

Development of materials for mini DMFC working at room temperature for portable applications

C. Coutanceau^{a,*}, R.K. Koffi^a, J.-M. Léger^a, K. Marestin^b,
R. Mercier^b, C. Nayoze^c, P. Capron^c

^a *Laboratoire de Catalyse en Chimie Organique, Equipe Electrocatalyse, UMR CNRS n° 6503,
40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

^b *Laboratoire des Matériaux Organiques à Propriétés Spécifiques, UMR CNRS – Université de Savoie n° 5041,
BP 24, 69390 Vernaison, France*

^c *Commissariat à l’Energie Atomique, Service de Conversion et de Stockage de l’Energie, Laboratoire des Sources d’Energie Miniature,
17 rue des Martyrs, 38054 Grenoble Cedex 9, France*

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Abstract

Methanol permeability measurements and direct methanol fuel cell tests were performed at room temperature with different commercially available or recast Nafion[®] membranes and sulfonated polyimide (SPI) membranes. Power densities as high as 20 mW cm⁻² could be obtained with Nafion[®] 115. However, in order to meet the technological requirements for portable applications, thinner membranes have to be considered. As the MeOH crossover increases greatly (from (7 to 20) × 10⁻⁸ mol s⁻¹ cm⁻²) while Nafion[®] membranes thickness decreases, non-perfluorinated polymers having high IEC are promising candidates for DMFC working at room temperature. The development catalysts tolerant to methanol is also relevant for this application. In spite of the low permeability to MeOH of SPI membranes, the obtained electrical performance with E-TEK electrodes based MEAs was lower than that obtained with Nafion[®] membranes. No significant increase of performances was neither evidenced by using homemade PtCr(7:3)/C and PtRu(4:1)/C catalysts instead of E-TEK electrodes with recast Nafion[®] based MEAs. However, MEAs composed with thin SPI membranes (50 μm) and homemade PtCr/C catalysts gave very promising results (18 mW cm⁻²). Based on experimental observations, a speculative explanation of this result is given.

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Keywords: Crossover; DMFC; Methanol tolerance; Nafion[®] membranes; Platinum based catalysts; Sulfonated polyimide membranes

1. Introduction

Nowadays, the technology for portable applications (computers, mobile phones, etc.) is in constant evolution for the development of smaller and lighter devices with more performing integrated functions. As a consequence, the on board energy density is a key parameter which has to be taken into account. Up to now, lithium based technology is currently used (volumic energy close to 500 Wh L⁻¹) [1,2], but mini fuel cells seem to be a very promising alternative as power supply for the next generation systems.

In spite of its high specific energy (32 Wh g⁻¹) [3] and because of storage problems in portable systems, the use of hydrogen as fuel is dismissed [4]. Liquid fuels as alcohols seem better adapted to the targeted technology. Indeed, alcohols are easy to store and have a relatively good energy density: 6.1 Wh g⁻¹ (4800 Wh L⁻¹) and 8.6 Wh g⁻¹ (6800 Wh L⁻¹) for methanol and ethanol, respectively [5]. According to the complete oxidation reaction of methanol into CO₂, one molecule of water is required to oxidize one molecule of methanol, as shown in the following equation:



Nevertheless, several problems have to be overcome. Low power densities are still currently obtained in DMFC [6] because of the difficulty to activate the oxidation reaction of alcohol and

* Corresponding author. Tel.: +33 5 49 45 48 95; fax: +33 5 49 45 35 80.
E-mail address: christophe.coutanceau@univ-poitiers.fr (C. Coutanceau).

the reduction reaction of molecular oxygen at room temperature. This problem could be solved by reducing the membrane thickness [7], i.e. to balance the loss of performance of the cell due to low reaction kinetics by the increase of the membrane conductivity. However, because high MeOH concentrations are required (5–10 M), the methanol crossover shall be severely increased. This could be detrimental to the fuel cell electrical performance as methanol acts as a poison for conventional platinum based catalysts present in fuel cell electrodes.

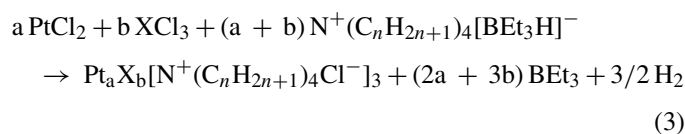
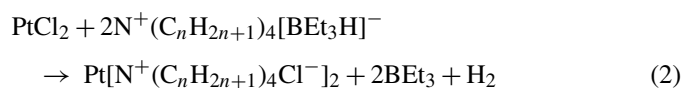
In order to improve the current DMFC performance, new materials have to be developed, namely new membranes having a low MeOH permeability [8,9] and new catalysts efficient for oxygen reduction at room temperature and more tolerant towards the presence of MeOH than classical platinum catalysts [10–15].

