Investigation of the through-plane effective oxygen diffusivity in the porous media of PEM fuel cells: Effects of the pore size distribution and water saturation distribution

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1. Abstract

A thorough understanding of the oxygen transport properties in the gas diffusion layers (GDLs) of polymer electrolyte membrane (PEM) fuel cells is crucial for improving cell performance. However, because of the complex pore structure of the GDLs and the presence of water in them, the effective oxygen diffusivity (EOD) in porous medium of a PEM fuel cell is still not precisely understood. In this paper, the EODs were measured in two typical porous materials (TGP-H-120 carbon paper and carbon cloth, commonly used as GDLs) by using an oxygen sensor based on a galvanic cell under both dry and partially saturated conditions. The measurements were performed for various pore size distributions (PSDs) and water saturation distributions (WSDs); different PSDs were obtained by increasing the PTFE loading and different WSDs were realized via two impregnation methods using liquid water, namely vacuum impregnation and moist air condensation impregnation. The EOD was found to strongly depend on the PSD and WSD in the GDL, not simply on the average porosity and average water saturation, as reported in previous studies. Finally, this paper presents the experimentally verified equations that account for PSDs and WSDs under both dry and partially saturated conditions for the prediction of the EODs in PEM fuel cells.

Keywords: PEM fuel cell, GDL, effective oxygen diffusivity, pore size distributions, water saturation distributions.

2. Introduction

Polymer electrolyte membrane (PEM) fuel cells, which convert chemical energy into electricity and release water and heat as byproducts, are promising energy conversion devices. They have already been adopted for commercial applications [1]. However, there are still many challenges to be overcome to further reduce their cost and enhance cell performance, and determining the effective oxygen diffusivities (EODs) in their gas diffusion layers (GDLs) is one of these challenges. A GDL is formed of porous media with a complex microstructure. Oxygen is transported through the GDL to participate in cathodic oxygen reduction reaction, which produces water. Higher complexity of the GDL microstructure will increase the tortuosity of the oxygen transport path. Furthermore, the accumulation of liquid water can block the pores of the GDL in a PEM fuel cell, and hinder oxygen transport to the active sites, consequently causing severe performance losses, especially at high current densities when the water removal is inadequate. Therefore, a thorough understanding of the oxygen transport properties is critical to improving cell performance [2, 3].

Fick's law is commonly used for the mathematical modeling of gaseous diffusion characteristics in porous media, such as the GDLs of PEM fuel cells:

$$\varepsilon \frac{\partial C}{\partial t} = D^{\text{eff}} \nabla^2 C \quad (1)$$

where ε is the porosity of the GDL, C represents the gaseous species concentration, and D^{eff} is the EOD of the gaseous species. Nearly all previous studies have correlated the EOD D^{eff} to the average porosity ε_{avg} and the average water saturation s_{avg} by modifying the bulk diffusion coefficient D^{bulk} , as follows:

$$D^{\text{eff}} = D^{\text{bulk}} f(\varepsilon) g(s) \quad (2)$$

where D^{bulk} is the bulk diffusion coefficient of the gaseous species, the normalized function $f(\varepsilon) = D_{\text{eff}}^{\text{dry}} / D^{\text{bulk}}$ represents the effect of the porosity (here, $D_{\text{eff}}^{\text{dry}}$ is the effective diffusivity of the gaseous species in dry porous medium), and the normalized function $g(s) = D_{\text{eff}}^{\text{sat}} / D_{\text{eff}}^{\text{dry}}$ represents the influence of water saturation (here, $D_{\text{eff}}^{\text{sat}}$ is the effective diffusivity of the gaseous species under partially saturated porous media).

In many publications [4-6], the Bruggeman correlation [7] has been applied to determine the EOD with the normalized functions as follows:

$$f(\varepsilon) = \frac{\varepsilon_{\text{avg}}}{\tau} \quad (3)$$

$$g(s) = (1 - s_{\text{avg}})^{\beta} \quad (4)$$

where τ is the tortuosity, defined as the ratio of the mean length of the actual flow path to the thickness of the porous media in the direction of gaseous diffusion:

$$\tau = \varepsilon_{\text{avg}}^{\alpha} \quad (5)$$

here, $\alpha = -0.5$ and $\beta = 1.5$ are adopted in Eq.(4) and (5), respectively.

