

Short communication

A novel PTFE-based proton-conductive membrane

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Available online 29 June 2005

Abstract

The demand for a solid polymer electrolyte membrane (SPEM) for fuel-cell systems, capable of withstanding temperatures above 130 °C, decreasing the electrode-catalyst loadings and reducing poisoning by carbon monoxide, has prompted this study. A novel, low-cost, highly conductive, nanoporous proton-conducting membrane (NP-PCM) based on a polytetrafluoroethylene (PTFE) backbone has been developed. It comprises non-conductive nano-size ceramic powder, PTFE binder and an aqueous acid. The preparation procedures were studied and the membrane was characterized with the use of: SEM, EDS, pore-size-distribution measurements (PSD), TGA–DTA and electrochemical methods. The ionic conductivity of a membrane doped with 3 M sulfuric acid increases with the ceramic powder content and reaches 0.22 S cm⁻¹ at 50% (v/v) silica. A non-optimized direct-methanol fuel cell (DMFC) with a 250 μm thick membrane has been assembled. It demonstrated 50 and 130 mW cm⁻² at 80 and 130 °C, respectively. Future study will be directed to improving the membrane-preparation process, getting thinner membranes and using this membrane in a hydrogen-fed fuel cell.

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Keywords: PCM; MEA; PTFE; Fuel cell; Membrane

1. Introduction

The proton-conducting membrane (PCM) is the key component in PCM-based fuel cells. One of the major problems with perfluorosulfonic acid (PFSA) membranes has been and still remains, to present day, their high cost (US\$ ~700 m⁻²). The high cost of PFSA membranes is due to the expensive fluorination step and lengthy preparation required in their making, thus creating an incentive for developing other types of PCMs [1]. Nafion[®], the most commonly used PFSA membrane and by far the most studied proton-conducting electrolyte, operates in fuel cells at near-room temperature (up to 80 °C). Nafion[®] membranes present poor barrier properties to methanol; allowing methanol crossover from the anode to the cathode in direct methanol fuel cells (DMFC). It also has high osmotic drag, which makes water management at high current densities difficult [2].

High-temperature operation (above 130 °C) of a SPEM fuel cell has been investigated [3–6] with a view to reducing the effects of carbon monoxide adsorption on the platinum electrocatalyst (carbon monoxide poisoning). In addition to increasing the tolerable carbon monoxide concentration in the anode fuel, higher-temperature operation can improve thermal management and heat utilization of the fuel-cell stack (possible use of co-generated heat), increase reaction rates at the anode and cathode (lower Pt loading), simplify fuel-cell water management [7,8] and in DMFCs, improve the kinetics of the methanol-oxidation reaction at the anode. However, low membrane hydration leads to large ohmic losses, which lower operating voltage, power, and efficiency at a given current. As a result, dehydration at higher temperatures could potentially offset any of the performance benefits mentioned above.

During the past decade, there has been an intensive effort to develop a low-cost SPEM to replace perfluorinated ionomer membranes, i.e. Nafion[®] [9]. Significant progress has been made and has stimulated a variety of approaches in the development of new and alternative polymeric membranes: perfluorinated ionomer composite,

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partially perfluorinated ionomer, partially perfluorinated ionomer composite, non-perfluorinated ionomer and non-perfluorinated composite membranes [10]. We have recently reported on the development of a novel nanoporous proton-conducting membrane (NP-PCM), which consists of ceramic powder, polymer binder and aqueous acid and on a direct-methanol fuel cell and direct-ethylene glycol fuel cell based on this membrane [11–14]. The NP-PCM has several advantages over the commercial Nafion[®] membrane: lower cost, higher conductivity, higher water permeation under hydraulic pressure and lower fuel crossover. The rapid water permeation also enables the use of a liquid–water barrier layer for internal water recycling, thus avoiding the necessity of a water-recycling pump [14,15]. It also reduces the relative humidity of the air (oxygen) that exits the cathode. As none of the previously reported membranes demonstrated a sufficiently long operating life at above 130 °C we decided to use the most stable polymer, i.e. PTFE, as the binder in the NP-PCM.

The objective of this work was to prepare and characterize a PTFE-based NP-PCM that would be more durable at elevated temperatures (≥ 130 °C). This preliminary characterization is achieved with the use of several techniques including: pore-size distribution (PSD), scanning electron microscopy (SEM), TGA–DTA and electrochemical measurements. The membrane consists, basically, of a nano-size inorganic ceramic powder with good acid-adsorption capacity, a polymer binder and an acid solution that fills the nano-size pores.

