Sulfonated derivatives of polyparaphenylene as proton conducting membranes for direct methanol fuel cell application

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Abstract

Proton conducting polymers derived from polybenzoyl-1,4-phenylene (PBP) and poly-*p*-phenoxybenzoyl-1,4-phenylene (PPBP) were synthesized by the 'Colon synthesis technique'. The sulfonation of these proton conducting polymers was carried out using either sulphuric acid or tetramethylsiliylchlorosulfonate (TMSCl) as sulfonating agent, and their thermal properties were evaluated. Both sulfonated PBP and PPBP are thermally stable up to at least 215 °C. The sulfonated sPPBP exhibited good conductivity as proton conducting membranes at room temperature and were tested as electrolyte membranes for a single direct methanol fuel cell (DMFC) in terms of water absorption, methanol permeability and electrical performance. The water uptake of the sPPBP was found to be larger than that of the sPBP, i.e., 65 and 43 mol%, respectively. The permeability to methanol was found to be 10 times lower than sPPBP and sPBP compared to a Nafion® membrane. In spite of this, performance in a single DMFC was found to be twice inferior to that with Nafion® 117. Optimisation of the sulfonation level and of the electrode-membrane interfaces was lead to better results.

1. Introduction

Fuel cells are promising energy converters because of the energy efficiency achievable is higher than that of internal combustion engines [1–4]. The use of methanol as a liquid energy carrier circumvents the difficulties of hydrogen storage. However, methanol permeation through the membrane leads to the depolarisation of the cathode and hence decreased performance of the direct methanol fuel cell (DMFC) [5–7].

Perfluorinated proton exchange membranes such as Nafion® or Flemion® have been extensively used as polymer electrolytes for fuel cells. These polymer electrolytes have suitable electrochemical and mechanical properties, as well as chemical and thermal stabilities. However, fuel cells equipped with these perfluorinated polymer electrolyte membranes tend to be expensive and have several problems especially for use in electric vehicles, i.e. crossover of methanol and relatively low operating temperature (up to 110 °C). To overcome these problems, the development of new proton conducting polymer electrolytes is necessary. Polymer electrolytes based on hydrocarbon polymers or inorganic polymers are promising materials for the development of new

polymer electrolyte membrane fuel cells (PEMFCs). A variety of polymer materials exists which can be chemically modified at low cost. In most cases, these polymer electrolytes have high water absorption and high proton conductivity at high temperatures and low relative humidity with adequate thermal and chemical stabilities [8, 9]. They can be used as proton conducting polymer electrolytes for new high performance PEMFCs that can be operated at high temperatures without humidification [10, 11]. However, extensive work is required to develop materials with sufficient long-term stability, mechanical strength and low methanol permeability for optimum performance in fuel cells.

This paper describes the preparation, sulfonation and determination of the thermal properties of proton conducting polymers based on thermostable polymers derived from polyparaphenylene backbone, i.e., the polybenzoyl-1,4-phenylene (PBP) and the poly-*p*-phenoxybenzoyl-1,4-phenylene (PPBP). These polymers were synthesized by the so-called Colon synthesis, first described at the end of the 1980s [12], consisting in a polycondensation using palladium catalytic coupling. Sulfonated sPPBP exhibited good conductivity as proton conducting membranes at room temperature

and were tested as electrolyte membranes in a single direct methanol fuel cell in for water absorption, methanol permeability and electrical performance.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich (except zinc powder purchased from Fluka) and used as received unless otherwise noted. N,N-dimethylacetamide (DMAc) was dried over calcium hydride and vacuum distilled before used. Triphenylphosphine was purified by recrystallisation in ethanol. The zinc powder was first washed with 1 M hydrochloric acid, then washed twice with diethyl ether and ethanol; it was then filtered and dried under vacuum before storage under inert atmosphere. The dichloro bis(triphenylphosphine)-nickel(II) catalyst was synthesized in our laboratory the day before the polymerisation was carried out and was stored under inert atmosphere. Sulphuric acid 95% and tetramethylsilylchlorosulfonate were used without further purification.

2.2. Characterizations

^{1}H and ^{13}C NMR Spectroscopy measurements were carried out in CD$_2$Cl$_2$ with a Bruker AC 200 and a Bruker AC 400 set up. FTIR Spectra were recorded using a Bruker IFS 55 instrument. Analytical GC was carried out on a Chrompack CP 9002 gas chromatograph equipped with a flame ionisation detector. The number average molecular weights and the weight average molecular weight were determined by Gel permeation Chromatography (GPC) system, relative to narrow polystyrene standards. This GPC system was equipped with a Waters R 4000 refractive index detector and with four ULTRASTYRAGEL® columns thermostated at 35 °C. THF was used as the mobile phase. The polydispersity index (I_p) is equal to M_w/M_n. Glass transition temperatures (T_g) were determined using a Differential Scanning Calorimeter (DSC 50-Shimadzu) with a heating rate of 10 °C min^{-1}. Thermogravimetric (TGA) analyses were carried out using a Setaram 24 with a heating rate of 10 °C min^{-1}.

2.3. Synthesis of monomers

The chemical structures of both monomers are shown in Figure 1. We report here the synthesis of the 2,5-dichloro-p-phenoxybenzophenone; similar procedures were involved in preparing the 2,5-dichlorobenzophenone.

10 g (0.05 mol) of acyl chloride and 12.2 g (0.07 mol) of diphenylether were vigorously stirred in a 250 mL three-neck flask (fitted with an argon inlet, a condenser and a thermometer) to homogenise the mixture. Because the reaction is exothermic, the flask was cooled at 0 °C in ice during the introduction of 8.3 g (0.06 mol) of aluminium chloride. The viscosity increased during the course of
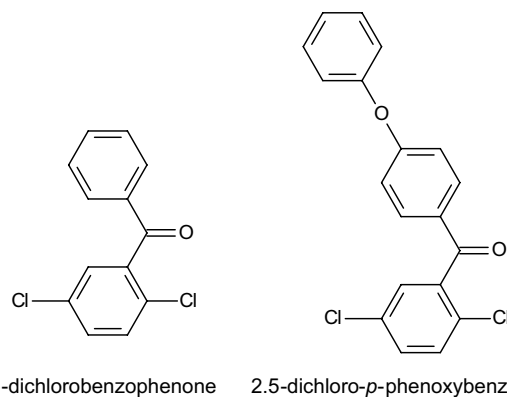
Fig. 1. Chemical structure of 2,5-dichlorobenzophenone and 2,5 dichloro-p-phenoxybenzophenone.

the reaction and the colour varied from blood red to dark. At the end of the reaction, the solution was hydrolysed in ice water to neutralize the excess aluminium chloride; the yellow paste obtained was stirred overnight. 45 mL of dichloromethane was then added to dissolve the yellow paste and the solution was filtered on celite. The residue was extracted three times with 20 mL of dichloromethane, and the brown organic phase obtained was dried on magnesium sulphate prior to filtration. The brown oil was recrystallised twice in 20 mL of ethanol, which was subsequently removed under reduced pressure. 10.3 g (0.03 mol) of 2,5-dichloro-p-phenoxybenzophenone were obtained which gave a yield of 58%. Both monomers were characterized by FTIR, NMR ^{1}H and ^{13}C.

