Workshop on Fuel Cell Operation at Sub-Freezing Temperatures

A Study on Performance Degradation of PEMFC by Water Freezing

Feb. 1-2, 2005

EunAe Cho
Fuel Cell Research Center
Korea Institute of Science and Technology



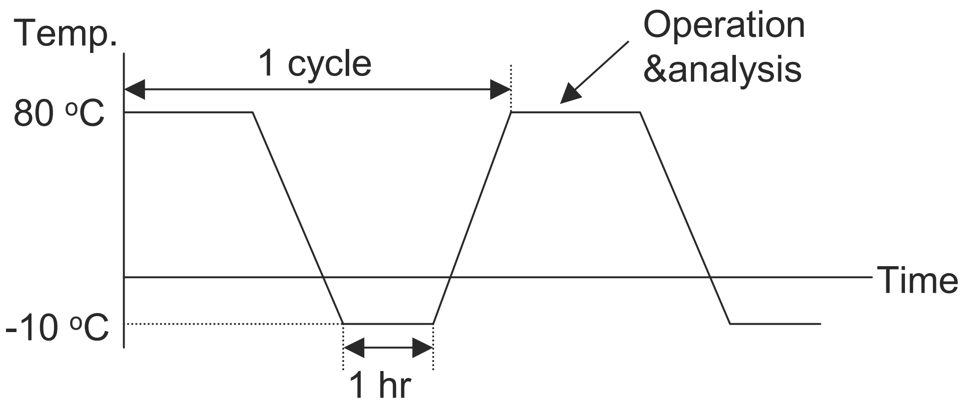

Overview

Study on performance degradation mechanism of PEMFC exposed to sub-freezing temperatures → Development of performance degradation prevention methods

- E.A. Cho et al., "Characteristics of the PEMFC Repetitively Brought to Temperatures below 0 ^{o}C", *J. Electrochem. Soc.*, **150** (12), A1667-A1670 (2003)
- E.A. Cho et al., "Effects of Water Removal on the Performance Degradation of PEMFCs Repetitively Brought to < 0 ^{o}C", *J. Electrochem. Soc.*, **151** (5), A661-A665 (2004)

