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Relationship between gas transport resistance in the catalyst layer and effective surface area of the catalyst

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ABSTRACT

A new method was developed for evaluating the gas transport resistance of the catalyst layer, R_{CL}, based on gas crossover through the Nafion® membrane. Using this method, gas transport resistance toward Pt catalyst (per unit of Pt surface area), $R_{micro,\mathrm{Pt}}$, was investigated for both hydrogen and oxygen. This method is applicable to low relative humidity (RH) conditions because of the extremely low limiting current density attributed to crossover gases. It was used to investigate the RH dependence of R_{CL} for hydrogen and oxygen, which has so far been difficult to measure. A comparison of the limiting current density due to the hydrogen oxidation reaction (HOR) with and without inert gas flow suggested that the decrease in the HOR current at a high potential is mainly due to mass transfer loss caused by a loss of effective surface area, S^{eff}, and not by a loss of inherent Pt activity. For hydrogen, it is possible with this method to evaluate the potential dependence of S^{eff} for the electrochemical reactions rather than the electrochemical surface area (ECA) determined by proton adsorption in the low potential region. It was found that $R_{micro,\mathrm{Pt}}$ increased for both hydrogen and oxygen with a lower RH. The trend of RH dependence and the impact of RH on $R_{micro,\mathrm{Pt}}$ were very similar to the tendencies observed for the Nafion® membrane. However, the gas transport resistance of the ionomer was notably higher for oxygen than for hydrogen, considering its relationship in the membrane. Adsorption of the ionomer onto the Pt/C catalyst might be one of the factors accounting for this difference.

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. Catalyst layers can play an important role in resolving these challenges. However, it is difficult to characterize and model the catalyst layers. For one reason, the transport of water, gas and protons occurs simultaneously with the electrochemical reactions in the catalyst layers. In addition, the catalyst layers have a very complicated microstructure. To design optimized catalyst layers, it is necessary to develop methods of evaluating and gaining an in-depth understanding of the phenomena involved [1].

The greatest challenge of all from an industrial point of view is to reduce the cost [2,3]. The most effective way to do that is to reduce the amount of Pt used. Fuel cell operation under low humidity and high current density is also desirable because it would allow the FC stack and its associated system to be simplified [4], resulting in lower cost. However, the increase in gas transport resistance, R_{gas}, stemming from lower Pt loading is an issue of concern [5,6]. Mass transport in the cathode catalyst layers in particular could cause performance loss under high current density. Moreover, improved performance under low RH conditions is required for dry operation. Therefore, it is essential to understand the gas transport properties of low Pt loading catalyst layers, especially through the ionomer, and their RH dependence.

In recent years, a method of evaluating gas transport in the catalyst layers, R_{CL}, by measuring the limiting current of diluted gases has been developed [7] and applied [5,6]. This method has good reproducibility and the advantage of enabling simultaneous evaluation of both gas transport resistance in the gas diffusion layer, R_{GDL} and R_{CL}. This method provides a basic understanding of phenomena in ideal RH conditions (e.g., 70–90% RH). However, it is not universally applicable. For one thing, the limiting current is uncertain when the proton conductivity of the catalyst layers is not high enough (with a low ionomer content or under low RH) because of the potential distribution attributed to the IR drop in the catalyst layers. For this reason, the RH dependence of R_{gas} has not been investigated thoroughly, although a low RH is essential for dry operation. What is more, the concentration distribution of the reactant from the inlet to the outlet makes it difficult to analyze this dependence.

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In this study, we investigated a new method for evaluating gas transport resistance based on gas crossover through the Nafion® membrane. Using gas crossover as a reactant source has several advantages. Specifically, it allows the method to be applied to low proton conductive conditions because the amount of the reactants is extremely small compared with that of the previous method [7], resulting in small limiting current densities (gas crossover: less than 1.6 mA cm^{-2} for hydrogen and 1.8 mA cm^{-2} for oxygen, previous method: less than 0.3 A cm^{-2} and 0.2 A cm^{-2} for oxygen). The concentration distribution in the gas flow direction can also be ignored because the flow direction does not matter for gas crossover from the counter electrode side. With this method, the RH dependence of R_{CL} was investigated and analyzed for both hydrogen and oxygen.

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/GKB (catalyst: 46 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 this study, oxygen transport resistance was measured using the gas crossover. Thereby, water electrolysis occurred on the counter side. If a carbon support had been applied, the carbon would have corroded. Therefore, Pt black was applied to the reference and counter electrodes, so as not to cause the morphological change in water electrolysis. Graphitized ketjen black, which has a very small number of primary pores, was used as the support in order to ignore gas transport in the primary pores.

