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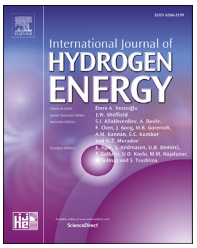

Short Communication

PEMFC modeling based on characterization of effective diffusivity in simulated cathode catalyst layer

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ABSTRACT

Oxygen diffusion in the cathode catalyst layer (CCL) is crucial to the high performance of polymer electrolyte membrane fuel cells (PEMFCs), especially in high current density or concentration loss regions. Recently, PEMFC performance has been reported to be enhanced by increasing CCL pore size and pore volume due to the reduction of diffusion resistance by capillary water equilibrium [Yim et al., Electrochimica Acta 56 (2011) 9064–9073]. Herein, we simulate these experimental results utilizing a new one-dimensional PEMFC model considering the effects of accumulated water film in CCL on oxygen diffusion. Two CCL microstructures were numerically generated based on agglomerate models to examine the experimental results obtained for two membrane electrode assembly (MEA) samples with different CCL porosity. The effective diffusivity of oxygen in the CCL was estimated by performing auxiliary simulations of oxygen concentration in CCL microstructures covered by a film of liquid water, with exponential correlation obtained between effective diffusivity and the thickness of the above film. Polarization curves predicted by the present model were in good agreement with experimental results. In agreement with the results of Yim et al., the present model predicts that the MEA featuring a CCL with smaller pores (which are more easily filled by liquid water) should exhibit a larger concentration loss at high current densities.

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Introduction

Hydrogen is a promising alternative to fossil fuels, being utilized in polymer electrolyte fuel cells (PEFCs) that can potentially be used as energy conversion devices for portable and stationary applications. However, this approach exhibits the disadvantages of high cost, low material durability, and complicated water/heat management. Water management in PEFCs is particularly difficult, significantly impacting overall system performance and reliability. For instance, the presence of excessive water in cells hinders gas transport to the electrode catalyst, causing a significant performance loss, whereas water deficiency results in significant ohmic resistance due to membrane dehydration, adversely affecting cell performance. Hence, water transport and balance in PEFCs have been extensively studied for the gas diffusion layer (GDL), microporous layer (MPL), and gas flow channels.

Among the above mentioned factors, water management in the catalyst layer (CL) is most critical, since this layer is a fundamental element of the fuel cell, directly affecting its performance. When the CL is covered with liquid water, the concentration of fuel participating in the electrochemical reaction is greatly decreased, resulting in a large concentration loss. Therefore, understanding CL water flooding is of great importance. Although the one-dimensional model of the cathode catalyst layer (CCL) has been extensively investigated [1–4], macroscale models reflecting the effect of liquid water flooding in CL microstructures are scarce. Recently, the CCL microstructure and its effect on water management have been extensively investigated [5–10], mostly by numerical modeling, with characteristics such as pore size distribution, porosity, and wetting properties reported as critical for oxygen transport. These parameters influence the capillary water equilibrium in nanoscale CCL pores, which drives liquid water accumulation and thus determines CCL wetting states [9–11]. A mesoscale two-phase modeling study also showed that the wettability of the CCL structure influences the corresponding flooding dynamics. It was reported that liquid water flooding in the CCL involves a transition from capillary fingering to a stable displacement pattern [8]. Wang et al. [7] examined liquid water distribution by performing a pore-scale two-phase lattice Boltzmann simulation, estimating the effective diffusion coefficient in the CL as a function of liquid water saturation. A comprehensive review of pore-scale modeling in the context of two-phase transport in PEFCs can be found in the work of Mukherjee et al. [6]. Very recently, Inoue et al. [5] have reported the relationship between a carbon black agglomerate structure and the ionomer adhesion condition based on numerical analysis of a real reconstructed structure and a simulated one. However, the aforementioned numerical studies have not been experimentally verified. Recently, Yim et al. [11] have reported the experimental results on the effects of CCL pore structure on cell performance at a constant catalyst loading, testing different MEAs with identical electrochemical characteristics but different CL pore structures. These differences in pore structure resulted in significantly dissimilar water management abilities and cell performances, even for CLs with identical catalyst loading. The increase of mass transport resistance with decreasing CCL pore size and volume suggests that water preferentially condenses and accumulates in CCLs with smaller pores. The accurate prediction of CCL water flooding and cell performance requires numerical modeling accounting for the effects of liquid water in the CCL microstructure, which involves a challenging computational analysis necessitating the computation of the two-phase flow of complex multi-scale CL microstructures from tens of nanometers to micrometers, as well as that of the transport phenomena of momentum, species, and energy dealt with in conventional fuel cell modeling.

Therefore, this study presents a simplified fuel cell model accounting for the CCL microstructure (simulated using a statistical technique) and the limitation of mass transport in the CCL by liquid water flooding. The effective diffusion coefficient in the liquid water film covering catalyst particles was derived by solving auxiliary diffusion equations for the CCL microstructure. To test the validity of the present model, we performed simulations implementing a correlation between effective diffusivity and liquid water film thickness and showed that polarization curves predicted by the present model were in good agreement with experimental results. In agreement with the work of Yim et al. [11], the present model also shows that catalyst layers with smaller pore sizes are more easily filled with liquid water, which results in a larger concentration loss.

The rest of the article is organized as follows. The modeling of the catalyst layer microstructure is presented in Section Modeling of the catalyst layer microstructure, and the effective diffusivity for the CCL microstructure is estimated in Section Estimation of effective diffusivity in simulated cathode catalyst layer. The results of fuel cell modeling using the diffusion coefficient proposed for the CCL are discussed in Section Fuel cell modeling using the diffusion coefficient proposed for the CCL, with conclusions presented in Section Conclusion.

Modeling of the catalyst layer microstructure

To elucidate transport phenomena inside the CL, we numerically described the CCL of sample MEAs employing the agglomerate model, as schematically shown in Fig. 1. In this model, the stochastic structure consists of primary (primary carbon particle) and secondary (particle agglomerate) spheres, with the location and diameter of each sphere being randomly chosen. However, to realistically represent the CL structure, the diameters of primary carbon particles and agglomerates were chosen to equal 28–32 and 150–300 nm, respectively. In the employed model, primary carbon particles existed only inside secondary spheres, with the contact shape of these particles realized by allowing each of them to intersect within a permissible range. This structure generation process was continued until reaching porosity that equaled the value experimentally determined for the modeled MEA.

To check the reliability of the thus generated CCL structure, its pore size distribution was compared to those of two different MEA samples employed in a previous experiment [11], MEA-10 and MEA-400. Fig. 2 shows the pore size distribution of these samples determined by mercury intrusion porosimetry, revealing that the microstructure of MEA-400

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