INVESTIGATING THE INFLUENCE OF CATALYST LAYER MORPHOLOGY ON FUEL CELL PERFORMANCE BY NUMERICAL SIMULATION

Uwe Beuscher
Gore Fuel Cell Technologies, W. L. Gore & Associates, Inc.
201 Airport Road, Elkton, MD 21921, USA

ABSTRACT

A one-dimensional model of all five domains of a Proton Exchange Membrane Fuel Cell has been developed to study the structure of the catalyst layer. The model is validated against experimental data of electrodes with different structural properties. The validated model provides insight into the processes inside the fuel cell and helps to assess the influence of material and structural properties on the overall performance of the fuel cell. A sensitivity analysis of critical catalyst layer morphology parameters was performed, which led to the suggestion of a design for an optimized electrode structure.

INTRODUCTION

The performance of a Proton Exchange Membrane (PEM) fuel cell is limited by electrochemical kinetics, proton conductance through the ionomeric material, and mass transport limitations. The electrochemical reaction itself takes place within the porous catalyst layer at the three-phase boundary on the surface of a platinum catalyst. A detailed one-dimensional model was developed to study the material and structural properties of the membrane, Catalyst Layer (CL), and Gas Diffusion Layer (GDL) of Gore™ PRIMEA® Membrane Electrode Assemblies (MEAs). The focus of this paper is the application of the model to study the catalyst layer of a PEM fuel cell.

The catalyst layer is a structure of three interpenetrating and continuous networks: a carbon phase for electron transport (which also provides the support for the platinum catalyst), an ionomer phase for proton transport, and porosity for gas and water transport. The design of this complex structure has to consider a balance between electron, proton, and gas transport. To reduce the cost of the PEM fuel cell system, it is desirable to minimize the amount of platinum in the catalyst layer. At the same time, it is important to maximize the utilization of the available platinum in the cell to optimize the fuel cell performance. Therefore, it is necessary to understand the influence of the morphological structure of the catalyst layer and how it influences the transport processes and electrochemical reaction.

Since it is challenging to experimentally measure concentrations and transport processes inside a running fuel cell, numerical modeling was chosen to provide a detailed
insight into the fuel cell. Numerical modeling of the PEM fuel cell including the transport phenomena in the catalyst layers is gaining more interest, e.g. refs. (1-6). The Gore Electrode Model (GEM) describes the transport and reaction phenomena in the catalyst layer in detail and also includes the other MEA components of the PEM fuel cell to explore the influence of their morphological structure on the overall cell performance. The model was validated against a set of experimental data of catalyst layers with varying structural properties. The model calculations represent the experimental data very well. The numerical results can be used to analyze potential and concentration profiles as well as the distribution of the fluxes and reaction rates throughout the MEA.

MODEL DESCRIPTION

The GEM model is a one-dimensional description of all five components of the MEA. All transport fluxes through anode GDL, anode CL, membrane, cathode CL, and cathode GDL are considered as outlined in Fig. 1. Hydrogen diffuses through the open space of anode GDL and CL, while oxygen diffuses through the cathode GDL and CL. No crossover through the membrane is currently considered. Electrons are generated in the anode CL from the hydrogen oxidation reaction and are conducted through the carbon phase of anode CL and GDL, through the external circuit, and finally through the cathode GDL and CL. Protons are generated inside the anode CL and are conducted through the ionomer phase of anode CL, membrane, and cathode CL, where they combine with the electrons and oxygen in the oxygen reduction reaction. Water is generated in the cathode CL and diffuses through all five domains. However, the direction of the flux is determined by the current density and the humidification of the reactant gases in the flow channels.

The model is isothermal and single phase, thus, no heat fluxes or condensation of water vapor is considered. Gas phase transport is described using Fick’s Law by

\[ N_j = -D_j \nabla C_j , \]  

where \( N_j \) is the molar flux, \( D_j \) the diffusion coefficient, and \( C_j \) the molar concentration of component j. Water transport inside the membrane is estimated by diffusion and electro-osmotic drag by

\[ N_w = -D_w \nabla C_w + n_d \frac{i}{F} , \]  

where \( N_w \) is the water flux, \( D_w \) the water diffusivity, and \( C_w \) the water concentration in the membrane, \( n_d \) the electro-osmotic drag coefficient, \( i \) the current density, and \( F \) the Faraday constant. Proton transport in the membrane and the ionomeric phase of the CL is calculated by

\[ i_{\text{H}_i} = -\sigma_i \nabla E_i , \]  

where \( i_{\text{H}_i} \) is the proton flux, \( \sigma_i \) is the ionic conductivity, and \( E_i \) is the ionic potential. Electrons are transported by conduction given by
\[ i_e = -\sigma_e \nabla E_e , \]  \hspace{1cm} [4]

where \( i_e \) is the electronic current density, \( \sigma_e \) the electronic conductivity, and \( E_e \) the electronic potential of the carbon phase. All transport parameters in the porous regions of the GDL and CL are corrected for volume fraction and tortuosity by

