Short communication

Solvent and acidification method effects in the performance of new sulfonated copolyimides membranes in PEM-fuel cells

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Abstract

A series of new sequenced sulfonated naphthalenic polyimides were synthesized containing a flexible aromatic–aliphatic diamine. The obtained membranes present the advantage of being soluble in N-methyl pyrrolidone (NMP) which is a less toxic solvent than the previously used m-cresol. In this work, we report on the solvent and acidification method effects on the properties of the membranes such as density, water uptake, proton conductivity as well as on the performance of these membranes in fuel cell operation. The membranes prepared from NMP solution and acidified with ion-exchange resins give the best results. They have good mechanical properties as well as high ionic conductivity (14.4×10^{-2} S cm^{-1} at 80 °C) and good performances as proton exchange membrane (PEM) in fuel cell at 70 °C.
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1. 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 have been used for this purpose due to their efficient proton conduction (10^{-1} S cm^{-1} in the fully hydrated protonic form) and long lifetime [5–8]. However, the high cost of this ionomer is the major drawback for the development of this technology. Lower cost polymers with similar properties are therefore strongly desired as alternative materials [9–13]. In the last few years, several non-fluorinated membranes have been studied as alternatives to Nafion such as the sulfonated polynaphthalimides. These naphthalenic polyimides described previously are however only soluble in m-cresol. In this paper, we describe the synthesis of new naphthalenic copolyimides obtained from 2,2′-benzidinedisulfonic acid (BDSA, a sulfonated diamine) and the bis[(4 aminophenyl-oxy)methyl] 2,2-propane (APMP, a non-sulfonated diamine). APMP diamine allows managing some important properties of the copolyimides [14–20], like the solubility in water and solvents, the mechanical properties and others. The APMP was selected because of its flexibility induced by the neopentyloxy catenation. Then, it has been possible to improve the solubility of such polymers in solvents different to m-cresol, such as NMP. This improvement offers to prepare membranes in better conditions. The goal of this paper is to investigate the properties of these new copolyimides such as proton conductivity, density and water sorption as well as their performance in fuel cell operation with respect to the casting solvent and the acidification method.

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2. Experimental

2.1. Starting materials

1-Chloro-4-nitro-benzene and 2,2-dimethyl-propane-1,3-diol, used for the synthesis of the non-sulfonated diamine as well as potassium carbonate, 10% palladium on activated carbon, benzoic acid, triethylamine, *N,N*-dimethylacetamide (DMAc), diethyl ether and *m*-cresol were purchased from Aldrich and used as received. The 4,4′-diamino-biphenyl 2,2′-disulphonic acid obtained from Tokyo Kasei Co. and was purified before the polycondensation reaction. The 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) from Aldrich was dried at 160 °C under vacuum before use.

2.2. Bis[(4 aminophenyl-oxy)methyl] 2,2-propane (APMP) synthesis

34.5 g (0.219 mol) of 1-chloro-4-nitro-benzene, 11.1 g (0.107 mol) of 2,2-dimethyl-propane-1,3-diol, 32.5 g (0.235 mol) carbonate potassium and 180 ml of DMAc with 10 ml of toluene were introduced in a three-necked flask fitted with a magnetic stirrer, a Dean-Stark trap, nitrogen pad and thermometer. The reaction mixture was heated at 170 °C for 24 h. After cooling at room temperature, the mixture was precipitated into water. The isolated powder was washed with diethyl ether, filtrated off and dried under vacuum at 60 °C to obtain 31.3 g of bis[(4-nitrophenoxy)methyl]2,2-propane (NPMP) with a yield of 84.5%. A mixture of 15.0 g (0.01 mol) of NPMP, 0.28 g of Pd/C catalyst and 100 ml of ethanol was placed in a hydrogen pressurized steel autoclave. When the hydrogen was no longer absorbed, the reaction mixture was filtered to separate the catalyst. After evaporation of the solvent, 13.1 g of the APMP diamine was obtained. ^{1}H NMR (CDCl$_3$, NMR spectrometer AC 250 Bruker at 30 °C): 1.10 (s, 6H, $-CH_3$); 3.23 (s, 4H, $-NH_2$); 3.74 (s, 4H, $-CH_2-$); 6.61 (dd, 2H, Ar); 6.73 (dd, 2H, Ar).

