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Note: Determination of effective gas diffusion coefficients of stainless steel films with differently shaped holes using a Loschmidt diffusion cell

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In this work, an in-house made Loschmidt diffusion cell is used to measure the effective O_2 – N_2 diffusion coefficients through four porous samples of different simple pore structures. One-dimensional through-plane mass diffusion theory is applied to process the experimental data. It is found that both bulk diffusion coefficient and the effective gas diffusion coefficients of the samples can then be precisely determined, and the measured bulk one is in good agreement with the literature value. Numerical computation of three-dimensional mass diffusion through the samples is performed to calculate the effective gas diffusion coefficients. The comparison between the measured and calculated coefficient values shows that if the gas diffusion through a sample is dominated by one-dimensional diffusion, which is determined by the pore structure of the sample, these two values are consistent, and the sample can be used as a standard sample to test a gas diffusion measurement system. [doi:10.1063/1.3385673]

I. INTRODUCTION

Gas diffusion through porous materials is of significance in various areas of both scientifically fundamental study and engineering applications, such as in catalyst research,^{1,2} environment study,³ and fuel cell development.^{4–6} People have made abundant efforts in theoretical study and experimental measurement of effective gas diffusion coefficients of porous materials.^{2,7}

On the one hand, satisfactory theoretical models are not easy to develop due to the complexity of the diffusion in porous materials of various pore networks.^{5,7} For example, porous gas diffusion layer (GDL) in a proton exchange membrane fuel cell is used for the transport of gas and liquid as well as electron conduction. The progress in the research and development of fuel cells depends heavily on the understanding of the transport phenomena in the cells. Due to the complexity of monitoring species transport experimentally, mathematical models are often used to investigate this transport, and various models are available for calculating the effective gas diffusion coefficient in the GDL.^{8–10} However, as a result of the geometry difference of different GDLs and the lack of experimental data for comparison, it becomes difficult to choose the most appropriate model.⁵

On the other hand, some measurement techniques, e.g., gas chromatography, pulsed field gradient nuclear magnetic resonance, and diffusion cell methods,^{7,11,12} have been devel-

oped to determine effective diffusion coefficients of porous materials. In order to establish the confidence in an experimental technique in terms of measurement accuracy and precision, it is ideal to have a sample that has a simple pore structure, and its effective diffusion coefficient can be easily predicted. The sample then can be used to test the measurement techniques.

In this work, we report an experimental method to measure the effective diffusion coefficients of four selected porous samples using an in-house made Loschmidt diffusion cell. The samples have simple pore structures and the measurement results are compared to that attained by numerical calculation. The experimental results demonstrate that the Loschmidt diffusion cell method can precisely measure effective diffusion coefficient, and one sample under investigation can be used as standard sample to test or calibrate a diffusion measurement system. Furthermore, the structure of perforated GDL, which is considered a promising new generation of GDL,¹³ is very similar to the sample; the measurement method reported in this paper can be employed to study the perforated GDL.

II. EXPERIMENTAL

An in-house made Loschmidt diffusion cell, as described in Refs. 5 and 6, was used in this work to measure binary diffusion coefficients of dry O_2 – N_2 through-plane diffusion of porous samples at 25 °C and 1 atmospheric pressure. A theoretical formula of one-dimensional mass diffusion

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FIG. 1. SEM images of photoetched sample cross-sections: straight (PE-A), coned (PE-B), and stepped (PE-C).

$$c(z, t) = \frac{1}{2} \left[c^b + c^t - (c^b - c^t) \operatorname{erf} \left(\frac{z}{2\sqrt{Dt}} \right) \right] \quad (1)$$

was applied to process the experimental data (e.g., least-square curve fitting method) to obtain the diffusion coefficient D .^{6,14,15} Here, c is the concentration of O_2 and c^b and c^t are the concentrations of O_2 at time $t=0$ in the bottom and top chambers of the cell, respectively. In the gas diffusion, the equivalent diffusion resistance R_{eq} to the diffusion can be written as $R_{eq} = \Delta z / D_{eq} A$,² where Δz is the diffusion distance in the diffusion direction, A is the cross-sectional area available to diffusion, and D_{eq} is the equivalent diffusion coefficient. The equivalent resistance, in the presence of a porous sample of a thickness l and an effective diffusion coefficient D_{eff} , can be expressed as^{2,6}

$$R_{eq} = \frac{\Delta z}{D_{eq} A} = \frac{\Delta z - l}{D_B A} + \frac{l}{D_{eff} A}. \quad (2)$$

