DESIGN CONSIDERATIONS FOR MEASURING THE KINETIC PARAMETERS OF ELECTROCATALYSTS IN AN OPERATING FUEL CELL

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ABSTRACT

Measurement of the electrocatalytic activity of an electrocatalyst in an operating polymer-electrolyte-membrane (PEM) fuel cell is complicated by the possibility of ohmic and mass-transfer losses in the porous structure of a PEM fuel-cell electrode and by uncompensated $iR$-drop in the bulk electrolyte. We review simple models that can provide guidance to selecting fuel-cell geometries and operating conditions under which a porous fuel-cell electrode is kinetically limited and accurate measurement of electrocatalytic activity is possible.

1. INTRODUCTION

When measuring the electrocatalytic activity of a new electrocatalyst, it is desirable to conduct the measurement with the high-surface-area form of the electrocatalyst and in the environment (e.g., temperature, pressure, electrolyte, reactant concentrations) in which the electrocatalyst is designed to be used. In the case of electrocatalysts that are designed for use in polymer-electrolyte-membrane (PEM) fuel cells, the most practical experimental setup to measure the electrocatalytic activity of the electrocatalyst is an operating fuel cell.

The operation of a fuel cell, particularly a PEM fuel cell, is nontrivial. This is due to the interaction of mass-transfer, ohmic, and kinetic effects during the operation of the cell. Some of the issues that arise from the interplay of these effects in an operating a fuel cell include the performance of the porous electrodes (both anode and cathode) and the potential distribution in the electrolyte as it applies to the potential drop between a working electrode and a reference electrode.

This paper reviews modeling efforts that should be undertaken to understand the interplay of these effects. Such an understanding is necessary to optimize the design of membrane and electrode assemblies (MEAs) in order to obtain accurate measurements of the kinetic parameters of electrocatalysts. The three types of studies that are reviewed here are:
• Porous electrodes as equipotential surfaces – this type of study determines under what conditions the porous electrode behaves as an equipotential surface operating under kinetic limitations.

• Water management and cathode flooding – this type of study determines the conditions under which cathode flooding would occur so as to avoid this situation in fuel cell operation and to ensure that the anode was the electrode limiting the performance of the test cell.

• MEA potential distribution – this type of study determines optimal electrode placement in a MEA to ensure reliable measurement and control of the working electrode potential relative to a reference electrode.

Before describing the models, it is instructive to describe the geometry of the fuel cell as it will be utilized in experimental studies. The fuel cell consists of a membrane and electrode assembly (MEA) which is comprised of an anode, cathode, and reference electrode hot-pressed onto a Nafion 117 membrane. The three electrodes are thin (1 to 10 μm thick) porous electrodes. The reference electrode is a reversible hydrogen electrode constructed from carbon-supported platinum and has a hydrogen stream routed over the back. The MEA is mounted in a test stand that provides electrical contact and reactant flow to the electrodes. The reactant flow is routed through a serpentine gas channel machined into a resin-impregnated graphite block that also provides the electrical contact to the electrodes. A diagram of these components is presented in Figure 1.

Figure 1. Schematic of MEA and fuel cell test stand.

2. POROUS ELECTRODES AS EQUIPOTENTIAL SURFACES

In order to quantify the effects of electrode potential on the reactions studied, the anode needs to behave as a planar electrode with a large surface area, and the reaction needs to be kinetically limited. However, the distributed nature of the porous electrode

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may result in the porous electrode behaving as a network of electrodes not necessarily at
the same potential or under the same controlling mechanism (e.g., kinetic control vs.
mass-transfer control, etc.).

2.1. Approach

The approach presented here follows that presented by Newman, Newman and
Tobias, and Newman and Tiedemann (1-3). The first step was first to derive
dimensionless groups that compare the relative importance of the different processes in a
porous electrode. These dimensionless groups were then used to determine what
conditions lead to a situation where the electrode is solely kinetically limited over the
entire expected range of operation.

