

Comparative Study of Polymer Single Cells Based on Sulfonated Linear and Star Butadiene–Styrene Block Copolymer Electrolyte Membranes

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ABSTRACT: Proton-conducting electrolytes based on a sulfonated hydrogenated poly-(butadiene–styrene) matrix were synthesized. Block copolymer ionomers were prepared through sulfonation of part of the styrene units. The free acid samples were characterized with X-ray photoelectron spectroscopy to quantify sulfonation. Microstructural and electrical characterizations of membranes obtained from sulfonated polymer and blends were carried out with dynamic mechanical analysis, differential scanning calorimetry, and impedance spectroscopy. Electrolytes exhibiting the highest conductivities were tested in a model hydrogen/oxygen single fuel cell working at a medium temperature range (30–80°C) and at 1 bar of pressure. The current and power densities obtained were compared with commercial Nafion electrolyte. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 367–377, 2002

Key words: polymer electrolytes; membranes; sulfonation; conducting polymers; fuel cell; polystyrene butadiene copolymers

INTRODUCTION

The industrial development of electrochemical devices in the medium temperature range relies on the synthesis and production of new protonic materials that are stable at a working temperature range and have high conductivities. Such ionic conducting materials, in the form of flexible, mechanically stable membranes, are solid electrolytes for energy conversion devices.^{1–5}

Extensive studies have been performed to develop new ion-conducting polymer electrolytes from aromatic polymer systems.^{6,7} Selective aromatic-ring sulfonation is one of the alternatives, offering good potential in this way.

Several investigations have been devoted to the study of the morphology and chemical and

physical properties of sulfonated polymer salts.^{8–11} In this article, we focus on the behavior of free-acid-form polymer and its blends. Recently, we reported on the synthesis and characterization of new blend membranes.¹² In this work, we describe the thermal, mechanical, and electrochemical characterization of the materials synthesized. The fuel cell application tests in hydrogen/oxygen up to 80°C of some of the developed membranes is also discussed.

EXPERIMENTAL

Sulfonation Reaction

Polymers used in this work were selectively hydrogenated poly(butadiene–styrene) linear tri-block copolymer (LHPBS) and star-branched (four arms) block copolymer (SHPBS). Polymers

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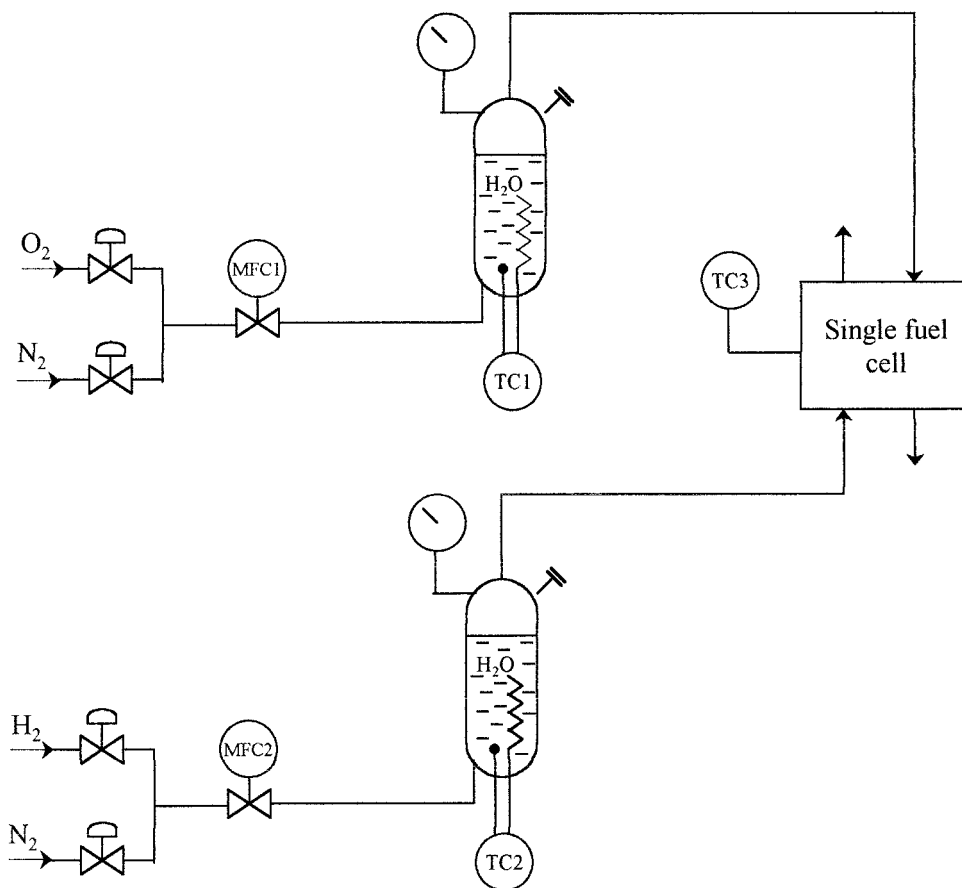


Figure 1 Experimental setup for polarization curve measurements.

commercially named Calprene, provided by Repsol, (Madrid, Spain), contained 30% wt and had an average molecular weight of 150,000. For styrene units, the sulfonating reagent was acetyl sulfate prepared by the reaction of acetic anhydride and concentrated sulfuric acid (96%). Sulfonation was carried out in 1,2-dichloroethane (DCE).

