Effective diffusivity of polymer electrolyte fuel cell gas diffusion layers: An overview and numerical study

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ABSTRACT

Published experimental and theoretical investigations conducted to estimate the effective diffusivity of the gas diffusion layers (GDLs) and other porous layers in polymer electrolyte fuel cells (PEFCs) have been reviewed. The main observations are that most of the diffusivity investigations were on the Toray carbon papers and that fewer studies have been conducted to estimate the effective diffusivity of the microporous layers (MPLs) and the catalyst layers. The main finding set by most of the reviewed investigations is that the Bruggeman relation significantly overestimates the effective diffusivity of the GDL. In order to evaluate how this overestimation is reflected on the performance of the fuel cell, a numerical study has been conducted. The outputs of this numerical study have shown that the Bruggeman relation significantly overestimates the performance of the fuel cell; this overestimation may be up to a factor of 2 or more. It is therefore recommended that empirical relations are used rather than the Bruggeman relation to calculate the effective diffusivity of the GDL materials. Also, the results suggest that a distinction between the GDL and the MPL in the single-phase modelled fuel cell should be made if the difference between the porosities of the two layers is significant.

Introduction

Gas diffusion layers (GDLs) are crucial components for polymer electrolyte fuel cells (PEFCs) and this is primarily due to their role in enhancing the utilisation of the catalyst by permitting lateral transport under the lands of the flow-field plates. The GDLs are normally composed of carbon fibres that are bound together by either weaving (carbon cloths) or by applying a binding material (carbon papers). They are typically treated with a hydrophobic agent, e.g. PTFE, to increase hydrophobicity. Also, they are coated with the so-called microporous layers (MPL), which normally consist of carbon black and PTFE particles, to enhance the contacts with catalyst layer and mitigate flooding in it.

Due to the low gas permeability of the currently-used gas diffusion layers (GDLs), the dominant transport mode for the gases in these layers is diffusion [1–3]. From a performance point of view, what matters is the diffusion of oxygen to the catalyst layer which is desired to be as

high as possible especially at high current densities. To this end, there have been several investigations to evaluate the diffusion resistance of the GDLs through estimating their effective diffusivity. Note that we use the word 'effective' since the diffusivity must be corrected for the structural restrictions imposed by the porous nature of the GDLs. The effective diffusivity, D_{eff}, is typically expressed as follows:

$$D_{eff} = f(\varepsilon)g(S)D \tag{1}$$

where D is the bulk diffusivity, ε is the porosity, S is the saturation of liquid water, and $f(\varepsilon)$ and $g(S)$ are relative functions of porosity and liquid saturation, respectively [4]. The focus in the present work is on the structure-related effects of the GDLs on the diffusivity of the gases. Therefore, to isolate the effects of water saturation, the function $g(S)$ is set to unity, thus implying that water is available only as a vapour. Equation (1) then becomes:

$$D_{eff} = f(\varepsilon)D \tag{2}$$

or

$$f(\varepsilon) = D_{eff}/D \tag{3}$$

The above expression is normally used to show how diffusive is the porous medium. The function $f(\varepsilon)$, which is an intrinsic property of the porous medium, is known in the literature as the 'diffusibility' [4], 'normalised effective diffusivity' [5] or 'effective relative diffusivity' [6]. In this paper, we will interchangeably use the terms 'effective relative diffusivity' and 'effective diffusivity'.

The gas diffusion in the GDLs has been one of the hot research topics in PEFCs in the last decade. One of the main motives behind this is the realisation that the normally-used analytical diffusion models for the porous media do not accurately describe the gas diffusion in the GDLs. Most of these models are based on the assumption that the porous medium is composed of spherical particles. Examples of these models are the Bruggeman relation [7], which is the most commonly-used diffusion model for porous media in PEFC modelling, and Neale and Nader [8]. Recently, Das et al. [9] proposed a similar expression to that of Neale and Nader; however, they stressed that a factor that accounts for the randomness and non-spherical nature of the fibres should be introduced into the proposed expression. The typical GDL materials are mainly composed of carbon fibres that are preferentially oriented in the in-plane directions, i.e. the directions parallel to the flow of the gases in the channels. Such a structure, compared to the idealised structure upon which the above analytical models are based, creates higher resistance to the diffusion of the gases especially in the through-plane direction, i.e. the direction normal to the catalyst layer. It is noteworthy that the relatively higher through-plane GDL resistance has been demonstrated to other modes of transport in our previous investigations, namely mass convection [10—12], electrical conduction [13] and thermal conduction [14,15]. In this paper, we review the investigations that have been conducted to estimate the effective diffusivity of the porous layers in PEFCs, particularly the GDLs. This review is followed by a numerical study to evaluate the predictions obtained by both the Bruggeman relation and an empirically-proposed relation.

Review

Most of the recent attempts to estimate the effective diffusivity of the GDLs (and other porous layers in PEFCs) are either experiment-based [4—6,16—22] or based on numerical models [23—37]; Table 1 lists these investigations, their types and the main findings for each one. Based on the findings given in Table 1, a number of observations are made:

- Toray carbon papers are the most characterised GDLs for the effective diffusivity. The reason behind this focus is often the tendency of the investigators to compare their effective diffusivity results with those of the previous works in which Toray papers were originally used and characterised.
- Relative to the GDLs, fewer investigations were conducted on estimating the effective diffusivity of the microporous layers (MPLs) or the catalyst layers. This is most likely due to the difficulty in experimentally handling the sub-100 μm layers and the rather complicated analysis of the results due to the emergence of Knudsen effects which become increasingly significant since the mean pore size becomes less than 1 μm as is the case for the MPLs and the catalyst layers [38,39].
- The representation of the GDL used in the numerical models is achieved through using pore networks [25,27,30,31] or the reconstruction of the GDL using stochastic models [24,29,32] or X-ray computed tomography [23,26,33]. It is noteworthy that Nanjundappa et al. [28] and Zhang et al. [34] reconstructed the MPL using a focused ion beam scanning electron microscopy. Fig. 1 shows examples of the above representations for the GDL.
- With the exception of the experimental works conducted by Kramer et al. [18] and Fluckiger et al. [6], the experimental setups were only capable of estimating the through-plane effective diffusivity of the GDLs [4,5,16,17,19—21]. This limitation is mainly due to the infinitesimally small cross-section of the GDL that imposes a technical challenge in estimating the effective diffusivity in the in-plane directions.
- Most of the experimental investigations to estimate the effective diffusivity of the GDLs are ex-situ in which closed diffusion cells [4,17,20,21], open diffusion cells [19] and electrochemical diffusimetry [6,18] were employed.
- There are two approaches to experimentally evaluate the effects of porosity on the effective diffusivity of the GDL, namely through (i) changing the PTFE content of the GDL (e.g. Ref. [4]) and (ii) subjecting the GDL to a set of gradually increasing compressions (e.g. Refs. [6,18]). Clearly both techniques decrease the porosity. However, one should be a little cautious when comparing the diffusivity results obtained from both techniques as increasing the PTFE content would decrease the porosity without causing a deformation to the structure of the GDL which is normally not the case when subjecting the GDL to practical compressions.