

Determination of the Physicochemical Characteristics and Electrical Performance of Postsulfonated and Grafted Sulfonated Derivatives of Poly(*para*-phenylene) as New Proton-Conducting Membranes for Direct Methanol Fuel Cell

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ABSTRACT: Poly(*para*-phenylene)s (PPPs) are an interesting class of rigid-rod polymers that have excellent thermal and mechanical properties. Because of their high degree of crystallinity and lower permeability to methanol, PPPs are insoluble and infusible. A number of methods have been developed to synthesize substituted sulfonated PPPs bearing lateral chains to improve their solubility. In this work, a comparison of the physicochemical properties of three PPP-based polymers is made with respect to Nafion membranes. One of these polymers was prepared with the postsulfonation method, and the other two were made with a new method of grafting developed in the Commissariat à

l'Energie Atomique laboratory (a grafted sulfonated PPP polymer and a grafted perfluorinated sulfonated polymer). The sulfonated PPP polymers were examined for their mechanical properties, small-angle X-ray scattering, water absorption, proton conductivity, and methanol permeability. Relations between structures and properties were also investigated. Performances in fuel-cell tests were also investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 944–952, 2006

Key words: poly(*para*-phenylene); electrochemistry; fuel cell; methanol

INTRODUCTION

Because of the difficulties in producing, storing, and distributing clean hydrogen of hydrolysis quality,^{1–3} the use of liquid fuels in polymer electrolyte membrane fuel cells (PEMFCs) has been proposed, and research has been conducted in the field of direct alcohol fuel cells.^{4–6} However, specific problems arise from the electrocatalysis of alcohol oxidation^{7,8} as well as alcohol permeation through the membranes.^{9,10}

For many years, polymer electrolytes bearing sulfonate groups have been investigated and used as cation-exchange resins or membranes. In the field of PEMFCs, efforts have been made to develop membranes that can serve as separators between the anodic

and cathodic compartments and transport protons from the anode to the cathode.^{11–13} Currently, sulfonated perfluorinated ionomer-based systems such as Nafion (produced by Dupont de Nemours) are used as proton-exchange membranes in most cases.^{14–20} Despite their technical advantages, high conductivity (close to 10^{-1} S/cm at room temperature), and good mechanical and chemical properties, some limitations exist that restrict their use in direct methanol fuel cells (DMFCs), such as low conductivity at low relative humidity, that is, at high temperatures ($>80^{\circ}\text{C}$), and high methanol (MeOH) permeability. Therefore, research to develop new membranes with better performances in comparison with that of Nafion is of great interest. These new membranes should exhibit long-term stability and good performance at high operating temperatures ($>80^{\circ}\text{C}$) and lower MeOH permeability. Moreover, the cost of such membranes must be reduced in comparison with that of Nafion if extensive applications are to be considered.

In a previous work,²¹ the possibility of using thermostable sulfonated polymers derived from a poly(*para*-phenylene) (PPP) backbone in a DMFC was

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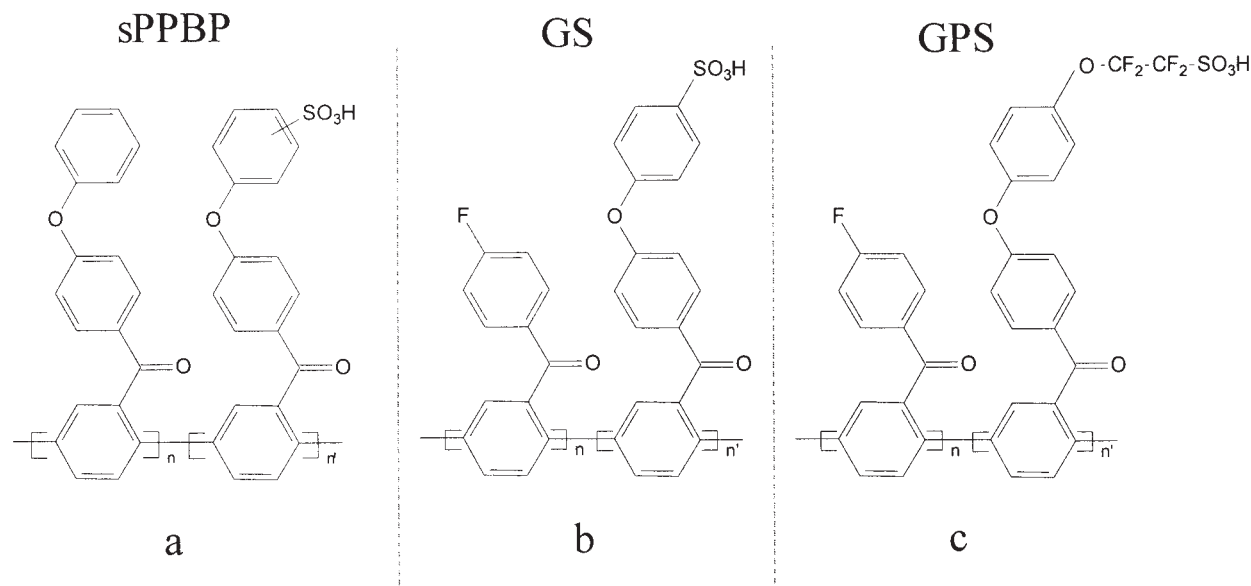


