly higher than that of Nafion, but values are enough stables, staying in the same order of magnitude, and even they lightly reduce with the temperature. This fact is indicating that the experimental membranes do not dehydrate when temperature increases, at least during the approximately 5 or 6 h that each experiment lasted.

In the charge transfer process, several aspects can be emphasized: R_1 values for the sample with 10 wt.% of silica are similar and even minor at 80 °C than that of Nafion 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 that the operation of the cell is optimum because R_m and R_1 values are similar. However, BG-22Vs membrane presents R_1 values higher than R_m values in both O_2/O_2 and H_2/H_2 testing, so in this case it could be important to improve the membrane–electrode interface for optimizing the cell operation.

4. Conclusions

The results indicate that experimental membranes, concretely BG-21Vs sample, can be a possible electrolyte for using in low temperature fuel cells. The ionic conductivity is similar to Nafion. The diffusion of methanol is much lower than Nafion, and the water uptake is higher than Nafion, probably due to the block structure of HSBS whose non-ionic blocks make a barrier effect to the diffusion and ionic blocks favor the water absorption and the protonic transport. And the most important aspect, the obtained power density values are higher than Nafion and moreover the single cell operation is optimum like single cell modeling demonstrates.

References

[1] M.K. Ravikumar, A.K. Shukla, J. Electrochem. Soc. 143 (1996) 2601.
[2] J. Cruickshank, K. Scott, J. Power Sources 70 (1998) 40.
[3] K. Scott, W.M. Taama, P. Argyropoulos, J. Membr. Sci. 171 (2000) 119.
[4] M. Takami, Y. Yamazaki, H. Hamada, Electrochemistry 69 (2001) 98.
[5] A. Mokrini, C. del Río, J.L. Acosta, Solid State Ionics 166 (2004) 375.
[6] C. Del Río, J.R. Jurado, J.L. Acosta, Polymer 46 (2005) 3975.
[7] A. Navarro, C. Del Río, J.L. Acosta, J. Membr. Sci. 300 (2007) 79.
[8] P.G. Escribano, A. Nácher, C. Del Río, L. González, J.L. Acosta, J. Appl. Polym. Sci. 102 (2006) 13.
[9] Y.A. Elabd, E. Napadensky, J.M. Sloan, D.M. Crawford, C.W. Walter, J. Membr. Sci. 217 (2003) 227.
[10] A.G. Hombrados, L. González, M.A. Rubio, W. Agila, J. Power Sources 151 (2005) 25.
[11] B.A. Boukamp, Equivalent Circuit Users Manual, University of Twente, The Netherlands, 1989.
[12] C.G. Bazuin, A. Eisenberg, Ind. Eng. Chem. Prod. Res. Dev. 20 (1981) 271.
[13] Y.A. Elabd, E. Napadensky, Polymer 45 (2004) 3037.
[14] Y.A. Elabd, C.W. Walter, F.L. Beyer, J. Membr. Sci. 231 (2004) 181.