

Proton-conducting membranes from phosphotungstic acid-doped sulfonated polyimide for direct methanol fuel cell applications

Francisco Alcaide · Garbiñe Álvarez ·
Larraitz Ganborena · Juan J. Iruin · Oscar Miguel ·
J. Alberto Blazquez

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Abstract A series of novel hybrid proton conducting membranes based on sulfonated naphthalimides and phosphotungstic acid (PTA) were prepared from N-Methyl Pyrrolidone (NMP) solutions. These hybrid organic-inorganic materials, composed of two proton-conducting components, have high ionic conductivities ($9.3 \times 10^{-2} \text{ S cm}^{-1}$ at 60 °C, 15% PTA), and show good performance in H₂|O₂ polymer electrolyte membrane fuel cells (PEMFC), previously reported by us. Moreover, they have low methanol permeability compared to Nafion[®]112. In this paper we describe, for the first time, the behaviour of these hybrid membranes as electrolyte in a direct methanol fuel cell (DMFC). The maximum power densities achieved with PTA doped sulfonated naphthalimide membrane, operating with oxygen and air, were 34.0 and 12.2 mW cm⁻², respectively; about the double and triple higher than those showed by the non-doped membrane at 60 °C.

Keywords Sulfonated polyimides · Ion-exchange membranes · Phosphotungstic acid · Direct methanol fuel cell · DMFC

Introduction

One recent and promising application of the polymeric materials is their use as ion-conductive membranes for batteries [1] or proton exchange membranes for fuel cells (PEMFC) [2–4]. For instance, perfluorosulfonated ionomer (Nafion[®]) membranes

F. Alcaide · G. Álvarez · L. Ganborena · O. Miguel · J. Alberto Blazquez (✉)
CIDETEC, Centro de Tecnologías Electroquímicas, Paseo Miramon 196,
20009 San Sebastian, Spain
e-mail: ablazquez@cidetec.es

J. J. Iruin
Departamento de Ciencia y Tecnología de Polímeros e Instituto de Materiales Poliméricos (POLYMAT), M. Lardizabal 3, 20018 San Sebastian, Spain

have been used for this purpose, due to their efficient proton conduction (10^{-1} S cm $^{-1}$ in their fully hydrated protonic form) and long lifetime [5–8]. Lower cost polymers with similar properties are strongly desired as alternative materials [9–13]. One of the most important areas of research in PEM fuel cells is the development of low cost membranes [14–20], with low methanol permeability for direct methanol fuel cells (DMFC), due to the limit of low operating cell temperature, as well as, the methanol crossover problems associated in common perfluorosulfonic acid membranes [21–23]. In DMFC the crossover of methanol from the anode to the cathode affects adversely the performance of the cell, since the presence of methanol at the cathode is in the origin of the poisoning of the catalyst sites for oxygen reduction [21].

Organic-inorganic composites as membranes for PEMFC have been investigated with the main objective of increasing the proton conductivity of the membrane [24–28]. The heteropolyacids are attractive inorganic fillers, because in their crystalline forms these materials have demonstrated to be highly conductive [21, 29].

In this paper, we describe the synthesis of hybrid organic-inorganic membranes based on sulfonated naphthalimides and phosphotungstic acid (PTA). The presence of phosphotungstic acid modifies some important properties of the copolyimides, such as the solubility in water and other solvents, as well as their mechanical properties [21, 24]. Thus, it has been possible to improve the solubility of such polymers in solvents different to the common *m*-cresol [24, 30], such as *n*-methyl pyrrolidone (NMP). This improvement allows preparing membranes in better conditions, as we have described previously [24]. The objective of this paper is to investigate the influence of dispersed PTA on different membrane properties such as water uptake, ion exchange capacity (IEC), proton conductivity, methanol permeability and their behaviour as electrolyte in direct methanol fuel cells.

Experimental

Starting materials

Benzoic acid, triethylamine, *N,N*-dimethylacetamide (DMAc), diethyl ether and *m*-cresol were purchased from Aldrich and used as received. The 4,4'-diaminobiphenyl 2,2'-disulphonic acid (BDSA), obtained from Tokyo Kasei Co, was purified in boiling water and dried at 140 °C under vacuum for 24 h, before the polycondensation reaction. The 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), the 4,4'-(4,4'-Isopropylidenediphenyl-1,1'-diyldioxy)dianiline (pAPI) and phosphotungstic acid were purchased from Aldrich and were dried at 160 °C under vacuum before use.

Polymer synthesis

All polyimides were prepared by the same method [30]. As a representative example, we describe in detail the synthesis procedure of the BDSA/NTDA/pAPI ($r = n_{\text{BDSA}}/n_{\text{APMP}} = 70/30$) copolyimide. In a three-necked flask fitted with

mechanical stirrer and nitrogen inlet, 9.0860 g (0.0262 mol) of BDSA containing 1.1% water (determined by thermogravimetric analysis on a TG-Q500 (TA Instruments) under nitrogen at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$) and 6.33 g (0.0626 mol) of triethylamine were introduced with 89 g of m-cresol. This mixture was stirred until solubilization of BDSA. Then 10 g (0.0372 mol) of NTDA, 4.5567 g (0.0111 mol) of pAPI diamine and 6.38 g (0.0522 mol) of benzoic acid were added. This reaction mixture was stirred a few minutes and then heated at $80\text{ }^{\circ}\text{C}$ for 4 h and then at $180\text{ }^{\circ}\text{C}$ for 20 h. Before cooling, 166 g of m-cresol were added, and the viscous polymer solution was poured into ethyl acetate. The precipitated polyimide was collected by filtration, washed with methanol and dried under vacuum at $100\text{ }^{\circ}\text{C}$.

