

Effect of freeze-thaw cycles on the properties and performance of membrane-electrode assemblies

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Received 21 January 2006; received in revised form 24 February 2006; accepted 27 February 2006

Available online 25 April 2006

Abstract

The effect of freezing of a membrane-electrode assembly on its physical properties and performance was investigated. It was found that freeze-thaw cycles caused the electrode (i.e., catalyst layer) of a fully hydrated membrane-electrode assembly (MEA), either as a freestanding piece or as assembled in a cell, to crack. Accompanying the cracking was a reduction in the electrochemical active surface areas of the electrodes as measured by cyclic voltammetry, but the short-term performance of the fuel cell did not show much effect. When dry reactants were used to remove some water from a cell that had been previously tested at fully hydrated condition, freeze-thaw cycling did not cause apparent damage to the appearance of the electrodes. Also, for freestanding MEAs that were taken directly from the manufacturing line and only exposed to ambient temperature (e.g., 23 °C) and relative humidity (e.g., <50% RH), freezing did not cause apparent damage to the appearance of the electrodes.

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Keywords: PEM fuel cell; Freezing; Freezing damage; Freeze-thaw cycles; Membrane-electrode assembly

1. Introduction

Water is required for the proper operation of a proton-exchange membrane (PEM) fuel cell. It hydrates the membrane and the ionomer within the electrodes (i.e., catalyst layers), enabling protons to be transported away from or to the reaction sites in the anode and cathode, respectively, and transported through the membrane from the anode to the cathode to complete the electrical circuit. High proton conductivity is desired in order to reduce the fuel cell performance losses associated with activation overpotential and ionic resistance.

Although a PEM fuel cell is intended to operate at a temperature above the freezing point of water, it is likely that it will experience some subzero temperatures during its lifetime. When the fuel cell is operating, the heat generated by the fuel cell itself is normally enough to keep water from freezing. But when the fuel cell is idle, or during its transportation and storage (especially in winter), it could experience subzero conditions. Using a heater (plus good insulation) could keep the fuel cell above subzero temperature and is manageable for a short time during

temporary exposure to cold weather such as during installation. However, using a heater to warm a fuel cell for long periods would be too costly and impractical.

Antifreeze agents such as conventional glycol-based liquids (e.g., ethylene glycol, propylene glycol, 1,3-butanediol, glycerol, and other alcohols) or their mixtures with water that possess low freezing temperatures are normally used as coolants to prevent a fuel cell stack from overheating [1,2]. Also, due to their low freezing points, these coolants will not freeze at normal winter temperatures, so freezing of coolants is normally of little concern. However, the presence of such low freezing point coolants within the stack coolant flow-fields does not mean that water within the fuel cell stack will not freeze.

At a subzero condition, water within the fuel cell stack is likely to freeze. The ice formed could block reactant passages and cause difficulty when the fuel cell is restarted. The passages include the pipelines transporting the reactants from sources to the stack, the manifolds within the stack, the flow-fields on the plates, and pores within the gas diffusion layers (GDL) and the catalyst layers. A variety of heating methodologies have been proposed to start a stack from subzero temperatures [3–13].

When water freezes to form ice, its volume will increase. The volume expansion and the stress associated with the volume

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expansion could damage fuel cell components such as the electrodes and the membrane. Removing some of the water before allowing a fuel cell to go below the freezing point could alleviate this problem, and vacuum drying has been suggested as one of the methods to remove water [14].

There are very limited data published about the effects of freezing on the physical properties and performance of a membrane-electrode assembly (MEA). Cho et al. thermally cycled MEAs between 80 and -10°C , and found that the thermal cycling degraded the fuel cell performance due to increased polarization resistance and ohmic losses [15]. They also found that thermal cycling increased the average pore size and decreased the electrochemical active surface area of the electrode. In this article, we report our studies on the effect of thermal cycling an MEA between 20 and -30°C on both the performance and the physical properties of the MEA. We chose a lower temperature limit of -30°C because such a temperature is possible in winter months in many regions and during fuel cell transportation by air freight.

2. Experimental

2.1. Fuel cell tests

Single fuel cell tests were performed using a homemade 50 cm^2 active area test fixture. The test fixture was composed of a pair of graphite plates with serpentine flow-fields for the reactants to flow. There were cooling channels on the back of the plates for liquid water to flow. Rod-shaped heaters were inserted into the plates to help control the cell temperature.