Sulfonation was carried out according to the procedure described by Makowski et al.^{13–14} In an agitated reactor, the polymer was dissolved in DCE at 52–56°C and purged with nitrogen. Then, acetyl sulfate was added, and the solution was stirred and purged with nitrogen during the experiment. The reaction was ended after the desired reaction time, and the reaction product was recovered by precipitation in deionized water (1 L per 10 g of polymer used). Sulfonated polymers (LHPBS-SH and SHPBS-SH) were filtered, washed many times with deionized water to ensure the complete removal of residual acid from the final product, and finally vacuum dried at 50–60°C for a few days.

Membrane Preparation

For preparation of the blends, two procedures were used in this study. For sulfonated hydrogenated poly(butadiene-styrene) (HPBS-SH)/hydrogenated poly(butadiene-styrene) (HPBS) blends, an open two-roll mill (friction 1:1.4) was used, with a conventional mixing procedure. The blending time was 20 min, to secure a good intermixture of the polymers.

For polypropylene (PP) and polystyrene (PS) blends, a torque rheometer (Brabender, Germany) was used for blend preparation. First, PP or PS was melted in the preheated thermoplastic mixing chamber; then, sulfonated polymers were added at a rotor speed of 60 rpm. The material remained in the mixing chamber for 10 min to ensure homogenization.

Membranes were prepared by hot-pressing the materials between Teflon sheets in a Collin 600 hydraulic press (Germany) at a temperature of 140–150°C and 200 bar pressure. Membranes obtained were 200–400 μm in thickness.

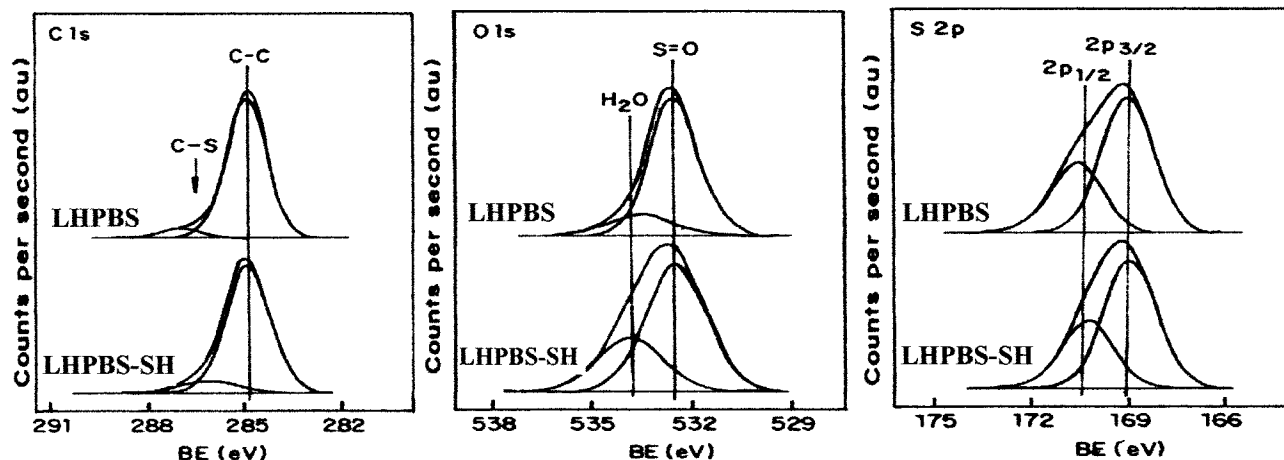


Figure 2 C_{1s} , O_{1s} , and S_{2p} core-level spectra of LHPBS and LHPBS-SH samples.

Characterization

Photoelectron spectra were acquired with a VG ESCALAB 200R spectrometer provided with MgK α radiation ($h\nu = 1253.6$ eV) and a hemispherical electron analyzer. The spectrometer was calibrated with the Cu 2p $_{3/2}$ and the Au 4f $_{7/2}$ peaks of a metallic sample. The C_{1s} , S_{2p} , and O_{1s} core-level spectra were recorded in kinetic energy ranges at a pass energy of 20 eV. Each spectral region was scanned between 40 and 100 times, depending on the intensity of the signal, to get an acceptable signal-to-noise ratio at reasonable acquisition times.

A Mettler (Switzerland) differential scanning calorimeter (model 30) calibrated with indium was used for the thermal analysis of the samples. To determine the glass-transition temperature (T_g), samples were first heated to 250°C at 30°C/min, then cooled to -140°C at 100°C/min, held at this temperature for 5 min, and then scanned at

10°C/min from -140 to 250°C. All the measurements were carried out under nitrogen atmosphere.

Dynamic mechanical analysis (DMA) measurements were performed with a TA Instrument 2980 dynamic mechanical analyzer, operating in the fixed frequency and film tension mode. The frequency used was 1 Hz, and the temperature was varied from -100 to 300°C with a heating rate of 5°C/min.

