

Hybrid SPEEK/Phosphonated silsesquioxanes membranes for PEMFC

1 Kelen Rossi de Aguiar MSc

Center of Technological Sciences, Santa Catarina State University–
UDESC, Campus Universitário s/n, Joinville-SC, Brazil

2 Guilherme Pelizzaro Batalha BEng

Center of Technological Sciences, Santa Catarina State University–
UDESC, Campus Universitário s/n, Joinville-SC, Brazil

3 Ailton Ramos DEng

Center of Technological Sciences, Santa Catarina State University–
UDESC, Campus Universitário s/n, Joinville-SC, Brazil

4 Estevam Vitorio Spinacé DSc

Nuclear and Energy Research Institute– IPEN-CNEN/SP, Cidade
Universitária, São Paulo-SP, Brazil

5 Marcelo Linardi Dr. Ing

Nuclear and Energy Research Institute– IPEN-CNEN/SP, Lineu Prestes,
Cidade Universitária, São Paulo-SP, Brazil

6 Adriana N. Geraldes DSc

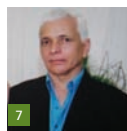
Nuclear and Energy Research Institute– IPEN-CNEN/SP, Lineu Prestes,
Cidade Universitária, São Paulo-SP, Brazil

7 Dionísio F. da Silva DSc

Nuclear and Energy Research Institute– IPEN-CNEN/SP, Cidade
Universitária, São Paulo-SP, Brazil

8 Sérgio Henrique Pezzin DSc

Center of Technological Sciences, Santa Catarina State University–
UDESC, Campus Universitário s/n, Joinville-SC, Brazil



In this work, the production and characterization of hybrid membranes of sulfonated poly(ether-ether-ketone; SPEEK) and phosphonated copolysilsesquioxanes (PCs) and its application in proton exchange membrane fuel cell (PEMFC) were studied. To improve the proton conduction and thermal stability of the polymer SPEEK, PCs were synthesized from diethylphosphatoethyltriethoxysilane (Ph-TEOS) and phenyltriethoxysilane (PTES), 90/10 mol/mol, by a hydrolysis/condensation procedure. The PCs were characterized by infrared thermal analysis. Hybrids membranes produced from SPEEK and 20 wt% PC were submitted to further hydrolysis to give semiinterpenetrating copolysilsesquioxanes networks. The hybrid membranes were also characterized according to their thermal behavior, proton conductivity, electrochemical performance in fuel cell, and oxidative stability. The proton conductivities (σ) of the membranes in the hydrated state at room temperature were determined by electrochemical impedance spectroscopy. It was verified that the proton conductivities of the hydrolyzed hybrid membranes were about 370% higher than the σ of plain SPEEK. The hydrolyzed membranes with 20% (90:10) PC showed the best performance in a PEMFC working with H_2/O_2 at 60°C.

List of notations

AC	Alternating current
ATR	Attenuated total reflectance
DMSO	Dimethyl sulphoxide
DSC	Differential scanning calorimetry
EDX	Energy dispersive x-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FC	Fuel cell
FTIR	Fourier transform infrared spectroscopy

HCl	Hydrochloric acid
PBI	Polybenzimidazole
PC	Phosphonated copolysilsesquioxanes
PEEK	Poly(ether-ether-ketone)
PEMFC	Proton exchange membrane fuel cell
PEO	Polyethylene oxide
Ph-TEOS	Diethylphosphato-ethyltriethoxysilane
PMMA	polymethylmethacrylate
PSU	Polysulfone

PTES	Phenyltriethoxysilane
SD	Sulfonation degree
SEM	Scanning electron microscopy
SPEEK	Sulfonated poly(ether-ether-ketone)
TGA	Thermogravimetric analysis
σ	Proton conductivity
V_{as}	Asymmetrical stretching
V_s	Symmetrical stretching

1. Introduction

Fuel cells (FC) offer potential technology for energy conversion due to its high thermodynamic efficiency, low emission of pollutants, and easy operation. A number of worldwide efforts have been made to develop systems and materials for this kind of technology (Costamagna and Srinivasan, 2001; Gottesfeld and Zawodzinski, 1997). Among different types of FC, the proton exchange membrane FC (PEMFC) emerges as the most promising because of its low-to-intermediate application temperature range (30°C–168°C; Gao *et al.*, 2011), efficiency (40%–60%), power versatility (from few watts to hundreds of kilowatts), and relatively low cost (US\$ 30–35 per watt), being suitable for stationary and auxiliary power applications for aviation, road, rail, and marine transportation. The considerable attention received by the solid polymeric electrolytes in the recent years resulted in the creation of many types of membranes with interesting mechanical and electrical properties, and long-term thermal stabilities (de Bruijn *et al.*, 2008). The PEMFC generates a specific power (W/kg) and power density (W/cm²) higher than any other type of FC. Hybrid polymeric membranes represent an important research field in respect to PEMFCs. These materials show high versatility because of the properties of both inorganic and organic constituents. In hybrid materials, the two phases, organic and inorganic, are intimately connected either through weak physical interactions (hybrid class I) or strong chemical covalent bonds (hybrid class II). The size of at least one domain ranges from a few angstroms to several nanometers and, consequently, the properties of hybrid materials are not just the sum of the individual contributions, but are greatly influenced by size confinement and interfaces between domains. Indeed, numerous hybrid materials are synthesized and processed by using soft chemistry routes based on, for example, the polymerization of functional organosilanes, macromonomers, and metallic alkoxides (Sanchez, 2005).