Recently, experimental measurements of different porous media with the same average porosity under dry conditions [8, 9] and with the same average water saturation under partially saturated conditions [10] have revealed significant differences in the EOD. In addition, for the same porous media, the in-plane and through-plane EODs observed at the same average porosity and water saturation also differ greatly [11]. Furthermore, Garcia-Salaberri *et al.*, in their work [12], highlighted this problem by performing the LBM simulations to determine the EODs based on an X-ray tomographic reconstruction of the invading water distribution. Therefore, simply using the average porosity and water saturation to determine the EOD is insufficient for porous media, because the distributions of pore size and water saturation also have a major impact on the gas diffusion behaviour.

Many efforts have been made to determine $f(\varepsilon)$ and $g(s)$. In numerical analysis, micropores have been modeled using parallel pore models [13, 14], random pore network models [15-18], pore network models [19-21, 36], fractal model [22], model analogous to electrical conductivity [23] and Lattice Boltzmann Method (LBM) models [11, 12, 24, 25], as summarized in Tab.1. On the whole, nearly all the above studies reported much lower values of $f(\varepsilon)$ and $g(s)$ compared with those predicted by the widely used effective medium and percolation theories, such as the Bruggeman correlation. However, most of those works applied the average porosity in the normalized function $f(\varepsilon)$ and the average water saturation rather than WSD in the

1 normalized function $g(s)$, which is worth to be investigated. The curves of $f(\epsilon)$ and
2 $g(s)$ for various present models and values of β are plotted in Fig. 1.

3 In experimental studies, most EOD measurements have been performed under
4 dry conditions [8, 26-30], and a few have been performed under partially saturated
5 conditions [1, 10, 31-34]. The methods used in these experimental measurements
6 include ex situ approaches such as conductivity cells [26], electrochemical
7 diffusimetry [27, 28], Loschmidt diffusion cells [29, 30] as well as in situ models
8 approaches such as neutron imaging and limiting current [31, 33]. For dry GDLs, the
9 experimental results reveal that the value of $f(\epsilon)$ strongly depends on the pore
10 structure, PTFE content, anisotropy, compression, and other factors. To fit the
11 measurement results, several parameters (for instance, a parameter representing the
12 effect of the PTFE content) have been introduced to modify the normalized function
13 $f(\epsilon)$ based on the present effective medium theory or percolation theory [21, 29].
14 However, seldom of them have further explored the effect of PSD on $f(\epsilon)$. Meanwhile,
15 for partially saturated GDLs, up to date, the very limited number of experimental
16 studies have revealed that the water-filling behavior and the alteration of the water
17 distribution caused by the addition of PTFE exert a considerable influence on the
18 EOD, in this case, the power-law function $g(s)$. Koresawa and Utaka [1] used a
19 galvanic cell oxygen absorber to measure the EOD in a GDL containing liquid water
20 and reported that the liquid water distribution affected the oxygen diffusion
21 characteristics of the carbon paper type GDL. Hwang and Weber [34] used the
22 limiting current method to experimentally examine the effect of PTFE loading on the
23 EOD and proposed an empirical relationship to calculate $g(s)$ based on a cumulative
24 log-normal function. Owejan *et al.* [33] combined in situ limiting current experiments
25 with neutron imaging to measure the liquid WSD and developed a modified
26 Bruggeman relationship (the power-law function $g(s)$) by correcting the exponent β .
27 Nevertheless, the directly experimental evidence is still needed to verify the strong
28 impact of the WSD on the power-law function $g(s)$, hence the EOD.