A Hewlett Packard 4192A impedance spectroscopy (IS) analyzer was used for impedance analysis. Small membrane-electrodes assemblies (MEAs) with 0.5 cm 2 electrodes area were prepared. Samples were sandwiched between two brass blocking electrodes in the measurement cell. Complex impedance measurements were carried out in alternating current (AC) mode in the frequency range 0.01–10,000 kHz and 1 V amplitude of the applied AC signal. The hydration pro-

Table I Binding Energies (eV) of Core Electrons, Surface Atomic Ratios, and Sulfonation Conversion of the Samples

Sample	C_{1s} (eV)	O_{1s} (eV)	S_{2p} (eV)	S/C Atom	Abundance SO_3H Groups (%)
LHPBS	284.9 (93)	532.7 (84)	169.1	0.017	0.88
	287.0 (7)	534.8 (16)			
LHPBS-SH	284.9 (85)	532.8 (73)	168.9	0.0232	12.09
	286.1 (15)	534.3 (27)			
SHPBS	284.9 (83)	532.6 (85)	168.8	0.0033	1.70
	285.9 (17)	533.9 (15)			
SHPBS-SH	284.9 (79)	532.9 (68)	168.9	0.0301	15.75
	285.8 (21)	534.2 (32)			

cedure used consisted of the introduction of the measurement cell in a closed vessel with a steam-water saturated atmosphere at different temperatures.

MEA Preparation

MEA consists of two electrodes with a thin layer of electrocatalyst bonded to either side of the proton exchange membrane. Electrodes used in this work were prepared in the Instituto de Ceramica y Vidrio (CSIC-Madrid) by deposition of a suspension containing approximately 40 wt % wt electrocatalyst, platinum in this case, on carbon paper. For the optimization of the membrane-electrodes interface, dissolutions of ion-conductive polymer were used for electrode impregnation. The complete MEA was hot-pressed at 80 bar of pressure. For IS analysis, small MEAs with 0.5-cm² electrodes were prepared, whereas MEAs for polarization curve measurements had 5-cm² electrodes.

Polarization Curve Measurements

The single fuel cell used for polarization curve measurements was a commercial cell (Electro-Chem Inc., USA) and consisted of two bipolar plates made of graphite, contacted on the external side by copper current collectors. In addition to the single cell, the experimental setup (Fig. 1), consisted of a control unit with mass flow controllers and temperature controllers. Gases were supplied humidified to the single cell on either side of the MEA through channels formed in the bipolar plates. The characterization of the MEA studied was evaluated through current density measurements obtained at different applied potentials. Measurements were performed at 40, 60, and 80°C, with humidified H₂ and O₂ at 1 and 2 bar of pressure (see Table V for measurement conditions). Before measurement, the MEA was immersed in water for 1 h and placed in the measurement cell; this was followed by humidification at 40°C for 12 h with moist nitrogen.

RESULTS AND DISCUSSION

Sulfonation

Sulfonation of LHPBS and SHPBS was carried out according to the procedure described previously. X-ray photoelectron spectroscopy was used to determine the chemical state of the elements at

Table II Composition of the Samples

Sample Name	LHPBS-SH (wt %)	LHPBS (wt %)	PP (wt %)	PS (wt %)
LA	100	—	—	—
LB	90	10	—	—
LC	90	—	10	—
LD	90	—	—	10

	SHPBS-SH (wt %)	SHPBS (wt %)		
SA	100	—	—	—
SB	90	10	—	—
SC	90	—	10	—
SD	90	—	—	10

the polymer surface and to quantify their abundance. LHPBS-SH and SHPBS-SH, together with nonsulfonated samples LHPBS and SHPBS as references, were used. Figure 2 displays C_{1s}, O_{1s}, and S_{2p} core-level spectra of the linear samples. The corresponding binding energies are summarized in Table I. To measure the abundance of sulfonic groups (percentage of sulfonated styrene groups in relation to 100 mol % of all present monomer units), atomic S/C ratios were calculated for all the samples and are summarized in Table I. The results show that percentage of sulfonated styrene groups was 12.1 and 15.8 mol % for LHPBS-SH and SHPBS-SH, respectively, and 0.88 and 1.70 mol % for the starting polymer, which was attributed to sulfur impurity of the samples.

For this study, sulfonated polymers (LHPBS-SH and SHPBS-SH) were kept in their acid form, and blends with the nonsulfonated polymers (SHPBS and LHPBS), PP, and PS were prepared. Table II lists the composition of the membranes selected for fuel cell tests.

Microstructural Characterization

The primary focus of this mechanical analysis was to evaluate the effect of sulfonation and blending on the structure of the polymers studied. All the samples analyzed showed the presence of two principal transitions, the lower one (at -50°C) was associated with T_g of the hydrogenated polybutadiene (HPB) blocks, and the higher one (at 90–130°C) was associated with that of PS domains. A *larger tan δ peak was observed for the sulfonated samples. Differential scanning cal-

Table III T_g 's Through DMA and DSC

Sample Name	DMA		DSC	
	$T_g^{(PS)}$ (K)	$T_g^{(PHB)}$ (K)	$T_g^{(PHB)}$ (K)	$T_g^{(PP)}$ (K)
SHPBS	360.8	222.5	222.35	—
SA	406.4	226.8	222.55	—
SB	401.6	222.9	222.65	—
SC	418.5	226.1	222.65	437.35
LHPBS	363.32	222.11	223.45	—
LA	393.33	227.10	224.35	—
LB	392.12	228.05	224.55	—
LC	416.28	229.82	224.15	435.55

orimetry (DSC) showed a lower sensitivity compared with DMA; only low T_g 's associated to the HPB unit and the melting temperature of PP could be determined.

