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Short communication

A novel method for effective diffusion coefficient measurement in gas diffusion media of polymer electrolyte fuel cells

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HIGHLIGHTS

- A novel method for measuring effective diffusion coefficient is developed.
- Establishment of O_2 concentration difference is realized in an air-breathing PEMFC.
- The O_2 concentration differences are correlated with the PEMFC voltage differences.
- This method is more reliable than conventional conductivity method.

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ABSTRACT

A novel method for measuring effective diffusion coefficient of porous materials is developed. The oxygen concentration gradient is established by an air-breathing proton exchange membrane fuel cell (PEMFC). The porous sample is set in a sample holder located in the cathode plate of the PEMFC. At a given oxygen flux, the effective diffusion coefficients are related to the difference of oxygen concentration across the samples, which can be correlated with the differences of the output voltage of the PEMFC with and without inserting the sample in the cathode plate. Compared to the conventional electrical conductivity method, this method is more reliable for measuring non-wetting samples.

1. Introduction

Transport phenomena in porous media has long been an important research subject because of the wide-ranging application of the porous materials in separation, catalysis, energy transformation and storage, and so on. A thorough understanding of the mass transport limitations in gas diffusion material (GDM) is crucial to provide insight into GDM design, as well as to improve the fuel cell performance. There are several mechanisms for mass transport in porous media: (i) ordinary diffusion, (ii) Knudsen diffusion, (iii) viscous flow, (iv) surface diffusion. It is a meaningful but challenging task to predict the effective diffusion coefficient in porous media, since no completely satisfied theory is available [1].

Gas diffusion coefficients can be measured by whether steady state (constant concentration boundary condition) or transient state methods (time-dependent concentration boundary condition) [2], such as closed-tube (Loschmidt), two-bulb, evaporation-tube, point-source method and so on; a detailed survey of this field can be found in reference [3]. All the methods involve establishing a concentration gradient and monitoring the flux (or gas concentration), usually requiring specially constructed diffusion cells and tracer/carrier gas [2–6]. Several researchers investigated *in situ* limiting current density of an operating fuel cell to characterize the mass transport properties of gas diffusion media in membrane electrode assembly (MEA) [7–11], however, one specified MEA need to be prepared for each test and the value measured is an overall mass transfer coefficient arising in flow channel, backing layer, microporous layer (MPL) and catalyst layer.

As Fick's first law is analogous to Ohm's law in mathematics, the determination of the effective conductivity can be translated immediately into equivalent results for the effective diffusion coefficient [12,13]. Researchers tend to measure the correction factor of diffusion coefficient, N_M, i.e., the MacMullin number, which is

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defined as the ratio of the resistivity of the porous media filled with electrolyte to the bulk resistance of the same electrolyte, based on electrical properties since the conductivity is easy to be measured [14–16]. N_M is a function of porosity (ε), tortuosity (τ) and the pore size distribution and connectivity [15,16]. Then the effective diffusion coefficient D_e can be expressed as:

$$D_e = \frac{D_o}{N_M} \tag{1}$$

where D_o is the diffusion coefficient in the open space. One problem to measure D_e by the conductivity method is that the hydrophobic pores in the sample might not be completely wetted, hence the measured resistance would be much greater than the true value.

In this communication we report a novel method to measure the effective diffusion coefficient under atmospheric circumstance, which does not require specially constructed diffusion cell and tracer/carrier gas, nor the analysis of gaseous streams. Both the establishment of oxygen concentration gradient and the determination of the ratio of oxygen concentration difference between the samples are realized in one air-breathing proton exchange membrane fuel cell (PEMFC). The method is validated by comparing the measured N_M value of perforated plates of different diameters with their corresponding theoretical values, and the N_M values of five different GDM were compared with the data acquired from the conventional conductivity method.

2. Methods and material

2.1. N_M measurement – steady-state diffusion method

The steady-state diffusion method was employed to measure the MacMullin number (N_M^t) by comparing the difference of oxygen concentration across the tested samples with that of standard sample under the same oxygen flux, as shown in Fig. 1a. The difference in oxygen concentration across the sample is established and measured in one air-breathing PEMFC with a sample holder in the cathode plate, as shown in Fig. 2a. Multiple holes with diameter of 3.00 mm were drilled in the cathode plate to serve as the passages for oxygen.