2. Experimental

PTFE-based NP-PCMs were formed incorporating, primarily, a drying, baking, rolling and sintering process. A viscous paste was formed by mixing a high-surface-area (consisting of nano-size particles) inorganic, electronically nonconductive powder having good acid-adsorption capacity with PTFE as a polymer binder and a solvent mixture. PTFE (Teflon[®] 30 by DuPont) was introduced in the form of a dispersion, which was a hydrophobic and negatively charged colloid, containing particles of 0.22 μm diameter suspended in water [16].

The membrane is not directly produced in the final thickness and width. Rather, it is made upon becoming a homogeneous mixture followed by calendaring and sintering. The PTFE-based NP-PCM can be reproduced in thicknesses ranging from 250 to 1000 μm , depending on the desired thickness needed. Following sintering, the film was doped with the acid by immersion. Using the given procedure, we prepared PTFE-based NP-PCMs with the following nano-size powders: amorphous fumed silicon dioxide—12 nm particle size, 99.8% (Aerosil 200[®], Degussa), 15 nm particle size, 99.8% (Alfa Aesar, Johnson–Matthey) and 16 nm particle size, 99.8% (Aerosil 130[®], Degussa). Typical solvents examined were: acetone, petroleum ether, cyclopentanone, isobutanol

and isopropanol. The volume fraction of the ceramic powder ranges between 5 and 50%. The best solvent mixture found in this work is isopropanol–water. A less viscous and more homogenous paste is achieved as the ratio of solvent mixture to polymer binder is increased.

The ionic conductivity of the PCM, held between two gold-plated electrodes (1 cm^2), was measured at room temperature (25 ± 3 °C) with the use of a Solartron model SF 1260 AC analyzer (four-point measurement). Before these measurements, samples of the membrane were immersed in a 3 M aqueous solution of sulfuric acid for 1 h at 70 °C.

The porosity of the PTFE-based NP-PCM was calculated by dividing the volume of pores, determined by the difference between the volume of the membrane and the sum of the volumes of its solid components, by the volume of the membrane. The porosity influences other parameters, such as conductivity, mechanical strength and permeability of the membrane to solvents.

The volume fraction of water in the saturated PCM was calculated by dividing the difference between the weight of the wet (saturated) membrane and the weight of the dry (dehydrated) membrane by its volume.

Since water does not penetrate neither the closed nor the hydrophobic pores the result obtained is a measure of the volume of the hydrophilic, “open”, pores. Samples were dried for 1 h in a convection oven at 100 °C. Saturating the samples was carried out by heating them for 1 h in an aqueous solution at 80 °C and then allowing the samples to rest in water at room temperature for another week.

Hydraulic water permeation of PTFE-based NP-PCM was measured by clamping the membrane sample in a ball joint between two gaskets. The upper end of the tube was covered with paraffin film to prevent loss of water by vaporization. The tube was filled with water to a height of 500 mm (0.05 atm water). The drop in the water level was measured and the permeation calculated in units of $\text{mg h}^{-1} \text{cm}^{-2}$.

PSD of dry PCMs (without acid) was carried out with a NOVA 2200[®] Quantachrome Surface Area gas sorption analyzer based on the density functional theory (DFT). SEM analysis was performed with a JSM-6300 Scanning Electron Microscope (JEOL). The TGA tests were carried out with a TA Instruments module SDT 2960. TGA–DTA runs were recorded at a scan rate of 20° min^{-1} up to 700 °C.

Preliminary performance tests of a 5 cm^2 non-optimized DMFC were carried out with the use of graphite plates on which flow fields were engraved. The membrane-electrode assembly (MEA) is based on a 250 μm thick nanoporous proton-conducting membrane (NP-PCM) made of PTFE and SiO_2 (10% v/v). It was hot-pressed (25 kg cm^{-2} , 1 min, 100 °C) between a Toray paper coated with a layer of anode catalyst on one side and an E-TEK[®] cathode (De Nora Elettrodi) on the other. The anode catalyst was platinum–ruthenium (1:1 atomic) nanopowder (Johnson–Matthey). The anode and the cathode Pt loading was 4 mg cm^{-2} . Dry air was fed, at 1–4 atm (abs), into the cathode compartment at a rate of 100–400 ml min^{-1} . During

cell operation an aqueous solution of 1 M methanol in 3 M sulfuric acid was circulated past the anode at a flow rate of 5 ml min^{-1} . Measurements of fuel crossover were carried out at several temperatures by feeding nitrogen instead of air into the cathode compartment (at ambient pressure) and feeding the methanol–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 [11,17].