Experimental

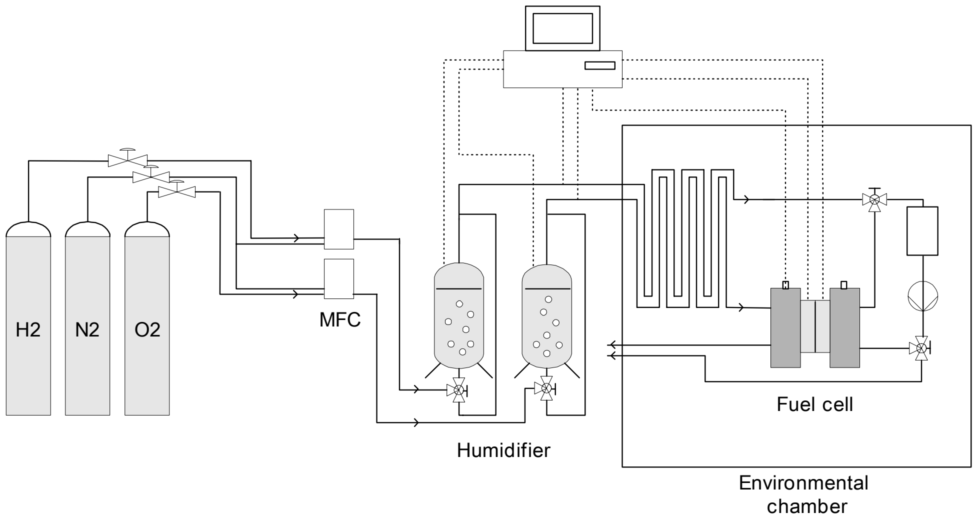
Thermal cycle



MEA fab. & operation condition

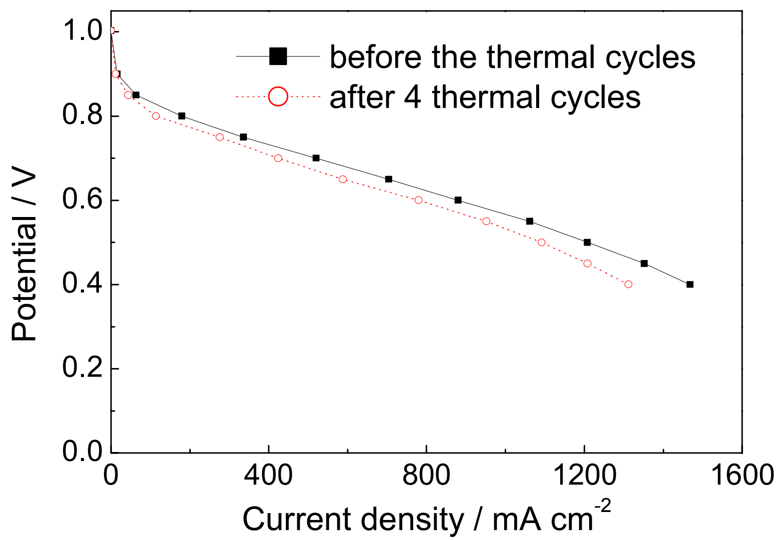
Item	Specification
Active area	25 cm^2
Anode Pt loading	0.4 mg/cm^2
Cathode Pt loading	0.7 mg/cm^2
Membrane	Nafion 115
Hot pressing	200 kg/cm^2 at 140 °C for 90 s
Operating temp.	80 °C
Operating pressure	1 atm
Gas stoichiometry	λ_{H2} = 1.5, λ_{O2} = 3
Humidifier temp.	An. : 80 °C Ca. : 75 °C

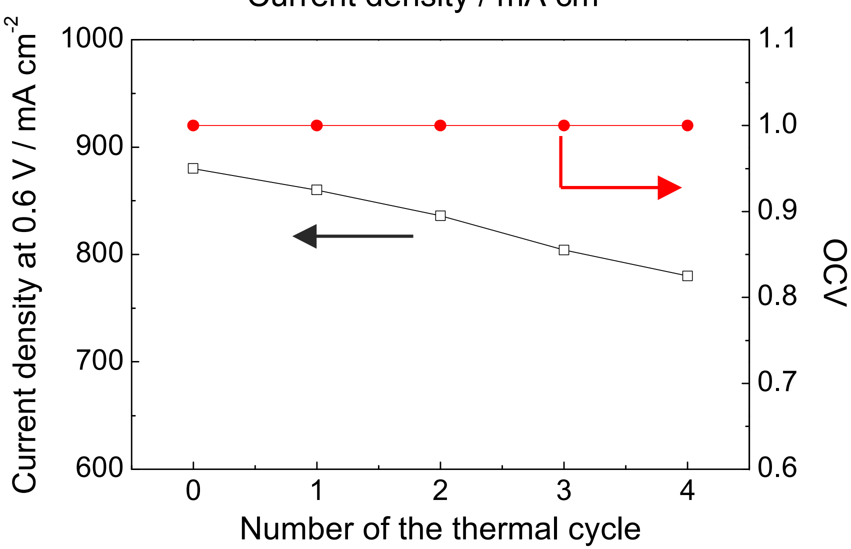
Apparatus



Performance Degradation

◈ Effects of the thermal cycles on performance





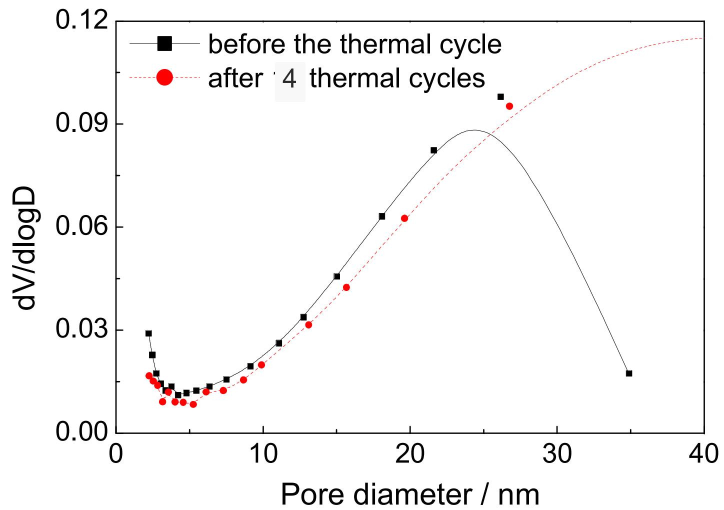
With the thermal cycle, current density measured at a cell voltage of 0.6 V was decreased while OCV remained almost constant.

