

Short communication

Effects of reverse voltage and subzero startup on the membrane electrode assembly of a PEMFC

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Abstract

Effects of reverse voltage and frozen fuel cell startup on the membrane electrode assembly (MEA) were investigated for a proton exchange membrane fuel cell (PEMFC). A single cell was started from a subzero temperature by applying reverse voltage. The voltages applied to the cell were 0.8 and 1.2 V. The fuel cell performance was measured with a polarization curve and by cyclic voltammetry (CV), electrochemical impedance spectra (EIS), linear scan voltammetry (LSV) after each experiment. From the results, it was concluded that the catalyst activity, electrochemical active surface area (ECA) and the membrane were not damaged by the reverse voltage if the voltage was below 0.85 V. In contrast, a reverse voltage improved cell performance slightly. If the reverse voltage was larger than 0.85 V, the cell performance degraded. Another single cell with an active area of 128 cm² was started up at -15°C by applying reverse voltage. The cell performance and MEA physical characteristic were tested before and after the freeze startup. From the results, the cell performance decayed MEA delamination was observed and the pore size distribution of the MEA changed.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) has attracted great attention in recent years as a promising replacement for traditional engines due to its high power density and ultra-low emission features. Especially, the automotive industry has pushed PEMFC development in the recent years. Beside the very high dynamic demands in cars, fuel cell systems must also be able to startup at temperatures below 0°C . For passenger fuel cell vehicles, customers will expect to startup the vehicle immediately, implying a very short time for the system warm up for full power. For the direct hydrogen system, the 2010 DOE requirement for cold startup is from -20°C to maximum power is 30 s [1]. The most significant problem for PEMFCs in cold weather is the frozen water, since water is required to keep the PEM moist, and is generated at the cathode as a consequence of the electrochemical reaction. Frozen water partially blocks

the passages or the reactant gases through a porous support medium, thereby partially inhibiting the electrochemical process. It may also degrade cell performance. To deal with this, many methods were proposed for a fast startup and for evaluating the performance degradation. Reiser [2], introduced a PEMFC cold startup using a hydrogen pump at a constant current density at -30°C . Matsuoka [3] reported a PEMFC cold start at -30°C . They found that the cell temperature reached 0°C in about 100 s. But the voltage applied to the stack reached 2.4 V. Hydrogen was generated by water electrolysis. Korytnikov [4] also tried a PEMFC startup at a subzero temperature using a hydrogen pump. The voltage applied to the cell was controlled to below 0.4 V. All of the mentioned research did not investigate the influence on the performance and electrochemical characteristics. Yan et al. [5] investigated the cold-start behavior and the effect of a subzero temperature on fuel cell performance. They concluded that MEA and backing layer were damaged after operation below -5°C . Catalyst layer delamination and cracks and pinholes in the membrane were observed. Oszipok et al. [6,7] used statistical analysis to study operational influences on the passive cold-start behavior of PEM fuel cells. Their exper-

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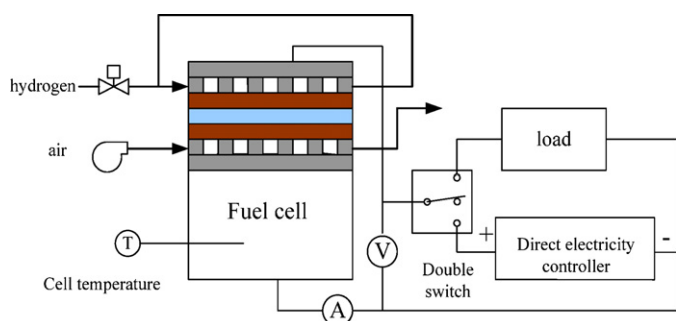


Fig. 1. Scheme of PEMFC rapid startup using hydrogen pumping.

iments showed that the initial current mainly depended on the membrane humidity and the operating voltage. The load level must be high to blow out the product water and for successful cold startup in fuel cell stacks the membrane should not be too dry.

