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Analysis of Ice Distribution in Cathode Catalyst Layer and Shutdown Mechanism at PEFC Cold Start

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In polymer electrolyte membrane fuel cells (PEFCs), freezing of produced water induces the extreme deterioration of cell performance below zero. This phenomenon is serious problem in cold regions and is needed to be solved to achieve the practical use of PEFCs. In this study, we investigated the freezing phenomena in the cathode catalyst layer (CL) by the experiments, and identified the effects of current density, cathode gas pressure, and oxygen concentration. Furthermore, we analyzed the factor dominating the uneven ice distribution and the operation shutdown by the model simulation.

A single cell with an active area of 25cm^2 was used for the experiments. 0.2mm thick carbon papers with micro porous layer (MPL) were used for gas diffusion layers (GDLs). Separators on the anode and cathode sides were made of carbon with straight channels.

The procedure of the cold start experiment consists of four steps in thermostatic chamber: preconditioning, gas purge, cool-down, and cold start. At the gas purge process, the initial water conditions in the cell were strictly controlled because residual water in the cell strongly affects the cold start characteristics. After the cell temperature was cooled down to -20ºC or -30ºC, the cold starts with pure hydrogen as the anode gas, and three kinds of gases as the cathode gas were conducted.

The amounts of ice formed in the cathode CL were estimated from the cold start characteristics (1). Figure 1(a) shows the amounts of ice for three current densities with air. As the current density increases, the amount of ice decreases. This is because ice is formed uniformly and almost all of the CL pores are finally filled with ice at low current density, but larger amounts of ice are finally present near the GDL interface and empty pores remain even after the shutdown at high current density (1).

Figure 1(b) shows the amount of ice for different cathode gases and pressure conditions, air at 1atm, nitrogen with oxygen 10% at 2atm, and air at 2atm. The current density was 0.08A/cm^2. In these operations where molecular diffusion coefficient and the oxygen molar concentration are changed, the ice amounts are very similar. This indicates that Knudsen diffusion is dominant in the CL, but it is difficult to explain the oxygen concentration dependency.

Figure 1(c) shows the amount of ice in the CL for three current densities with pure oxygen. The amounts of ice are similar to those with air (Fig. 1(a)) in each current density. Figure 2 is example of the cryo-SEM images of the cathode CL cross-section after the -30ºC shutdowns at 0.2A/cm^2 with (a) air and (b) oxygen. Lager amounts of ice are formed near the GDL interface and empty pores remain even with pure oxygen. These results mean that the ice formation process is less affected by oxygen concentration and it may be concluded that the oxygen supply is not dominant to the uneven ice distribution and the shutdown. Here, we arrive at a hypothesis that increase in electrical resistance inside the CL due to ice formation dominates the ice formation process.

To examine the effect of increase in electrical resistance on the ice distribution in the CL, the model simulation was conducted using the agglomerate model (1). In the previous model, the change in thickness direction, *z*, of the cathode overpotential, $d\eta/dz$, was calculated considering only the effect of the proton current. In this study, the effect of the increase in electrical resistance due to ice formation was introduces as the following equation.

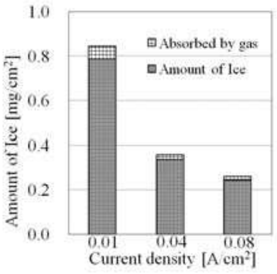
$$\frac{d\eta}{dz} = \frac{i_{H^+}}{\kappa^{eff,CL}} + A \cdot m_{ice} \cdot i_{e-}$$

Here, A is an adjusting parameter, m_{ice} is the local amount of ice in the CL, and i_{e-} is the electron current.

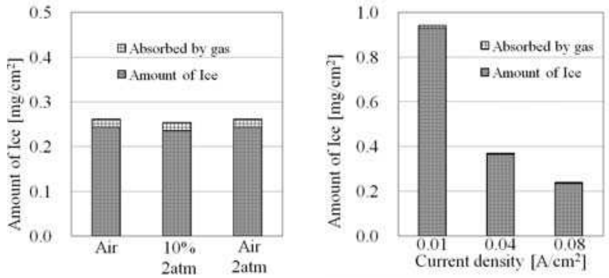
Figure 3 shows the calculation results of the ice distribution within the cathode CL for two current densities with $A=1.3\times10^2$. The abscissa is dimensionless z position; $z/\delta=0$ and 1 are the polymer membrane and GDL interfaces. At 0.01A/cm^2, ice is formed uniformly at the shutdown of 630s, while at 0.08A/cm^2 more ice is formed near the GDL interface at the shutdown of 50s. Here, ice filling the CL pores completely with 0.64mg/cm^2 blocked the oxygen supply and caused the shutdown. These results correspond to the experimental results, and it was confirmed that the change in the ice distribution is independent of the oxygen concentration and the pressure.

Reference

1. R. Ichikawa, Y. Tabe and T. Chikahisa, *ECS Transactions*, **41** (1), 733 (2011).

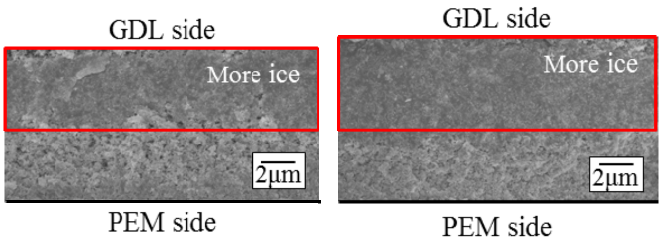


(a) With air



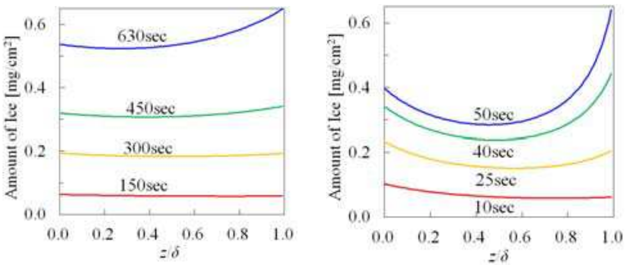
(b) With 2atm gas pressure (c) With pure oxygen

Figure 1. Amount of ice in the CL at -20ºC



(a) with air (b) with pure oxygen

Figure 2. Cryo-SEM images of the CL cross-section after the shutdown of the cold start at -30ºC



(a) At 0.01A/cm^2 (b) At 0.08A/cm^2

Figure 3. Ice distribution in the CL at -20ºC