

Short communication

Operation of a proton-exchange membrane fuel cell under non-humidified conditions using thin cast Nafion membranes with different gas-diffusion media

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Abstract

Thin membranes in polymer electrolyte membrane fuel cells (PEMFCs) enhance the back diffusion of water from cathode to anode and allow operation of the PEMFC under dry conditions. In this work, thin cast Nafion membranes are prepared to operate the PEMFC under non-humidified conditions at various temperatures. Also, the effect of gas-diffusion media (GDM) on cell performance is examined using two different GDM that have distinct physical properties. Single cells with thin cast membranes provide better performance than those with commercially available Nafion 112. This improvement is due to better back-diffusion of water and lower membrane resistance. The performance of cell using GDM with low porosity is superior to that of a cell using GDM with high porosity. The fuel cell can be operated successfully under non-humidified conditions with a thin cast membrane and low porosity GDM.

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1. Introduction

The proton-exchange membrane fuel cell (PEMFC) has drawn much attention as an alternative power source for transportation and stationary applications [1,2]. Perfluorosulfonic acid membranes such as the Nafion are currently used as the electrolyte due to their favourable chemical and mechanical stabilities together with their high proton conductivity [3]. The membranes have to be hydrated to provide satisfactory proton conductivity and fuel cell performance. Therefore, the reactants are humidified through an external humidification system prior to entry into the cell. Operation of a PEMFC

without external humidification can simplify the whole system and offer significant cost savings [4].

If a fuel cell is operated under dry conditions, water from the electrochemical reaction is the only source of humidification. Therefore, effective water management within the cell is very important. Depending on the hydration state of the membrane, proton migration is associated with a drag of water molecules from the anode to the cathode [5]. This so-called electro-osmotic drag, together with electrochemical water production, results in an accumulation of water at the cathode side. In turn, the water concentration gradient between the anode and the cathode causes back-diffusion, which works against drying of the membrane from the anode side. The water concentration gradient between the anode and the cathode is influenced by the thickness of the membrane, the water content of the membrane, and the humidity of the

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reactant gases. It has been found that the back-diffusion of water from the cathode to the anode is the dominant process for water management in the cell over a wide range of operating conditions. According to Fuchi and Srinivasan [6], water production from the cathode was sufficient to keep the anode in a humidified state at temperatures up to 70 °C at ambient pressure.

Appropriate water management can be achieved by the design and operation of a PEMFC [7]. There are several reports of the operation of PEMFCs under non-humidified conditions using modified Nafion-type membranes. Among them, the use of self-humidifying membranes by incorporating inorganic materials into proton-conducting polymer membranes is presently attractive [4,8–13]. Even though these modified membranes improve the cell performance under non-humidified conditions by retaining water in the membrane even at high temperatures, incorporation of inorganic particles mostly increase the electrolyte resistance. Also, these membranes require tedious preparation procedures. Most models and experiments [4,14–16] found that effective water management in the fuel cells under dry conditions was possible by controlling parameters such as the fuel/oxidant stoichiometry, the cell temperature, and the pressure gradient between the anode and the cathode compartments. On the other hand, some workers have achieved effective water management inside the cell by modification of the gas diffusion layer (GDL) [17–20]. The basic function of the GDL is to provide a homogenous distribution of reactant gases from the flow-field of the bipolar plates to the reaction sites. With proper modification of the GDL, it is expected that additional functions, such as appropriate water management, can be obtained, and result in adequate hydration of the polymer electrolyte so that flooding of the electrode is minimized. Recently, Ahn et al. [21] reported the operation of a fuel cell under non-humidified conditions using cast membranes. Since the membrane was thick, the cell gave a low performance and could only be operated at room temperature.

In this study, non-humidified operation of a PEMC has been achieved by employing a thin cast Nafion membrane. The cell was operated at various temperatures using these membranes under non-humidified conditions. Two different gas-diffusion media (GDM) that have distinct properties have been used and their water management has been investigated.