Figure 1 Chemical structures of (a) sPPBP, (b) GS, and (c) GPS.

validated in terms of the mechanical properties, water uptake (WU), and MeOH permeation. In this work, proton-conducting polymers were prepared either with the postsulfonation method or through the grafting of sulfonate-containing groups. In this way, a new method of substitution was developed in the Commissariat à l'Énergie Atomique laboratory, which consisted of grafting sulfonated perfluorinated pendent chains onto the polymer backbone. Polymers were synthesized via polycondensation with palladium catalytic coupling (Colson synthesis).²² The grafted perfluorinated sulfonated materials appear to be promising materials and are helpful in understanding the relations between the properties and structures of membranes for fuel-cell applications. Before DMFC tests, all membranes that were produced were characterized in terms of their mechanical properties, small-angle X-ray scattering, water absorption, proton conductivity, and MeOH permeability.

EXPERIMENTAL

The base structure of the polymers studied in this work was the PPP backbone, from which poly(*p*-phenoxybenzoyl-1,4-phenylene) (PPBP) and poly(*p*-benzoyl-phenylene) (PBP) were prepared. Their synthesis and functionalization as protonic conductor membranes have been described elsewhere.²¹ The sulfonated substituted PPPs were dissolved in *N*-methylpyrrolidinone (NMP; 8–10 wt %) at 80°C under an argon atmosphere for several days. The NMP solutions were then filtered, and the polymer film was cast onto a glass sheet. The solvent was evaporated via heating to 60–70°C until the membranes were dry. The chemical formulas are presented in Figure 1(a) for

sulfonated poly(*p*-phenoxybenzoyl-1,4-phenylene) (sPPBP), which was sulfonated with a medium sulfonation agent [tetramethylsilylchlorosulfonate (TMSCl)], in Figure 1(b) for the grafted sulfonated poly(*p*-benzoyl-phenylene) (GS), and in Figure 1(c) for the grafted perfluorinated sulfonated poly(*p*-benzoyl-phenylene) (GPS). To compare the different polymers, the sulfonation level was controlled to obtain for each of them an ionic exchange capacity (IEC) of 1.3 mequiv of H⁺/g.

Small-angle neutron scattering (SANS) experiments were performed with a focus camera at the European Synchrotron Radiation Facility. The spectrometer was built to produce a focused X-ray beam on the sample. In these experiments, the beam size on the sample was 10 × 10 μm (width at half-maximum). The experimental setup allowed the location of the detector (a charged coupling device camera) at a distance between 1 and 10 m from the sample. The chosen incident wavelength was 0.1 nm, which corresponded to an energy of 12.4 keV. The brilliance of the beam light was defined as the photon density per solid angle unity and area ($h\nu \text{ s}^{-1} \mu\text{m}^{-2} \text{ rad}^{-2}$). Before the SANS measurements, the membranes were hydrated in deionized water for 72 h at 25°C. The time of exposure was close to 100 ms. The spectra were recorded after one acquisition and presented after correction for the detector deviation and background noise.

The mechanical resistance measurements were carried out with a traction microplate with an associated optical transmission microscope fitted with a polarizer/analyzer filter system, which allowed visualization of the deformation field of the polymeric films. Tests were performed at 25°C at an elongation rate of 500 μm/min on membranes 2.5 mm long, 2 mm wide, and

23 μm thick. The force applied to the samples before the experiments was 0.1 N. All samples were hydrated in deionized water for 72 h at 25°C before mechanical resistance measurements.

WU was estimated through the weighing of the membranes in an infrared desiccator. The membranes were hydrated in deionized water for 72 h at 25°C, and their wet weight was measured. The membranes were then dried for 15 min at 140°C. At the end of the cycle, WU was determined with the following equation:

$$\text{WU} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where w_w is the weight of the wet polymer and w_d is the weight of the dry polymer.

From the WU determination, the number of water molecules per acid site (λ) could be calculated as follows:

$$\lambda = \frac{\text{WU}}{M_{\text{H}_2\text{O}} \times \text{IEC}} \quad (2)$$

where $M_{\text{H}_2\text{O}}$ is the molecular weight of water (18 g/mol) and IEC is recorded as milliequivalents of H^+ per gram.

The permeability of the membranes to MeOH was determined in a two-compartment glass cell, as described elsewhere.²³ One compartment (volume = 40 mL) was filled with a 1M MeOH solution, and the other (volume = 40 mL) was filled with deionized water. The membrane (3.14 cm in diameter) was clamped between the two compartments. Both compartments were vigorously stirred during the permeation experiments. The concentrations of MeOH in the second compartment were determined by high-performance liquid chromatography. The MeOH permeability was calculated from the slope of the straight lines of the MeOH concentration versus time (see ref. 23).