In this work, phosphonated copolysilsesquioxanes (PC) from diethylphosphato-ethyltriethoxysilane (Ph-TEOS) and phenyltriethoxysilane (PTES) were chosen as the inorganic component for the preparation of hybrid membranes, based on sulfonated poly(ether-ether-ketone; SPEEK), to produce a silsesquioxane semiinterpenetrating network into the polymer matrix. The choice of these silane precursors aimed to provide protogenic phosphonic groups ($-\text{PO}_3\text{H}_2$), from Ph-TEOS, and promote higher thermal and chemical stabilities, using PTES, further exploring a possible

interaction of the aromatic rings from PTES and SPEEK. The hybrid membranes were obtained by casting and characterized regarding their thermal and chemical stability (oxidative stability), proton conductivity, and electrochemical performance in hydrogen PEMFC.

2. Experimental

2.1 Materials

Poly(ether-ether-ketone; PEEK), in powder form (Victrex® PEEK™, 450 PF) was kindly supplied by Victrex USA, Inc. Diethylphosphatoethyltriethoxysilane (Ph-TEOS, 95%) e PTES (98%) were purchased from ABCRGmbH (Karlsruhe, Germany). Dimethylsulfoxide (DMSO; Vetec), absolute ethanol (Vetec), ferrous sulfate heptahydrate 98% (ABCR), hydrogen peroxide 36.5% (Nuclear), sulfuric acid 97% (Cinética), hydrochloric acid 37% (Cinética) were used without further purification. For the preparation of the FC electrodes, 20 wt% Pt/C E-TEK® catalyst (BASF) and a 5 wt% Nafion® 115 isopropyl alcohol solution were used.

2.2 Methods

2.2.1 Synthesis of SPEEK

SPEEK with sulfonation degrees (SD) between 60%–70% was synthesized following the procedure described by Jiang *et al.*, 2005. The sulfonation reaction was carried out dissolving PEEK in 97% sulfuric acid under vigorous stirring in a capped Erlenmeyer at room temperature for 24 h. The PEEK/H₂SO₄ ratio was 5/95 (w/v). The solution was then carefully poured on ice-cooled deionized water under mild stirring. The precipitated polymer, in fibers, was thoroughly washed until pH > 5 and left under deionized water overnight. The pale yellow SPEEK was dried in a vacuum oven at 60°C for 24 h. The SD was determined by elemental analysis, as described by Nolte *et al.*, 1993.

2.2.2 Synthesis of PCs

PCs were synthesized from Ph-TEOS and PTES in a 90:10 Ph-TEOS:PTES molar ratio following the procedure described by Nieuwenhuyse *et al.*, 2008. The reagents were added to a capped flask and homogenized for ca 3 minutes before the addition of the catalyst (0.1 mol/l HCl). After catalyst addition, the solution was left under stirring for 24 or 96 h. A transparent viscous liquid was obtained after solvent evaporation. A silsesquioxane oligomer was obtained containing phosphonic groups in the ester form.

2.2.3 Synthesis of hybrid membranes

The hybrid membranes were produced in two steps. In the first step, membranes containing 20 wt% of PCs produced after 24 h or 96 h were prepared. The second one consisted in the hydrolysis of the hybrid membranes, by refluxing with 37% HCl, to convert the phosphonic groups in the ester form into free phosphonic acid.

The hydrolysis followed the procedure described by Pezzin *et al.*, 2008.

2.3 Characterization

2.3.1 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded using a Perkin-Elmer Spectrum One B spectrometer, in ATR mode, after 12 scans from 4000 cm^{-1} to 650 cm^{-1} .

2.3.2 Differential scanning calorimetry (DSC)

DSC analyses were carried out in a NETZSCH Jupiter STA 449C equipment under nitrogen atmosphere (30 ml/min). In the first heating, the sample was heated at 10 K/min from room temperature to 150°C and, after 1 min at 150°C, was quenched with $\text{N}_{2(\text{g})}$ to -60°C. The second heating was performed from -60°C to 300°C at 10 K/min.

2.3.3 Thermogravimetric analysis (TGA)

The samples were heated under nitrogen from room temperature to 600°C at 10 K/min. At this temperature, the atmosphere was changed to synthetic air and the system was further heated to 800°C at 10 K/min to promote the thermal oxidation of the material.

2.3.4 Electrochemical impedance spectroscopy (EIS)

Proton conductivities (σ) of the hybrid membranes were measured by electrochemical impedance spectroscopy (EIS) in alternating current (AC), using an Agilent Precision Impedance Analyzer 4294A, in the frequency range from 40 to 40×10^6 Hz and a voltage source of 500 mV. All measurements were made at room temperature in the transverse direction of the membrane, taking an average of 20 runs. Five membranes of ca. 100 μm thickness each were compressed between two stainless steel electrodes of 8.75 mm diameter in an open cell. The membranes were stored for at least 24 h in deionized water before the measurements.