2. Experimental

2.1. Membrane preparation

Solution cast membranes were prepared from 20 wt.% (EW 1100) commercial Nafion solution (Dupont Fluoroproducts) and dried under ambient conditions, followed by curing at 120 °C (higher than the glass-transition temperature, T_g , of Nafion) for 3 h. Each membrane was treated by boiling for over 1 h each with 5% H_2O_2 , 0.5 M H_2SO_4 and deionized water to obtain the acid form of the membrane. They were

stored in deionized water. The thickness of each membrane was about 25 μm in dry state.

2.2. Preparation of membrane electrode assemblies (MEAs)

Catalytic inks for the electrodes were prepared by mixing 40 wt.% Pt/C (E-Tek Inc.), 5 wt.% Nafion solution (Dupont), and isopropyl alcohol (Baker analyzed HPLC grade reagent). The inks were sprayed on to the pretreated cast membrane with platinum loadings of 0.3 and 0.4 mg cm^{-2} for the anode and the cathode, respectively. The catalyst-coated membrane (CCM) was dried overnight at 50 °C. The same preparation method was used to make a MEA with a commercially available Nafion 112 membrane to compare the effect of thickness on cell performance.

2.3. Single cell tests

Single cells were assembled with CCMs, gas diffusion media (Sigracet GDL 30 BC and 10 BC), Teflon gaskets and graphite blocks. Hydrogen and oxygen were fed to the anode and the cathode, respectively, at flow rates of 400 cc min^{-1} under ambient pressure.

The single cell was activated at 80 °C with 100% humidification at the anode and the cathode, which had temperatures of 80 and 75 °C, respectively. The cell was operated in the galvanostatic mode at 1 A cm^{-2} for 5 h under the above conditions. Then, the cell temperature decreased to ambient temperature and was operated with dry reactant gases at 1 A cm^{-2} for 24 h before evaluating the I - V characteristics. Subsequently, the cell was operated at various temperatures with dry reactants. Also, an experiment was performed without activation of the cell. The performance of the cell was evaluated by measuring the I - V characteristics using an electric load (Daegil Electronics, EL500P).

2.4. SEM analysis

Scanning electron microscopy (Hitachi S-4200) was used to observe the morphology of the cast membrane and the gas-diffusion media.

3. Results and discussion

3.1. Effect of membrane thickness in water back-diffusion

The morphology of the surface and cross-section of the cast membrane is presented in Fig. 1. The surface of the membrane does not display any cracks or defects. The cross-section of the membrane shows the thickness to be about 25 μm .

In order to understand the role of the thin membrane in water back-diffusion, the cell was operated with a thin cast membrane ($\sim 25 \mu\text{m}$). The single-cell performance is pre-

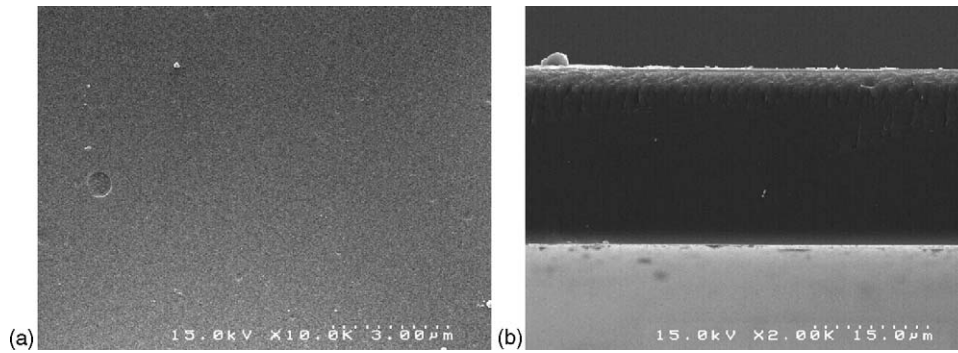


Fig. 1. Scanning electron micrographs of (a) surface morphology of cast membrane (b) cross-sectional view of cast membrane.