3. Results and discussion

In this paper we wish to present preliminary results regarding the initial characterization of PTFE-based NP-PCMs. Such membranes have the appearance of plastic films and maintain chemical and electrochemical stability at elevated temperatures. This is achieved by the use of PTFE, which is chemically inert in both oxidizing and reducing atmospheres,

as a backbone. The perfluorinated composition of the polymer imparts chemical and thermal stability rarely available with non-fluorinated polymers.

SEM analysis is used to characterize the surface area of the membranes at the microscopic level, while examining the influence of the different membrane content on the topography and morphology. Analysis shows that the membrane does not contain any contaminants and has two main ingredients: polymer binder and ceramic powder (Fig. 1). The surface of the membrane (Fig. 1a) consists of 50–200 nm spherical particles. Some nano-size voids, up to about 200 nm in size, are seen among these particles. On rolling the membrane to a thickness of less than $250 \mu\text{m}$, cracks begin to form (Fig. 1d). However, these are not through cracks. The PTFE fibers can be seen on the surface of the membrane and inside the cracks.

PSD measurements, based on the DFT method, on a dry PTFE-based NP-PCM, containing 30% (v/v) ceramic powder, show two groups of pores (Fig. 2). One group ranged from 0.7 to 2.5 nm and the second has a peak at about 7 nm and decays toward 50 nm. In the fuel cell these pores are filled