2.3.1. Characterization of monomer 1: 2,5-dichlorobenzophenone
NMR ^{1}H (CD$_2$Cl$_2$): δ (ppm) 7.3–7.8. NMR ^{13}C (CD$_2$Cl$_2$): δ (ppm)=129.1; 129.2, 129.8, 130.3, 131.5, 131.7, 133.2, 134.4; 136.2, 140.2, 193.8. FTIR (KBr/cm^{-1}): 1650 (i) C=O stretching; 1610 (i), 1520 (m), 1510 (i), 1440 (f) C=C aromatic stretching; 1350 (m); 1260(i) Ar—C=O, 1097 (m) C—Cl.

2.3.2. Characterization of monomer 2: 2,5-dichloro-p-phenoxybenzophenone
NMR ^{1}H (CD$_2$Cl$_2$): δ ppm=7.0 (d, 2H;^3J=9 Hz); 7.1 (d, 1H;^3J=8 Hz); 7.2 (m; 5H); 7.4(dd, 1H; ^3J=8 Hz; ^4J=2 Hz); 7.7 (d, 1H;^4J=2 Hz); 7.8 (d; 2H;^3J=9 Hz). NMR ^{13}C (CD$_2$Cl$_2$): δ ppm=117.5; 120.7; 125.3; 129.0; 129.6; 130.5; 130.7; 131.3; 131.6; 132.7; 133.2; 140.4; 155.4; 163.3; 192.2. FTIR (KBr/cm^{-1}): 1690 (i) C=O stretching; 1610 (i), 1520 (m), 1510 (i), 1440 (f) C=C aromatic stretching; 1350 (m); 1260(i) Ar—C=O; 1260 (i), 1190 (m) Ar—O—Ar; 1100 (m) C—Cl, 780 (m); 700 (m).

2.4. Synthesis of the polymers

The polymerisation scheme is represented in Figure 2. Only the synthesis of the 2,5-dichloro-p-phenoxybenzophenone to form polymers is reported here.
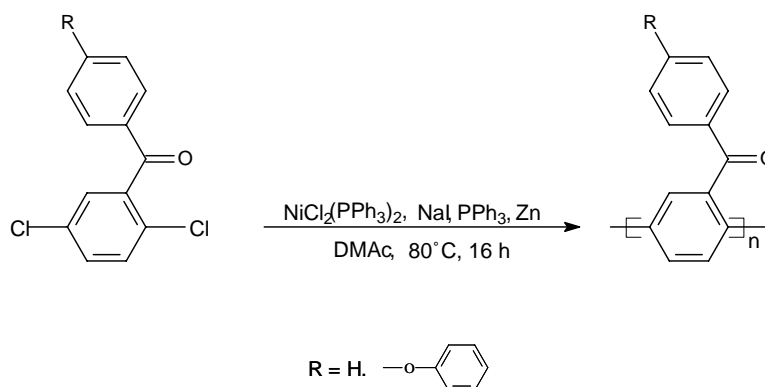
Fig. 2. Synthesis scheme of the poly(p-phenylene) derivatives.

In a 250 mL round bottomed, three-neck flask were placed successively the catalyst (0.5 g, 0.8×10^{-3} mol), sodium iodide (0.2 g, 0.8×10^{-3} mol), triphenylphosphine (2.0 g, 8×10^{-3} mol), 20 mL of N,N dimethylacetamide and the zinc powder (1.9 g, 0.03 mol). The green solution became yellow then bloody which is a characteristic colour of the activation of the reaction medium. 2 g (5.8×10^{-3} mol) of monomer were then added. The solution was heated to 80 °C with stirring for 16 h. Because the reaction is exothermic, the flask was cooled in ice during the introduction of aluminium chloride. The colour of the solution (first blood red) became darker as the polymerisation reaction occurred. The viscosity increased during the course of the reaction. The day after, the mixture turn into a black viscous solution. After hydrolysis in 1 M methanol solution to remove excess of aluminium chloride, the mixture was filtered and washed with THF. 1.4 g (5.2×10^{-3} mol) of a yellow powder of poly(p-phenoxybenzoyl-1,4-phenylene) was obtained corresponding to a good yield of 90%. Both polymers (PBP and PPBP) were characterised by FTIR, NMR ^{1}H and ^{13}C, TGA, DSC and by SEC to determine their molecular weight.

2.4.1. Characterization of the polymer 1: poly(benzoyl-1,4-phenylene) – PBP
NMR ^{1}H (CD$_2$Cl$_2$): δ=7.3–7.8 ppm. NMR ^{13}C (CD$_2$Cl$_2$): δ=125.4–133.2; 142.8; 195.2–195.3 ppm. GPC (THF): M_{w}=1 10 000; M_{n}=40 000, I_{p}=2.7. FTIR (KBr/cm^{-1}): 1650 (i) C=O stretching; 1610 (i), 1520 (m), 1510 (i), 1440 (f) C=C aromatic stretching; 1350 (m); 1260 (i) Ar—C=O. TGA (N$_2$): weight loss of 23.7% at 567 °C. DSC (air): T_{g}=160 °C and beginning of degradation at 437 °C.

2.4.2. Characterization of the polymer 2: poly(p-phenoxybenzoyl-1,4-phenylene) – PPBP
NMR ^{1}H (CD$_2$Cl$_2$): δ=7.3–7.8 ppm. NMR ^{13}C (CD$_2$Cl$_2$): δ=115.5–119.1; 127.5–132.5; 144.9; 154.7; 161.2; 195.3–195.5 ppm. GPC (THF): M_{w}=75 000; M_{n}=26 000, I_{p}=2.9. FTIR (KBr/cm^{-1}): 1690 (i) C=O; 1610 (i), 1520 (m), 1510 (i), 1440 (f) C=C aromatic stretching; 1350 (m); 1260(i) Ar—C=O; 1260 (i), 1190

(m) Ar—O—Ar; 780 (m); 700 (m). TGA (N$_2$): weight loss of 21.3% at 548 °C. DSC (air): T_{g}=153 °C and beginning of degradation at 440 °C.

2.5. Sulfonation of polymers

200 mg of pulverized polymer were dissolved in 2 mL sulphuric acid under an argon atmosphere at room temperature. The solution was held at the desired temperature for a preset time and then mixed with a large excess of water. The precipitate was filtered and then washed with water. It was then pulverised and washed further with water until a neutral pH was reached. Both polymers were sulfonated in this manner.

Tetramethylsilylchlorosulfonate (TMSCl) was used only for the sulfonation of the poly-p-phenoxybenzoyl-1,4-phenylene. 200 mg (7.3×10^{-4} mol) of poly-p-phenoxybenzoyl-1,4-phenylene (PPBP) were dissolved in 1 mL dichloromethane and 0.11 mL (7.3×10^{-4} mol) of trimethylsilylchlorosulfonate was carefully added. The obtained solution was held at room temperature for a set time and then poured into a large excess of water. The precipitate was filtered and washed with water. It was then pulverised and washed with water until a neutral pH was reached.

The degree of sulfonation was estimated by elemental analysis and titration using the following procedure: 1.0 g of the sulfonated polymer was placed in a sodium hydroxide saturated aqueous solution, and the solution was kept at room temperature for 1 day. The solution was then back titrated with 1 M HCl using phenolphthalein as an indicator.