2.3.5 Scanning electron microscopy (SEM)

Morphological characterization and semiquantitative energy dispersive spectroscopy (EDS) analyses were made using a SHIMADZU EDX-550 microscope. The samples were cryofractured in liquid N_2 and recovered with a thin gold layer.

2.3.6 Fenton test

A piece of membrane was immersed in Fenton solution (3% H_2O_2 and 2 ppm Fe^{2+}) for 10 h at 70°C (Asano *et al.*, 2006). The membranes were then evaluated by FTIR and mass loss ($M\% = (m_{\text{dry}} - m_{\text{aged}})/m_{\text{dry}}$) where m_{dry} is the mass of the dry membrane without treatment and m_{aged} is the mass of the dry membrane after treatment with Fenton reagent.

2.3.7 FC measurements

The hydrogen FC performances were determined in a single cell with an area of 5 cm^2 . The tests were performed at 1 bar and 100 % RH. The temperature varied from 60°C to 90°C for the FC and

was set at 80°C and 90°C for the oxygen and hydrogen humidifiers, respectively. Oxygen and hydrogen flows were regulated at 50 ml/min and 80 ml/min, respectively. Polarization curves were obtained by using a TDI RBL 488 electronic load.

3. Results and discussion

3.1 Synthesis of PCs

The synthesis of the prepolymer (sol) in a 90:10 (Ph-TEOS:PTES) molar ratio yielded viscous, transparent and water-soluble silsesquioxanes oligomers, for both 24 or 96 h of reaction time, due to the highly polar structure, rich in silanol groups (Khramov *et al.*, 2006). The high Ph-TEOS content aimed to increase the phosphonic group density in the polysilsesquioxane chain.

To evaluate the prepolymer formation, FTIR spectra of the products were collected after 24 h (PC [90:10]-24) and 96 h (PC [90:10]-24) of reaction time (Figure 1). Both spectra show typical bands related to the absorption of siloxane groups (Si-O-Si), which were characterized by the appearance of bands at 1020 cm^{-1} and 865 cm^{-1} , attributed to their asymmetric (ν_{as}) and symmetric (ν_{s}) stretchings, respectively. An intense band at 950 cm^{-1} is attributed to silanol groups (Siuzdak *et al.*, 1999).

In Figure 1, two other bands, at 1090 cm^{-1} and 958 cm^{-1} , attributed to ν_{as} and ν_{s} of Si-O-C bonds, respectively, are also observed. This shows that the conversion of these bonds to siloxane bonds is not complete. Potentially, both Ph-TEOS functionalities, ethoxysilane, and ethoxyphosphonate groups, are hydrolysable, but the latter are more stable in dilute acidic media (Aliev *et al.*, 2000; Jurado-Gonzales *et al.*, 2002). The presence of a band at 1050 cm^{-1}

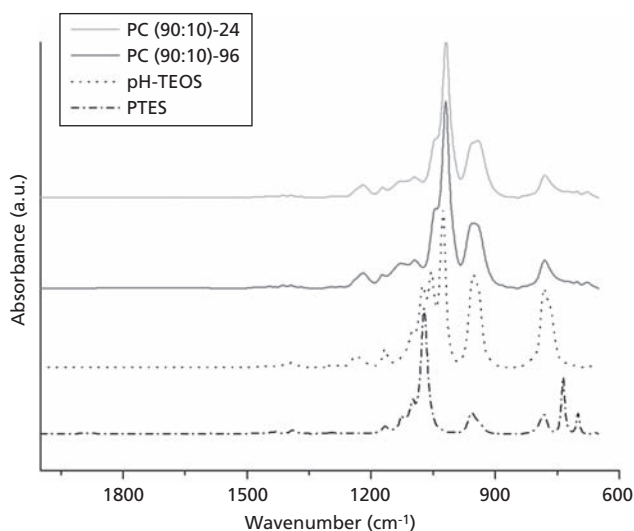


Figure 1. FTIR spectra of the starting silanes and PCs obtained after 24 h and 96 h of reaction time.

characterizes ν_{as} of P-O-C bonds, showing that these are stable even after hydrolysis and condensation reactions for obtaining PCs. A previous FTIR analysis confirmed the condensation of the siloxane precursors, which was evidenced by the presence of Si-O-Si characteristic bands. Diethylphosphonate groups were also stable during the copolymerization of the silanes.

3.2 Synthesis of hydrolyzed hybrid membranes

The hybrid membranes were produced from SPEEK ($SD \approx 65\%$) and PC prepolymers by casting. These membranes were then treated with concentrated HCl (37%) at 70°C to hydrolyze the diethylphosphonate groups and to obtain a semiinterpenetrating network of PCs containing free phosphonic acid groups. Moreover, this posttreatment contributes to the complete hydrolysis of the silanes, increasing the cross-linking of the inorganic phase and promoting a network formation. This membrane can be classified as a hybrid class I (with van der Waals interactions between organic and inorganic phases). After hydrolysis and network formation, the membranes (ca $100\ \mu\text{m}$ thick) became opaque with a pearl brightness.

3.3 Morphological characterization

Figure 2 shows the SEM images for the hydrolyzed 20% PC(90:10)-96 membrane. It is observed a porous microstructure after hydrolysis, differing considerably from the SPEEK dense microstructure. The pores have approximately $1\ \mu\text{m}$ and are well distributed throughout the membrane.