2.2. Assumptions.

In developing the model, the following assumptions are made:
• The electrode consists of two phases, one ionically conducting and one
electronically conducting with no bulk gas phase present.
• The electrode can be treated as a superposition of the two phases and each phase
can be treated in a continuum approximation.
• Dilute-solution transport theory is a good approximation of the transport
processes in the electrode structure.
• Only one electrochemical reaction takes place in the electrode.

The electrode is modeled as a porous medium with porosity \( \varepsilon \) and specific surface
area \( a \) with the coordinate system illustrated below.

![Diagram of porous-electrode model with coordinate system and dimensions labeled.]

Figure 2. Geometry for porous-electrode model.

2.3. Governing Equations

2.3.1. Kinetic vs. Mass-Transport Control. As can be seen in Figure 2, the electrode
extends from \( x = 0 \) to \( x = L \) with a current collector at \( x = 0 \) and the polymer electrolyte
membrane at \( x = L \).
To describe the transport processes in the porous electrode, we begin with the equation of change in porous media:

$$\frac{\partial (\rho \sigma_i)}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i.$$  \[1\]

The flux of species $i$ is a combination of a diffusion flux, a migration flux, and a convective flux:

$$\mathbf{N}_i = -\varepsilon D_i \nabla c_i - z_i F \alpha_i \varepsilon \nabla \Phi + \alpha_i \mathbf{v}$$  \[2\]

where $u_i$ is the mobility of species $i$ and $\Phi$ is the electrostatic potential. A reaction involving species $i$ can be written in the form:

$$\sum_i s_i M_i = ne^-$$  \[3\]

where $s_i$ is the stoichiometric coefficient for species $i$, denoted as $M_i$. The accumulation of species $i$ per unit volume due to a given electrochemical reaction [3] is given by:

$$R_i = \frac{-s_i a_i}{nF}$$  \[4\]

where $a$ is the specific surface area of the electrode and $i$ is the current density normalized to the true surface area of the electrode using the convention that anodic current densities are positive.

Combining [1] through [4], and assuming steady-state operation, constant diffusion coefficients, constant mobilities, and no convective flow in the electrode gives the following result for neutral species such as fuels and oxidants (assuming one-dimensional concentration gradients and current densities):

$$i^* = \frac{nF \varepsilon D_i c_i^0}{s_i \alpha(i) L^2} \frac{d^2 c_i^*}{dz^2}.$$  \[5\]

[5] has been cast in non-dimensional form using the following dimensionless variables:
where \( \langle i \rangle = \frac{I}{aL} \) is the average current density for the superficial current density \( I \), \( c_i^0 \) is the concentration of species \( i \) at \( x = 0 \), and \( L \) is the thickness of the porous electrode layer.

If we define:

\[
\alpha_i = \frac{nF\varepsilon D_i c_i^0}{s_j a(i)L^2},
\]

then \( \alpha_i \) represents the dimensionless ratio of the diffusive flux of species \( i \) to the flux needed to sustain current density \( i_m \). If \( \alpha_i >> 1 \), the diffusion of species \( i \) is able to sustain current density \( i_m \). If there is negligible potential drop across the electrode due to ohmic limitations in either the ionically conductive phase or the electronically conductive phase, then the entire electrode will be operating under kinetic control.

It is useful to note that Newman quotes a dimensionless group without explicit derivation, \( \chi \), which is essentially \( \alpha_i^{-1} \) (4):

\[
\gamma = \frac{s_j IL}{nF\varepsilon D_i c_i^0}.
\]

2.3.2. Kinetic vs. Ohmic Control. If charged species are considered in the derivation of [5], a second term appears on the right side of [5] which can be used to estimate the relative importance of ohmic losses in the electrolyte phase. However, this procedure does not provide any information about the electronically conducting phase. In order to treat the ohmic losses in the porous electrode structure more accurately, a flooded-pore model is used to describe the electronic and ionic conduction in the electrode structure.

