

Progress in the development of a high-power, direct ethylene glycol fuel cell (DEGFC)

V. Livshits, E. Peled*

School of Chemistry, Tel-Aviv University, Tel Aviv 69978, Israel

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Abstract

We recently reported on a high-power nanoporous proton-conducting membrane (NP-PCM)-based direct methanol fuel cell (DMFC) operated with triflic acid. However, accompanying the advantages of methanol as a fuel, such as low cost and ease of handling and storage, are several pronounced disadvantages: toxicity, high flammability, low boiling point (65 °C) and the strong tendency to pass through the polymer-exchange membrane (high crossover). The focus of this work is the development of a high-power direct ethylene glycol fuel cell (DEGFC) based on the NP-PCM. Ethylene glycol (EG) has a theoretical capacity 17% higher than that of methanol in terms of Ah ml⁻¹ (4.8 and 4, respectively); this is especially important for portable electronic devices. It is also a safer (bp 198 °C) fuel for direct-oxidation fuel cell (DOFC) applications. Maximum power densities of 320 mW cm⁻² (at 0.32 V) at 130 °C have been achieved in the DEGFC fed with 0.72 M ethylene glycol in 1.7 M triflic acid at 3 atm at the anode and with dry air at 3.7 atm at the cathode. The cell platinum loading was 4 mg Pt cm⁻² on each electrode. The overpotentials at the cathodes and at the anodes of the DEGFC and DMFC were measured, compared and discussed.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising electrochemical power generators for a variety of applications. This liquid-feed system is relatively simple, compact and does not require any fuel processing unit. Therefore, great potential is foreseen in applications including transportation, decentralized power generation and, most importantly, portable devices [1–16]. We recently reported on a high-power (0.5 W cm⁻²) nanoporous proton-conducting membrane (NP-PCM)-based direct methanol fuel cell (DMFC) operated with triflic acid [17]. The use of the NP-PCM in the DMFC offers several advantages over the Nafion-based DMFC: much lower membrane cost, higher conductivity and lower fuel crossover. Its hydraulic water permeation is more than ten times that of Nafion 117 [18–22]. Therefore, the water flux through the NP-PCM is much smaller, leading to water-neutral operating conditions, to reduced cathode-catalyst flooding and to low relative humidity in

the cathode flow field, thus to a high oxygen partial pressure and to improved cell performance [17,22,23]. In addition, the use of the NP-PCM significantly reduces the need for oxidant humidification. The recirculation of the acid-based aqueous electrolyte, which seems to be the main drawback of the NP-PCM-based FC, is also one of its advantages, since, unlike Nafion, the electrolyte can be easily replaced in case of contamination or degradation.

Up to now, methanol has been found to be the best fuel for DOFCs. However methanol is toxic, highly flammable and has a tendency to pass through the fuel-cell membrane. As a result, in a Nafion-based DMFC, it must be diluted to a concentration of 3–6% before being fed into the cell. Therefore finding alternative fuels to MeOH is very important. To replace MeOH in DOFCs, one must look for a fuel with the following characteristics: low to no toxicity, safe handling, and high energy density. Moreover, an appropriate fuel would be one that is oxidized completely to CO₂ with few or no by-products, has a high boiling point (to be used at $T > 100$ °C at near ambient pressure) and should be commercially available and inexpensive. Ethylene glycol (EG) complies favorably with these requirements. EG has a theoretical capacity 17% higher than that of methanol in terms of Ah ml⁻¹ (4.8 and 4, respectively) which is especially important for portable

* Corresponding author. Tel.: +972 3 640 8438; fax: +972 3 641 4126.
E-mail address: peled@post.tau.ac.il (E. Peled).