The topic of this paper is to present results obtained under DMFC operating conditions at room temperature, with non-conventional MEAs. For that purpose, sulfonated polyimide membranes (SPI), and anodic PtRu(4:1)/C and cathodic PtCr(7:3)/C catalysts were prepared and tested. The results were compared to those obtained with Nafion[®] membranes and commercial E-TEK catalysts. The effect of the methanol concentration on the tolerance of cathodic catalysts will also be discussed in order to explain the DMFC results.

2. Experimental

2.1. Catalytic powders preparation

Colloidal precursors are synthesized according to the procedure described by Bönemann et al. [16], but slightly modified. All experiments were carried out under argon, using anhydrous salts and dry solvents. Reducing agent $N^+(C_nH_{2n+1})_4[BEt_3H]^-$ is prepared by mixing stoichiometric amounts of tetraalkylammonium bromide [$N^+(C_nH_{2n+1})_4Br^-$] and potassium triethylborohydride [$K(BEt_3H)$] in tetrahydrofuran (THF). While added to this solution, the metallic salts (PtCl₂, RuCl₃, CrCl₃-Alfa Aesar) were reduced according to the following reactions:



where X = Cr or Ru.

Any agglomeration of the metallic particles was prevented by the presence of $N^+(C_nH_{2n+1})_4Cl^-$, which acts as a protecting surfactant. The colloidal precursors were dispersed onto a high specific area carbon substrate (Vulcan XC72), which was preliminary thermally treated at 400 °C under nitrogen for 4 h, in order to clean it. The carbon supported metal powders were then prepared by thermal treatment of these precursors at 300 °C under air for 1 h. Thermogravimetric analysis evidenced the complete elimination of the surfactant without modifying drastically the particle size. Bimetallic PtRu/C powder of atomic ratio

4:1 and PtCr/C powder of atomic ratio 7:3 were thus obtained [15,17,18].

2.2. Fabrication of the sulfonated polyimides (SPI) membranes

SPI polymers were synthesized by polycondensation of 2,2'-benzidine disulfonic acid (BDSA) as sulfonated monomer, a non-sulfonated diamine (bis[4 aminophenyl-oxy)methyl]2,2'-propane (APMP)) and a naphthalenic dianhydride (NTDA). The ionic exchange capacity (IEC) of the final polymer was controlled by the initial amount of sulfonated monomer introduced and was fixed to 1.98 meq_{H+} g⁻¹. The general copolymerization procedure is described elsewhere [19]. SPI NMP solutions were acidified with acidic ionic exchange resins. Acidified SPI membranes were directly obtained by casting of the solution.

2.3. Fabrication of the recast Nafion[®] membranes

Nafion[®] membranes were obtained by classical coating technology from Nafion[®] solution provided by Dupont. The solution was cast onto a glass plate at ambient temperature. Then, after removing of the solvents, the membrane undergoes a thermal annealing at 80 °C for 3 h in order to improve its mechanical properties. The membrane is washed in deionized water for 2 h before testing. The IEC of the Nafion[®] membranes were 1.1 meq_{H+} g⁻¹.

2.4. Electrodes and membrane electrode assemblies (MEAs) fabrication

The electrodes supplied by E-TEK were composed of 60 wt.% Pt–Ru/C (1/1 atomic ratio) for the anode and 40 wt.% Pt/C for the cathode. The average metal loading of each electrode was 2 mg cm⁻². Both electrodes contained 0.8 mg cm⁻² Nafion[®] in the active layer and 30 wt.% Teflon in the diffusion layer.

The homemade electrodes for DMFC were prepared from an ink composed of a Nafion[®] solution (5 wt.% from Aldrich), isopropanol and the catalytic powder, brushed on a carbon gas diffusion electrode. Carbon gas diffusion electrodes were homemade using a carbon cloth from Electrochem. Inc., on which was brushed an ink made of Vulcan XC72 carbon powder and PTFE dissolved in isopropanol. The gas diffusion electrodes were loaded with 3.5 mg cm⁻² of a mixture of carbon powder and 20 and 30 wt.% PTFE for the anodes and the cathodes, respectively. The metal loading was close to 2 mg cm⁻² and the Nafion[®] loading was 0.8 mg cm⁻². Nafion[®] based MEAs were prepared either with or without hot pressing of the electrodes onto Nafion[®] membranes at 130 °C for 90 s under a pressure of 3.43 MPa (35 kg cm⁻²). Because of the high glass transition temperature of SPI, hot pressing was not considered, as it would require to high pressing temperatures. As a consequence, for SPI based MEAs, electrodes were only pressed at room temperature.