The hydrolysis with hydrochloric acid was effective for the formation of the network, which is associated to the fact that acid protons can diffuse through the membrane and promote the formation of the PC semiinterpenetrating network.

To evaluate the density of copolysilsesquioxane domains in the hybrid membranes, it was performed an EDS elemental mapping of phosphorous and silicon distribution throughout the membrane

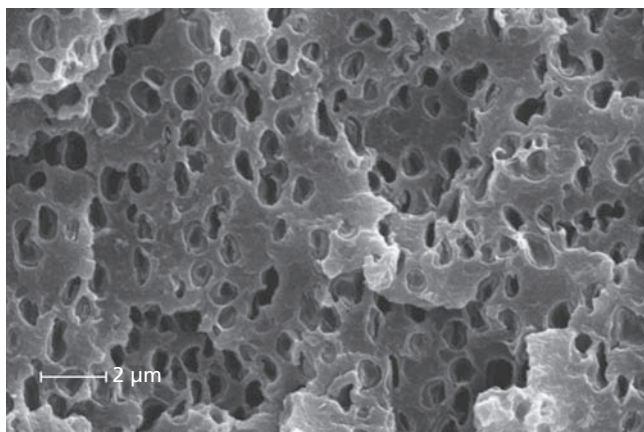


Figure 2. SEM image of the cryogenic fracture of the hydrolyzed 20% PC(90:10)-96 membrane.

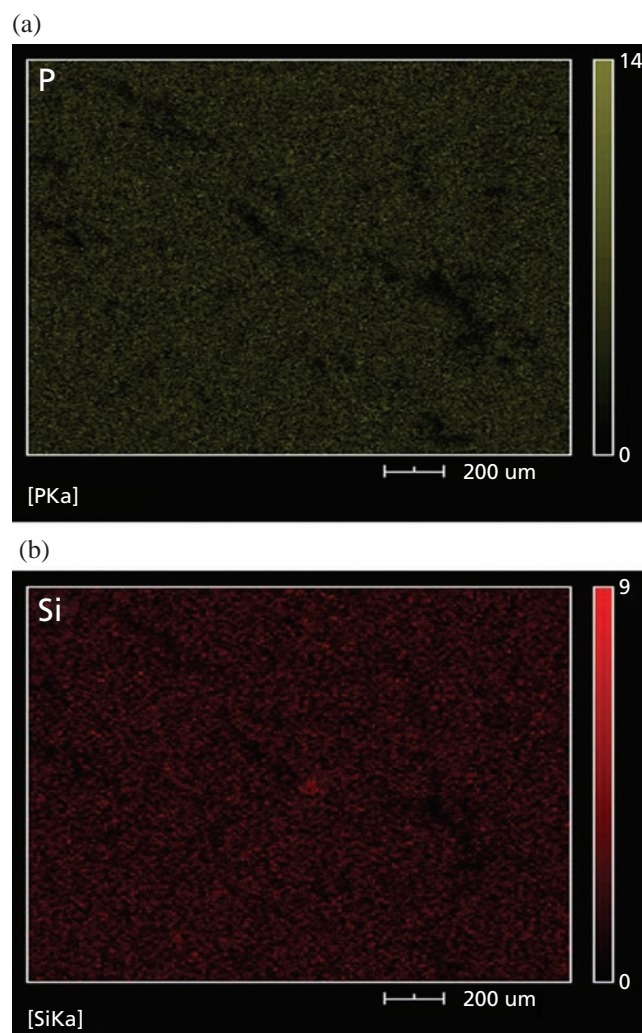


Figure 3. (a) Phosphorous (P) and (b) silicon (Si) EDS mapping at the fractured surface of a hydrolyzed 20% PC(90:10)-96 membrane.

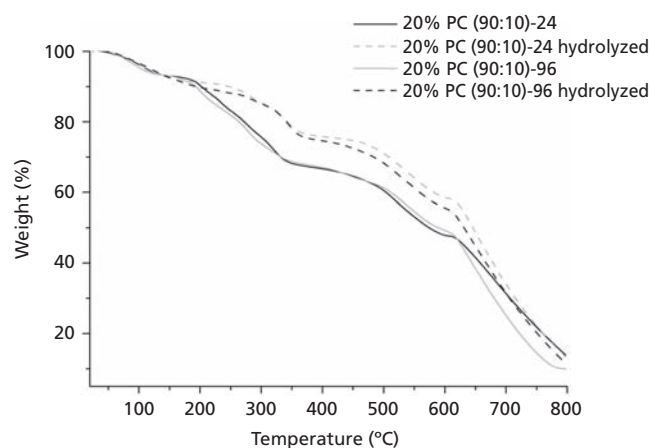


Figure 4. TGA curves for hydrolyzed and nonhydrolyzed hybrid membranes.

(Figure 3). Both evaluated elements, Si and P, are well distributed across the membrane, indicating a homogenous distribution of the inorganic domains into the SPEEK polymer matrix.