Pure hydrogen and air were used as the reactants at the anode and cathode, respectively. The cell temperature was controlled at 65°C , and both reactants were 100% humidified by pass-

ing them through humidifiers prior to supplying them to the cell.

Commercial MEAs with a total Pt loading slightly lower than 1.0 mg cm^{-2} were used in the study. The membrane was about $30\text{ }\mu\text{m}$ thick, and was made of perfluorinated sulfonic acid ionomer. Carbon paper-type GDLs were used as the backing.

2.2. Cyclic voltammetry (CV)

An EG & G Potentiostat (Model 263 A) was used to perform the cyclic voltammetry. When the CV of the cathode (or anode) was measured, the anode (or cathode) was supplied with pure hydrogen to function as the counter and reference electrode, and the cathode (or anode) side was supplied with an inert gas such as nitrogen. Both hydrogen and nitrogen were fully humidified, and their flow rates were set at 0.523 and 2.073 SLM respectively. The cell temperature was controlled at 65°C . The potential was scanned between 50 and 500 mV at a scan rate of 20 mV s^{-1} .

2.3. Scanning electron microscopy (SEM) and energy disperse spectrometry (EDS)

A JEOL 6400 SEM was used for microscopic analysis. EDS was performed using software and hardware manufactured by IXRF Systems, Inc. The EDS was coupled with the SEM.

2.4. Freeze-thaw cycles

The experiment was conducted in an environmental chamber (CSZ, ZH-32, Cincinnati Sub-Zero Products, Inc.). The temperature was cycled between 20 and -30°C with 30 min of heating and cooling time, and the temperature was held at -30°C for 6 h during each cycle.

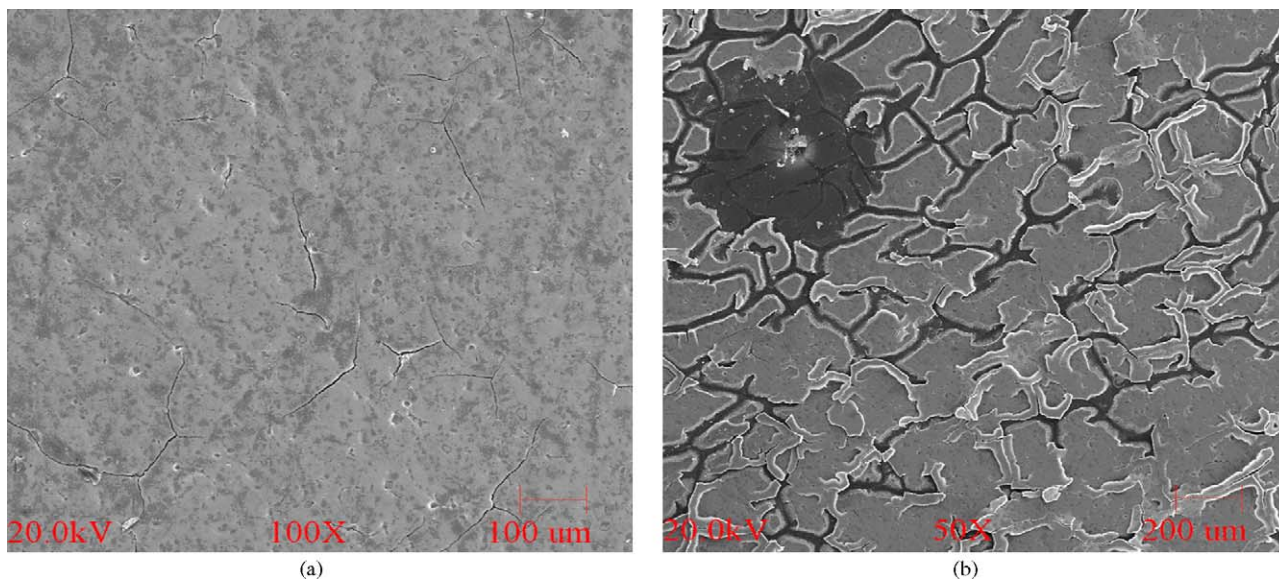


Fig. 1. SEM of the cathode side of freestanding MEAs after six freeze-thaw cycles between 20 and -30°C : (a) MEA was only exposed to ambient temperature and relative humidity before going through the freeze-thaw cycles; $100\times$ magnification. (b) MEA that was fully hydrated in water at 80°C for 10 min before going through the freeze-thaw cycles; $50\times$ magnification.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