Freezing of water in PEMFC degraded the cell performance by increasing activation losses and ohmic losses without affecting internal current.

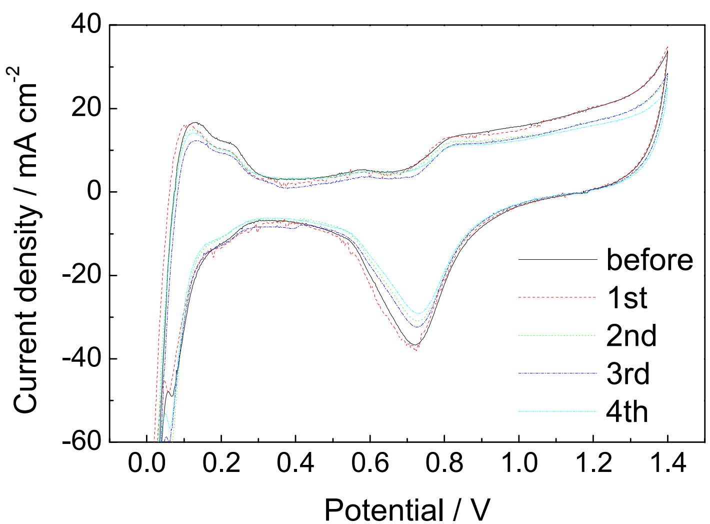
Electrode Degradation

Korea Institute of Science and Technology
Fuel Cell Research Center

- Pore size distribution by nitrogen adsorption



- Cyclic voltammogram

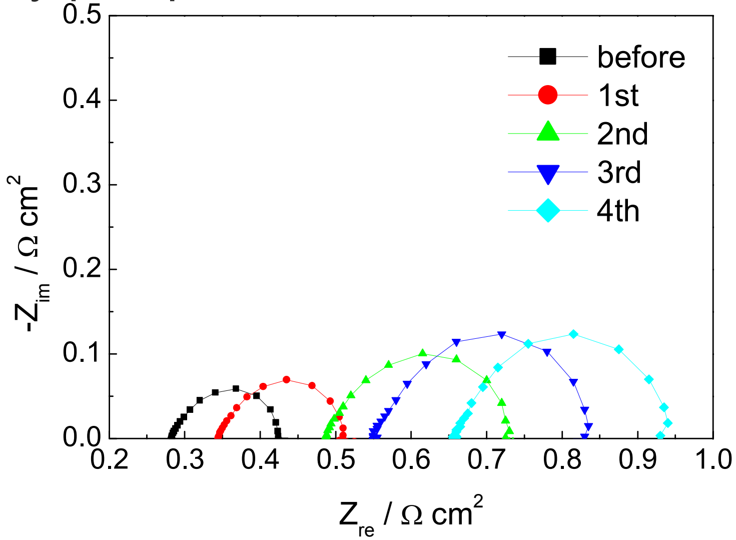


By the thermal cycles and the resulting volume changes of water, pore size was increased with decrease in specific surface area, electrochemical active surface area and, hence, utilization of platinum catalysts.

