Water-neutral micro direct-methanol fuel cell (DMFC) for portable applications

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Abstract

Water loss and water recycling in direct-methanol fuel cells (DMFCs) is a major issue that affects the complexity, volume and weight of the system and becomes of greater concern as the size of the DMFC decreases. Flat micro DMFCs were built in a plastic housing with a water-management system that controls the flux of liquid-water through the membrane and the loss of water during operation. These cells contain a nanoporous proton-conducting membrane (NP-PCM). Methanol consumption and water loss were measured during operation in static air at room temperature for up to 900 h. Water flux through the membrane varied from negative, through zero, to positive values as a function of the thickness and the properties of the water-management system. The loss of water molecules (to the air) per molecule of methanol consumed in the cell reaction (defined as the *W* factor) varied from 0.5 to 7. When *W* equals 2 (water flux through the membrane equals zero) there is no need to add water to the DMFC and the cell is operating under water-neutral conditions. When *W* is smaller than 2, water must be removed from the cell and when it is larger than 2, water must be added. The cell showed stable operation up to 900 h and its maximum power was 12.5 mW/cm^2.
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1. Introduction

The growing demand for power and energy for portable devices such as cellular phones, PDAs, portable computers, etc. on the one hand and the limited energy density of the Li-ion batteries on the other, makes the direct-methanol fuel cell (DMFC) an attractive candidate [1–10] for powering these devices. We have recently reported on the development of a novel nanoporous proton-conducting membrane (NP-PCM) and a direct-methanol fuel cell based on this membrane [11–14]. This membrane has several advantages over the commercial Nafion membrane—lower cost, higher conductivity and lower fuel crossover. Crossover current density for Nafion 117 at 20 °C was found to be 40 mA/cm^2 [15].

A major problem in the use of micro DMFCs is the loss of water due to electromigration of water from the anode side to the cathode side. Water osmotic drag is about three molecules of water at 20 °C and up to 3–4.5 at 100 °C [16,17] for each proton passing the membrane. Most of this water exits the cathode in the form of small droplets [17] and some water evaporates. If all the electromigrated water

would exit the cathode, then for each gram of methanol consumed in the cell reaction, about 10 g of water would have to be added to the fuel tank or to the anode compartment. In continuous operation of a DMFC, a large tank of water or some kind of condenser and mechanical pump for recycling the water from the cathode back to the anode compartment or to the water tank must be used. Both solutions would add to the complexity, to the volume and to the weight of the system.

In this report, we describe a novel way of managing the water loss from the DMFC and the water flux through the PCM (recycling of liquid-water) in a flat micro DMFC (based on a nano nonporous proton-conducting membrane). This solution does not require pumps or mechanical recycling systems. It is possible to control the water flux through the membrane from negative through zero and up to positive values and to reach water-neutral operating conditions.

2. Experimental

The flat fuel-cell housing (including the fuel tank) was made of 3–6 mm plastic. The membrane used in these cells was made of PVDF (Elf Atochem), nanopowder SiO$_2$

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(Degussa), its porosity was about 50% and its thickness was 250–300 μm [11,12]. The cathode ink was made by mixing 75 wt.% Pt catalysts "Johnson–Matthey" nanopowder, 15 wt.% Nafion and 10 wt.% carbon powder. The ink was applied directly on the membrane. The cathodic catalyst loading was between 4 and 7 mg/cm^2. The anodic-catalyst (Pt-Ru 1:1 "Johnson–Matthey") loading was between 5 and 7 mg/cm^2. The anodic ink was applied on a Toray paper. Water flux through the PCM was managed by the use of a liquid-water leak-proof system, it consists of several sub layers placed on both side of the cathode current collector. The material for the hydrophobic liquid-water leak-proof layer is a paste that consists of 20–50% (w/w) PVDF or Teflon, carbon powders such as: Black Pearl 2000, XC 72 and Shawingan black. Using a plastic knife, the paste is inserted into the pores of the wet proofed Toray paper to form a layer inside the Toray paper, close to its surface. Several such paste insertions are made. Up to 5–7 layers of leak-proof material are needed in order to receive a uniform coating of 20–50 μm thick. After a satisfactory morphology is reached, the Toray paper with the leak-proof material is cured at 150–250 °C for 0.5–2 h. The hydrophobic embedded liquid-water leak-proof layer is free of pores or cracks larger than 0.5 μm, thus it restricts the leak of liquid-water.

The MEA was hot-pressed at 80–100 °C for 1 min. The MEA (6 cm^2) was glued to the plastic housing and the tank was filed with 2 M H_2SO_4 and 1–6 M methanol. All cells were operated at room temperature (20–25 °C).