sented in Fig. 2. After activation, and the cell was operated at 34 °C with dry reactants at 1 A cm⁻² for 24 h and the *I*–*V* characteristics were obtained. Each point for the polarization curve was taken every 5 min. This procedure was chosen to facilitate sufficient hydration in the membrane. In order to evaluate the influence of temperature on cell performance, the cell was operated with dry reactants at 50, 60 and 70 °C. In general, the performance of PEMFCs shows a strong dependence on operating temperature. With increase in operating temperature, a higher rate of evaporation occurs and the reactant gases can take up more water vapor because of the higher saturation pressure [22]. The polarization curves indicate that the cell gives good performance at 34 °C. At 50 and 60 °C, however, it shows high activation overpotential but the performance improves in the high current density region and the polarization curves tend to merge with that at 34 °C. In the low current density region, however, the performance is poor at these temperatures. This can be explained by the fact that only a small amount of water is produced by the electrochemical reaction at low current densities, and back diffusion is

limited. This, in turn, leads to membrane dehydration at the anode side and therefore poor proton conductivity. As water production is increased at high current density, the cell performance increases with back diffusion of water. At 70 °C, even though the electrochemical reaction rate is increased, the cell performance is lower over the entire region due to water loss in the cell by evaporation and thereby resulting in low proton conductivity.

The performance of a cell operated with a thick Nafion 112 (50 μm) membrane is shown in Fig. 3. The performance decreases as the temperature is increased. At 50 °C the cell performance is low over the entire region and this is contrary to that for a cell with a thin cast membrane. Even though the cell temperature is low, the membrane at the anode side is dehydrated due to poor back-diffusion of water from the cathode because of the thick membrane. In addition, the cell performance deteriorates at 60 and 70 °C in the ohmic region. This may be due to severe water loss together with poor back-diffusion of water compared with a cell that uses a thin cast membrane.

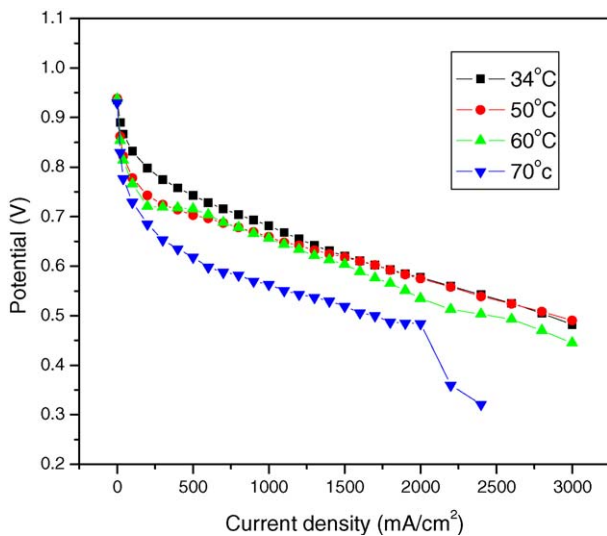


Fig. 2. Polarization curves at various temperatures using MEAs fabricated with a cast membrane and SGL 30 BC GDM, and operation with dry H₂ and O₂ (with activation).

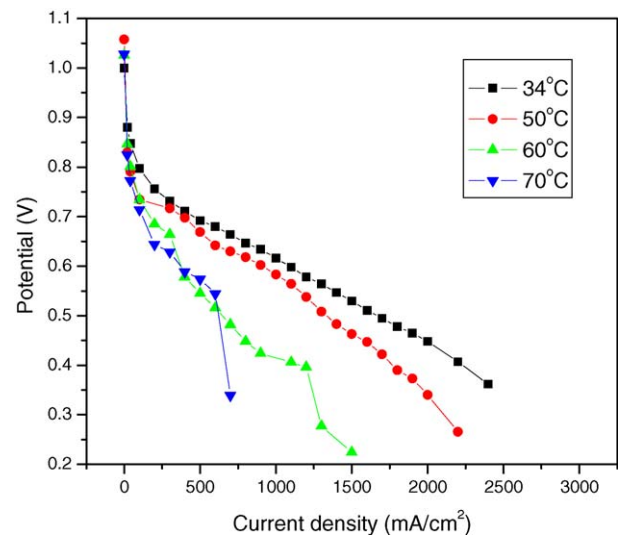


Fig. 3. Polarization curves at various temperatures using MEAs fabricated with Nafion 112 and SGL 30 BC GDM, and operation with dry H₂ and O₂ (with activation).