2.3. Polymer synthesis

All polyimides were prepared by the same method. As a representative example, we describe in detail the synthesis procedure of the BDSA/NTDA/APMP ($r = n_{BDSA}/n_{APMP} = 70/30$) copolyimide. In a three-necked flask fitted with mechanical stirrer and nitrogen pad, 9.0860 g (0.0262 mol) of BDSA containing 1.1% water and 6.33 g (0.0626 mol) of triethylamine were introduced with 89 g of *m*-cresol. The water amount on the BDSA was determined by thermogravimetric analysis on a TG-Q500 (TA Instruments) under nitrogen at a heating rate of 5 °C min^{-1}. This mixture was stirred until solubilization of BDSA. Then 10 g (0.0372 mol) of NTDA, 3.2035 g (0.0111 mol) of APMP diamine and 6.38 g (0.0522 mol) of benzoic acid were added. This reaction mixture was stirred few minutes and then heated at 80 °C for 4 h and at 180 °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 °C.

2.4. Film preparation

Membranes of the sulfonated polynaphthalimides were obtained by solution casting from a polymer solution using either *m*-cresol or NMP as solvent. The films were dried on a heating plate for 1 h at room temperature, 3 h at 50 °C, 3 h at 100 °C and 1 h at 120 °C. The polymer film was unstuck from the glass plate support by immersion in water. All membranes were washed three times by keeping them in methanol at 50 °C for 1 h each time. Series of tough sulfonated polyimide films were obtained with controlled thickness from 45 to 70 μm. Membranes were acidified using three different methods. The method A which is the acidification of the polymer in solution using an ionic interchange resin during 1 week. This method is only possible when NMP is used as solvent. Using *m*-cresol the solutions are too viscous to be filtrated after the acidification. For polymers with ion-exchange capacity (IEC) less than 1.5 it was not possible to use this method because the acid form polymer tend to precipitate during the treatment. For method B the polymer was acidified as membrane form with a 0.1 M H$_2$SO$_4$ solution at ambient temperature during 14 h and then rinsed with water. Finally, method C is also an acidification of the polymer membrane with 0.1 M H$_2$SO$_4$ at 80 °C during 4 h and subsequently washed with water.

2.5. Polymer characterization

2.5.1. Density measurements
Density of films has been determined using a gradient density column with CCl$_4$ and toluene as miscible liquids. With these mixtures, densities density ranging from 1.59 to 1.23 g cm^{-3} can be determined. In order to wet conveniently the membranes, three samples of each membrane were placed in the liquid column for 1 day before the measurements.

2.5.2. Water uptake and water sorption
The water uptake of membranes was determined by soaking in water at room temperature. The membrane was first dried for 1 week in a vacuum oven at 100 °C and weighted. Then the membrane was immersed in water at room temperature at different times. The membrane was then wiped with a dry paper and quickly weighted. This procedure was repeated until to obtain a constant weight.

The equilibrium water uptake WS of membranes is the amount of water per gram of the original dry membrane and was determined using the following relation:

$$WS = \frac{W_S - W_d}{W_d}$$

where W_d and W_S are the weight of the dry and wet membranes, respectively. From this value, the number of water

molecules per ionic group was calculated as:

$$\lambda = \frac{n(\mathrm{H_2O})}{n(\mathrm{SO_3}^-)} = \frac{\mathrm{WS}}{18\,\mathrm{IEC}}$$

where $n(\mathrm{H_2O})$ is the $\mathrm{H_2O}$ mole number, $n(\mathrm{SO_3}^-)$ the $\mathrm{SO_3}^-$ group mole number, WS the water uptake previously defined, IEC the theoretical ion-exchange capacity (in eq $\mathrm{H^+\,g^{-1}}$) and 18 corresponds to the water molecular weight ($18\,\mathrm{g\,mol^{-1}}$).