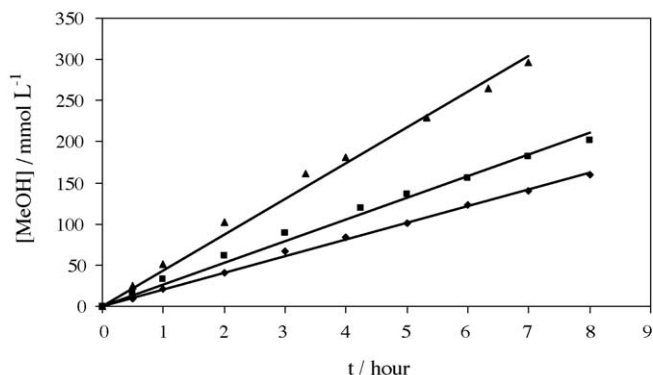


Fig. 1. Measurements of methanol cross-over for Nafion® 112 (▲), Nafion® 115 (■) and Nafion® 117 (◆) at $T=25\text{ }^{\circ}\text{C}$.

2.5. Electrochemical measurements

DMFC tests were carried out in a 5 cm^2 single cell using a Globe Tech Inc. fuel cell test station, equipped with humidification bottles having pressure and flow rate controls of both reactants: 5 M methanol and pure oxygen. Before the measurements, the membrane electrode assembly (MEA) was hydrated and equilibrated in the cell with a 5 M methanol solution at room temperature for 1 h. The fuel cell tests were carried out at room temperature under 1 bar of oxygen (30 mL min^{-1}) and 1 bar of methanol solution (2 mL min^{-1}).

The E versus j and P versus 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. Nafion® membranes

Because of the dramatic effect of the presence of methanol at the cathode side, and in order to optimize the MEAs, the permeability of different Nafion® membranes to methanol were evaluated before fuel cell tests (Fig. 1). Methanol crossover was measured as described elsewhere [9]. The thickness of the membranes are reported in Table 1 as well as the methanol crossover rate J and the diffusion coefficient D , which were calculated using the first Fick's law [9]. As expected, the crossover rate J decreases with the membrane thickness [7,9].

The electrical characteristics of these MEAs were evaluated under DMFC working conditions with commercial E-TEK electrodes hot pressed onto different Nafion® membranes

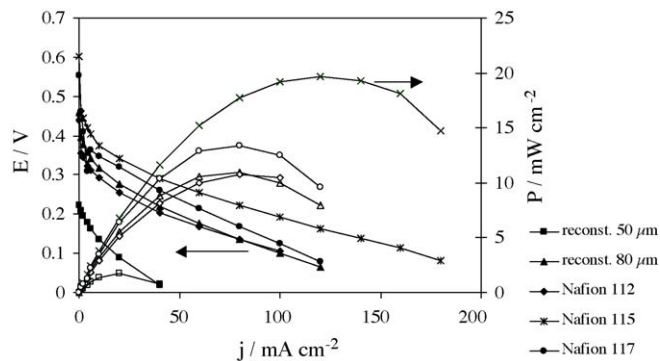


Fig. 2. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with different Nafion® membranes in a single 5 cm^2 DMFC at $T=25\text{ }^{\circ}\text{C}$ (5 M MeOH, $P_{\text{MeOH}}=1\text{ bar}$, 2 mL min^{-1} ; $P_{\text{O}_2}=1\text{ bar}$, 20 mL min^{-1}). The MEA was made with E-TEK electrodes (cathode: Pt/C, 2.0 mg cm^{-2} Pt loading; anode: PtRu(1:1)/C, 2.0 mg cm^{-2} metal loading) and hot pressed 3 min at $130\text{ }^{\circ}\text{C}$ and 35 kg cm^{-2} (3.43 MPa).

(Fig. 2). Unfortunately, we did not succeed to make MEA with the thinnest Nafion® membrane ($30\text{ }\mu\text{m}$ thickness) without a total loss of electrical characteristics (open circuit voltage close to 0 V). The best power densities (20 and 13 mW cm^{-2}) were, respectively, obtained with Nafion® 115 and 117 based MEAs. These values are in good accordance with those reported in literature [20]. For lower membrane thickness, the electrical performances were lower but still relatively acceptable: close to 11 mW cm^{-2} with both $80\text{ }\mu\text{m}$ recast Nafion® membrane and Nafion® 112 membrane. However, surprisingly, only very low electrical performances (2 mW cm^{-2}) could be obtained with a $50\text{ }\mu\text{m}$ recast Nafion® membrane.

