Measurement of Water Transport Properties Through Membrane Electrode Assemblies

Part II. Cathode Diffusion Media

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This paper presents an in situ method to characterize the effective water diffusivity (D_e) of cathode diffusion media in an operating fuel cell. The D_e values of self-made gas diffusion layers (GDLs) and a commercial GDL were experimentally determined to be about one order of magnitude lower than the theoretical value. The effects of several factors such as the inert gas component and cathode pressure as well as the presence of microporous layer (MPL) on D_e were studied, and the mechanism of water transport through cathode diffusion media was explored. It was found that the water transport is largely controlled by molecular and Knudsen diffusion through the catalyst layer. The MPL does not exhibit a dominant resistance to water transport. Interrelations of D_e with the net water transport coefficient through the membrane and membrane resistance were also examined, suggesting that good balance between suitable membrane hydration and cathode flooding avoidance can be achieved by optimizing cathode diffusion media. The capability to measure D_e reported in this work provides a diagnostic tool for screening cathode diffusion materials.
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Diffusion media or gas diffusion layers (GDLs) are a vital component for attainment of high performance in proton exchange membrane fuel cells (PEMFC). One essential requirement for an ideal GDL is that it should have proper hydrophobicity so that excellent reactant supply can be attained while anode dehydration and cathode flooding are avoided. This is particularly critical for the cathode side because product water, existing as a liquid under many conditions, may accumulate and lead to flooding if the excessive water cannot be efficiently removed out of diffusion media.[1,2]

A schematic of the GDL is shown in Fig. 1. It is typically a double-layer carbon-based porous substrate placed between the flow field and the catalyst layer (CL). The first layer in contact with the flow field is a macroporous substrate of either carbon cloth or carbon paper. It is usually treated with polytetrafluoroethylene (PTFE) to increase hydrophobicity for favorable water management. It also serves as a current collector, a physical support of the CL, and an elastic component of a membrane electrode assembly (MEA). The second layer adjacent to the CL is a thinner microporous layer (MPL) consisting of carbon or graphite particles mixed with a polymeric binder, usually PTFE. The MPL helps to improve the water management of a fuel cell.[1]

A key function of the GDL is for water management. Much effort has been made to optimize its morphology, structure, and composition for this purpose, leading to enhanced fuel cell performance.[3-9] However, these approaches have been mostly guided by empiricism due to lack of effective measurement tools or characterization methods to evaluate the water retention/removal properties of GDLs. The net water transport coefficient through the membrane, α, defined as the ratio of the net water flux from the anode to cathode to the protonic flux (mol H_2O/mol H^+), is often used as a quantitative measure of water management in a PEMFC. When $\alpha > 0$, the net water transported through the membrane from the anode to cathode combined with product water of oxygen reduction reaction (ORR) on the cathode is removed by cathode gas, thus termed cathode water removal. In contrast, when $\alpha < 0$, product water will be removed via the anode fuel stream, thus termed anode water removal.[10] The minimum α is equal to -0.5. In This case all product water of ORR is removed through the membrane into the anode. Numerous studies have examined the effects of operating conditions, e.g., stoichiometry and relative humidity of gas streams, current density, and pressure on the α value.[11,12] However, no attempt

has been made in the literature to quantify a direct relationship between the water transport capability of cathode diffusion media and the net water transport coefficient through the membrane. Development of such a relationship will provide a rational guideline to tailor diffusion media for innovative water management strategies.

In this study, we develop an in situ technique to determine experimentally the effective water diffusivity through the entire cathode including the CL, MPL, and substrate diffusion layer. The effects of the inert gas component, cathode pressure, and the presence of MPL on cathode effective water diffustiy were explored. The objective of this paper is to provide (*i*) a measurement technique for the water transport property of the entire cathode for better understanding of the water transport mechanisms, (*ii*) a screening tool for cathode component materials required in fuel cell optimization, (*iii*) reliable input for fuel cell modeling, in which the GDL is included as an important component, and (*iv*) a diagnostic tool to characterize mass transport properties of aged electrodes and GDLs in situ.