3.4 Thermal behavior of hydrolyzed hybrid membranes

TGA curves (Figure 4) for hydrolyzed and nonhydrolyzed membranes, containing 20 wt% of PC(90:10)-24/96, show that the hydrolyzed membranes have better thermal stability in comparison with nonhydrolyzed ones. Five mass loss steps were observed. The first mass loss, below 100°C, corresponds to the adsorbed water desorption (ca 8 wt%). This step is slightly larger (ca 10 wt%) for the hydrolyzed membranes, probably because of the higher concentration of hydrophilic groups, which present better water adsorption.

Between 200°C and 350°C, two mass loss steps are observed, because of the leaving of sulfonic groups ($-\text{SO}_3\text{H}$; Xing *et al.*, 2004a) and thermal degradation of diethylphosphonate groups ($\text{P-OC}_2\text{H}_5$; Parvole and Jannasch, 2008). The presence of polar phosphonic acid groups into the hydrolyzed membranes retards the exit of $-\text{SO}_3\text{H}$ groups, shifting the temperatures from 170°C–190°C (for nonhydrolyzed membranes) to 250°C–270°C, probably because of the formation of hydrogen bonds between these groups. At ca 260°C, the thermal oxidation of diethylphosphonate groups occur, whereas above 350°C, the leakage of P–C bonds (Parvole and Jannasch, 2008), and possibly the formation of phosphorous pentoxide (Schuster *et al.*, 2005), takes place, followed by the exit of aromatic rings from PC chains. The oxidative degradation of the PEEK backbone takes place at ca 610°C after changing atmosphere from N_2 to synthetic air to promote the removal of the residual organic material.

Figure 5 shows the DSC curves (second run) of the hybrid membranes. The glass transition temperatures for the membranes and the PCs, obtained from the DSC curve derivatives (DDSC), are summarized in Table 1. Three Tgs ($\text{Tg}^{1\text{m}}$, $\text{Tg}^{2\text{m}}$, e $\text{Tg}^{3\text{m}}$) are observed for all hybrid membranes. $\text{Tg}^{1\text{m}}$ (between 40°C and 60°C) and $\text{Tg}^{3\text{m}}$ (between 245°C and 270°C) are related to the formation of the semiinterpenetrating network, and correspond to the Tg^1 and Tg^2 of the copolysilsesquioxanes. $\text{Tg}^{2\text{m}}$, observed at intermediary temperatures (130°C–160°C), corresponds to the glass transition of the organic polymer phase of the membranes.

3.5 Proton conductivity

Proton conductivities of fully hydrated membranes were measured by EIS at room temperature in an open cell and used to evaluate their possible application in a PEMFC, in comparison with Nafion® 115 at the same conditions. The membranes with 20 wt% of hydrolyzed PC(90:10)-24/96 presented reasonable proton conductivity results at room temperature. Their proton conductivity behavior against frequency is shown in Figure 6.

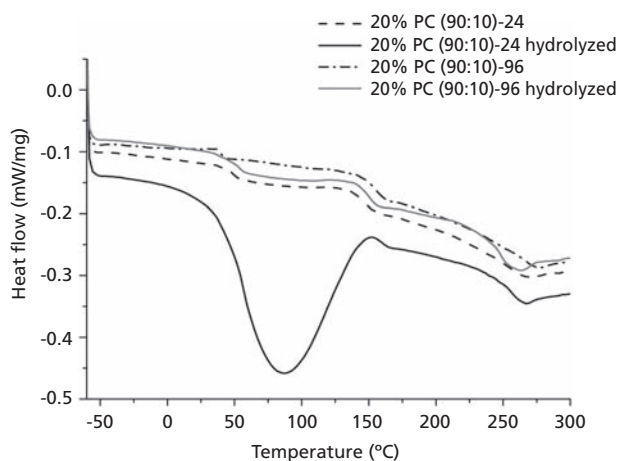


Figure 5. DSC curves of hydrolyzed and nonhydrolyzed hybrid membranes.

Membrane	$\text{Tg}^{1\text{m}}$	$\text{Tg}^{2\text{m}}$	$\text{Tg}^{3\text{m}}$
20% CF(90:10)-24	49	145	ND
20% CF(90:10)-24H	56	160	247
20% CF(90:10)-96	40	155	268
20% CF(90:10)-96H	53	150	248
Copolysilsesquioxane	Tg^1		Tg^2
CF(90:10)-24	35	—	239
CF(90:10)-96	37	—	249

Table 1. Tgs of hybrid membranes and copolysilsesquioxanes.

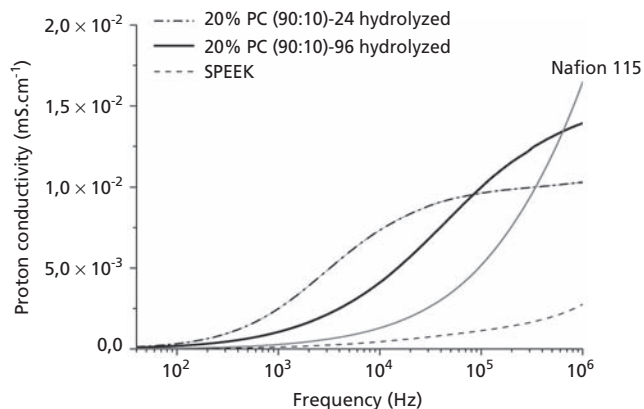


Figure 6. Proton conductivity behavior of hydrated membranes in the 40 Hz to 1 MHz range.