Using the same geometry as in Figure 2, we begin with conservation of charge in the region \( 0 \leq x \leq L \):

\[
\nabla \cdot \mathbf{i} = 0.
\]

We now treat the porous electrode as a superposition of two phases, an electronically conductive phase (phase 1) and an ionically conductive phase (phase 2):
\[ i = i_1 + i_2. \] \[ \text{[10]} \]

Since the change in current density in the electronically conductive phase is due to Faradaic reactions at the interface between the two phases. If it assumed that there is only a single reaction taking place, then the change in current density in the electronically conductive phase is given by:

\[ \nabla \cdot i = -\frac{s_i a_i n}{n} \] \[ \text{[11]} \]

where \( s_i \) is the stoichiometric coefficient of the charge carrying ion, \( i_n \) is the current density normal to the interface between the two phases with positive current densities taken as anodic current densities, and \( a \) is the specific surface area.

By assuming that \( i_n \) is given by a Butler-Volmer current-potential relationship, that the electronic and ionic conductivities are uniform, and noting that \( \phi_1 - \phi_2 = \eta \), in the limit of low overpotential the following result is obtained for current densities in one-dimension:

\[ \frac{d^2 \psi}{dz^2} = \frac{L^2 s_i a_i n F}{nRT} \left( \alpha_a + \alpha_\epsilon \right) \left( \frac{1}{\sigma} + \frac{1}{\kappa} \right) \psi; \psi = (\phi_1 - \phi_2) \left( \frac{a F}{RT} \right). \] \[ \text{[12]} \]

If we define:

\[ \beta_i = \frac{L^2 s_i a_i n F}{nRT} \left( \alpha_a + \alpha_\epsilon \right) \left( \frac{1}{\sigma} + \frac{1}{\kappa} \right), \] \[ \text{[13]} \]

then \( \beta_i \) is a dimensionless ratio of the potential drop across the electrode due to ohmic losses to the potential drop due to kinetic polarization.

Again, Newman has presented a dimensionless group, \( \nu^2 \), which is similar to \( \beta_i \) presented in this work (\( \nu^2 = \beta_i \) for \( s_i = n \))(5):

\[ \nu^2 = \left( \alpha_a + \alpha_\epsilon \right) \frac{F a_i L^2}{RT} \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right). \] \[ \text{[14]} \]
If the overpotential cannot be assumed to be small relative to \( \frac{\alpha F}{RT} \), then [12] is not valid and should not be used. In this situation, a superficial current density can be utilized to obtain a dimensionless group similar to \( \beta \).

The resulting non-dimensionalized equation written in terms of the superficial current density, \( I \), is:

\[
\frac{d^2 \psi}{d \zeta^2} = \frac{\alpha_s F L I}{nRT} \left( \frac{1}{\sigma} + \frac{1}{\kappa} \right) \tag{15}
\]

since \( I = a_i L \).

For the case where \( s_i = n \), the dimensionless group on the right side of [15] has been denoted by Newman as \( \delta \):

\[
\delta = \frac{\alpha_s F L I}{RT} \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) \tag{16}
\]

which is another dimensionless ratio of the potential drop across the porous electrode due to ohmic losses to the potential drop in the porous electrode due to kinetic polarization.

Thus if \( \beta_i > 1 \) or \( \delta > 1 \), then the electrode is ohmically limited and there is significant potential drop across the electrode. Conversely, if \( \beta_i < 1 \) and \( \delta < 1 \), then the electrode is kinetically limited, and there is negligible potential drop through the electrode in either the ionically conducting phase or the electronically conducting phase. In the absence of any mass-transfer limitations, the electrode will act as an equipotential surface, as desired.