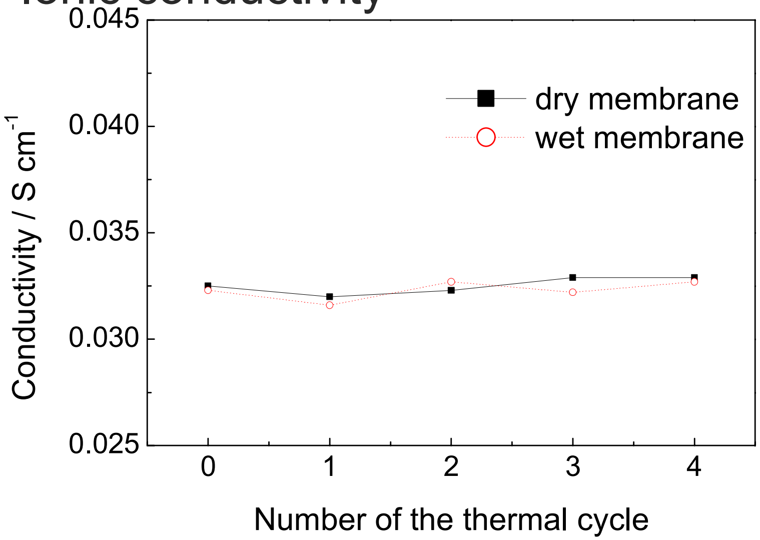
Deformation of the catalytic layer would cause degradation of the cell performance by increasing the activation polarization, making the contact between catalyst powders and membrane loose, and breaking down the network structure of Nafion ionomers in the catalytic layer.

Interface Degradation

Nyquist plots



Ionic conductivity



During the 4 thermal cycles, freezing of water in PEM results in the increase of ohmic resistance and charge transfer resistance and in the performance degradation.

For both wet and dry PEM, the proton conductivity was almost constant, independent of the number of the thermal cycles.

The increase in ohmic resistance by the thermal cycles is not attributed to the increase in proton conductivity of PEM, but probably due to an increase in the contact resistance between electrodes and PEM.

Conclusions

- A repetitive freezing and melting of water in PEMFC, accompanied by volume change, degraded the cell performance by increasing polarization resistance and ohmic resistance.

- The volume change of water increased the pore size of catalytic layer, which might make the contact between catalyst powders and membrane loose and break down the network structure of Nafion ionomers in the catalytic layer, and decreased electrochemical active surface area. Deformation of the catalytic layer resulted in increase in contact resistance and activation polarization.

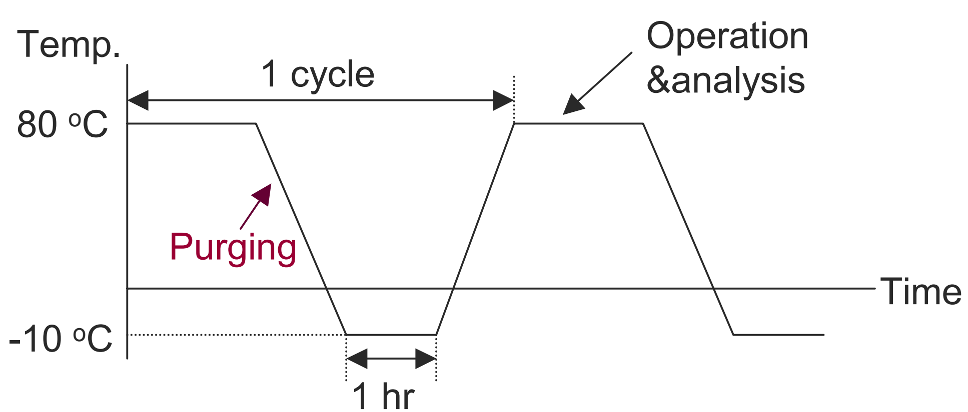
- Charge transfer resistance and ohmic resistance were increased by the repetitive freezing and melting of water in PEMFC while proton conductivity of PEM was almost constant. This implies that the increase in ohmic resistance was attributed to an increase in contact resistance between the electrode and membrane, in accordance with the results obtained from the analysis of electrode structure.