SEM was used to study the surface morphology change of MEAs having different hydration levels following freeze-thaw cycles. Fig. 1 shows the microstructure of the cathode side of freestanding MEAs. In Fig. 1(a), the MEA was only exposed to ambient temperature (ca. 23 °C) and relative humidity (e.g.,

<50% RH) after it had been fabricated before going through six freeze-thaw cycles between 20 and –30 °C. A smooth catalyst layer surface was observed, indicating that little damage was done to the MEA by the six freeze-thaw cycles. Fig. 1(b) shows the results from a similar MEA that was fully hydrated in water at 80 °C for 10 min before going through the six freeze-thaw cycles. After the hydration step, the water on the surface of the MEA was removed using Kimwipes. The picture shows that the catalyst layer was seriously damaged, with severe cracks and

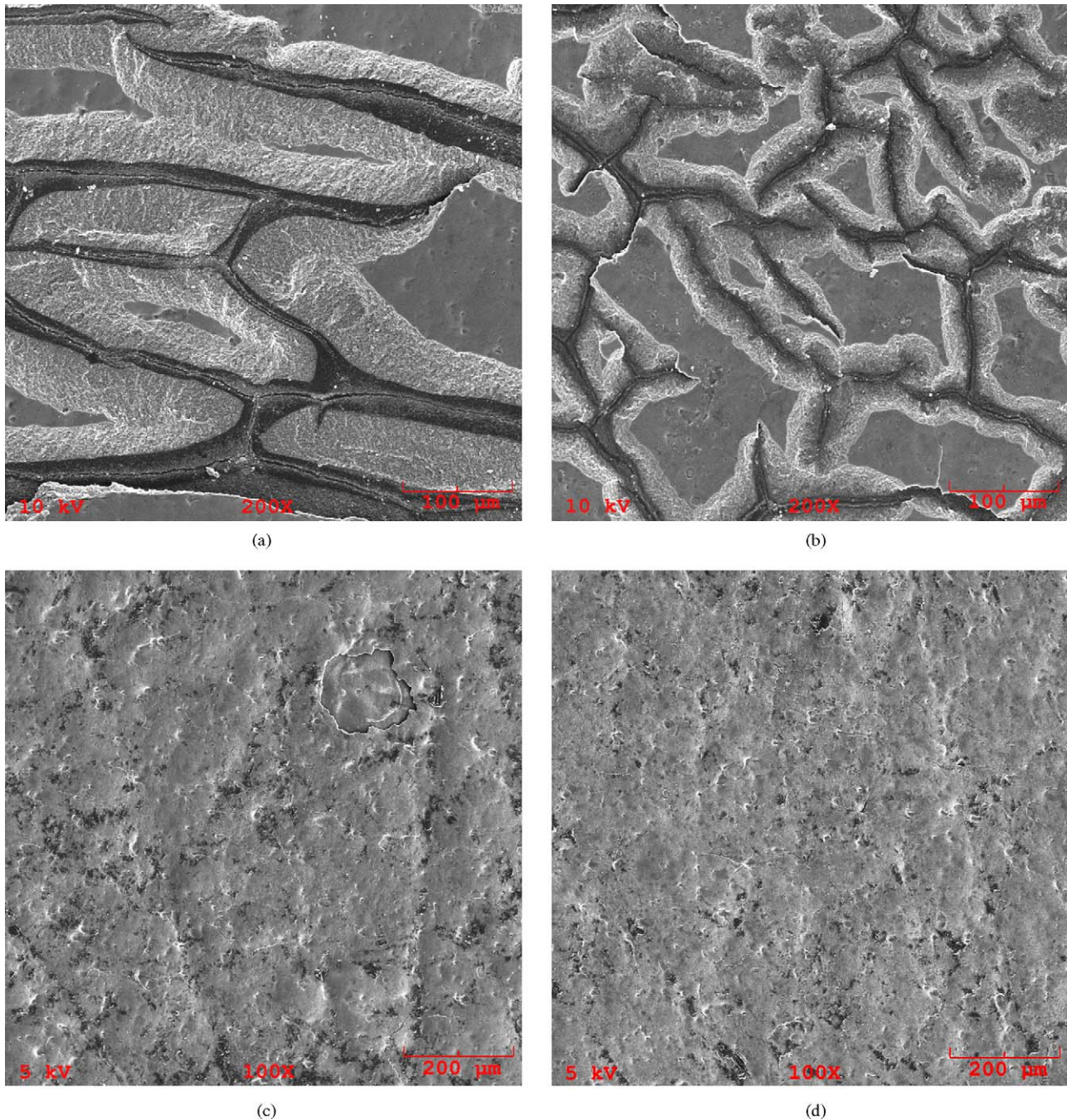


Fig. 2. SEM of MEAs that were assembled within single cell fixtures after freeze-thaw cycles between 20 and –30 °C: (a, b) MEA was fully humidified during testing and no dehydration step was taken before going through 10 freeze-thaw cycles; 200× magnification; (c, d) MEA was fully humidified during testing and a dehydration step was taken by passing dry reactants through both the anode and cathode compartments before going through nine freeze-thaw cycles for 10 min; 100× magnification. (a) and (c) are anodes, and (b) and (d) are cathodes.

segregation of catalyst domains. There were also areas where the catalyst materials became detached (and lost) from the membrane. Those areas and the ditches between catalyst domains showed nearly no EDS signals from the catalysts, indicating the exposed areas were the membrane that was initially underneath the catalyst layer. It is inferred that this kind of catalyst layer damage could cause delamination of the catalyst layer from either the membrane or the GDL. Such delamination could then increase the contact resistance.

Fig. 2 shows the freeze-thaw effect on MEAs that were assembled and kept in a 50 cm² single cell fixture. In Fig. 2(a) and (b), after the MEA was exposed to fully humidified anode and cathode reactants, the cell was shut down and the reactant flows were stopped immediately. Then the entire single cell fixture was placed into the temperature chamber for 10 freeze-thaw cycles