electronic devices. It is a more efficient [20,22] and safer (bp 198 °C) fuel for DOFC applications. Vielstich et al. studied the electrocatalysis of ethylene glycol oxidation in acidic solution [24] and included a very good summary of previous publications in this area. They found that on a Pt–Ru catalyst, CO₂, glycolic acid and possibly oxalic acid are formed in parallel reactions. The catalytic activity increases with the Ru content, but the complete oxidation of EG to CO₂ is favored by a high Pt content. Recently, a study of the electro-oxidation of a series of polyhydric alcohols in three different electrolytes (H₂SO₄, KOH, and K₂CO₃) on a platinum electrode was reported by Ogumi et al. [25]. EG showed the highest reactivity of all the polyhydric alcohols studied and low activity decay in alkaline solutions. Very low EG oxidation to CO₂ (6%) was measured at room temperature with the use of a flow cell [26]. The reasons for these low values is the use of a flow cell at room temperature where the EG intermediates are flushed away from the electrodes. As opposed to this, we reported on very high EG fuel utilization (over 95%) as measured in a DEGFC at 80 °C and on up to three times lower crossover current density than that for methanol [20,21]. A DEGFC based on a homemade NP-PCM and fed by a sulfuric acid-fuel solution and by dry oxygen delivered 300 mW cm⁻² at 130 °C [21]. In this paper we report on progress in the development of a DEGFC and we present comparative performance analyses of a single DEGFC and a DMFC based on NP-PCM. Maximum power densities of 80, 285 and 320 mW cm⁻² have been achieved in a 5 cm² NP-PCM-based DEGFC under dry-air feed at 80, 110 and 130 °C, respectively.

2. Experimental

The FC setup described previously [17–21] was used here. The test vehicle was a 5 cm² DOFC. The fuel-cell housing was built from synthetic graphite blocks (Poco Inc.), in which serpentine flow fields were engraved. The composition of the nanoporous proton-conducting membrane (NP-PCM) was 28% (v/v) poly(vinylidenedifluoride) (PVDF), 12% SiO₂, and 60% liquid volume (that is filled with an acid-fuel solution). It was produced on a semi-industrial coater (Dixon) at a rate of 15 m² h⁻¹ (IPRC). The thickness of the NP-PCM was 70–100 μm. At 130 °C, the conductivity of the NP-PCM was 0.15 S cm⁻¹ for the homemade membrane with 3 M sulfuric acid and 0.17 S cm⁻¹ for the machine-made membrane with 1.7 M triflic acid [17]. The anode ink was prepared from unsupported Pt–Ru (1:1 atomic) nanopowder (Johnson Matthey) and spread over unteflonated Toray paper (loading was 4–5 mg Pt cm⁻²). An E-TEK cathode with 4 mg Pt cm⁻² was used. The membrane-electrode assembly (MEA) was hot-pressed at 100 °C at a pressure of 24–56 kg cm⁻².

A solution of 1 M methanol or 0.72 M ethylene glycol and 1.7 M triflic acid or 0.5 M ethylene glycol and 2 M sulfuric acid was circulated over the anode at 0–3 atm (g.) and at 5 ml min⁻¹, and dry air at 0–3.7 atm (g.) was fed to the cathode. Cell resistance was measured with a Solartron 1260. Cells were tested with a Maccor model series 4000 battery tester. Anode potentials were measured vs. reference hydrogen electrode (RHE). Similar to a regular FC, graphite blocks-based fuel cell, in which