- *To operate the PEMFC at temperatures below 0 °C, the removal of water from the cell is essential.*

Water Removal Methods

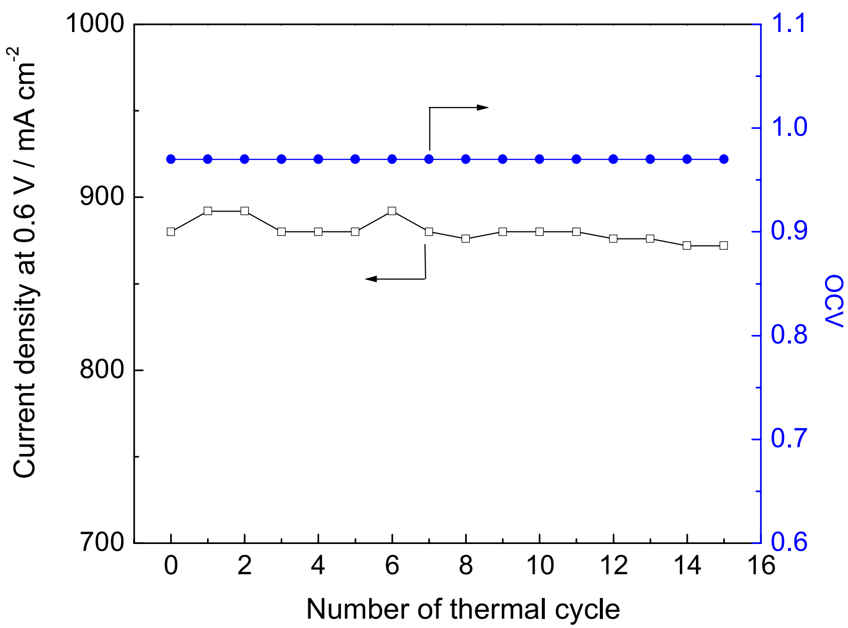
Korea Institute of Science and Technology
Fuel Cell Research Center

- Two candidates for water removal from PEMFC
  - Dry gas purging
    - N_2/O_2
    - RH of outlet gas < 3 %, 20 min.
  - Anti-freezing solution purging (freezing point = -20 °C)
    - 30 % MeOH, 35 % Ethylene glycol
    - 30 % EtOH, 47 % Iso-propanol : low dimensional stability