between 20 and –30 °C. Both the anode and cathode catalyst layers were badly damaged, and fracture of the catalyst surface was observed. The catalyst domain segregation seemed to be not as severe as that observed with the freestanding MEA shown in Fig. 1(b). This difference could be due to the following reasons: First, the stacking force applied onto the MEA that was assembled in a cell helped maintain the integrity of the MEA during the freeze-thaw cycles. Second, the MEA inside the cell was less hydrated than the one that was treated in water at 80 °C.

In Fig. 2(c) and (d), after the MEA was exposed to fully humidified anode and cathode reactants, a dehydration step was taken by passing unhumidified (dry) reactants through both the anode and cathode compartments for 15 min at flow rates of 0.42 and 1.66 SLM respectively. It was then followed by a dry nitrogen purge of both sides for 1 min at a flow rate of 1.66 SLM. During these processes, the gas inlet pressure was about several psig, and the cell temperature was around 65 °C. The major purpose of the final 1 min nitrogen purge was to remove hydrogen and oxygen from the anode and cathode chambers, respectively. Then the test fixture was transferred from the station to the environmental chamber for nine freeze-thaw cycles between 20 and –30 °C. SEM results indicated that the surface of neither the anode nor the cathode was apparently damaged. Thus, removing water from the MEA reduced the likelihood of damage during freeze-thaw cycles.

3.2. Electrochemical active surface area

Fig. 3(a) and (b) show the cathode and anode active area changes, respectively, of an MEA associated with freeze-thaw cycles performed under similar conditions as in Fig. 2(a) and (b). The electrochemical active surface area was estimated by the areas under the hydrogen desorption peaks (i.e., the shaded area for curve 4 in Fig. 3(a)). Apparent electrochemical active surface area loss was observed for both electrodes. For the cathode, the electrochemical active surface area decreased by 23% from 1800 to 1390 mC per 50 cm² after 20 freeze-thaw cycles. For the anode, the electrochemical active surface area decreased by 15% from 650 to 550 mC per 50 cm² after 20 cycles. The features and shapes of the hydrogen adsorption and desorption peaks showed little change accompanying the freeze-thaw cycles.