29 Recently, Garcia-Salaberri *et al.* [12] determined the EOD by performing the
30 LBM simulations based on an X-ray tomographic reconstruction of the invading

1 water distribution; and they highlighted that the WSD through the porous media,
 2 especially the peak water saturation, rather than the average water saturation was the
 3 dominant factor in determining the EOD. Following the pioneering work of
 4 Garcia-Salaberri *et al.*, this paper measured the EODs in two typical porous materials
 5 (TGP-H-120 carbon paper and carbon cloth, commonly used as GDLs) under both dry
 6 and partially saturated conditions using an oxygen sensor based on a galvanic cell. In
 7 this manner, the effects on the EOD of the PSD, as achieved by increasing the PTFE
 8 loading and measured via mercury injection, and of the WSD, as determined by
 9 adopting different methods of liquid water impregnation, could be quantitatively
 10 analyzed by using distribution equations of pore size and water saturation.

11 3. Experimental Apparatus and Method

12 The EOD measurements were performed using a galvanic battery type oxygen
 13 concentration sensor, the configuration of the experimental apparatus was depicted in
 14 Fig. 2. It consisted of a lead anode and a gold cathode; over the cathode was placed a
 15 gas permeable membrane, above which lay a porous medium holder for holding the
 16 porous specimens. The length of the porous medium holder (L) in the gas diffusion is
 17 between 5 mm and 100 mm, and its inner diameter (d) is 5 mm. One side of the holder
 18 is exposed to the ambient environment, and the other side faces the cathode of the
 19 sensor. And it can be seen, there is a gap between porous medium holder and gas
 20 permeable membrane. During each measurement, oxygen in the air permeated the
 21 porous medium and the gas permeable membrane to arrive at the boundary of the
 22 cathode, where it reduced by the electrochemical reaction as shown in Eq. (6):

23 At the same time, the lead anode is oxidized as shown in Eq. (7)

24 The lead dissolves in the alkaline electrolyte and the same quantity of water is
 25 generated as the amount consumed at the cathode, as expressed in Eq. (8)

26 The mass fraction of the oxygen, w_1 , at the porous specimen surface facing the

cathode and the quantity of oxygen, M_{O_2} , consumed by the electrochemical reactions at the cathode can be calculated by the output current I , and then the EOD of the porous specimens, D^{eff} , can be obtained as follows

$$w_1 = w_0 \frac{I}{I_0} \quad (9)$$

$$M_{O_2} = \frac{I}{4F} \quad (10)$$

$$D^{\text{eff}} = -22.4 \times 10^{-3} \frac{M_{O_2} L}{A} \cdot \frac{273.15 + t}{273.15} \cdot \frac{1}{\ln\left(\frac{1 - w_0}{1 - w_1}\right)} \quad (11)$$

where w_0 is the oxygen mole fraction at the porous specimen surface exposed to the ambient environment, I_0 is the output current without the porous specimens and holder, F is the Faraday constant, A is the cross-sectional area of the holder. t is the ambient environment temperature.

To evaluate the effect of the WSD on the EOD, two impregnation methods were adopted for experiments using the apparatus, as depicted in Fig. 3. The vacuum impregnation method is illustrated in Fig. 3(a); in this procedure, the porous specimen was immersed in pure water in a pressure tight case, which was then placed under vacuum to cause the water to impregnate the specimen. Fig. 3(b) illustrates the moist air condensation impregnation method. Moist air was passed through a cooler, at the center of which lay the porous specimens, where the water vapor condensed because of the low temperature in the cooler. Hence, porous media with different WSDs were obtained, and the EODs of the specimens were then measured in the experimental apparatus of the galvanic battery type.