The proton conductivity was measured by impedance spectroscopy. A sinusoidal voltage of 10 mV was applied to the sample in the frequency range of 10⁷ to 10 Hz, and the resulting current was recorded. The apparatus consisted of a Solartron 1255 A frequency analyzer (Solartron Analytical, Farnborough, UK) associated with a Novocontrol BDS electrochemical interface (Novocontrol, Hundsangen, Germany). A two-platinum electrode cell was used to carry out the measurements of the membrane conductivity, the samples being put between the two platinum electrodes. Springs were used to apply a constant pressure to the electrodes, facilitating good contact with the membranes. The cell was then placed in a deionized water bath to carry out conductivity measurements on water-saturated membranes. The system was con-

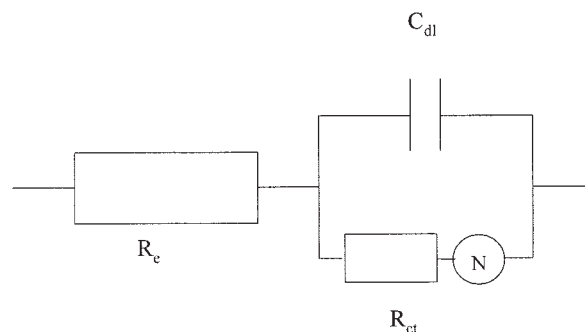


Figure 2 Equivalent circuit used for fitting the impedance spectroscopy Nyquist plots.

trolled with Windeta software (Novocontrol, Hundsangen, Germany). Data were then analyzed with Z-View software (Huntington Beach, CA) with Nyquist diagrams [imaginary part of the complex impedance of the circuit (Z'') vs the real part (Z') for each imposed frequency]. To analyze the data, the equivalent electric circuit shown in Figure 2 was considered. The useful information for our purpose was the resistance of the solid polymer electrolyte. Conventionally, Nyquist diagrams are presented by a nonperfect half-circle at medium and high frequencies and by a linear line at low frequencies. The intersection of the quasi-half-circle at high frequencies (close to 10⁵ Hz) with the X axis (Z') led to the evaluation of the resistance of the electrolyte and furthermore the conductivity with the following equations:

$$Z = Z' + jZ'' \quad (3)$$

$$Z = R_e + \frac{R_{ct}}{1 + jR_{ct}C_{dl}\omega} \quad (4)$$

$$\sigma = \frac{1e}{R_e S} \quad (5)$$

where R_e is the resistance of the membrane, R_{ct} is the resistance of the charge transfer, C_{dl} is the electrode double-layer capacitance, ω is the angular frequency, σ is the conductivity of the membrane (S/cm), e is the thickness of the membrane, and S is the surface area of the membrane. The Nernstian element (N) of impedance $Z(\omega)$ in series with R_{ct} takes into account the mass-transport limitation occurring at low frequencies²⁴ and can be neglected to evaluate the resistance of the electrolyte measured at a high frequency (close to 10⁵ Hz).

The fuel-cell performances were determined in a single DMFC with 5-cm² electrodes with a Globe Tech test bench (Globe Tech, College Station, TX). The membrane electrode assemblies (MEAs) were just pressed in the cell; no previous hot pressing of the