Glass transition temperatures, defined as the inflection point in DSC thermograms and as the maximum signal of $\tan \delta$ in DMA, are summarized in Table III.

T_g associated with HPB units [$T_g^{(HPB)}$] was insensitive to sulfonation and blending; the maximum variation observed was about 7°C, whereas

$T_g^{(PS)}$ related to styrene blocks increased considerably after sulfonation [$\Delta T_g^{(PS)} \cong 30^\circ\text{C}$ for LH-PBS and 45°C for SHPBS]. The augmentation in T_g was directly associated to ion content.¹⁵ This was the result of the restrictions on the segmental movements in the styrene blocks because of the hydrogen bonding of sulfonic groups introduced.

In the case of blends, the same tendency was observed for $T_g^{(HPB)}$, whereas in the case of sulfonated PS blocks, T_g seemed to be affected by the incorporation of PP.

Electrochemical Analysis

Ionic conductivity of membranes was determined with the complex impedance method. Values were calculated from Nyquist plots. As an example, impedance spectra for the sample LA electrolyte at a temperature ranging from 30 to 90°C are illustrated in Figure 3. The spectra comprised two well-defined regions, a high-frequency zone that was related to conduction processes in the bulk of the electrolyte and a low-frequency region, which was attributed to the solid electrolyte–electrode interface. The bulk resistance was obtained from the intercept of high-frequency curves with the real axis. This resistance was smaller for samples with higher conductivities.

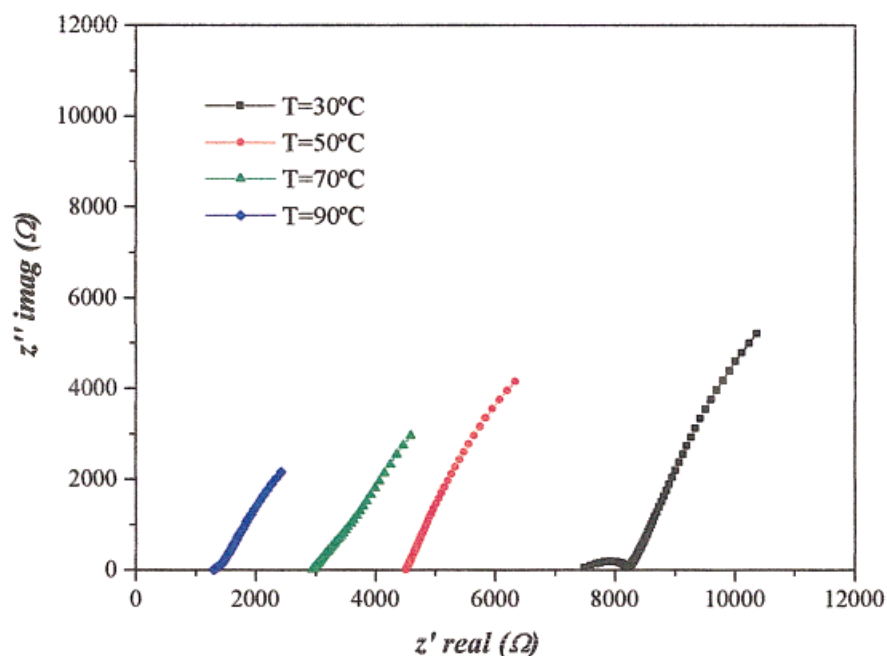


Figure 3 Impedance spectra for MEA with the LA electrolyte after 4 h hydration time at 30, 50, 70, and 90°C (AC mode, 1 V amplitude of applied signal, frequency range = 0.01–10,000 KHz). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table IV Conductivity Data Before and After 4 h Hydration Time

Sample Name	Membrane Thickness (μm)	Prehydration Conductivity (S/cm)	Posthydration Conductivity (S/cm)			
			30°C	50°C	70°C	90°C
LA	310	4.20E-07	2.14E-03	3.96E-03	1.59E-02	1.45E-01
LB	270	4.43E-06	5.00E-03	5.00E-03	1.52E-04	7.00E-05
LC	210	8.00E-07	5.25E-03	8.49E-03	3.45E-02	8.53E-02
LD	300	2.76E-06	3.57E-03	8.33E-03	8.00E-03	1.47E-02
SA	320	3.12E-07	7.66E-03	1.99E-02	2.25E-02	2.82E-02
SB	250	1.25E-08	1.64E-03	2.01E-04	8.18E-05	1.75E-05
SC	210	7.35E-09	8.51E-04	2.71E-03	4.47E-03	2.91E-02
SD	370	2.78E-08	1.36E-04	2.64E-04	4.54E-04	4.08E-03
Nafion	180	5.30E-04	2.0E-02	1.30E-01	—	—

All impedance measurements were done before and after hydration of the MEAs. Electrolytes in dry form exhibited conductivities between 10^{-6} and 10^{-9} S/cm; the entire conduction process occurred through the ionization of sulfonic groups in water incorporated into the polymer structure after hydration. Data obtained before and after hydration are represented in Table IV.

As shown, the ionic conductivity of membranes increased several orders of magnitude after a few hours of hydration and remained within the same order of magnitude for longer hydration times. As shown in Figure 4, conductivities obtained were plotted as a function of temperature for all of the membranes studied. In general, an increase in ionic conductivity with temperature was observed, except in the case of blends containing nonsulfonated HPBS polymers (LB and SB samples).

