Understanding formation mechanism of heterogeneous porous structure of catalyst layer in polymer electrolyte fuel cell

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ABSTRACT

In order to elucidate a porous structure consisting of carbon aggregate and ionomers, the agglomeration mechanism of carbon black in CL is examined based on the experimental results of particle diameter distribution of carbon black in CL ink with or without an ionomer and the transmission electron microscopy image of carbon black dispersion. A theoretical model of the attraction and repulsion between carbon particles is also discussed, and compared with experimental results. From this model and the measured particle distribution data, it is supposed that the structure with large isolated pores results from carbon black dispersion in CL slurry, and the interaction phenomenon of each carbon black particle depends on the weight ratio of ionomer and carbon. Furthermore, the carbon black aggregate and the agglomerate structure in CL are reproduced numerically, and the effects of the heterogeneous structure on gas diffusion performance are examined by simulations. These results suggest that gas diffusion performance depends on pore size and ionomer adhesion. In particular, ionomer migration near large pores strongly affects gas diffusion performance because of the existence of isolated pores. In addition, better gas diffusion needs a certain amount of pores of non-uniform sizes.

Introduction

Polymer electrolyte fuel cell (PEFC) is a potential power source for new-generation automobiles like fuel cell vehicles (FCV) that run on hydrogen energy. The most important characteristics of PEFCs are low operation temperature and quick start and shutdown. To develop high performance FCVs and fuel cell systems, various investigations are required, such as the development of innovative catalysts and electrolyte materials [1,2], optimization of catalyst layer [3—6], measurement of actual porous structure [7,8], simulation of mass transport and internal reaction [9—14], and understanding the mechanism of electrochemical reaction and mechanical durability [15—22]. These papers have helped in improving the cell output performance and durability. However, in order to obtain high electrochemical activity, Pt particle catalyst is used as both anode and cathode of PEFCs. Thus, the most important obstacle to be overcome is the high cost of PEFCs [23]. Although the Pt catalyst is the costliest among all the components of available PEFC systems, the total PEFC stack cost cannot reach the target value even if the cost of Pt had been

zero. Not only is the development of a technique that uses small amount of the Pt catalyst or an innovative new catalyst other than Pt but also the cost reduction of all components is necessary. One of the approaches for cost reduction is to increase the output power density. Realizing high current densities will reduce the electrode area on the PEFC stack, leading to cost reduction. Since oxygen reduction reaction (ORR) at the cathode is the limiting reaction in PEFCs, ORR activity of the catalyst and mass transport for the ORR reactants, oxygen, proton and electron, have to be increased. Fig. 1 shows the schematic of cathode mass transport and reaction. Under normal operating conditions, oxygen transfer is the dominant factor for limiting current density. Therefore, oxygen transfer must be increased from the gas channel to the Pt surface through various porous media and various components, such as the gas diffusion layer (GDL), the micro porous layer (MPL), the CL, the micro and nano-scale pores, and ionomers near the Pt surface.

Recently, oxygen transport phenomena near the Pt surface has been focused on to understand and solve the dominant factor of nano-scale oxygen transfer, such as oxygen dissolution and diffusion in ionomers, oxygen adsorption on the Pt surface, oxygen transfer through nanopores inside the carbon support, etc. [24–26]. These studies contribute new material and new structure design for PEFC research. On the other hand, meso-scale oxygen diffusion through porous media is also important. The oxygen diffusion resistance of each component was reported Yokoyama et al. [27]. The diffusion resistances of GDL, MPL, and CL are 25, 10, and 16 s/m, respectively (total pressure = 103.3 kPa). Other researchers have already reported that the overvoltage (O$_2$ and electron transfer) is reduced by using a cell without GDL [28]. However, in order to further reduce oxygen diffusion resistance, the mechanisms of the dominant phenomena of oxygen transfer in MPL and CL have to be elucidated.