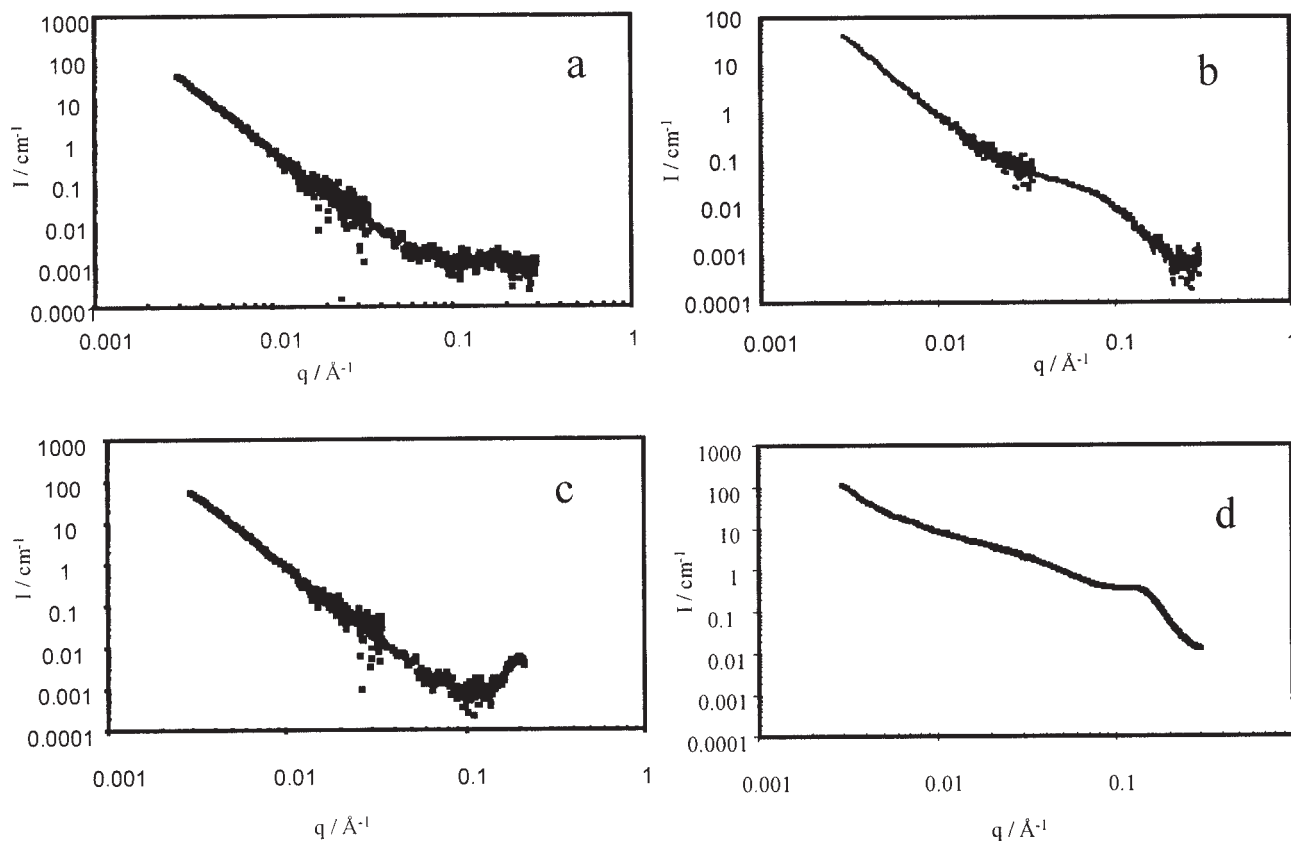


Figure 3 SANS measurements for (a) a 260- μm -thick hydrated sPPBP membrane, (b) a 140- μm -thick hydrated GS membrane, (c) a 145- μm -thick hydrated GPS membrane, and (d) a 125- μm -thick hydrated Nafion 115 membrane as a reference.

electrode to the membrane was performed. The E - j and P - j curves were recorded with a high power potentiostat (model HP 88, Wenking, Bank Elektronik, Zellerfeld, Germany) interfaced with a personal computer to control the current sequences and for data storage and a variable resistor cell current discharge. The electrodes (anode and cathode) were supplied by E-TEK (De Nora Fuel Cell Division, Somerset, NJ). The electrocatalysts were 60 wt % Pt-Ru/C (1/1 atomic ratio) for the anode and 40 wt % Pt/C for the cathode. The average platinum loading of each electrode was 2 mg/cm^2 . Both electrodes were loaded with 0.8 mg/cm^2 Nafion in the active layer and 30 wt % Teflon in the diffusion layer.

RESULTS AND DISCUSSION

SANS measurements

Spectra of the different PPP-based copolymers with an IEC of 1.3 mequiv of H^+/g are presented in Figure 3 (as well as a spectrum of a Nafion 115 membrane) in protonic and hydrated forms. In the so-called Guinier range of small angles, $q \ll 1$, one may obtain information about the form and size of the domains in the polymer if the distance between them is large enough.

In this technique, q represents the transfer momentum, which is the modulus of the vector corresponding to the difference between the incident and diffracted wave vectors:

$$q = \frac{4\pi}{\lambda} \sin \theta \quad (6)$$

where θ is the diffusion angle and λ is the wavelength of the incident light beam.

Only a few observations could be made on the spectrum obtained for the sPPBP polymer [Fig. 3(b)]. No characteristic peaks or ionomer peaks are visible. This polymer appears to be nonorganized: that is, no domains of the characteristic size between 2 and 60 nm are detected. Assuming that the ionic groups are uniformly distributed in the polymer matrix, it seems that the sulfonation does not modify the nanosized structure of the material. The increase in the signal toward small-angle values just corresponds to a dense system without fluctuation of well-defined electronic density. However, prudence is required in the interpretation of the spectrum; the measurements were made only in the plane of the membrane, and according to Blachot et

TABLE I
Physicochemical Characterization of the Different Polymers Used in this Study and Recorded at 20°C with Hydrated Membranes

	sPPBP	GS	GPS	Nafion 117	Nafion 115	sPI
IEC (mequiv of H ⁺ /g)	1.3	1.3	1.3	0.9	—	1.3
Organization of nanodomains (nm)	—	6–10	3	—	7	—
Young's Modulus (MPa)	—	1800	1400	—	—	1000
Strain rupture parameter (MPa)	—	103	74	—	—	50
Deformation rupture parameter (%)	—	10–15	5–10	—	—	37
Membrane thickness (μm) used for the permeability measurements	100	60	40	175	125	—
J for MeOH ($10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$)	0.1	0.2	1.3	0.7	0.9	—
J_{norm} for MeOH ($10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$)	0.1	0.1	0.5	1.2	1.1	—
Diffusion coefficient ($10^{-7} \text{ cm}^2 \text{ s}^{-1}$)	1.0	1.2	5.2	12.2	11.2	—
λ (H ₂ O/H ⁺)	25	20	33	20	—	26
σ (10^{-3} S/cm)	2.0	1.8	8.5	30.0	—	—

al.,²⁵ in the case of polyimide polymers for which a lamellate structure is assumed, the structure is anisotropic and different normal to the plane than parallel to the plane of the membrane.