3. Results and discussion

Fig. 1 shows a typical polarization curve for this 6 cm^2 flat plastic cell operating with a water-management system at room temperature under normal breathing conditions (no forced air). The cell reached a maximum power of 12.5 mW/cm^2. The hydraulic pressure that developed in the cathodic catalyst layer forced some or most of the liquid-water that

had formed there or had reached it by electro-migration, to the anode side. This process depends on the properties, the number of sub-layers and the thickness of the liquid-water barrier layer. The water flux and water loss were measured for several cells with different liquid-water barrier layers. We define a factor "*W*" as the ratio between the moles of water lost from the cell (to the air) to moles of fuel consumed. In the case of methanol, the net reaction in the fuel cell is:

$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$$
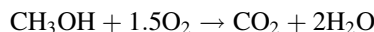
The desired value for *W* is 2 (i.e. the stochiometric number for water), which means that only the water formed by oxidation of the methanol exits the cathode to the air and thus there is no need to add water to the anode side. In this case, the net water flux equals zero. These are called water-neutral test conditions. For *W* > 2, it was necessary to add water to the anode compartment since the cell loses more water (probably due to electromigration) than is formed by oxidation of the fuel. For *W* < 2 (a negative water flux), water had to be removed from the cell since both the water formed by oxidation and the water reaching the cathode by electromigration are cycled back to the anode compartment. We tested (at constant voltage) several sets of cells with full or partial water-management and without it. Each cell was weighed before and after operation. The amount of methanol consumed was calculated from the charge passed through the cell including an estimate for crossover current. "*W*" was calculated after a weight balance was made that included weight loss due to the evolution of CO_2 and weight gain due to O_2 absorption. For cells without a water-management system, the typical value for *W* was in the range of 5–7, while for cells having it we measured values between 2 and 0.5. It was possible to observe the rising water level in the fuel tank in cells which exhibited *W* = 0.5.

Two DMFCs were operated for 144 h. The first cell contained a full water management where the water evolved at the cathode as a result of electromigration is cycled back
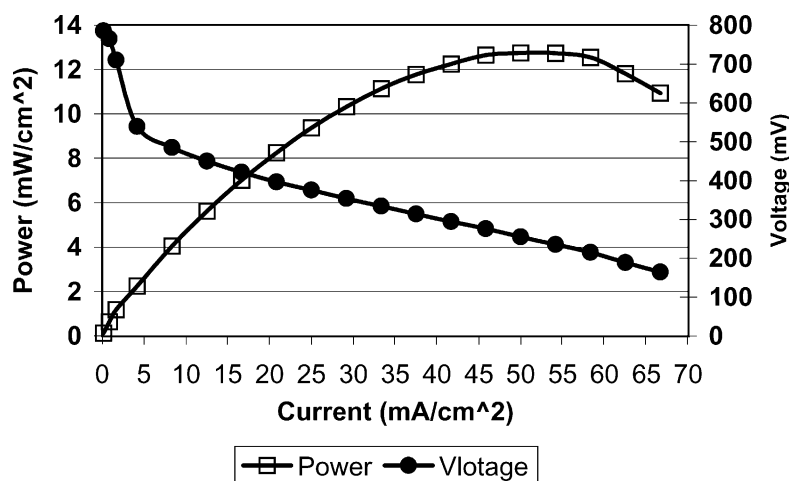

Fig. 1. Polarization curve for a 6 cm^2 cell, at room temperature, static air.
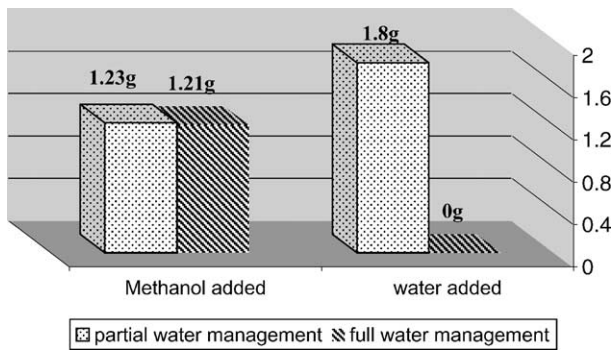
Fig. 2. Water and methanol consumption in two types of cells.

