Impact of Cathode Fabrication on Fuel Cell Performance

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Hydrophobicity is generally believed to be key to water management in polymer electrolyte fuel cells (PEFCs). However, we reported that the membrane electrode assembly (MEA) using a hydrophilic micro porous layer (MPL) showed much better performance in a wide range of pressure and humidity conditions than that using a hydrophobic MPL. When operating an MEA, it usually needs to be humidified in order to maintain conductivity of the membrane. Operation without humidification is critical to the commercialization of PEFCs for backup power and automotive applications. We, therefore, evaluated MEAs at 60°C, at the Hydror stoichiometric ratio of 1.45:0.1, without humidification, in addition to the normal conditions of 80°C, 100 & 30% RH. We found that the MEA employing a gas diffusion electrode (GDE) method on the hydrophobic MPL showed the best performance under a very dry condition, suggesting that the first interface between the catalyst layer and the MPL plays a crucial role in determining MEA performance, particularly under dry conditions.

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PEFCs have been investigated as a promising power source for electric vehicles and other applications because of their high performance and environmental benefits. A typical MEA in PEFC consists of an ion-exchange membrane with a pair of electrodes on opposite faces of the membrane. The MEA is sandwiched between two gas diffusion layers (GDLs). These layers are typically treated with a hydrophobic material such as polytetrafluoroethylene (PTFE), in order to remove the product water from the cathode side of the fuel cell. In addition, a micro porous layer (MPL), consisting of carbon black mixed with a PTFE binder, is generally applied to the GDL substrates for better water removal from the catalyst layer. If the water removal rate does not keep up with the generation rate, excessive water will accumulate, causing flooding in the catalyst layer, which will result in covering up active sites of the catalysts and hampering the gas transportation.

On the other hand, water taken in the ionomer and membrane is essential for optimal proton conductivity in the catalyst layer and in the membrane. Dehydration of the ionomer and membrane increases the resistance to the proton transport, causing ohmic losses. Water management, therefore, is key to improve performance of a PEFC. A lot of work has been carried out to understand the water transport mechanism in a PEFC, using experimental techniques, such as transparent fuel cells, neutron imaging,12 and X-ray radiography.13 Besides a great number of studies concerning hydrophobic GDLs for the cathode side, efforts have been made to study the use of hydrophilicity in designing MEAs. In 2003, Töber et al.1 reported that the MEA using a hydrophilic carbon paper, which has no MPL, demonstrated higher current densities than that using a hydrophobic carbon paper, but they were unable to perform sustained measurements with stable hydrophilic conditions of the carbon papers because the hydrophilic effect degraded. Introduction of silicon dioxide (SiO2) either in the catalyst layer, on the gas diffusion layer or on the membrane were studied,14 with the intention of improving PEFC performance under low humidity conditions. Use of a mixture of hydrophilic and hydrophobic materials for the MPL was studied to facilitate liquid water removal from the cathode catalyst layer by incorporating hydrophilic pathways. Wang et al.15 developed an MPL by using two carbon blacks with different hydrophilic porosity into one layer with PTFE. Mutukand et al.16 reported an improvement in PEFC performance using an MPL which contains 10 wt% hydrophilic aluminate fibers in the carbon black PTFE paste. Recently, hydrophobic/hydrophilic double MPLs coated on the GDL substrate have been presented by Kitahara et al.17,18 The hydrophilic layer, which consists of carbon black and polyvinyl alcohol (PVA) or titanium dioxide (TiO2), was coated on the hydrophobic MPL, resulting in enhancing PEFC performance under no-humidification at the cathode.

In 2010, we conceived21 the idea of hydrophilic MPLs, which is PTFE-free and instead contains hydrophobic ionomer and vapor grown carbon fiber (VGCF-H, Showa Denko K. K.). We reported22 that MEA performance is largely dependent on the combinations of hydrophobic and hydrophilic materials used for anode and cathode GDLs; the best performance was obtained for the MEA using a hydrophilic MPL for the cathode side, and it was proved to be advantageous by demonstrating stable performance for 200 hours at 2.0 A/cm2, at 64°C 100% RH. We also showed23 the difference in MEA structure and performance between the MEA using a hydrophobic MPL for the cathode GDL and that using a hydrophilic single-layer MPL for the cathode GDL. In the MEA operation without humidification, the MEA using a hydrophobic MPL showed a rapid drop in cell voltage with a rise in temperature, whereas the MEA employing a single hydrophilic MPL maintained fairly high cell voltage even at 95°C, suggesting that the hydrophilic MPL helps prevent membrane dehydration under a dry condition. Here we report the impact of cathode fabrication on MEA performance, taking into account the hydrophilic or hydrophobic surface property of the MPL for the cathode GDL.

Experimental

Hydrophobic MPL coating.— Hydrophobic MPLs were prepared by coating the slurry (consisting of carbon fiber, mixed with ionomer in a water-ethanol (1:1) mixture) on the GDL substrate. The carbon fiber was used as received. Vapor grown carbon fiber (VGCF-H, Showa Denko K. K.), ionomer dispersion (Flemion, 910 equivalent weight (EW), Asahi Glass Co., Ltd.), water, and ethanol were mixed with an ultrasonic homogenizer to prepare MPL coating slurries. The solid content of the slurry was 20 wt% and the ionomer contents were 33.3 wt%. The slurry was then applied on the GDL substrate (Improved H2315, hydrophobic treated GDL, without an MPL, Freudenberg-NOK) using a wire rod coater, so that the amount of solid would be 3.0 mg/cm2, and the coated GDL was dried in a convection oven at 80°C for 30 min.

Hydrophobic MPL.— A commercial GDL with a hydrophilic MPL (H2315 T10X6 CX96 by Freudenberg-NOK) was used. The thickness of the MPL, which is composed of carbon black and PTFE, is about 40 μm.

Catalyst coating.— The anode and cathode catalyst inks were prepared by mixing catalyst, water, ethanol, and ionomer dispersion (Experimental fluorinated polymer, equivalent weight (EW) 650; Asahi Glass Co., Ltd.) with a planetary ball mill (LP-4, Itoh Seisakusho Ltd.). The ratio of ionomer to carbon support was 0.8. Carbon-supported Pt catalyst (20 wt%Pt, Tanaka Kikinzoku Kogyo) and carbon-supported Pt-Co catalyst (53wt%Pt+7wt%Co, 0.8nm particle size) were prepared and coated on MPL, respectively, using the slurry method. The thickness of the catalyst layer was 10 μm and 5 μm for the anode and cathode catalysts, respectively.