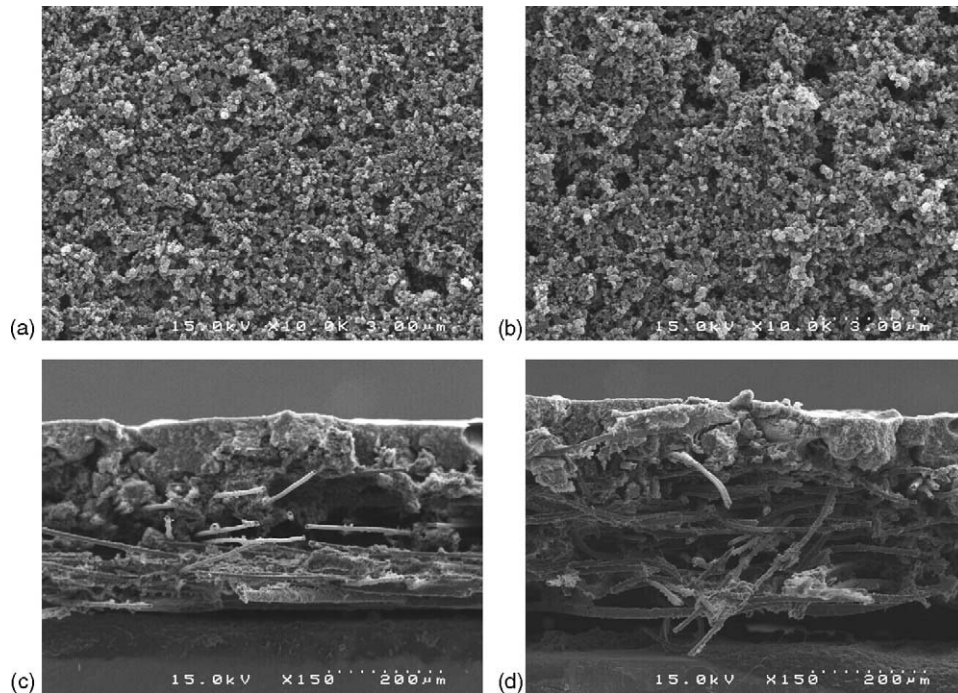


Fig. 4. Scanning electron micrograph of: (a) surface morphology of SGL 30 BC GDM (microporous layer); (b) surface morphology of SGL 10 BC GDM (microporous layer); (c) cross-sectional view of SGL 30 BC GDM; (d) cross-sectional view of SGL 10 BC GDM.

3.2. Effect of gas-diffusion layer in water management

A thin gas-diffusion layer improves the gas supply and facilitates the removal of product water, but it has high electronic resistance and poor mechanical properties. On the other hand, a thick layer hampers the accessibility of gas due to the lengthened transport layer and has poor diffusivity [17]. To evaluate the role of gas-diffusion media (GDM) in water management, two different GDM (Sigracet GDL 30 BC and 10 BC) that have different porosity, density and thickness have been examined. The characteristics of these GDM are shown in Table 1. The surface morphology and cross-sectional view of the GDM are presented in Fig. 4. The microporous layer structure of both the GDM appears to be similar and it is difficult to distinguish between them. From the cross-sectional view, however, it can be observed that the SGL 30 BC has a denser and thicker microporous layer than the SGL 10

Table 1
GDM properties given by manufacturer

	Sigracet GDL 10 BC	Sigracet GDL 30 BC
Thickness (μm)	415	330
Areal weight (g m^{-2})	135	140
PTFE content (%)	5 (substrate)	5 (substrate)
Air permeability ($\text{cm}^3 \text{cm}^{-2} \text{S}^{-1}$)	1.45	0.50
Through plane specific electrical resistance ($\text{m}\Omega \text{cm}^2$)	<13	<16
Special treatment	Microporous layer	Microporous layer

BC specimen, and is also supposed to have a better water-retaining capability.