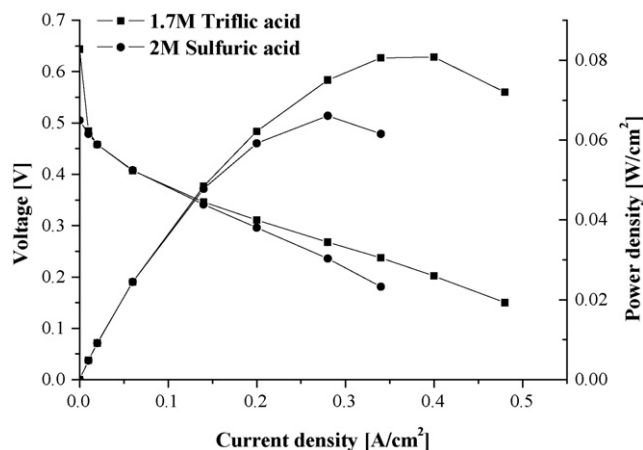


Fig. 1. Effect of the type of acid on the performance of the DEGFC at 80 °C. 0.5 M EG, ambient air and electrolyte pressures, 100 μm NP-PCM, 4 mg Pt cm⁻² on each electrode.

standard Pt-based MEA was constructed, was used as the RHE. The RHE was connected to the fuel solution/electrolyte feeding pipe between the fuel solution/electrolyte tank and the fuel cell, i.e. the same electrolyte flowed through one side of the RHE and the anode compartment of the fuel cell. Pure hydrogen was fed to the opposite side of the RHE. Thus, the potential measured between the fuel cell anode and the hydrogen side of the RHE was taken as the anodic overpotential (η_a). As the E^0 values for methanol and ethylene glycol are very close to the RHE potential (20 and 10 mV, respectively [24,27]), we considered the potentials measured *versus* RHE as the methanol or ethylene glycol electrode overpotentials with no further correction. The cathodic overpotential was calculated according to Eq. (1):

$$\eta_c = E^0 - E_{\text{cell}} - \eta_a(-IR) \quad (1)$$

3. Results and discussion

We recently reported on the replacement of sulfuric acid by triflic acid and the use of a higher quality nanoporous proton-conducting membrane (NP-PCM) in our DMFCs [17]. This led to an increase in DMFC power by up to 250% (up to 0.5 W cm⁻² at 130 °C) and to a decrease in both anodic and cathodic overpotentials [17]. It was found [28] that bisulfate adsorbs most strongly on the 1 1 1 planes of platinum and this leads to the decrease in its catalytic activity; triflic acid does not behave in this way [28,29].

In this paper, we report on the progress achieved in the direct ethylene glycol fuel cell (DEGFC) by the implementation of the abovementioned modifications and we compare the electrode characteristics of the DEGFC with those of the DMFC. Fig. 1 shows the effect of the type of the acid on the performance of the DEGFC at 80 °C. A higher OCV (0.64 V *versus* 0.51 V), higher potentials under load (0.26 V *versus* 0.22 V at 0.3 A cm⁻²) and a higher maximum power (0.081 W cm⁻² *versus* 0.066 W cm⁻²) were measured in the triflic acid-based cell. At low current densities, both cells have the same voltage, but at current densities higher than about 0.15 A cm⁻², the voltage of the triflic acid-based cell is higher. The reasons for this differ-

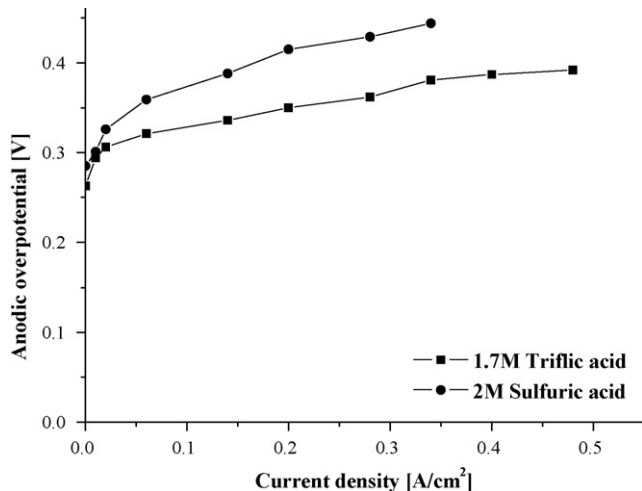


Fig. 2. Effect of the type of acid on the anodic overpotential of the DEGFC at 80 °C. 0.5 M EG, ambient air and electrolyte pressures, 100 μm NP-PCM, 4 mg Pt cm^{-2} on each electrode.

