Lattice Boltzmann Pore-Scale Investigation of Coupled Physical-electrochemical Processes in C/Pt and Non-Precious Metal Cathode Catalyst Layers in Proton Exchange Membrane Fuel Cells

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ABSTRACT

High-resolution porous structures of catalyst layers (CLs) including non-precious metal catalysts (NPMCs) or Pt for proton exchange membrane fuel cells are reconstructed using the quartet structure generation set. The nanoscale structures are analyzed in terms of pore size distribution, specific surface area, and phase connectivity. Pore-scale simulation methods based on the lattice Boltzmann method are developed to predict the macroscopic transport properties in CLs. The non-uniform distribution of ionomer in CL generates more tortuous pathways for reactant transport, greatly reducing the effective diffusivity. The tortuosity of CLs is much higher than that adopted by the Bruggeman equation. Knudsen diffusion plays a significant role in oxygen diffusion and significantly reduces the effective diffusivity. Reactive transport inside the CLs is also investigated. Although the reactive surface area of the non-precious metal catalyst (NPMC) CL is much higher than that of the Pt CL, the oxygen reaction rate is lower in the NPMC CL due to the much lower reaction rate coefficient. Although pores of a few nanometers in size can increase the number of reactive sites in NPMC CLs, they contribute little to enhance the mass transport. Mesopores, which are a few tens of nanometers or larger in size, are shown to be required in order to increase the mass transport rate.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are of great technological interest for vehicular and stationary power applications. Several technical barriers must be overcome before widespread commercialization of PEMFC technology. These barriers include high cost, material durability and water and heat management [1]. The utilization of precious metal-based catalysts, particularly platinum (Pt), contributes significantly to the cost of PEMFCs. Most of the utilized Pt catalyst is loaded at the cathode side due to the inherently sluggish oxygen reduction reaction (ORR) in the cathode catalyst layer (CCL). ORR reaction kinetics on the CCL have been shown to be five orders of magnitude slower than that of the hydrogen oxidation reaction (HOR) in the anode CL [2]. Cost reduction can be realized by optimizing CL design to enhance Pt utilization and thus to reduce Pt loading [3]. The limited availability and increased demand for Pt, however, is likely to raise the price of Pt [4]. An alternative to using Pt-based CLs is to develop active, selective, and durable non-precious metal catalysts (NPMCs) based on earth-abundant materials [3,5–15].

Different approaches have been proposed to develop different NPMC materials for ORR [5]. To date, the most promising NPMCs are a class of pyrolyzed transition metal nitrogen-carbon (M-N-C) complexes [5], which are obtained via heat-treatment of precursors including elemental transition ions, carbon and nitrogen [5,6]. For example, for the Polyaniline-FeCo-C (PANI-FeCo-C) NPMC developed by Wu et al. [11], the precursors are Ketjenblack, aniline oligomer, and cobalt nitrate and/or iron chloride. To replace Pt, the activity, selectivity, and durability of the NPMCs need to be improved [5]. The volumetric activity of an NPMC is the product of the active site density and the single-site activity [16]. With

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extensive efforts, NPMC volumetric activity has been improved significantly by deliberately selecting synthesis techniques [8,9]. However, the volumetric activity is measured under relatively high potential (0.8 V vs RHE (Reversible hydrogen electrode)), under which the dominant limiting factor is the electro-catalytic process. When fuel cells operate at low potentials (high current densities), transport limitations play a significant role in controlling ORR reaction rates. Therefore, NPMC activity and mass transport contributions must be combined in order to fully understand PEMFC performance [5]. To achieve higher activity, the thickness of NPMC CLs are usually ten times thicker than that of C/Pt CLs, leading to higher mass transport resistance in the NPMC CLs [6]. To date, many studies have focused on enhancing the NPMC activity with very little focus on the exacerbated mass transport issues [10]. Enhancing the transport efficiency inside the NPMC CL would lead to dramatic improvement in PEMFC performance but requires a more in depth understanding of the transport/structure relations in these CL systems.

Successful improvements of CLs are significantly dependent upon the fundamental understanding of the complex structures of CLs as well as the physicochemical reactions occurring in CLs. Typically, these structures contain nanometer scale features and can span many orders of magnitude in length making it extremely difficult to implement experimental investigations of in-situ reactive transport processes. Therefore, numerical simulations capable of spanning these length scales provide a promising method for gaining meaningful insights into the coupled electrochemical processes in a CL. Over the past two decades, numerical investigations of the Pt-based CL have progressed from ultra-thin interface models [17], to homogeneous models [18], to agglomerate models [19], and most recently to pore-scale models [20–28]. Each advancement corresponds to a higher resolution of the nanoscale porous structures at the cost of more complicated numerical models [19]. Pore-scale simulations, for instance, are based on explicitly resolving the realistic microstructures of porous media. Therefore, they do not require empirical relationships between statistic structural parameters and macro transport properties (such as porosity vs. effective diffusivity). Pore-scale simulations can be used to improve the fundamental understanding of reactive transport processes in porous media. The importance of pore-scale simulations is reflected in the increasing number of studies about pore-scale studies of reactive transport phenomena in Pt-based PEMFCs [20–36]. However, pore-scale studies related to NPMCs-based PEMFCs has not been reported.