Film preparation

Sulfonated polynaphthalimides membranes were obtained by solution casting from a m-cresol polymer solution. Hybrid proton-conducting membranes were obtained by solution casting from a polymer solution using NMP as solvent. When the phosphotungstic acid was completely dissolved, the corresponding amount of polymer was added to obtain different hybrid membranes with a different degree of phosphotungstic acid, 15, 30 and 45% in weight. The films were dried on a heating plate for 1 h at room temperature, 2 h at $80\text{ }^{\circ}\text{C}$, 4 h at $120\text{ }^{\circ}\text{C}$ and finally 2 h at $180\text{ }^{\circ}\text{C}$. The polymer film was separated from the glass plate support by immersion in water. All membranes were washed three times by keeping them in methanol at $50\text{ }^{\circ}\text{C}$ for one hour. Series of tough sulfonated polyimide films were obtained with controlled thickness between 45 and $50\text{ }\mu\text{m}$. Membranes were acidified with a $0.1\text{ M H}_2\text{SO}_4$ solution at room temperature during 14 h and then rinsed with water. The hybrid membranes were rinsed with water during the necessary time up to observing that the weight was constant (72 h). In all cases we observed that the loss of weight was lower than 5% of added PTA, due to the strong interactions between the polyimide and the PTA [24].

Polymer characterization

Density measurements and FTIR study

The density values of the membranes were measured by the picnometry technique, using toluene as a media in which the membranes do not dissolve. It is consequently assumed that the total volume is the additive sum of the polymer and the liquid. FTIR spectra were performed on a Nicolet Magna 560 infrared spectrophotometer.

Water uptake

The water uptake was determined by soaking the membranes in liquid water at room temperature. Previously, they were dried for 1 week under vacuum at $100\text{ }^{\circ}\text{C}$ and weighted. The dry membranes were then immersed in water at room temperature for

different periods of time. Finally, the membranes were wiped with a dry paper and quickly weighted. This procedure was repeated until a constant weight was obtained.

The equilibrium water uptake (WS) of a membrane is the amount of water per gram of the original dry membrane (composed of polymer and inorganic charge) and was determined using the following relation:

$$WS = \frac{(W_s - W_d)}{W_d} \quad (1)$$

where W_d and W_s are the weight of the dry and the wet membrane, respectively. From this value, we can define the “corrected water uptake” (WS') as the amount of water per gram of polymer using the following relation:

$$WS' = \frac{WS}{\%pol} \times 100 \quad (2)$$

where $\%pol$ is the percentage of polymer in the hybrid membrane. Using this procedure it is possible to compare the water sorption of the hybrid membranes and that of the pure polymer, in order to evidence the real effect of the PTA.

Proton conductivity

The conductivity was determined using the complex impedance spectroscopy method in a frequency range between 1 MHz and 1 Hz (at 20 frequencies per decade, amplitude 10 mV), using a potentiostat Autolab PGSTAT30 equipped with a FRA2 module. A membrane ($1.0 \times 0.5 \text{ cm}^2$) and two platinum electrodes were set in a Teflon cell. The distance between the two electrodes was 0.5 cm. The cell was placed in a thermostatic chamber in order to control the temperature, as this parameter affects the proton conductivity. All measurements were carried out in deionized water (at 100% relative humidity). The resistance value related to the membrane conductance (R) was determined from the high-frequency intercept of the impedance with the real axis. Proton conductivity was calculated from the following equation:

$$\sigma = \frac{D}{L \times B \times R} \quad (3)$$

where D is the distance between the two electrodes, L and B are the thickness and width of the membrane, respectively, and R is the resistance value measured.

Methanol crossover

Methanol crossover was measured using a PTFE gravimetric cell [31, 32]. Briefly, it consists of a small container partially filled with the liquid under study in equilibrium with its vapor. The top of the container was sealed with the polymeric membrane. When the gravimetric cell was placed downward, the liquid came in contact with the membrane allowing the determination of the liquid permeation. The liquid inside the cell permeated the polymeric membrane and evaporated into the

air. This process is reflected as a reduction in the overall weight of the cell. After an induction time, a stationary process is usually exhibited from which the permeability of the penetrant can be calculated. In the present case, we used a computer-connected Sartorius analytical balance with a sensitivity of 10^{-5} g to record the weight loss.

First of all, the original films were submitted to a 100% relative humidity during 3 weeks before measuring the crossover, using a K_2SO_4 saturated aqueous solution. Then, the PTFE cell was filled with an aqueous methanol solution of 2 M, a typical concentration value in the DMFC cells using membranes as those employed in this paper. The temperature was 30 °C. Given that water also permeates through the cell and in order to know the amount of methanol that has permeated, it is necessary to quantify the concentration of methanol both in the initial (2 M) and the final aqueous solution. In this context we can define the methanol crossover by means of the expression:

$$J = \frac{1}{S} \left(\frac{N_{\text{initial}} - N_{\text{final}}}{t} \right) \quad (4)$$

where S is the membrane exposed area (2.54 cm^2 in our case), N_{initial} and N_{final} the moles of methanol in the initial and final aqueous solutions and t is the time of the measurement. In order to have a constant and representative value of J for the methanol crossover, the experimental time t should be enough to assure that the permeation process was in a stationary state, as evidenced by the evolution of the PTFE cell weight.