For instance, Fig. 4 shows the experimental results for GDL of carbon paper type subject to vacuum impregnation method. (A) and (J) in Fig. 4 illustrate the output values measured without porous medium holder and when the cathode of the sensor was exposed to the ambient environment; (B) in Fig. 4 illustrates the output values when the holder with dry specimens was installed to the experiment apparatus; (C) to (H) in Fig. 4 illustrate the output values measured when the holder with saturated specimens was installed. As can be observed from (C) to (H) in Fig. 4, at the

beginning, the vacuum impregnation method resulted into high water saturation of the porous specimens, which approximated 0.9. In the experiment, the liquid water in the porous specimens slowly evaporated from the surface exposed to the ambient environment (evaporation side), however, there was no evaporation from the other side, which facing the cathode of the sensor (no-evaporation side). At regular interval, the holders with porous specimens were taken down from the experimental apparatus for the measurement of their quality (the quality of the holders with porous specimens under high saturated and dry state were measured in advance), and then the average water saturation from 0.9 to 0 could be obtained in this way successively. Since the evaporation rate was relatively slow under ambient environment, the evaporation of liquid water can be neglected during each measurement of the quality of the holders with porous specimens. As also can be seen in Fig. 4, with the decrease in the water saturation, the curve of the output values shows a no-linear increase.

The measurement data for GDL of carbon paper type subject to moist air condensation impregnation method can be obtained by using the means above as well. From those experimental results, conclusions regarding the effect of the WSD on the EOD could be drawn. The validity of this method of measuring for the EOD using an oxygen sensor based on a galvanic cell has previously been confirmed by Utaka *et al.*, [8]. The experiments presented in this paper were performed at an ambient temperature of 24°C.

4. Results and Discussion

4.1. Effective Oxygen Diffusivity in Dry Porous Media

The EOD under dry conditions was measured for TGP-H-120 (carbon paper) and carbon cloth, whose porosity and PSD were measured via mercury intrusion porosimetry. Fig. 5 shows micrographs of the two types of GDL materials without PTFE loading. In the carbon paper, the fibers are uniformly stacked and the pores are randomly distributed, whereas in the carbon cloth, the fibers are knitted together and the pores are connected through spaces in the mesh among the fibers. Tab. 2 summarizes the properties of the two materials, and Fig. 6 illustrates their PSDs.

Although both materials have nearly the same porosity, with values of 0.81 and 0.78, the PSDs are significantly different. The representative pore diameter of the carbon cloth (with a peak value at 100 μm) is three times larger than that of the TGP-H-120 carbon paper (with its peak value at 30 μm), as shown in Tab. 2.

Fig. 7 shows the measured EOD results for two specimens of these materials without PTFE loading. The EOD values for the TGP-H-120 (carbon paper) and carbon cloth are $6.47 \times 10^{-6} \text{ m}^2/\text{s}$ and $1.20 \times 10^{-5} \text{ m}^2/\text{s}$, respectively. If the bulk EOD in air is assumed to be 100%, then the ratio of the EODs in the TGP-H-120 (carbon paper) and carbon cloth to the bulk EOD will be approximately 31% and 58%, respectively. The difference in EOD between the two specimens can be explained in the terms of the different natures of the two porous media. Although the two specimens have nearly the same porosity, their pore structures are considerably different, as reflected by the PSDs in Fig. 6. Hence, the value of the EOD in the carbon cloth is greater than that in the TGP-H-120 (carbon paper) by a factor of about two.

A further study of the effect of the PSD on the EOD under dry conditions is discussed below. Fig. 8 plots curves representing the PSDs of TGP-H-120 (carbon paper) specimens with various PTFE loadings. As increasingly high mercury pressure are applied, smaller pores in the GDL are invaded. Once pores of $\sim 30 \text{ }\mu\text{m}$ are invaded, a percolation threshold is reached and the entire sample fills rapidly. This indicates a mean pore size of 30 μm in the material, as shown in Fig. 8a; simultaneously, the curves of the log differential intrusion volume reach their peak values, reflecting the aggregation of the representative porosity, as indicated in Fig. 8b. Furthermore, the curves exhibit a volume reduction in the GDLs with an increase in the PTFE loading. These experimental results are in good agreement with the previous literature [27, 28]. Treatment with PTFE is an effective method of water removal; however, the addition of PTFE can induce significant structural changes, such as changes to the PSD in the GDL, thereby increasing the tortuosity τ of the oxygen transport path. Thus, the tortuosity τ must be calculated before the EOD in a GDL can be determined. Here, a correlation proposed by Hager [35] is adopted to calculate the tortuosity τ of porous

