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Gas transport inside and outside carbon supports of catalyst layers for PEM fuel cells

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ABSTRACT

A new method of evaluating gas transport resistance inside and outside the carbon supports of fuel cell catalyst layers has been developed using a partial CO covering technique. This method was developed to examine the effectiveness of the Pt catalyst deposited inside and outside the primary pores of the carbon supports. Gas transport resistance for Pt located outside a carbon support was measured by selectively deactivating Pt inside the support with CO. Gas transport resistance for Pt inside the carbon support was estimated from the total gas transport resistance and that for Pt outside the support. Gas transport resistance for Pt inside the carbon support per unit Pt surface area, $r_{micro,in}$, was slightly greater than that for Pt outside the support, $r_{micro,out}$. This indicates that Pt inside carbon supports is not as effective as that outside the supports.

Transport resistance inside the carbon support was investigated in more detail by controlling the degree of CO covering by varying the RH condition for CO oxidation. Gas transport resistance for Pt that became active at higher RH was higher than that for Pt that became active at lower RH. This indicates that gas transport resistance inside carbon supports strongly depends on the pore geometry.

1. Introduction

A polymer electrolyte fuel cell (PEFC) is a promising primary power source and is expected to be used on vehicles in the future. There are still challenges to be addressed in the commercialization of fuel cell electric vehicles (FCEVs), including power density, durability, sub-zero startup, and cost reductions. The greatest challenge of all from an industrial point of view is cost reduction. According to a U.S. Department of Energy report, Pt accounts for about a quarter of the total fuel system cost [1]. The most effective measure for this issue is to reduce the loading of the Pt noble metal and to use it more effectively.

In recent years, various core–shell catalysts have been researched to reduce Pt usage by replacing the core of a Pt particle, which does not directly contribute to electrochemical reactions, with other materials such as Au, Pd, and other metals or alloys [2,3]. Another expected benefit of replacing the core is the improvement of area-specific activity. This kind of approach is focused on the catalyst itself, while, on the other hand, the modification of catalyst supports also contributes to improving electrochemical reactions. Carbon supports with high surface areas (HSA carbon) usually have high electrochemical surface areas (ECA), resulting in high mass-specific activity [4,5], although they also result in poorer proton conductivity in the catalyst layer [6–8]. Moreover, they may also have poorer durability against both carbon corrosion [9,10] and Pt dissolution [11,12], due to the instability of carbon and high roughness and smaller Pt particle size, respectively.

Even though they may have negative repercussions with respect to proton conduction and durability, HSA carbon supports look promising because they are useful in designing the catalyst layer microstructure as well as in increasing the ECA. HSA carbon usually has numerous primary pores of several nm in diameter, and Pt can be deposited inside the pores, resulting in higher ECA. Our previous studies suggest that the ionomer cannot penetrate into the primary pores of the carbon support [6–7,13]. This is also substantiated by simulations based on coarse-grained molecular dynamics [14,15]. Since the ionomer is not present inside the primary pores, the ionomer coverage on Pt strongly depends on the presence of the primary pores, as indicated by an in situ analysis of ionomer coverage on Pt [13]. Although Pt particles inside the primary pores are not in contact with the ionomer, they could be electrochemically active because water condensed in the primary pores could contribute to proton transport from the ionomer to the Pt particles.

A recent study indicated that the oxygen reduction activity of Pt located inside the primary pores is higher than that of Pt located outside the pores and covered with the ionomer [16]. However, it is still controversial whether the effectiveness of Pt in the primary pores is as good as or better or worse than that located outside the pores. That is because since there are no effective

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methods of evaluating the transport property of reactants towards Pt inside and outside the primary pores separately. It is important to understand the transport property of reactants towards Pt inside and outside the carbon primary pores separately in order to use the precious Pt catalyst effectively.

Among various phenomena occurring in the catalyst layer, gas transport is an issue of concern because gas transport resistance, R_{gas}, increases with lower Pt loading [17]. We established a method for evaluating R_{gas} in the catalyst layer using gas crossover and analyzed the phenomenon [18]. As a result, gas transport resistance that takes place towards Pt on a micro scale was successfully identified from the overall resistance. The method, however, did not enable us to separate R_{gas} for Pt inside the primary pores, Pt_{in}, from that for Pt on the outer surface of the support, Pt_{out}. We also established an in situ technique for analyzing ionomer coverage [13]. Under a certain condition in the analysis process, only Pt located outside the primary pores and covered with the ionomer was activated. In that condition, it is likely that the electrochemical and mass transport properties of Pt_{in} and Pt_{out} can be separately evaluated. In this study, we applied the evaluation method for R_{gas} to the catalyst layer in which only Pt_{in} was deactivated by CO adsorption. That made it possible to evaluate the gas transport resistance of the reactant towards Pt inside and outside the primary pores separately.