With the intention of determining the final concentration of methanol in the aqueous solutions the area of its ^1H NMR signals [33, 34] were measured with reference to an internal standard. The standard was the sodium salt of 2,2-(dimethyl)-2-sylpentan-5-sulfonic (DSS). It is soluble in water and it gives a clear and strong singlet signal to reference the other signals ($\delta = 0.00 \text{ ppm}$).

In a NMR tube 200 μl of the aqueous methanol solution, 400 μl of D_2O (its signal served as the field frequency lock) and 100 μl of standard DSS, of concentration $8.3 \times 10^{-3} \text{ M}$ were successively added. Using a Bruker DRX-500 spectrometer, 500 MHz ^1H NMR spectra were recorded. One hundred and twenty-eight scans of 64 K data points were acquired with a spectral width of 8,012 Hz (16 ppm), an acquisition time of 4.09 s, a recycle delay of 1 s and a flip angle of 90°. Water signal suppression was achieved using the Watergate pulse sequence [35]. The data, acquired under an automation procedure, required about 11 min. per sample. Preliminary data processing was carried out with the Bruker software, version 2.5. The FIDs were Fourier transformed (0.4 Hz line broadening), the spectra phased and baseline corrected. The resulting spectra then aligned by right or left shifting if necessary (using the DSS signal as reference), saved as ASCII files and transferred to a PC. Data analysis was achieved with Mestre-C software package [36].

All the results shown in the present work represent the average of three independent experimental measurements.

Fabrication of membrane electrode assemblies and fuel cell testing

Membrane electrode assemblies, MEAs, used in this work consisted of two single sided ELAT V2.1 gas diffusers (E-Tek, Inc.) and a catalyst coated membrane [37]. Briefly, the catalyst was first dispersed in ultra pure water (Millipore Milli-Q system; conductivity lower than $6 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$), with appropriate amounts of 5% wt. Nafion[®] solution (1100 EW, Aldrich) and 1-methyl-2-pyrrolidone (Fluka). The anode contained 4 mg cm^{-2} of unsupported platinum/ruthenium black (Pt:Ru 1:1 atomic ratio, Alfa Aesar), while the cathode contained 4 mg cm^{-2} of platinum black (E-Tek, Inc.). Then, both anode and cathode catalyst inks were directly painted onto either side of the sulfonated polyetherimide-based membrane. The MEA had an active area of 5 cm^2 .

The MEAs were characterized in commercial fuel cell hardware (ElectroChem Inc., FC05-01SP). The current collectors were made of low-porosity, high-purity graphite blocks with serpentine flow fields. The MEA, flanked by the two current collectors, was held between two gold-plated copper contact plates using a set of retaining bolts positioned around the periphery of the cell. Electrical heaters were placed behind each of the copper plates.

All of the measurements reported here were carried out feeding the anodic compartment with 2.0 mol dm^{-3} aqueous CH_3OH at 2.0 ml min^{-1} from a reservoir at 60°C . Dry high purity oxygen (Praxair, 99,999%) or synthetic air (Praxair, 99,999%), both at a fixed flow rate of 100 ml min^{-1} at room temperature, were flowing through the cathodic compartment. No backpressure was used in any of the experiments. The cell temperature was set at 60°C .

Cell polarization measurements were performed using a 1287A Potentiostat (Solartron Analytical). Current vs. voltage data were recorded from open cell voltage down to 0.1 V at a scan rate of 1 mV s^{-1} until a reproducible curve was obtained. These current-voltage curves were compared with those obtained by consecutive voltage steps (50 mV ; current recorded after 180 s), and no significant differences were found.

Results and discussion

Synthesis of sulfonated polynaphthalimides

All polyimides were prepared by copolymerization of the naphthalic anhydride NTDA in a mixture of the sulfonated diamine BDSA and the aromatic diamine pAPI (see Fig. 1). A series of copolymers were prepared by varying the relative ratio between BDSA and pAPI. More precisely, two different values of ion-exchange capacities were fixed: 2.5 and $1.98 \text{ meq H}^+/\text{g}$. These sulfonated polyimides present a very poor solubility in the most common solvent as NMP, DMAc, etc. Interestingly, these copolyimides are soluble in NMP when some phosphotungstic acid is previously dissolved in NMP, due to the appropriate interactions between the polymer and the PTA, as we have described previously [24].

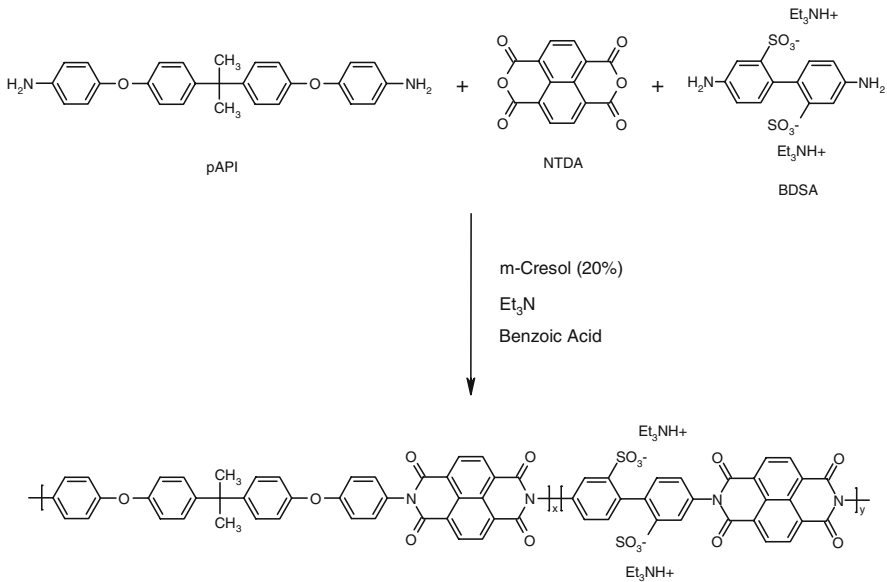


Fig. 1 General scheme of the synthesis of a novel sulfonic polyimide BDSA/NTDA/pAPI