Generally, ionic conduction in polymer electrolytes was dominated by the amorphous elasto-

meric phase. In the case of the blends of sulfonated and nonsulfonated HPBS, the presence of nonconducting microdomains dispersed in the matrix phase involved spacing out of sulfonic acid groups, which explained the decrease in ionic conductivity with blending in general.

After hydration of the MEAs and before polarization curve measurements, impedance spectra were recorded to ensure good assembly of fuel cell. Nyquist plots obtained are represented in Figure 5. The current density–voltage data obtained in a H_2/O_2 single cell for all the MEAs studied are reported in Figure 6, where the samples are compared with Nafion 117 MEA. Experiments were carried out at temperature range of 40–80°C and 1–2 bar of pressure. The open circuit voltage value obtained for all the MEAs was near 1 V (similar to Nafion); however, a lower cell voltage was obtained for sulfonated HPBS MEAs. The MEA with LB membrane could not be measured because of the swelling of the membrane

Table V Experimental Conditions for Polarization Curve Measurements

Sample	Pt (mg/cm^2)		Thickness		Conditions			
	Anode	Cathode	MEA (mm)	Membrane (mm)	T (°C)	P (bar)	H_2 (cm^3/min)	O_2 (cm^3/min)
Nafion	0.5	0.5	0.75	0.18	60	1	12.5	6
AM-10	0.6	0.6	1.05	0.54	40,60,80	1–2	12.5	6
AM-21	0.5	0.5	0.89	0.35	40,60,80	1–2	12.5	6
AM-31	0.5	0.5	0.94	0.53	40,60,80	1–2	12.5	6
AME-10	0.6	0.6	0.93	0.48	40,60,80	1–2	12.5	6
AME-11	0.5	0.5	1.1	0.48	40,60,80	1–2	12.5	6
AME-21	0.6	0.6	0.85	0.34	40,60,80	1–2	12.5	6
AME-31	0.8	0.6	0.98	0.58	40,60,80	1–2	12.5	6

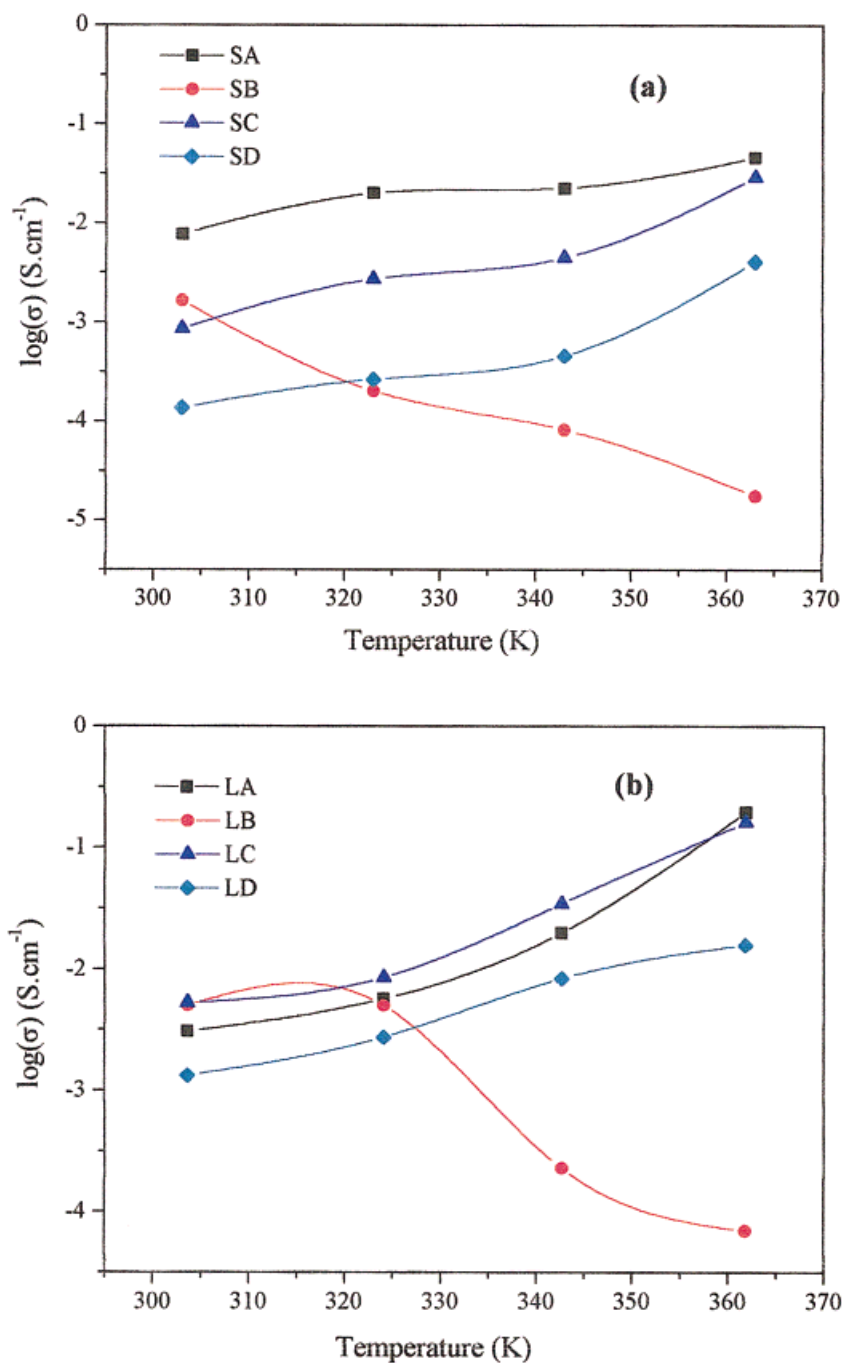


Figure 4 Logarithm of the ionic conductivity of the samples as a function of temperature: (a) SHPBS-SH and (b) LHPBS-SH blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and the lost contact between bipolar plates of the cell.

