Gas permeability of catalyzed electrodes in polymer electrolyte membrane fuel cells

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HIGHLIGHTS

- Measured permeability of fuel cell electrodes for air, oxygen and nitrogen.
- Investigated the effect of catalyst layers as well as catalyst loading and type.
- Observed 58–77% reduction in permeability for electrodes with catalyst layers.
- Found small effect of temperature and gas species on permeability.
- Measured effective gas permeability of $(1.5–3.7) \times 10^{-15}\,\mathrm{m^2}$ in catalyst layers.

ARTICLE INFO

ABSTRACT

For polymer electrolyte membrane (PEM) fuel cells, the importance of mass transport property, gas permeability, in gas diffusion layer (GDL) is widely recognized with less attention being paid to catalyzed electrode (GDL with a catalyst layer). In this study, the contribution of the catalyst layer to the overall gas permeability of the electrode is experimentally investigated for different catalysts with a range of Pt loadings at various temperatures for air, oxygen and nitrogen gases. Results indicate that the gas permeability of the GDLs can be reduced by 58–77% with the presence of a catalyst layer. For the constant Pt loadings, the electrodes with higher Pt/C ratios (e.g., 60% Pt/C) show larger gas permeability than those with lower ratios (e.g., 30% Pt/C) due to their smaller thicknesses and higher porosity. Similarly, for the electrodes with the same type of catalysts, the gas permeability is higher for lower Pt loadings. Further, the effective gas permeability of the catalyst layers alone is about two orders of magnitude smaller than that of the GDLs. Additionally, operating at higher temperatures slightly enhances the permeability. Oxygen gas has a higher permeability than air and nitrogen, but the differences are small. These results highlight the importance of catalyst layer, hence the Pt loadings and Pt/C ratios, in determining the mass transport throughout the entire electrode in PEM fuel cells.

1. Introduction

Mass transport limitation is increasingly becoming a bottleneck for the performance enhancement of polymer electrolyte membrane (PEM) fuel cells [1–3], because PEM fuel cells are increasingly designed to operate at higher power densities. Mass transport is accomplished through both convection due to pressure gradients and diffusion arising from molecular motion. Mass diffusion has been extensively studied for electrodes with and without the catalyst layers (CLs) [4–8]; however, gas permeability representing convection capability for electrodes is relatively paid less attention, especially for electrodes with CLs [2,9–11].

A porous electrode in a PEM fuel cell in general consists of a CL and a gas diffusion layer (GDL). The CL, where electrochemical reaction occurs, is made of carbon-supported platinum (Pt/C) particles and ionomers [12]. The GDL, which supports the CL, is usually made of two layers: the carbon fiber paper and micro-porous layer (MPL) [13–15]. The MPL, adjacent to the CL, is made of carbon particles with PTFE binder, and it provides a good connection between the carbon paper and CL because its porosity and pore size are in between those of the CL and carbon paper, reducing the interfacial resistance and enhancing the performance of the PEM fuel cells [14,16,17]. In standard operating conditions, the reactants are pressurized in the flow channels and continuously consumed at the CLs, thus generating a pressure gradient

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Table 1
Models to predict the gas permeability of the porous media in PEM fuel cells.

Model	Material	Note	Reference
$k = \frac{\varepsilon}{K_c}\left(\frac{V_p}{S_p}\right)^2$	General porous media	ε – porosity K_c – Kozeny constant V_p – pore volume S_p – pore surface	[20]
$k = \frac{r^2\varepsilon}{4K_c(\ln\varepsilon)^2}$	Random overlapping fiber structures	r – fiber radius ε – porosity K_c – Kozeny constant	[20,21]
$k = \frac{r^2\varepsilon^3}{4K_c(1-\varepsilon)^2}$	Random non-overlapping fiber structures	r – fiber radius ε – porosity K_c – Kozeny constant	[20,22]
$k = r^2 \frac{\varepsilon(\varepsilon-0.11)^{\alpha+2}}{8(\ln\varepsilon)^2(1-\varepsilon)^{\alpha}[(\alpha+1)\varepsilon-0.11]^2}$	Fibrous material	r – fiber radius ε – porosity α – 0.785 through-plane 0.521 in-plane	[20,23]
$k = \frac{d^2\varepsilon^3}{150(1-\varepsilon)^2}$	Spherical particles	d – particle diameter ε – porosity	[24,25]
$k = \frac{d^2\varepsilon^{5.5}}{5.88}(0.35 < \varepsilon < 0.7)$	Spherical particles	d – particle diameter ε – porosity	[24,26]

Note: Kozeny constant K_c is an unknown parameter for most porous materials.

on both sides of the porous electrode. The resulting pressure gradient determines the mass transport mechanisms in the porous electrodes. When the pressure gradient is sufficiently large, the convection of the reactant gases through the porous electrode dominates the diffusion mechanism [15,18,19], especially for high power or current density operations. The mass transport rate is then determined by the gas permeability, which is a crucial property of the electrode impacting the cell performance.