Fig. 4. Crossover current density vs. applied potential at different fuel concentrations.

into the fuel tank without any pumps or other mechanical means. The second cell was fitted with a partial water-management system. Methanol was added to both cells as needed according to the charge delivered by the cells (taking into account the crossover current). Water was added to both cells whenever needed, i.e. whenever a water loss was detected. Fig. 2 compares the water and fuel consumption for both cells after 144 h of operation. The cell with partial water management consumed 1.21 g of methanol and 1.8 g of water while the cell with full water management consumed 1.23 g of methanol and no water had to be added to the fuel tank—the water remained at its original level. In this case, the loss of water equals its formation in the cell reaction and the net water flux in the membrane equals zero.

Another set of DMFCs with partial or no water management was operated continuously for 900 h. They were refueled (typically three times a day) to compensate for methanol consumption. Both cells consumed about 13.5 g of methanol. To the cell having a partial water-management system, 2.6 g of water was added and to the one without it, 38 g of water was needed. Fig. 3 depicts the current versus time of operation at constant cell voltage measured immediately after the addition of methanol. As can be seen, there are some fluctuations in the current (probably due to variation in methanol concentration) but the average current is steady and there is no permanent degradation over 900 h.

Crossover tests were carried at methanol concentrations between 1 and 6 M. Negative potentials of 0.6–1.1 V were applied to the cell (minus on the anode) and the current was recorded. The measurements shown in Fig. 4 were taken after the current was stabilized (typically 5 min). Fig. 4 shows plots of crossover-current density as a function of the
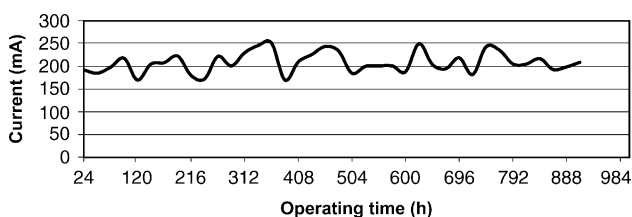
applied voltage for different fuel concentrations. The maximum crossover-current density was obtained at a voltage of 0.9 V. Fig. 5 shows the dependence of the crossover-current density, measured at 0.9 V, on methanol concentrations (between 1 and 6 M). The crossover currents at 0.9 V show a linear dependence on concentration, starting from about 2.5 mA/cm^2 for 1 M of methanol up to 26 mA/cm^2 for 6 M.

Fuel utilization was measured for 1 M methanol by running cell at constant voltage until the current dropped to about zero. 0.13 ml methanol fed into the cell (equivalent to 510 mAh) and the cell delivered 470 mAh it means fuel utilization of 92%.

Fig. 6 shows a hybrid power pack consisting of a series of three flat micro fuel cells connected in series to a dc-to-dc converter. The fuel cells, via the dc-to-dc converter, supply power both for holding the phone in stand-by mode and for charging a miniature lithium-ion battery. When the phone is switched to talk mode, the supplementary power needed is supplied from the lithium-ion battery and when switched back to stand-by mode, the battery is recharged. In portable applications the acid–fuel solution in the anode compartment will be immobilized by a gel.

On the basis of the results of crossover tests (5 mA/cm^2 for NP-PCM at 1.5 M methanol) and fuel utilization, we performed a simulation for the energy and the methanol consumed by a cellular phone. We assumed that the phone operates for 16 h a day, part of the time in talk mode and the rest of the time in stand-by mode and it is refueled by a 10 ml methanol cartridge. The average power consumption for talk mode was taken as 650 and 12 mW for stand-by. The dc-to-dc efficiency was taken as 0.8.

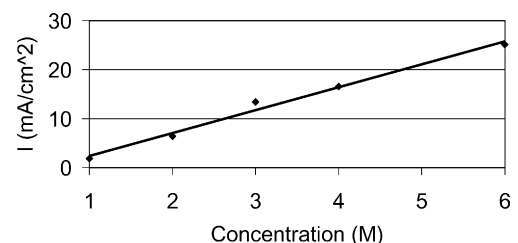Fig. 3. Cell's current at constant voltage as a function of operating time.

Fig. 5. Crossover current density vs. methanol concentration (M) at 0.9 V.

Table 1
Fuel consumption for NP-PCM based DMFCs powered cellular phone at various talk times

Talk time per day (min)	Methanol utilization (ml per day)	Cartridge capacity (ml)	Time between refuelling (days)	Total talk time (h)	Total STB time (h)
75	1.25	10	8	10	642
165	2.3	10	4.3	11.8	642

Fig. 6. Cellular phone powered by hybrid fuel cells.