Water vapour sorption at different water vapour activities ($a_w < 1$) was performed at $35\,^\circ\mathrm{C}$ using the IGA-2 electrobalance supplied by HIDEN, UK. The water uptake was gravimetrically monitorized. The dry weight of the membrane samples used was in the range of 35–75 mg.

2.5.3. Proton conductivity measurements and fuel cell test

The conductivity was determined using the complex impedance spectroscopy method measured between 1 MHz and 1 Hz (at 20 frequencies per decade) and with amplitude of 10 mV, using an Autolab PGSTAT30 with a FRA module. A membrane ($1.0\,\mathrm{cm} \times 0.5\,\mathrm{cm}$) and two platinum electrodes were set in a Teflon cell. The distance between two electrodes was 0.5 cm. The cell was placed in a thermo-controlled chamber to control the temperature, which 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:

$$\sigma = \frac{D}{L \times B \times R}$$

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

To perform the fuel cell tests of different membranes the membrane–electrode assembly (MEA) were prepared by setting a polymer membrane between two electrodes ELAT V2.1 (E-TEK) without pressing. The MEA was then set up in a commercial $16\,\mathrm{cm^2}$ single cell (Fuel Cell Technology). Hydrogen and oxygen were humidified by flowing them through bubble humidificators at a set temperature of $60\,^\circ\mathrm{C}$, and then fed to the anode and cathode at 100 and 80 m lSTP min^{-1}, respectively. Operating fuel cell temperature was $70\,^\circ\mathrm{C}$ at a pressure of 1 atm. Performance of the fuel cell was evaluated by measuring the voltage versus the intensity current using an electronic loader (Amrel Fel 60-1).

3. Results and discussion

3.1. Synthesis of sulfonated naphthalimides

All polyimides were prepared by copolymerization of the naphthalic anhydride NTDA and a mixture of the sulphonated diamine BDSA and the aromatic/aliphatic diamine NePa (Fig. 1). A series of copolymers were prepared by varying the relative ratio between BDSA and APMP. More precisely, three different values of ion-exchange capacities were fixed:
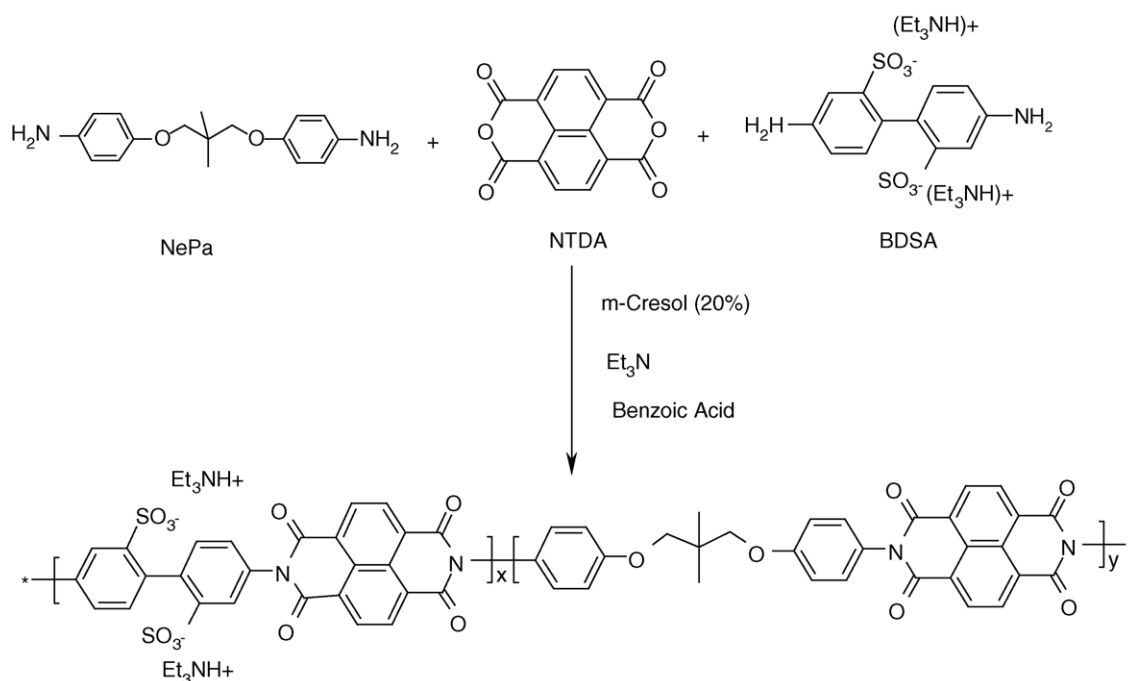