Table 1 Experimental measurements of membranes with different IEC and PTA content

IEC	Solvent	PTA (%)	WS ^a (%)	WS ^b (%)	Methanol crossover ($\times 10^{-8}$ mol s ⁻¹ cm ⁻²)	ρ^c	$\sigma^d \times 10^{-2}$ (S cm ⁻¹) 25 °C
2.5	m-cresol	0	61.6	61.6	15.1	1.51	8.3
	NMP	15	46.9	55.2	12.3	1.73	6.1
		30	34.5	49.3	11.7	2.00	5.1
2.0	m-cresol	0	39.6	39.6	7.7	1.48	2.9
	NMP	15	27.3	32.1	4.2	1.65	2.4
		30	20.4	29.1	2.2	1.95	2.1
		45	15.5	28.2	1.9	2.22	1.9
Nafion112		0	–	–	21.3	–	4.1

^a Water uptake per gram of membrane

^b Water uptake per gram of polymer

^c Density in g cm⁻³ at 35 °C

^d Conductivity

Density measurements and FTIR analysis

As reported in Table 1, the density of the membranes increases when the PTA content is raised. This is related to the higher density of the inorganic charge with respect to that of the polymer. On the other hand, a decrease in the IEC of the membrane leads to a decrease in the membrane density, at constant PTA content.

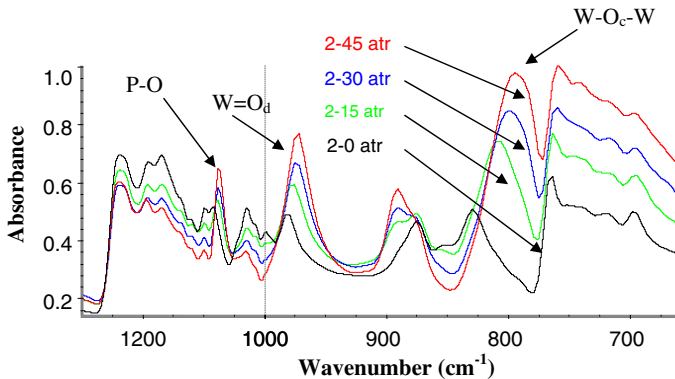


Fig. 2 IR spectra of hybrid membranes obtained from a sulfonated polyimide ($\text{IEC} = 1.98 \text{ meqH}^+/\text{g}$) and different PTA content

This fact is a consequence of the lower proportion of the flexible non sulfonated diamine (pAPI) incorporated in the polymer chain.

Figure 2 shows the IR spectra of membranes having an IEC of $1.98 \text{ meq. H}^+/\text{g}$ with different PTA contents. It can be observed from the FTIR spectra the following facts: (a) there is no change in the position of P–O stretching band; (b) the terminal oxygen band ($\text{W}=\text{O}_d$) appears at the same wave number that those of the secondary structure of the PTA; (c) in the case of lower contents of polyimide, the wave numbers of the bridging oxygen bands are near to the primary structure. However, a progressive shift of ($\text{W}-\text{O}-\text{W}_c$) band is observed with increasing polyimide content, whereas there is no change in the case of ($\text{W}-\text{O}_b-\text{W}$) [21]. A similar frequency shift was also observed in two cases: (1) in PTA-supported silica, which was attributed to the interaction of the corner-shared oxygen of PTA with silica surface [21] and (2) PTA-poly (vinyl alcohol) [21]. These specific interactions could explain the solubility of the polymer in NMP in the presence of PTA, as well as, the retention of the PTA in the membrane after being immersed in water for hours [24].

Water uptake analysis

Figure 3 illustrates that for a given IEC value the water vapor sorption and the liquid water uptake, at different relative humidities, decrease when the PTA content increases. One possible explanation could be related with the low PTA water sorption capacity compared to the polymer water sorption [38, 39]. This contrasts with other systems like those reported by Li and Wang [38, 39], in which the matrix is less hydrophilic than the PTA. However, the corrected water uptake (which would be constant) decreases when the PTA content increases. This trend could arise from the higher density and lower free volume of our membranes [21]. In a similar way, in partially sulfonated poly(arylene ether sulfone) copolymer/heteropoly acid composite membrane, the water uptake decreases as the filler content increases, mainly due to strong interaction between sulfonic acid on the polymer backbone and PTA [40].

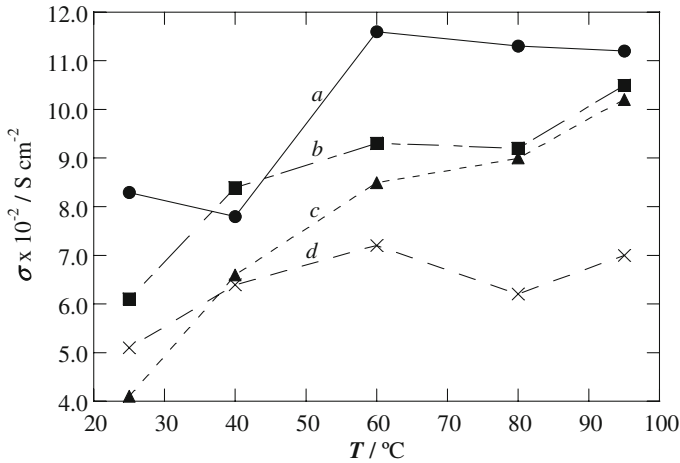


Fig. 3 Temperature dependence of the ionic conductivity values of pure and hybrid membranes obtained from sulfonated polyimides having the same IEC (2.5 meq. H⁺/g polym.) and different PTA content: (a) pure copolyimide with 0% PTA (b) 15% PTA (c) 30% PTA, and (d) Nafion[®] 112

On the other hand, for membranes with the same PTA content and different IEC, one can observe that the water uptake decreases when the IEC value decreases because of the sulfonic groups are the principal responsible in the absorption of water [30].