Because suspecting the hot pressing treatment of thin membranes to be at the origin of such results, different MEAs were realized without hot pressing of the electrodes onto 30, 50 and $80\text{ }\mu\text{m}$ recast Nafion® membranes. As shown in Fig. 3, the electrical performance obtained with the $30\text{ }\mu\text{m}$ Nafion® membrane reaches 7 mW cm^{-2} , which confirms that hot pressing damages the membrane. But, hot pressing leads to enhance the electrical performance of MEAs made with thicker membranes, the maximum power density, achieved for example, in the case of the $80\text{ }\mu\text{m}$ membrane increasing from 9 mW cm^{-2} (Fig. 3) without hot pressing to 11 mW cm^{-2} with hot pressing (Fig. 2). However, the $50\text{ }\mu\text{m}$ membrane displays once again very poor electrical performance, which now could be attributed to some problems related to the membrane preparation and not to the hot pressing procedure. Song and Pickup [21] claimed that hot pressing (43 and 155 kg cm^{-2}) of electrodes onto a Nafion® 115 membrane generally led to decrease the electrical performance. It was pro-

Table 1
Thickness, crossover rate J and diffusion coefficient D of different Nafion® membranes

	Membrane Nafion®						
	Reconst. 1	Reconst. 2	112	Reconst. 3	Reconst. 4	115	117
Thickness (μm)	30	50	51	60	80	127	178
J ($\text{mol s}^{-1}\text{ cm}^{-2}$)	20×10^{-8}	16×10^{-8}	15.3×10^{-8}	15×10^{-8}	13×10^{-8}	9.3×10^{-8}	7.2×10^{-8}
D ($\text{s}^{-1}\text{ cm}^{-2}$)	6×10^{-7}	8×10^{-7}	7.8×10^{-7}	9×10^{-7}	10.4×10^{-7}	11.8×10^{-7}	12.8×10^{-7}

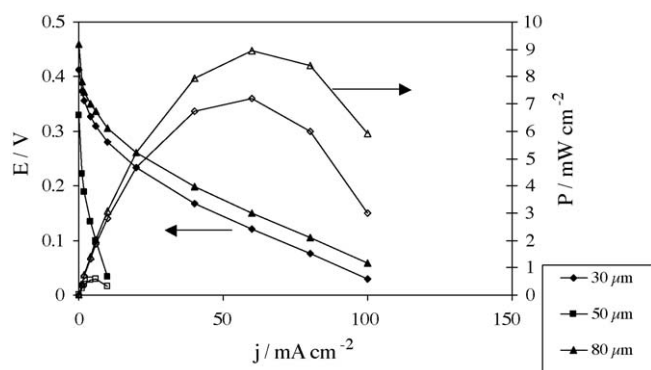


Fig. 3. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with different Nafion[®] membranes in a single 5 cm² DMFC at $T=25\text{ }^{\circ}\text{C}$ (5 M MeOH, $P_{\text{MeOH}}=1\text{ bar}$, 2 mL min^{-1} ; $P_{\text{O}_2}=1\text{ bar}$, 20 mL min^{-1}). The MEA was made with E-TEK electrodes (cathode: Pt/C, 2.0 mg cm^{-2} Pt loading; anode: PtRu(1:1)/C, 2.0 mg cm^{-2} metal loading) without hot pressing.

posed that the elevated temperature and pressure led to collapse the pore within the catalytic layer. However, in our study, the loss of performance was only observed with the thinnest membrane (30 μm) and was thought to be likely due to its mechanical fragility. In fact, in the work of Song and Pickup [21], the MEA pressed at 43 kg cm^{-2} led to electrical performance, in terms of peak power, a little higher than that with the not pressed MEA. It can then be proposed that an optimum in the pressure could exist below 43 kg cm^{-2} . Moreover, Le Ninivin et al. [9] showed that, in single DMFC fitted with a Nafion[®] 117 and working at $90\text{ }^{\circ}\text{C}$, the same hot pressing procedure as used in this work led to increase the maximum achieved power density by a factor 3 compared with a not pressed MEA. It was then proposed that hot pressing led to reach the glass transition temperature of the Nafion[®] membrane and of the Nafion[®] polymer present in the catalytic layer of the electrodes and to paste the electrodes to the membrane, which leads to a better membrane–electrode interface by diminishing the interfacial resistance.