On the other hand, in the spectrum of the grafted sulfonated polymer (GS), a bump appears centered in the range of $0.06 \text{ \AA}^{-1} < \mathbf{q} < 0.1 \text{ \AA}^{-1}$, which can be interpreted as an indication of an electronic density correlation. It is likely that the GS polymer contains ionic aggregates in a size range that can be determined with the following equation:

$$L = \frac{2\pi}{\mathbf{q}} \quad (7)$$

where L is the interaggregate distance. The low and high values of \mathbf{q} are close to 0.03 and 0.2 \AA^{-1} , respectively, leading to a distance between the ionic domains in the range of 10–6 nm.

In the case of the grafted perfluorinated sulfonated copolymer (GPS), the spectrum is very interesting [Fig. 3(c)]. A well-defined peak is visible, centered at $\mathbf{q} = 0.2 \text{ \AA}^{-1}$, which can be characteristic of the repetition of an aggregate structure in a size range of 3 nm. Two explanations for this peak can be formulated: first, this peak can be considered an ionomer peak, similar to that observed in the SANS spectrum of Nafion 115 [Fig. 3(d)], and is characteristic of the interionic cluster distance, assuming that the ionic part is sufficiently distant from the rigid hydrophobic skeleton of the polymer. Second, this peak can correspond to a typical copolymer sequencing, in which the PPP skeleton is decorated by sulfonic groups. However, this material appears to be more organized than the previous one, and so the first hypothesis is accepted. The well-defined differences in the structures of the PPP-based polymers revealed by SANS were rather unexpected as these polymers were assumed to have relatively similar structures and morphologies.

Mechanical tests

Because of the high brittleness and lack of ductility of the base PPBP polymer, no mechanical results about this material could be obtained. The mechanical properties of hydrated GS and GPS polymers are presented and compared with those of a sulfonated polyimide (sPI) of the same IEC. Table I presents the values of the Young's modulus and rupture parameters (deformation and strains). Looking to the rupture strain parameter, we find that the grafted sulfonated PPP polymers are sturdier than sPI, and this is consistent with the increase in the flexibility given to the rigid polyaromatic skeleton by the pendent chains in the case of grafted PPP. The low values of the rupture deformation parameter indicate that the three materials are still weakly tensile. However, in the sulfonated PPP family of materials, the grafted sulfonated polymers are the least brittle and more tensile.

The IEC has also an influence on the mechanical properties of the polymer. As an example, Figure 4

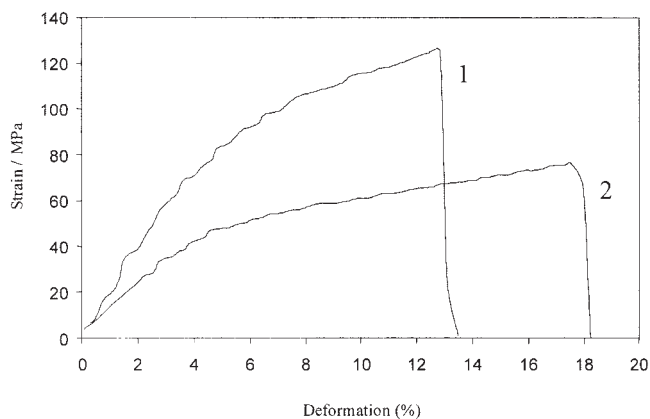


Figure 4 Applied strain as a function of deformation for hydrated GS membranes recorded at 20°C with IECs of (1) 1.3 and (2) 1.0 mequiv of H⁺/g.

TABLE II
Data from Permeability-to-MEOH Measurements for Nafion Membranes Having Different Thicknesses

	Thickness (μm)	J ($10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$)	J_{norm} ($10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$)	Diffusion coefficient ($10^{-7} \text{ cm}^2 \text{ s}^{-1}$)
Nafion ^a	40	1.5	0.6	6.0
Nafion 112	50	1.5	0.7	7.5
Nafion ^a	70	1.2	0.8	8.4
Nafion 115	125	0.9	1.1	11.2
Nafion 117	175	0.7	1.2	12.2

^a Nafion membranes from recast Nafion solutions.

presents the traction curves for two GS polymers with IEC values of 1.3 and 1.0 mequiv of H^+ /g. The Young's modulus is higher for the polymer with the higher IEC, as well as its rupture strain parameter. In this case, the hardness of the polymer seems to increase with increasing IEC, in contrast to some radiation-grafted sulfonated membranes. However, the deformation values at the material rupture (13 and 18% for IEC values of 1.3 and 1.0 mequiv of H^+ /g, respectively) indicate that both materials are rather fragile and undergo rupture after too little deformation.

Water sorption

The determination of WU constitutes very important data for a fuel-cell membrane's application. The presence of sulfonic functions in the PPP polymers will cause the swelling of the membranes when they are soaked in water, as is the case for the majority of ionic polymers. WU is essential for the protonic conductivity of membranes, but too large WU can lead to degraded mechanical properties and undesirable solubility of the polymer in water. However, well-hydrated membranes are important for optimal properties.

