

# High-power direct ethylene glycol fuel cell (DEGFC) based on nanoporous proton-conducting membrane (NP-PCM)

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## Abstract

We recently reported the development of a new nanoporous proton-conducting membrane (NP-PCM) and have applied it in a direct methanol fuel cell (DMFC) and in other direct oxidation fuel cells. The use of the NP-PCM in the DMFC offers several advantages over the Nafion-based DMFC including lower membrane cost, lower methanol crossover which leads to a much higher fuel utilization and higher conductivity. In this work, we found that the 90 °C swelling of the NP-PCM is only 5–8% and that the diffusion constant of methanol at 80–130 °C is higher by a factor of 1.5–3 than that of ethylene glycol (EG). The maximum power density of methanol/oxygen and EG/oxygen FCs equipped with a 100 μm thick NP-PCMs is 400 and 300 mW/cm<sup>2</sup> respectively, higher than that for a DMFC based on Nafion 115 (260 mW/cm<sup>2</sup> [Electrochem. Solid-State Lett. 4 (4) (2001) A31]). This puts the DEGFC in direct competition with both DMFC and indirect methanol FC. Ethylene glycol (EG) is well known in the automobile industry and in contrast to methanol, its distribution infrastructure already exists, thus it is a promising candidate for practical electric vehicles. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Direct methanol fuel cell; Ethylene glycol; Direct-oxidation fuel cell

## 1. Introduction

A fuel cell (FC) is an electrochemical device that converts, with high efficiency, the chemical energy of a fuel-oxidation reaction directly into electrical energy. Fuel cells employing organic fuels are extremely attractive as power sources for electric vehicles, and for both stationary and portable applications. A direct-oxidation fuel cell (DOFC) is a device in which the organic fuel is fed directly into the fuel cell without any previous chemical modification. In the cell, the fuel is oxidized at the anode and oxygen is reduced to water at the cathode. Hence, DOFCs offer a considerable weight and volume advantage over indirect fuel cells, in which the fuel is converted by a reformer into hydrogen.

Up to now methanol has been considered to be the “best” fuel [1–12]. It is cheap and is more efficiently oxidized, under certain conditions, than other alcohols or aqueous hydrocarbons. However, the use of methanol as a fuel presents several problems: methanol is toxic, it is highly flammable, has a low boiling point (65 °C) and is highly prone to pass through the polymer–electrolyte membrane (high crossover). Fuel crossover lowers the operating potential of the oxygen electrode and results in the consumption of

fuel and generation of heat without the production of useful electrical energy. It is obviously desirable to minimize the rate of fuel crossover. Hydrocarbons and aliphatic alcohols are very difficult to electrooxidize completely [11–16], the main products of aliphatic alcohols being aldehydes or ketones, CO<sub>2</sub> and acids or esters. The yield of electrooxidation of ethylene glycol (EG) to CO<sub>2</sub> on a platinum electrode in acid solution and at room temperature is only 5% [16]. It was suggested that the intermediate reduction products are strongly adsorbed and this slows further reaction. An appropriate fuel would be one that is oxidized completely to CO<sub>2</sub> with no, or minor, side products.

We recently reported the development of a new nanoporous (1.5 nm typical pore size) proton-conducting membrane (NP-PCM) [17] that consists of a ceramic nanopowder and PVDF and an acid and have applied it in a direct methanol fuel cell (DMFC) [18]. The use of the NP-PCM in the DMFC offers several advantages over the Nafion-based DMFC: (1) lower membrane cost (by more than two orders of magnitude); (2) smaller pores (by a factor of two); (3) lower methanol crossover (by up to an order of magnitude). This leads to much higher fuel utilization; (4) higher conductivity (by up to four times); (5) the ionic conductivity of the NP-PCM, unlike Nafion, is not affected by heavy-metal impurities; (6) as the corrosion products of heavy metals do not affect its conductivity it permits the use of cheaper catalysts and hardware materials.

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Using a NP-PCM based fuel cell we found that the electrooxidation of both EG and dimethyl oxalate (DMO) is possible [19–21] and, moreover at 60 °C, their fuel utilization is very high (94%). EG is more efficient, safer than methanol and has a capacity density (in terms of Ah/g) 14% lower than that of methanol. EG is well known in the automobile industry and, as opposed to methanol, its distribution infrastructure already exists, thus it is a promising candidate for practical electric vehicles and for mobile and stationary applications.