The effective gas diffusion resistance has to be reduced by optimizing the porous structure. In porous media, the effective gas diffusion coefficient (D^{eff}) is determined based on Knudsen effect, which occurs by the interaction between the gas molecules and solid wall of the nano-space; as expressed in following eqs. (1) and (2) [29],

$$D^{eff} = \frac{\varepsilon}{\tau} \frac{D^K D^{bulk}}{D^K + D^{bulk}} \tag{1}$$

$$D^K = \left(\frac{2}{3}\right)\left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} r \tag{2}$$

where D^{bulk} is the bulk gas diffusion coefficient, D^K is the Knudsen diffusion coefficient ε is the porosity, and τ is the tortuosity (the ratio between the curved length of the transport paths in porous media and the straight apparent transport length). The smallest possible value of the tortuosity is 1, corresponding to a straight path. In addition, the relative gas diffusion coefficient (D^R) is the ratio between the effective and bulk gas diffusion coefficients, given by eq. (3).

$$D^R = \frac{D^{eff}}{D^{bulk}} = \frac{\varepsilon}{\tau} \frac{D^K}{D^K + D^{bulk}} \tag{3}$$

These equations suggest that in order to increase the effective gas diffusion coefficient, structures with high porosity and low tortuosity are required. Because electronic conductivity is required within the acidic environment of a proton-conduction PEFC, carbon materials are the primary choice of material for the structural frameworks of GDL, MPL, and CL. The most common GDL material is a fibrous porous medium with a mean pore size of ~20 μm. The MPL consists of a primary aggregate of carbon black particles having diameters in the range of 20–50 nm. The length of the aggregate is 100–300 nm. PTFE is typically used as a binder, with a mean pore size of ~0.1 μm. Many researchers have already studied the relationship between these heterogeneous porous structures and their mass transport properties, both experimentally and numerically.

Recently, various observation technologies have contributed to enhanced understanding of an actual heterogeneous structure. The most popular three-dimensional observation technologies are X-ray computed tomography (X-ray CT) and focused ion beam–scanning electron microscopy (FIB-SEM). These have been applied for studying PEFC porous structures [30,31]. The structure of the CL has to be observed under small space resolutions, and the relationship between an actual porous structure and mass transport performance has to be elucidated. Usually, the CL is an accumulated layer of carbon-black-supported Pt catalysts and ionomers (electrolytic polymers) that constitute the proton conduction path; the mean pore size of CLs is 0.1 μm. However, the relationship between the heterogeneous porous structures of PEFC components and mass transport performance has not
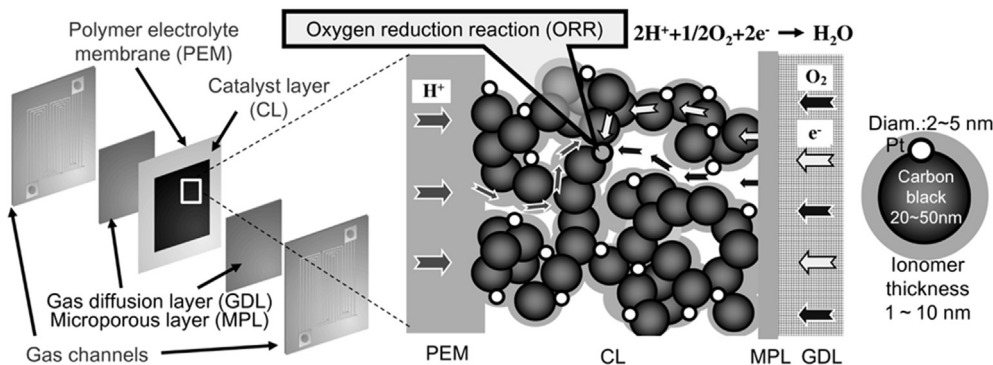

Fig. 1 – Schematic of the cathode reaction and mass transport in the catalyst layer (CL).