Taking into account the apparent conductance of the membrane as well as the methanol crossover, 127 μm thick membranes (Nafion[®] 115) seem to be most promising. However, the dimensional requirements for portable applications impose the use of membranes thinner than 100 μm . When comparing Nafion[®] 112 and 80 μm recast Nafion[®] membranes, better electrical performance was obtained with the thickest membrane at low current densities ($<80\text{ mA cm}^{-2}$). One possible explanation is related to its lower methanol permeability. This hypothesis is confirmed by the higher value of the open circuit voltage (OCV = 0.46 V) recorded with the recast membrane compared to that obtained with the Nafion[®] 112 membrane (OCV = 0.44 V). On the other hand, as it could be expected, the slope of the

polarization curve $j(E)$ is higher with the recast membrane than with the Nafion[®] 112. This observation can be related to the difference in thickness of the two membranes [7].

Based on the above-mentioned results, 80 μm recast Nafion[®] membranes were chosen as a reference for this work.

3.2. SPI membranes

SPIs as proton exchange membranes are promising candidates for DMFC working at room temperature. Indeed, this kind of structure enables the synthesis of polymers with high IEC, insoluble in water and displaying very low dimensional variations. These properties are key parameters for the elaboration of membranes highly conductive at room temperature. Moreover, aromatic and heterocyclic structures are known to present limited MeOH permeability [22].

In order to evaluate the MeOH permeability of these polymers and to compare it to the crossover of MeOH through Nafion[®] membranes, SPI membranes with different thickness were prepared and tested. Results are reported in Table 2. As expected, the thicker is the membrane, the lower is the permeability. However, in all case SPI membranes present a far reduced MeOH permeability: the measured values are more than twice lower than those obtained with Nafion[®] membranes. This result is particularly interesting as the SPI membranes tested have a very high IEC (1.98 meq_{H+}/g) compared to that of the Nafion[®] membranes (1.1 meq_{H+}/g) and thus are expected to induce high conductivities and good electrical performances at room temperature.

As mentioned earlier, SPI based MEAs were prepared by pressing the electrodes onto the membranes at room temperature. In a first set of experiments, E-TEK electrodes were used. The polarization curves $j(E)$ and the corresponding power densities $P(j)$ curves are reported in Fig. 4. From these graphs, two main results can be drawn. First, the OCV recorded from the SPI based MEA (0.49 V) is 30 mV higher than the that recorded from the Nafion[®] based MEA (0.46 V). This result is consistent with the lower MeOH permeability of the sulfonated polyimide polymer. The second observation concerns the fuel cell performance: the better electrical performance obtained with the 50 μm thick membrane (6 mW cm^{-2}) is slightly lower than those obtained with 80 μm recast Nafion[®] membranes.

3.3. Electrical behavior of the membranes with homemade electrodes

From the previous results and according to the dimensional targets for mini DMFC application, the 80 μm recast membrane Nafion[®] and the 50 μm SPI membrane, which led to the best

Table 2
Thickness, crossover rate J and diffusion coefficient D of different SPI membranes

	Membranes SPI				
	30 μm	40 μm	50 μm	60 μm	80 μm
J (mol s ⁻¹ cm ⁻²)	9.1×10^{-8}	9.3×10^{-8}	4.6×10^{-8}	6.4×10^{-8}	4.6×10^{-8}
D (s ⁻¹ cm ⁻²)	2.7×10^{-7}	3.7×10^{-7}	2.3×10^{-7}	3.8×10^{-7}	3.7×10^{-7}

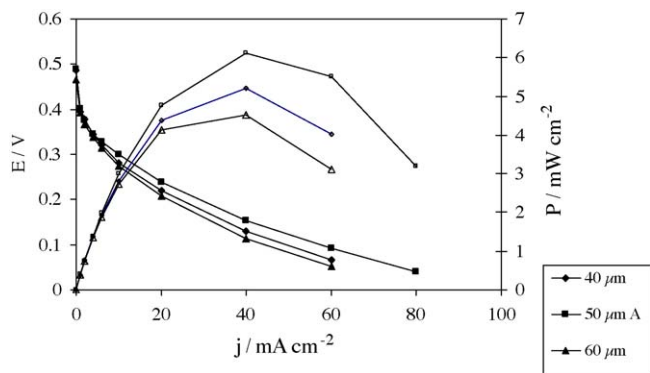


Fig. 4. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with different SPI membranes in a single 5 cm^2 DMFC at $T=25^\circ\text{C}$ (5 M MeOH , $P_{\text{meOH}} = 1 \text{ bar}$, 2 mL min^{-1} ; $P_{\text{O}_2} = 1 \text{ bar}$, 20 mL min^{-1}). The MEA was made with E-TEK electrodes (cathode: Pt/C, 2.0 mg cm^{-2} Pt loading; anode: PtRu(1:1)/C, 2.0 mg cm^{-2} metal loading) without hot pressing.

electrical characteristics with E-TEK electrodes were used to realize MEAs based on home-made catalysts: PtCr(7:3)/C at the cathode and PtRu(4:1)/C at the anode.

