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Effective diffusivity of gas diffusion layer in proton exchange membrane fuel cells

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HIGHLIGHTS

► We develop a comprehensive diffusivity model for gas diffusion layers (GDLs) in proton exchange membrane fuel cells (PEMFCs).
► The analytical model agrees excellently with experimental results and numerical data available in literature.
► The influences of microstructures of GDLs are extensively explored.

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ABSTRACT

In gas diffusion layers (GDLs) of proton exchange membrane fuel cells (PEMFCs), effective gas diffusivity is a key parameter to be determined and engineered. Existing theoretical models of effective diffusivity are limited to one-dimensional (1D) regular fiber arrays. Numerical simulations were carried out to simulate gas diffusion through more realistic fibrous materials like GDLs, in which fibers are randomly distributed in a two-dimensional (2D) plane or three-dimensional (3D) space, but they could not fully reveal the underlying mechanisms. In this paper, we propose an analytical model to predict the effective diffusivities of 1D, 2D and 3D randomly distributed fiber assembles. The present model is established by extending the model of 1D regular fiber alignments to 1D random fiber arrangements through Voronoi Tessellation method, and using the 1D local diffusivities to determine the 2D and 3D diffusivities based on mixing rules. The predicted effective diffusivities agree well with experimental results and numerical data. With the new model, the influences of porosity, fiber distribution, and fiber orientation are analyzed in this study.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is considered to be one of the leading candidates for the power sources of mobile, stationary, and portable devices [1]. The gas diffusion layer (GDL) of PEMFCs is a fibrous porous material with a layered structure, which not only provides the support of the fuel cell membrane, but also allows the transport of reactant products. For example, oxygen diffuses through the GDL from the gas channel (GC) to the catalyst layer (CL), where it is combined with the protons and electrons from the anode to produce water [2]. The produced water could condense and even block the porous GDL. Therefore, effective diffusivities of water vapor, oxygen, and hydrogen strongly affect the PEMFC's performance.

The movement of gas molecules caused by concentration difference in a porous medium is known as diffusion [3]. It takes place when the concentration of the molecules is higher in one region than the other. Gas molecules will not stop migrating until there is an equalized concentration configuration throughout the carrier. The moving paths of molecules during diffusive motion process are random, but the most preferred migration of molecules will be in the direction of decreasing concentration. Generally, gas diffusion through a medium can be phenomenologically described by Fick's law:

$$J = D_{\text{eff}} \nabla C, \tag{1}$$

where, J is the diffusive flux, D_{eff} is the effective diffusivity and ∇C is the concentration gradient. Fick's law states that the average flux in the fibrous structure is directly proportional to the gas

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concentration gradient, and the effective diffusivity tensor D_{eff} lumps all the complex interactions between gas and fiber. Accurate determination of effective diffusivity, therefore, is essential to characterize the diffusion process.

The effective diffusivity of fibrous materials can be determined through Eq. (1) by experimentally measuring the diffusive flux and the directional concentration gradient. Early in 1940, through-plane diffusion coefficient of a steel wool sample was measured using carbon disulfide and acetone vapor [4]. In 1984, Bateman et al. [5] employed NO gas to transfer through a 2D cellulosic filter and calculated its effective diffusivity. Recently, Gibson et al. [6] applied a dynamic diffusion test cell method to measure vapor diffusivity of fibrous media. Two parallel gas flows with different water vapor humidity were directed to a test cell, with which vapor diffused through the sample between the gas flows, and the effective diffusivity was determined by measuring the relative humidity of gas flows leaving the cell [6]. Huang and Qian [7] modified the dynamic cell method by providing a water vapor source on one side of the sample. Effective diffusivities of GDLs were also obtained indirectly by measuring ionic conductivity for the soaped electrolyte based on the analogy between Ohm's law and Fick's law [8–10]. Using a dynamic diffusion cell, LaManna and Kandlikar [11] recently investigated the effects of Microporous Layer (MPL) coatings, GDL thickness, and polytetrafluorethylene (PTFE) loadings on the effective water vapor diffusion coefficient of GDLs. Instead of measuring the effective diffusivity, many measured the evaporative moisture vapor resistance, which is inversely related to the vapor diffusivity [12,13].