With Eq. (2), we determined the effective diffusion coefficient D_{eff} of a porous sample by measuring the bulk diffusion coefficient D_B (without the porous sample) and the equivalent diffusion coefficient D_{eq} (with the porous sample) using Eq. (1).

Four stainless steel porous samples were investigated. Among them, three photoetched MicroEtch Screens (stainless steel alloy 316/316L) were from Tech-Etch, Inc., named as PE-A, PE-B, and PE-C in this paper. Another sample was a stainless steel sheet sample with holes created by Alase Technologies, Inc. using laser microdrilling technique. Figure 1 presents the scanning electron microscope (SEM) images of sample cross-sections. The hole radii (r_1 and r_2) on two surfaces of each sample and the distance between the holes (d) were measured with surface SEM images (not shown in this paper), and the results are listed in Table I.

III. RESULTS AND DISCUSSION

Typical concentration evolution patterns of the gas diffusion measured by the oxygen sensor in the diffusion cell can be found in Ref. 6. The D can be attained by least-square curve fitting of Eq. (1) to experimental data as described in

TABLE I. Geometrical parameters of the holes of the samples.

Sample	l (μm) ($\pm 1\%$)	r_1 (μm) ($\pm 3\%$)	r_2 (μm) ($\pm 3\%$)	d (μm) ($\pm 3\%$)	r_1/d	Hole profile
PE-A	50	90.9	90.9	163.0	0.557	Straight
PE-B	153	173.8	221.2	422.1	0.412	Coned
PE-C	200	202.5	312.5	595.1	0.339	Stepped
Laser-drilled	506	40.7 ^a	60.5 ^a	105	0.397	Coned

^a $\pm 5\%$.

Ref. 6. The bulk diffusion coefficient D_B was found to be $D_B = (0.202 \pm 0.001) \text{ cm}^2 \text{ s}^{-1}$ at 25°C and 1 atmospheric pressure with dry gases, which is well consistent with the literature value.¹⁶ More than 30 measurements were performed for each sample and the results of the equivalent diffusion coefficient D_{eq} for all the samples are listed in Table II. The mean free path for O_2 , estimated using the kinetic theory of gases, is $\sim 60 \text{ nm}$.¹⁷ At pore sizes much larger than the mean free path, surface adsorption leading to capillary condensation or Knudsen diffusion in a confined space is assumed to be negligible. The fact that for all the samples the standard deviation of D_{eq} was less than 1% of the mean value demonstrates that precise experimental results can be achieved with the Loschmidt diffusion cell and Eq. (1).

The measured effective diffusion coefficients D_{eff} of the samples were compared to the calculated ones using numerical three-dimensional diffusion computation. The finite element method (FEM) was used to solve for the effective gas diffusion coefficient through the samples.¹⁸ Only one segment of each sample was considered as the computational domain, as shown in Fig. 2(a).

The Fick's law of diffusion and the associated boundary conditions are given by

$$\begin{cases} \nabla(D_B \nabla c) = 0, & (x, y, z) \in \Omega_{\text{pore}} \\ \frac{\partial c(x, y, z)}{\partial n} = 0, & (x, y, z) \in S_1, S_2, S_3, S_4 \\ c(x, y, z) = c_L & (x, y, z) \in S_L \\ c(x, y, z) = c_R & (x, y, z) \in S_R \\ \frac{\partial c(x, y, z)}{\partial n} = 0, & (x, y, z) \in S_I \end{cases}, \quad (3)$$

where Ω_{pore} represents pore space; S_I represents the interface between solids and pores; S_1 , S_2 , S_3 , and S_4 are, respectively, the segment surfaces where there are zero fluxes normal to them; and S_L and S_R are the two outer surfaces where differ-

TABLE II. Results of the diffusion coefficients and the ratios of effective diffusion coefficients to bulk diffusion coefficient.