First, the new electrodes were tested in DMFC conditions with the recast Nafion[®] membrane, after hot pressing. As shown in Fig. 5, comparing with the values obtained with E-TEK electrodes, no significant enhancement of the electrical performances occurred (12 and 11 mW cm^{-2} , respectively). However, the OCV was 90 mV higher with the homemade catalysts based MEAs, reaching 0.550 V instead of 0.46 V with E-TEK electrodes based MEAs. This may be due to the higher tolerance of PtCr catalyst towards the presence of methanol. However, in the low current density range (from 0 to 20 mA cm^{-2}), the shift towards lower voltages of the DMFC working with the new electrodes was more important than that with the commercial electrodes. This should be attributed to the difference in the catalysts composition of the anode, and especially to the higher ruthenium content in the commercial catalysts (50% atomic ratio against 20% atomic ratio for the homemade catalysts), which

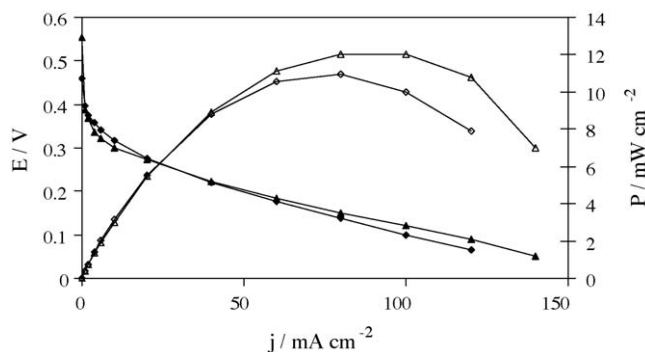


Fig. 5. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with a $80 \mu\text{m}$ thickness Nafion[®] membrane in a single 5 cm^2 DMFC at $T=25^\circ\text{C}$ (5 M MeOH , $P_{\text{meOH}} = 1 \text{ bar}$, 2 mL min^{-1} ; $P_{\text{O}_2} = 1 \text{ bar}$, 20 mL min^{-1}). The MEA was made either with (\blacklozenge , \diamond) E-TEK electrodes (cathode: Pt/C, 2.0 mg cm^{-2} Pt loading; anode: PtRu(1:1)/C, 2.0 mg cm^{-2} metal loading) or (\blacktriangle , \triangle) homemade electrode (cathode: PtCr(7:3)/C, 2.0 mg cm^{-2} metal loading; anode: PtRu(4:1)/C, 2.0 mg cm^{-2} metal loading) and hot pressed 3 min at 130°C and 35 kg cm^{-2} (3.43 MPa).

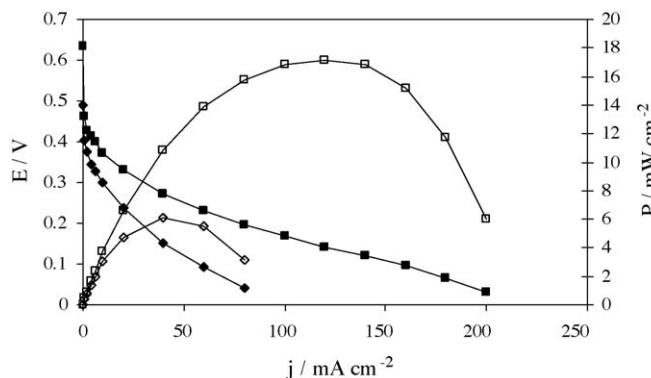


Fig. 6. Polarization curves $E(j)$ and power density curves $P(j)$ recorded with a $50 \mu\text{m}$ thickness SPI membrane in a single 5 cm^2 DMFC at $T=25^\circ\text{C}$ (5 M MeOH , $P_{\text{meOH}} = 1 \text{ bar}$, 2 mL min^{-1} ; $P_{\text{O}_2} = 1 \text{ bar}$, 20 mL min^{-1}). The MEA was made either with (\blacklozenge , \diamond) E-TEK electrodes (cathode: Pt/C, 2.0 mg cm^{-2} Pt loading; anode: PtRu(1:1)/C, 2.0 mg cm^{-2} metal loading) or (\blacksquare , \square) homemade electrode (cathode: PtCr(7:3)/C, 2.0 mg cm^{-2} metal loading; anode: PtRu(4:1)/C, 2.0 mg cm^{-2} metal loading) without hot pressing.

leads to decrease the platinum poisoning at low anode potentials [17,23]. Indeed, according to the bifunctional mechanism [24,25], at low anode potentials, platinum is needed to adsorb dissociatively methanol into CO species and ruthenium to activate water and to bring the additional oxygen atom necessary to complete the oxidation of adsorbed CO species into CO_2 . But, in the higher current density range, i.e. current densities higher than 20 mA cm^{-2} , the tendency is reversed and the PtRu (80:20)/C catalyst leads to better electrical performance of the DMFC. This can be explained by the fact that at high anode potentials, i.e. low cell voltages, platinum is able to activate water and then the kinetics of the oxidation reaction of methanol is increased [26,27].

