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Incorporating Embedded Microporous Layers into Topologically Equivalent Pore Network Models for Oxygen Diffusivity Calculations in Polymer Electrolyte Membrane Fuel Cell Gas Diffusion Layers

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ABSTRACT

In this work, a voxel-based methodology is introduced for the hybridization of a pore network with interspersed nano-porous material elements allowing pore network based oxygen diffusivity calculations in a 3D image of a polymer electrolyte membrane (PEM) fuel cell gas diffusion layer (GDL) with an embedded microporous layer (MPL). The composite GDL is modeled by combining a hybrid network of block MPL elements with prescribed bulk material properties and a topologically equivalent network of larger discrete pores and throats that are directly derived from the 3D image of the GDL substrate. This hybrid network was incorporated into a pore network model, and effective diffusivity predictions of GDL materials with MPL coatings were obtained. Stochastically generated numerical models of carbon paper substrates with and without MPLs were used, and the pore space was directly extracted from this realistic geometry as the input for the pore network model. The effective diffusion coefficient of MPL-coated GDL materials was predicted from 3D images in a pore network modeling environment without resolving the nano-scale structure of the MPL. This method is particularly useful due to the disparate length scales that are involved when attempting to capture pore-scale transport in the GDL. Validation was performed by comparing our predicted diffusivity values to analytical predictions, and excellent agreement was observed. Upon conducting a mesh sensitivity study, it was determined that an MPL element size of 7 μm provided sufficiently high resolution for accurately describing the MPL nano-structure.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are a viable alternative for stationary and portable power production due to their high efficiency, zero-local emissions, and rapid start-up capability. During PEM fuel cell operation, reactant gases travel through a conductive, porous material named the gas diffusion layer (GDL) to reach the reaction sites. PEM fuel cell performance is strongly influenced by the diffusion resistance of the GDL (also known as the porous transport layer or diffusion medium), as the Nernst potential of the cell is directly related to the oxygen concentration at the reaction sites. Therefore, a full understanding of GDL mass transport limitations, especially at high current densities, is crucial for informing preferred GDL designs for optimum cell performance. A hydrophobic microporous layer (MPL) can be added to one face of the GDL to improve mass transfer and fuel cell performance by altering the distribution of liquid water in the cell and creating more pathways for oxygen diffusion to the reaction sites [1–4]. Moreover, the addition of the MPL has been shown to reduce the contact resistance between the GDL and the catalyst layer, provide mechanical support to the catalyst layer, and prevent catalyst layer degradation [5,6]. Gas transport through the GDL occurs in both in-plane and through-plane directions; however, the addition of the MPL has a major effect on oxygen diffusion in the through-plane direction [7].

The effective diffusivity of the GDL is a unique characteristic of the material, which is expressed as a function of the GDL microstructure and the bulk diffusivity [8].

$$D_{eff} = \alpha D_b \quad (1)$$

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Nomenclature

List of symbols

D	Diffusivity
D_{eff}	Effective diffusivity
D_b	Bulk diffusivity
α	Effective diffusion coefficient
L	Diffusion length
l	Diffusion length
A	Diffusion area
n_{O_2}	Oxygen flux
C	Oxygen concentration
C_{in}	Inlet oxygen concentration
C_{out}	Outlet oxygen concentration
g	Diffusive conductance
d	Pore/throat diameter
a	MPL element length
R	Diffusive resistance

where $D_{eff}$is the effective diffusivity of the GDL, α is the GDL effective diffusion coefficient, and D_b is the bulk oxygen diffusivity in air. Many analytical and theoretical correlations are available in the literature for estimating the GDL effective diffusion coefficient [9–12]; however, the effective diffusion coefficient of the GDL can be over- or under-predicted [13] when formulations for porous media are simplifications of the GDL.

Several authors have explored the use of in-situ and ex-situ experimental methods for measuring the effective diffusivity of GDL materials. These techniques include using a diffusion bridge [14–16], a Loschmidt cell [13,17,18], and a limiting-current method [19–21], among others [22,23].