material based on the measured PSD results, as follows:

$$\tau = \sqrt{\frac{\rho}{24K_g(1+V\rho)}} \int_{\eta=r_{c,\min}}^{\eta=r_{c,\max}} \eta^2 f_v(\eta) d\eta \quad (12)$$

where ρ denotes the apparent density of the porous material, K_g denotes the gas permeability of the porous material, V denotes the total pore volume, $f_v(\eta)$ represents the function describing the PSD, and $r_{c,\max}$ and $r_{c,\min}$ represent the maximum and minimum pore diameters, respectively.

A comparison between the experimental values and computed results predicted by using Eq. 12 in Eq. 3 is presented in Fig. 9. The computed results agree well with those determined in the experiments. The existing theories for predicting $f(\varepsilon)$, such as the widely used effective medium and percolation theories, are also compared with the present experimental and computed results. The $f(\varepsilon)$ curves plotted based on the Bruggeman correlation with an exponent of $\alpha = -0.5$ and several other models show significant deviations from the present results; nearly all these models considerably overpredict the value of $f(\varepsilon)$. However, the curve generated using the Bruggeman correlation with an exponent of $\alpha = -3.0$ show good agreement with the present works, therefore, when information regarding the PSD is unavailable, the Bruggeman correlation with an exponent $\alpha = -3.0$ can be used to determine the value of $f(\varepsilon)$.

4.2. Effective Oxygen Diffusivity in Partially Saturated GDLs

EOD measurements in partially saturated GDLs (TGP-H-120 carbon paper and carbon cloth without PTFE) were performed at various WSDs established using two water impregnation methods, namely, vacuum impregnation and moist air condensation impregnation. Fig. 10 shows the experimental results for the normalized function $g(s)$ for TGP-H-120 (carbon paper) and carbon cloth without PTFE subject to vacuum impregnation. As shown in Tab. 2, the two materials exhibits nearly identical porosities; however, a remarkable difference in the value of $g(s)$ is observed between TGP-H-120 (carbon paper) and carbon cloth, as shown in Fig.10. This difference can be understood to be an effect of the pore structure. The fibers of the TGP-H-120 (carbon paper) are uniformly stacked on each other and the pores are randomly

distributed, compared with carbon cloth. Whereas the fibers of the carbon cloth are knitted together, resulting in dense parts (fibers present) and non-dense parts (mesh spaces among the fibers), as shown in the Fig. 5. When impregnated by vacuum method, the carbon cloth tends to maintain the liquid water in the small pores of the fibers, and it is presumed that oxygen transport channels tend to be formed in the mesh spaces among the fibers, as a result, at a given water saturation, the carbon cloth show higher value of $g(s)$ than the TGP-H-120 (carbon paper). It also can be observed in Fig. 10 that both specimens exhibited a non-linear increase in $g(s)$ with a decrease in the average water saturation (due to the evaporation of water from the porous medium).

Comparisons of the results of vacuum and moist air condensation water impregnation are provided in Fig. 11 and 12 for TGP-H-120 (carbon paper) and carbon cloth, respectively. For carbon cloth, the specimens impregnated using the two methods reveal no obvious differences in $g(s)$ at the same average saturation. However, for carbon paper, a significant difference was apparent. At an average saturation of $s = 0.3$, as shown in Fig. 12, the TGP-H-120 (carbon paper) impregnated using moist air condensation method yielded a higher value of $g(s)$ than did the specimen treated using the vacuum method. Because the measurements presented in Fig. 12 were acquired for the same type of specimen (TGP-H-120 carbon paper without PTFE), and the properties (average porosity and PSD) remained unchanged, the only possible reason for the different $g(s)$ values observed in these TGP-H-120 (carbon papers) is a difference in the water distributions resulting from the two impregnation methods. In a previous neutron radiography study [32], it was demonstrated that water tended to aggregate near the no-evaporation side of the TGP-H-120 (carbon paper) specimen when the vacuum water impregnation is applied, causing the domains to exhibit severe resistance to oxygen transport and resulting in a much lower value of $g(s)$. However, when the air condensation water impregnation is used, the values of $g(s)$ in present study show reasonably good agreement with those reported in [12] and [34] for the case in which the area of high transport resistance near the no-evaporation side is excluded, as illustrated in Fig. 13.