The obtained results are presented in Table I. First, the number of molecules of water per acid site determined for the Nafion 117 membrane (20 ± 2 water molecules per acid site) is consistent with that given in the literature.²⁶ Recently, Silva et al.²⁷ also showed that Nafion has a maximum of $\lambda = 23$ water molecules per ionic exchange site. The number of water molecules per ionic sulfonate group was found to be dependent on the polymer structure but independent of the IEC for a given polymer.

The grafted sulfonated polymer (GS) has almost the same λ value as the Nafion membrane (close to 20 ± 2), whereas the sPI, postsulfonated polymer (sP-PBP), and grafted perfluorinated sulfonated polymer (GPS) have a higher number of molecules of water (26 ± 1.9 , 25 ± 1.9 , and 33 ± 1.5 , respectively). The grafting of a perfluorinated side chain on a thermostable backbone leads to a considerable increase in the WU of

the membrane. The position of the sulfonic group at the end of the perfluorinated polar chains away from the bulky and less polar aromatic rings may favor the accessibility of water. λ for Nafion 117 is lower than that for the GPS polymer. In a comparative study of a Dow membrane and a Nafion membrane, Zawodzinski et al.²⁶ showed that the shorter the side chain, the higher the WU per ionic site: increasing the length of the perfluorinated chain increases the hydrophobic character of the polymer because of the presence of fluorine.

MeOH permeability measurements

The measurement of permeability allows the evaluation of the flux density (J) of MeOH through the membranes and the diffusion coefficient of MeOH in the membranes with Fick's first law of diffusion.²¹ However, the diffusion of MeOH in the different membranes is dependent not only on the chemical nature of the polymers but also on their structure, which can differ not only with the method of membrane preparation (extrusion or solution casting) but also with the structural differences in the percolation network of the polymer induced by the thickness of the membrane. Therefore, the normalized flux density (J_{norm}), defined as the flux density per 100 μm of polymer thickness, is used to compare different polymers, whereas J is more appropriate for characterizing the permeability of membranes of different thicknesses and is the pertinent parameter for comparison with DMFC performances. For example, consider the commercial Nafion 117, 115, and 112 membranes and two recast Nafion membranes obtained by classical coating technology from a 20 wt % Nafion solution in aliphatic alcohols provided by Dupont (Fayetteville, NC) (see Table II for the MeOH permeation characteristics of these membranes). J_{norm} appears to be of the same order (ca. $0.7 \times 10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$) for both reconstituted membranes and for the Nafion 112 membrane and almost 2 times higher for the Nafion 115 and 117 membranes (ca. $1.2 \times 10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$). On the other hand, the values of the diffusion rate, dC/dt , and of J as a func-

tion of the membrane thickness decrease quasilinearly and show that thinner membranes have higher diffusion rates. Because of this, the permeability of the different PPP polymers is characterized by J_{norm} to compare the polymer types, whereas the permeability of the membrane, J , is used to determine the pertinent value for the DMFC tests. The results are listed in Table I. The permeability of the PPP membranes is lower than that of the Nafion membranes. Looking at the normalized diffusion density, we find that the functionalization of the PPP polymer with the TMSCI medium sulfonating agent (sPPBP) or by grafting (GS) leads to the same permeability to MeOH; however, the grafted perfluorinated sulfonated polymer demonstrates a permeability 5 times higher. The main conclusion is that the introduction of the perfluorinated side chains onto the thermostable backbone of the PPP polymer led to a permeability value similar to that obtained with perfluorinated Nafion 112 membranes. Finally, we did not observe the expected lowering of the permeability to MeOH of the polyaromatic polymers in comparison with the high permeability of the perfluorinated polymers such as Nafion. This indicates that the structures of the GPS polymer and the Nafion polymers did not differ as much as expected. Indeed, in the vicinity of the sulfonic group in a Nafion or grafted perfluorinated sulfonated PPP, the chemical structures of the pendent chains are very similar ($\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_3\text{H}$ in each case), and it can be reasonably assumed that the organizations of the hydrophilic domains in both structures are similar, as are the characteristics of both polymers in term of flexibility, acidity, and bulkiness. Therefore, the pathway of a polar molecule such as MeOH through the membrane is probably the same in both perfluorinated polymers, leading to the very close values of permeability that are observed.

Conductivity measurements

The results of the conductivity measurements are also reported in Table I. The grafted sulfonated (GS) membrane and the postsulfonated (sPPBP) membrane displayed the same conductivity (2 mS/cm). These values, obtained at room temperature and 100% relative humidity, are 10 times lower than that obtained with Nafion 117 and are consistent with that given in the literature.^{28,29} These authors reported a conductivity of 10^{-2} S/cm for 65 mol % sPPBP at 100°C and 100% relative humidity.