2.4. Model Results

In order to utilize the porous electrode to obtain kinetic parameters, the electrode parameters and operating conditions must be such that \( \alpha_i > 1 \), \( \beta_i < 1 \), and \( \delta < 1 \). In the example of a direct ethanol PEM fuel cell, Table 1 lists the physical parameters and estimated values that determine \( \alpha_{\text{EOH}} \), \( \beta_{\text{proton}} \), and \( \delta \).
Table 1 Physical parameters for determining $\alpha_{\text{EtOH}}$, $\beta_{\text{proton}}$, and $\delta$.

| Parameter | Value       | Parameter | Value       | Parameter | Value       |
|-----------|-------------|-----------|-------------|-----------|-------------|
| $L$       | $10^{-3}$ cm| $L$       | $10^{-3}$ cm| $L$       | $10^{-3}$ cm|
| $A$       | $2.5 \times 10^6$ cm$^3$ | $a$       | $2.5 \times 10^6$ cm$^3$ | $a$       | $2.5 \times 10^6$ cm$^3$ |
| $\epsilon$ | 0.5        | $\sigma$  | $400$ $\Omega^{-1}$ cm$^{-1}$ | $\sigma$  | $400$ $\Omega^{-1}$ cm$^{-1}$ |
| $\langle i \rangle$ | $2 \times 10^{-4}$ A cm$^{-2}$ | $\kappa$  | $0.1$ $\Omega^{-1}$ cm$^{-1}$ | $\kappa$  | $0.1$ $\Omega^{-1}$ cm$^{-1}$ |
| $D_{\text{EtOH}}$ | $10^{-6}$ cm$^2$ s$^{-1}$ | $i_0$     | $10^{-6}$ A cm$^{-2}$ | $\langle i \rangle$ | $2 \times 10^{-4}$ A cm$^{-2}$ |

With these parameters, $\alpha_{\text{EtOH}} = 1.16$ for complete oxidation of 1 M EtOH, $\beta_{\text{proton}} = 0.0093$, and $\delta = 0.093$. It is apparent that an electrode having these parameters should not be ohmically limited, but may approach a mass-transport-limited region. It should be noted that the maximum superficial current density corresponding to the value of $\langle i \rangle$ given in Table 1 is 500 mA/cm$^2$. It is questionable as to whether or not such a high current density will be obtained in a direct ethanol PEM fuel cell. Also of concern is the possibility that the ethanol may not be completely oxidized, thus increasing the possibility of entering a mass-transfer-limited region. Therefore, the value of $\alpha_{\text{EtOH}}$ was investigated for several values of superficial current density, feed concentration, and degree of electrooxidation.

Figure 3. Effect of current density and degree of oxidation on the parameter $\alpha_{\text{EtOH}}$.

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In Figure 3, current density normalized to the true surface area of electrocatalyst in the electrode has been calculated assuming an average particle size of 25 nm. It can be seen that for complete oxidation (n = 12), mass-transfer limitations are not expected to be encountered until current densities greater than 500 mA/cm² have been reached. However, in the case where ethanol is oxidized to acetaldehyde (n = 2), mass-transfer limitations can be expected for current densities as low as 100 mA/cm² if 1 M ethanol is utilized as the feed concentration. In both cases, the mass-transfer-limited current density increases with increasing concentration. This is not surprising as the diffusive flux of ethanol in this model is directly proportional to the concentration gradient.

In this example, the model predicts that a porous electrode described by the parameters in Table 1 should operate as an equipotential surface at current densities that can be estimated from Figure 3 or similar estimation of \( a_e \). A comparison of the current densities obtained in fuel cell operation with the curves in Figure 3 can be used to verify that the electrode is not mass-transfer limited.

3. WATER MANAGEMENT AND CATHODE FLOODING

In the case where we are interested in examining the kinetic performance of the anode, even if a half-cell experiment is used in which the potential of the anode vs. a suitable reference electrode is controlled, as opposed to the cell potential, it is important to have a cathode that does not limit the performance of the cell as a whole. If the transport of oxygen to the cathode is significantly limited (e.g., by the flooding of the cathode structure), the potential at the cathode will decrease until cathodic evolution of hydrogen proceeds at a rate sufficient to match the current passing through the anode. This situation is undesirable since hydrogen that is generated at the cathode may diffuse across the polymer-electrolyte membrane and interfere with the electrochemical processes one wishes to investigate at the anode.