It was verified by a significant proton conductivity (σ) enhancement with the addition of the inorganic phase in the SPEEK polymer matrix. The hydrolyzed membrane containing 20 wt% PC(90:10)-96

presented an increase of ca 370% in the σ when compared to plain SPEEK. Polar phosphonic groups ($-\text{PO}_3\text{H}$) are capable of retaining a higher water content in the pores of the membrane and have a pronounced amphoteric character (Schuster and Meyer, 2003). The water works, in general, as a nonprotonated vehicle that transports protons as H_3O^+ through the basic mechanism of vehicle transportation (Kreuer, 1996). As the Grotthuss mechanism for the conductivity involves the proton exchange from a donator [$-\text{SO}_3\text{H}$, PO_3H] to a suitable acceptor [$-\text{SO}_3^-$, $-\text{P}(\text{OH})_2\text{O}^-$], the amphoteric character of the phosphonic groups favor the proton transport across the membrane (Paddison *et al.*, 2006). Hydrophilic domains are formed, when the material is hydrated, by the aggregation of sulfonic groups with water molecules. Then, the dissociated protons resulting from the solvation of the acidic groups become mobile, facilitating the transport of protons through the membrane (Jung *et al.*, 2004).

The frequency behavior of the proton conductivity, shown in Figure 6, is characterized by a frequency-dependent heterogeneous dispersion curve (Park *et al.*, 2005). At higher frequencies, the process can be described as a symmetrical distribution of relaxation times and is typically attributed to the rotation of the hydrogen bonds between sulfonic groups and water, whereas the behavior at low frequencies is attributed to interfacial polarization effects (Tsonos *et al.*, 2000). Impedance measurements, later transformed into conductivity, were scanned in the 40 Hz to 1 MHz range, however, the conductivity values considered for comparison between the different materials were taken at 1 MHz, to avoid the effects of interfacial polarization and for the smaller dependence of the conductivity with frequency. Thus, at this frequency, it is ensured that the behavior of the conductivity is inherent to the membrane and that there is some stability in conductivity values with frequency variation.

The highest proton conductivity presented by a hybrid membrane (14 mS/cm) was that obtained for the hydrolyzed 20% PC(90:10)-96 membrane, ca 12% lower than that for a Nafion® 115 membrane measured at the same conditions of analysis, but still very satisfactory for a nonfluorinated polymer. The conductivity of the dry membranes was in the order of 10^{-7} S/cm, which confirms the real necessity of filled water channels for proton transportation. Other nonfluorinated polymers, like PBI doped with phosphoric acid presented proton conductivities between $1.20\text{--}5.22 \times 10^{-3}$ S/cm at 20°C and 100% relative humidity (He *et al.*, 2008); PEO/ SiO_2 hybrids had a conductivity of 1×10^{-4} S/cm at 160°C (Honma *et al.*, 1999), while composite membranes based on PSU/PMMA and BPO_4 presented a maximum conductivity of 2×10^{-3} S/cm (Savadogo, 2004).

3.6 Electrochemical performance in hydrogen FC

The tests in a single hydrogen FC were performed using hydrolyzed 20% CF(90:10)-24/96 and Nafion® 115 membranes, at the conditions summarized in Table 2.

Temp. H ₂ (°C)	Temp. O ₂ (°C)	Cell temp. (°C)	H ₂ flux (ml/min)	O ₂ flux (ml/min)
90	80	60	80	50
90	80	70	80	50
90	80	80	80	50

Table 2. Working parameters for the hydrogen fuel cell tests.

Figure 7 presents the typical polarization and power curves (V–I) of the PEMFCs using different membranes.

In all curves, it was possible to verify the presence of regions of activation polarization, at low currents, and polarization by ohmic loss, at intermediate currents. None of the tests presented a region of mass transport polarization, as the FC did not work at currents high enough to visualize the effects of this loss. Matos (2008) has observed this region at currents over 1A in tests with Nafion® at 80°C. Considering that the linear region of ohmic loss is due to the resistivity (R) of the membrane and is governed by the Ohm Law ($V = I.R$), it was possible to calculate the membrane resistivities ($R = \Delta V/\Delta I$) and the proton conductivities ($\sigma = d/R.A$) at the different working temperatures (Wagner, 2002). Table 3 summarizes the values of R and σ from the FC tests.

It is known that the membrane resistivity depends on the concentration of water, temperature and current of the cell, which is directly proportional to the flow of water in the membrane. At 70°C and 80°C, there was a reduction in proton conductivity and a decrease in current density. At these temperatures it is also observed, besides the reduction of ionic conductivity, the decrease in the affinity for water, loss of mechanical stability due to the softening of the polymer, and losses due to fuel permeation (Smitha *et al.*, 2005). All these factors contribute to the observed performance of the membranes at 80°C, and these may be related to a decrease in current density and proton conductivity observed for the tested membranes. SPEEK membranes with different degrees of sulfonation showed similar behavior (Zaidi *et al.*, 2000).