Fig. 1. General scheme of the synthesis of a novel sulfonic polyimide BDSA/NTDA/NePa.

Table 1
Experimental measurements with membranes prepared using different solvents and acidification methods

IEC (meq H$^+$ g^{-1} polymer)	Solvent	Acidification methods	Water uptake (%, w/w)	λ	$d^{25\,°C}$	$\sigma(\times10^{-2}\,S\,cm^{-1})$			
						25 °C	40 °C	60 °C	80 °C
2.50	NMP	A	55.6	12.5	1.464	19.0			
		B	48.1	11.0	1.458	8.4			
		C	49.0	11.0	1.454	11.0			
	m-Cresol	B	49.7	11.0	1.451	5.3			
		C	49.6	11.0	1.464	7.5			
1.98	NMP	A	48.4	13.5	1.439	4.3	6.9	8.4	14.4
		B	46.6	13.0	1.431	6.7	8.2	10.3	12.8
		C	44.3	12.5	1.429	1.5	2.3	2.8	3.2
	m-Cresol	B	44.5	12.5	1.431	3.8	4.6	6.4	10.9
		C	44.8	12.5	1.427	4.5	6.4	7.9	10.9
1.50	NMP	B	26.1	10.5	1.401	1.1			7.1
		C	25.0	9.5	1.416	0.3			2.8
	m-Cresol	B	25.4	9.5	1.409	0.8	3.1	5.3	5.9
		C	26.6	10.0	1.407	0.9	2.3	5.0	5.3

A, acidification with an ionic interchange resin in solution; B, acidification with H$_2$SO$_4$ 0.1N, 14 h at 25 °C; C, acidification with H$_2$SO$_4$ 0.1N, 4 h at 80 °C; d, density en g cm^{-3}; σ, conductivity; λ, number of water molecules per ionic group.

2.5, 1.98 and 1.5 meq H$^+$ g^{-1}. Interestingly, these copolyimides are soluble in NMP. As a consequence, we were able to question whether the solvent used to prepare the membranes and/or the acidification method used have an effect on the electrochemical properties and the performances of membranes.

3.2. Density measurements and water uptake analysis

As mentioned in the experimental part, membranes were prepared using two different solvents (m-cresol, NMP) and treated by three different acidification methods (A–C). As reported in Table 1, density values show that for membranes with a given IEC, the density is slightly higher for the acidification method A than the other ones (methods B and C). This could be due to the fact that, the acidification is carried out in solution, increasing the accessibility of the sulfonic groups and thus leading to a higher acidification degree. In other words, the acidic form of sulfonic acid groups could lead to a better stacking of polymer chains.

