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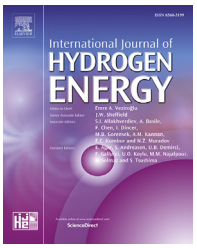

Pore structure and effective diffusion coefficient of catalyzed electrodes in polymer electrolyte membrane fuel cells

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ABSTRACT

For polymer electrolyte membrane (PEM) fuel cells, the pore structure and small effective diffusion coefficient (EDC) of the catalyst layers have significant impact on the cell performance. In this study, both the pore structure and EDC of the catalyst layers are investigated experimentally; the pore structure of the catalyst layer is characterized by the method of standard porosimetry, and the EDC is measured by a modified Loschmidt cell for oxygen-nitrogen mixture through the catalyzed electrodes. It is found that Pt loading has a direct impact on the pore structure and consequently the EDC of the catalyzed electrodes. As the Pt loading is increased, the porosity and mean pore size of the catalyzed electrode decrease, and the EDC decreases accordingly, however, it is increased by 15–25% by increasing the temperature from 25 °C to 75 °C. The EDC of the catalyst layer is about 4.6×10^{-7} m^2 s^{-1} at 75 °C, compared with 25.0×10^{-7} m^2 s^{-1} for the uncatalyzed electrode at the same temperature.

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Introduction

Gas diffusion in the electrode of polymer electrolyte membrane (PEM) fuel cell is one of the dominant mechanisms of transporting the reactants from the flow channels to the reaction sites [1–3]. The gas diffusion in the porous electrode is commonly represented by the effective diffusion coefficient (EDC) [4–8], and higher values of EDCs indicate better capabilities of gases to penetrate through the porous electrode, which is beneficial for fuel cell performance [9,10]. In a single PEM fuel cell, the reactant diffusion occurs in both the gas diffusion layer (GDL) and catalyst layer (CL), which constitute the electrode. The EDC, in turn, is governed by the pore structures of these porous layers at the cell operating condition, and is instrumental to fuel cell operation at high current densities, which is essential for practical applications [7].

Great efforts have been made to reconstruct the micromorphology of electrode materials and to optimize the microstructure of the electrodes through three-dimensional pore-scale simulation [11–14]. The pore structure of the electrode is complex due to the presence of various materials in different layers [15–18]. The catalyst layer, adjacent to the membrane, is made of carbon-supported platinum (Pt/C) particles and ionomer. The solid structure provides electrochemical reaction sites as well as electronic and protonic pathways, while the remaining pores for the reactant diffusion and water management. The catalyst layer is protected

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and supported by the GDL, which is made of a carbon paper or cloth and a micro-porous layer (MPL). The carbon paper/cloth is often treated by Polytetrafluoroethylene (PTFE) in order to improve its hydrophobicity, while the MPL, made of carbon particles with PTFE binders, provides a good connection between the carbon paper/cloth and catalyst layer, reducing the interfacial resistance and enhancing the performance of the PEM fuel cells [1,19,20]. The pore structure of the GDLs has been extensively investigated in terms of fiber diameter, fiber direction, layers of fibers, PTFE treatment, as well as MPL coating [21–24]; however, the factors affecting the pore structure of the CLs including the types of catalyst and ionomer, CL composition, as well as Pt loading have not been investigated adequately, although pore structure of the catalyst layer has been shown to have significant impact on the cell performance [15,25].

Various techniques for the characterization of the pore structure in terms of the porosity and pore size distribution (PSD) have been employed including mercury porosimetry [26,27], gas adsorption [28], capillary condensation [29,30], small-angle X-ray scattering [31], displacement method [32], and optical and electronic microscopy [33]. However, each of these methods has its own limitations on testing the GDL and CL [26–34]. The method of mercury porosimetry might deform the target pore structure due to the high pressure of mercury [35–37]. The methods of gas adsorption, capillary condensation, and small-angle X-ray scattering are suitable for small pores (up to 50 nm), while the displacement method works well only for large pores (10–200 μm) [28–35]. The PSD obtained from the optical microscopy and electronic microscopy depends on the data-processing algorithm, and the pore size is calculated mostly from surface images. Volfkovich et al. [35–37] developed the method of standard porosimetry (MSP) based on capillary equilibrium, which is able to measure the GDLs and CLs in a wide range of pore sizes (0.3 nm - 300 μm) under room conditions.