ence become clear upon examination of Figs. 2 and 3. At 80 °C and at low current densities (about 10 mA cm^{-2}), the overpotential values measured at both the anode and the cathode are the same for both acids. At higher current densities, the replacement of sulfuric acid by triflic acid results in a pronounced decrease in the anodic overpotential; at the cathode, no beneficial effect was obtained. At 0.34 A cm^{-2} the anodic overpotential drops from 0.44 to 0.38 V. This phenomenon is in agreement with the difference in adsorption of triflic and sulfuric acids on the Pt catalyst. In addition, it was found that the cathodic overpotential is greater than the anodic overpotential in both types of cells. In other words, the voltage loss at the cathode is higher than that at the anode at all current densities. This can be explained by some kind of poisoning of the air electrode catalyst by EG that crosses over to the cathode side and by its partially oxidized species (adsorbed on the platinum nanoparticles). As we see later, this poisoning is lessened by raising the temperature of operation. Fig. 4 depicts triflic acid-based DEGFC performance at several temperatures: 65 and 80 °C (at 0.9 atm dry air), 110 and 130 °C (at 3.7 atm dry air). Maximum power densities of 45, 80, 285 and 320 mW cm^{-2} , respectively, have been achieved, under these conditions. In terms of power per gram Pt (at the anode) the values are 16, 57 and 64 W g^{-1} at 80, 110 and 130 °C, respectively. These values are close to those for the DMFC. Platinum loading could be reduced by using carbon-supported catalysts and a more active catalyst which will be tailored to the electro-oxidation of EG. At 0.28 A cm^{-2} , the operating voltage rises from 0.15 V at 65 °C to 0.5 V at 110 and 130 °C. The current density at maximum power also increases with temperature. It is 0.2, 0.4, 0.8 and 1.05 A cm^{-2} at 65, 80, 110 and 130 °C, respectively. It is interesting to note that raising the temperature from 110 to 130 °C resulted in little gain in performance especially up to 0.6 A cm^{-2} . This temperature effect on performance is explained by the faster oxygen-reduction and EG-oxidation reaction kinetics at elevated temperatures and also by a lessening in the poisoning of the Pt catalyst of the oxygen electrode by EG that crosses over to the cathode side and by its partially oxidized species. The same explanation holds for the fact that the OCV at 110 and 130 °C is higher than that at 65–80 °C. The voltage drop on the membrane is relatively small, as the cell resistance (for both cells) is lower than 0.08 and 0.07 Ωcm^2 at 110 and 130 °C, respectively. This is a unique feature of the NP-PCM, since for PEMs, the resistance of the membrane rises with temperature over this temperature range [30].

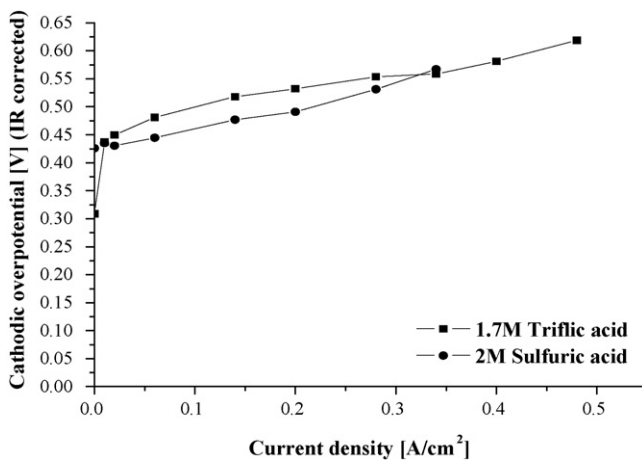


Fig. 3. Effect of the type of acid on the cathodic overpotential of the DEGFC at 80 °C. 0.5 M EG, ambient air and electrolyte pressures, 100 μm NP-PCM, 4 mg Pt cm^{-2} on each electrode.

