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Computational prediction of nanoscale transport characteristics and catalyst utilization in fuel cell catalyst layers by the lattice Boltzmann method

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ABSTRACT

In the present study, a three-dimensional lattice Boltzmann model based on the quasi-random nanostructural model is proposed to evaluate the mass transport properties and catalyst utilization of fuel cell catalyst layers in pursuance of catalyst performance improvement. A series of catalyst layers is randomly generated with statistical significance at the 95% confidence level to reflect the heterogeneity of the catalyst layer nanostructures. The nanoscale gas transport phenomena inside the catalyst layers are simulated by the D3Q19 (*i.e.*, three-dimensional, 19 velocities) lattice Boltzmann method, and the corresponding mass transport characteristics are mathematically modeled in terms of structural properties. Considering the nanoscale reactant transport phenomena, a transport-based effective catalyst utilization factor is defined and statistically analyzed to determine the structure-transport influence on catalyst utilization. The tortuosity estimation results clearly show that the classic Bruggeman equation underestimates the tortuosity of the catalyst layers and should be modified for PEFC applications. Subsequently, the effective mass diffusion coefficient is calculated by applying the tortuosity factors to the Knudsen diffusion coefficient in the catalyst layers, and it shows good agreement with published experimental data. These results indicate that Knudsen diffusion is the dominant mass transfer mechanism for fuel cell catalyst layers and that the pre-estimated tortuosity accurately reflects the mass transfer phenomena in the catalyst layers. Furthermore, catalyst utilization can be affected by excessive Pt/C catalyst loading due to the lack of pore interconnections, and it is significantly limited by the substantive reactant mass transport path inside the fuel cell catalyst layers.

1. Introduction

In polymer electrolyte fuel cell (PEFC) systems, the utilization of precious metal catalysts is considered to be a major determining factor of fuel cell performance and the cost of the system [1–3]. In conventional fuel cell catalyst layers, platinum/carbon (Pt/C) catalysts, ionomers, and pores form mostly heterogeneous interconnected transport paths for electrons, ions, and reactants, respectively, to facilitate complete electrochemical reactions, as shown in Fig. 1 (a). These intrinsically heterogeneous morphological structures of catalyst layers may provide various pore structures, and the corresponding pore volume fraction available for mass transport can be remarkably different from the initial superficial porosity of catalyst layers, as depicted in Fig. 1 (b). More specifically, the reactants are primarily transported through the vacant spaces of the interconnected pore structures, whereas the reactants in dead-end pores have limited contribution to reactant mass transport owing to the morphological structure. Furthermore, the reactants cannot reach the catalyst sites that are present on disconnected pores (*i.e.*, closed pores) [4,5]. Consequently, Pt catalysts located on dead-end or closed pores cannot successfully participate in the electrochemical reactions and may lead to underutilization of the Pt catalyst. Therefore, it is of great importance to simulate mass transport phenomena inside nanoscale pore structures of catalyst layers to elucidate structure-transport influences on catalyst utilization.

The most common mathematical expression for evaluating catalyst utilization is the effectiveness factor proposed by Thiele, which is defined as the ratio of catalytic activity to the maximum catalytic activity [6]. Based on this definition of the effectiveness

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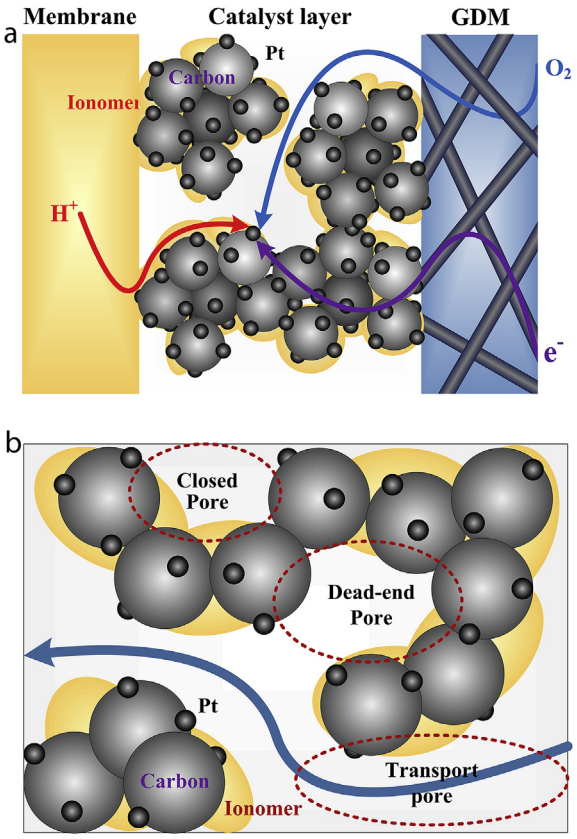

Fig. 1. Schematic diagrams of (a) the conventional catalyst layer structure for fuel cell applications, and (b) nanoscale pore structure within the catalyst layers.

