ANALYTICAL MODEL FOR PEM FUEL CELLS INCLUDING WATER TRANSPORT AND IMPLICATIONS FOR IMPROVING THE MEA STRUCTURE

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ABSTRACT
This paper presents a method for calculating the relative effectiveness of each mass transfer processes in the PEM fuel cell electrode. Such a method is useful for determining the feasibility of a new electrode material or design. The method was applied to MEAs fabricated in our laboratory and found ionic conductivity in the membrane and electrode dominating the transport losses in the cell. Since conductivity is a function of the water content in the electrolyte, MEA structures fabricated in our laboratory with substrate layers designed to increase the water content in the electrolyte showed significant improvement. These new MEA structures not only improved performance while operating humidified, but also while operating with a dry gas feed.

1. INTRODUCTION
Research on polymer electrolyte fuel cell electrodes is moving from the proof-of-concept stage into commercialization. Research efforts have begun to engineer and optimize the polymer electrolyte membrane (PEM) fuel cell electrode and system. This paper presents a method for calculating the relative effectiveness of each mass transfer processes in the electrode. Such a method is useful for determining the feasibility of a new material and for identifying what needs to be improving in existing designs.

The power plant for light weight transportation applications requires a low-cost, low-maintenance fuel cell system. This requires the membrane and electrode assembly (MEA) to contain only small amounts of platinum and the fuel cell to operate with a relatively simple gas humidification system. MEAs designed to meet these goals were analyzed using the relative effective current method and ionic conductivity dominated the transport
losses in the cell. The ionic conductivity can be increased by increasing the water content of the electrolyte. Previous attempts to achieve this goal include water injection techniques (1) and insertion of catalyst into the membrane (2). As a much simpler solution, MEAs with new substrate structures were designed to increase the water content in the electrolyte and they showed significant improvement while operating on humidified and dry gas at atmospheric pressure and 50°C.

2. RELATIVE EFFECTIVE CURRENT OF EACH MASS TRANSFER PROCESS

The components of the fuel cell are multiphase structures such that increasing the transport facility in one phase usually decreases the transport ability of the other phases. For maximum power, it is desirable to design an electrode such that all the transport and kinetic processes in the cell are balanced, i.e. no single process is much more rate limiting than the others. The effective resistance of each process is a non-linear function of current and potential; therefore, one must define an operating point at which the balancing will take place. In this analysis, the fraction of the intrinsic kinetic current that is limited by a mass transfer process defines the operating point used as a basis. This fraction is called the effectiveness factor, $Z$, and is defined as the true current resulting from limitations by mass transfer, $i_m$, divided by the intrinsic kinetic current, $i_k$. It is a function of the dimensionless rate modulus, $\phi$, which is defined as the intrinsic kinetic rate divided by the inherent mass transfer rate, $\alpha$. The square root of the rate modulus as defined here is commonly known as the Theile modulus in heterogeneous catalysis.

$$i_m = i_kZ(\phi)$$

where

$$\phi = \frac{i_k}{\alpha} = \frac{\text{intrinsic kinetic rate}}{\text{inherent mass transfer rate}}$$

The electrode needs to be designed such that at a desired operating current, all the mass transfer processes are contributing with equal effectiveness. Conversely, it needs to be designed such that at a tolerable effectiveness factor, each mass transfer process has about the same relative rate. The effectiveness factor used in the evaluation will depend on the loss of kinetic utilization that can be afforded as determined by the designer.

2.1 Intrinsic Kinetic Rate

The amount and activity of the catalyst determines the intrinsic kinetic current. In acid polymer electrolyte fuel cells, the cathode reaction is rate limiting and almost completely determines the kinetic rate. Therefore, the derivations shown here are for the cathode; a similar analysis can be performed on the anode. The Tafel equation with a constant transfer coefficient is sufficient to model the kinetic rate as a function of potential within the operating range of the fuel cell (0.8 to 0.5 volts). The intrinsic kinetic current flux of the electrode, $i_k$, is a function of the potential, $V$, the oxygen partial pressure, $x_{O_2}P$, the activity of the catalyst surface, $k$, the active platinum surface area per unit volume, $\alpha_r$, and the depth of the active region, $L$. 
2.2 Effectiveness Factors for the Mass Transfer Processes

The effectiveness factor of a mass transport process comes from the analytical solution of the volume averaged material balance which considers only kinetics and that mass transport process. The effectiveness factor functions for each mass transfer process have been derived and are summarized in Table I and plotted in Figure 1.

