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Effect of porous structure of catalyst layer on effective oxygen diffusion coefficient in polymer electrolyte fuel cell

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HIGHLIGHTS

- The low gas diffusion coefficient of catalyst layer is studied by simulation.
- Carbon black aggregate structure and ionomer adhesion are modeled.
- Effect of porous structure with carbon agglomerate simulation model is studied.
- The possibility to improve gas diffusion by structure design is understood.

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ABSTRACT

It is important to reduce the oxygen diffusion resistance through PEFC porous electrode, because it is the key to reduce the PEFC cost. However, the gas diffusion coefficient of CL is lower than MPL in spite of framework consisted of same carbon blacks. In this study, in order to understand the reasons of the lower gas diffusion performance of CL, the relationship between a carbon black agglomerate structure and ionomer adhesion condition is evaluated by a numerical analysis with an actual reconstructed structure and a simulated structure. As a result, the gas diffusion property of CL strongly depends on the ionomer adhesion shape. In the case of adhesion shape with the same curvature of ionomer interface, each pore can not be connected enough. So the pore tortuosity increases. Moreover, in the case of existence of inefficient large pores formed by carbon black agglomerate and ununiformly coated ionomer, the gas diffusion performance decrease rapidly. As the measurement values in actual CL are almost equal to that with model structure with inefficient large pores. These characteristics can be confirmed by actual cross-section image obtained by FIB-SEM.

1. Introduction

Polymer electrolyte fuel cell (PEFC) is expected to be used widely as a high-efficient electric generator to the stationary power supply and fuel cell vehicle (FCV). Recently, the cell performance, the cost and durability increased by developing new low-platinum technology and innovative membrane materials. However, in order to develop the utilization of FCV, the cost is required to be reduced further more [1]. As approaches for them, it is very important to increase current density as well as to develop new materials such as non-platinum catalysts and low-platinum technologies. Realizing high current densities will make it possible to reduce the electrode area on the PEFC stack, and thus that helps to reduce the amount of material and leads to reduce the cost. In present PEFC, the reaction and transport resistance to the oxygen reduction reaction (ORR) at the cathode are the rate-limiting factor, and many studies have focused on the cathode. In particular, an insufficient supply of oxygen to the electrode surface obstructs to achieve high current densities, and thus it is important to improve the oxygen transport rate.

Recently, in order to understand the oxygen mass transport resistance through ionomers, some researchers have already tried to obtain the effective diffusion coefficient through ionomers by experiments with a very thin ionomer layer [2–5]. On the other hand, mass transport resistance through porous media cannot be also ignored. And as the gas diffusion property strongly depends on the porous structure, it is extremely important to know the actual heterogeneous porous structure of PEFC component and to understand the dominant structural property for mass transport and

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cell performance. It is already reported that some reconstruction techniques of porous media [6], Epting et al., is useful to obtain the numerical reconstructed catalyst layer by nano-X-ray CT with 50 nm resolution. Furthermore, the characteristics of porous structure are evaluated, such as aggregate size and pore size [7]. Kotaka et al., reconstructed the three-dimensional structure of MPL and GDL with two types of X-ray CT measurement similarly, and the effect of porous structure on effective gas diffusion coefficient and effective electrical conductivity is considered [8]. Mukherjee and Wang reported the technique of calculation method of mass transport and reaction in heterogeneous porous structure of catalyst layer. In this simulation, the catalyst layer is reconstructed by 2D TEM image and the statistics of porous structure [9]. From these studies, the oxygen diffusion resistance and the relationship between porous structure and gas diffusivity become clear quantitatively. However, there are few studies to reconstruct catalyst layer and the oxygen diffusion performance in catalyst layer because a catalyst layer has small pore as approximately 100 nm and the resolution of nano X-ray CT and 2D TEM method are not enough to understand the heterogeneous porous structure. As the background information, Takahashi et al., reported that porous structure of catalyst layer strongly depends on the solvent condition in slurry at fabrication process and that this structure affects the cell performance [11]. They considered some mechanism of oxygen transfer through void space and inside agglomerate. So, the effect of oxygen transfer performance on cell output has already reported, and it is important to know the effective gas diffusion coefficient in void space of catalyst layer. From this viewpoint, In our other study, relative gas diffusion coefficients, which are defined by the ratio between the effective gas diffusion coefficient and the bulk molecular gas diffusion coefficient, in various PEFC porous media, such as gas diffusion layer (GDL), microporous layer (MPL) and catalyst layer (CL) were measured experimentally. Moreover, these values were compared with simulation results obtained with a reconstructed structure of each porous media by focused ion beam scanning electron microscopy (FIB-SEM) and X-ray computed tomography (X-ray CT). The dominant factors of the gas diffusion properties in each porous electrode were considered by comparing model structures, such as a vertical orientation structure, a particle packing structure and a fibrous structure [10]. And the relationship between porosity of the relative diffusion coefficient of each porous media in PEFC was obtained by simulation and direct measurement. From this result, the relative diffusion coefficients for the various material elements were organized by the value of ε^{γ}. In addition, it is noteworthy that the relative gas diffusion coefficient of CL was lower than MPL in spite of the framework consisted of the same carbon black. Fig. 1 shows the cross-section view of MPL and CL obtained with FIB-SEM and relationship between the porosity and the relative diffusion coefficient of various porous media in PEFC from Ref. [10]. These data are shown with experiments by direct measurement, the calculation with reconstructed structure by FIB-SEM and the theoretical model of some structures. The relative gas diffusion coefficient of MPL without Knudsen effect was almost close to physical limits estimated by simulations of a primary particle packing structure. The value could be expressed by the squared porosity. In the case with Knudsen effect, the data was close to the equation of the fourth power of porosity. On the other hand, In the case of CL, the relative diffusion coefficients of CL with and without Knudsen effect were expressed by the fourth power of porosity and the sixth power of porosity respectively. As the reason, the following factors could be considered,