Samples	D_{eq} ($\text{cm}^2 \text{ s}^{-1}$)	D_{eff} ($\text{cm}^2 \text{ s}^{-1}$)	D_{eff}/D_B	
			Measured	Simulated
PE-A	0.2005 ± 0.0009	0.057 ± 0.009	0.27 ± 0.03	0.282
PE-B	0.190 ± 0.001	0.026 ± 0.002	0.13 ± 0.009	0.168
PE-C	0.185 ± 0.001	0.0232 ± 0.0009	0.110 ± 0.005	0.150
Laser-drilled	0.181 ± 0.001	0.042 ± 0.003	0.21 ± 0.02	0.175

FIG. 2. (a) Unidirectional diffusion process for a segment of a sample and (b) cross-sections used in the calculations for PE-A (straight), PE-B (coned), PE-C (stepped), and laser-drilled (coned) samples.

ent gas concentration boundary conditions are applied.

For each sample, we meshed the entire pore volume of the cross-section of each sample shown in Fig. 2(b) and the geometrical parameters in Table I. We solved the gas diffusion equation throughout the entire pore volume by using the FEM package, ANSYS. The effective diffusion coefficient D_{eff} of the porous segment, as shown in Fig. 2(a), is defined as the flux across the surface S_R over the flux through the homogeneous segment, which has exactly the same size and the same boundary conditions as the porous segment. It can be expressed as

$$D_{\text{eff}} = \frac{\int \int_{S_R} D_B \left(\frac{\partial c}{\partial z} \right)_{z=l} dx dy}{\frac{(C_R - C_L)}{l} S_R}. \quad (4)$$

The experimentally measured and numerically calculated ratios of the effective diffusion coefficient to bulk one, D_{eff}/D_B , for each sample is presented in Table II.

From Table II, we can see that for sample PE-A, the numerical calculated and experimentally measured ratios are consistent with a relative difference of about 4%. This consistency indicates that this sample can be used as a standard sample to test or calibrate a diffusion measurement system. For PE-B and PE-C samples, the relative difference are about 29% and 36%, respectively. Two factors may contribute to these large relative differences. First, the theoretical model for the experimental measurements of the effective diffusion coefficients is one-dimensional. As shown in the Table I, samples PE-B and PE-C have smaller values of r_1/d and larger thicknesses than that of sample PE-A, which cause the deviation of the one-dimensional approach from the three-dimensional one. Second, the shapes of the sample cross-sections used in the three-dimensional numerical computation [Fig. 2(b)] are different from the real ones (Fig. 1). The difference in the cross-section shapes contributes to the rela-

tive difference of the ratio D_{eff}/D_B of these photoetched samples. For the laser-drilled sample, the relative difference the ratio is about 16%. Besides the foregoing two factors, the nonuniform surface shapes (can be seen in the surface SEM images) of the holes of the sample could be another factor for the relative difference. The deviation of the measured results from the calculated diffusivity leads to a consideration that further refinement of both the theoretical description of irregular morphology in the actual porous media, and the need for an increasingly complex morphological model.

IV. CONCLUSIONS

Together with the formula of one-dimensional mass diffusion, a Loschmidt diffusion cell was employed to measure effective binary gas diffusion coefficients of porous samples of different simple pore structures. It was found that this technique could precisely measure both bulk diffusion coefficient and the effective diffusion coefficients of the porous samples. The measured values of the effective gas diffusion coefficients were compared to the ones calculated using numerical computation of three-dimensional gas diffusion. The measured effective diffusion coefficient of the sample PE-A of large r_1/d was well consistent with the calculated one, and this sample can be used as a standard sample for a gas diffusion measurement system assessment or calibration.

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