Table I. Summary of effectiveness factors for transport processes

| Transport mechanism | Mass transport inherent rate | Effectiveness factor, Z |
|---------------------|-----------------------------|-------------------------|
| 1) gas diffusion in active region (gas diffusion in agglomerates) | $\alpha_{\text{o}_2,\text{act}} = \frac{4FCD_{\text{o}_2}}{L}$ | $Z_{\text{o}_2,\text{act}} = \frac{\tanh\sqrt{\phi}}{\sqrt{\phi}}$ |
| 2) proton (electron) migration in active region | $\alpha_{\text{H}^+,\text{act}} = \frac{L}{\kappa_{\text{H}^+}^{\text{act}}}h$ | $Z_{\text{H}^+,\text{act}} = \frac{\sin[\sigma]}{\sqrt{\phi/2}}, \sigma = \frac{\phi}{2} \cos[\phi]$ |
| 3) gas diffusion through substrate | $\alpha_{\text{o}_2,\text{sub}} = \frac{4FCD_{\text{o}_2}}{L}$ | $Z_{\text{o}_2,\text{sub}} = \frac{1}{1 + \phi}$ |
| 4) proton migration in membrane (electron in current collector) | $\alpha_{\text{H}^+,\text{mem}} = \frac{R_{\text{mem}}}{b}$ | $Z_{\text{H}^+,\text{mem}} = \exp[-Z_{\text{H}^+,\phi}]$ |
| 5) gas convection in the flow field | $\alpha_{\text{o}_2,\text{flow}} = \frac{x_q 4FQ}{A}$ | $Z_{\text{chan}} = \frac{1 - \exp(-\phi)}{\phi}$ |

The rate modulus, $\phi$, will have a certain value at a chosen mass transport effectiveness, $Z_r$. Since $\phi = i_r/\alpha$, the relative effective current, $i_r$, can be defined in terms of the transport parameter, $\alpha$, and the chosen mass transport effectiveness $Z_r$.

$$i_r = \frac{\phi (Z_r)}{Z_r}$$  [3]

For example, the relative effective currents at $Z_r = \frac{1}{2}$, called here the half-effective currents, are shown in Table II.
2.3 Analysis of MEA Design

The mass transport rates in a typical PEM fuel cell electrode were compared using the relative effective current analysis. Table II also displays estimated values of the half effective currents in a typical PEM fuel cell MEA with low-cost components including a total platinum loading of 0.25 mg/cm² and Nafion 112 membrane and operating with air at atmospheric pressure and 50°C. Values for the parameters were estimated from experimental data collected in our laboratory and a number of parameter estimation techniques available in the literature (3-5).

Table II. Half effective currents for mass transfer processes

| Transport mechanism                        | Half effective current | Approximation of \( i_{1/2} \) for PEMFCs with low catalyst cathodes |
|--------------------------------------------|------------------------|---------------------------------------------------------------------|
| reactant gas in active region              | \( i_{1/2} = 1.84 \frac{x4FcD_{O^2}}{L} \) | \( 1.2 \frac{A}{cm^2} \)                                           |
| reactant gas in agglomerates               | \( i_{1/2} = 1.84a_o \frac{4Fc_{O^2}D_{O^2}}{\delta} \) | \( 14.4 \frac{A}{cm^2} \)                                          |
| reactant gas through substrate             | \( i_{1/2} = 0.5 \frac{x4FcD}{L} \) | \( 1.9 \frac{A}{cm^2} \)                                           |
| proton in active region                    | \( i_{1/2} = 2.5 \frac{b\kappa_{\text{eff}}}{L} \) | \( 0.84 \frac{A}{cm^2} \)                                          |
| proton in membrane                         | \( i_{1/2} = 0.693 \frac{b\kappa}{L} = 0.693 \frac{b}{R} \) | \( 0.28 \frac{A}{cm^2} \)                                          |

According to this study, proton transport in the membrane and proton transport in the active region had lower half-effective currents than the other processes. Therefore, the MEA performance could be improved by increasing the proton conductivity even at the expense of electron conductivity or some oxygen diffusion in the substrate. The effective proton current could be increased in the membrane by reducing the membrane thickness, in the active region by increasing the polymer volume fraction, or in both layers by increasing the water content in the polymer electrolyte. Reducing the membrane thickness is limited by mechanical stability and gas crossover. An increase of the polymer volume fraction in the active layer will significantly decrease the oxygen diffusivity. Thus, our efforts focused on increasing the water content in the electrolyte by changing the substrate design. The polymer will contain a certain number of water molecules per sulfonic group when equilibrated with fully humidified gas (about 14 in Nafion® membranes with equivalent weight of 1100) (6). The water content almost doubles when equilibrated with liquid water which results in twice the conductivity.
3. WATER TRANSPORT IN THE CELL

The PEM fuel cell requires a careful balance of water content. High ionic conductivity demands the presence of liquid water on the interface of the polymer electrolyte. However, excess water in the porous electrode will block the gas pores and lower the oxygen diffusion from the gas flow fields to the electrode catalyst layer. The ideal electrode will be designed to maintain a high concentration of water in the electrolyte while keeping the gas diffusion layer clear of water.

