Numerical Analysis on Water Transport in Alkaline Anion Exchange Membrane Fuel Cells

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Abstract

We present an isothermal, one-dimensional, steady-state model for an alkaline anion exchange membrane fuel cell (AAEMFC), in which the conducting ions (OH\(^-\)) move from the cathode to the anode. While water is produced at the anode, it is consumed at the cathode along with oxygen. The water transport in the membrane comprises water flux by the electro-osmotic drag and the diffusive water flux because of the gradient of water concentration across the membrane. The present model is validated with the experimental data in the literature and the water transport in AAEMFC is discussed. By performing numerical simulations of four cases of humidity conditions (dry or fully humidified conditions for each anode and cathode), it is reconfirmed theoretically that anode humidification is more essential to secure good AAEMFC performance. In addition, water transport through the gas diffusion layers of anode and cathode as well as the membrane is examined to provide fundamental information about water management in the AAEMFC operations.

Keywords: Anion Alkaline Fuel Cell, Anion-exchange Membrane, Water Flux, Humidified Condition

1. Introduction

Recent studies on proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC), wherein a cation (H\(^+\))-conducting polymer membrane was used as an electrolyte, have indicated the possibility of active commercialization of the membranes for various applications because of their high conductivity and durability. However, the use of acidic polymeric electrolytes in PEMFC or DMFC has the limitations such as (i) slow electrode-kinetics, (ii) CO poisoning of Pt and Pt-based electrocatalysts at low temperatures and (iii) high costs of the membrane and catalyst.

On the other hand, when an anion-conducting alkaline electrolyte was used, ORR kinetics was significantly enhanced in comparison with an acidic medium. This led to the use of low-cost, non-precious catalysts (e.g., Ni, Ag, and Mn), thereby allowing much higher price competitiveness. However, the conventional alkaline fuel cells (AFCs) suffer from the leakage of liquid electrolyte and electrode flooding by electrolytes. Recently, ammonium-based alkaline anion exchange membranes (AAEMs) have been used instead of the liquid electrolyte to overcome the disadvantages of liquid electrolyte in AFCs.

Most of the previous researches on AAEM fuel cells (AAEMFCs) has focused on the synthesis and characterization of AAEMs\(^{1-11}\) and the development of non-Pt catalysts.\(^\text{12-14}\) In addition to the development of suitable materials for AAEMFCs, it is also important to investigate the cell performance under various operating conditions. It has been reported that the humidified conditions significantly influence the AAEMFC performance.\(^\text{15}\) In contrast to PEMFCs, water is produced at the anode, which should be consumed by the ORR at the cathode in AAEMFCs as shown in Fig. 1. Therefore, the water management strategies obtained from the studies of PEMFCs cannot be directly applied to the AAEMFCs. Research on the water transport in AAEMFC under various humidified conditions could provide important strategic information for operational control of the AAEMFC system; however, such research has been scarce hitherto.\(^\text{16}\)

![Figure 1. Schematic of alkaline anion exchange membrane fuel cell model.](http://dx.doi.org/10.5796/electrochemistry.83.80)
The water flux by the electro-osmotic drag (EOD) can be determined from,

\[ N_{W,\text{drag}} = n_d J / F = n_d 2I, \]  

(10)

where \( n_d \) is the EOD coefficient in the membrane and it is calculated by the following empirical relation of Huo et al.\(^8\)

\[ n_d = 0.183t + 1.3, \]  

(11)

where the water content (\( \lambda \)) is given as a function of RH (0 < \( \phi \) ≤ 1) at 30, 40, and 60°C:\(^9\)

\[ \lambda_{30} = 0.158 + 21.14 \phi - 42.09\phi^2 + 34.2\phi^3 \]
\[ \lambda_{40} = 0.117 + 23.4\phi - 47.74\phi^2 + 39.0\phi^3 \]
\[ \lambda_{60} = 0.423 + 19.3\phi - 30.76\phi^2 + 26.9\phi^3. \]  

(12)

The diffusive water flux through the membrane, \( N_{W,\text{diff}} \) can be expressed as,

\[ N_{W,\text{diff}} = D_w c_w^m - c_w^m / \tau_w, \]  

(13)

where \( D_w \) denotes the water diffusivity of the membrane and \( \tau_w \) is the thickness of the membrane. Note that the linear profile of water concentration is assumed in the diffusive water flux. The water diffusivity in the A201 membrane is reported as a function of the average water content in the membrane:\(^9\)

\[ D_w (x_0^{-10^{-10} m^2 s^{-1}}) = \begin{cases} -79.826 + 17.928l - 1.3329l^2 + 0.03337l^3 & (30°C) \\ -312.23 + 63.058l - 4.2255l^2 + 0.09468l^3 & (40°C) \end{cases} \]  

(14)

The water concentration in the membrane \( c^m \) can be expressed in terms of the water content of the membrane \( \lambda \) as,

\[ c^m = \lambda / k^m, \]  

(15)

where \( k^m \) is the fixed charge (quaternary ammonium group) concentration in the membrane (1.7 × 10^7 mol m^−3 for the A201 membrane)\(^3\).

By solving the diffusion equation for the GDLs (Eqs. 5–7) with an initial guessed value of \( \alpha \), the diffusive water flux through the membrane can be calculated from Eq. (13). However, when \( \alpha \) is not appropriately chosen, the diffusive water flux does not satisfy the water molar flux balance of Eq. (9); hence, we employed the Newton iterative method to find the appropriate value of \( \alpha \). With this value, the fuel concentration was calculated at the reaction site and used for calculating the overpotential losses. We assumed that the anodic overpotential was negligible and considered only the cathodic potential.