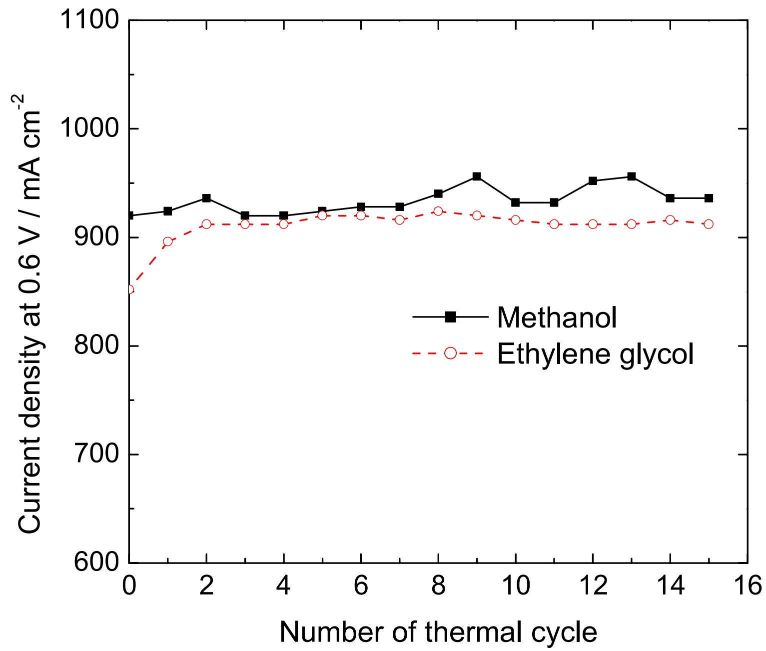


Performance Conservation

- Gas purging method



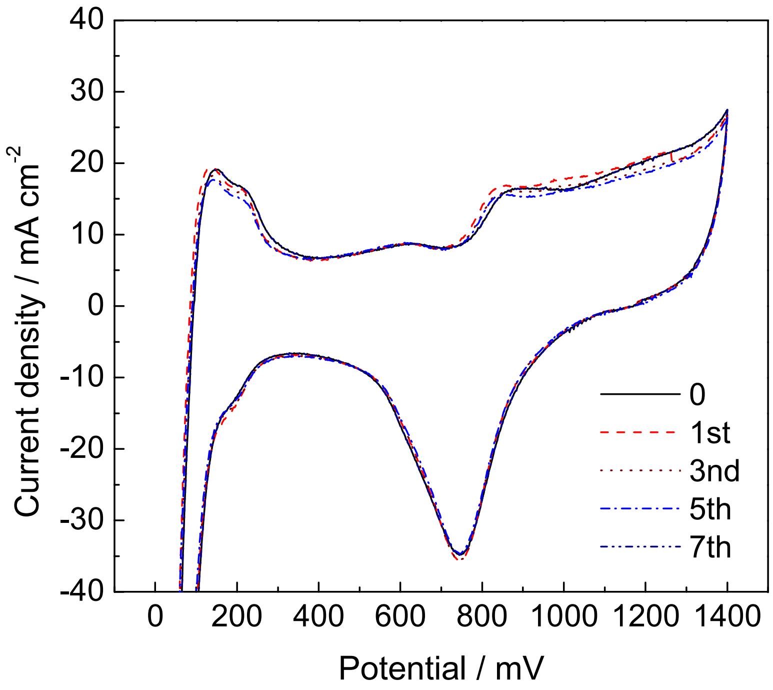
- Anti-freezing solution purging method



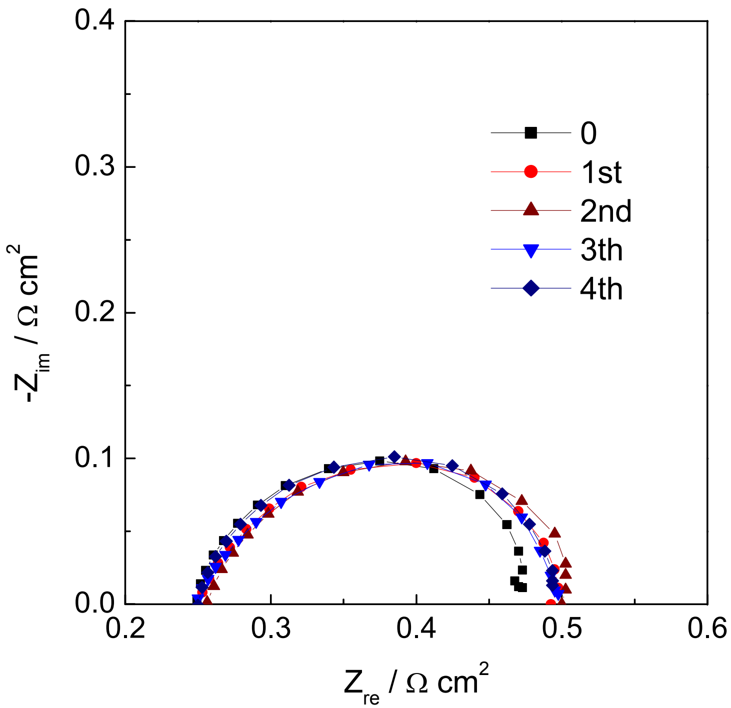
Electrode & Interface Conservation

Korea Institute of Science and Technology
Fuel Cell Research Center

◈ Nyquist plots



◈ Cyclic voltammogram



Conclusions

Korea Institute of Science and Technology
Fuel Cell Research Center

- The gas purging method, by which water was removed from the PEMFC by feeding dry nitrogen and oxygen gases to the anode and the cathode, respectively, before cell temperature fell down below 0 ^{o}C, significantly reduced the performance degradation rate.

- Considering time restriction in a mobile application, anti freezing solutions, instead of the dry gases, were supplied to PEMFC. By using the solution purging method employing either 30 % methanol or 35 % ethylene glycol solution as an anti-freezing solution, the performance degradation was successfully prevented.