In this study, the reverse voltage and freeze startup effect on cell performance and MEA electrochemical characters were investigated. As shown in Fig. 1, a dc power is placed in series with fuel cell. Namely, the positive was applied to the fuel cell cathode side, and the negative was applied to the fuel cell anode side. So, the voltage applied to the fuel cell is called “reverse voltage”. Initially, a fuel cell with 4 cm^2 active area was employed to investigate the effect of reverse voltage on cell at room temperature. A single cell with active area of 128 cm^2 were employed to investigate the PEMFC startup behavior at subzero temperatures using applying reverse voltage. The single cell was housed in an environmental chamber that allowed the cell to be subjected to temperatures ranging from sub-freezing conditions to normal operation. During the startup at subzero and room temperature using applying reverse voltage, there was no humidification. Protons move from one side of the membrane to the other side of the membrane due to the reverse voltage. So, this process is also called a “hydrogen pumping”.

2. Experimental

2.1. Test bench

A test bench was set-up, which enabled fuel cell operation under nearly isothermal conditions. The temperature was controlled by a thermostatic bath, which was connected to the fuel cell cooling plates. The gas humidity is adjusted up to 100% by conventional bubble humidifiers. The gas inlet pressure and the temperature were monitored. The whole test bench is controlled by a PC and all signals were recorded. Digital mass flow controls were used for gas regulation. The electronic load had an operating range up to 300 A.

For simulating a subzero environment, a climate chamber was used. The temperature ranges were between -40 and $80\text{ }^\circ\text{C}$. A dc power source is connected in series with the fuel cell. The current ranged up to 120 A with the voltage up to 100 V. The fuel cell was placed in the climate chamber. Dry air and hydrogen were supplied by the test bench. The whole test bench was controlled by PC and all signals are recorded.

2.2. Fuel cell, MEA and performance measurements

The gas diffusion electrodes (GDEs) were fabricated using a 20 wt.% home-made Pt/C (Vulcan XC-72) catalyst, Toray carbon paper, Nafion[®] solution and PTFE suspension. The Pt loading of the GDEs is totally 1 mg cm^{-2} and the dry Nafion[®] content is about 1.0 mg cm^{-2} for either anode or cathode. Two electrodes and a N212 membrane were hot-pressed to form a MEA.

A single cell with a 4 cm^2 active area consisted of a membrane electrode assembly (MEA), two graphite monopolar plates and two organic glass end plates. The graphite monopolar plates used as current collectors were machined with parallel flow channels. The other side of the graphite planar plate was machined with coolant channels. A silicon O-ring was used as a seal. The fuel cell test station consisted of temperature controllers, humidifiers, mass-flow controllers, pressure regulators and an impedance meter (KFM2030 Kikusui, Japan). The experimental data were recorded by Fuel Cell Load & Impedance software from Kikusui. The cell was operated at 0.03 MPa and $60\text{ }^\circ\text{C}$, while the reactant humidification temperatures were set at 5 and $10\text{ }^\circ\text{C}$ above the cell temperature. The heating tape temperatures were $7\text{ }^\circ\text{C}$ higher than the humidification temperatures to avoid water condensation. The cathode and anode outlet gas flows were controlled at a constant flow rate of 100 and 40 mL min^{-1} . The cell was operated at 0.5 A cm^{-2} until the voltage became stable. Then, the polarization curve was recorded. The polarization curves of the cell were measured by scanning the current from 0 to 6 A with $0.2\text{ A}/10\text{ s}$ increments and simultaneously measuring the voltage.

The single cell had an active area of 128 cm^2 . The flow-field has a parallel structure with a channel width of 1 mm, depth 0.8 mm and a ligament width of 1 mm. Bipolar plates were made of a metal compound with a graphite parallel flow-field. The current collectors were made of stainless steel and the end plates of a non-metallic material. The single cell was operated at an ambient pressure and $65\text{ }^\circ\text{C}$, while the reactant humidification temperatures were set at $5\text{ }^\circ\text{C}$ above the cell temperature. The heating tape temperatures were $7\text{ }^\circ\text{C}$ higher than the humidification temperatures to avoid water condensation. The cathode and anode inlet gas, oxygen and hydrogen or air and hydrogen, flows were controlled at a constant flow rate of 0.9 and 1.2 or 3 and 1.2 L min^{-1} . The cell was firstly operated at 0.5 A cm^{-2} until the performance was steady. The polarization curves of cell were measured by scanning the current from 0 to 150 A with $10\text{ A}/30\text{ s}$ increments and simultaneously measuring the voltage.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) was implemented to determine the electrochemical surface area (ECSA) of the cathode available for hydrogen adsorption or desorption. Fifty millilitre per minute ultrahigh purity nitrogen gas of and 100 mL min^{-1} humidified hydrogen were fed to the cathode and the anode. The reference and counter electrode leads were connected to the anode while the working electrode lead was connected to the cathode. For the CV, three cycles were performed at a sweep rate of 50 mV s^{-1} and cell potential was scanned from -0.05 to 1.0 V . After each