Proton conductivity measurements

Table 1 shows the proton conductivity of membranes at different temperatures. The conductivity increased with the ion exchange capacity, showing values in the order of 10⁻¹ S cm⁻¹. In contrast, the conductivity decreased slightly as the PTA content increased (see Fig. 3). This phenomenon may be due to the lower water sorption of the hybrid membranes [24], and to the less ionic conductivity of the PTA than the polymer.

Methanol crossover

Using aqueous methanol solutions and the corresponding ¹H NMR spectra a calibration graph (Fig. 4) was obtained, by plotting the ratio between the peak areas of methanol (A) and the internal standard DSS (A_{SD}) against the methanol wt.%, at the selected chemical shifts (Fig. 5). Processing of the data with the aid of the program SPSS 11.0 generated the following equation:

$$A/A_{DSS} = (2.087 \pm 0.029)C(\%) - (2.143 \pm 3.70)10^{-2}$$

$$(n = 7, r = 0.9995, S_{y/x} = 3.682 \times 10^{-2}).$$

The limit of detection, calculated from “3S_{y/x} + intercept”, was 0.053% methanol by weight.

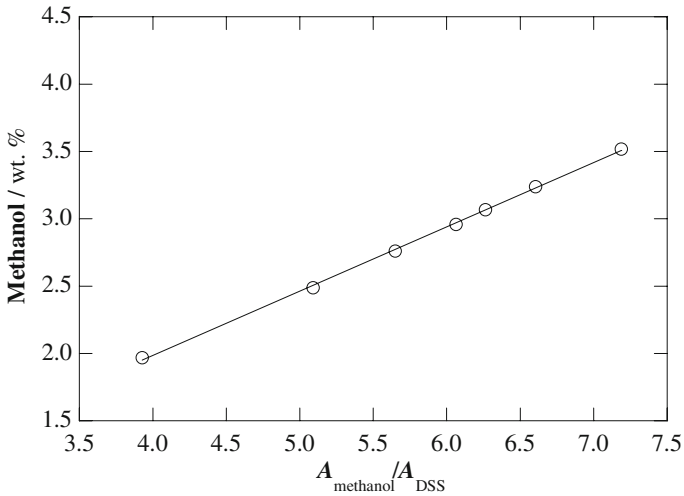


Fig. 4 Calibration graph, obtained by plotting the ratio between the peak areas of methanol (A) and the internal standard DSS (A_{SD}) against methanol wt. %

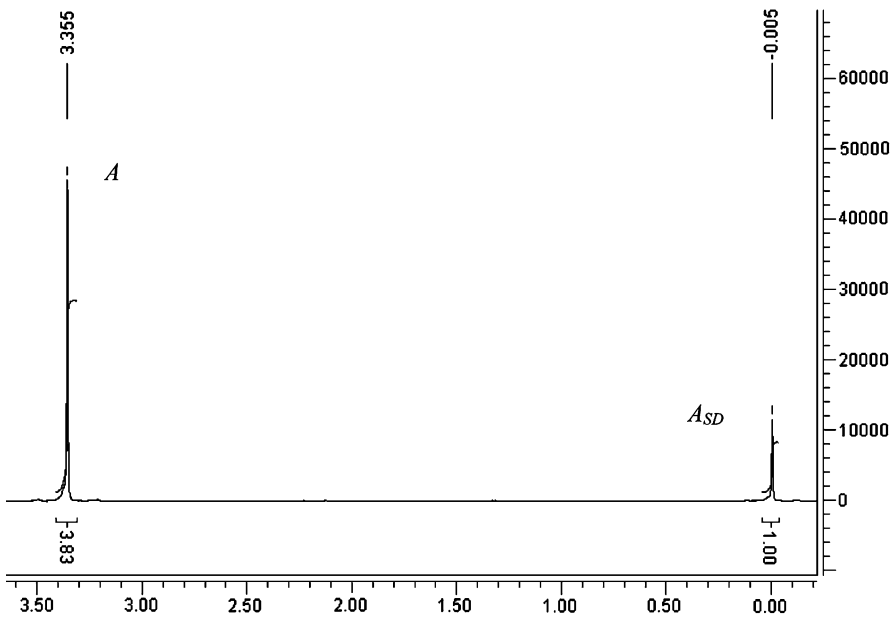


Fig. 5 ^1H NMR of samples containing methanol (A) and the internal standards DSS (A_{SD})

With the aid of this calibration equation, the methanol crossover of pure and hybrid sulfonated polyimide membranes was evaluated after measuring the steady-state concentration of methanol in the permeation cell. Figure 6 shows how the methanol crossover decreased when the concentration of the inorganic component