As expected, membranes with low proton conductivity showed low performance (Fig. 6). Higher efficiency was observed for Nafion in general. Calculated current density distribu-

tion profiles were related to the used fraction of catalyst particles, the electrodes active area, the thickness of solid electrolyte, gas flow rates, and so on. The larger thickness of sulfonated HPBS electrolytes (five times) with respect to Nafion, and consequently, the important ohmic

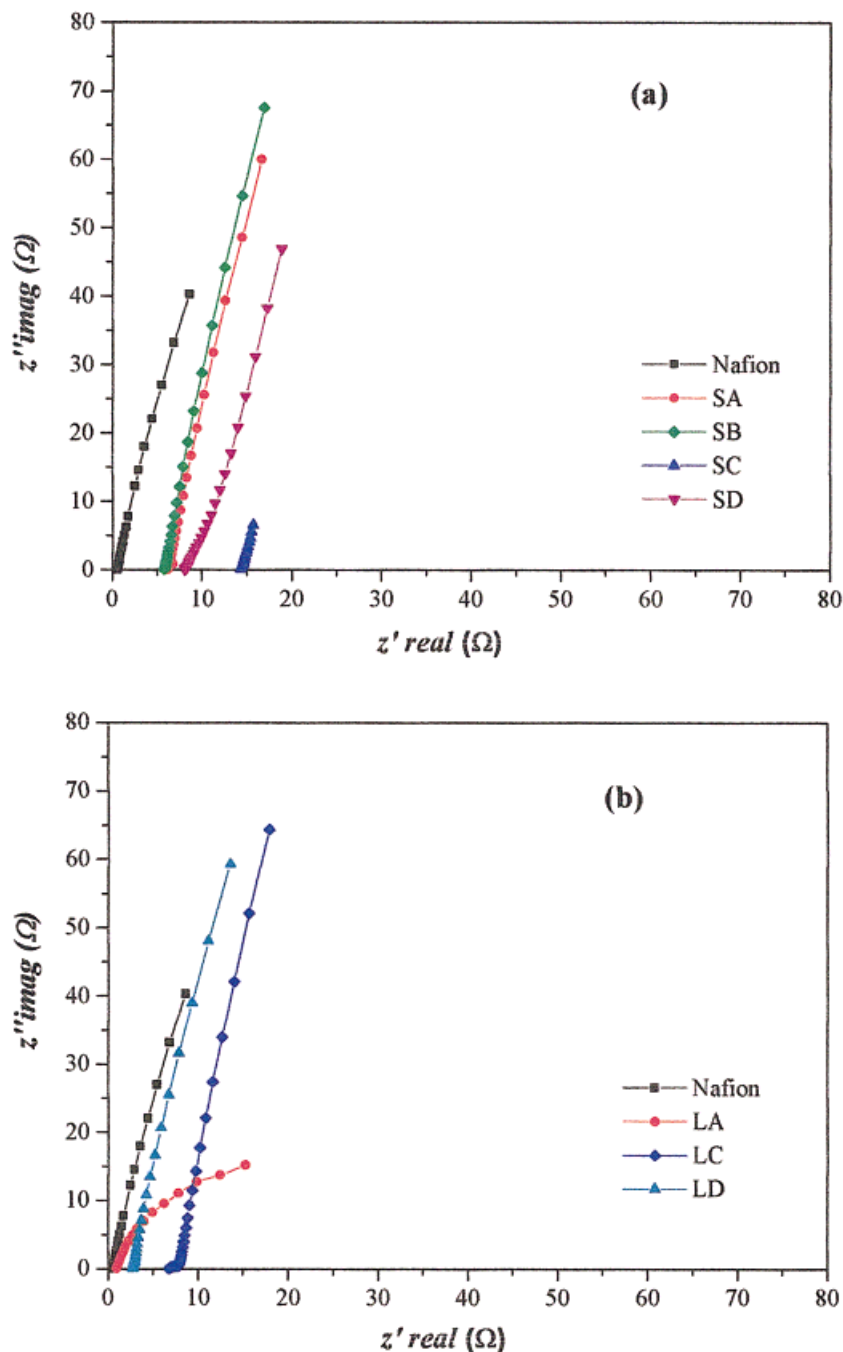


Figure 5 Impedance spectra for MEAs before polarization curve measurements after 14 h hydration time with moist N_2 at $40^\circ C$: (a) Nafion and SHPBS-SH and (b) Nafion and LHPBS-SH blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

losses, was the principal explanation. The possible existence of simultaneous chemical reactions that increased the gas permeability and, consequently, decreased the cell performance was also probable.