\[ k_{\text{eff}} = k_{\text{bulk}} \frac{\varepsilon}{\tau}, \]  \hspace{1cm} [5]

where \( k_{\text{eff}} \) is the effective parameter in the porous structure, \( k_{\text{bulk}} \) the respective bulk parameter, \( \varepsilon \) the volume fraction of the respective phase, and \( \tau \) the tortuosity parameter for the phase. All gas diffusivities and ionic and electronic conductivities were adjusted by Eq. [5]. The electrochemical reactions inside the CLs where modeled as pseudo-homogenous. The surface reaction term of the platinum site is multiplied by the volumetric surface area of the platinum in the CL structure by

\[ i_{v} = i_a a_v , \]  \hspace{1cm} [6]

where \( i_v \) is the volumetric reaction rate or current density, \( i_a \) the intrinsic current density per surface area of platinum, and \( a_v \) the surface area of platinum per volume of CL. The electrochemical surface reaction is described by the Butler - Volmer equation according to

\[ i_a = i_0 \frac{C_j}{C_{j,\text{ref}}} \left[ \exp \left( \frac{\alpha F}{RT} (E_i - E_e) \right) - \exp \left( -\frac{(1-\alpha) F}{RT} (E_i - E_e) \right) \right] , \]  \hspace{1cm} [7]

where \( i_0 \) is the intrinsic exchange current density, \( C_j \) the concentration of reactant \( j \), \( C_{j,\text{ref}} \) the reference concentration of the reactant \( j \), \( \alpha \) the transfer coefficient, \( R \) the gas constant, and \( T \) the cell temperature. The concentration of oxygen and hydrogen inside the CLs influence the reaction through Eq. [7] as well as the equilibrium potential, \( E^* \), through the Nernst equation,

\[ E^* = E_o + \frac{RT}{nF} \ln \left( \frac{C_{O_2}}{C_{H_2}} \right) , \]  \hspace{1cm} [8]

where \( E_o \) is the reference potential. An additional mass transport resistance inside the CL had to be introduced to fit the experimental data. The film model (7) was used to estimate the local mass transport resistance at the platinum site. A thin ionomer (or water) layer covers the platinum site as illustrated in Fig. 2. The oxygen and hydrogen molecules have to diffuse through this layer before the reaction takes place. The linearized flux through this layer may be described by

\[ N_j = \frac{D_j S_j}{L} \Delta C_j , \]  \hspace{1cm} [9]
where $D_j$ is the diffusivity, $S_j$ the solubility, and $L$ the thickness of the film. The unknown parameters can be combined to a surface resistance by

$$R_s = - \frac{L}{D_j S_j}$$

where $R_s$ represents a mass transport resistance with units of time per length.

**MODEL VALIDATION**

Since it is very difficult to measure local fluxes within the MEA structure, it is necessary to validate the model calculations to an appropriate set of experimental data. Since the GEM model focuses on the description of the CL morphology, a set of electrodes with different structural properties was chosen. This set consists of Gore™ PRIMEA® Series 5510 electrodes with loadings of 0.05, 0.1, 0.2, 0.3, and 0.4 mg Pt/cm².

Since the GEM model is a one-dimensional description, it is important to also approximate one-dimensional experimental fuel cell data. Thus, experiments were performed with hydrogen and oxygen as the reactant gases, 100% relative humidity on both anode and cathode side, and under high stoichiometry to eliminate concentration gradients in the flow channels between inlet and outlet of the cell.

The input parameters for the model calculations were the GDL and CL structural parameters as well as the membrane conductivity and water transport properties, which were either determined ex-situ or taken from the literature. The experimentally determined open circuit potential was used in the calculations since it is influenced by phenomena like gas crossover, electrical shorting, and platinum oxide formation, which are not considered in this model.

The model contains three adjustable parameters: the oxygen reduction reaction transfer coefficient, $\alpha$; the exchange current density, $i_0$, in Eq. [7]; and the film resistance, $R_s$, in Eq. [10]. The hydrogen oxidation kinetic parameters were defined by comparison to the oxygen reduction parameters. The three adjustable parameters were simultaneously fit to the entire set of five polarization curves. The results are shown in Fig. 3. The model calculations show an excellent fit to the experimental data over a wide range of current densities and electrode morphologies. It was concluded that the GEM model provides a good approximation of the transport phenomena inside the MEA.

**GEM CAPABILITIES**

Since the model describes all five domains of the MEA, the change of various variables throughout the MEA can easily be investigated. For example, the current distribution is illustrated in Fig. 4. The current is carried by electrons in the GDLs and by protons in the membrane. The transfer between the electronic and ionic currents is illustrated inside the CLs and may be used to explore its effectiveness. Similarly, the electronic and ionic potential distribution can be studied throughout the MEA. The profiles of gas and water vapor concentration may be explored to assess the open edges of the membrane.
structure of the GDL and CL morphology, which influence the distribution of the water content of the ionomer phase in the CLs and membrane shown in Fig. 5. This information may be used to investigate the local hydration state and conductivity of the ionomer in the MEA.