2.6. Casting of the membranes

The sulfonated polymers (sPBP and sPPBP) were dissolved in N-methyl-pyrrolidinone (NMP) at 80 °C under argon atmosphere for several days. Then, the NMP solution was filtered and cast on a glass sheet. The solvent was evaporated by heating from 60 to 70 °C until the membranes were dry.

2.7. *Physical characterization of the sulfonated polymers*

2.7.1. *Methanol permeability measurements*
A two-compartment glass cell was utilized for permeability measurements as described elsewhere [13]. One compartment (V_A=40 mL) was filled with a 1 M solution of methanol in deionised water and the other (V_B=40 mL) was filled with deionised water. The membrane (3.14 cm diameter) was clamped between the two compartments, which were stirred during the experiment. A methanol flux establishes across the membrane owing to the concentration difference between the two compartments. V_A and V_B were chosen sufficiently large that a pseudo steady state condition prevailed during these experiments. The concentration of methanol in compartment B was determined as a function of time using high liquid performance chromatography. The methanol permeability was calculated from the slope of the straight-line plot of methanol concentration vs permeation time.

2.7.2. *The electrodes*
The electrodes (anode and cathode) were supplied by E-TEK. 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}. The two electrodes contained 0.8 mg cm^{-2} Nafion$^{®}$ in the active layer and 30% mass of Teflon in the diffusion layer.

2.7.3. *The single cell*
A single DMFC was mounted on a Globe Tech Inc fuel cell test station. This station was equipped with humidification bottles with pressure and flow rate control of both reactants: 2 M methanol and pure oxygen. Preliminary to the measurements, the membrane electrode assembly (MEA) was installed in the cell and hydrated with a 2 M methanol solution at 50 °C for 24 h. The fuel cell tests were carried out at 50, 70 and 90 °C at oxygen pressures of 1.4, 1.8 and 2.3 bar and methanol pressures of 1.2, 1.4 and 1.8 bar.

2.7.4. *The experiment*
The fuel cell tests in a single DMFC with electrodes of 5 cm^2 geometric surface areas were carried out using a Globe Tech test bench. The E vs. j and P vs. j curves were recorded using a high power potentiostat (Wenking model HP 88) interfaced with a PC to apply the current sequences and to store the data, and a variable resistance in order to fix the applied current to the cell.

3. Results and discussion

3.1. *Sulfonation of PBP and PPBP*

Sulfonation is a powerful and versatile method for polymer transformation into proton conductors. This reaction appears to be the most useful way to produce sulfonated polymers; it was studied for most of the non-perfluorinated polymers to be used as proton exchange membrane in fuel cells [14–16]. However, sulfonation with fuming chlorosulphonic acid or concentrated sulphuric acid may cause severe degradation of the polymer skeleton. The reaction is not selective in terms of attack sites and hardly reproducible. Moreover, the direct sulphuric acid procedure cannot be used to produce truly random polymers because sulfonation and dissolution in acid sulphuric occur in a heterogeneous environment. This is the reason why the post-sulfonation needs to be optimised; it depends on the polymer backbone, the time and the temperature of reactions, as well as the sulfonation agent used.

Ionic substitutes have been introduced on lateral groups of both PBP and PPBP by the classic way of sulfonation. The degree of sulfonation of PBP and PPBP as a function of reaction time and temperature is presented in Figures 3–5. Because sulfonation is an
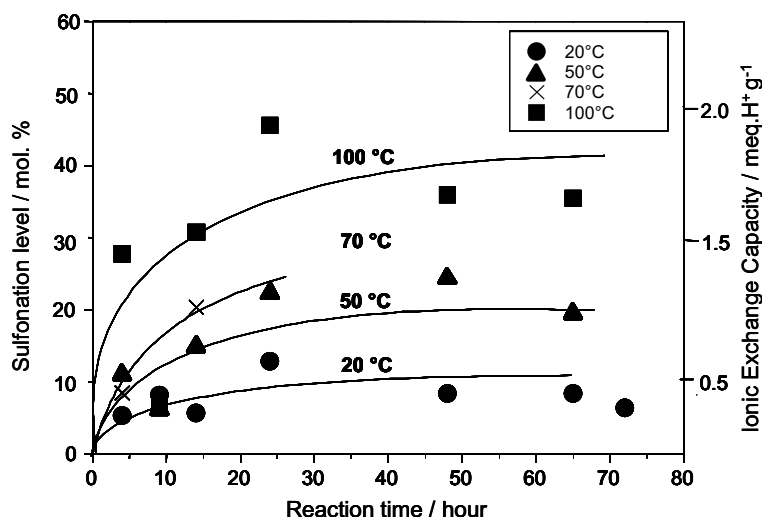

Fig. 3. Kinetics of the sulfonation reaction of poly(benzoyl-1,4-phenylene) and ionic exchange capacity vs. time.
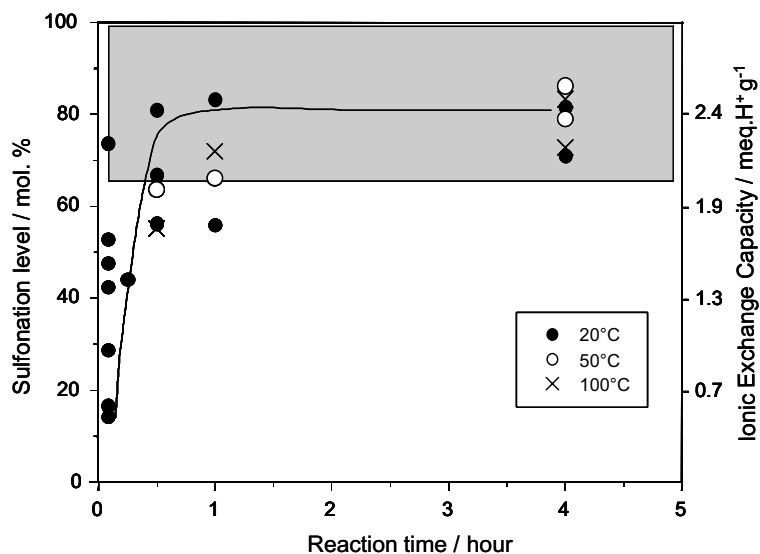
Fig. 4. Kinetics of the sulfonation reaction by H$_2$SO$_4$ of poly(*p*-phenoxybenzoyl-1,4-phenylene) and ionic exchange capacity vs. time. The dotted frame corresponds to the water soluble copolymer area.
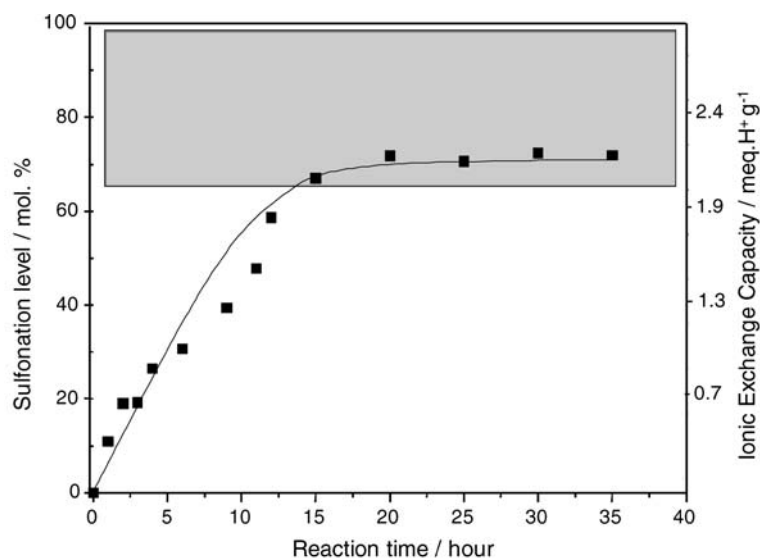