experiment CV was measured. A TDI3691 potentiostat (Tian-Jing ZhongHuan, China) was used. For the LSV, the sweep rate of 4 mV s^{-1} and the potential range of 0–0.5 V were selected.

In situ electrochemical impedance spectra were measured by a KFM2030 impedance meter. The perturbation amplitude for the sinusoidal signal was 165 mA (peak to peak) over a frequency range of 10 kHz to 0.1 Hz. Impedance measurements were performed after the polarization test. The cell was stabilized at 0.5 and 1 A cm^{-2} , respectively, for 3 min, before the perturbation was added to the cell.

2.4. Applying reverse voltage at room temperature

A single cell with 4 cm^2 active area was first operated at 60°C . After stable cell performance was achieved, the cell performance was tested by measuring the polarization curve (IV). Electrochemical characteristics such as cyclic voltammetry (CV), electrochemical impedance spectra (EIS) and linear scan voltammetry (LSV) were also measured. After purging the anode and the cathode sides using 50 ml min^{-1} dry hydrogen and air for 60 s, the air and hydrogen were supplied to the cathode and the anode. The flow rates of the reactant gases were 80 mL min^{-1} of dry air and 20 mL min^{-1} of dry hydrogen. Then the reverse direct electricity was applied to the cell by using a dc power source. The voltage was controlled at 0.8 and 1.2 V. The time was lasted 20 min. The cell temperature, current and voltage were recorded. After each experiment, the cell was operated for 30 min at 500 mA cm^{-2} , 0.03 MPa and 60°C . Then the cell performance and electrochemical characters by measuring IV, EIS and LSV were tested. The scheme of hydrogen pumping is given in Fig. 1. Here, a dc power source was used.

2.5. Cold startup

Single cell with active area of 128 cm^2 cold startup using applying reverse voltage were performed at -15°C . The single cell was operated at ambient pressure, 65°C , until its performance was steady. Then cell performance (IV) was tested. The dry nitrogen was supplied to the cell cathode and the anode, and the flow rate were all 5 L min^{-1} . The whole purging processing lasted about 5 min. The relative humidity (Rh) of flow gas was 30%. After the purging, the cell was insulated, then, put into the climate chamber. After the cell temperature dropped to the temperature cell start from, the cell was kept for about 2 h. The dc power source was applied in reverse to the cell. Namely, it was placed in series with the fuel cell. Dry air and hydrogen were supplied to the cathode and the anode, respectively. After the cold startup by applying reverse voltage, the cell performance was tested after it was operated about 30 min at 500 mA cm^{-2} , 65°C and ambient pressure. The scheme of PEMFC cold start using applying reverse voltage was given Fig. 1.

2.6. Physical characteristic

The SEM measurement was performed on JEOL (JSM-5600LV) scanning electronic microscope. After startup experiments, MEAs were taken out from the cells. To avoid a