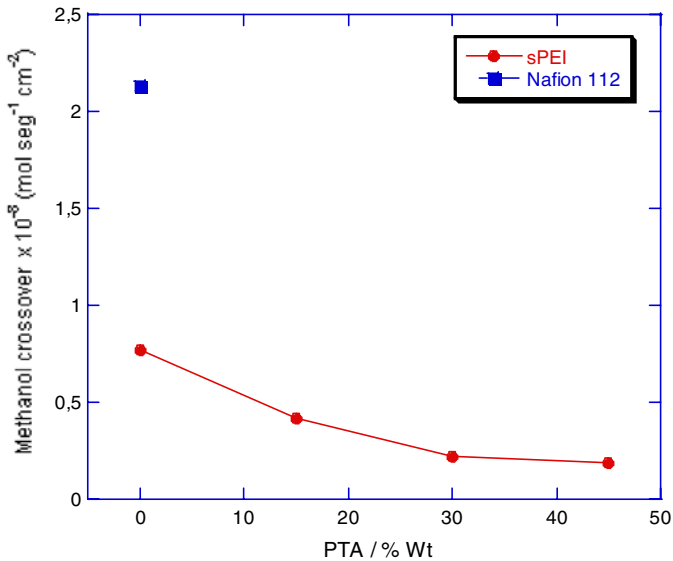


Fig. 6 Influence of PTA content on methanol crossover through hybrid membranes. Methanol crossover through Nafion[®] is also included for comparison

(PTA) in the hybrid membranes increased. This behaviour corresponds to hybrid membranes in which the pure polymer has an ion exchange capacity of 2.0 meq H^+ /g polym. When PTA increases from 0 to 45%, the methanol crossover reduces three times, providing an indirect proof that hybrid system becomes denser (its free volume is reduced) with the PTA doping [21]. For comparative purposes, a membrane of pure Nafion[®] 112 was also measured under similar conditions and the result is shown in Fig. 3. Compared to our hybrid system, the Nafion[®] 112 show less resistance to methanol crossover, being similar to that reported by others authors, which used different methods for methanol crossover measurements [21, 41, 42].

Performance of direct methanol fuel cells, DMFCs, with sulfonated polyimide-based membranes

Figure 7 shows the current density-cell voltage curves of the cells based on sulfonated polyetherimide and that of Nafion[®] 112 membranes with oxygen or air fed cathodes and 2 M fed methanol anode. The performance of the cells improved considerably during the first 2 days. After that, it did not show any further improvement.

The open circuit voltage of the sulfonated polyetherimide membrane (15% charge) cell was 0.120 V higher than that of the non-charged membrane due, mainly, to its lower methanol permeability. In addition, and over the entire current density region, the cell voltage of the polyetherimide sulfonated membrane (15% charge) cell was higher than that of non-charged membrane cell. A similar behaviour was observed when air, instead oxygen, was fed to the cathode of the

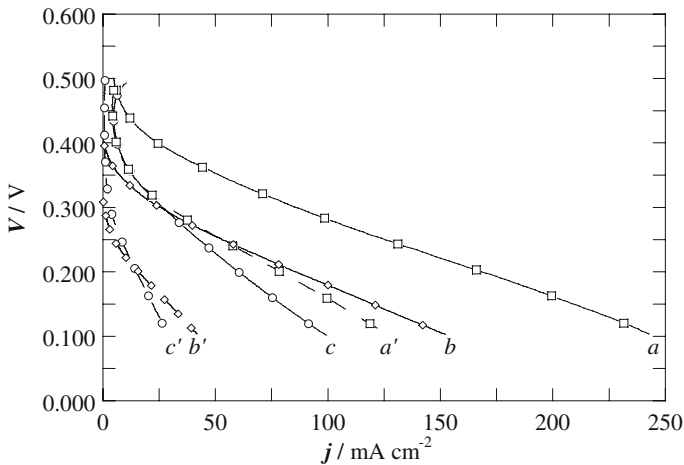


Fig. 7 DMFC performance of pure and hybrid IEC = 2.5 meq. H^+ /g polym. membranes: (a, a') 15% PTA loading; NMP processed; (c, c') pure copolyimide with 0% PTA; m-cresol processed. The DMFC performance of Nafion[®] 112 membrane was included for comparison (curves b, b'). *Solid lines*: pure oxygen as oxidant (curves a, b, and c); *-dotted lines*: air as oxidant (curves a', b' and c')

cells. Subsequently, cell polarization curves clearly show that charge in the membrane increases the performance of DMFCs. This behaviour could be explained taking into account the low methanol permeability of doped membranes. At 0.300 V (see Fig. 7), the cell with sPEI (15% PTA), curve *a*, yields 85 mA cm^{-2} , whereas the cell with sPEI (0% PTA), curve *c*, yields 26 mA cm^{-2} .

On the other hand, the maximum power densities achieved with sPEI (15% PTA) membrane are 33.7 and 12.2 mW cm^{-2} , using oxygen or air, respectively, whereas the maximum power densities reached with sPEI (0% PTA) are 16.0 and 3.3 mW cm^{-2} , when the cell operate with oxygen or air.

It is interesting to compare the performance of the cells with sPEI membranes with those which use Nafion[®] 112 membranes. The sPEI (15% PTA) cell voltage was higher than that of Nafion[®] 112 cell over the whole current density region, irrespective of the cathode fed (compare curves *a*, *a'* and *b*, *b'* in Fig. 7). In contrast, the sPEI (0% PTA) cell voltage decreased with respect to the Nafion[®] 112 cell voltage when the current density increased. This behaviour was reported by Song et al. [43], who attributed it to the fact that the polarization at the cathode of sPEI (0% PTA) cell increased more rapidly than that of Nafion[®] 112 cell.