Experimental

Commercially available 5 cm^2 Gore-PRIMEA-18 MEAs were used in this study. The MEA consists of an 18 μm membrane and 12 μm thick catalyst layer with a Pt loading of 0.4 mg/cm^2. The investigated GDLs were self-prepared by a paste casting process using TGPH-60 Toray carbon paper as the macroporous substrate. The paste mixture was made by dispersing PTFE powder into an appropriate solution of Vulcan XC-72R. The paste was applied onto the carbon paper using a doctor blade in a controlled thickness. The as obtained MPL has 40 wt % PTFE after drying and heat-treatment. For comparison purpose, a commercially available SGL GDL with MPL was also included in this work. The experimental setup and procedure were the same as those in the fuel cell mode described in Part I of this series.
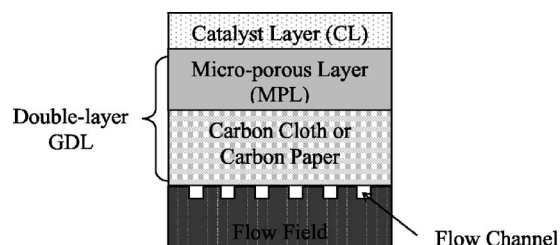
Figure 1. Schematic of a double-layer gas diffusion medium.

Results and Discussion

Effective water diffusivity through the entire cathode.— Based on the diffusion-type model,[12-14] the effective water diffusivity through the cathode including GDL composite media can be defined by

$$J_{c,w} = D_e \frac{C_{c,m} - C_c}{l_{CL+MPL+CP}} = D_e \frac{P_{sat}}{RT} \frac{RH_{c,m} - RH_c}{l_{CL+MPL+CP}} \quad [1]$$

where $J_{c,w}$ and D_e are the net water flux and the effective water diffusivity through the cathode diffusion media, respectively. $l_{CL+MPL+CP}$ is the total thickness of the composite diffusion media including CL, MPL, and carbon paper. $C_{c,m}$, C_c, $RH_{c,m}$, and RH_c are the concentration and relative humidity of water vapor at the membrane/cathode catalyst layer (CCL) interface and the cathode bulk gas stream in the channels, respectively. P_{sat} is the saturated water vapor pressure at the cell temperature, T, and R is the gas constant.

As introduced in Part I, we have the following water balance equations

$$J_{c,w} = J_{net} + J_{prod} \quad [2]$$

and

$$J_{net} = J_{a,in} - J_{a,out} \quad [3]$$

or

$$J_{net} = J_{c,out} - J_{c,in} - J_{prod} \quad [4]$$

We define the net water flux through the membrane as

$$J_{net} = \alpha \frac{I}{F} \quad [5]$$

where α is called the net water transport coefficient through the membrane. The other terms have the same physical meaning as described in Part I.

The experimental conditions were also the same as those in Part I for the fuel cell mode. For example, the flow rates of the hydrogen and air were 0.28 and 0.70 slm, respectively, and the average RH level in the gas streams on the both sides ranged between 35% and 100%. At each RH level, the fuel cell was operating at three constant current densities of 0.4, 0.8, and 1.2 A/cm², respectively. Sufficient time was taken in each experiment to ensure steady state required of Eq. 2-4. The same procedures were applied for the measurements of water flux and high-frequency resistance (HFR) values as well as for the determination of $\lambda_{c,m}$, which can be converted into $C_{c,m}$ or $RH_{c,m}$. Using Eq. 1, D_e can be obtained when $\lambda_{c,m}$ becomes known. Figure 2 displays the values of D_e in air through the entire cathode for the self-made and SGL GDLs and their comparison with the theoretical value.[15,16] Note that D_e values do not show much variance with the RH level and current density, and their average values are about one order of magnitude lower than the theoretical diffusion coefficient of water in air. Here we must emphasize that the values obtained at high RH levels (around 100% RH) might not be reliable due to difficulty in determination of accurate $\lambda_{c,m}$ with possible presence of liquid water. Therefore, the average values of D_e over the entire RH range denoted by horizontal lines in Fig. 2 were acquired mostly based on the data points at relatively low RH levels. Our result of the significantly lower D_e values is consistent with a most recent finding for the oxygen diffusion coefficient. Stumper et al.[17] reported that their experimentally obtained oxygen diffusivity value (6.1 × 10⁻⁷ m²/s) through a similar cathode diffusion media in an operating fuel cell was about one-tenth of the theoretical value (8.83 × 10⁻⁶ m²/s). They concluded that a transport-limiting step in the active catalyst layer seemed the most plausible explanation for such a low diffusivity.