As shown in Fig. 2, for a given IEC value the water vapour sorption at different relative humidity extent as well as the liquid water uptake seem to be independent of the acidification method and of the solvent used for the preparation of the membrane. Moreover, as expected, it appears that in both cases (liquid water or water vapour sorption), the greater the IEC, the higher the water uptake. However, it is worth noticing some differences of the water uptake behaviour when the membranes are kept in the presence of water or water vapour. Indeed, by comparing Table 1 and Fig. 2, it is clear that the membranes uptake more water in the presence of liquid water ($a_w = 1$) than in the case of water vapour at activities close to one. This has been observed by other groups [20–22] and
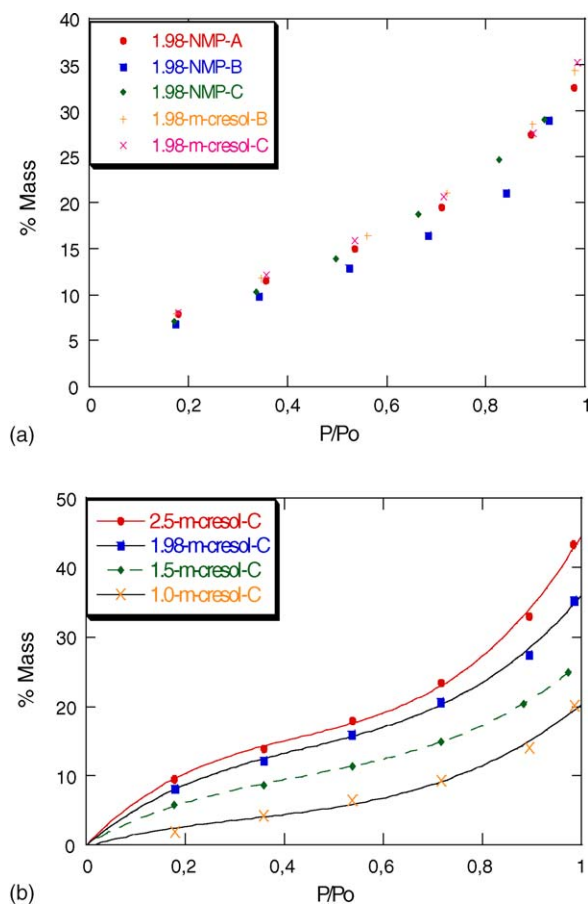

Fig. 2. (a) Water vapour sorptions of membranes with IEC equal to 1.98 meq H$^+$ g^{-1} polymers and different preparation methods; (b) water vapour sorptions of membranes with different IEC and the same preparation method.
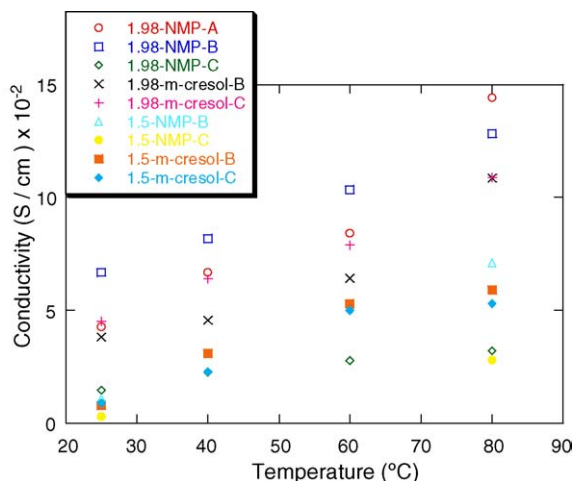
Fig. 3. Temperature dependence of the ionic conductivity values of membranes with different IEC and different preparation methods.

Fig. 4. Fuel cell tests of membranes with IEC equal to 1.98 meq $H^+ g^{-1}$ polymer prepared in NMP, acidified with resin; with IEC equal to 1.98 meq $H^+ g^{-1}$ polymer Prepared in m-cresol with H_2SO_4 0.1N at ambient temperature and with IEC equal to 1.5 meq $H^+ g^{-1}$ polymer prepared in m-cresol with H_2SO_4 0.1N at ambient temperature. These membranes are compared with the Nafion 112 in the same conditions.

it could be due to the extensive water molecules clustering in the vicinity of $a_w = 1$. In fact, the Zimm and Lundberg model [23–25] applied to different polymer/water systems usually predicts higher values of the water uptake at $a_w = 1$ than those extrapolated from water vapour measurements at different water activities (or relative humidity values). This would indicate that the number of water molecules per cluster increases dramatically as the activity tends to one, thus contributing to a higher water uptake.