1 A comparison of the experimental data measured for TGP-H-120 (carbon paper)
 2 in the present study with the data reported in previous works is provided in Fig. 13;
 3 and a rather wide spread can be observed in this figure, even with the exclusion of the
 4 domain of the high oxygen transport resistance. This is because the internal WSD of
 5 the porous medium plays an important role in determining the EOD. As is well known,
 6 the transport and distribution of liquid water in the porous medium are governed by
 7 capillary forces, and a significant amount of efforts have been made on determining
 8 the WSDs based on it. Hence, various through-plane WSDs in GDL can be found in
 9 [12, 19, 33, 35-37]. The approximately linear water saturation profiles predicted in
 10 [36, 37] are shown in Fig. 14. Therefore, linear profiles were assumed to represent
 11 those in Fig. 14 and equations $s(x)$ can be reasonably proposed to describe the WSDs,
 12 as follows:

$$13 \quad s(x) = -(2s_{\text{avg}} - 2s_0)x + 2s_{\text{avg}} - s_0 \quad (13)$$

14 where s_{avg} ($0 \leq s_{\text{avg}} \leq s(x) < 1$) is the corresponded average water saturation and s_0
 15 ($0 \leq s_0 \leq s(x) < 1$) is the initial saturation in the GDLs.

16 Fig. 15(a) and (b) plot the water saturation profiles predicted by $s(x)$ for
 17 $s_0 = 0$ and $0 < s_0 < 1$, respectively. The dashed lines represent flat water saturation
 18 profiles (average water saturation), whereas the solid lines represent linear water
 19 saturation profiles. For instance, in Fig. 15(a), the solid line in red represents the
 20 linear water saturation profile, whose corresponded s_{avg} is 0.4. Linear water saturation
 21 profiles with a initial water saturation can be seen from Fig. 15(b). In general, the
 22 water saturation value in an operation PEM fuel cell is approximately 0.4; thus, values
 23 of $s_{\text{avg}} = 0.1$ and $s_{\text{avg}} = 0.4$ were selected. Once the water saturation profiles have been
 24 obtained, the normalized function $g(s)$ can be calculated by integrating them over the
 25 GDL thickness from 0 to 1 in a normalized manner. Here, $\beta = 3.0$, following previous
 26 work [12].

$$27 \quad \sum_{x=0}^{x=1} \frac{x}{g(s(x))} = \frac{1}{g(s)} \quad (14)$$

$$g(s) = \frac{1}{\int_0^1 [1-s(x)]^{-3.0} dx} \quad (15)$$

Fig. 16 shows a comparison of the results obtained via integration in this manner and in our previous work [9] with the experimental data obtained using the two water impregnation method and in a previous work [34]. This figure shows that the $g(s)$ curves plotted using Eq. 15 are significantly different from the results predicted using the average saturation, $(1 - s_{avg})^{3.0}$. For a given average saturation, the value of $g(s)$ predicted by the flat water saturation profile is higher than that predicted by the linear water saturation profile. When $s_0 = 0$, the $g(s)$ curve tends to exhibit better agreement with the present result. However, with an increase in s_0 , the $g(s)$ curve begins to approximate $(1 - s_{avg})^{3.0}$. This is because the water saturation profile approaches the flat water saturation profile. Thus, when predicting the EOD, an analysis of the effect of the WSD is significant important; it is insufficient to consider only the average saturation, which have recently been highlighted by Garcia-Salaberri *et al.* [12]. In the absence of information regarding the WSD, however, a power-law relation of the form $(1-s)^\beta$ with $\beta = 4.0$ can be used to predict the value of $g(s)$.