Fig. 5. Kinetics of the sulfonation reaction by TMSCI of poly(*p*-phenoxybenzoyl-1,4-phenylene) and ionic exchange capacity vs. time. The dotted frame corresponds to the water soluble copolymer area.

electrophilic reaction, its application depends on the substitutent on the ring. Electron donating substitutent will favour the reaction, whereas electron accepting substitutent will not. Indeed the kinetics of sulfonation for poly-benzoyl-1,4-phenylene and poly-*p*-phenoxybenzoyl-1,4-phenylene is totally different.

With concentrated sulphuric acid at room temperature, the sulfonation of PBP leads to a threshold of almost 10% mol within 10 h whereas the sulfonation of PPBP leads to a threshold of 80% within 4 h (Figure 3). The level of sulfonation of PBP became saturated at 20 mol% per repeating unit for the temperature range from 50 to 70 °C. Above this temperature, the level of sulfonation is less than 40 mol% per repeating unit. The FTIR spectra (see Figure 6) show a real change in the

structure, more particularly around the carbonyl functional group which can be interpreted as a degradation of the structure. Three types of behaviour have been observed for different temperatures.

As expected, after these different experiments, the sulfonation of the polymer was found to be very difficult. This phenomenon is explained by the structure of the lateral pendant group of the poly-*p*-phenylene backbone. In the literature, the carbonyl group is described as a deactivating group. It deactivates the aromatic ring where the sulfonic group attack takes place [17], as in the case of poly-*p*-phenylene structure. This phenomenon was already observed and described, especially in the case of the poly(ether ether ketone) family [18]. In the case of
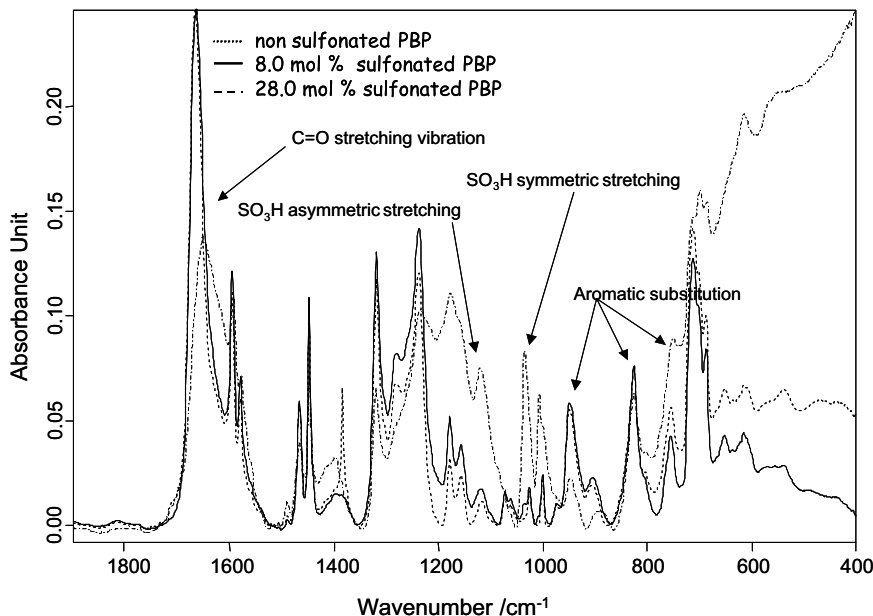
Fig. 6. Infra red spectra of poly(benzoyl-1,4-phenylene) for different sulfonation levels.

poly-*p*-phenoxybenzoyl-1,4-phenylene (PPBP), the ionic groups were introduced in the same way as in PBP. The polymer was dissolved in concentrated sulphuric acid. The level of sulfonation reached a threshold at 80 mol.% within 4 h (Figure 4). This result is in good agreement with those obtained by Rikukawa et al. [19–21]. The limit of water solubility was also in agreement with the work of the group of Rikukawa, i.e., close to 60 mol.%. However, the kinetics of reaction is totally different. The time necessary to reach the threshold was around 200 h whereas, in our study, it was about 100 min. Because the conditions of sulfonation were the same, the differences may be due to the polymer structure, especially its molecular weight. Rikukawa et al. [19] claimed an average molecular weight M of 25 000 for their polymer whereas the weight average molecular weight M_w of our sample was found to be 80 000. This probably influenced the kinetics of the sulfonation reaction. Moreover, the lower limit of the weight average molecular weight M_w to obtain polymer films with sufficient mechanical properties was found close to 60 000.

To have a better control on the course of the reaction, a mild sulfonating reactant, trimethylsilylchlorosulfonate (TMSCl), was used (Figure 5). This sulfonating agent has already been used to perform the sulfonation of other kind of polymers [22, 23]. In order to control the homogeneity of the reaction, the polymer was dissolved in dichloromethane before sulfonation. The sulfonation saturation level was almost the same as that obtained using sulphuric acid as sulfonating agent, i.e. more than 70 mol% per repeating unit. However, 15 h of reaction were needed to reach this level of sulfonation, whereas with sulphuric acid as reactant only one and half hours were needed. The water solubility was reached for a sulfonation of 65 mol.% per repeating unit.

The substituted polyparaphenylene PBP and PPBP were soluble in common organic solvent such as chloroform, dichloromethane and tetrahydrofurane whereas sPBP and sPPBP were insoluble in these solvents. However, sPBP and sPPBP were soluble in DMF, DMSO, and NMP after heating at 60 °C, or more in the case of PBP. Above 60% sulfonation, sPPBP swelled in water and methanol.