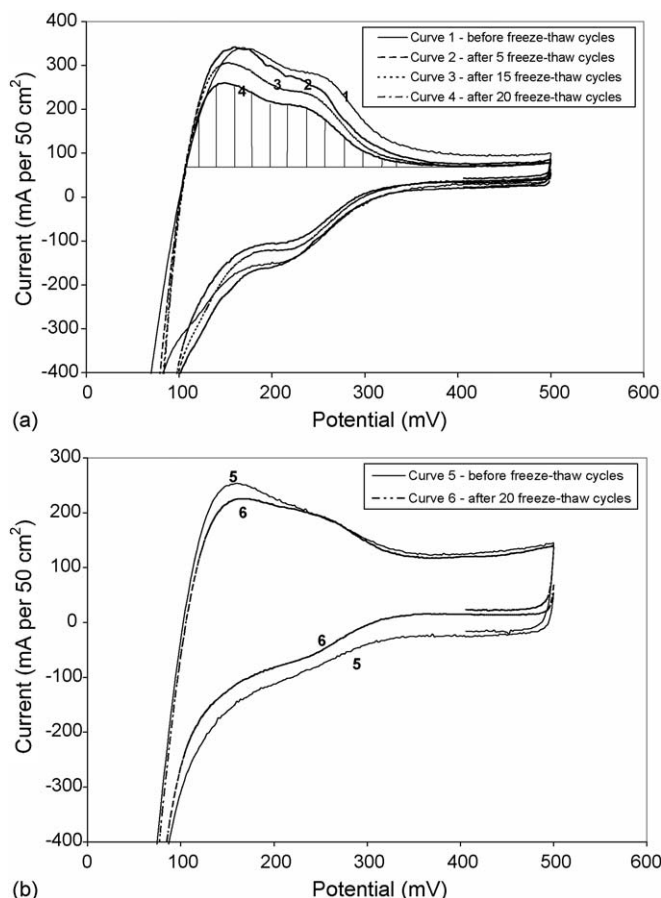


Fig. 3. Cyclic voltammograms of (a) cathode and (b) anode of an MEA after 0–20 freeze-thaw cycles at fully humidified state.

3.3. Fuel cell performance

Fig. 4 shows the fuel cell performance after a fully humidified MEA kept in a single-cell fixture went through different numbers of freeze-thaw cycles. Full humidification was achieved by using saturated reactants for both the anode and cathode, and no dehydration action was taken before the freeze-thaw cycles. The cell voltage at a current density of 0.6 A cm⁻² is plotted. It was found that the fuel cell's short-term performance did not change significantly after a total of 20 freeze-thaw cycles, although the catalyst layers were severely cracked and segregated as illustrated by Fig. 2(a) and (b) for another MEA thermally cycled under similar conditions. However, we do expect that the damage to the catalyst layer will shorten the lifetime of the MEA.

Another MEA was subjected to a similar process with the exception that dehydration was performed by passing dry reactants through the anode and cathode channels before the freeze-thaw cycles; the results are shown in Fig. 5. In this experiment, each freeze-thaw process was limited to only one cycle. Again, the fuel cell's short-term performance was not noticeably affected by the freeze-thaw cycles. Please note that there are time gaps on the x-axis in both Figs. 4 and 5.

It was noticed that the performance in both Figs. 4 and 5 seemed to fluctuate frequently. This could imply that the MEAs became more readily flooded after the freeze-thaw cycles.

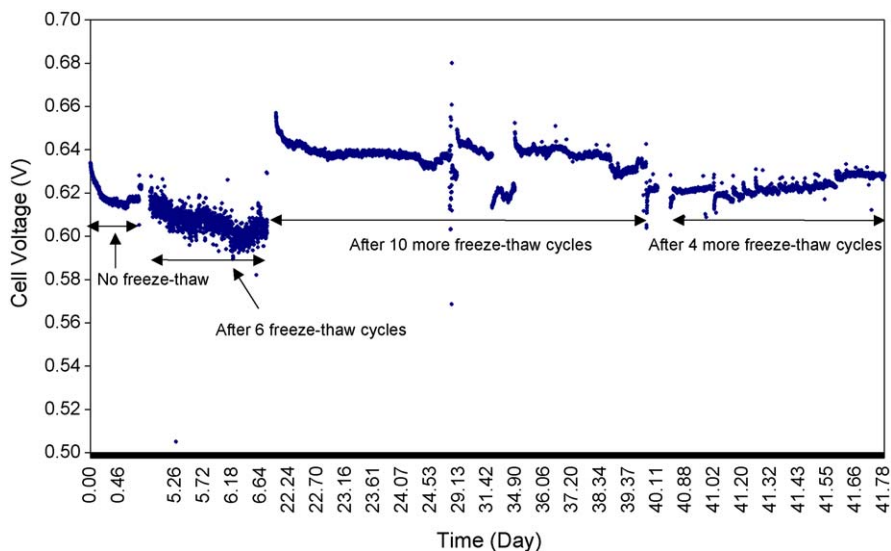


Fig. 4. Fuel cell voltage at a current density of 0.6 A cm^{-2} before and after 6, 10, and 4 successive freeze-thaw cycles, respectively. The MEA was fully humidified before each freeze-thaw cycle. Cell temperature 65°C , 100% RH for both anode and cathode reactants, $1.5/2.0 \text{ H}_2/\text{air}$ stoichiometry.