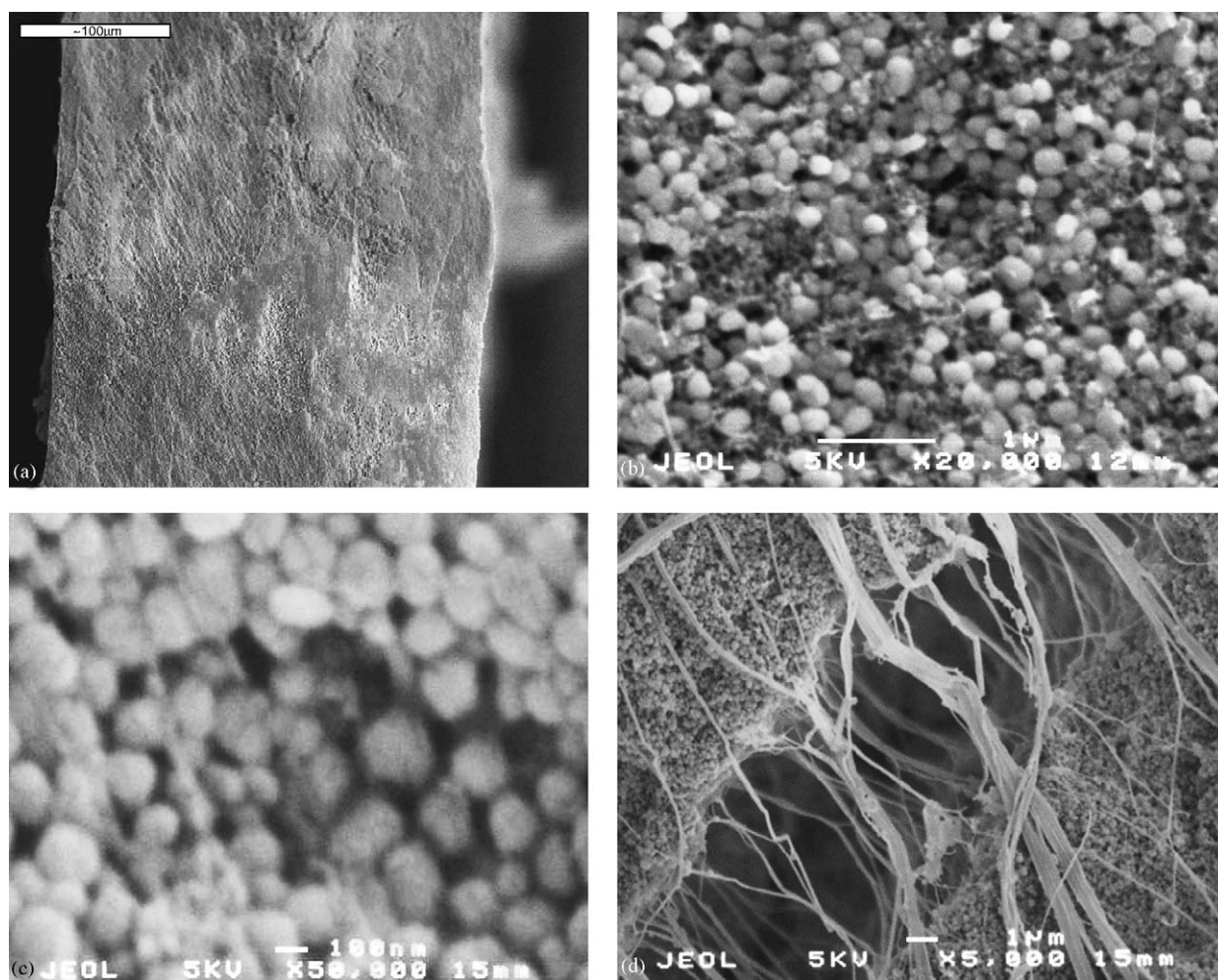


Fig. 1. SEM micrographs of gold plated PTFE-based NP-PCM. Composition of samples consists of 13% (v/v) ceramic powder: (a) cross-section image, magnification $\times 300$, $250 \mu\text{m}$ thickness; (b) surface image, magnification $\times 20,000$, $250 \mu\text{m}$ thickness; (c) surface image, magnification $\times 50,000$, $200 \mu\text{m}$ thickness; (d) surface image, magnification $\times 5,000$, $200 \mu\text{m}$ thickness.

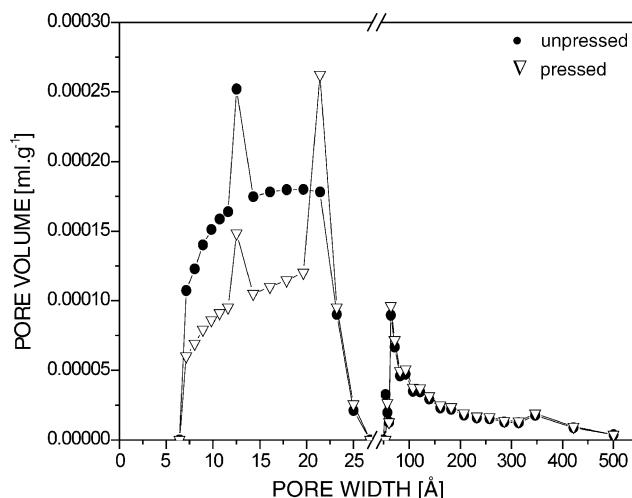


Fig. 2. PSD of PTFE-based NP-PCM, demonstrating the influence of pressing the membrane as function of the PSD.

with aqueous acid and thus allow ionic conductivity to take place. The PVDF-based NP-PCM has a similar pore distribution [13] with a smaller contribution from the second group (7–50 nm) of pores. For comparison, Nafion[®] TM 117 has a wide spectrum of pore sizes ranging from 1 to 100 nm with an average value of about 2 nm [18]. Hot pressing decreases the volume of the small pores by about 40% but has no effect on the second group (Fig. 2). These pores are small enough to maintain a large gas pressure difference when filled with water.

Fig. 3 shows the effect of ceramic powder content on the porosity and on water-uptake presented as the percentage of the membrane volume filled with water. The difference between these curves is the volume of closed and hydrophobic pores. Porosity and water uptake rise from 40 and 22% at 8% silica up to 63 and 50%, respectively, at 25% silica. On the other hand, the volume percentage of closed and hydrophobic pores decreases from 16% at 8% silica to 12% at 25% silica.

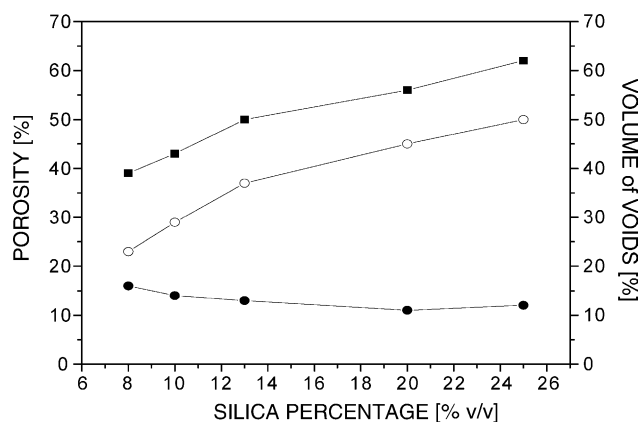


Fig. 3. Effect of ceramic powder content on the porosity and on the volume of empty and water full voids: (■) membrane porosity; (○) volume of voids full with water (water-uptake); (●) volume of closed and hydrophobic voids.