FTIR spectra of PBP, PPBP and their sulfonated derivatives are shown respectively in Figures 6 and 7. The PBP polymer is mainly characterized by absorption bands at 1666 cm^{-1} (which are assigned to the stretching mode of the carbonyl function), at 826 cm^{-1} (which is assigned to the aromatic substitutions in position 1, 2, 4 of the benzene ring) and at 713 and 755 cm^{-1} (which correspond to the monosubstituted benzene ring) [24, 25]. The FTIR data obtained after sulfonation can be classified in two groups. The first corresponds to low sulfonation levels (5–15 mol% per repeating unit) and shows a global feature very similar to that of the non sulfonated polymer. The second, corresponding to high sulfonation levels (>30 mol% per repeating unit), shows spectra with drastic changes. For example, the absorption band close to 1666 cm^{-1} assigned to the carbonyl group became larger and is shifted by 15 cm^{-1} towards lower wave numbers. Moreover, four characteristic absorption bands due to sulfonation, at 1177, 1121, 1035 and 1008 cm^{-1} [24, 25] were observed. The disappearance of the absorption band close to 713 cm^{-1} is related to the monosubstituted ring and indicates that poly-substitution of the ring could occur. After sulfonation, and whatever the sulfonation level, only this band disappeared, the absorption band at about 750 cm^{-1} being still present. Therefore, it can be stated that poly-substitution occurred partially. However, the domain around 700 cm^{-1} is compatible with a monosubstitued ring or di-substituted in meta position or
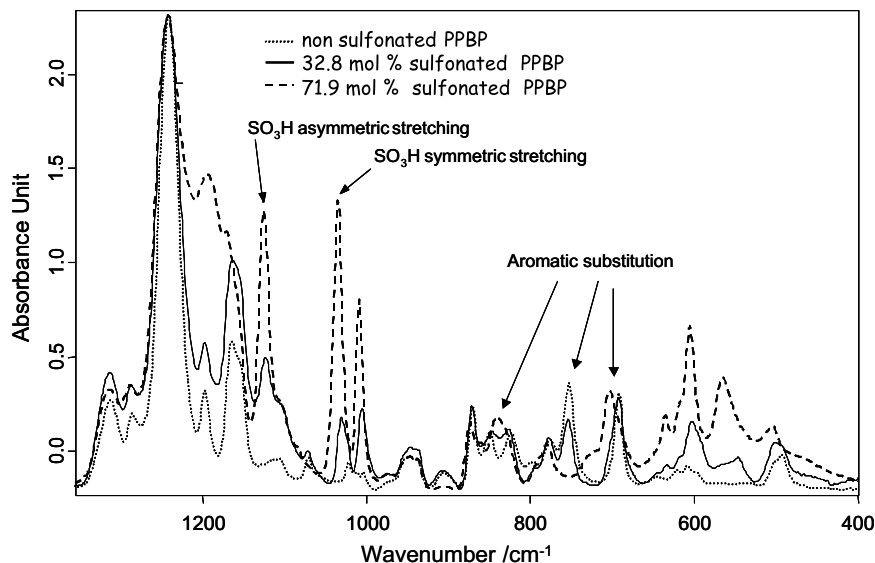
Fig. 7. Infra red spectra of poly(*p*-phenoxybenzoyl-1,4-phenylene) for different sulfonation levels.

tri-substituted in 1, 2, 3 (700 and 770 cm^{-1} [24, 25]) or 1, 3, 5 (700 and 845 cm^{-1} [24, 25]) position. Then, it was not possible to conclude on the sulfonation position.

There are major differences between the spectra of PPBP and its sulfonated derivatives (Figure 7). After sulfonation, we note the appearance of four absorption bands at 1195, 1126, 1035 and 1009 cm^{-1}. Two of them are directly related to sulfonation [24, 25]. Indeed, the aromatic sulfonic acid group gives two absorption bands with good intensity in the wavenumber ranges from 1230 to 1120 (asymmetric stretching vibration of the sulfonic group) and from 1120 to 1025 cm^{-1} (symmetric stretching vibration of the sulfonic group). Rikukawa et al. [21] have also observed the appearance of these bands. We also observed a decrease of the intensity of the absorption band close to 1070 cm^{-1}. This band is assigned to the monosubstitued benzene ring and decreases when the sulfonation level is increased. However, the disappearance of the bands at 753 and 692 cm^{-1} confirms that poly-substitution of the benzene ring occurs. The sulfonation of the polymer is evidenced by the numerous absorption bands present in the IR spectra in the range from 700 to 900 cm^{-1}. The main bands located at 704, 780, 840 and 873 cm^{-1} are assigned to the disubstituted and trisubstituted benzene ring [24, 25].

3.2. *Thermal properties*

The thermal stability of dry sPBP and sPPBP was investigated by DSC and TGA analysis. The glass transition temperatures T_g measured for the PPBP (153 °C) and the PBP (160 °C) are in good agreement with those given in the literature [26, 27]. The lower T_g of PPBP is due to the phenoxy group, which probably modifies the organization of the macromolecule and leads to a better flexibility of the side chain. This observation is in good agreement with results obtained by Simon et al. [27]. These authors concluded that PPBPs with large side units and poor packing had a lower glass transition temperature. In contrast, the glass transition temperatures were not observed for both sulfonated polymers. This can be explained by the fact that the glass transition temperature increases with the sulfonation level, as was observed with thermostable polymers like sulfonated polyethersulfone [28]: the determination of the T_g becomes impossible beyond a given level of sulfonation. The introduction of a functional group on a rigid backbone may create hydrogen bonds and, as a consequence, may increase the T_g of the polymer which can become higher than the temperature of degradation of the polymer; this is the case for polyoxadiazole and polyphenylene [29]. The method used in this work is not suitable for evaluating the T_g of the sulfonated polymers; the use of the DMA (Dynamic Mechanical Analysis) technique maybe more appropriate.

The thermogravimetric diagram of the sulfonated PBP gives information about the starting temperatures of degradation of the sulfonate groups and of the degradation of the polymer backbone, which are 215 and 567 °C, respectively. The weight loss due to SO$_3$H group degradation takes place up to 400 °C, whereas the total degradation of the backbone polymer was reached at 590 °C. Similar observations were made with sulfonated PPBP polymer in the thermogravimetric diagram presented in Figure 8. In this case, the SO$_3$H groups begin to degradation at 310 °C, in good agreement with the temperature given in the literature [30]. The weight loss at 580 °C corresponds to the degradation of the polymer backbone, as was observed in DSC.

From these results, it appears that both sulfonated PBP and PPBP are thermally stable at least up to 215 °C. The operating temperature range in DMFC being from 50 to 150 °C, the sulfonated polymers
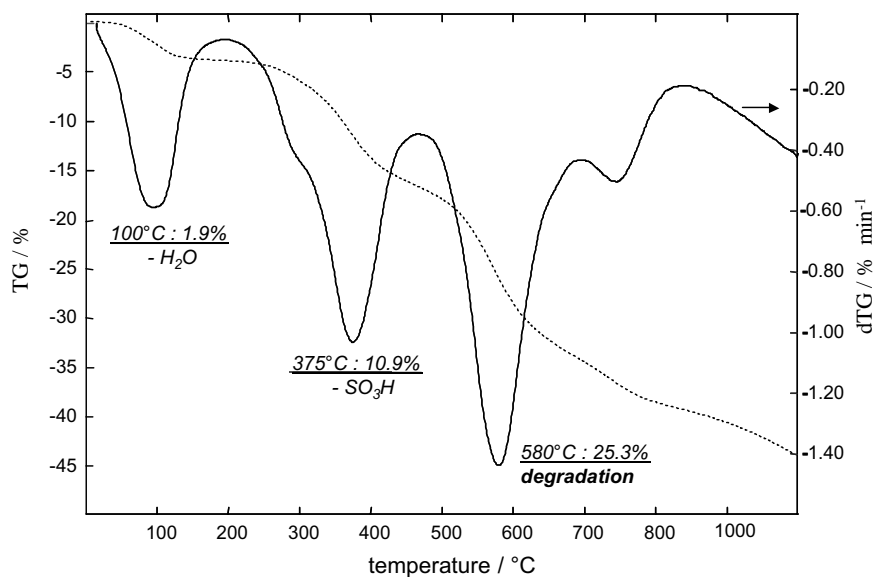
Fig. 8. Thermogravimetric diagram of sulfonated poly(p-phenoxybenzoyl-1,4-phenylene).

prepared in this work can be envisaged for this application (in terms of thermal stability).