Fig. 6 shows the polarization curves of a fuel cell before and after a dehydrated MEA went through nine freeze-thaw cycles (surface morphologies of the MEA are shown in Fig. 2(c) and 2(d)). Almost identical $V-I$ curves were obtained, indicating that the dehydration step and the following freeze-thaw cycles had little effect on the short-term performance of the MEA. In addition, we found that the frozen cell could be restarted immediately and that it regained its previous performance quickly.

Although the membrane could contain about 30% water by weight in the fully hydrated state, apparent physical damage to the membrane was not observed during these short-term

freeze-thaw cycles. One hypothesis is that since there is a high electrolyte concentration within the membrane (e.g., about 2 M sulfonic acid groups for Nafion 1100 equivalent weight materials) and the channels or pores hosting water are on the scale of nanometer dimensions, water does not freeze easily within the membrane due to freezing point suppression. According to the studies by Saito et al. and Cappadonia et al. water within Nafion membranes (EW 1100) partially freezes around -20°C , but non-freezing water remains in the membranes at even much lower temperatures [16,17]. The situation is quite different within the catalyst layers (and the GDLs) where low (and

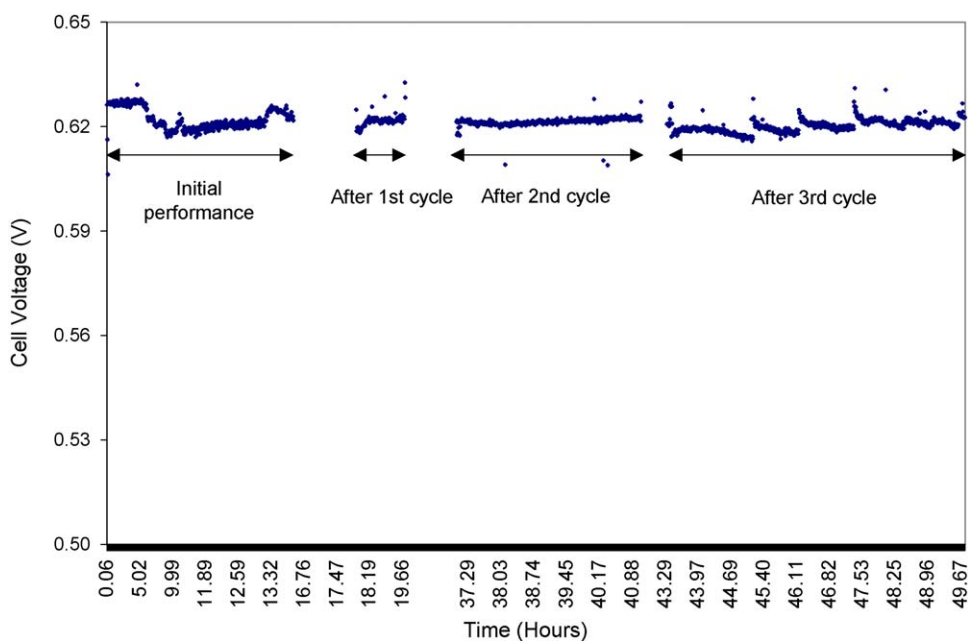


Fig. 5. Fuel cell voltage at a current density of 0.6 A cm^{-2} before and after 1, 1, and 1 successive freeze-thaw cycles, respectively. Before each freeze-thaw cycle, the MEA within the cell was dehydrated by passing dry reactants through both the anode and cathode compartments for 10 min. Cell temperature 65°C , 100% RH for both anode and cathode reactants, $1.5/2.0 \text{ H}_2/\text{air}$ stoichiometry.