LHPBS-SH copolymer electrolytes showed higher performance than SHPBS-SH. The cross-link network in the star-branched copolymer retained more sulfonic acid groups without a real chemical link with styrene groups. There was a

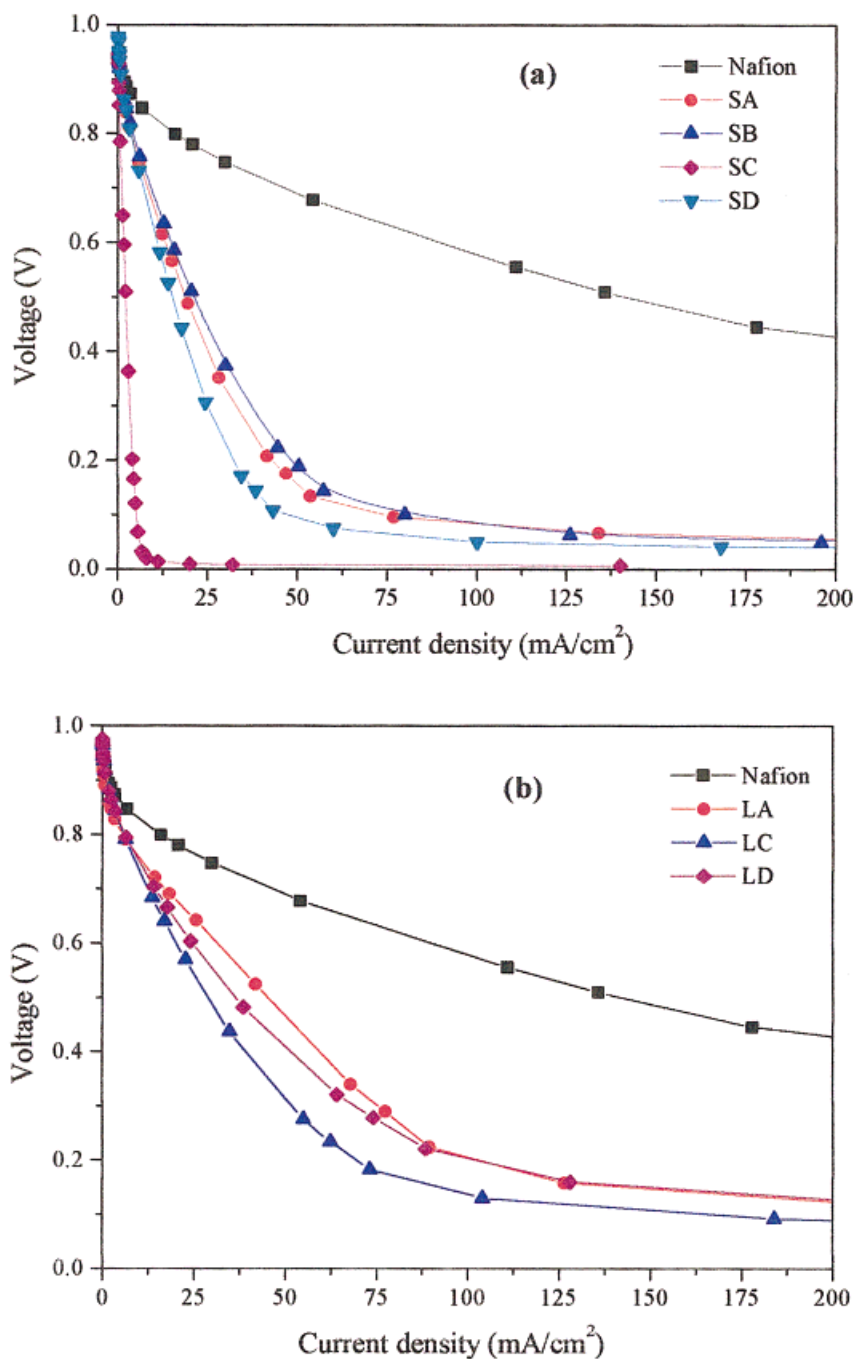


Figure 6 Polarization curves of MEAs ($T = 60^{\circ}\text{C}$, $P = 1$ bar, $\text{H}_2 = 12.5$ cm³/min, $\text{O}_2 = 6$ cm³/min): (a) Nafion and SHPBS-SH and (b) Nafion and LHPBS-SH blends electrolytes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

progressive loss of sulfonic acid groups during membrane performance and hydration. Moreover, the decrease of polymer segmental mobility (due to the network polymer) resulted in a decrease in proton conductivity.