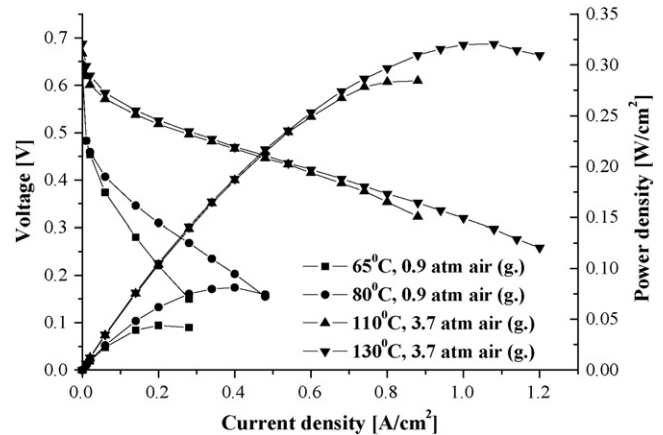


Fig. 4. NP-PCM-based DEGFC performance at 65–130 °C. Eighty-five micrometer NP-PCM, 0.72 M EG, 1.7 M triflic acid, no air humidification, 4 mg Pt cm^{-2} on each electrode. Operating pressure: 0.9–3.7 atm (g.) at the cathode and 0–3 atm (g.) at the anode.

performance at several temperatures: 65 and 80 °C (at 0.9 atm dry air), 110 and 130 °C (at 3.7 atm dry air). Maximum power densities of 45, 80, 285 and 320 mW cm^{-2} , respectively, have been achieved, under these conditions. In terms of power per gram Pt (at the anode) the values are 16, 57 and 64 W g^{-1} at 80, 110 and 130 °C, respectively. These values are close to those for the DMFC. Platinum loading could be reduced by using carbon-supported catalysts and a more active catalyst which will be tailored to the electro-oxidation of EG. At 0.28 A cm^{-2} , the operating voltage rises from 0.15 V at 65 °C to 0.5 V at 110 and 130 °C. The current density at maximum power also increases with temperature. It is 0.2, 0.4, 0.8 and 1.05 A cm^{-2} at 65, 80, 110 and 130 °C, respectively. It is interesting to note that raising the temperature from 110 to 130 °C resulted in little gain in performance especially up to 0.6 A cm^{-2} . This temperature effect on performance is explained by the faster oxygen-reduction and EG-oxidation reaction kinetics at elevated temperatures and also by a lessening in the poisoning of the Pt catalyst of the oxygen electrode by EG that crosses over to the cathode side and by its partially oxidized species. The same explanation holds for the fact that the OCV at 110 and 130 °C is higher than that at 65–80 °C. The voltage drop on the membrane is relatively small, as the cell resistance (for both cells) is lower than 0.08 and 0.07 Ωcm^2 at 110 and 130 °C, respectively. This is a unique feature of the NP-PCM, since for PEMs, the resistance of the membrane rises with temperature over this temperature range [30].

In spite of the fact that the performance achieved with DEGFC is among the highest in the literature for direct oxidation fuel cells, there is still a gap between it and the performance of a DMFC based on NP-PCM. This gap is a result of the greater potential losses at both the anode and the cathode (Figs. 5 and 6). The major potential loss was measured at 80 °C for the cathode of the DEGFC. At 0.48 A cm^{-2} it is 0.62 V in the DEGFC and only 0.42 V in the DMFC. Raising the operating temperature of the DEGFC from 80 to 110 °C resulted in significant improvement in the performance of both electrodes. The improvement is more pronounced for the air electrode (Fig. 6).