Theoretically, the EDC in the porous media is related to the volume fraction of the void region (i.e., porosity Φ), the length fraction of the tortuous flow path to the straight line length (i.e., tortuosity τ), and the bulk diffusion coefficient [38]. The EDC of porous media can be calculated using the following equation [38]:

$$D_{\text{eff}} = \frac{\varnothing D_{\text{bulk}}}{\tau} \quad (1)$$

However, the tortuosity, τ, is unknown for the porous electrode in PEM fuel cells. For simplicity, many models have been developed for the EDC of porous materials as a function of porosity only [39–45], as summarized in Table 1. However, these models are built based on the assumption that the materials are made of either fibers or particles; therefore, these models may not be suitable for the PEM fuel cell electrodes because their pore structure is more complex with agglomerates, binders, and ionomers.

Various methods have been developed to experimentally measure the EDCs of the porous layers in PEM fuel cells. Baker et al. [46] determined the EDC of the GDLs using water vapor in air mixture through the method of limiting current. LaManna and Kandlikar [47] investigated the water vapor diffusion coefficients of various GDLs with and without MPLs using a dynamic diffusion test cell. Casalegno et al. [48] utilized a single fuel cell with humidified and dry air flow to measure water vapor concentrations for GDLs. Kramer et al. [49] and Flückiger et al. [50] employed the electrochemical impedance spectroscopy to determine the effective relative diffusivity for GDLs under compression conditions. Shen et al. [8] and Chan et al. [51] modified the Loschmidt cell (also referred to as the closed-tube method) to investigate the EDCs of the nitrogen-oxygen gas pair for the GDLs and Al_2O_3-membrane-supported catalyst layers, respectively. Of all the above methods, the Loschmidt cell is one of the most commonly used methods to determine the diffusion coefficients of the gas pairs because of its feasibility of modification for different porous media, high accuracy, short experimental execution time, ease of operation, and simple experimental configuration [8,38,52]. Further, the measured EDC of a carbon paper was found to be in good agreement with the three-dimensional (3D) simulation result of gas diffusion in the sample [44], indicating the advantages of the Loschmidt cell in studying the porous layers in PEM fuel cells.

Despite the fact that the pore structure and EDCs of the GDLs have been widely investigated, few studies have been directed to the practical catalyst layers or the GDL-supported catalyst layers which are the complete paths for the gas transport in PEM fuel cells. Therefore, the objective of the present study is to experimentally investigate the effect of the catalyst layers, with a focus on Pt loadings, on the pore structure and EDC of the catalyzed electrodes. In this study, the catalyzed electrodes with the Pt loadings of 0.1, 0.2, 0.3,

Table 1 – Various models for the effective diffusion coefficient (EDC) of porous materials.

Model	Effective diffusion coefficient	Note	Source
Bruggeman (1937)	$D_{\text{eff}} = \varnothing^{1.5} D_{\text{bulk}}$	Spherical particles	[39,40]
Neale and Nader (1973)	$D_{\text{eff}} = [2\varnothing/(3-\varnothing)]D_{\text{bulk}}$	Spherical particles	[41]
Tomadakis and Sotirchos (1993)	$D_{\text{eff}} = \varnothing[(\varnothing - 0.037)/0.963]^{0.661} D_{\text{bulk}}$	Fibers	[42]
Mezedur et al. (2002)	$D_{\text{eff}} = [1-(1-\varnothing)^{0.46}]D_{\text{bulk}}$ $(0 \le \varnothing \le 0.65)$	Tetragonal network	[43]
Zamel et al. (2009)	$D_{\text{eff}} = \left\{1 - 2.76\varnothing\cosh(3\varnothing - 1.92)\left[\frac{3(1-\varnothing)}{3-\varnothing}\right]\right\} D_{\text{bulk}}$ $(0.33 \le \varnothing \le 1)$	Fibers	[44]
Das et al. (2010)	$D_{\text{eff}} = D_{bulk} - \frac{\frac{3(1-\varnothing)D_{\text{bulk}}}{3D_{\text{bulk}}}}{\frac{D_{\text{bulk}}}{\frac{2f_m D_m}{3-f_m}} - \varnothing}$	Catalyst layers	[45]

Note: D_m is the diffusivity in ionomer and f_m is the volume fraction of ionomer.

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