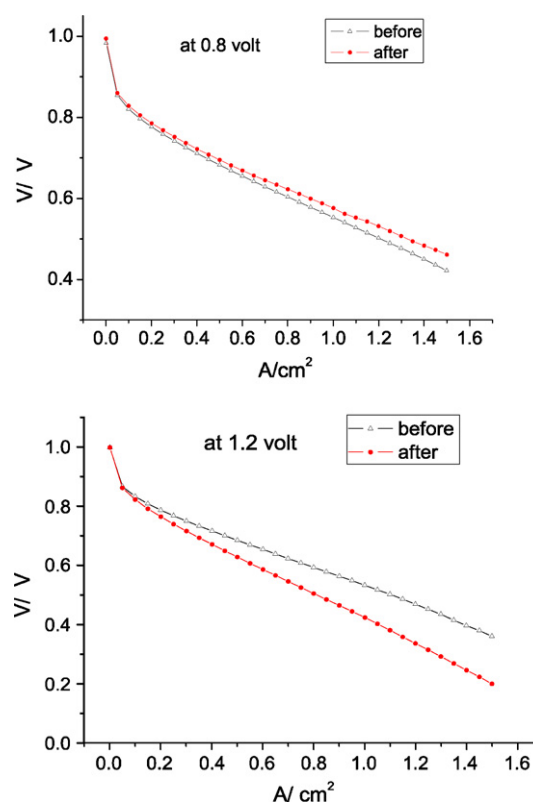


Fig. 2. Cell performance before and after applying reverse voltage of 0.8 and 1.2 V.

freezing effect during the process of sample preparation, liquid nitrogen was not used to prepare the specimens. The specimens for SEM were prepared by cutting the MEA by surgical knife. PoremasterGT60 (Quantachrome) was applied to measure the porosity of the MEAs. Information was obtained from the amount of mercury intrusion as a function of the applied pressure. The pressure is from 1.38×10^3 to 4.13×10^7 Pa (0.2 – 6.0×10^4 psi) and the mercury contact angle is 140° .

3. Results and discussions

3.1. Effect of reverse voltage at room temperature

The hydrogen pump effect of the single cell at room temperature was studied by measuring the polarization curve of the cell operation at 60°C . The polarization curves after the hydrogen pump process at different applied voltages are shown in Fig. 2. The polarization curves show that the performance does not degrade when the reverse voltage is 0.8 V. In fact, the reverse voltage applied on the fuel cell may improve the cell performance. But, at 1.2 V of reverse voltage, the cell performance degraded significantly. The reversed electricity did not degrade the catalyst if the reverse voltage did not exceed the Pt oxidation potential. In the hydrogen pump process, hydrogen was generated in the catalyst layer and released. The hydrogen may drive the water on the surface of the catalyst out. So the catalyst active surface area increases. This can be seen in the CV results in Fig. 4. Once the reverse voltages exceed the oxidation voltage

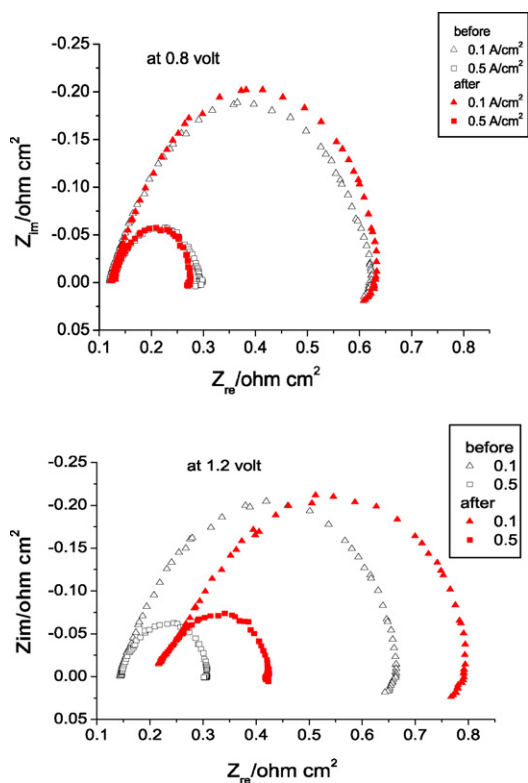


Fig. 3. The EIS responses before and after applying reverse voltage of 0.8 and 1.2 V.

of Pt. Oxidation of Pt makes the ECA decrease. This can also be seen in the CV results in Fig. 4.

The dynamic EIS response of a fuel cell can provide information about interfacial kinetics, electrode transport process and membrane hydration [9,10]. The electrochemical impedances of the cell operating at 0.1 and 0.5 A cm⁻² were measured after each experiment. For different applied voltages, the hydrogen pump effect on the EIS responses of cell are shown in Fig. 3. The impedance spectrum included a high frequency intercept with the real axis, a high frequency arc and a low frequency arc. From Fig. 3, at 0.8 V, the sum of the membrane resistance and the contact resistance between the membrane, electrodes and bipolar plates was constant, at about 0.125 Ω cm². In addition, it can be concluded that the charge transfer resistance did not change significantly. But, at a 1.2 V applied voltage, the corresponding value was about 0.225 Ω cm². It can be concluded that during the hydrogen pumping process the membrane and electrolyte are not destroyed if the reverse voltage is less than oxidation potential of Pt.