Traditionally, a hydrophobic agent, Teflon®, has been impregnated into the substrate layer to keep liquid water out. However, the water transport mechanism is not understood and remains one of the challenges to reliable fuel cell stack systems. PEM conductivity is kept high in laboratory evaluations by super-saturating the reactant gas. The parasitic energy required to super-saturate the gas is undesirable and super-saturation creates a problem with two-phase flow in the gas distributors of larger electrode areas and stacks. The efficiency of the fuel cell system can be improved if the reactant gas does not need to be super-saturated. By understanding the water transport mechanisms through the substrate, one should be able to improve the substrate structure so that oxygen diffusion and electrolyte hydration can be balanced at a maximum.

Water flux occurs in the vapor, polymer, and liquid phases. A concentration gradient and interaction with the reactant gas flux drives water transport in the gas phase. A concentration gradient and a drag exerted by the moving protons drives water transport in the polymer phase. Water in the liquid phase may be driven out of the cell by capillary pressure or by a dynamic process of evaporation and condensation that occurs while the interface is at equilibrium, or by a convective turbulence that reaches into the depths of the layer from the gas stream in the channels. From experiment, it has been determined that water is primarily transported in the vapor phase. The effective water vapor diffusivity of the substrate layer most likely includes thermal and capillary pressure effects, because it was found to be higher than an expected gas phase diffusivity estimated from the bulk phase water diffusivity multiplied by the porosity and divided by the tortuosity.

A qualitative model for water transport can be put together based on volume averaged material balances and empiricism. Figure 2 shows a physical picture of the water transport model. The most simplistic method to describe the water concentration in the multiphase porous media uses a single, dimensionless, volume averaged variable called the relative saturation, $S$. At $S = 0$, the cell is completely dry. At $S = 1$, the pores are flooded which means there is enough water present to block the major gas pathways. In the membrane, the relative water saturation is a function of the water content and relative liquid pressure. In the membrane, the relative saturation is not restricted to a maximum of unity because a liquid pressure gradient across the membrane can increase its value.

For each layer except the cathode, the transport equation for water is:
\[ N_w = -D_w \nabla S + \xi i/2F \]  \hspace{1cm} [4]

and at each boundary between layers "a" and "b", \( S_a = S_b \). \( D_w \) is the effective water diffusivity and \( \xi \) is the interaction drag between water and a moving species in the layer. Since water is produced in the cathode, the material balance for this layer will include the divergence term:

\[ D_w \nabla^2 S + \frac{j}{2F} = 0 \]  \hspace{1cm} [5]

where \( j \) is the local reaction current per volume. The drag term is neglected in the active layer for simplicity and because oxygen drags water toward the membrane in the gas phase and protons drag water away from the membrane in the electrolyte phase; any discrepancy will most likely be internally balanced by inter-phase transport. The overall water balance in the cell from anode to cathode is:

\[ N_{\text{cathode}} - N_{\text{anode}} = i/2F. \]  \hspace{1cm} [6]

In this study, the model was used to determine how changes in the diffusivity of water in the substrate would affect the water content in the membrane and electrode. As discussed earlier in the paper, the relative limiting current analysis determined that the cell performance could be improved by increasing the water content in the membrane and electrode. Once the desired diffusivity change was identified, mechanistic models of the water transport helped identify new substrate designs that might accomplish the goal. The results of one of these new substrate designs is presented in the following section.

4. MEAS WITH IMPROVED WATER SATURATION IN THE ELECTROLYTE

The substrate layer was altered to increase the liquid hold up in the electrode and membrane. The MEAs were fabricated as presented previously in the literature (7,8) with Nafion® 112 membranes and a total platinum loading of 0.25 mg/cm² for the low platinum content MEAs and 1.30 mg/cm² for the high platinum content MEAs. The old type of substrate consisted of a 15 wt% Teflon and Shawnagan Black mixture painted onto a carbon cloth. The new type of substrate used a composite of different polymer/carbon mixtures painted onto a carbon cloth.

The performance of cells with the new substrate design were compared with the standard MEA design at a cell temperature of 50°C, under atmospheric pressure, and using a humidified gas feed. The decrease in the slope of the linear region of the oxygen curve shows that the ionic resistance decreased in the cells with the new substrate in 5 cm² tests as seen in Figure 3. The air curve indicates a slight decrease in the oxygen diffusivity, but overall performance is still improved with the new substrate layer. A
second test with 50 cm² electrodes operating at an oxygen stoichiometry of 2.5 reconfirmed these results as shown in Figure 4.

