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A fractal analytical model for the permeabilities of fibrous gas diffusion layer in proton exchange membrane fuel cells

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ABSTRACT

The study of water and gas transport through fibrous gas diffusion layer (GDL) is important to the optimization of proton exchange membrane fuel cells (PEMFCs). In this work, analytical models of dimensionless permeability, and water and gas relative permeabilities of fibrous GDL in PEMFCs are derived using fractal theory. In our models, the structure of fibrous GDL is characterized in terms of porosity, tortuosity fractal dimension (D_T), pore area fractal dimensions (d_f), water phase ($d_{f,w}$) and gas phase ($d_{f,g}$) fractal dimensions. The predicted dimensionless permeability, water and gas relative permeabilities based on the proposed models are in good agreement with experimental data and predictions of numerical simulations reported in the literature. The model reveals that, although water phase and gas phase fractal dimensions strongly depend on porosity, the water and gas relative permeabilities are independent of porosity and are a function of water saturation only. It is also shown that the dimensionless permeability decreases significantly with the increase of tortuosity fractal dimension. On the other hand, there is only a small decrease in the water and gas relative permeabilities when tortuosity fractal dimension increases. One advantage of the proposed analytical model is that it contains no empirical constant, which is normally required in past models.

1. Introduction

The proton exchange membrane fuel cells (PEMFCs) are promising energy devices for stationary and mobile applications because of high power density, high efficiency, low operating temperature, low emissions, low noise, and great environmental compatibility [1–9]. The PEMFCs are composed of gas diffusion layer (GDL) including gas diffusion backing (GDB) and microporous layer (MPL), membrane electrode assembly (MEA), and bipolar plates with gas channels. The fibrous GDL is a core component of a PEMFC, enabling transport of gases, liquids and electricity within the cell. One of the major limitations to the performance of PEMFCs is flooding of water, which hinders the transport of reactant gas to the reaction sites, deteriorating the power output. It is therefore crucial to understand the transport of water and gas through the fibrous GDL in PEMFCs. Hence, the study of permeability, water and gas relative permeabilities of fibrous GDL has attracted the attention of many researchers. For example, Cindrella and Kannan [4] provided a comprehensive and systematic review of the published work on the GDL including, the essential properties of the GDL, the characterization techniques for GDL, the current status and future directions of GDL in PEMFCs, etc. Zhu [7] derived an improved fractal model to estimate through-plane liquid water permeability of GDL in PEMFCs. In this model [7], the porous structure of GDL was modeled as a combination of parallel and perpendicular channels to the fluid flow direction. Benziger et al. [10] investigated the water flow in GDL of PEMFCs experimentally and showed that only a few percent of the void fraction of the GDL was necessary for water transport and the smaller pores could be remained free for the diffusion of reactant gas. Zamel et al. [11] developed a morphology model to study the effects of water on the diffusion process in GDL of PEMFCs. Rama et al. [12] considered three different types of treatments, viz. electrochemical, fluid dynamics and porous flow treatments, for the transport mechanistic models of fluids in GDL of PEMFCs. Numerical simulator, like MUFTE_UG [13], was also applied to study the water and gas transport based on extended Darcy's law and experimentally determined porosity and tortuosity. The complex behavior of two-phase flow in the GDL of PEMFCs was also studied using lattice Boltzmann method (LBM) [14]. Besides, Hao and Cheng [15] investigated the relative permeabilities of GDL in PEMFCs using the free energy multiphase LBM. Because LBM requires regular

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square grids, it is only approximate when applied to the curved surface of fibers. Dawes et al. [16] proposed a three-dimensional numerical model to study the effects of water flooding on cell performance parameters. In the model [16], parametric analyses were undertaken, which consisted of investigations into the influences of diffusivity and permeability, to determine the way to simulate the transport restrictions caused by liquid water flooding. However, in order to reduce the complexity of the simulation, the most important liquid phase of water cannot be modeled directly in their work [16]. Additionally, Fan and He [17] obtained a fractal derivative model for air permeability in hierarchic porous media. The proposed model [17] was successfully used to explain the novel air permeability phenomenon of cocoon. Recently, Xiao and Fan [18] applied Monte Carlo technique to predict the relative permeability of unsaturated fractal porous media, considering the effect of capillary pressure. Monte Carlo simulation is complementary to analytical methods, but does not give exact results. Based on the assumption that GDL consists of many periodical unit cells, Shou and Fan [9] also established semi-analytical equations to determine the effective diffusivities of GDL in PEMFCs. Although the prediction of Shou and Fan's model [9] agrees well with experimental results and numerical data, the assumption was idealized because most fibrous structures are not composed of periodical unit cells.

Although many researchers have studied the transport properties of fibrous GDL through experimental investigation and numerical simulations, analytical studies is needed to further elucidate the relationship between the micro-structure of fibrous GDL and its water and gas relative permeabilities. In this study, fractal theory is applied to model the permeabilities of fibrous GDL, as it has been well established that fibrous porous media are fractal objects [19–26].