The curves in Figure 8 show that all the membranes presented an increase of proton conductivity at the three different cell temperatures, in comparison with the conductivities measured at room temperature. It was observed that the membranes have shown the best conductivity values at 60°C, and the highest value was obtained for the 20% PC(90:10)-24 membrane. This membrane has also presented the higher conductivity and the best performance at 80°C. In general, all membranes have shown a satisfactory performance in the FC tests, but the highest current ($\approx 800 \text{ mA/cm}^2$) and power ($\approx 226 \text{ mW/cm}^2$) densities were obtained at 60°C, as shown in Figure 7.

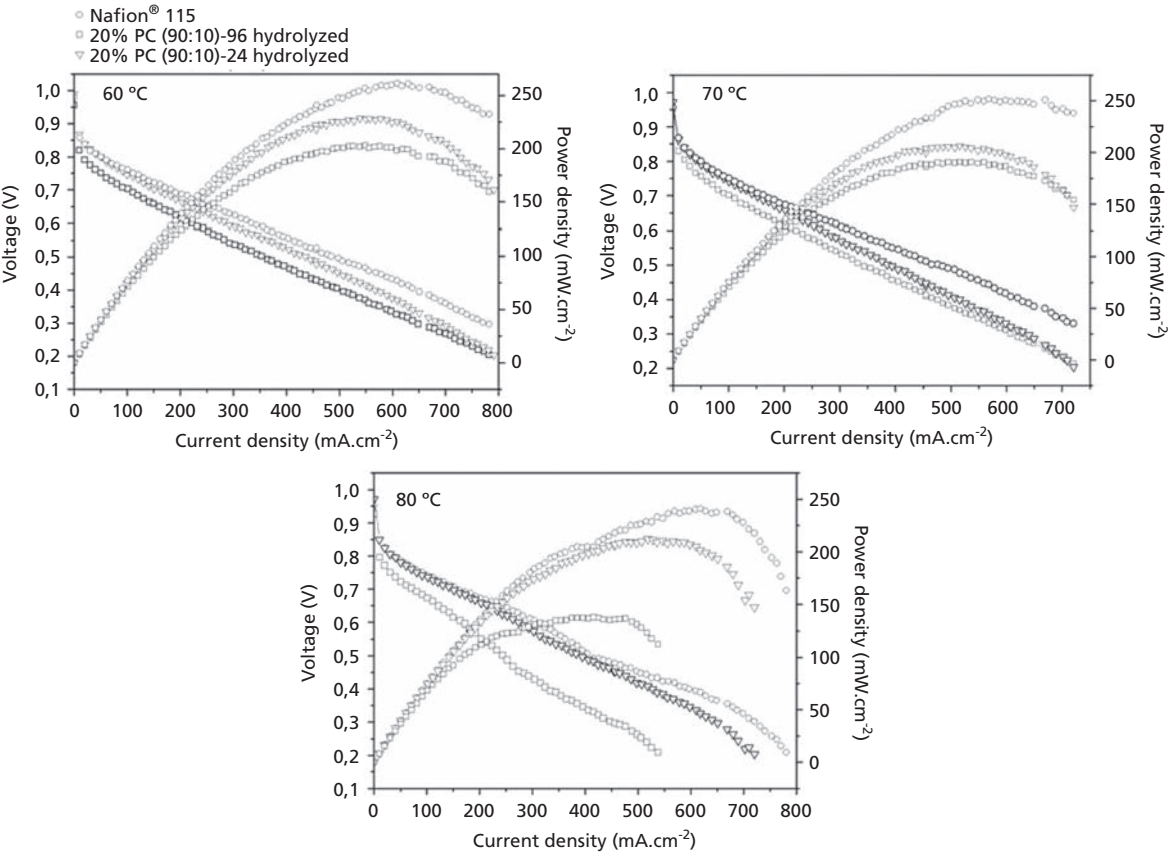


Figure 7. Polarization (potential–V × current density–I) and power (power density × current density) curves obtained for the PEMFC operating at 60°C, 70°C, and 80°C.

Membrane	Thickness (d) (μm)	Resistance (R; Ω.cm²)			σ (mS/cm)		
		60°C	70°C	80°C	60°C	70°C	80°C
20% PC(90:10)-24 hydrolyzed	250	0.70	0.86	0.82	35.7	29.06	30.48
20% PC(90:10)-96 hydrolyzed	250	0.79	0.82	1.15	31.64	30.48	21.73
Nafion® 115	150	0.66	0.65	0.78	22.72	23.07	19.23

A = 5 cm² (Surface area of the membranes).

Table 3. Proton conductivities (σ) and resistivity of hydrolyzed 20% PC(90:10)-24/96 and Nafion® 115 membranes obtained from V–I plots.

3.7 Fenton test

Fenton reaction is a catalytic oxidation process using a mixture of hydrogen peroxide (H₂O₂) containing trace amounts of ferrous ions (Fe²⁺), resulting in a complex redox reaction (see Equation 1; Walling, 1998). The degradation occurs by the action of •OH and •HO₂ radicals (Liu and Zuckerbrod, 2005). This reaction

has become a common *ex situ* aging test to evaluate the durability of membranes. The typical concentration of 3% H₂O₂ is much larger than the typical amounts of H₂O₂ found in the FC (Xing et al., 2004a, 2004b). A high concentration of radicals can result in additional routes of degradation, limiting the lifetime of the membrane.