The goals of this work are to characterize the NP-PCM at high temperatures and to study the performance of a DEGFC employing a 100  $\mu\text{m}$  thick NP-PCM at 130 °C.

## 2. Experimental

We used the same FC setup described in [18,19]. Our test vehicle was a 5 or 7  $\text{cm}^2$  DOFC operating at various oxygen pressures. The fuel cell housing was built from synthetic graphite blocks provided by Globetech, in which serpentine flow fields were engraved, one for the organic fuel solution and the other for oxygen or air.

The membrane electrode assembly (MEA) was based on a 100 or 240  $\mu\text{m}$  thick nanoporous proton-conducting membrane (NP-PCM) made of PVDF and  $\text{SiO}_2$ . It was hot pressed between a Toray paper coated with an anode catalyst layer on the one side and an E-TEK cathode on the other. The anode catalyst was platinum-ruthenium (1:1 atomic) nanopowder (Johnson-Matthey). The anode and the cathode platinum loading was 4  $\text{mg}/\text{cm}^2$ . Oxygen was fed, at 1–4 atm (abs), into the cathode compartment through a water bubbler at 65–95 °C and at a rate of 40–60 ml/min. During cell operation an aqueous solution of 3 M sulfuric acid and a fuel (0.5–2 M methanol or EG) was circulated past the anode at a flow rate of 15 ml/min.

Measurements of fuel crossover were carried out at several temperatures by feeding nitrogen instead of oxygen

into the cathode compartment (at ambient pressure) and feeding organic fuel-acid solution into the anode compartment. Cell voltage was reversed; hydrogen was evolved at the fuel electrode while fuel that crossed over to the cathode side was oxidized. The current that flows at 0.8–1 V was found to be the limiting current for fuel-oxidation [18,19].

## 3. Results and discussions

We recently found [20] that in a 240  $\mu\text{m}$  thick NP-PCM-based DEGFC the anodic and the cathodic overpotentials decrease markedly with temperature rise and above 110 °C the cathodic overpotential in the DMFC is similar to that of the DEGFC. At 130 °C the anodic overpotential was found to be smaller than that of the cathode [20] and the maximum power density of the DEGFC was 180  $\text{mW}/\text{cm}^2$ , similar to that of the DMFC (215  $\text{mW}/\text{cm}^2$ ). In this work, in order to gain more power, we reduced the thickness of the membrane from 240 to 100  $\mu\text{m}$ .

One of the biggest advantages of the NP-PCM is its relatively higher resistance to fuel permeation. Table 1 summarizes crossover test results at 80–130 °C for three membranes. The crossover current density rises with temperature and with fuel concentration and decreases with increase in the thickness of the membrane. In all cases, for the same membrane, concentration and temperature, the crossover current density for EG is lower than that for methanol. This difference decreases with temperature. It must be kept in mind that oxidation of EG is a 10 electron reaction while oxidation of methanol involves only six electrons. Thus, a better way to analyze the results is to look at the  $D$  (diffusion coefficient) values or the normalized flux. When the number of electrons is taken into account and the fuel flux in terms of  $\text{mol}/\text{s}/\text{cm}^2$  is normalized to 1 M fuel, it can be seen (Table 1) that the permeability (flux) of EG, at 80 °C, is one-third that of methanol.  $D$  values have been

Table 1  
Crossover tests for methanol and ethylene glycol

Fuel	Temperature (°C)	Concentration (M)	Crossover current density ( $\text{A}/\text{cm}^2$ )	Fuel flux <sup>a</sup> ( $\text{mol}/\text{s}/\text{cm}^2$ ) $\times 10^{-8}$	Fuel $D_{\text{ap}}$ <sup>b</sup> ( $\text{cm}^2/\text{s}$ ) $\times 10^{-6}$
Ethylene glycol	80	0.5	0.019 <sup>c</sup>	3.9	1.2
	80	1.0	0.041 <sup>c</sup>	4.2	1.3
	110	1.0	0.130 <sup>d</sup>	13	3.2
	110	1.0	0.200 <sup>e</sup>	20	2.1
	130	2.0	0.740 <sup>e</sup>	38	3.8
	130	1.2	0.500 <sup>e</sup>	42	4.3
Methanol	80	1.0	0.076 <sup>c</sup>	13	3.9
	110	1.5	0.230 <sup>d</sup>	26	6.4
	130	1.5	0.290 <sup>d</sup>	33	8.0
	130	1.0	0.340 <sup>e</sup>	59	5.9

<sup>a</sup> Normalized to 1 M fuel.