In addition to the IV curve, a diagnostic test of the CV measurement was carried out to get the ECA of the Pt catalyst. The ECA is the area under the H-desorption peak in the CV curve. The ECSA can be calculated with the following equation [8]:

$$\text{ECA (m}^2 \text{ g}^{-1}) = \text{charge area } (\mu\text{C cm}^{-2}) \times 10 \times 210 (\mu\text{C cm}^{-2}) \times \text{catalyst loading (mg cm}^{-2})$$

The CVs are shown in Fig. 4. The ECA becomes slightly larger after hydrogen pumping at 0.8 V. At 1.2 V, the ECSA

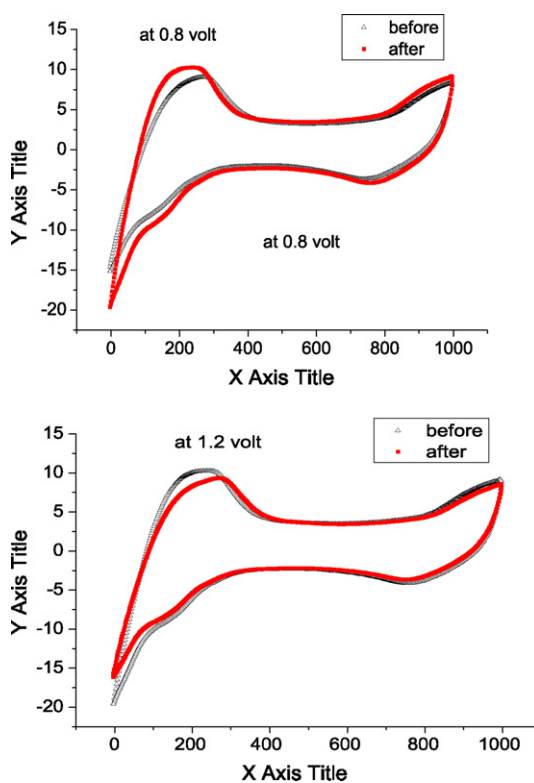
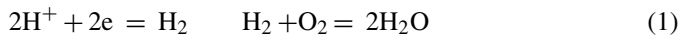


Fig. 4. The CV responses before and after applying reverse voltage of 0.8 and 1.2 V.

becomes smaller after hydrogen pumping. The ECA results are consistent with the IV performance.

LSV measurement was also employed to investigate the effect of hydrogen pumping on the membrane. During the hydrogen pumping, protons penetrated through the membrane and reacted with oxygen at the cathode as in reaction (2). Protons may also combine with electrons to generate hydrogen then the hydrogen reacted with oxygen as in reaction (1). The reaction (1) may be likely to cause some hot points, and may induce cracks and pinholes in the membrane. But, from Fig. 5, the crossover hydrogen current was constant, so that the hydrogen pumping did not induce these phenomena.



3.2. Cold startup and effect on the MEA

A single cell with an active area of 128 cm² was tested from -15 °C. The cell temperature, voltage and current were recorded and are shown in Fig. 6. The IV curves before and after the cold startup were measured. The reactants were pure oxygen and air with pure hydrogen. The performance degradation is shown in Fig. 7. From Fig. 7, the performance degradation with air and hydrogen was more significant than that with oxygen and hydrogen. It may be caused by diffusion layer degradation. During the cold startup process, water is generated and diffuses through the diffusion layer. At subzero temperatures, however, some water freezes in the diffusion layer. The pore structure in