The performance of a cell with a SGL 10 BC diffusion layer, which has higher porosity than the SGL 30 BC variant is given in Fig. 5. At low temperature, the cell performance shows the same trend as that of SGL 30 BC (Fig. 2). At high temperatures however, the cell performance decrease due to water evaporation. This may be explained by the porosity

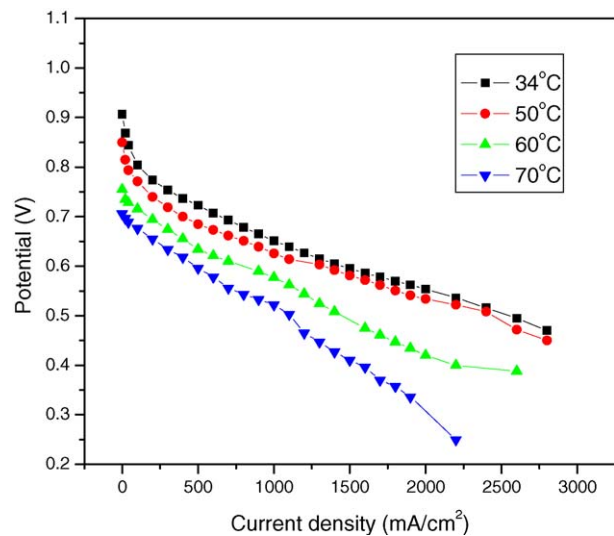


Fig. 5. Polarization curves at various temperatures using MEAs fabricated with cast membrane and SGL 10 BC GDM, and operation with dry H_2 and O_2 (with activation).

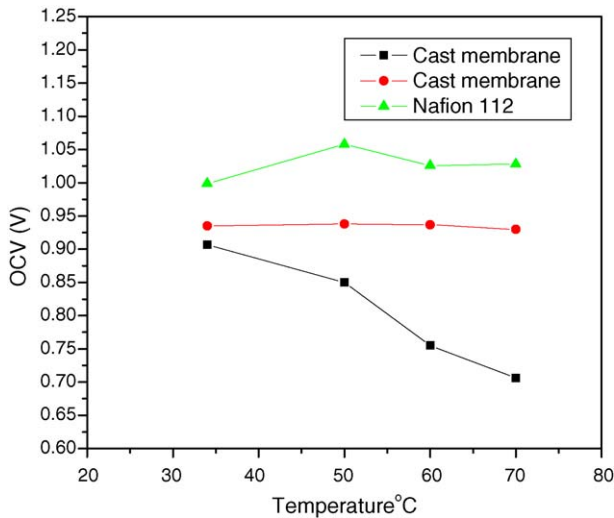


Fig. 6. Comparison of open-circuit voltages of cells fabricated with (■) SGL 10 BC and (●) (▲) SGL 30 BC GDM.

and thickness of the microporous layer of the GDM. Because of its high porosity, SGL 10 BC cannot hold water inside; this behaviour is opposite to that exhibited by SGL 30 BC with low porosity. This difference is reflected in the open-circuit voltage (OCV) at each cell temperature. The OCV of the cell with SGL 30 BC (using Nafion 112 and cast membrane) is compared with that of the cell with SGL 10 BC (cast membrane) in Fig. 6. Using SGL 30 BC, the OCV is almost constant for all operating temperatures. With SGL 10 BC, however, the OCV decreases as the temperature is increased. This is due to water loss at high temperature and membrane dehydration, which leads to cross-over of reactants through the membrane.

In an attempt to operate a single cell with dry hydrogen and air, the cathode gas was changed from oxygen to air.

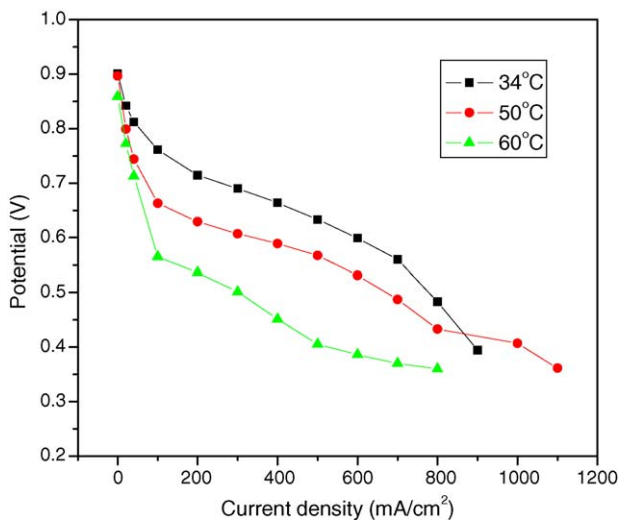


Fig. 7. Polarization curves at various temperatures using MEAs fabricated with cast membrane and SGL 30 BC GDM, and operation with dry H₂ and air (with activation).