To explore the mechanism of water transport through the cathode diffusion media, the effects of the inert gas component and cathode pressure as well as the presence of MPL on D_e were studied. Note
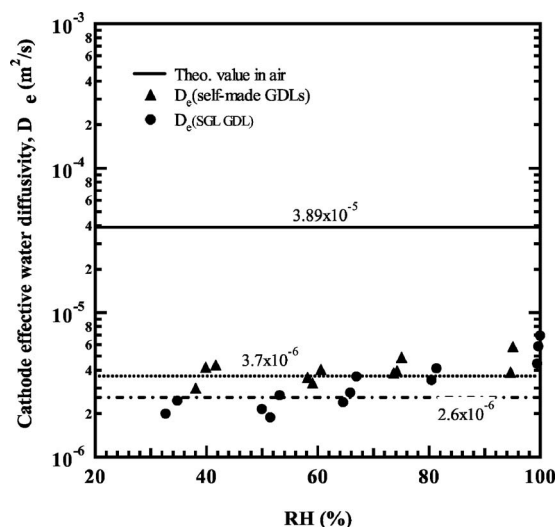

Figure 2. Cathode effective water diffusivity values of the self-made and SGL GDLs.

that there are generally two types of diffusion mechanisms through a porous medium like GDL, i.e., molecular diffusion and Knudsen diffusion. Molecular diffusion depends on the inert gas component and the total pressure, whereas Knudsen diffusion does not.[1,18] We thus examined the effective water diffusivity in helox (79% He/21% O₂) and that under increased cathode pressure (i.e., 2 atm) while all other conditions were kept the same. To investigate which layer is dominant for water transport resistance, we also checked the values of D_e for a GDL without a MPL (bare carbon paper). Figure 3 shows the values of D_e under these varied conditions. For comparison purpose, the corresponding theoretical values calculated from Ref. 15 are also included in this figure. It can be seen that the average D_e increases from 3.7 × 10⁻⁶ m²/s in air by about 1.5 times up to 5.7 × 10⁻⁶ m²/s in helox, while it decreases by less than half down to 2.1 × 10⁻⁶ m²/s under 2-atm cathode pressure. In contrast, the theoretical value in helox was estimated to be 2.4 times that in air from the theory of binary diffusion coefficients.[15] It is then concluded that the water transport through the cathode diffusion media is largely controlled by molecular diffusion with Knudsen diffusion playing some role.
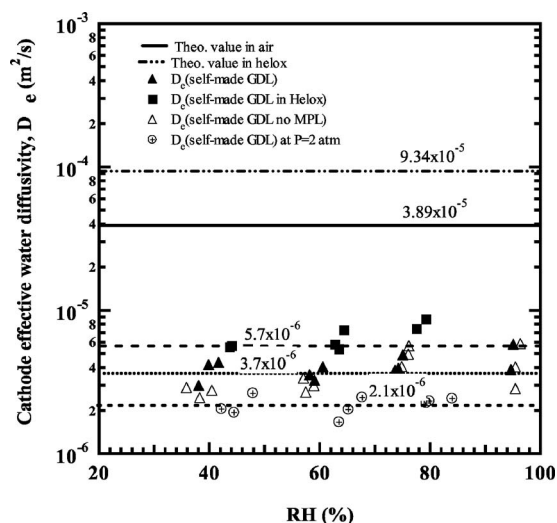