1. Effect of the carbon black aggregate structure which is different from uniform primary particles
2. Effect of ionomer coating and adhesion shape

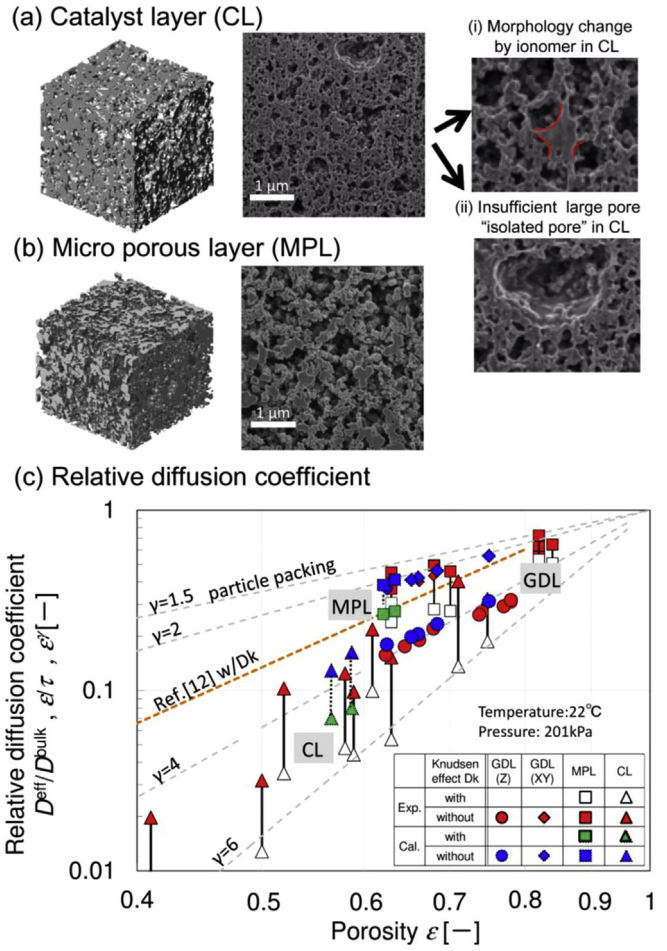

Fig. 1. Reconstructed structure and cross-section view of MPL and CL obtained with FIB-SEM and relationship between porosity and relative diffusion coefficient of various porous media in PEFC from Ref. [10]. These data are shown by the experiment of direct measurement, the calculation with reconstructed structure from FIB-SEM and the theoretical model of some structures.

3. Effect of heterogeneous structure in CL

About the first point, in usual, carbon black is used for a supporter and an electrical conductive material in CL and MPL respectively. As it is not primary particle, the relative gas diffusion coefficient of packed carbon black aggregate cannot always be expressed in the equation of $D^{R} = \varepsilon^{\gamma}$. So it can be considered that the exponent γ in the equation of D^{R} may depend on the porosity if the carbon morphology affects it.

About the second point, although the PTFE used as binders in the MPL is a particulate substance, ionomers, which are dispersed in the form of a catalytic ink, covers the entirety of the carbon black during the drying process, and may adhere in a way that partially fills pores and change their shape in CL. This characteristic could be confirmed in Fig. 1 (a).

About the third point, the existence of extremely large pores was observed from Fig. 1 (a). A characteristic feature here is that ionomers adhere in large numbers in the vicinity of the pores like a wall. Therefore, it is possible that these pores form isolated pores which are ineffective for gas diffusion, whereupon the structure deviates significantly from those of the MPL.

However, these possibilities were referred qualitatively by comparing with each image. The effects of these possibilities have to be examined quantitatively to understand dominant factor more