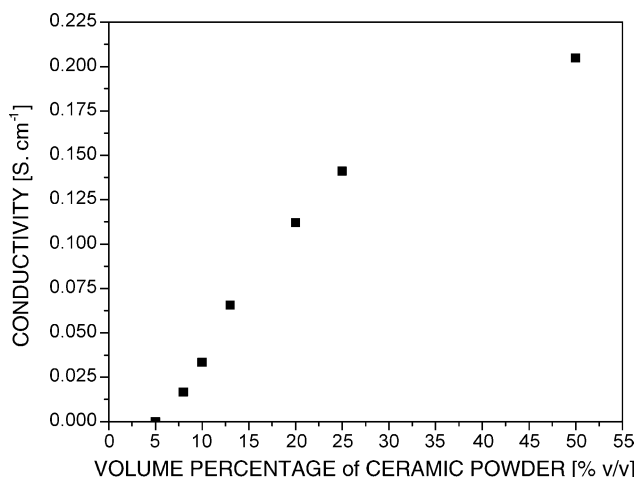


Fig. 4. Effect of ceramic powder content on the ionic conductivity of PTFE-based NP-PCM (3 M H₂SO₄).

The ionic conductivity of a membrane doped with a 3 M aqueous solution of sulfuric acid increases with the ceramic powder content, as shown in Fig. 4. It reaches 0.11 and 0.22 S cm⁻¹ at 20 and 50% silica, respectively. The incorporation of hydrophilic nano-ceramic powder into the perfluorinated polymer membrane results in the formation of nano-size hydrophilic pores that absorb aqueous solution. In order to be able to conduct ions, these pores must be connected. At silica content lower than 5% the conductivity is zero as a result of percolation limitation (lack of continuity of hydrophilic pores). Measurements of the resistance as function of the membrane thickness revealed (Fig. 5) that it rises with thickness but does not pass through the origin. We presume that this can be explained by another resistance, apart from the bulk resistance, referred to as the surface-film resistance. This film resistance varies with the silica content and as a result the film resistance measured is 0.06 and approximately 0.1 Ω cm² for a membrane consisting of 13 and 20–50% silica, respectively. Thus, one concludes that

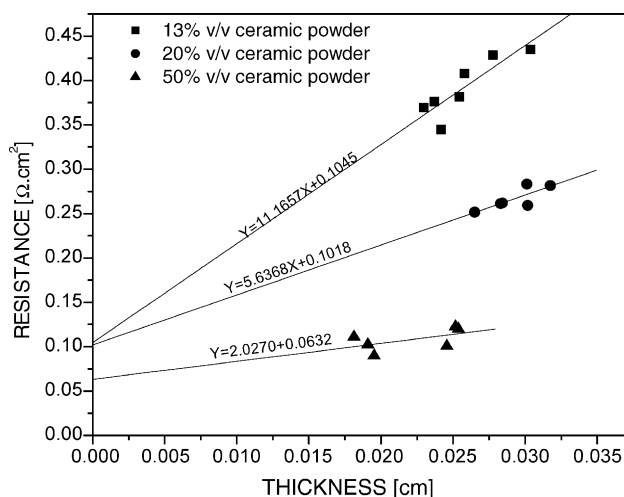


Fig. 5. Plots of membrane resistance as function of thickness.