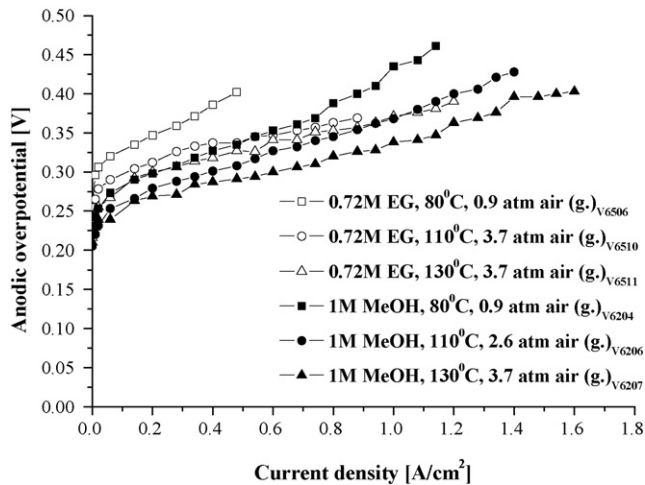


Fig. 5. Comparison of anodic overpotentials for NP-PCM-based DMFC and DEGFC at 80–130 °C. Operating pressure: 0.9–3.7 atm (g.) at the cathode and 0–3 atm (g.) at the anode.

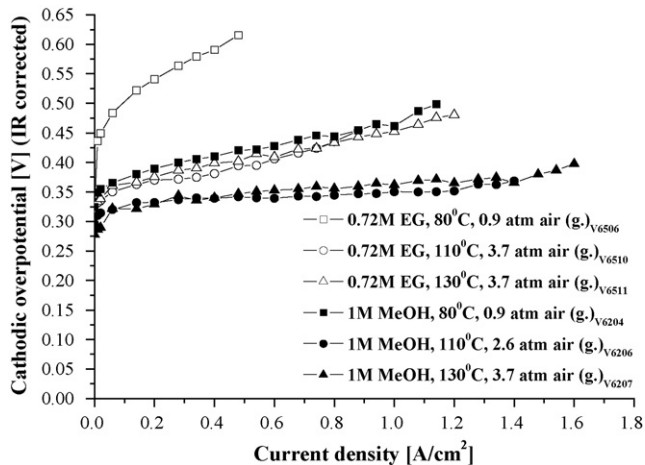


Fig. 6. Comparison of cathodic overpotentials for NP-PCM-based DMFC and DEGFC at 80–130 °C. Operating pressure: 0.9–3.7 atm (g.) at the cathode and 0–3 atm (g.) at the anode.

The cathode overvoltage at 0.48 A cm^{-2} dropped from 0.62 V at 80 °C to 0.39 V at 110 °C. At the anode, the relevant voltage drop is from 0.41 to 0.33 V (Fig. 5). At all temperatures and current densities, the voltage losses at the air electrode are larger than those at the EG electrode. At 110 and 130 °C, the difference between the voltage losses at the anode of the DEGFC and at the anode of the DMFC is typically smaller than 50 mV, while at the cathode the voltage-loss difference increases from about 50 mV at low current densities to over 100 mV at high current densities. This indicates that the poisoning caused by methanol and its oxidized species at the cathode is less severe than the poisoning caused by EG and its oxidized species.

4. Summary

In this paper we report on progress in the development of the DEGFC and we present a comparative performance analy-

sis of a single DEGFC and a DMFC, both based on NP-PCM. Maximum power densities of 80, 285 and 320 mW cm^{-2} have been achieved in a 5 cm^2 NP-PCM-based DEGFC under dry-air feed at 80, 110 and 130 °C, respectively. Raising the operating temperature of the DEGFC from 80 to 110 °C resulted in a significant improvement in the performance of both anode and cathode. The improvement is more pronounced for the air electrode and is explained by a lower level of poisoning of the Pt catalyst by EG and its oxidized species. Poisoning of the cathode by EG and its oxidized species is more severe than that caused by methanol and its oxidized species.

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