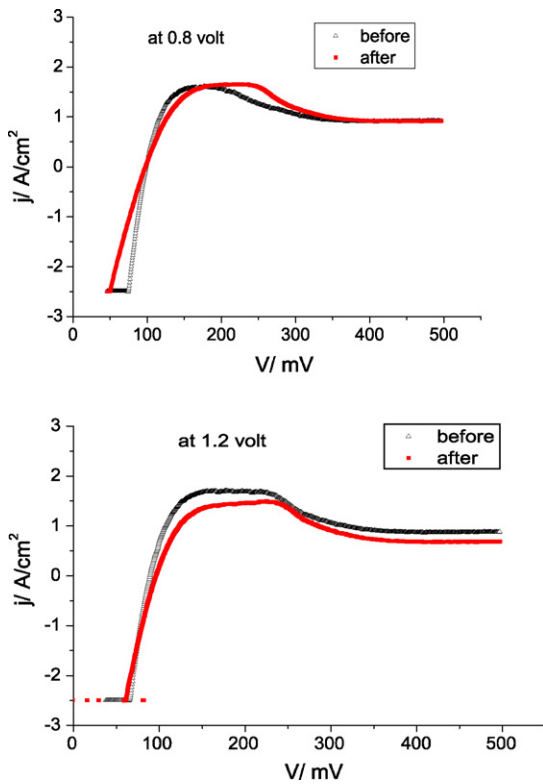


Fig. 5. The LSV responses before and after applying reverse voltage of 0.8 and 1.2 V.

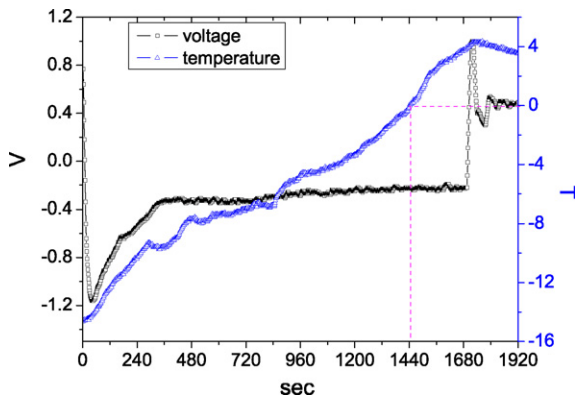


Fig. 6. Cell temperature and voltage variations during the single cell cold start at -15°C by applying reverse voltage.

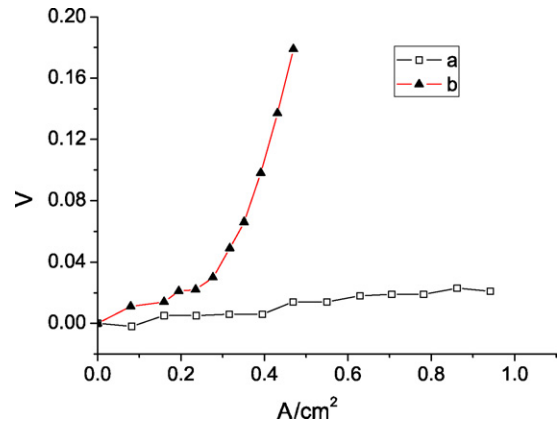


Fig. 7. Cell performance degradation with air/hydrogen (b) and oxygen/hydrogen (a).

the diffusion layer becomes larger or hydrophilic and reduces the reactant diffusion to the catalyst layer.

To investigate the morphology change of the MEAs, cross-sections of fresh MEA (a) and MEA (b) after cold startup at -15°C are compared in Fig. 8. The smooth components in the middle of the pictures is the membrane and the left side is the cathode. From Fig. 8a, the cathode or anode contacts the membrane intimately. The cross-section of the MEA (b) in Fig. 8b is different from a fresh one. Delamination did occur in the MEA. During cold startup by applying reverse voltage, water was generated in the catalyst layer on the cathode side. For temperatures below 0°C , water froze in the catalyst layer and caused the MEA delamination.

The pore size distribution of the MEA after cold startup was also investigated, as shown in Fig. 9. The important characteristic in the figure is the peak in the size range of $10\text{--}100\ \mu\text{m}$. The diameter corresponding to the peak can be called “mode pore diameter” of the GDL since the pore diameter in the CL is generally smaller than $10\ \mu\text{m}$ [9]. The mode pore diameters for the MEAs after cold startup become larger and the pore number in the size range of more than $30\ \mu\text{m}$ increases. Most of the water exists in the GDL and the gas channels. As a result, the mode pores diameter becomes larger and the number of the pores increases due to volume changes. The passages for water and gas are all destroyed. Since the pores are structurally changed, the PTFE impregnating the pores most likely breaks off. This will