Lin et al. [22] reported the use of proton conducting hybrid membranes from phosphotungstic acid (PTA)-doped polyvinyl alcohol (PVA) for DMFC applications. The *j*-*E* curve for a DMFC based on PVA (20% wt.)PWA(80% wt.) hybrid membrane showed that at 0.300 V the cell delivered 25 mA cm^{-2} , under similar experimental conditions to those used in this study (2 M methanol fed anode, O_2 fed cathode, and temperature $60 \text{ }^\circ\text{C}$).

On the other hand, Song et al. [43] reported the direct methanol fuel cell performance of a sulfonated polyimide membrane. At 0.300 V the cell gave 313 mA cm^{-2} operating at $80 \text{ }^\circ\text{C}$ and ambient pressure, with 1 M methanol at

50 °C (1 ml min⁻¹) and humidified oxygen at 20 °C (20 ml min⁻¹). However, in spite of this value, if one takes the performance of a Nafion[®] 112 membrane cell as a baseline, at 0.300 V the current density in the sPEI-DMFC reported by Song increased by a factor of 1.1, respect to that of the Nafion[®] 112-DMFC, whereas in the sPEI (15% PTA)-DMFC reported in this work, the current density increased by a factor of 3.3. This result supports the goodness of the sPEI membranes developed in the present work.

Conclusions

A series of sulfonated polyimides soluble in NMP in the presence of phosphotungstic acid have been synthesized.

A new method has been proposed to determine the methanol crossover through DMFC membranes. The method enables a simple fast and effective determination of membrane methanol permeability in the presence of the water generated during the process. Its easy and reliable implementing makes it particularly promising for analyzing crossover with every kind of membranes. It is also useful in order to determine the permselectivity of a membrane for a given mixture of liquids and vapours.

The membranes containing PTA and processed in NMP seem to be more efficient than classical sulfonated polyimides membranes processed in m-cresol in a DMFC environment, yielding the former more than three times the current yield by the latter at 0.300 V, operating with liquid methanol and oxygen as oxidant. Using air instead oxygen, membranes with PTA give more than eight times de current given by classical sulfonated polyimides without PTA.

In summary, in this paper we have demonstrated that sulfonated polyetherimide membranes doped with phosphotungstic acid could be attractive to DMFC applications, because their limited methanol permeability with respect to the classical sulfonated polyimides. Further modifications of the hybrid membranes, as well as, the improvement in the preparation of membrane electrode assemblies (MEAs) will lead to an increase of performance in the temperature range of operation of DMFCs, suitable for portable applications.

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References

1. Samuelson LA, Anagnostopoulos A, Alva KS, Kumar J, Tripathy SK (1998) Biologically derived conducting and water soluble polyaniline. *Macromolecules* 31:4376
2. Yeager AL, Steck A (1981) Cation and water diffusion in nafion ion exchange membranes: influence of polymer structure. *J Electrochem Soc* 128:1880
3. Scherer GG (1990) Polymer membranes for fuel cells. *Ber Bunsenges Phys Chem* 94:1008
4. Steele BCH, Heinzel A (2001) Materials for fuel-cell technologies. *Nature* 414:345

- Zawodzinski TA, Neeman M, Sillerud LO, Gottesfeld S (1991) Determination of water diffusion-coefficients in perfluorosulfonate ionomeric membranes. *J Phys Chem* 95:6040
- Sone Y, Ekdunge P, Simonsson DJ (1996) Proton conductivity of nafion 117 as measured by a four-electrode ac impedance method. *J Electrochem Soc* 4(143):1254
- Silva RF, De Francesco M, Pozio A (2004) Tangential and normal conductivities of nafion® membranes used in polymer electrolyte fuel cells. *J Power Sources* 134:18
- Fontanella JJ, Edmondson CA, Wintersgill M, Wu Y, Greenbaum SG (1996) High-pressure electrical conductivity and nmr studies in variable equivalent weight nafion membranes. *Macromolecules* 29:4944
- Miyateke K, Shouji E, Yamamoto K, Tsuchida E (1997) Synthesis and proton conductivity of highly sulfonated poly(thiophenylene). *Macromolecules* 30:2941
- Wycisk R, Pintauro PN (1996) Sulfonated polyphosphazene ion-exchange membranes. *J Membr Sci* 199:155
- Wang F, Chen T, Xu J (1998) Synthesis of poly(ether ether ketone) containing sodium sulfonate groups as gas dehumidification membrane material. *Macromol Rapid Commun* 19:135
- Nikitina TS (1990) $\alpha\beta$ -trifluorostyrene and polymers based on it. *Rus Chem Rev* 59:575
- Przyluski J, Poltarzewski Z, Wieczorek W (1998) Proton-conducting hydrogel membranes. *Polymer* 39:18
- Faure S, Mercier R, Aldebert P, Pineri M, Sillion B (1996) Gas separation polyimide membranes used to prepare ion-exchange membranes for use in manufacture of fuel cells. *French Pat* 9605707
- Faure S, Cornet N, Gebel G, Mercier R, Pineri M, Sillion B (1997) Proceedings of second international symposium on new materials for fuel cell and modern battery systems, Montreal, Canada, July 6–10, 1997, p 818
- Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M (2001) Soluble sulfonated naphthalenic polyimides as materials for proton exchange membranes. *Polymer* 42:359
- Genies C, Mercier R, Sillion B, Petiaud R, Cornet N, Gebel G, Pinéri M (2001) Stability study of sulfonated phthalic and naphthalenic polyimide structures in aqueous medium. *Polymer* 4:5097
- Cornet N, Diat O, Gebel G, Jousse F, Marsacq D, Mercier R, Pinéri M (2000) Sulfonated polyimide membranes: a new type of ion-conducting membrane for electrochemical applications. *J New Mat Electrochem Syst* 3:33
- Choonkeun L, Saimani S, Jinuk K, Haksoo H (2004) Structure-property correlations of sulfonated polyimides. I. Effect of bridging groups on membrane properties. *J Polym Sci Part A Polym Chem* 42:3612
- Yin Y, Fang J, Cui Y, Tanaka K, Kita H, Okamoto K (2003) Synthesis, proton conductivity and methanol permeability of a novel sulfonated polyimide from 3-(2',4'-diaminophenoxy)propane sulfonic acid. *Polymer* 44:4509
- Lin CW, Thangamuthu R, Yang CJ (2005) Proton-conducting membranes with high selectivity from phosphotungstic acid-doped poly(vinyl alcohol) for DMFC applications. *J Membr Sci* 253:23
- Savadogo O (2004) Emerging membranes for electrochemical systems: Part II. High temperature composite membranes for polymer electrolyte fuel cell (PEFC) applications. *J Power Sources* 127:135
- Savadogo O (1998) Hydrogen/oxygen polymer electrolyte membrane fuel cells (PEMFCs) based on alkaline-doped polybenzimidazole (PBI). *J New Mater Electrochem Syst* 1:47
- Blázquez JA, Mecerreyes D, Miguel O, Rodriguez J, Cendoya I, Ajuria J, Iruiñ JJ, Santos JJ, Marestin C, Mercier R (2006) Hybrid proton-conducting membranes as fuel cells solid polyelectrolytes. *J Fuel Cell Sci Technol* 3:309
- Shao Z-H, Xu H, Li M, Hsing I-M (2006) Hybrid nafion/inorganic oxides membrane doped with heteropolyacids for high temperature operation of proton exchange membrane fuel cell. *Solid State Ionics* 177:779
- Shao Z-H, Joghee P, Hsing I-H (2004) Preparation and characterization of hybrid nafion-silica membrane doped with phosphotungstic acid for high temperature operation of proton exchange membrane fuel cells. *J Membr Sci* 229:43
- Kim YM, Choi SH, Lee HC, Hong MZ, Kim K, Lee H-I (2004) Organic/inorganic composite membranes as addition of SiO₂ for high temperature-operation in polymer electrolyte membrane fuel cells (PEMFCs). *Electrochim Acta* 49:4787
- Ramani V, Kunz HR, Fenton JM (2004) Investigation of Nafion®/HPA composite membranes for high temperature/low relative humidity PEMFC operation. *J Membr Sci* 232:31
- Kreuer KD (1996) Proton conductivity: materials and applications. *Chem Mater* 8:610