In Fig. 6 are reported the polarization curves obtained with two different MEAs based on $50 \mu\text{m}$ SPI membrane, either with commercial or homemade electrodes. The homemade electrodes based MEA presents a far better performance. Indeed, the maximum power density, which initially was close to 6 mW cm^{-2} with conventional catalysts, raised up to 18 mW cm^{-2} . The increase of the OCV is also significant (40 mV).

It can thus be concluded that the use of homemade electrodes is much more beneficial with SPI based MEAs than with Nafion[®] based MEAs.

Obviously, this shift in the OCV is lower than that observed with the Nafion[®] membrane. The SPI membrane being less permeable to methanol, one can expect that the cathode depolarization will be lower under DMFC working conditions with a SPI membrane than with a Nafion[®] one. On the other hand, the OCVs of the cell working with SPI membranes are always lower than those recorded when using Nafion[®] membranes under the same conditions, which indicates the important role of the hot pressing to enhance the membrane electrode assembly.

Comparing the electrical performance of Nafion[®] and SPI based MEAs (Fig. 7), it appears that results obtained with SPI membranes–homemade catalysts MEA are particularly interesting as the power density is increased by a factor two with respect to Nafion[®]–homemade catalysts MEA. As Nafion[®]–E-

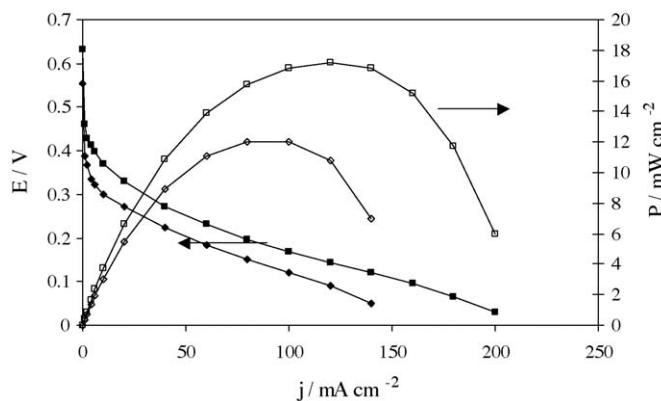


Fig. 7. Comparison of the polarization curves $E(j)$ and power density curves $P(j)$ recorded with (◆; ◇) a hot pressed MEA based on a 80 μm thickness Nafion[®] membrane and (■; □) a non hot pressed MEA based on a 50 μm thickness SPI membrane in a single 5 cm^2 DMFC at $T=25^\circ\text{C}$ (5 M MeOH, $P_{\text{MeOH}}=1$ bar, 2 mL min^{-1} ; $P_{\text{O}_2}=1$ bar, 20 mL min^{-1}). The MEAs were fitted with homemade electrodes (cathode: PtCr(7:3)/C, 2.0 mg cm^{-2} metal loading; anode: PtRu(4:1)/C, 2.0 mg cm^{-2} metal loading).

TEK based MEAs always presented higher power densities than SPI-E-TEK based MEAs, this result could seem surprising. However, such a behavior can be easily explained.

On the anode side, the lower permeability of the SPI membrane is consistent with an increase of the local methanol concentration in the catalytic layer and therefore to a reduction of the problems related to mass transport limiting reactions. However, this phenomenon is unlikely the only parameter responsible of the observed increase of the electrical performance, especially as fuel cell tests are performed at high methanol concentration (5 M). As discussed earlier, more important is the impact of the low permeability of SPI membranes to limit the effect of cathode depolarization. Surprisingly, in the presence of E-TEK catalysts, only a small benefit could be evidenced at low current densities. In order to understand this observation, the nature of the catalyst has to be taken into account. It is well known [15,28] that the tolerance towards methanol of PtCr catalysts depends on the MeOH concentration: the higher the concentration, the lower the tolerance. Whereas PtCr catalysts are less poisoned than Pt catalysts at low MeOH concentrations, their tolerance is similar at high MeOH concentrations.