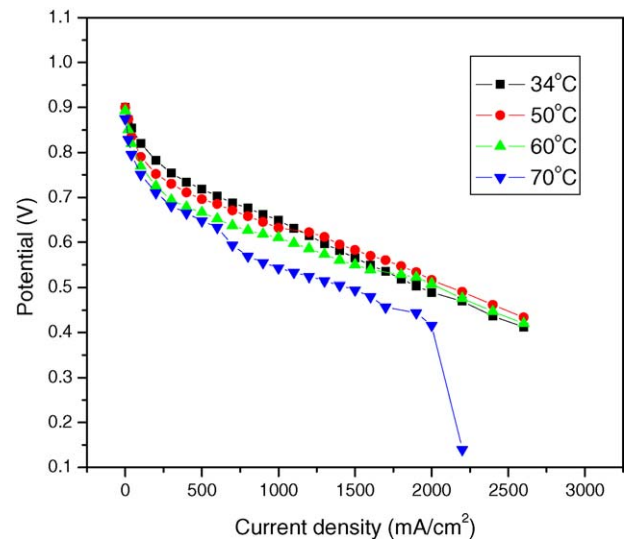


Fig. 8. Polarization curves at various temperatures using MEAs fabricated with cast membrane and SGL 30 BC GDM, and operation with dry H₂ and O₂ (without activation).

The single-cell performance with air is presented in Fig. 7. There is a severe decrease in performance as the temperature increases. This is due to the high flow rate of air that removes water from the cell and dehydrates the membrane.

Finally, the single cell was operated using a thin cast membrane without any activation. The polarization curves with dry H₂/O₂ and dry H₂/air are given in Figs. 8 and 9, respectively. The cell performance is similar to that with activation, except that, the current density at each operating potential is lower. The high performance of the cell with activation is due to the fact that the water uptake capacity of the membrane and the catalyst layer is enhanced at high cell temperature (80 °C) during the activation, and this increases the proton conduc-

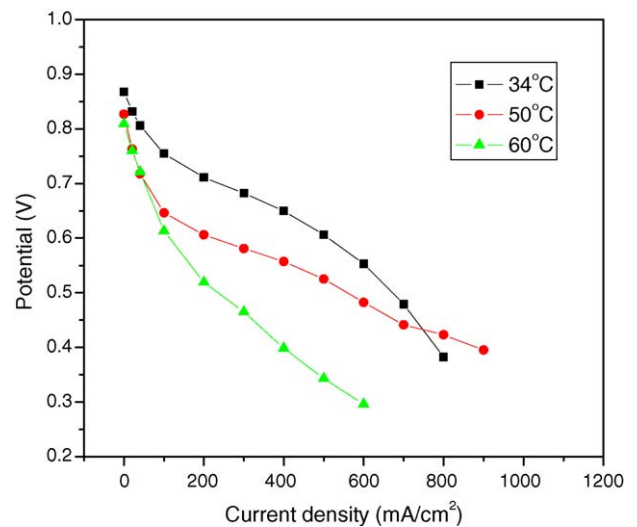


Fig. 9. Polarization curves at various temperatures using MEAs fabricated with cast membrane and SGL 30 BC GDM, and operation with dry H₂ and air (without activation).

tivity of the membrane and the electrochemical activity of catalyst layer.

4. Conclusion

Thin cast membranes have been prepared from Nafion solution and used for PEMFC operation under non-humidified conditions at various cell temperatures. A single cell with a thin cast membrane exhibits good performance at low cell temperature compared with that of a cell with a Nafion 112 membrane. The cell performance decreases at high temperatures. This reflects membrane dehydration due to severe water loss by evaporation. The single cell has also been operated with two different gas diffusion media (GDM) that have different porosities. Due to its better water retaining capacity, a GDM with low porosity exhibits better performance than a GDM with high porosity.

With effective water management inside the cell, single cells using thin cast membranes exhibit superior high cell performance to cells with commercial, thick Nafion membranes under non-humidified conditions. It is possible to operate a PEMFC successfully at ambient temperature when using a thin cast membrane together with proper GDM under non-humidified conditions.

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