30. Blázquez JA, Irui JJ, Eceolaza S, Marestin C, Mercier R, Mecerreyes D, Miguel O, Vela A, Marcilla R (2005) Solvent and acidification method effects in the performance of new sulfonated copolyimides membranes. *J Power Sources* 151:63
31. Miguel O, Fernandez-Berridi MJ, Irui JJ (1997) Survey on transport properties of liquids, vapors, and gases in biodegradable poly(3-hydroxybutyrate) (PHB). *J Appl Polym Sci* 64:1849
32. Földér RM, Huvard GS (1980) *Methods of experimental physics*. Academic Press, New York 16c:315
33. Berregi I, Santos JI, Del Campo G, Miranda JI, Aizpurua JM (2003) Quantitation determination of chlorogenic and in cider apple juices by ^1H -RMN spectrometry. *Anal Chimica Acta* 486:269
34. Berregi I, Santos JI, Del Campo G, Miranda JI (2003) Quantitative determination of (-)-epicatechum in cider apple juices by ^1H -RMN. *Talanta* 61:139
35. Liu M, Mao X, He C, Huang H, Nicholson JK, Lindon JC (1998) Improved WATERGATE pulse sequences for solvent suppression in NMR spectroscopy. *J Magn Reson* 132:125
36. Cobas C, Sardina FJ (2002) Mestre-C, 4.9 version. University of Santiago de Compostela, Spain
37. Wang S, Sun G, Wang G, Zhou Z, Zhao X, Sun H, Fan X, Yi B, Xin Q (2005) Improvement of direct methanol fuel cell performance by modifying catalyst coated membrane structure. *Electrochem Comm* 7:1007
38. Li L, Wang Y (2002) A hybrid membrane of poly(vinyl alcohol) and phosphotungstic acid for fuel cells. *Chin J Chem Eng* 10:614
39. Li L, Wang Y (2003) Novel proton conducting composite membranes for direct methanol fuel cell. *Matter Lett* 57:1406
40. Kim YS, Wang F, Hickner M, Zawodzinski TA, McGrath JE (2003) Fabrication and characterization of heteropolyacid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$)/directly polymerized sulfonated poly(arylene ether sulfone) copolymer composite membranes for higher temperature fuel cell applications. *J Membr Sci* 212:263
41. Coutanceau C, Koffi RK, Léger JM, Marestin K, Mercier R, Nayoze C, Capron P (2006) Development of materials for mini DMFC working at room temperature for portable applications. *J Power Sources* 160:334
42. Einsla BR, Kim YS, Hickner MA, Hong Y-T, Hill ML, Pivovar BS, McGrath JE (2005) Sulfonated naphthalene dianhydride based polyimide copolymers for proton-exchange-membrane fuel cells: II. Membrane properties and fuel cell performance. *J Membr Sci* 255:141
43. Song JM, Miyatake K, Uchida H, Watanabe M (2006) Investigation of direct methanol fuel cell performance of sulfonated polyimide membrane. *Electrochim Acta* 51:4497–4504