Figure 3. Effect of inert gas, cathode pressure, and MPL on cathode effective water diffusivity of the self-made GDLs.
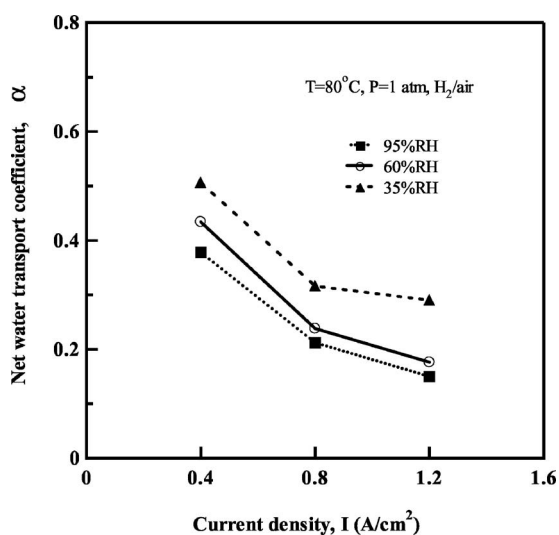
Figure 4. Dependence of the net water transport coefficient through the membrane on current density.

Figure 5. Dependence of the net water transport coefficient on relative humidity of gas streams.

From Fig. 3 it is also observed that there was not much difference between the average D_e values for the GDLs with and without MPL, indicating that the MPL does not constitute a dominant resistance to water transport. Because carbon paper, the substrate layer of the GDL, has macroporous structure, which may not be a controlling layer in water transport,[1] we hypothesize that the catalyst layer comprises a significant part of the total resistance. Furthermore, water transport in the active catalyst layer is largely dominated by molecular diffusion with high tortuosity, while Knudsen diffusion may play a part when partially flooded pores in the catalyst layer becomes sufficiently small to be comparable with the mean free path of water molecules.

Net water transport coefficient.— The net water transport coefficient through the membrane is a quantitative index of water management in a fuel cell system. It is a combined result of the electro-osmotic drag and back diffusion through the membrane, and thus is a reflection of the membranes overall water transport property. α also relies on the property of the diffusion media and on the operating conditions. In this study, we measured α values and analyzed their dependence under several experimental conditions. Figure 4 and 5 show the dependence of α on current density and the gas RH level, respectively. It is noticed that α considerably decreases with increasing current density at a certain RH level, and this tendency remains the same over a large RH range between 35% and 95%. At a constant current density, α slightly decreases with the increasing RH level of the gas streams. This occurs because at higher current densities the back diffusion of water is more significant as more water builds up at the membrane/CCL interface. When the gas stream at the cathode has higher RH, water is removed less efficiently from the catalyst layer to the gas channel due to the smaller water concentration gradient, resulting in a smaller α value. Our results are different from measurements reported by Janssen and Overvelde,[11] where the α value depended more significantly on the gas RH conditions rather than on the current density. This difference might be caused by the membrane thickness; in their study much thicker membranes were used, i.e., Nafion 105 and 112.

Effect of D_e on α and membrane resistance.— The water removal capability through the cathode is characterized by D_e. It is thus interesting to explore how D_e affects the net water transport through the membrane, i.e., α, and membrane resistance. These interrelations are shown in Fig. 6 and 7. It can be observed that D_e noticeably affects the α value and membrane resistance. Larger D_e results in larger α and larger membrane resistance, implying that
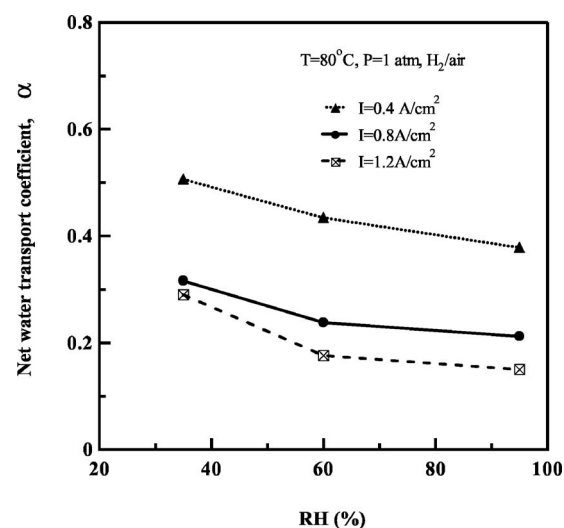
cathode diffusion media with strong water removal capability result in higher net water flux through the membrane and may dehydrate the membrane due to weak back diffusion of water. However, on the other hand, larger D_e indicates that water is more efficiently removed from the cathode to the gas channel, which is helpful to avoid cathode flooding. Therefore, cathode diffusion media must be engineered to maintain a suitable water retention/removal capability so that good balance can be achieved between the membrane hydration and cathode flooding avoidance.