3.3. Proton conductivity measurements

Fig. 3 shows the proton conductivity of membranes at different temperatures. Not surprisingly, whatever the solvent used for membrane preparation and the acidification method, conductivity increases with the ion-exchange capacity, showing values in the order of $10^{-1} S cm^{-1}$. However, membranes with the highest IEC value (2.5 meq $H^+ g^{-1}$ polymer) are soluble in water at temperatures higher than 40 °C, preventing its use in fuel cells. Comparison of membranes prepared from NMP and m-cresol shows that the proton conductivities are not drastically different. In any case, it seems that the values are always slightly higher for the membranes prepared from NMP solution than the one involving m-cresol. One possible explanation could be a difference of morphology of the membranes, induced by specific interactions between the solvent and the polymer. Small angle neutron scattering analysis (SANS) of both membranes is under investigation in order to confirm this hypothesis. This interesting fact confirms the interest to NMP as a solvent.

The effect of the acidification method in the proton conductivity was also studied. It was then observed that the acidification of the membranes at 80 °C with 0.1 M H_2SO_4 (method C) leads to better conductivity but results in a significant decrease of the mechanical properties of the final membranes. For this reason, we consider that the acidification at 80 °C of membranes is not a suitable procedure. On the
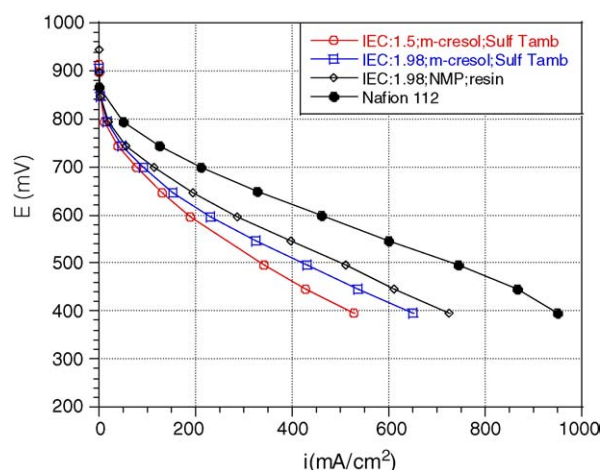
other hand, the two acidification methods tested (A, using ion-exchange resins) and (B, 0.1 M H_2SO_4 at room temperature) have a similar effect on the ionic conductivity of membranes. In the case of the ion-exchange resins treatment of polymers, the efficiency of the acidification was evidenced by ^1H NMR analysis, by following the disappearance of peaks relative to triethylammonium counter-ions. This method leads to a very interesting conductivity ($14.4 \times 10^{-2} S cm^{-1}$ at 80 °C for a membrane with a IEC of 1.98 meq g^{-1}).

3.4. Fuel cells test

Fig. 4 shows the fuel cell performances of the sulfonated polynaphthalimide membranes and the classic Nafion 112, which are used as reference.

Comparing two membranes obtained from m-cresol solution and acidified at room temperature in H_2SO_4, we can observe, as expected, that the higher the IEC, the better the performances. Although the membranes prepared from NMP solution and acidified with H_2SO_4 at ambient temperature have high conductivities (Table 1), it was not possible to perform a complete fuel cell test as the membrane was fragilized by this acidification treatment.

More interesting is the behaviour of the membrane prepared from NMP solutions with the polymer acidified with ionic exchange resins. Indeed, this mild and efficient procedure does not affect the mechanical properties of the membrane and the performances obtained were better than those obtained with a membrane done from m-cresol solution and acidified in H_2SO_4 0.1N. One speculative explanation for the better performances should be related to a particular morphology of the membrane, which could be induced by the casting of the polymer solution directly in its acidic form. To this end, SANS experiments are currently under investigation.

4. Conclusions

Using a flexible non-sulfonated diamine we were able to synthesize a series of sulfonated polyimides soluble both in NMP and in *m*-cresol. We have shown that the nature of the solvent used for casting the membranes induces rather small differences in conductivity. The NMP appeared as a better solvent to this point.

The acidification of the polymer with ionic exchange resins in NMP seems to be more efficient than the classical acidification methods with strong acid (0.1 M H_2SO_4 at ambient temperature) and results in better performances in the fuel cell test. This procedure seems very promising and could be envisioned for other type of polymers.

Acknowledgements

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