Performance of MEAs with high platinum loading (1.25 mg/cm²) did not improve in the 5 cm² tests as shown in Figure 5, but did show significant improvement in the 50 cm² tests as shown in Figure 6. Both 5 cm² and 50 cm² tests with high platinum content MEAs show a slight increase in the kinetic rate from the cells with the new substrate layer. This may reflect an increase in the ionic conductivity in the substrate side of the active region which increases the utilization of the catalyst. This effect was predicted by the water transport model. The 5cm² test with air does show the onset of oxygen diffusion limitations due to the new substrate layer.

MEAs with thin active layers are more susceptible to the lower water saturation level in the electrolyte because the narrow transition between the “dry” (water vapor) gas diffusion layer and the “wet” (liquid water) electrolyte layer provides a steep water concentration gradient for a fast water flux. As a result, MEAs with thin active layers (low platinum loading) typically exhibit a higher ionic resistance than MEAs with thick active layers. The thicker active region will have a smaller water concentration gradient between the electrolyte membrane and the substrate for slower mass transfer which means a larger build up of the water concentration in the electrolyte. MEAs with thicker active layers can even operate reasonably well when fed dry gas (8).

A 50 cm² MEA with the redesigned substrate layer was tested while fed completely dry gas at 50°C and atmospheric pressure. Typical MEA’s fabricated in our laboratory show significant performance loss while operating on dry air. There is almost no performance difference when the low loaded and high loaded MEAs with the new substrate layer were operated with dry air as shown in Figure 7 and Figure 8.

5. CONCLUSIONS

A relative effective current analysis can indicate how to better balance the transport losses in the PEM fuel cell for better overall performance. Such an analysis would be useful for optimizing any multiphase electrochemical system. The analysis presented here showed that ionic conductivity in the membrane and active layer were the most rate limited processes in the current MEA design.

PEM cells are very sensitive to water content and understanding the water flux and saturation properties is essential to designing better MEAs and operating procedures. The substrate is a key part to balancing the water content in the MEA. The experiments presented here show that a new substrate layer which increases the water holdup in the electrode and membrane can increase cell performance while operating with humidified air and operate with almost no loss of performance when fed dry air.
NOTATION

\[ a \] area of catalyst per volume of reaction region (cm\(^2\)/cm\(^3\))
\[ N \] molar flux (mol/cm\(^2\)-s)
\[ P \] pressure (atm)
\[ A \] electrode area (cm\(^2\))
\[ Q \] molar gas flow (mol/s)
\[ b \] effective Tafel slope (mV)
\[ R \] resistance (\(\Omega\cdot\text{cm}^2\))
\[ c \] molar concentration (mol/cm\(^3\))
\[ S \] water saturation
\[ D \] effective diffusivity (cm\(^2\)/s) or for water model (mol/cm\(^2\)-s)
\[ V \] electric potential (V)
\[ Z \] effectiveness factor
\[ F \] Faraday’s constant (C/equiv)
\[ \alpha \] mass transfer intrinsic rate (A/cm\(^2\))
\[ i \] electrode current flux or current density (A/cm\(^2\))
\[ \delta \] agglomerate effective thickness (cm)
\[ j \] current flux produced in a volume of the reaction region (A/cm\(^3\))
\[ \phi \] rate modulus
\[ k \] electrokinetic rate constant (A/cm\(^2\)-s-atm)
\[ \kappa \] effective conductivity (S/cm)
\[ L \] depth of a layer (cm)
\[ \xi \] interaction drag coefficient

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Figure 1. Effectiveness factors as a function of the rate modulus for transport processes in the MEA. Solid line - proton transport in active region; Short dash - oxygen transport in active region; Medium dash - proton transport in membrane; Long dash - oxygen transport in substrate.

Figure 2. Physical Picture of the water transport model. Layers are not scaled to thickness.
Figure 3. 5 cm$^2$ tests of low platinum content MEAs comparing the new substrate layer with the existing substrate layer. Gas flow was humidified and high stoichiometry.

Figure 4. 50 cm$^2$ tests of low platinum content MEAs comparing the new substrate layer with the existing substrate layer. Gas flow was humidified and $1.1\text{H}_2/2.5\text{O}_2$ stoichiometry.
Figure 5. 5 cm² tests of high platinum content MEAs comparing the new substrate layer with the existing substrate layer. Gas flow was humidified and high stoichiometry.

Figure 6. 50 cm² tests of high platinum content MEAs comparing the new substrate layer with the existing substrate layer. Gas flow was humidified and 1.1H₂/2.5O₂ stoichiometry.
Figure 7. 50 cm² tests with low loaded electrodes showing air curves for old substrate and new substrate operating on dry gas compared to new substrate operating on humidified gas. Gas flow stoichiometry was $1.1H_2/2.5O_2$.

Figure 8. 50 cm² tests with high loaded electrodes showing air curves for old substrate and new substrate operating on dry gas compared to new substrate operating on humidified gas. Gas flow stoichiometry was $1.1H_2/2.5O_2$. 