It is interesting to note that the experiments and analysis described in this work can also be applied to aged cells with degraded CL and GDL. This allows in situ diagnosis of mass transport characteristics through degraded CL and GDL as well as altered water transport through the membrane, thus providing important information on PEFC durability.

Conclusions

A method to characterize the effective water diffusivity of cathode diffusion media has been developed. It is found that the overall water diffusivity was about one order of magnitude lower than the theoretical value. Water transport through the entire cathode includ-
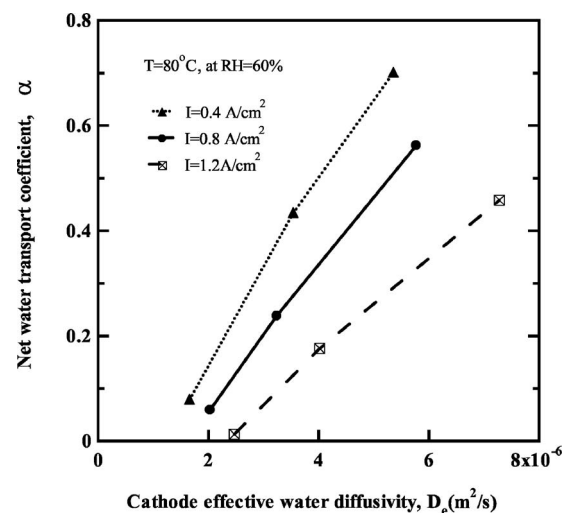

Figure 6. Interrelation between water transport through the membrane and that in cathode diffusion media.
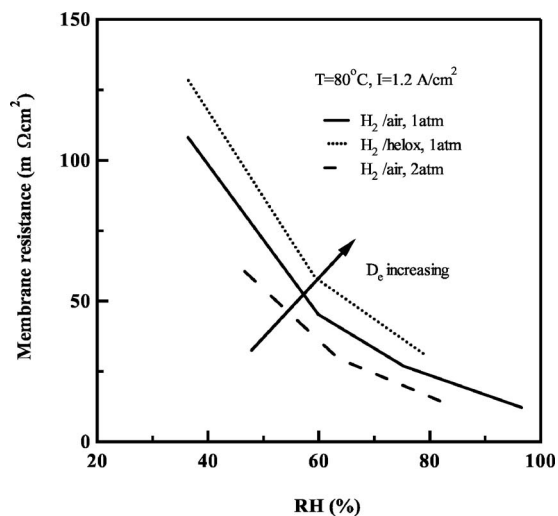
Figure 7. Effect of water transport through cathode diffusion media on the membrane resistance.

ing CL, MPL, and carbon substrate layer is largely controlled by molecular and Knudsen diffusion through the active catalyst layer. The inert gas component and cathode pressure have considerable effects on the water diffusivity, and the MPL does not exhibit a dominant resistance to water transport.

The net water transport coefficient noticeably decreases with increasing current density over the RH range studied; while it slightly decreases with an increasing RH of the gas streams under the same other conditions. It is also found that the overall cathode diffusivity markedly affects the membranes water transport and ohmic resistance. A good compromise is required between maintaining high membrane hydration and avoiding cathode flooding in fuel cell design, and this optimization can be realized by engineering cathode diffusion media. The ability to measure D_e in situ as described in

this work provides an effective approach for screening of cathode diffusion medium materials as well as for interrogating degradation mechanisms of degraded cathodes and diffusion media.

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