The grafted perfluorinated sulfonated (GPS) membrane displayed a conductivity of 8.5 mS/cm, which is a value only 3–4 times lower than that obtained under the same conditions with Nafion 117. This encouraging result is due to the lower normalized MeOH permeability of the GPS polymer in comparison with the Nafion 117 polymer, and hence the use of a thinner

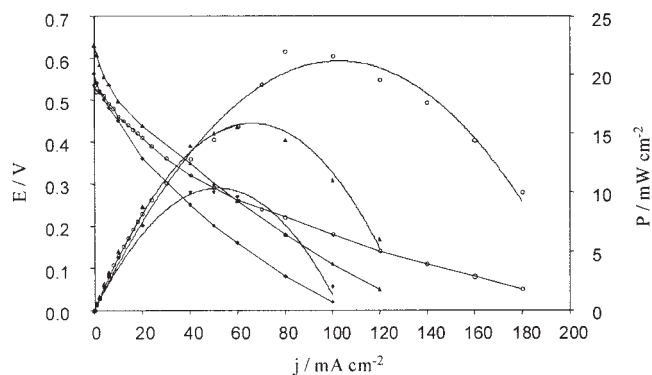


Figure 5 Comparison of the fuel-cell performance at 90°C with different membranes in 5-cm² DMFCs: (◆) GS membrane, (▲) sPPBP membrane, and (○) GPS membrane. MEAs were assembled in cells with no previous hot pressing (2M MeOH solution flow rate = 2 mL/min, $T_{\text{MeOH}} = 95^\circ\text{C}$, $P_{\text{MeOH}} = 1.8$ bar, pure O₂ flow rate = 150 mL/min, $T_{\text{O}_2} = 95^\circ\text{C}$, $P_{\text{O}_2} = 2.3$ bar).

membrane can be considered, which would lead to an increase in the area conductance (i.e., a decrease in the electrolyte resistance) and an enhancement of the DMFC performance.

DMFC performance

The two major requirements for using a membrane in a DMFC are low MeOH crossover and high ionic conductivity. However, although a membrane material exhibits low MeOH permeation in nonelectrochemical tests, the MeOH crossover, when operated under fuel-cell conditions, may still be significant because of electro-osmosis drag. If we consider the ionic conductivity, it may also be perturbed by the working temperature of the DMFC, typically 60–100°C, which can either increase the conductivity of the membrane or decrease it because of the dehydration of the membrane. Therefore, fuel-cell tests are necessary to compare the different membranes.

First, the two grafted materials (GS and GPS) and the postsulfonated material (sPPBP), having the same IEC, were compared with respect to performance in an operating DMFC (Fig. 5). The values of the open circuit potential are 0.1 V higher with the PPBP and GS membranes than with the GPS membrane, and this is consistent with the value of the MeOH permeability of the membranes, as discussed earlier. However, the decrease in the potential with the current density is more drastic with the PPBP and GS membranes in comparison with the GPS membrane. Again, this result is fully consistent with the conductivity evaluated earlier. The peak power densities achieved with the sPPBP, GS, and GPS membranes at current densities of 50, 70, and 110 mA/cm² are 10, 15, and 22 mW/cm², respectively.

Generally, the catalyst layers of the electrodes for fuel cells and particularly DMFCs load with Nafion, which acts as a binder and as an ionic bridge between the catalyst and the membrane electrolyte, facilitating proton transfer.^{14–20,30,31} To optimize the MEA, the Nafion-containing electrodes were hot-pressed against the Nafion membrane. However, when the membrane differed significantly in terms of the chemical composition from Nafion, no good interface could be obtained in this way. The modification of the membrane with a functionalized perfluorinated sulfonated group was assumed to improve this interface. However, no enhancement of the DMFC performance was observed upon hot pressing with PPP-based membranes. However, when we compared the DMFC performances obtained with a Nafion membrane without hot pressing and a GPS membrane at 90°C (Fig. 6), the performances were nearly identical. In the whole current density range, the curves are very close. The lower voltage at an open circuit in the case of the GPS membrane is due to the increased MeOH permeability, which is 2 times higher with the 40- μm GPS membrane than with the Nafion 117 membrane ($J = 1.3 \times 10^{-7}$ and 0.7×10^{-7} mol s⁻¹ cm⁻², respectively). The difference between both open circuit voltages (which is close to 0.05 V) is constant over the whole current density range, confirming this. The $j(E)$ polarization curves have similar slopes, which indicate that the resistances of both membranes are close. Indeed, the conductivity was found to be 3–4 times lower for the GPS polymer than for the Nafion membrane, whereas the GPS membrane is more than four times thinner than the Nafion 117 membrane; this leads to similar area resistances.