5. Conclusions

Precise determination of the EODs in GDLs is crucial for the accurate prediction of cell performance, because it provides a more reliable numerical model for the optimization of PEM fuels. In this paper, the EODs in two commonly used GDL materials, carbon paper and carbon cloth, were measured under both dry and partially saturated conditions. The measurements were performed by using an oxygen sensor based on a galvanic cell developed in our previous studies.

For dry GDLs, the experimental investigations demonstrated that most previous models had considerably overestimated the ability for oxygen transport. An investigation of the effect of the PSD on the EOD revealed that the PSD, in addition to the average porosity, had a significant impact on the EOD. Hence, a relation accounting for the PSD proposed by Hager was introduced to calculate the EOD, and

the calculated data were found to agree well with the experimentally measured values. In the absence of information regarding the PSD, the Bruggeman correlation with an exponent of $\alpha = -3.0$ can be used to determine the EOD.

For partially saturated GDLs, the effects on the EODs of different WSDs obtained from using two water impregnation methods were analyzed. It was observed that carbon cloth specimens impregnated by using the two methods exhibited no significant difference in EOD at the same average water saturation, whereas, the EODs of carbon paper specimens impregnated by using the vacuum method declined more rapidly with an increase in water saturation than did the EOD of identical specimens impregnated by using the moist air condensation method. The experimental results confirmed the previous finding that the WSD exerted a considerable influence on the EOD (at least for carbon paper specimens here). Furthermore, experimentally verified equations were proposed to analyze the present experimental results. The $g(s)$ results calculated by using power-law relation of the form $(1 - s)^{3.0}$ with the application of the WSD equations were observed to fit the existing experimental data well. Nonetheless, in the absence of information regarding the WSD, a power-law relation of the form $(1-s)^\beta$ with $\beta = 4.0$ can be used to determine the value of $g(s)$. Finally, the need remains for a more detailed study of the effect of the WSD.

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Table and Figure Captions

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1 Fig. 16. Comparison between the results predicted by predicted using $s(x)$ and
2 $(1 - s_{\text{avg}})^\beta$ (with $\beta = 3.0$ and $\beta = 4.0$) and the experimental data.
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1 Table 1. Models of effective diffusivity reported in the literature

Theory	$f(\epsilon)$	$g(s)$	References
Effective medium	$\epsilon_{\text{avg}}^{1.5}$	1	Bruggman [7]
Percolation	$\epsilon_{\text{avg}} \left(\frac{\epsilon_{\text{avg}} - 0.037}{1 - 0.037} \right)^{0.661}$	1	Tomadakis and Stotirchos[15]
Effective medium	$1 - \frac{3(1 - \epsilon_{\text{avg}})}{3 - \epsilon_{\text{avg}}}$	1	Das <i>et al.</i> [16]
Pore net work	$1 - (1 - \epsilon_{\text{avg}})^{0.46}$	1	Mezedur <i>et al.</i> [18]
Pore net work	$\epsilon_{\text{avg}} \left(\frac{\epsilon_{\text{avg}} - 0.11}{1 - 0.11} \right)^{0.785}$	$(1 - s_{\text{avg}})^{\beta}$ $\beta = 2.0 \sim 3.0$	Nam and Kaviany [19]
Pore net work	$f(\epsilon)$	$(1 - s_{\text{avg}})^{\beta}$ $\beta = 5.0$	Gostick <i>et al.</i> [20]
Pore net work	$f(\epsilon)$	$(1 - s_{\text{avg}})^{\beta}$ $\beta = 2.6 \sim 3.6$	Wu <i>et al.</i> [21]
Empirical	$\epsilon_{\text{avg}}^{3.8}$	1	Martínez <i>et al.</i> [26]

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Table 2. Properties of the two materials

Material	PTFE loading(%)	Porosity	Pore size (μm)
Carbon Cloth	0	0.78	97
Carbon Paper TGP-H-120	0	0.81	32
TGP-H-120	20	0.74	32
TGP-H-120	70	0.61	31
TGP-H-120	97	0.57	32
TGP-H-120	120	0.52	30
TGP-H-120	150	0.43	32

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