<sup>b</sup> Apparent fuel diffusion constant for the membrane (calculated assuming:  $I_{\text{co}} = I_1$ ).

<sup>c</sup> PCM A, 300  $\mu\text{m}$  [20].

<sup>d</sup> PCM B, 240  $\mu\text{m}$ .

<sup>e</sup> PCM C, 100  $\mu\text{m}$ .

calculated assuming that the crossover current density equals the limiting current density of the fuel in the membrane. At 80 °C,  $D$  for methanol is about three times that for EG. This ratio  $D(\text{methanol})/D(\text{EG})$  decreases with temperature and at 130 °C it is only 1.5.

The swellings of these PCMs in 3 M  $\text{H}_2\text{SO}_4$  and 2 M methanol solution have been measured at 90 °C. PCM samples (100  $\mu\text{m}$ , 5 cm  $\times$  5 cm) have been immersed for 1 h in this solution and the changes in the  $X$  and  $Y$  directions were measured. The change in  $X$  was found to equal the change in  $Y$ . Thus the volume change, or the swelling, was calculated assuming an equal change in the  $Z$  direction (a change of a few percents in the thickness is difficult to measure). The swelling (volume change) from complete dryness (100 °C in vacuum) to immersion at 90 °C was found to be 5–8%.

In this paper, we report preliminary results obtained with non-optimized Pt-Ru catalysts as used for methanol. It is not clear whether the methanol catalyst is the best one for EG electrooxidation. We are sure that much better performance can be achieved following dedicated catalyst development and after cell optimization.

Fig. 1 shows polarization curves for 2 M methanol and 1.5 M EG in 3 M  $\text{H}_2\text{SO}_4$  fed into a 100  $\mu\text{m}$  thick, 5  $\text{cm}^2$ , NP-PCM fuel cell at 130 °C and at 4 atm (abs) oxygen pressure (the back pressure was also 4 atm). The operating voltage of the DEGFC is about 50–70 mV lower than that of the DMFC. With the use of a reference electrode it was found that, at 110 °C, the overpotential of the EG electrode is larger than that of the methanol electrode and the voltage losses at the oxygen electrodes are almost identical or a little bit larger in the case of DEGFC at higher current densities [20]. This probably means that EG, which crosses over to the cathode side, slows or deactivates oxygen reduction. This point will be rechecked in the future. In addition, it was found [20] that the cathodic overpotential is greater than the anodic, so the cathode must be improved. A polarization curve for 2 M methanol in a 115 Nafion (125  $\mu\text{m}$  thick) based DMFC run under the same conditions, 130 °C and oxygen at 4 atm [4], is shown in Fig. 1. At low current densities, i.e. at the activation overpotential region, the Nafion-based DMFC has a higher operating voltage. However, at high current densities, where both the mass-transport phenomenon and the membrane resistance are important, the voltages of both the DEGFC and DMFC based on NP-PCM are higher than that for Nafion-based DMFC. Both have similar membrane thickness. The open circles in the polarization curves are a short extrapolation we made in order to find the maximum power of the cell (our power supply was limited to 5 A). Fig. 2 depicts power density plots for the data in Fig. 1. It can be seen that the maximum power densities for Nafion-based DMFC, NP-PCM-based DEGFC and NP-PCM-based DMFC are 260, 300 and over 400  $\text{mW}/\text{cm}^2$ , respectively. The DEGFC was not optimized with respect to concentration and other test conditions, whereas more time was devoted to get the maximum power for the