The objective of the present study is to develop a pore-scale model based on the lattice Boltzmann method (LBM) for the coupled physic-electrochemical processes in both C/Pt and NPMC cathode CLs in PEMFCs. To the best of our knowledge, only Kim et al. [22] has adopted a LBM approach for transport processes in CL, however they did not consider the coupled electrochemical reactions. The present study applies a pore-scale model to CLs to evaluate the effects of nanoscale structural characteristics on the macroscopic transport properties, thus improving the fundamental understanding of reactive transport processes in the nanostructures of CLs. While there are a number of pore-scale studies of mass transport in Pt-based CLs [20–32], there is no such study on NPMC CLs. Our pore-scale model will be applied to the reactive transport processes in both Pt CLs and NPMC CLs, representing the first such study on NPMC CL systems. The rest of this paper is arranged as follows. In Section 2, the reconstruction processes of nanostructures of CLs are introduced. In Section 3, the physico-electrochemical model for reactive transport processes within the CLs is established. In Section 4, the numerical details of the LBM methodology are introduced. In Section 5, effects of CL morphology on the effective transport coefficients of oxygen and protons are

investigated. The predicted effective transport coefficients are compared with results from the literature. Particular attention will be paid to differences between Pt and NPMC CLs and how those differences affect the reactive transport processes. Finally, conclusions are discussed in Section 6.

2. Reconstruction of nanostructures of the catalyst layers

The final nanostructures and performance of M-N-C catalysts are strongly affected by several factors including the type of precursors and synthesis conditions [11]. Therefore, we need to select a representative NPMC structure for this study. We have chosen the PANI-FeCo-C NPMC developed by Wu et al. [11]. The synthesis of this catalyst is as follows (also shown in Fig. 1). First, Ketjenblack, aniline oligomer and transition metal salts are mixed. Ammonium is added into the mixture to polymerize aniline. Then, the composite is dried and subjected to heat treatment in nitrogen in the temperature range of 400–1000 °C. The heat treated product is acid leached, after which a second heat treatment in nitrogen is implemented. The PANI-FeCo-C shows excellent performance, achieving a maximum power density of 0.55 W cm^{-2} at a cell voltage of 0.38 V (fuel cell voltage without correction of the voltage drop caused by membrane ionic resistance), and excellent performance retention after 700 h of potential hold at 0.4 V [11]. Fig. 2 shows a SEM of the nanoscale structures of PANI-FeCo-C with heat treatments of 900 °C [11], where formation of agglomerates with typical size of hundreds of nanometers can be seen.

The electrochemical reaction kinetics, structural morphology, and reactive site distributions of PANI-FeCo-C CLs are different from Pt CLs. First, Pt CLs are nanoscale porous media with random three-phase composites of pores, carbon-supported Pt (C/Pt), and ionomer (electrolyte). For the PANI-FeCo-C CL, the solid phase consists of carbon black, graphitic PANI, and metal aggregates. Second, in Pt CLs, ORR takes place on Pt particles surrounded by oxygen transporting void, electron conducting solid, and proton conducting ionomer phases. Together, these three phases constitute the triple-phase-boundary (TPB) [37,38]. The exact nature of the active ORR sites in NPMCs, however, is still under debate [11,39]. The doped nitrogen is likely critical to the active site formation [11]. Additionally, unlike in the Pt CL systems, there is no distinction between catalyst and the support in the considered NPMC as active sites are part of the support.

Although there are many differences between Pt CLs and NPMC CLs, we choose to focus on how reactive transport changes due to the different distribution of ORR active sites. Comparing SEMs of a NPMC CL in Fig. 2 with that of a Pt CL shown in Ref. [24] (Fig. 1 in Ref. [24]), it can be found that the porous structures of the two different catalysts are quite similar at the scale of hundreds of nanometers, showing formation of agglomerates with approximately equal size of primary particles. This observation leads to the assumption in the present work that the NPMC CL has the same solid structure as the Pt CL at the agglomerate scale. This assumption allows for direct comparison between localized active site distributions (Pt CL-like) and diffuse active site distributions (NPMC CL-like). The first step then is to generate the solid structure to be used for the comparative simulations.

The nanoscale topology of a CL can be achieved via computational reconstruction algorithms using experimental input from techniques such as SEM. In the literature, several reconstruction methods have been developed for Pt CLs including the Gaussian random field method proposed by Want et al. [20,21], the sphere-based annealing method by Kim and Pitsch [22], and the random carbon sphere method by Lange et al. [23,26,27]. Recently, Siddique and Liu [24] developed a reconstruction method based on the specific synthesis process used in fabricating a given CL structure. The computational