The counter electrode consisted of a Pt black catalyst layer that was spray-coated on a square perfluorosulfonic acid (PFSA) membrane (Nafion® NR211, thickness = 25 μm) measuring 72 mm on one side and then dried for 30 min at 80 °C to remove the organic solvent. The working electrode, consisting of Pt/C, was then fabricated on the other side and dried. The membrane was masked beforehand with a 25-μm-thick polyethylene naphthalate (PEN) film (Q51, Teijin-DuPont) having a 10 cm^2 open area (2 cm vertical × 5 cm horizontal) on both sides so as to prevent any gap between the film and the catalyst layer. This was done because gas crossover through the gap might affect the analysis, albeit not so significantly. The film also provided reinforcement. Pt loadings on the counter electrode and the working electrode were 0.6 and 0.12 mg cm^{-2}, respectively. The Pt loading of the counter electrode was determined from an engineering point of view. The catalyst layer of the counter electrode is quite thin when approximately the same Pt loading is applied to both the counter and working electrodes because the former electrode does not have a carbon support. Therefore, high Pt loading was applied to the counter electrode to prevent the gas diffusion layer (GDL) from attacking the membrane directly. The thickness of the catalyst layer was observed using 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 counter electrode and the working electrode, respectively. A GDL without a microporous layer was desirable for the working electrode to make it easier to analyze gas transport phenomena. The MEA was formed by assembling the GDLs on both sides of the catalyst coated membrane (CCM). It was assembled in a single cell between bipolar plates with a straight flow field made of graphite and gaskets made of silicone rubber. The compression pressure was kept uniform by measuring it with pressure-sensitive paper (Prescale, Fuji Film). An schematic image of the MEA is shown in Fig. 1 with the experimental setup.

2.2. Principle of the measurement and analysis

Crossover hydrogen has generally been measured electrochemically with inert gas flowing to the working electrode [8]. Strictly speaking, crossover hydrogen can exit the system through the cathode GDL and gas channels in this case because the cathode side is not hermetically closed. Usually, this should not matter because the GDLs are much thicker than the catalyst layers, in other words, gas transport resistance in the GDLs, R_{GDL}, is much larger than that in the catalyst layers, R_{CL}. Both the thickness and Pt loading are key factors of R_{CL} because R_{CL} is a function of the Pt surface area as reported in the literature [5,6]. It was found that R_{CL} increased when the Pt loading was reduced. Accordingly, the amount of gas crossover detected in the catalyst layer should decrease when the Pt loading is reduced even if the same membrane and GDLs are used.

An equivalent circuit model for gas transport in the MEA and a schematic diagram of the flux of each component are shown in Fig. 2. The relationship among the flux that goes through the GDLs, N_{GDL}, the flux that is consumed in the catalyst layer, N_{CL}, R_{CL} and R_{GDL} is expressed as

$$\frac{N_{CL}}{N_{GDL}} = \frac{R_{GDL}}{R_{CL}} \qquad (1)$$

Therefore, it is possible to obtain R_{CL} using R_{GDL}, N_{GDL} and N_{CL}. Here, N_{CL} can be simply measured by the conventional method [8] and N_{GDL} is obtainable from the flux through the membrane, N_{total}, and N_{CL}. In Fig. 2, R_{CL} is expressed as a parallel circuit consisting of gas transport resistance in the through-plane direction, which corresponds to gas transport resistance in the macropores of the catalyst layer, R_{macro}, and the gas transport resistance toward the Pt surface, namely, gas transport resistance through the ionomer, R_{micro}. R_{CL} was calculated with this type of equivalent circuit model having 100 segments in the catalyst layer region. When R_{GDL} is infinite all the reactant should be consumed in the catalyst layer. Such a condition can be created just by closing the inlet and outlet valves on the working electrode side. In this way, N_{total} was measured by consuming all the reactant leaked through from the counter electrode side with the valves on the working electrode side

Table 1
Specifications of the MEA.

	Counter and reference electrodes	Working electrode
Catalyst	Pt black	Pt/GKB (46 wt.%)
Carbon support	–	Graphitized ketjen black
Loading	0.6 mg-Pt cm^{-2}	0.12 mg-Pt cm^{-2}
Ionomer	Nafion® (D2020, EW1000, DuPont)	Nafion® (D2020, EW1000, DuPont)
Ionomer/carbon weight ratio	0.17 (I/Pt)	0.9 (I/C)
Geometrical electrode area (cm^2)	10	10
GDL	Carbon paper with MPL (25BCH, SGL Carbon)	Carbon paper without MPL (TGP H120, Toray)