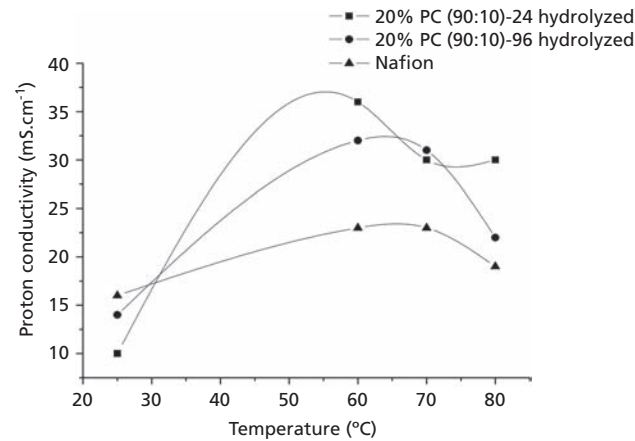


Figure 8. Proton conductivity variation with temperature at fuel cell tests.

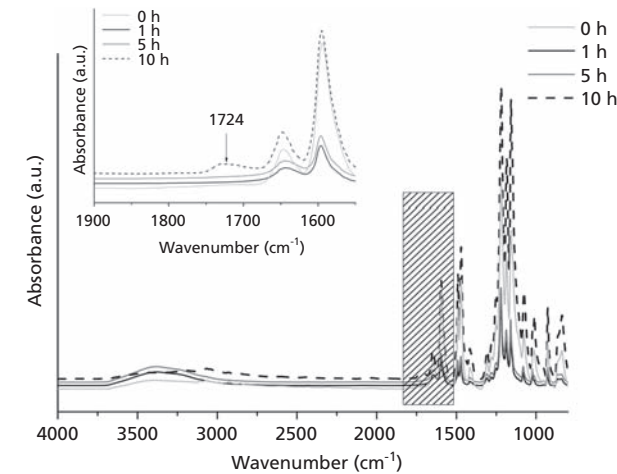
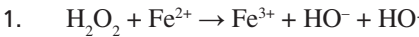


Figure 9. Overlay of FTIR spectra of hydrolyzed 20% CF(90:10)-96 membrane aged for 1, 5, and 10 h in Fenton reagent and nonaged membrane.



FTIR spectra of the hydrolyzed 20% CF(90:10)-96 membrane aged for 1, 5, and 10 h and the nonaged membrane (0 h) are shown in Figure 9.

No significant changes between the aged and the reference (0 h) membrane were observed for 1 and 5 h of treatment, except for the increased intensity of the band in the region from 3700 to 3000 cm^{-1} . This region is associated with OH vibrations and can be the result of phenols, a primary product of degradation. At 10 h, there was the appearance of a shoulder at 1724 cm^{-1} which suggests the formation of new products containing carbonyl groups, different from the ketone carbonyl, which appears at 1650 cm^{-1} (Perrot *et al.*, 2010). Another way to assess the *ex situ* degradation

Membrane	Initial mass (g)	Final mass (g)	Mass loss (%)
20% PC(90:10)-24 hydrolyzed	0.022	0.021	1
20% PC(90:10)-96 hydrolyzed	0.027	0.026	3
SPEEK	0.020	—	Dissolved

Table 4. Mass loss of the membranes after 10 h at 70°C in Fenton reagent.

is by mass loss measurements. Table 4 shows the mass loss results for the hybrid membranes after 10 h subjected to Fenton’s oxidant environment.

Tested membranes became brittle and dark after 10 h of contact with the Fenton solution at 70°C and the mass difference evaluation revealed a small loss of 3% for hydrolyzed 20% PC(90:10)-96 membrane. The addition of the PC to the SPEEK matrix favored a relatively high oxidation resistance for the hybrid membranes, as the pure SPEEK dissolved completely under the same conditions. The weakness may be associated with a reduction in the polymeric chain length (Perrot *et al.*, 2009).

4. Conclusions

The methods of synthesis of phosphonatedsilsesquioxane precursors and hydrolyzed hybrid membranes through hydrolysis/condensation processes have been effective, allowing the development of membranes with potential application in FC technology. Flexible and self-standing membranes with adequate thermal and oxidative stability were produced. Proton conductivities of ca 14 mS/cm and 10 mS/cm at room temperature were achieved for hydrolyzed membranes containing 20% PC(90:10)-96 and 20% PC(90:10)-24, respectively. At 60°C, proton conductivities 2 to 3 times greater than at room temperature were achieved. Membranes produced with 20% CF (90:10) 24/96 showed a very satisfactory performance in the hydrogen PEMFC operating at 60°C, 70°C, and 80°C. The efficiency shown by these hybrid materials was in average 54% at 60°C. Compared with Nafion®, the performance of the hybrid membrane in the hydrogen FC showed that this type of nonfluorinated polymer has potential for application in PEMFC operating between 60°C and 80°C at high relative humidity. The process of production of the hybrid membrane by forming a semi-interpenetrating network of copolysilsesquioxanes is a relatively simple way to chemically modify a polymeric material, such as SPEEK, increasing their properties for application in hydrogen FC technology, which plays an important role in the alternative energy scenario.

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