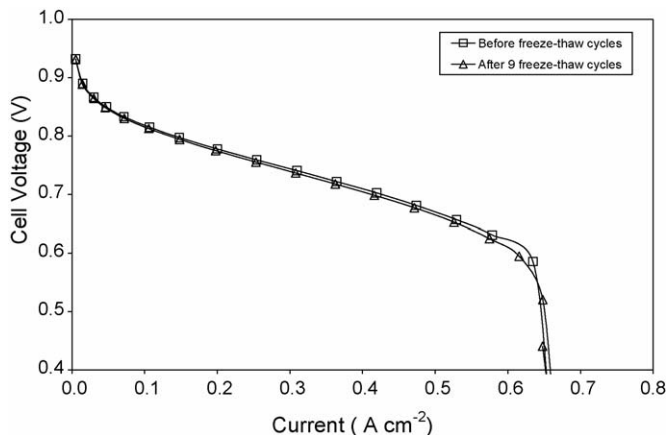


Fig. 6. Polarization curves before and after nine freeze-thaw cycles. Before the freeze-thaw cycles, the MEA within the cell was dehydrated by passing dry reactants through both the anode and cathode compartments for 10 min. Cell temperature 65 °C, 100% RH for both the anode and cathode reactants, constant reactant flow rates with 1.5/2.0 H₂/air stoichiometry at a current density of 0.6 A cm⁻².

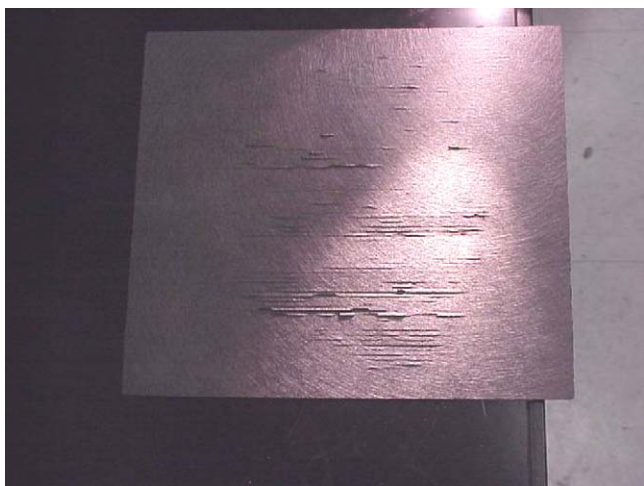


Fig. 7. Picture of the backside of a GDL obtained from a disassembled fuel cell system. The fuel cell system went through some idle periods during a winter.

zero) electrolyte concentration exists, and there are pores on the order of microns or larger scales where water will freeze more readily.

For MEAs assembled into a fuel cell, the volume expansion accompanying ice formation could create significant stress in all directions, including the direction perpendicular to the electrode surface. At the same time, the membrane, GDL and catalyst layer could become slightly more brittle under freezing conditions. The combination of brittleness and stress could lead to crushing of the MEA structure and perforations of the entire MEA become possible. Fig. 7 illustrates a picture of the backside of a GDL that was obtained from a disassembled fuel cell system. The fuel cell went through some idle periods in a winter. Obviously, the GDL was seriously crushed, and portions of the flow-field pattern can be seen.

4. Conclusions

Severe physical damage to the electrodes – cracks and catalyst domain segregation – were observed when a fully hydrated membrane-electrode assembly, either as a freestanding piece or as assembled in a single cell fixture, was subjected to multiple freeze-thaw cycles between 20 and –30 °C. The electrochemical active surface areas measured from hydrogen desorption peak areas decreased in conjunction with the electrode damage. However, the short-term fuel cell performance did not show apparent decline due to such damage. On the other hand, freezing did not cause apparent damage to membrane-electrode assemblies that were partially hydrated by exposing them to only ambient temperature and relative humidity before going through the freeze-thaw cycles. Also, when the MEA was dehydrated by passing dry gases through both the anode and cathode compartments after a cell had been tested at fully humidified conditions, no apparent physical damage was observed to the MEA by the freeze-thaw cycles either. These observations suggest that lowering the water content within an MEA could be an effective method to prevent it from being severely damaged due to freeze-thaw cycles [14,18].

Acknowledgements

The authors are grateful to Mr. Mike Knussman and Mr. Tim Phillips for performing the SEM/EDS analyses and single cell tests, respectively. We thank Ms. Cynthia Mahoney White, Mr. Daniel Beaty, Mr. Jeffrey Boyer, and Dr. Richard Pollard of Plug Power for their critical reviews of this article.

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