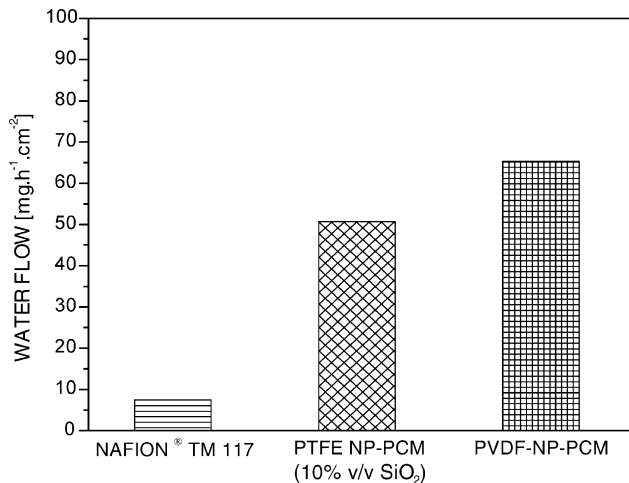


Fig. 6. Hydraulic water permeation of PTFE, PVDF-based NP-PCMs and of Nafion® TM 117. Measurements were carried out at a water-column height of 500 mm (0.05 atm water) [15].

a membrane with higher polymer content will have higher-surface film resistance. Similar behavior was also found both in PVDF-based NP-PCMs (unpublished results) and both in PFSA membranes. The preparation of our membrane involves vaporization of solvents and additives during the drying stage. Although solvents and additives are vaporized, the polymer binder remains on the surface area of the membrane, as a polymer-rich thin film [19–21]. As a result of the described phenomena, the surface film acts as a barrier and partially blocks the pores. This surface film adds another resistance to the bulk resistance of the membrane and subsequently reduces the formally calculated ionic conductivity of the membrane.

The importance of the use of a proton-conducting membrane with high water permeability has been recently demonstrated [15]. It reduces the hydraulic pressure in the cathode

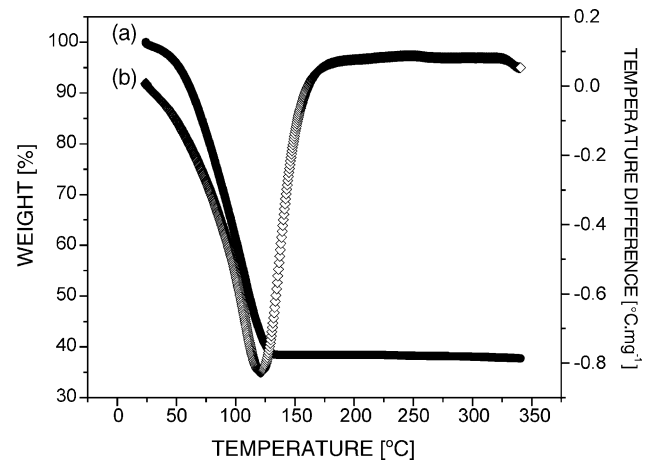


Fig. 7. Thermal analysis thermograms (TGA–DTA) of PTFE-based NP-PCM: (a) TGA curve; (b) DTA curve.

catalyst layer and in the GDL (by transferring water through the membrane back to the anode side) and this leads to a decrease in cathode flooding and to a lowering of the water vapor partial pressure in the cathode and in the cathodic flow field. Both phenomena enable a higher mass transport of oxygen thus higher power. The water permeation of a membrane depends upon the number, size and shape of the interconnecting hydrophilic pores. Pores that are sealed have no effect upon permeation. The hydraulic water permeation of PTFE-based NP-PCMs was measured and compared to that of PVDF-based NP-PCMs [15] and to that of Nafion® TM 117 (Fig. 6). It can be seen that the hydraulic water permeation of PTFE-based NP-PCMs, 10% (v/v) nano-size silica, is close to that of PVDF-based NP-PCMs and seven times that of Nafion® TM 117. As a result, fuel cells using PVDF- and PTFE-based NP-PCMs allow for higher power and for simpler and less complex fuel-cell systems. Nafion® has a