**SENSITIVITY ANALYSIS**

To illustrate the usefulness of the GEM model, a sensitivity analysis of the cathode CL properties was performed. The operating conditions for the calculations were 70°C cell temperature, 100% relative humidity on both anode and cathode side, and 0 psig back pressure. The reactant gases were hydrogen and air. Three parameters were varied: the ionic conductivity, which determines the rate of proton transport in the CL, the catalytic activity, which controls the reaction rate, and the film resistance, which dominates the oxygen transport in the catalyst layer. Each variable was varied independently to one half and twice its standard value. Finally, calculations were performed for an optimized CL with reduced catalytic activity.

Fig. 6 shows calculated polarization curves for varying ionic conductivity, $\sigma_i$. The base case refers to calculations performed with the parameters determined during the model validation. The two other curves represent the results for calculations with twice and half the base value for the ionic conductivity, respectively. The performance for all three cases is very similar up to a current density of about 0.5 A/cm$^2$. The difference between the polarization curves increases with current density and the effect of ionic conductivity becomes very significant above 1.5 A/cm$^2$.

The comparison of fuel cell performance for varying catalyst activity is illustrated in Fig. 7. Catalyst activity is represented by the product of intrinsic exchange current density and volumetric surface area of the platinum sites ($\nu_i$). A change in this parameter may be achieved by a change in intrinsic catalytic activity, a change in platinum dispersion, or a change in mass loading on the carbon. Fig. 7 shows that a change in ($\nu_i$) results in a constant offset of about 20 mV for the entire current density range. This is consistent with an estimate using Tafel kinetics for a change in exchange current density by a factor of 2. Thus, the influence of ($\nu_i$) has a larger relative effect at smaller current densities.

The influence of the film resistance, $R_s$, is illustrated in Fig. 8. Calculations with twice and half the base value show very little effect up to about 1 A/cm$^2$. At higher current densities, however, the effect becomes very significant and the performance with twice the base value reaches a low limiting current at a potential just below 0.5 V.

Finally, Fig. 9 shows a calculation for an optimized cathode catalyst layer structure with lower catalyst activity. These calculations were performed with half the catalyst activity ($\nu_i$), half the film resistance ($R_s$), and twice the ionic conductivity ($\sigma_i$) compared to the base case. The simulations show that the performance of the optimized structure with half the catalyst activity is very similar to the base case up to 1 A/cm$^2$. The optimized structure even outperforms the base case at higher current densities. These results show that the catalyst layer morphology has a significant impact on performance and may be optimized for better fuel cell performance. The fabrication of an actual
catalyst layer with lower catalyst activity, higher ionic conductivity, and lower film resistance, however, is a challenging task and remains the focus of ongoing work.

SUMMARY

The Gore Electrode Model (GEM), which describes all five domains of the MEA in great detail, is a powerful tool for continued product improvement. The calculations provide insight into the processes inside the fuel cell. Performance and conditions can be evaluated locally throughout the MEA and the effect of material properties of the various components of the MEA can be assessed. The limiting parameters for the fuel cell performance can be identified and optimized. Finally, these calculations can provide guidance for the design of prototypes with improved performance or reduced cost.

ACKNOWLEDGMENTS

The author would like to acknowledge the assistance and support of the Gore Fuel Cell Technologies technical team throughout this work.

REFERENCES

1. L. Pisani, M. Valentini, and G. Murgia, J. Electrochem. Soc., 150, A1558 (2003)
2. T.-C. Jen, T. Yan, and S.-H. Chan, Int. J. Heat Mass Transfer, 46, 4157 (2003)
3. H.-K. Hsuen, J. Power Sources, 123, 26 (2003)
4. Q. Wang, M. Eikerling, D. Song, Z. Liu, T. Navessin, Z. Xie, and S. Holdcroft, J. Electrochem. Soc., 151, A950 (2004)
5. B. Hum and X. Li, J. Appl. Electrochem., 34, 205 (2004)
6. K.T. Jeng, C.P. Kuo, and S.F. Lee, J. Power Sources, 128, 145 (2004)
7. Y. Bultel, P. Ozil, and R. Durand, Journal of Applied Electrochemistry, 29, 1025 (1999)

PRIMEA, GORE and designs are trademarks of W. L. Gore & Associates, Inc.
Figure 1. Transport processes considered by the GEM model.

Figure 2. Film model on the active surface of the catalyst.
Figure 3. Comparison of experimental data with different platinum electrode loadings (symbols) and model calculations (lines) in linear (a) and logarithmic coordinates (b) at 70°C, 100%RH, H₂/O₂, 0 psig.
Figure 4. Current distribution inside the MEA.

Figure 5. Water content of the ionomer phase throughout the MEA.
Figure 6. Calculated polarization curves for different values of the ionic conductivity, $\sigma_i$.

Figure 7. Calculated polarization curves for different values of the catalyst activity, $i_0^*a_v$. 
Figure 8. Calculated polarization curves for different values of the film resistance, $R_s$.

Figure 9. Calculated Polarization curves for an optimized morphology with lower catalyst activity compared to the base case.