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.

© 2007 The Electrochemical Society. [DOI: 10.1149/1.2737384] All rights reserved.
Results and Discussion

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

\[ J_{\text{c.w}} = D_{\text{e}} \frac{C_{\text{c.m}} - C_{\text{c}}}{l_{\text{CL+MPL+CP}}} = D_{\text{e}} \frac{P_{\text{sat}} \text{RH}_{\text{c.m}} - \text{RH}_{\text{c}}}{RT} \frac{1}{l_{\text{CL+MPL+CP}}} \]  \[ 1 \]

where \( J_{\text{c.w}} \) and \( D_e \) are the net water flux and the effective water diffusivity through the cathode diffusion media, respectively. \( l_{\text{CL+MPL+CP}} \) is the total thickness of the composite diffusion media including CL, MPL, and carbon paper. \( C_{\text{c.m}}, C_{\text{c}}, \text{RH}_{\text{c.m}}, \) and \( \text{RH}_{\text{c}} \) 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. \( P_{\text{sat}} \) 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

\[ J_{\text{c.w}} = J_{\text{net}} + J_{\text{prod}} \]  \[ 2 \]

and

\[ J_{\text{net}} = J_{\text{in}} - J_{\text{out}} \]  \[ 3 \]

or

\[ J_{\text{net}} = J_{\text{out}} - J_{\text{in}} - J_{\text{prod}} \]  \[ 4 \]

We define the net water flux through the membrane as

\[ J_{\text{net}} = \frac{J_{\text{in}} - J_{\text{out}}}{F} \]  \[ 5 \]

where \( \alpha \) 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 \( \lambda_{\text{c,in}} \) which can be converted into \( C_{\text{c.m}} \) or \( \text{RH}_{\text{c.m}} \). Using Eq. 1, \( D_e \) can be obtained when \( \lambda_{\text{c,m}} \) becomes known. Figure 2 shows the values of \( D_e \) in air through the entire cathode for the self-made and SGL GDLs and their comparison with the theoretical values.\(^{15,16}\) 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 \( \lambda_{\text{c,m}} \) 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 diffusion value \((6.1 \times 10^{-7} \text{ m}^2/\text{s})\) through a similar cathode diffusion media in an operating fuel cell was about one-tenth of the theoretical value \((8.83 \times 10^{-6} \text{ m}^2/\text{s})\). 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 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. 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 \( 3.7 \times 10^{-6} \text{ m}^2/\text{s} \) in air by about 1.5 times up to \( 5.7 \times 10^{-6} \text{ m}^2/\text{s} \) in helox, while it decreases by less than half down to \( 2.1 \times 10^{-6} \text{ m}^2/\text{s} \) 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.\(^ {17} \) 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.
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.\(^\text{20849}\) Also, it relies on the property of the diffusion media and on the operating conditions. In this study, we measured $\alpha$ values and analyzed their dependence under several experimental conditions. Figure 4 and 5 show the dependence of $\alpha$ on current density and the gas RH level, respectively. It is noticed that $\alpha$ 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, $\alpha$ 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 $\alpha$ value. Our results are different from measurements reported by Janssen and Overvelde,\(^\text{11}\) where the $\alpha$ 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 $\alpha$ 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., $\alpha$, and membrane resistance. These interrelations are shown in Fig. 6 and 7. It can be observed that $D_e$ noticeably affects the $\alpha$ value and membrane resistance. Larger $D_e$ results in larger $\alpha$ 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-
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.

Acknowledgments

We acknowledge ECEC industrial sponsors for the financial support of this work and W. L. Gore & Associates for donation of various fuel cell materials.

The Pennsylvania State University assisted in meeting the publication costs of this article.

References