Table 1 depicts the intervals between 10 ml methanol refueling of our cell in a cellular phone for several durations of talk time. As can be seen, for 75 min per day of talk time, the fuel cell has to be refueled every 8 days and for 165 min per day of talk time it has to be refueled every 4.3 days. Due to the low crossover current a 10 ml methanol cartridge is expected to supply 642 h of stand-by mode. Cells based on PEM having larger crossover have to be fueled more often.

4. Summary

Water loss (to the air) and water flux in the PCM was controlled by a water-management system that consists of several liquid-water barrier layers. W (water molecules lost per molecule of methanol consumed in the cell reaction) was reduced from 7 to 2 and even down to 0.5. When W equals 2 (water flux through the PCM equals zero) there is no need to add water to the DMFC and the cell is operating under water-neutral conditions. When W is smaller than 2, water must be removed and when it is larger than 2, water must be added to the cell. The cell exhibited stable operation up to 900 h and its maximum power was 12.5 mW/cm^2. Fuel utilization of 90–95% was measured for 1 M methanol.

References

[1] S.R. Narayanan, T. Valdez, N. Rohatgi, J. Christiansen, W. Chun, G. Voecks, G. Halpert, in: S. Gottesfeld, T.F. Fuller (Eds.), Proton Conducting Membrane Fuel Cells II, The Electrochemical Society Proceedings Series, vol. PV 98-27, Pennington, NJ, 1999, p. 316.

[2] S.R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M. Smart, S. Surampudi, G. Halpert, in: S. Gottesfeld, G. Halpert, A. Langrebe (Eds.), Proton Conducting Fuel Cells I, The Electrochemical Society Proceedings Series, vol. PV 95-23, Pennington, NJ, 1995, p. 261.

[3] S.R. Narayanan, W. Chun, T.I. Valdez, B. Jeffries-Nakamura, H. Frank, S. Surumpudi, G. Halpert, J. Kosek, C. Cropley, A.B. La Conti, M. Smart, Q.J. Wang, G.S. Prakash, G. Olah, in: Recent Advances in High-Performance Direct-Methanol Fuel Cells, 1996, NASA JPL web site: http://techreports.jpl.nasa.gov/jpltrs.cgi?fuel+cell.

[4] G. Halpert, S. Surampudi, S. Narayanan, H. Frank, A. Kindler, T. Valdez, in: Proceedings of the Paper Presentation at the Windsor Workshop on Transportation Fuels, Windsor, Ont., Canada, 10 June 1997, NASA JPL web site: http://techreports.jpl.nasa.gov/jpltrs.cgi?-fuel+cell.

[5] S. Gottesfeld, T.A. Zawodzinski, in: R.C. Alkire, H. Gerischer, D.M. Kolb, C.W. Tobias (Eds.), Advances in Electrochemical Science and Engineering, Wiley, New York, 1997, p. 197.

[6] S.C. Thomas, X. Ren, S. Gottesfeld, in: S. Gottesfeld and T.F. Fuller (Ed.), Proton Conducting Membrane Fuel Cells II, The Electrochemical Society Proceedings Series, vol. PV 98-27, Pennington, NJ, 1999, p. 327.

[7] K. Scott, P. Argyropoulos, K. Sundmacher, J. Electroanal. Chem. 97 (1999) 477.

[8] K. Scott, W.M. Taama, P. Argyropoulos, K. Sundmacher, J. Power Sources 83 (1999) 204.

[9] O. Savadogo, New Mater. Electrochem. Syst. 1 (1998) 47.

[10] S.J. Warthesen, D.A. Shores, in: Proceedings of the Extended Abstracts of the 3rd International Symposium on New Materials for Electrochemical Systems, Montreal, Canada, 4–8 July 1999.

[11] E. Peled, T. Duvdevani, A. Aharon, A. Melman, Electrochem. Solid-State Lett. 12 (2000) 525.

[12] E. Peled, V. Livshits, T. Duvdevani, J. Power Sources 106 (2002) 245.

[13] E. Peled, T. Duvdevani, A. Melman, in: Proceedings of the Second International Symposium on Proton Conducting Membrane Fuel Cells II, The Electrochemical Society, Pennington, NJ, USA, 1999, p. 66.

[14] E. Peled, T. Duvdevani, A. Melman, Electrochem. Solid-State Lett. 5 (1998) 210.

[15] S.R. Narayanan, in: Proceedings of the DOE/ONR Fuel Cell Workshop, 1999, JPL web site: http://www.lanl.gov/energy/est/transportation/trans/pdfs/workshop/narayanan.pdf.

[16] T.A. Zawodzinski, C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 1041.

[17] X. Ren, S. Gottesfeld, J. Electrochem. Soc. 148 (2001) 87.