To calculate the overpotential, we used the simple Tafel expression given as,

\[ J = J^0 \exp \left( \frac{C_{O_2} C_{H_2O}}{C_{O_2}^0 C_{H_2O}^0} \right) \left( \frac{\alpha_k F}{RT} \right) n_{\text{over}} \]  

(16)

The exchange current density \( J^0 \) is referenced to the fully humidified oxygen with RH 100% at 1 atm and 50°C. A linear fitting of Eq. (16) to the experimental data of Varcoe et al.\(^{13}\) in the semi-log plot of \( \eta \) vs. \( J \) gives \( \alpha_k \approx 0.79 \) and \( J^0 \approx 1.17 \text{ Am}^{-2} \).

Previous experimental studies\(^5,6\) reported that the ionic conductivity of AAEMs increases with cell temperature and water content (\( \lambda \)) and some modeling works based on the dusty fluid model (DFM)\(^3,4\) have successfully predicted the hydroxyl anion conductivity in AAEMs. Here, the ionic conductivity is calculated by the following equations based on the experimental results of Varcoe\(^5\)

\[ \sigma \times 10^{-4} \text{ S/cm} = 0.00324t^4 - 0.1516t^3 + 2.221t^2 - 2.68t \]  

(17)

Then, the ohmic loss was calculated as follows,
Finally, the cell voltage corresponding to the initially specified current density was calculated as,

$$V_{\text{cell}} = V_{\text{oC}} - \eta_{\text{ohmic}} - \eta_{\text{over}}$$

(19)

3. Results and Discussion

We performed simulations using the operating conditions listed in Table 1 to test the present model against the experimental results of Isomura et al.15 Figure 2 shows that the predicted polarization curves are in good agreement with the experimental results (denoted by symbols) for different humidified conditions. Dry gas conditions for both anode and cathode result in extremely poor performance. However, cell performance for a dry cathode with a 100% RH anode was similar to that of a 100% RH anode with a 100% RH cathode. We also tested the dry anode with the 100% RH cathode, which results in a significant decrease in the cell performance as compared to the case of 100% RH anode with a dry cathode. This numerical result implied that anode humidification was crucial to the AAEMFC performance. Figure 3 shows that the decrease in the cell performance was mainly owing to an increase in the ohmic losses of the membrane, which was closely related to the water content of the membrane, thereby suggesting that meticulous water management was indispensable for AAEMFC operations.

Figure 4 shows the net water flux from the cathode to the anode through the membrane.
However, for a dry anode with a 100% RH cathode, the net water flux was toward the anode in the AAEM. Our results suggested that the diffusion process was more dominant in the water transport through the membrane compared to electro-osmotic drag. Varcoe et al.\textsuperscript{13} have also experimentally reported that minimizing the AAEM thickness enhances the cell performance by increasing the water diffusion across the membrane and by reducing the ohmic loss. Notably, the magnitude of water flux for the dry anode condition was smaller than that of the dry cathode condition. This difference was attributed to the decrease in the gradient of water concentration across the membrane in the dry anode condition wherein water is produced at the anode catalyst layer during the operation.

Finally, the water flux through the anode and cathode GDLs under various humidified conditions are shown in Fig. 5. A positive value of the water flux represented that the water was transported toward the catalyst layer, across the GDL for each side. For both the 100% RH anode and 100% RH cathode conditions (Fig. 5a), in the cathode GDL, the net water flux was directed away from the catalyst layer for all the current densities. However, in the anode GDL, the water was transported to the catalyst layer at very low current density (<300 mA cm\textsuperscript{-2}) whereas the water flux direction was away from the catalyst layer at higher current density (>300 mA cm\textsuperscript{-2}). This direction change of water flux in the anode GDL can be attributed by the imbalance between the linear increase of water production rate at anode catalyst layer with the current density and nonlinear increase of the net water flux in the AAEM. For a 100% RH anode with a dry cathode (Fig. 5b), water was supplied to the membrane through the anode GDL as expected, which later moved toward the cathode catalyst layer in AAEM (Fig. 4) and was finally transported out toward the cathode GDL. This suggested that the water was transported in a single direction from the anode to the cathode in the AAEMFC operation under this humidified condition. For a dry anode with 100% RH cathode, the water transport in the through-plane direction was opposite, i.e., the water transported through the cathode GDL was supplied to the membrane and was partially consumed by the ORR at the cathode catalyst layer, followed by a movement toward the anode GDL.

\section*{4. Conclusions}

A simple one-dimensional isothermal model has been developed for numerical analysis of water transport in the alkaline fuel cell with an anion-exchange membrane. By testing four cases of humidified conditions (dry or fully humidified conditions for each anode and each cathode), we theoretically reconfirmed that anode humidification was essential to secure a good AAEMFC performance. The examination of water flux through the AAEMFC revealed that for both the 100% RH anode and 100% RH cathode conditions, the water was transported away from the catalyst layers in both the anode and cathode GDLs at high current density operation. Moreover, the water moved from the anode to the cathode in the membrane, consistent with the Isomura’s experimental measurements. For a 100% RH anode with a dry cathode, the water was transported in a single direction from the anode to the cathode; however, the water flux was in the opposite direction for the dry anode with a 100% RH cathode. The present modeling approach is expected to be useful for strategizing the operational control of high-performance AAEMFC systems. It should be noted that water is assumed to exist only in vapor form in the present model. However, it is expected that the cell performance could be significantly affected by flooding at the anode side under fully-humidified condition. To address the flooding effects, the distribution of liquid water saturation will be examined in the future work by performing multi-phase model simulation on AAEMFC.

\section*{References}