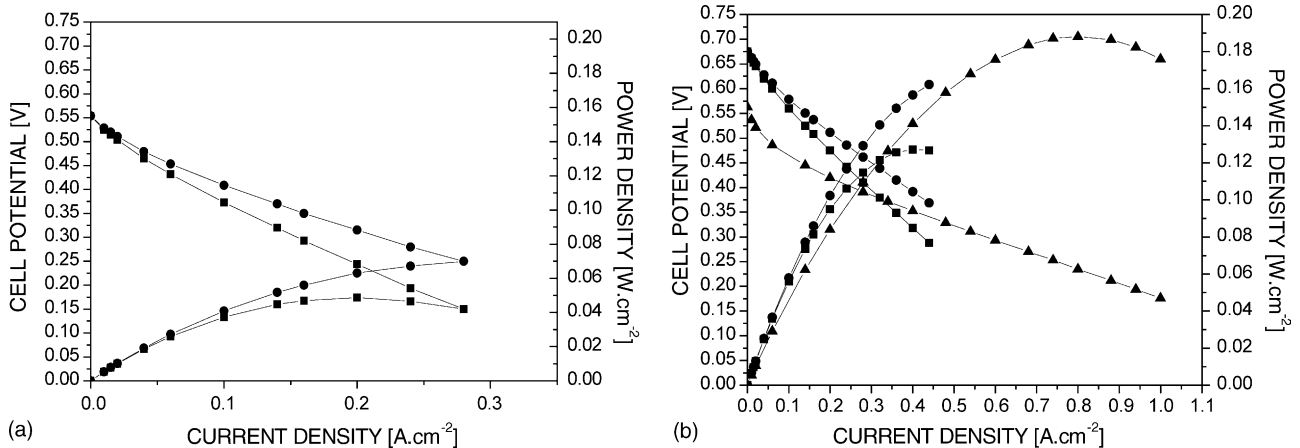


Fig. 8. (a) Cell polarization and power curves for a non-optimized DMFC containing a PTFE-based NP-PCM at 80 °C, 1 M MeOH, 3 M H₂SO₄, 3 atm(g) dry air at 180 ml min⁻¹, E-TEK® cathode, home made anode (4 mg Pt cm⁻²): (■) ~250 μm PTFE-NP-PCM, 180 ml min⁻¹; (●) ~250 μm PTFE-NP-PCM, +50% *iR* correction. (b) Polarization and power curves for the same DMFC compared to a PVDF based NP-PCM at 130 °C, 1 M MeOH, 3 M H₂SO₄, 3 atm(g) dry air, E-TEK® cathode, home made anode (4 mg Pt cm⁻²): (■) ~250 μm PTFE-NP-PCM, 180 ml min⁻¹; (●) ~250 μm PTFE-NP-PCM, +50% *iR* correction; (▲) ~65 μm NP-PCM, 240 ml min⁻¹ (1.5 M MeOH).

much lower water hydraulic permeation and thus dries during fuel-cell operation as a result of water dragging by the proton [22,23].

Simultaneous TGA–DTA analysis reveals that the membrane is thermally stable, up to 300 °C (Fig. 7). This is of great significance, as we are looking for fuel-cell systems, capable of withstanding temperatures above 130 °C for long operation times.

Preliminary performance tests of non-optimized DMFC were carried out (Fig. 8a). Three molar sulfuric acid and 1 M methanol solution were circulated through the anode compartment at 5 ml min⁻¹ and dry air fed at 180 ml min⁻¹.

The open-circuit voltage (OCV) was 0.56 and 0.65 V at 80 and 130 °C, respectively. The methanol crossover obtained was 0.27 and 0.56 A cm⁻² at 80 and 130 °C, respectively. The maximal power density is 50 and 130 mW cm⁻² at 80 and 130 °C, respectively. As the cell resistance was very high 0.5 Ω cm² (due to the use of a thick membrane) the polarization curves and the power curves were re-plotted after correction for 50% of the IR loss (this is equivalent to the use of a half thick (or 125 μm) membrane). After this correction the polarization and power curves are similar to those measured for PVDF-based DMFC (Fig. 8b). In the near future our main task is to improve the membrane preparation process in order to get a crack free thinner membrane and to test it in both hydrogen and direct methanol FCs.

4. Summary

In this paper, we describe the groundwork for a novel low-cost, highly conductive, NP-PCM based on a PTFE backbone for high temperature fuel cells. The work includes the various stages of preparation and characterization of the membrane.

The membrane consists of 50–200 nm spherical particles with nano-size voids among these particles. PSD tests reveal two groups of pores: one ranged from 0.7 to 2.5 nm and the second one has a peak at about 7 nm and decays toward 50 nm. The room-temperature conductivity exhibited a higher value than that of Nafion[®]. Preliminary performance tests of non-optimized DMFC assembled with a 250 μm membrane were carried out and demonstrated 50 and 130 mW cm⁻² at 80 and 130 °C, respectively. Future study will be oriented to reducing membrane thickness and applying this membrane in a hydrogen-fed fuel cell.

Acknowledgements

We express our gratitude to RAMOT—(Tel-Aviv University Authority for Applied Research and Industrial Development Ltd.), to the GM Foundation and to the European Community for their partial support on this project.

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