Obviously, during the hot pressing of classical commercial E-TEK electrodes against a Nafion 117 membrane, a much more higher power density is

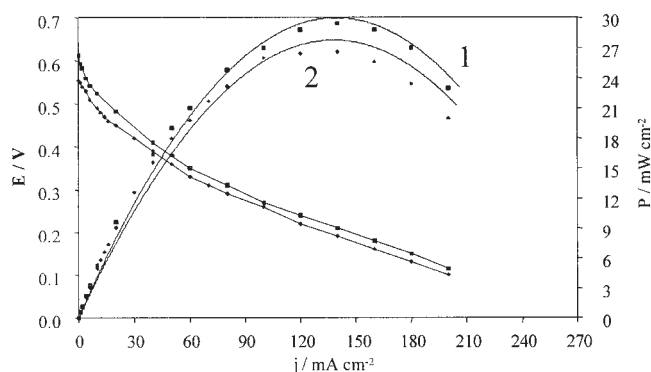


Figure 6 Comparison of the electrical performance at 90°C with different membranes in 5 cm² DMFCs: (1) Nafion 117 membrane and (2) GPS membrane. MEAs were assembled in cells with no previous hot pressing (2M MeOH solution flow rate = 2 mL/min, $T_{\text{MeOH}} = 95^\circ\text{C}$, $P_{\text{MeOH}} = 1.8$ bar, pure O₂ flow rate = 150 mL/min, $T_{\text{O}_2} = 95^\circ\text{C}$, $P_{\text{O}_2} = 2.3$ bar).

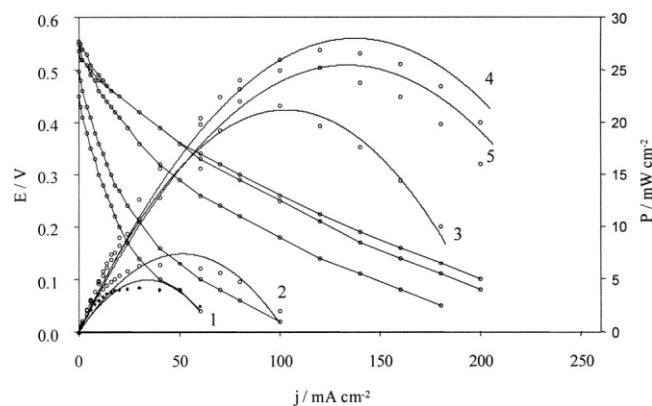


Figure 7 Temperature effect in $E(j)$ and $P(j)$ curves obtained in a 5-cm² DMFC fitted with a GPS membrane. MEAs were assembled in cells with no previous hot pressing (2M MeOH solution flow rate = 2 mL/min, pure O₂ flow rate = 150 mL/min): (1) 50°C ($T_{\text{MeOH}} = 55^\circ\text{C}$, $P_{\text{MeOH}} = 1.2$ bar, $T_{\text{O}_2} = 55^\circ\text{C}$, $P_{\text{O}_2} = 1.5$ bar), (2) 70°C ($T_{\text{MeOH}} = 75^\circ\text{C}$, $P_{\text{MeOH}} = 1.5$ bar, $T_{\text{O}_2} = 75^\circ\text{C}$, $P_{\text{O}_2} = 1.8$ bar), (3) 90°C ($T_{\text{MeOH}} = 95^\circ\text{C}$, $P_{\text{MeOH}} = 1.9$ bar, $T_{\text{O}_2} = 95^\circ\text{C}$, $P_{\text{O}_2} = 2.3$ bar), (4) 100°C ($T_{\text{MeOH}} = 95^\circ\text{C}$, $P_{\text{MeOH}} = 1.9$ bar, $T_{\text{O}_2} = 95^\circ\text{C}$, $P_{\text{O}_2} = 2.3$ bar), and (5) 110°C ($T_{\text{MeOH}} = 95^\circ\text{C}$, $P_{\text{MeOH}} = 1.9$ bar, $T_{\text{O}_2} = 95^\circ\text{C}$, $P_{\text{O}_2} = 2.3$ bar).

achieved,³² indicating that the optimization of the MEA is a major issue to be considered for developing new polymer electrolyte membranes for DMFC applications.

The effect of the working temperature of a DMFC fitted with a GPS membrane is shown in Figure 7. Increasing the temperature from 50 to 100°C led to an increase in the performance from 5 to 30 mW/cm². A higher temperature operation led to the performance of the cell decreasing (20 and 25 mW/cm² at 110°C). When the temperature was decreased to 100°C, the performance was recovered, and this indicated that no degradation of the membrane took place. At temperatures higher than 100°C, the GPS membrane underwent a dehydration that reduced its conductivity.

CONCLUSIONS

Membranes intended for fuel cells must have a low MeOH permeability to prevent a reduction of the cell efficiency due to the depolarization of the cathode. In nonperfluorinated phenylene membranes, the MeOH permeabilities were lower than those of Nafion 112, 115, and 117.

The DMFC performances obtained with the GS membrane and sPPBP membrane were half than that of the Nafion 117 membrane with nonoptimized and non-hot-pressed MEA. Further research is required to optimize several aspects of the membranes. Notably, the sulfonation level has to be more controlled with this new grafting method developed in the Commissariat à l'Énergie Atomique laboratory. Moreover, be-

cause of the advantages of this polymer family, especially the low cost of the matrix polymers and the large variety of substituting groups available, investigations into PPP membranes are promising. The grafting of a sulfonated perfluorinated chain led to a performance similar to that obtained with a nonoptimized, non-hot-pressed Nafion 117 MEA. Optimization of the chain length, the electrode–membrane interface, and the ionic conductor binder in the electrodes represents the direction of research required to develop new membranes (alternative to Nafion) for applications in DMFCs.

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