In this perspective, the low MeOH permeability of SPI membranes is a key parameter: as the MeOH concentration is greatly reduced, homemade electrodes based on PtCr become particularly tolerant in the fuel cell test conditions. The association of a membrane with a low MeOH permeability and of catalysts tolerant towards MeOH are thus responsible of the better performances obtained.

4. Conclusion

The aim of this work was to prepare new MEAs based on SPI membranes and homemade catalysts for DMFC applications at room temperature. Low thickness SPI membranes (50 μm) having interesting properties for portable applications, namely a weak dimensional variation at the swollen

state and a low methanol permeability were prepared. As the methanol crossover was highly reduced through these membranes, cathodic PtCr(7:3)/C catalysts were particularly efficient. The concomitant use of membranes having low MeOH permeability and PtCr/C catalysts is particularly promising as it was possible to obtain a far better electrical performance under DMFC working conditions with this system than with thin Nafion[®] membranes (<100 μm).

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References

- [1] M. Broussely, G. Archdale, J. Power Sources 136 (2004) 386.
- [2] K. Takei, K. Ishihara, K. Kumai, T. Iwahori, K. Miyake, T. Nakatsu, N. Terada, N. Arai, J. Power Sources 136 (119–121) (2003) 887.
- [3] C. Lamy, J.-M. Léger, J. Phys. IV 4 (1994) C1.
- [4] L. Zhou, Renew. Sust. Energy Rev. 9 (2005) 395.
- [5] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, J. Appl. Electrochem. 34 (2004) 439.
- [6] M. Hogarth, R. Ralph, Platinum Metals Rev. 46 (2002) 146.
- [7] M. Shen, S. Roy, J.W. Kuhlmann, K. Scott, K. Lovell, J.A. Horsfall, J. Memb. Sci. 251 (2004) 121.
- [8] X. Ren, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 92.
- [9] C. Le Ninivin, A. Bolland-Longeau, D. Demattei, C. Coutanceau, C. Lamy, J.-M. Léger, J. Appl. Electrochem. 34 (2004) 1159.
- [10] S. Baranton, C. Coutanceau, C. Roux, F. Hahn, J.-M. Léger, J. Electroanal. Chem. 557 (2005) 223.
- [11] J.-F. Drillet, A. Ee, J. Friedemann, R. Kötz, B. Schnyder, V.M. Schmidt, Electrochim. Acta 47 (2002) 1983.
- [12] A.K. Shukla, R.K. Raman, N.A. Choudhury, K.R. Priolkar, P.R. Sarode, S. Emura, R. Kumashiro, J. Electroanal. Chem. 563 (2004) 181.
- [13] H. Yang, N. Alonso-Vante, J.-M. Léger, C. Lamy, J. Phys. Chem. B 108 (2004) 1938.
- [14] H. Yang, C. Coutanceau, J.-M. Léger, N. Alonso-Vante, C. Lamy, J. Electroanal. Chem. 576 (2004) 305.
- [15] R.K. Koffi, C. Coutanceau, E. Garnier, J.-M. Léger, C. Lamy, Electrochim. Acta 50 (2005) 4117.
- [16] H. Bönnemann, W. Brijoux, R. Brinkmann, R. Fretzen, T. Jousen, R. Köppler, B. Korall, P. Neiteler, J. Richter, J. Mol. Catal. 86 (1994) 129.
- [17] L. Dubau, C. Coutanceau, E. Garnier, J.-M. Léger, C. Lamy, J. Appl. Electrochem. 33 (2003) 419.
- [18] L. Dubau, F. Hahn, C. Coutanceau, J.-M. Léger, C. Lamy, J. Electroanal. Chem. 554–555 (2003) 407.
- [19] C. Genies, R. Mercier, B. Sillon, N. Cornet, G. Gebel, M. Pinéri, Polymer 42 (2001) 359.
- [20] T. Shimizu, T. Momma, M. Mohamedia, T. Osaka, S. Sarangapani, J. Power Sources 137 (2004) 277.
- [21] C. Song, P.G. Pickup, J. Appl. Electrochem. 34 (2004) 1065.
- [22] W. Youngtai, O. Seyoung, K. YongSoo, J. Bumsuk, J. Memb. Sci. 220 (2003) 31.
- [23] J. Goodenough, R. Manoharan, Chem. Mater. 1 (1989) 391.
- [24] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 275.
- [25] P. Waszczuk, A. Wieckowski, P. Zelenay, S. Gottesfeld, C. Coutanceau, J.-M. Léger, C. Lamy, J. Electroanal. Chem. 511 (2001) 55.
- [26] H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Cairns, J. Electrochem. Soc. 141 (1994) 1795.
- [27] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 267.
- [28] Roger K. Koffi, Ph.D. Thesis, Poitiers, 2004.