The gas permeability of the electrode (i.e., GDL and CL combined) is controlled by its overall porous structure. Many models have been developed based on the pore structure to predict the gas permeability of different porous layers in PEM fuel cells. Table 1 summarizes the most commonly used models for the porous layers in PEM fuel cells [20–26]. These models are widely employed for porous media consisting of either spherical particles or fibers. Tomadakis et al. [20–23] developed different models based on fibrous materials with various structures. These models indicated that the permeability of the fibrous materials is significantly affected by the fiber diameter, porosity, and fiber direction. The other models are established based on spherical particles [24–26], and these models showed that the permeability is dependent on the spherical particles' diameters and porosity. A considerable amount of effort has been devoted to developing a general formula to estimate the permeability of different porous layer structures [20,26]; however, such a general formula does not exist yet because the permeability depends on the fiber/particle shape, size distribution, and their packing structure [24,26,27]. In PEM fuel cells, the porous electrode is a combination of the carbon fibers, carbon particles, Pt/C particles, PTFE, and ionomers, and its complex structure makes these models fail to predict the permeability of the electrode. Further, the gas permeability also can be affected by many other factors. Klinkenberg (1941) pointed out that the gas permeability also depends on the gas properties, and the experimental results indicated that the air permeability of the Jena glass filter can be 28% smaller than hydrogen permeability in the same materials [28]. Zamora et al. (2015) also proved that the permeability of the MPL made of Vulcan XC72 particles for hydrogen is about 20% higher than that for the oxygen and air [29]. This observation implies that the hydrogen is easier to pass through the GDL and CL than the air in operating PEM fuel cells. In addition, the mean pressure of the gases in the porous samples also influences the permeability of gases because the mean free path of the gas varies with pressure [28].

Due to its unique structure of limited small dimensions in thickness

and the presence of electrical current, it is challenging to conduct in-situ experimental measurement of various properties in an operating PEM fuel cell, and numerical models and simulations have been instrumental in providing an understanding of PEM fuel cell operation and performance [9,30]. PEM fuel cell operation and performance are essentially determined by the balance between the mass transport of gases through GDL and CL and the electrochemical reactions occurring on the catalyst surface. It is hence well known that in PEM fuel cells the mass transport of gases through GDL and CL is very significant factors affecting their performance [31]. However, due to the lack of experimental data in literature, many modeling and simulation studies, even some recent ones, either take the permeability values of the CLs or electrodes from another modeling and simulation study in literature, or simply assume some guessed values [30,32,33], and the value used in the modeling and simulation studies varies by many orders of magnitude, for example, from 10^{-15} to 10^{-12} m^2 [9,30,32,33]. Some other modeling and simulation studies may just estimate the permeability values from some theoretical models as shown in Table 1. But as discussed earlier, these models in Table 1 may not be suitable for the catalyzed electrodes or catalyst layers because of their uniquely different compositions and structures. Therefore, ex-situ experimental study to measure gas permeability of GDLs, CLs and catalyzed electrodes is urgently required for the modeling and simulation as well as design calculation of PEM fuel cells.

The permeability of the porous layers of PEM fuel cells is commonly measured experimentally based on Darcy's law by measuring the pressure drop at a specific flow rate across the samples [4,34,35]. Table 2 summarizes some experimental data on the permeability for the GDLs in PEM fuel cells. It suggests that the permeability of the carbon paper/cloth is in the order of 6–70×10^{-12} m^2, and that of the GDL (i.e., carbon paper/cloth + MPL) is in the range of 0.3–1.1×10^{-12} m^2. However, the experimental data on the gas permeability of the CLs or the entire electrodes of PEM fuel cells is unavailable in the literature. Further, it must be noticed that the experimental data in Table 2 are obtained under room conditions.

It is evident that despite its importance, the effect of CL on the permeability of the entire electrode of PEM fuel cells has not been investigated adequately. Therefore, the objective of the present study is to measure the permeability of the GDL with and without CL and the CL through ex-situ experiments such that the measured permeability values can be useful for modeling and simulation studies. The CL structure is considered in terms of the two important parameters: catalyst loading