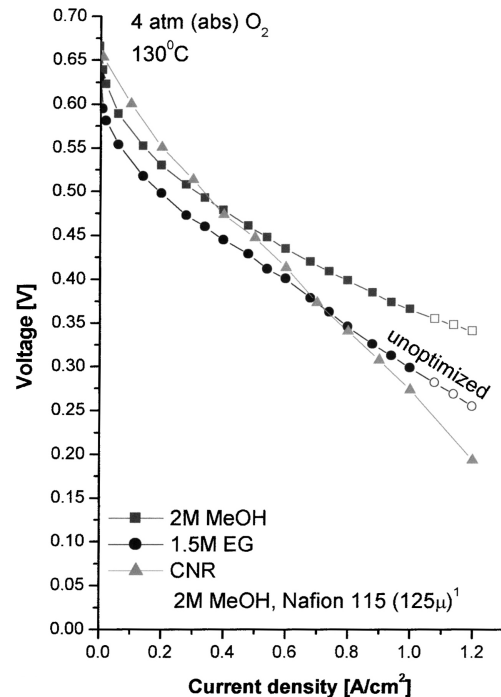


Fig. 1. Polarization curves for DMFC and DEGFC based on 100  $\mu\text{m}$  NP-PCM.

DMFC. The maximum power density obtained in the NP-PCM fuel cells is higher than that of the Nafion-based fuel cell under similar test conditions. We attributed this difference to the higher conductivity of the NP-PCM and its greater resistance to fuel permeation [17–20]. Higher power is expected when a thinner NP-PCM will be used. In

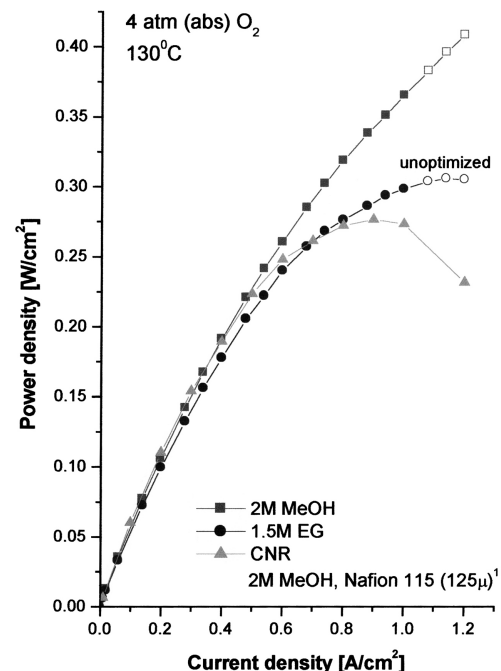


Fig. 2. Power density of DMFC and DEGFC based on 100  $\mu\text{m}$  NP-PCM.

addition, it is important to develop better catalysts for both EG and oxygen electrodes and to lower the crossover of EG and methanol. The high-power density already shown by these NP-PCM-based fuel cells and the possibility of obtaining higher values put them in direct competition with both Nafion-based DMFC and even with indirect methanol FC (reformat hydrogen fuel cells). The projected power density (on the stack basis) for both DEGFC and DMFC based on NP-PCM (at 130–150 °C) for transport applications is 1 kW/l (based on 0.2 W/cm<sup>2</sup> and 2 mm thick cells). This is close to that for hydrogen PEM FC. There are two disadvantages; in multicell stacks there will be a minor drop in efficiency due to shunt currents and the use of aqueous acid will require the use of corrosion-resistant materials for the peripheral systems. DMFC has some advantages over DEGFC, the theoretical capacity of methanol is 14% higher and so far it has about 10% higher operating voltage but about 10% lower fuel utilization. This makes the energy-conversion efficiency of both fuel cells roughly equal.

#### 4. Summary

The use of the NP-PCM in DOFCs offers several advantages over the Nafion-based DOFC, including lower membrane cost, lower fuel crossover, which leads to a much higher fuel utilization and higher conductivity. In this work we found that the 90 °C swelling of the NP-PCM is only 5–8% and that the diffusion constant of methanol at 80–130 °C is higher by a factor of 1.5–3 than that of EG. The maximum power density of methanol/oxygen and EG/oxygen FCs having a 100 µm thick NP-PCM is 400 and 300 mW/cm<sup>2</sup>, respectively, higher than the power density obtained from a DMFC based on Nafion 115 (260 mW/cm<sup>2</sup> [4]). This puts the DEGFC in direct competition with both DMFC and indirect methanol FC. EG is well known in the automobile industry and in contrast to methanol, its distribution infrastructure already exists, thus it is a promising candidate for practical electric vehicles.

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