Many researchers modeled the gas diffusion through fibrous materials. The simplest model assumes the fibrous material consisting of a bundle of tortuous channels. So the effective diffusivity is related to the bulk diffusivity in the void through porosity and tortuosity, given by a normalized form [14], viz:

$$\frac{D_{eff}}{D_b} = \frac{\varepsilon}{\tau}, \tag{2}$$

where D_b is the gas diffusivity in the void, ε is the porosity, and τ is the tortuosity. Although porosity is easy to be calculated or measured, the applicability of Equation (2) is tarnished by the difficulty in accurately determining the value of tortuosity [15]. A pore-scale model was presented to predict the effective diffusivity of unconsolidated porous media based on a rectangular representative unit cell, in which the tortuosity was expressed as the ratio of the diffusive path length to the streamwise displacement [16]. However, the regular geometry of the diffusive streamlines in the pore-scale model is over-idealized.

Apart from the pore-based models above, fiber-based models were developed. Shen and Springer [17] calculated diffusive transport across 1D impermeable cylinders with square packing configuration in a rectangular unit cell, and the model of effective diffusivity was expressed as:

$$\frac{D_{eff}}{D_b} = 1 - 2\sqrt{\frac{1-\varepsilon}{\pi}}, \tag{3}$$

which was widely applied to evaluate the influence of water vapor diffusion on the mechanical properties of composites [18]. Nevertheless, this model did not consider the varying width of the gaps between cylindrical fibers and hence under-estimates the effective diffusivity. The varying width of the gap between cylindrical fibers was later considered by Li et al. [19] for both square and hexagonal fibers arrangement, but their model over-predicts the diffusivity as the gas concentration is assumed to be constant at any cross-section in the channel between the fibers. In the PEMFC literature, the Bruggeman model has attracted most of the attention [20]. The Bruggeman model is based on effective medium approximation and is given by:

$$\frac{D_{eff}}{D_b} = \varepsilon^{1.5}. \tag{4}$$

However, the Bruggeman model was derived for uniformly packed spherical particles rather than differently oriented cylindrical fibers.

In order to model gas diffusion through more realistic fibrous structures, a number of researchers applied a variety of numerical simulation techniques. Tomadakis and Sotirchos [14] performed Monte Carlo simulations for 1D, 2D and 3D randomly oriented fibers and calculated the effective diffusivity. They measured the mean traveling distances of diffusive molecules inside the numerical fiber network, and proposed the following model for the randomly oriented fibrous systems:

$$\frac{D_{eff}}{D_b} = \varepsilon\left(\frac{\varepsilon-\varepsilon_p}{1-\varepsilon_p}\right)^{\beta}, \tag{5}$$

where, ε_p is the percolation threshold and β is an empirical constant determined by a least squares fit to the simulation results. In another numerical study, the local effective diffusivity of a GDL medium was determined as a function of the local porosity and the local water saturation by a network model, where the solid structure was simulated as layers of fiber screens and each layer was shifted by a randomly selected in-plane distance [21]. In 2008, Becker et al. [22] numerically reconstructed a fibrous structure from a 3D tomography image of the GDL, and proposed the effective diffusivity as a function of the saturation of the GDL. Later in 2011, Becker et al. [23] extended their work to consider the effect of Microporous Layer (MPL).

Although many analytical models have been proposed for determining the effective diffusivity of fibrous materials, they are limited to 1D fiber arrays. For more realistic fibrous materials where fibers are 2D or 3D oriented, only numerical studies have been conducted, which cannot fully reveal the underlying mechanisms of gas diffusion. In this work, we propose a generalized analytical model of effective diffusivity of fibrous materials. The new model is established through first extending the model of regular 1D fiber arrays to random 1D fiber arrays by Voronoi Tessellation approximation, and then applying them to 2D and 3D random fiber assembles by mixing rules.

2. Model generation

In this paper, fibrous media are assumed to be composed of periodical unit cells representing the geometrical nature of the microstructures. The present model is established by extending the model for regular 1D fiber arrays, since although the architectures of fibrous media vary from simple 1D regular type to complex 2D and 3D cases, they can be approximately represented by mixtures of 1D fibers arrays [24,25]. The following assumptions are made:

1. The fibrous matrix is made up of straight and circular fibers with relatively high porosity.
2. All the fibers are impermeable and the gas diffusion takes place only in the void areas between fibers.
3. The fibrous media have relatively high porosity and the spacing between fibers is much larger than the mean free path of diffusing species.

The simplest representative cell for 1D fibrous media is regular array of parallel fibers as shown in Fig. 1. The diffusivity in the open