The influence of temperature and pressure were also studied. As shown in Figure 7(a), higher power density values were observed at higher temperatures for all the MEAs. This is an interesting result, when the diminution of

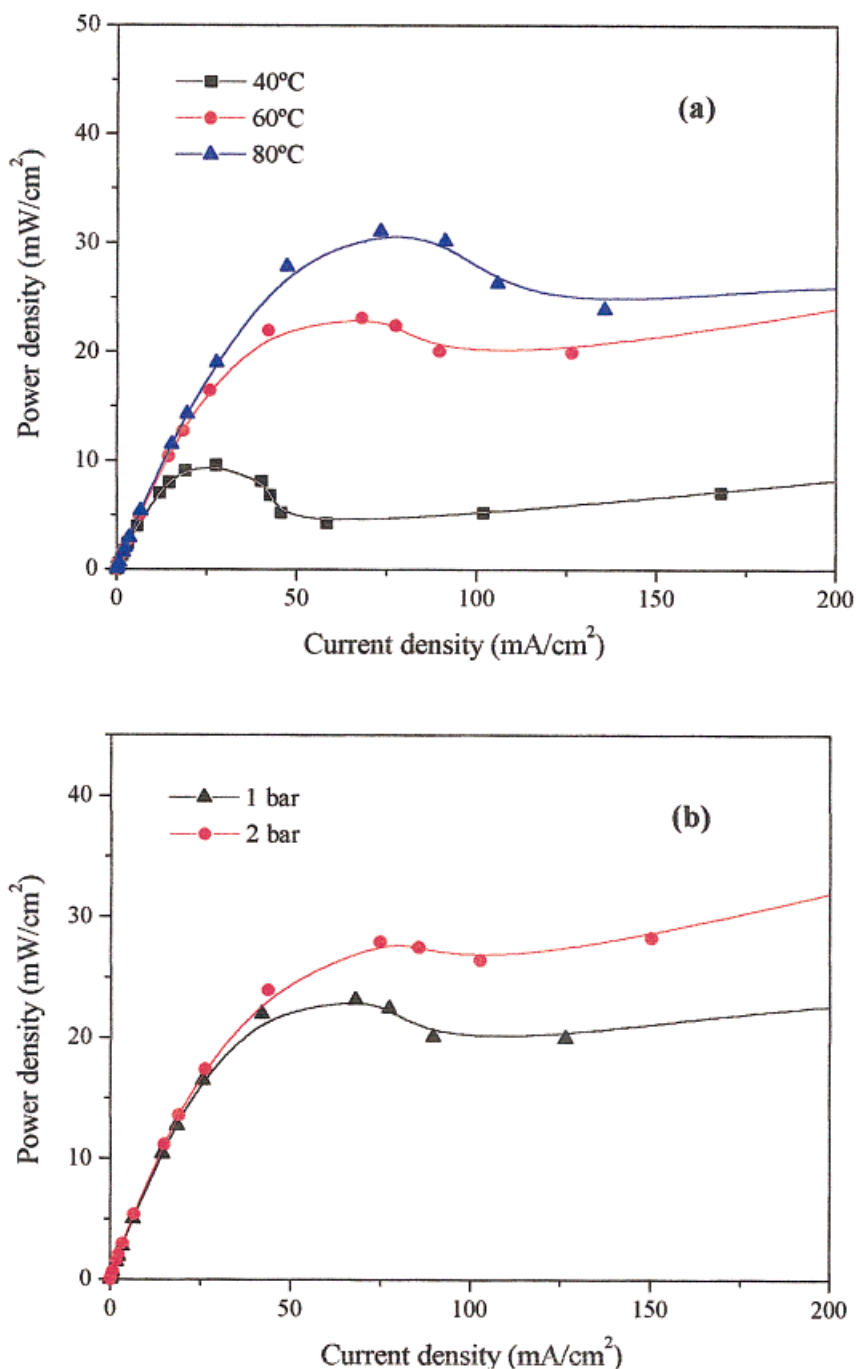


Figure 7 Power density as a function of current density curves for MEA with the LA electrolyte ($H_2 = 12.5 \text{ cm}^3/\text{min}$, $O_2 = 6 \text{ cm}^3/\text{min}$): (a) influence of temperature at $P = 1$ bar and (b) influence of pressure at $T = 60^\circ\text{C}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water content of the electrolyte increasing temperature and the difficulty to work with Nafion at temperature greater than 70°C is considered. Figure 7(b) shows that when pressure increased, the performance of the fuel cell in-

creased. This increment in efficiency was accompanied by an increase in water generation of the fuel cell. There were some problems with regulation of the pressure in our fuel cell setup, which did not include condensers.

CONCLUSIONS

LHPBS-SH and SHPBS-SH copolymers were prepared by partial sulfonation of the styrene blocks. DMA showed that T_g of the PS domain increased considerably after sulfonation, whereas T_g of the HPB phase remained practically constant.

In the case of impedance analysis, all the samples before hydration presented ionic conductivities in the range of 10^{-6} – 10^{-9} S/cm. After hydration, conductivities increased several orders of magnitude; the higher value obtained was 1.5×10^{-1} S/cm and corresponded to the LA sample. The general tendency when sulfonated polymers were blended was a diminution of film thickness but also of electrical properties. Results were compared with those of commercial Nafion; the data obtained showed in general higher conductivities for Nafion, but we also have to consider the very low thickness of Nafion membranes.

The current density–voltage data obtained in a H_2/O_2 single cell for all the MEAs studied showed that electrolytes based on LHPBS-SH copolymer exhibited higher performance than the star block copolymer. Increasing temperature and pressure was favorable for improving the efficiency of the fuel cell. The highest current and power densities obtained were approximately 100 mA/cm^2 and 30 mW/cm^2 , respectively. Results were compared with those of commercial Nafion; data showed in general a higher performance for Nafion MEA.

A decrease in the thickness of the membranes and, consequently, the ohmic losses, and optimization of the MEAs, as well as a better compre-

hension of the transport properties in relation to the structure may be very necessary to improve the performance of these new polymer electrolytes.

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