A typical carbon-paper GDL consists of a paper-like, highly porous, carbon fiber substrate, coated with PTFE to render the material hydrophobic. Recent studies have shown that the addition of the MPL to the carbon fiber substrate can improve fuel cell performance [24,25]. The MPL is a thin, porous layer that is commonly made of carbon black and PTFE with pore sizes ranging between 20 and 300 nm [26]. The MPL is either used as a sheet at the interface between the catalyst layer and the substrate or is directly coated onto the substrate. In the latter case, the MPL coating can take on a complex structure within the GDL, which necessitates a more sophisticated mass transport model for resolving the interactions between the nano-pores of the MPL and the micro-pores of the substrate. Fishman and Bazylak [27,28] found that in commercial GDL materials, the MPL penetrates the substrate non-uniformly. Thus, the MPL and the substrate cannot be assumed to be separate and distinct layers, which further emphasizes the need to examine the transport properties of the material as a composite.

Experimental methods have been used to directly measure the mass transport properties of MPL/substrate materials [16,17,29–31]. In some studies, the properties of the plain substrate and the MPL/substrate assembly were measured separately, and the MPL properties were obtained by subtracting the properties of the substrate [17]. Despite the large volume of available experimental results, the experimental measurements of GDL diffusivity remain expensive and time consuming to conduct. In addition, it is difficult to resolve and explain the impact of the heterogeneous microstructure of the GDL through experimental approaches.

Numerical techniques have been highly valuable for investigating the microstructure of the substrate and its effect on gas transport through this porous medium [31–35]. Although most numerical studies have concentrated on investigating gas diffusion in a standalone MPL [31,36–42], there are studies that utilize numerical methods to study gas diffusion in bilayered GDLs. Becker et al. [7] developed a multi-scale model that accounted for Knudsen diffusion for determining the binary diffusion coefficient of MPL/substrate materials. They found that the presence of the MPL had a larger effect on oxygen diffusion in the through-plane direction compared to the in-plane direction. Using a similar technique Zamel et al. [43] investigated the effect of MPL thickness, porosity, and penetration depth into the substrate on the effective diffusivity of the MPL/substrate assembly. Wargo et al. [44] applied micro X-ray computed tomography and focused ion beam-scanning electron microscopy (FIB-SEM) to obtain the microstructure of the material and used numerical methods to calculate the mass transport characteristics of MPL/substrate assemblies. They found that the addition of the MPL led to a decrease of ~50% in the effective diffusion coefficient of the MPL/substrate assembly. However, previously reported numerical estimations of the MPL/substrate effective diffusion coefficient have not accounted for the non-uniform MPL intrusion into the substrate.

Although the GDL is hydrophobically treated, the microstructure can become partially saturated with liquid water due to the capillary transport of water from locations of condensation to the gas flow channels. This liquid water accumulation blocks oxygen diffusion pathways in the GDL and can become a major impediment to high current density operation when both water production levels and oxygen consumption levels are at their highest.

Several authors have explored the use of computational fluid dynamics (CFD) methods along with realistic pore geometries to study the transport properties of the GDL [45–47]. James et al. [46] investigated the effect of compression on the porosity and effective gas diffusivity and electrical conductivity of a commercial GDL material using X-ray computed tomography and CFD analysis. Didari et al. [47] generated representative GDL geometries using a geometric modeling scheme and calculated the permeability and tortuosity of the samples using CFD methods. Furthermore, direct simulation methods can be utilized to study multiphase transport in the GDL and investigate the performance of the cell and GDL transport properties under wet conditions [48–52]. However, analyzing multiphase transport processes using CFD methods requires the calculation of material bulk properties, which are the inputs for CFD models [53–55]. Moreover, it can be challenging to resolve the microscale liquid water distribution in the GDL, even with the use of the volume of fluid technique that assigns the liquid/gas phases as a fractional value between 0 and 1 in each element.

Pore network modeling (PNM) is a pore-scale, numerical modeling approach which has become widely popular for studying transport phenomena in the porous layers of PEM fuel cells due to its computational efficiency (allowing for the simulation of a large area of porous media with relatively low computational burden) and its ability to incorporate the capillary transport of liquid water [56–61]. PNM was initially developed and employed in petroleum-related problems for studying the distribution of fluids in porous rocks [62]. This numerical method represents porous media with a simplified network of pores connected with throats. The main advantage of this approach is that it does not require a prior knowledge of the multiphase transport properties of each porous material, as it examines the material properties at the pore level. Recently, pore network models have been employed to investigate the effects of the presence of the MPL on water transport in the GDL [61,63,64]. Gostick et al. [63] used PNM with invasion percolation to simulate the breakthrough process and concluded that the presence of an MPL significantly reduces the GDL water saturation at breakthrough. Wu et al. [64] employed PNM to find the preferred