In-situ Detection of Hydrogen Peroxide in PEM Fuel Cells

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To establish polymer electrolyte membrane (PEM) fuel cells as an alternative power source for residential and automotive markets, one has to offer a system which supplies high performance for over an extended period of time: 50,000 hours for residential power, and 5,000 hours for automotive applications. However, it has been widely observed, that proton-conducting membranes have a strong tendency to develop pinholes in the time range from a few hundred to a few thousand hours depending on operation conditions. Such defects can cause steep performance decay or catastrophic failure of the whole system.

SEM analysis revealed that severe membrane degradation frequently occurred near pinhole areas. It was believed that such degradation was caused by chemical attack of ionomer from hydroxyl free radicals generated by H_2O_2 that was present during fuel cell operation. However, direct evidence of the presence of H_2O_2 in a fuel cell and further knowledge such as the concentration of H_2O_2 as a function of membrane thickness or operation condition can guide efforts of improving membrane durability. Hence, it was the goal of this study to detect H_2O_2 *in-situ* during fuel cell operation.

Electrochemical techniques using Pt wires as working electrodes were chosen in this study. Cyclic Voltammetry (CV) and Open Circuit Potential (OCP) measurements were performed to detect local chemical species and the electrochemical potential during fuel cell operation. First, electrochemical "signatures" of H_2O_2 in an acid environment were established by performing CV scans using a Pt microelectrode in pure 4N H_2SO_4 acid saturated with air and H_2 . Second, Pt microelectrodes were assembled into a MEA, and the MEA was then built into a test cell and operated under various conditions. CV scans taken from the Pt microelectrodes in the cell were compared with the scans taken from the Pt probe that was in the controlled acid environment.

Figure 1 compares a CV scan of pure H_2SO_4 acid saturated with H_2 with an in-situ background scan taken from a Pt probe of a MEA with 3 layers of 10 μ m GORE-SELECT[®] membrane when cell was exposed to H_2 on the anode side and N_2 on the cathode side. Figure 2 compares a CV scan of H_2SO_4 acid (saturated with H_2) containing 6.6ppm H_2O_2 with an in-situ scan taken from a Pt probe when the cell was operating under 700mA/cm² in H_2 and air at 60°C.

Comparing the CV scans obtained from the Pt probes in the fuel cell and in the acid, two conclusions can be extracted. First, Pt microprobes assembled in the MEA worked properly as an independent working electrode, which detects the electrochemical environment of its surrounding area. Second, H_2O_2 did, in fact, exist in the fuel cell environment when air was present.

In conclusion, H_2O_2 was observed to be the dominant electrochemically active species in a fuel cell environment, with or without the cell being on load.



Figure 1. Comparison of CV scan of pure acid saturated with H_2 and an in-situ background scan (in-situ cell: 60°C, H_2/N_2 ; pure acid: 4N H_2SO_4 saturated with H_2 , room temperature).



Figure 2. Comparisons of CV scan of H_2O_2 in acid and an in-situ scan taken when fuel cell is on load.