factor, several modeling methods have been proposed to evaluate the utilization of PEFC catalysts at a single Pt/C-ionomer agglomerate-level [7–11]. For instance, Wang et al. proposed a Pt/C agglomerate model of catalyst layers to evaluate catalyst utilization in terms of the effectiveness factors [7]. The PEFC catalyst layers were simplified as a spherical Pt/C agglomerate without addressing the heterogeneity of the pore structures or overall transport phenomena through the catalyst layers. However, these modeling approaches have limitations with respect to the mass transport effects throughout the entire pore structure of the catalyst layers because, by definition, the effectiveness factor inherently cannot address the effects of mass transport phenomena [9–11]. Therefore, these effectiveness-factor-based modeling methods rely on semi-empirical macroscopic relationships, which may not be suitable for heterogeneous porous structures, such as the PEFC catalyst layers, when estimating mass transport properties and overall fuel cell performance [12–14].

In this respect, the lattice Boltzmann method (LBM) is a promising approach to predict the mass transport properties in porous media because the LBM directly simulates the pseudo-fluid particle behavior according to the Boltzmann equation [15–17]. Indeed, several studies have reported that the LBM has relative advantages for simulating mass transport phenomena in random heterogeneous porous materials and that it is easily applicable to the catalyst layers in fuel cell systems [18–20]. Gao applied the LBM to the simplified catalyst layer model to simulate gas flow in the nanopores of catalyst layers [19]. In the modeling study, computationally reconstructed catalyst layer structures obtained by FIB/SEM images were used to estimate the pore diameters of the catalyst layers, and based on this pore size distribution, the pore structures of the catalyst layers were simplified into a bundle of pore tubes. However, these simplified cylindrical pore structures may affect the effective mass transport properties and the corresponding catalyst utilization of the catalyst layers. Therefore, this model can be improved by considering the heterogeneous pore structures of catalyst layers and the substantive tortuous reactant flow paths in the PEFC catalyst layers. Chen et al. developed pore-scale simulation methods based on the LBM to predict the mass transport properties in catalyst layers [20,21]. Quartet structure generation set was employed to reconstruct the tortuous nanoscale pore structures of the catalyst layers. The effective diffusion coefficient was estimated from the computed reactant concentration data, and the average tortuosity of the reactant flow paths was indirectly calculated from the estimated effective diffusion coefficient. In consequence, the estimated effective diffusion coefficient showed perceptible discrepancy.

Even when catalyst layers are fabricated with the same composition and using the same method, the catalyst layers are not expected to have exactly the same transport characteristics because the catalyst layers are highly heterogeneous and the nanostructures are rarely reproducible. In this regard, Shin et al. proposed stochastic quasi-random nanostructural modeling (QRNM) to model heterogeneous nanostructures of catalyst layers and to deduce the corresponding statistical variation of the mass transport characteristics [22,23]. A series of catalyst layers was generated at the 95% confidence level, and various compositions of catalyst layers were simulated to elucidate the nanostructural effects on catalyst utilization. The morphologically interconnected Pt/C catalysts, ionomers, and pores were classified as potential electron, ion, and reactant transport pathways, respectively, without considering the reactant transport phenomena. Thereby, the Pt/C catalysts that were simultaneously connected with interconnected Pt/Cs, ionomers, and pores, were classified as morphologically utilized catalysts. Additionally, the morphology-based effective catalyst utilization factor was introduced as an indicator of the maximum amount of catalysts that could theoretically participate in electrochemical reactions.

In the present study, a three-dimensional LBM model based on QRNM is proposed to predict the mass transport characteristics and substantive catalyst utilization in PEFC catalyst layers. The nanoscale mass transport phenomena in heterogeneous catalyst layer structures were simulated by the single-relaxation time (SRT) LBM. Although some research groups prefer to use the multiple-relaxation time (MRT) LBM [24,25], the SRT lattice Boltzmann method is still worthy to investigate the micro and macroscale descriptions and is applicable to simulate microscale fluidic motion in the heterogeneous porous structures, as reported in previous studies [26–28].

The resulting reactant flow paths were visualized by directly tracking the motions of the reactant particles. The effective mass transport properties, such as the tortuosity, through-plane permeability, and effective mass diffusion coefficient, were then predicted by numerically detecting the local velocity and pressure of the reactant flow. Subsequently, the mathematical correlations between structural properties and mass transport characteristics were derived by statistical analysis. Finally, considering the nanoscale reactant transport phenomena, a transport-based effective catalyst utilization factor was defined in pursuance of catalyst performance improvement, and it was statistically compared with the morphology-based effective catalyst utilization factor to elucidate the structure-transport influence on catalyst utilization.

2. Methods

2.1. Quasi-random nanostructural modeling of catalyst layers

In QRNM method, the morphological structures of the fuel cell