The standard sample is a perforated Acrylonitrile Butadiene Styrene (ABS) plate of 2.60 mm in thickness. The sizes and positions of the holes for the standard sample are completely the same as those for the cathode plate. Hence the MacMullin number of the standard sample is 1. The properties of the tested samples (carbon paper) are listed in Table 1. Eight sheets of carbon paper are layered to a total thickness of about 1.6 mm to reduce the measurement error.

The measurements were carried out as follows: (1) record the voltage (E_0) of the PEMFC discharging at a certain current density for 3 min using an Arbin E-load (to avoid water flooding, the cell is operated at a low current density in the range of 150–200 mA cm^{-2}); (2) insert the standard sample ($N_M^s = 1$) and record the voltage (E_s) of the PEMFC under the same current density as step 1; (3) keep the standard sample fitted in and insert the tested sample, and then record the voltage (E_t) of the PEMFC under the same current density as step 1. We denote $\Delta E_s = E_s - E_0$ and $\Delta E_t = E_t - E_s$.

The concentration difference ΔC across the samples is equal to the difference in value between the oxygen concentration (C_1) in the catalyst layer without sample in path and that (C_2) with sample (assuming a simple one-dimensional diffusion model). We can deduce the relationship between the voltage difference of the cell and concentration difference from Nernst equation:

$$\Delta E = \frac{RT}{nF}\ln\frac{C_1}{C_2} = \frac{RT}{nF}\ln\left(1+\frac{\Delta C}{C_2}\right) \tag{2}$$

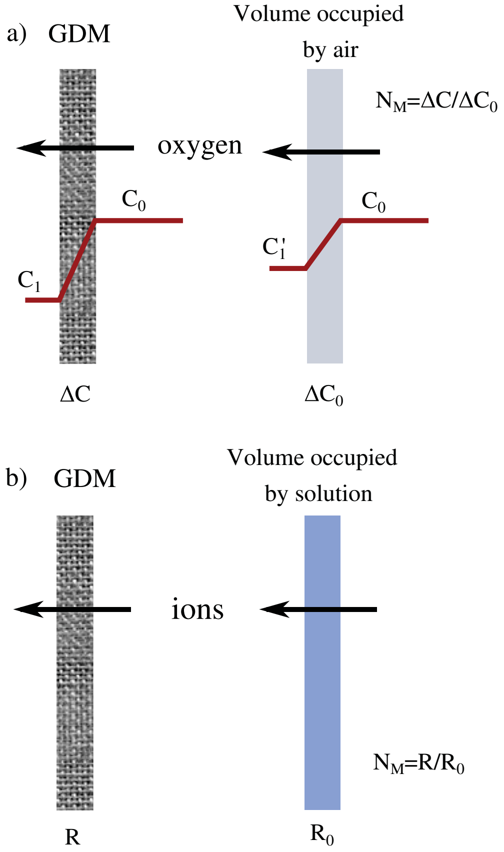

Fig. 1. Illustration of MacMullin number measurement. a) For a steady-diffusion method, N_M is the ratio of the concentration difference with the porous media in the path to that without the porous media. b) For an electrical conductivity method, N_M is defined as the ratio of the resistivity of the porous media filled with electrolyte to the bulk resistance of the same electrolyte.

where R, T, F denote the ideal gas constant, absolute temperature and Faraday's constant. Using the Taylor expansion, we get

$$\Delta E = \frac{RT}{nF}\ln\left(1+\frac{\Delta C}{C_2}\right) = \frac{RT}{nF}\left(\frac{\Delta C}{C_2} - \frac{1}{2}\left(\frac{\Delta C}{C_2}\right)^2 + \frac{1}{3}\left(\frac{\Delta C}{C_2}\right)^3 + \cdots\right) \tag{3}$$

For $\Delta C/C_2$ with a small value, the terms after $\Delta C/C_2$ can be neglected. Hence the concentration difference is proportional to the voltage difference:

$$\Delta C \propto \Delta E \tag{4}$$

Using Fick's law, we find

$$\frac{h_s N_M^s}{h_t N_M^t} = \frac{\Delta C_s}{\Delta C_t} = \frac{\Delta E_s}{\Delta E_t} \tag{5}$$

here h_s, h_t denote the thickness of the standard sample and the test sample, respectively.

2.2. N_M measurement – electrical conductivity method

The method described here is similar to that reported by Martínez et al., in which ion diffusion was used to obtain the effective transport coefficient (see Fig. 1b), and more details can be found in Ref. [16]. The resistivity cell apparatus, as shown in Fig. 2b, consists of a polycarbonate reservoir (15 cm × 10 cm × 10 cm) with a center