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Effects of Pt and ionomer ratios on the structure of catalyst layer: A theoretical model for polymer electrolyte fuel cells

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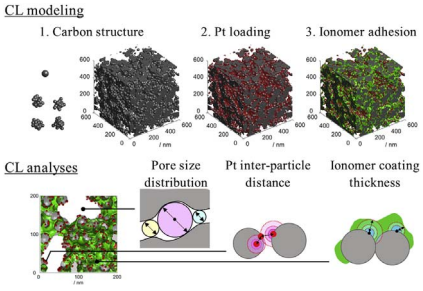
HIGHLIGHTS

- 3D catalyst layer (CL) structure in polymer electrolyte fuel cells is modeled.
- Calculated pore, Pt particle, and ionomer configurations validated with experiments.
- Effects of Pt/C and ionomer/C ratios on CL structure and performance are estimated.
- New design concepts based on balancing several trade-offs are proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The 3D structure of the catalyst layer (CL) in the polymer electrolyte fuel cell (PEFC) is modeled with a Pt/carbon (Pt/C) ratio of 0.4–2.3 and ionomer/carbon (i/C) ratio of 0.5–1.5, and the structural properties are evaluated by numerical simulation. The models are constructed by mimicking the actual shapes of Pt particles and carbon aggregates, as well as the ionomer adhesion in real CLs. CLs with different compositions are characterized by structural properties such as Pt inter-particle distance, ionomer coating thickness, pore size distribution, tortuosity, and ionomer coverage on Pt. The results for Pt/C = 1.0, i/C = 1.0 with Pt loading of 0.3 mg cm^{-2} and 50% porosity are validated against measured data for CLs with the same composition. With increasing i/C ratio, the smaller pores disappear and the number of isolated pores increases; while the ionomer connection and its coverage on Pt are significantly enhanced at i/C ~1.0. With increasing Pt/C ratio, the Pt inter-particle distance decreases as the particles connect with each other. The tortuosity of the pores and the ionomer exhibits a trade-off relation depending on the ionomer volume. Further CL design concepts to optimize both O_2 diffusion and H^+ conduction are discussed.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted much attention as power sources for automobiles and stationary cogeneration systems. However, for the widespread commercialization of PEFCs, several economic and technological barriers need to be overcome. For example, the PEFC stack in the fuel cell vehicle (FCV) consists of about 200–400 membrane electrode assemblies (MEAs), including ca. 10–50 g of Pt metal per stack as catalyst. This configuration results in high material costs. According to the U.S. Department of Energy, the fuel cell stack accounts for 50–60% of the overall fuel cell (FC) system cost in the FCV [1]. Hence, it is important to reduce Pt loadings in the MEAs while

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maintaining the cell performance. One approach to this goal is to enhance the catalytic activity of Pt, such as by alloying it with Co, Fe, and Ni [2,3] or controlling the crystal facets of Pt [4,5]. Another approach is to enhance the utilization and the effectiveness of Pt. In this approach, the Pt catalyst in the MEA is loaded in the catalyst layer (CL), which is a nanoscale porous structure typically consisting of Pt, carbon, ionomer, and pores. During fuel cell operation, the carbon, ionomer, and pores provide pathways for the transfer of electrons, H^+, and gas; while the electrochemical reaction occurs on the Pt surface. Clearly, the structures of carbon, ionomer, and pores in the CL should be optimized, in order to reduce the mass transfer resistances to electrons, H^+, and gas; as well as to improve the Pt utilization and cell performance. In other words, it is important to find the best shape, volume, and connectivity of carbon and ionomer materials and the pores in the CL. Especially, the CL structure in the cathode needs to be optimized, because Pt loading is much higher there than in the anode owing to the low activity of Pt for the oxygen reduction reaction (ORR).

The CL is fabricated and evaluated in the following processes. First, a carbon-supported Pt (Pt/C) catalyst, an ionomer (e.g. Nafion), and solvents (e.g. water and isopropanol (IPA)) are mixed and dispersed by ultrasonic homogenization or ball milling. The formed catalyst ink is sprayed or cast onto the electrolyte membrane or gas diffusion layer (GDL). After dried in air or heated oven, the CL is formed. Then, the MEA is fabricated by pressing the GDL, CL, and membrane together and assembling them into the cell. In fuel cell tests, the CL performance is typically evaluated by the i-V curve and cyclic voltammetry (CV). Furthermore, various factors that affect the voltage drop, such as O_2 diffusion overvoltage, H^+ conduction overvoltage, and electrochemical reaction overvoltage are assessed by measuring the O_2 gain, electrochemical impedance, and Tafel slope, respectively. To improve the cell performance, many new structural designs for the CLs have been reported. For example, the effects of the Pt/C and ionomer/carbon (i/C) ratios on the structure were examined and correlated to the cell voltages [6–8]. The effects of solvents in the catalyst ink on the CL formation process were also investigated and correlated with the resulting structure [9,10]. Regarding the CL preparation method, the ink dispersion, ink coating, and solvent drying processes have all been reported to influence the CL structure formation [11–13].