3.3. *Water absorption of PBP and PPBP*

Membranes were hydrated in deionised water for 72 h and their weight measured. Water uptake was estimated by weighing the membranes in an infrared dessicator. The membranes were then dried for 15 min at 140 °C.

PBP and PPBP have similar structures; the difference is that PPBP has pendant phenoxy benzoyl groups on the poly-p-phenylene backbone. However, it was difficult to compare the two polymers because, due to their different sulfonation levels, they had different ionic exchange capacities (IEC), i.e. the number of SO₃H mole per gram of polymer. The higher this number, the more the polymer is sulfonated. Nevertheless, comparisons were made between sPBP with IEC=0.7 and sPPBP with IEC=1.3. The water uptake (calculated using Equation 1) of the sPPBP polymer having a sulfonation level of 40 mol% per repeating unit was found to be larger than that of sPBP polymer having the maximum sulfonation level of 20 mol% per repeating unit, i.e. 65 and 43 mol%, respectively. The water uptake was calculated according to the formula:

$$\text{Water uptake} = \frac{w_{\text{w}} - w_{\text{d}}}{w_{\text{d}}} \times 100 \tag{1}$$

where w_{w} is the weight of wet polymer; w_{d} the weight of dry polymer.

Rikukawa et al. [19] compared sPPBP and sPEEK membranes having equivalent sulfonation level and explained that polyparaphenylene have a higher water uptake because of the flexible pendant side chain of poly-p-phenoxybenzoyl-1,4-phenylene. It can be as-

sumed that the same phenomenon occurs between the two-substituted polyparaphenylene because of the shorter and more rigid (due to the carbonyl function) side chain in the PBP polymer. Indeed, the phenoxybenzoyl group enhances the flexibility. The plasticity, the water penetration and the water absorption in the terminal sulfonic groups were enhanced, allowing the membrane to maintain a more hydrated state above 100 °C. This latter property gives this material an advantage over Nafion® membranes and other hydrocarbon polymers, which become less conductive because of dehydration at temperatures higher than 100 °C.

3.4. *Methanol permeability*

The methanol permeability of sulfonated poly-benzoyl-1,4-phenylene (sPBP) and sulfonated poly-p-phenoxybenzoyl-1,4-phenylene (sPPBP) membranes was determined at room temperature (Figure 9). The thickness of the membrane was 100 μm for the sPPBP membrane and 110 μm for the sPBP membrane, i.e., thinner than the Nafion®115 membrane (close to 125 μm) and Nafion®117 (close to 178 μm). Using Fick's first law (Equation 2), the diffusion coefficient D and the methanol flow per square centimetre of membranes, standardized to a thickness of 100 μm ($J_{\text{stand.}}$) or not (J), were determined.

$$J = \frac{1}{S}\left(\frac{dN}{dt}\right) = \frac{V}{S}\left(\frac{dC}{dt}\right) = -D\left(\frac{C}{\delta}\right) \tag{2}$$

where S is the membrane surface area, δ the thickness of the membrane, V the volume of methanol solution (40 mL) and dC/dt is the slope of the obtained straight lines $C_{\text{MeOH}} = f(t)$ (Figure 9). Equation 2 can be integrated as follows:
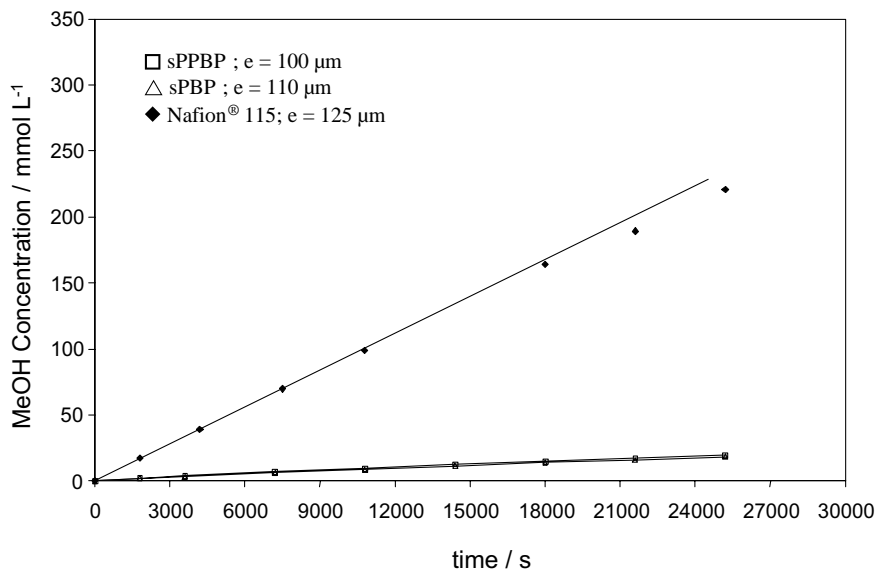
Fig. 9. Measurements of methanol cross-over for Nafion®115, Nafion®117, sPPBP and sPBP membranes at $T = 25$ °C.

$$\int_0^t -\frac{DS}{\delta V}\mathrm{d}t' = \int_{C_0}^C \frac{\mathrm{d}C'}{C'} \Leftrightarrow -\frac{DS}{\delta V}t = \ln\frac{C}{C_0} \qquad (3)$$

then, by neglecting in first approximation the variation of volume (which is very low):

$$C(t) = C_0 \mathrm{e}^{-\frac{DS}{\delta V}t} \qquad (4)$$

which can be approximated by $C_0 - C(t) = \frac{DS}{\delta V}t$ for $\frac{DS}{\delta V}t \ll 1$.

The results obtained are given in Table 1. The normalized permeability to methanol of poly-*p*-phenoxybenzoyl-1,4-phenylene and poly-benzoyl-1,4-phenylene membranes is found to be 11–13 times lower than that of the Nafion®115 and 117 polymers. The non-normalized permeability, which characterizes rather the membranes than the polymers, are in a ratio close to 7–11 to 1 between sPBP and sPPBP and Nafion®.

Again, the membranes prepared in this work display a better property for methanol permeability than a Nafion® membrane, which could be interesting for a DMFC application.

3.5. *Direct methanol fuel cell performance*

The results on sPBP and sPPBP (sulfonation level, IEC and water uptake studies) suggested that the latter

Table 1. Diffusion data obtained at 25 °C for different membranes

	$10^7 \times D$ /cm^2 s^{-1}	e /μm	$10^8 \times J$ /mol s^{-1} cm^{-2}	$10^8 \times J_{stand.}$ /mol s^{-1} cm^{-2}
sPBP	1.4	110	0.8	0.9
sPPBP	1.0	100	1.0	1.0
Nafion®115	11.2	125	9.0	11
Nafion®117	12.2	178	7.0	12

membrane should give better performance in DMFC that the former one. However, the sPBP appears to be less permeable to methanol than sPPBP. The performances of both membranes are compared in Figure 10. sPPBP displays the highest electrical performance in a single DMFC. Indeed, higher open circuit voltage (OCV) as well as higher current and power densities were achieved with this membrane.