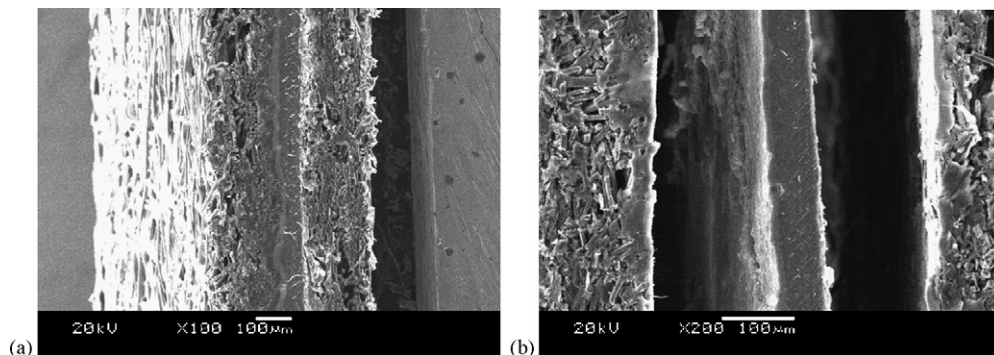


Fig. 8. Cross sections of the different MEAs: (a) fresh MEA and (b) MEA after cold startup from -15°C .

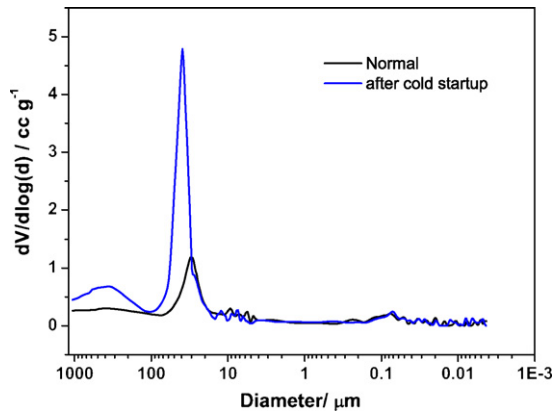


Fig. 9. Pore size distribution of the fresh MEA and MEA after cold startup.

induce easy flooding at high current density. This might be one of the reasons why the cells have poor mass transport performance after the cold startup.

4. Conclusions

Reverse voltages applied to the cell did not degrade the cell performance and electrochemical characteristics if the voltage did not exceed 0.85 V. In fact, the cell performance was improved. When the reverse voltage exceeded 0.85 V, cell performance degraded. The electrochemically active surface area decreased. Cell performance degradation occurred after cold startup using applying reverse voltage above 0.85 V, and the pore structure in the diffusion layer was changed significantly,

due to the volume change of water and ice phase transition. MEA delamination was also found after the cell experienced cold startup.

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References

- [1] U.S. Department of Energy, Fuel Cell for Transportation, Annual Progress Report, Washington, DC, 2001 (introduction).
- [2] C.A. Reiser, Battery-boosted, Rapid Startup of Frozen Fuel Cell, United States Patent 0207162 A1 (2003).
- [3] N. Matsuoka, United States Patent 0013915 A1 (2004).
- [4] K. Korytnikov, Peter Novak, Method and Apparatus for Cold-starting A PEM Fuel Cell System, United States Patent 0227126 A1 (2005).
- [5] Q. Yan, H. Toghiani, Y.-W. Lee, K. Liang, H. Causey, J. Power Source (2006).
- [6] M. Oszcipok, D. Riemann, U. Kronenwett, M. Kreideweis, M. Zedda, J. Power Sources 145 (2) (2005) 407–415.
- [7] M. Oszcipok, M. Zedda, D. Riemann, D. Geckeler, J. Power Sources (2005).
- [8] T.R. Ralph, G.A. Hards, J.E. Keating, et al., J. Electrochem. Soc. 144 (1997) 3845.
- [9] M. Watanabe, M. Tomikawa, A. Motoo, J. Electroanal. Chem. 195 (1985) 81.
- [10] V.A. Paganin, C.L.F. Oliveira, E.A. Ticianelli, et al., Electrochim. Acta 43 (24) (1998) 3761.