Many other studies have focused on the CL structural properties and their effects on the cell performance. For example, properties such as pore size distribution (PSD), Pt inter-particle distance (IPD) distribution, ionomer coating thickness distribution (CTD), and the tortuosity of pores and ionomer could influence the cell performance, due to the changes in O_2 diffusion, H^+ conduction, and electrochemical reaction in the CL. These structural properties have been characterized by analytical methods, such as mercury porosimetry [14], N_2 adsorption [15], and 3D microscopy. Especially, 3D microscopy techniques including computational image reconstruction have made remarkable progress in recent years for characterizing the 3D morphology of CLs [16] at multiple spatial scales. For example, in the macroscale analysis of the whole CLs, 3D X-ray computed tomography (X-ray CT) was applied with a resolution of ca. 50 nm to observe both the size and distributions of pores and carbon agglomerates [17,18]. The validity of the CL computational reconstruction was confirmed by comparison with the transmission electron microscopy (TEM) images and PSDs of the real CL. For the mesoscale analysis, focused ion beam scanning electron microscopy (FIB-SEM) has commonly been used due to its higher resolution of 2–15 nm [19]. Thiele et al. have developed the slice and view techniques in FIB-SEM, such as alignment and displacement of the images. They also extracted the CL structures in a cubic region 1–5 μm in size with a resolution of 2.5 nm/pixel in the x-y direction (SEM imaging direction) [20]. These authors further developed image segmentation techniques, such as intensity analysis, masking, and thresholding from the series of sliced SEM images. As a result, the accuracy of the 3D reconstruction was enhanced significantly [21]. The PSDs were calculated from the reconstructed 3D images, and the mass transport mechanism for O_2 and liquid water in the CL was discussed. Other studies used FIB-SEM to examine the relationship between CL morphology and O_2 diffusion coefficient [22,23]. Inoue et al. and Yokoyama et al. calculated the effective O_2 diffusion coefficient from the tortuosity of the FIB-SEM reconstruction data, and compared the results with the experimental ones based on the mutual diffusion resistance of O_2 and N_2 in the CL [24,25]. For the nanoscale properties (such as the shape of carbon aggregates, distribution of Pt, and adhesion of ionomer), the 3D-TEM tomography techniques have also been developed recently [26,27]. In this approach, a series of TEM images with a resolution of ~1 nm were obtained with rotating the sample by 90°–120°. Then, 3D structures were reconstructed based on the brightness and tomographic image processing. To increase the contrast in the electron image, ionic clusters of the ionomer were stained by Cs^+ ions, and both the ionomer adhesion structures and Pt distribution on carbon were visualized. Using computational structural analysis, properties of both Pt (such as particle number, size, and density) and ionomer (such as ionomer size, adhesion shape, and coating thickness on carbon) were obtained.

However, given the large number of parameters to optimize, these experimental CL designs and analyses still require a long time and considerable fabrication cost. Furthermore, even with state-of-the-art techniques, it remains difficult to modify CL morphologies flexibly and analyze them accurately due to their heterogeneous nanoscale structure. Modeling techniques have been developed to mitigate these experimental difficulties and improve the design flexibility and analysis accuracy. For example, on the mesoscale, Mukherjee and Wang reported a stochastic reconstruction technique using the statistical information obtained from 2D TEM images of a real CL [28,29]. By applying the Gaussian random field method, a 3D structure of the CL could be generated without first measuring the 3D tomography. Kim et al. improved the stochastic reconstruction by applying the sphere-based simulated annealing method, and the flexibility of the reconstruction was enhanced [30,31]. Furthermore, the ionomer and carbon structures could be distinguished based on the ionomer volume, PSD, and the assumption of Pt/C spheres covered by ionomer. Then, pore properties such as porosity, PSD, and tortuosity were correlated to the gas diffusivity with Knudsen effect. Another approach focuses on the random structure modeling without using the actual microscopic images. Siddique et al. applied this technique by mimicking the experimental CL fabrication process [32]. Random CL nanostructures were reconstructed by “growing” carbon aggregates by depositing Pt and ionomer on carbon based on the statistical probability, until the desired material composition was achieved. The validity of the reconstruction was confirmed by comparing to the agglomerate size, pore size, and morphology to those from the actual CL images obtained by SEM. Furthermore, after including mass transfer models such as Lattice Boltzmann method (LBM) or Knudsen diffusion and addressing the electrochemical reaction, not only the structural properties, but also their effects on O_2 diffusion, H^+ conduction, and cell performance could be numerically investigated [33,34]. Molecular dynamics (MD) is another modeling approach that has been applied to CLs at the sub-nanometer scale [35,36]. This approach permits the modeling of Pt, carbon, and ionomer at the molecular scale, as well as simulating the transfer and reaction of O_2, H^+, and electrons on the Pt surface. However, the high computational cost of MD limits the scale of the system, making it almost impossible to study CL morphology at the sub-micrometer scale. Hence, meso-scale modeling, which assumes the shape of the material as a mesh and adding the physical properties as needed, is more commonly used for the CL structure simulation.

Inoue et al. modeled the CL by random reconstruction while mimicking the actual shape of carbon aggregates and ionomer adhesion [37]. Carbon aggregates were formed by applying pseudo inter-particle forces between the carbon primary particles with controlling the probability density function and the morphology parameters. The ionomer adhesion model was originally developed to simulate the actual