2. Existing models of permeability of fibrous porous media

So far, the most widely known model of the intrinsic or absolute permeability of porous materials is the Kozeny–Carman equation:

$$K = \frac{\phi^{n+1}}{C(1-\phi)^n} \tag{1}$$

where, K is the intrinsic or absolute permeability of porous medium, ϕ is the porosity of fibrous porous media, n and C are the exponent and empirical constant, respectively. However, the Kozeny–Carman equation is a semi-empirical formula, which has its limitations since its inception. The n and C may vary with different porous materials, and they are only valid for given empirical constants. For the purpose of predicting the intrinsic permeability of the carbon paper GDL, $n=2$ [27], $n=2.04\sim3.57$, and $C=0.0045\sim0.024$ were proposed for different fibrous mats [28]. Feser et al. [29] validated the Kozeny–Carman equation using experimentally measured intrinsic permeability of GDLs made of woven and non-woven carbon fibers. Two computed empirical constants ($C^{-1} = 1.267\times10^{-11}$, $n=2$) for TGP-60-H were introduced into Kozeny–Carman equation. Besides, Yu et al. [30] pointed out that another weakness of Kozeny–Carman equation was that two empirical constants (viz. n and C) lacked physical significance.

Based on lattice Boltzmann method, a model of the dimensionless permeability of 3D random fiber webs was derived [31]:

$$K/D_f^2 = \frac{A}{4[e^{B(1-\phi)}-1]} \tag{2}$$

where D_f is the average diameter of the fiber. The calculated permeability [31] of the web was found to be in good agreement with experimental data, when two empirical constants $A=5.55$ and $B=10.1$ are given. The authors acknowledged that they had no theoretical arguments to support their above model [31].

A more comprehensive equation to calculate the dimensionless permeability in the in-plane and through-plane directions for randomly overlapping fiber structures based on random-walk simulation was derived [27]

$$K/D_f^2 = \frac{\phi(\phi-\phi_p)^{\alpha+2}}{32(\ln\phi)^2(1-\phi)^{\alpha}[(\alpha+1)\phi-\phi_p]^2} \tag{3}$$

where ϕ_p and α are two empirical constants. In Eq. (3), ϕ_p is the percolation threshold and α depends on the structure and the flow direction. Tomadakis and Robertson [27] obtained that $\phi_p = 0.11$ regardless of flow direction, and $\alpha = 0.521$ and $\alpha = 0.785$ for the in-plane and through-plane directions, respectively.

Shou and Fan [32] applied an effectual difference-fractal approach to study the hydraulic permeability of fibrous porous media:

$$K/D_f^2 = \frac{\pi}{6.376}\frac{\phi(\phi-0.11)^{0.785}}{1-\phi}\left(2+\frac{\pi}{2\ln\phi}\right)^2\frac{2-d_f}{4-d_f}\left(\frac{d_f-1}{d_f}\right)^2 \tag{4}$$

The validity of proposed model [32] is verified by experimental data. However, the model did not consider the effects of tortuosity fractal dimension (D_T) on permeability. Actually, most flow paths are tortuous, which implies the importance of tortuosity fractal dimension on mass transport through porous fibrous media. Besides, in order to calculate permeability, Shou and Fan [32] used several empirical equations for the parameters, leading to the need for empirical constants (viz. 6.376 and 0.785) in Eq. (4).

Furthermore, using Darcy's Law, Tamayol and Bahrami [33] proposed an approach for evaluating the parallel permeability of square fiber arrangements:

$$K/D_f^2 = \frac{[-1.479-\ln(1-\phi)+2(1-\phi)-0.5(1-\phi)^2-0.0186(1-\phi)^4]}{16(1-\phi)} \tag{5}$$

Although Eq. (5) is in good agreement with the collected experimental data, the model [33] holds only to square fiber arrangements. Besides, Eq. (5) contains several empirical constants.

In addition to the models reviewed above, numerical simulations were carried to predict permeability of porous fibrous media, however numerical simulations do not provide exact relationship between the permeability and geometrical parameters of fibrous media.

3. Fractal characteristics of porous fibrous GDL

The transfer routes of fluids in porous media have fractal characteristics and can be described as random fractal curves [20]. The fibrous GDL of PEMFCs is typically a dual-layer carbon-based porous substrate. Experimental investigations on permeation have shown that the tortuous capillaries in porous fibrous GDL are fractal objects [24,25]. Fig. 1 shows an example of a porous random fibrous structure in GDL. Due to the complexity of the fibrous structure, it is difficult to directly determine the permeability and relative permeabilities of fibrous GDL by solving the fluid dynamics equations. We assume that the fibrous structure of GDL is made up of a bundle of fractal tortuous capillaries with different pore sizes, as shown in Fig. 2, and the water and gas permeation within the GDL is equivalent to that within the capillaries channels with various sizes. Let the diameter of a capillary tube in GDL be λ, and its tortuous length along the transport direction be $l_t(\lambda)$, the actual length $l_t(\lambda)$ for liquid or gas traveling in GDL is related to the capillary size through the following fractal relationship [20]:

$$l_t(\lambda) = \lambda^{1-D_T} l_0^{D_T} \tag{6}$$

where l_0 is the length of straight capillary, equal to the thickness of the GDL, and D_T is the tortuosity fractal dimension, with $1 \le D_T \le 2$, representing the extent of convolutedness of capillary pathways for water or gas flow through the porous fibrous GDL. High value of D_T