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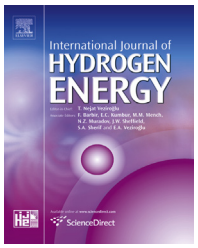

An analytical relationship for calculating the effective diffusivity of micro-porous layers

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ABSTRACT

Gas diffusion layer, GDL, properties are crucial in determining the polymer electrolyte membrane fuel cell performance. The micro-porous layer, as a thin layer coated on the GDL that has a smaller pore size than the fibrous substrate, creates a considerable mass transport barrier to the incoming gases from the flow channels. Hence, the effective diffusivity of MPL can affect the overall performance of PEM fuel cell. In the present investigation, a new analytical model is developed, based on the unit cell approach, to find the effective diffusivity of the MPL. A compact relationship is proposed that can be used to estimate the effective MPL diffusivity as a function the MPL pore size distribution and porosity. The developed model is also used to find the sensitivity of the aforementioned design parameters on the effective diffusivity. It is found that the MPL pore size is as influential as the porosity on the effective diffusivity.

Introduction

The membrane electrode assembly (MEA) used in polymer electrolyte fuel cells consists of a membrane, two electrodes (anode and cathode), and two gas diffusion layers (GDLs). The GDL is responsible for providing the pathways for transport of the reactant gases from the flow channels to the catalyst layers. Hence, the mass transport resistance of this layer should be minimized for high performance operation. The GDL is typically a dual-layer carbon-based material composed of a macro-porous substrate, which usually contains carbon fibers, binder, and PTFE, and a thin delicate micro-porous layer (MPL), which is usually made of carbon nano-particles and PTFE. Usually spherical carbon nano-particles of 20–100 nm in diameter construct the complex structure of the MPL. Small pore sizes and highly hydrophobic characteristics are the two main specifications of the MPL.

Several reasons are behind the application of MPL inside the MEA. The main incentive for using this vulnerable layer is the enhancements achieved in fuel cell performance due to its assistance in the liquid water management [1,2]. This is

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mainly a result of the small pore sizes and hydrophobic nature of the MPL that acts as an obstacle for penetration of liquid water into the fibrous substrate. Therefore, it forces the water to diffuse into the membrane, which helps the membrane hydration and reduces the ohmic losses in the membrane. Further, it reduces the chances of flooding in the GDL by transferring the liquid water from the cathode side towards the anode side through the electrolyte membrane. MPL also enhances the overall thermal/electrical conductivity of the MEA by reducing the contact resistances between the fibrous substrate and catalyst layer [2]; however, there are some other experimental evidences that show the MPL increases the overall thermal resistance by introducing a new layer [3].

Wide application of the MPL in the recent MEAs, rises the need for accurate models for estimating its transport properties. The effective diffusivity of the MPL is a key property in determining the fuel cell performance. However, since the MPL is a recently developed material, the number of published works with the focus on this thin and delicate layer is limited [4–14]. The number of publications are even less if one is looking for the effective transport properties, i.e., thermal/electrical conductivity, diffusivity [3,15–18]. Measuring the MPL diffusivity is a challenging task since the MPL needs a physical support and cannot be analyzed as a separate layer [16]. Similar to its measurements, modeling the MPL diffusivity is a difficult task [15,19], since it involves the reconstruction of the complex structure numerically and solving the diffusion equation in the nano-scale pores where the continuum assumption may be invalid and the Knudsen diffusion may prevail. Usually, complex numerical algorithms are employed to reconstruct a small portion of the MPL. This step is followed by a computationally intensive stage to solve the diffusion equations inside the void spaces of the reconstructed domain [15]. Although this approach leads to reliable and accurate results, an analytical relationship that correlates certain design parameters to the MPL diffusivity could be helpful and requires much less computational efforts.

Present relationships are either based on the effective medium theory [20,21], pore network models [22], percolation theories [23], or stochastic-based numerical modeling [24]. However, none of the existing methods are capable of providing an accurate, generally applicable function for the MPL diffusivity. Unit cell approach is another way of modeling the transport properties of porous materials. A unit cell is a simple geometry that inherits the most important specifications of a porous medium and roughly represents the entire medium structure. This approach is previously used by our colleagues in Refs. [3,25] to model the thermal conductivity of GDL and it is proven to be well applicable to model the transport properties of the fuel cell components. Hence, in this investigation an analytical modeling is performed based on the unit cell approach.

The main objective of this work is to propose a relationship for calculating the effective diffusivity of MPL. Hence, the heat and mass transfer analogy is utilized to find the effective diffusivity for a unit cell, which represents an MPL. The proposed relationship is suitable for implementation in complex performance models that require an accurate estimation of the effective transport properties.

Mathematical model

Unit cell geometry

A fully analytical solution of the mass transport equation inside a randomly structured porous material is not feasible. Simplifying assumptions are therefore required to derive an analytical model for predicting the transport properties of porous structures. In this work, the unit cell approach is used for modeling the effective diffusivity of MPL. Scanning electron microscopy, SEM, images from the surface and cross section of MPL helped us selecting a simplified geometry that represents the MPL structure. Fig. 1 shows an SEM image from the cross section of a typical MPL [13]. The structure of the MPL is complex and random; however, it is possible to divide structure into two domains: domain I that constitutes of large pores and domain II that is the packed bed of agglomerates surrounding those large pores. In Fig. 1 circles show the large pores (domain I) and their surrounding squares represent the packed bed of agglomerates (domain II).

In this investigation, a unit cell is devised that has both of these domains. The considered unit cell, which is shown in Fig. 2, is a cube that has a spherical pore with diameter d_I in the middle. The sphere is domain I, and its surrounding region in domain II, which is a homogeneous porous zone with the porosity of ε_{II} and the pore size of d_{II}. The relationship between the overall MPL porosity and the unit cell dimensions is found from the geometrical interrelations.

$$\varepsilon_{MPL} = \frac{V_{void}}{V_{tot}} = 1 - (1 - \varepsilon_{II})\left[1 - \frac{\pi d_I^3}{6a^3}\right] \quad (1)$$

In Eq. (1), the secondary domain's porosity, ε_{II}, primary pore diameter, d_I, and unit cell length, a, are unknown. Once the pore size distribution is known, these parameters can be calculated through a procedure that will be explained in the following paragraphs.

The average pore size for a porous zone can be found based on the probability density function of its pores. Hence, the average MPL pore size in this work is obtained from the following relationship.

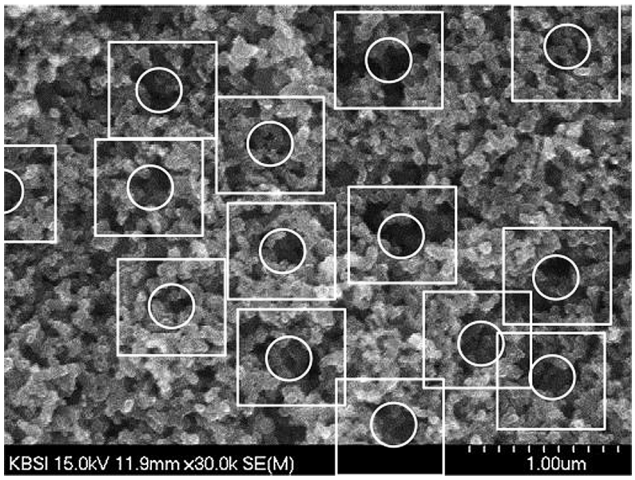

Fig. 1 – An SEM image from a cross section of an MPL [13].