Experiments on sPPBP were carried out to assess the influence of the operating temperature on the electrical performance (Figure 11) at 50, 70 and 90 °C. Increasing the temperature leads to improved performance of the DMFC. The maximum power density at 50 °C (4 mW cm^{-2}) is greatly enhanced (4 times higher) when the temperature reaches 90 °C. This fact confirms the difficulty to oxidize methanol and the necessity to work at temperatures higher than 90 °C to enhance the electrode kinetics and thus the performance of a DMFC.

After the large potential drop at low current density in the $E(j)$ polarization curves (due mainly to the activation overvoltage of the reduction and oxidation reactions at the electrode materials) a quasi linear behaviour of the polarization curves is observed. This is mainly due to the ohmic resistance of the membrane and of the interfaces. Afterwards, in the diffusion limited regime, a further potential decay progressively occurs. The shape of the polarization curves is similar in the whole temperature range investigated (50–90 °C). A peak power density of about 16 mW cm^{-2} is obtained at 60 mA cm^{-2} at 90 °C (Figure 11).

The influence of the membrane thickness on the DMFC performance was investigated at 90 °C. Two membranes with different thickness (80 and 50 μm) were tested as shown in Figure 12. For the thinner membrane, a drastic decrease in cell voltage occurs at low current densities and the open circuit voltage (OCV) is 0.1 V lower than for the thicker membrane. The
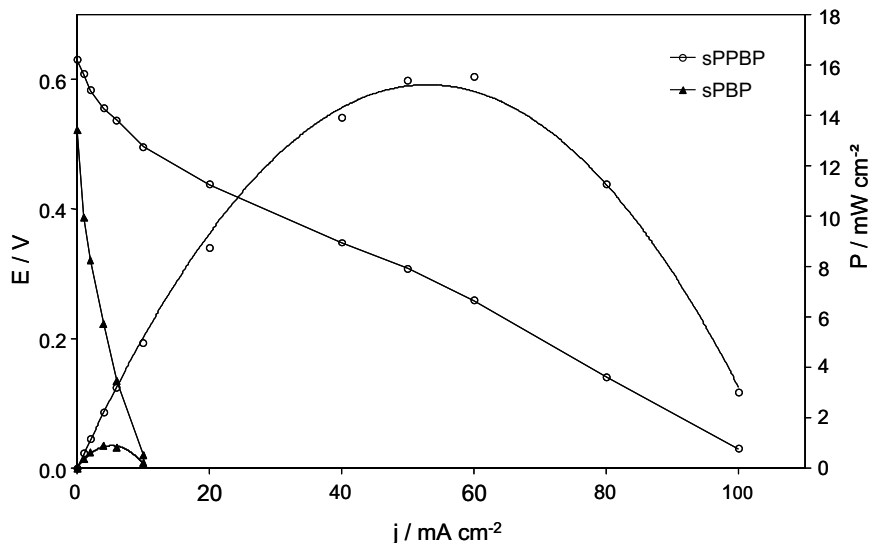
Fig. 10. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with a sPPBP and with a sPBP membranes in a single 5 cm^2 DMFC at $T = 90$ °C (2 M MeOH, $P_{\text{meOH}} = 1.8$ bar, 2 mL min^{-1}; $P_{O_2} = 2.3$ bars, 120 mL min^{-1}).
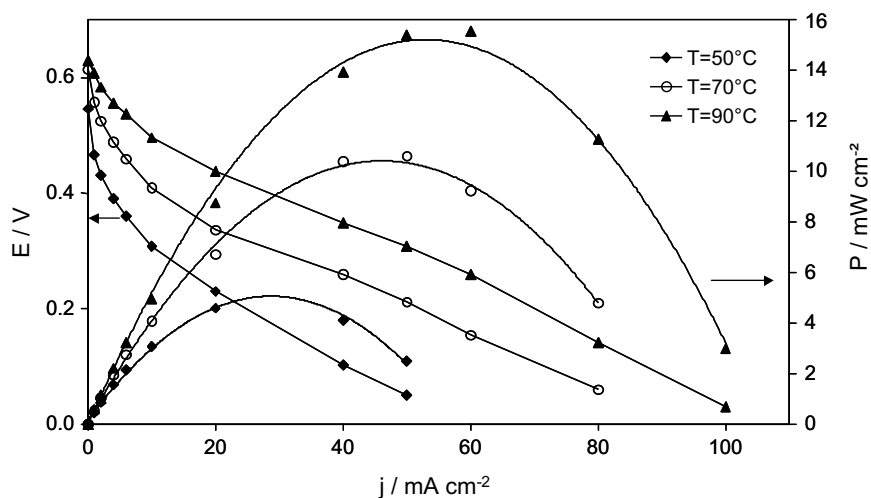

Fig. 11. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with a sPPBP in a single 5 cm^2 DMFC at different temperatures: 50 °C (2.0 M MeOH, $P_{\text{MeOH}} = 1.2$ bar, 2 mL min^{-1}; $P_{O_2} = 1.4$ bar, 120 mL min^{-1}), 70 °C (2.0 M MeOH, $P_{\text{MeOH}} = 1.4$ bar, 2 mL min^{-1}; $P_{O_2} = 1.8$ bar, 120 mL min^{-1}) and 90 °C (2 M MeOH, $P_{\text{MeOH}} = 1.8$ bar, 2 mL min^{-1}; $P_{O_2} = 2.3$ bar, 120 mL min^{-1}).

methanol crossover through the thinner membrane is likely more pronounced, thus inducing higher cathode depolarisation and a lower OCV. As a consequence, the maximum power density was four times lower.

To allow comparisons of performance with Nafion®117 in a DMFC at 90 °C, Membrane electrodes assemblies (MEA) of commercial E-TEK electrodes and Nafion®117 were prepared in the same way as MEAs with sPPBP membrane, i.e. without hot pressing. A higher open circuit voltage was observed with the sulfonated polyparaphenylene, due to the lower methanol permeability of the membrane (Figure 13). Even though the maximal power density obtained with sPPBP is two times lower than that with Nafion®, this result is rather encouraging because it is a validation of the concept of this kind of membranes as alternative to Nafion® for DMFC. The polarization curve drops more drastically in the case of sPPBP which is the result of a more important intrinsic resistance compared to Nafion®117.