2. Experimental

2.1. Preparation of MEA

Table 1 shows the membrane electrode assembly (MEA) specifications used in this study. Two catalyst inks were prepared respectively by mixing Pt black (manufactured by TKK, Japan) with the Nafion® ionomer dispersion (D2020, EW1000, DuPont), and Pt/C based on a porous carbon support (catalyst: 45 wt.%) with the Nafion® ionomer dispersion so that the weight ratio of the ionomer content was 0.17 relative to the Pt black and 0.9 to the carbon support. In order to investigate R_{gas} in the primary pores, a carbon support having numerous primary pores was used.

The anode side consisting of Pt black was fabricated on perfluorosulfonic acid (PFSA) square (72 mm on one side) membranes (Nafion® NR211, thickness = 25 μm) by a spray coating method and then dried for 30 min at 80 °C to remove the organic solvent. The cathode side consisting of Pt/C was then fabricated on the other side and dried again. The membrane was masked with polyethylene naphthalate (PEN) films (Q51, 25 μm, Teijin-DuPont) having 10 cm^2 (vertical direction: 2 cm, horizontal direction: 5 cm) of open area on both sides beforehand so as not to create any gaps between the film and the catalyst layer. This was done because gas crossover through such gaps could affect the analysis, although its effect would probably be small. The film also provided reinforcement. Pt loadings of the anode and the cathode were 0.6 and 0.15 mg cm^{-2}, respectively. The anode layer would have been very thin if the Pt loading had been almost the same as on the cathode side because it did not contain a carbon support. Therefore, a higher Pt loading was applied on the anode side in order to prevent the gas diffusion layer (GDL) from attacking the membrane directly. The thickness of the catalyst layer was observed with a scanning electron microscope (SEM) and found to be around 2 μm.

GDLs with a microporous layer (25BCH, SGL Carbon) and without a microporous layer (TGP-H120, Toray) were used for the anode and cathode side, respectively. A GDL without a microporous layer was desirable for the cathode side in order to avoid affecting the measured gas transport resistance. The MEA was formed by assembling the GDLs on both sides of the catalyst coated membrane (CCM). The MEA was assembled in a single cell between bipolar plates with a straight flow field consisting of graphite and gaskets made of silicone rubber. The compression pressure was kept uniform by measuring it with pressure-sensitive paper (Prescale, Fuji Film).

2.2. Experimental conditions

To deactivate Pt, 1% CO gas balanced with N_2 was used. All the measurements using CO were carried out at 30 °C to enhance CO adsorption. As it is difficult to control RH just by heating a bubbler tank at such low temperature, it was controlled by mixing dry gas and the wet gas that goes through the bubbler. The flow system used in this study is illustrated in Fig. 1. The flow rates of the dry and wet gases were controlled with mass flow controllers to prepare the specified RH condition in Table 2 and then mixed in a mixer tube right before entering the cell. An HZ-3000 electrochemical measurement system (Hokuto Denko, Japan) was used to perform the electrochemical measurements.

The entire process for analyzing gas transport resistance in the primary pores will be explained in the following section. The whole experiment was conducted according to the procedure shown in Fig. 2.

3. Method

3.1. Measurement of gas transport resistance

Gas transport resistance in the catalyst layer, R_{CL}, for hydrogen was measured under the conditions shown in Table 2. R_{CL} was obtained from the limiting current due to oxidation of hydrogen that leaked through the membrane from the anode side with and without cathode gas flow. Although the details of the gas transport resistance measurement were described in our previous study [18], the method is briefly explained here. Firstly, pure H_2 and N_2 were fed to the counter (and reference) and working sides respectively at 30 °C. After a certain waiting period, the potential was held at 0.95 V vs. RHE for 10 min and then set at 0.9 V for 5 min. Potential step voltammetry was conducted from 0.9 V to 0.2 V in 0.1 V increments at intervals of 5 min. The valves on the working side were then closed. Potential step voltammetry was conducted under a condition without inert gas flow to the working side in

Table 1
Specifications of the MEA.

	Anode	Cathode
Catalyst	Pt black	Pt/C (Pt 45 wt.%)
Carbon support	–	Porous carbon black
Loading	0.6 mg-Pt cm^{-2}	0.15 mg-Pt cm^{-2}
Ionomer	Nafion® (D2020, EW1000, DuPont)	Nafion® (D2020, EW1000, DuPont)
Ionomer/carbon weight ratio	0.17 (I/Pt)	0.9
Active electrode area / cm^2	10	10
GDL	Carbon paper with MPL (25BCH, SGL Carbon)	Carbon paper without MPL (TGP H120, Toray)