MEAs made by hot pressing Nafion® and electrodes at 130 °C, 35 kg cm^{-2} for 3 mn were prepared and tested. Hot pressing allows one to reach the glass transition temperature of the Nafion® and to paste the electrodes (which contain Nafion®) to the membrane. This leads to increased performance by a factor of 3 (Figure 14). Nafion® penetrates the catalyst layer and serves as an ionic bridge between the active sites of the electrocatalyst and the membrane surface thus facilitating proton transfer. The hot pressing leads to better membrane – electrode interface which diminish the interfacial resistance.
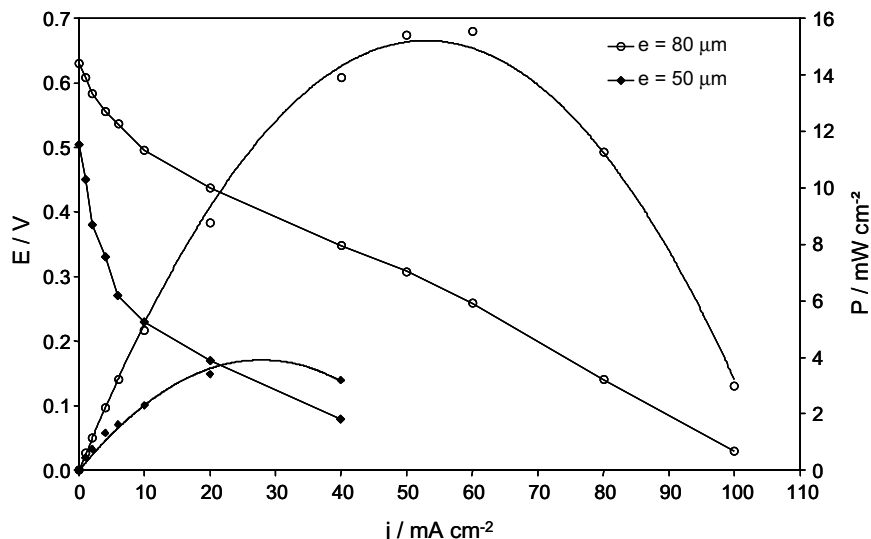
Fig. 12. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with sPPBP membranes of different thickness (50 and 80 μm) in a single 5 cm^2 DMFC at 90 °C (2 M MeOH, P_{MeOH} = 1.8 bar, 2 mL min^{-1}; P_{O_2} = 2.3 bar, 120 mL min^{-1}).

The interfaces in the MEAs made from PPBP were not optimised. Indeed, Nafion® and sPPBP are not 'compatible' and hot pressing did not allow the preparation of better MEAs, because the electrodes did not paste to the membrane. Knowledge of the T_g of the polymer (from Dynamic Mechanical Analysis) would be very useful in preparing MEAs by hot pressing with DMFC electrodes containing a PBPPs polymer solution, in order to improve the membrane-electrode interface.

4. Conclusion

Sulfonated PPP membranes were prepared. Sulfonation was demonstrated by elemental and FTIR analyses.

Both sPBP and sPPBP materials show high thermal stability.

Membranes to be used in fuel cells must have a low methanol permeability to prevent a reduction of the cell efficiency by depolarisation of the cathode. In poly(p-phenylene) membranes the methanol permeability appears to be lower than that of Nafion® membranes. Membranes have to endure harsh conditions in DMFCs, due to the necessity of high operating temperatures to activate electrochemical oxidation of methanol and achieve acceptable electrical performance. The polybenzoyl-1,4-phenylene membrane was not appropriate for fuel cell application due to its poor conductivity. Conversely, the power density obtained with poly-p-phenoxybenzoyl-1,4-phenylene membrane is promising. Even though the performance obtained is about half that of Nafion® 117, optimisation of the membrane and
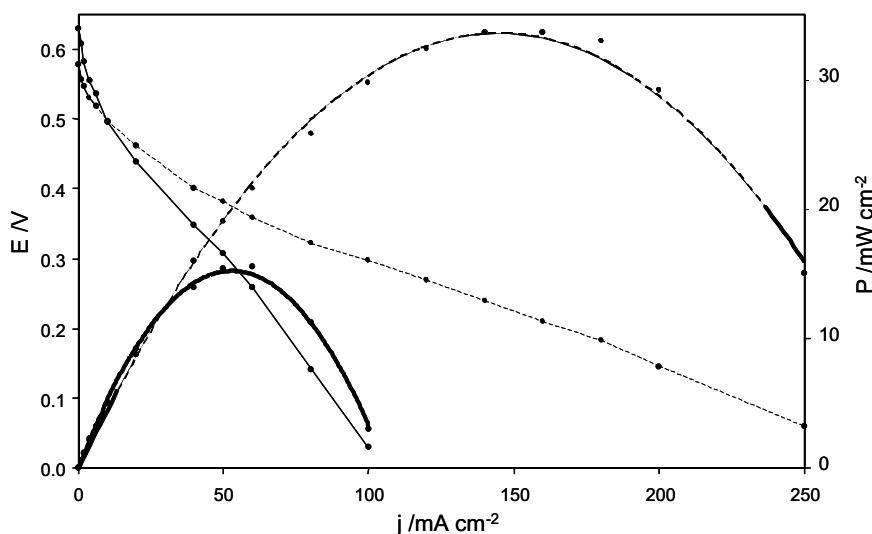

Fig. 13. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with a sPPBP and a Nafion®117 membranes in a single 5 cm^2 DMFC at 90 °C (2 M MeOH, P_{MeOH} = 1.8 bar, 2 mL min^{-1}; P_{O_2} = 2.3 bar, 120 mL min^{-1}).
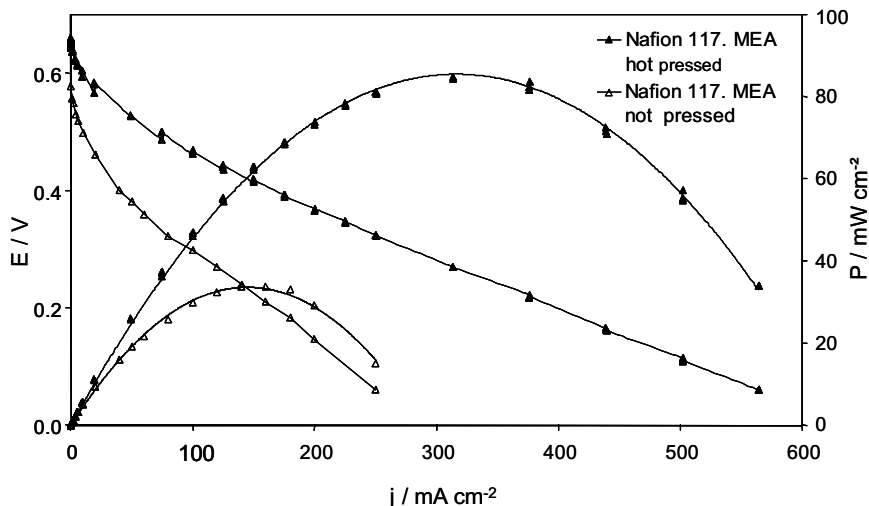
Fig. 14. Polarization curves *E*(*j*) and power density curves *P*(*j*) recorded with a non pressed Nafion®117 membrane and with a hot pressed Nafion®117 membrane (130 °C, 35 kg cm^{-2}, 3 min) in a single 5 cm^2 DMFC at 90 °C (2 M MeOH, P_{MeOH} = 1.8 bar, 2 mL min^{-1}; P_{O_2} = 2.3 bar, 120 mL min^{-1}).

interfaces could lead to better results. Moreover, the sulfonation level must be better controlled, and a new grafting method was developed in our laboratory to achieve this goal. Low cost of the matrix polymers and the large variety of substitutents available are good reasons to continue investigations on poly(paraphenylene) membranes.

Acknowledgements

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