3.1 Approach

A simple model can be used to describe the simultaneous heat- and mass transfer occurring within the gas-diffusion layer. The partial pressure of water and the temperature within the gas-diffusion layer can be estimated based on the partial pressure of water and temperature in the cathode gas channel, an estimated mass-transfer coefficient, and an estimated heat-transfer coefficient. The boundary conditions in the gas channel are determined by integrating the flux of heat and mass into or out of the gas channel along the length of the channel.

A schematic diagram of the geometry and boundary conditions for this model is presented in Figure 4 below.
3.2. Assumptions

The model is subject to the following assumptions:

- All of the heat and water that are produced at the cathode leave through the cathode and not through the polymer electrolyte.
- The reversible heat generated by the Faradaic reaction is small compared to the irreversible heat.
- There is no accounting for the electro-osmotic drag of water from the anode to the cathode with the passage of current.
- There is no heat or mass transfer in the z-direction within the gas-diffusion layer. This last assumption is a good approximation for mass transfer in the case of small diffusion coefficients or small gradients in partial pressures in the z-direction. Likewise, for the heat-transfer model, this is a good assumption in the case of low thermal conductivity or small gradients in temperature in the z-direction.

3.3. Governing Equations

The temperature and partial pressures of the components in the gas-diffusion layer are given in terms of the temperature and partial pressures in the gas channel by:

$$\frac{d^2 P}{dx^2} = 0; \quad \frac{d^2 T}{dx^2} = 0$$

subject to the boundary conditions for the mass and heat fluxes:
At $x = 0$, \[ N_j = \frac{s_j i}{nF}; \quad q = -\eta i. \] \[ \text{[18]} \]

At $x = L$, \[ N_j = \frac{k_j}{RT} \left( P_j^\ast - P_j^\ast \right); \quad q = h(T^\ast - T^\ast). \] \[ \text{[19]} \]

In this case, as for the previous model, the current density $i$ is positive for an anodic current. Since this model deals with the cathode, $i$ is necessarily negative for an operating fuel cell.

Considering heat transfer first:

\[ T(x, z) = T^\ast(z) + \eta i \left( \frac{x - L}{\kappa^\ast h} \right). \] \[ \text{[20]} \]

If $Lh << \kappa^\ast$, then the temperature gradient in the $x$ direction can be considered negligible, and the gas-diffusion layer will be at a uniform temperature in the $x$-direction, $T_{GDL}$. Assuming that the gas-diffusion layer is isothermal in the $x$-direction gives a simplified form for the partial pressures of the components in the gas phase analogous to [20]:

\[ P_j(x, z) = P_j^\ast(z) + \frac{s_j iRT}{nF} \left( \frac{x - L}{D_j^\ast h} \right). \] \[ \text{[21]} \]

The values for $P_j^\ast$ and $T^\ast$ are determined by stepping along the gas channel according to:

\[ \frac{dF_j(z)}{dz} = -\frac{s_j iw}{nF}; \quad P_j^\ast(z) = P_j^\ast \sum_j F_j(z). \] \[ \text{[22]} \]

\[ \frac{dT^\ast}{dz} = -\eta iw - U \left( T^\ast - T_{\text{ocen}} \right) w \sum_j F_j \tilde{C}_{p,j} \] \[ \text{[23]} \]

where $F_j$ is the molar flow rate of species $j$ in the gas channel ($z$-direction), $U$ is an overall heat-transfer coefficient between the gas channel and the outside environment, $w$ is the width of the gas channel, and $\tilde{C}_{p,j}$ is the molar heat capacity of species $j$. 

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The initial values (at \( z = 0 \)) of \( F_j \) and \( T^* \) are determined by the inlet conditions of the cell, and \( P^\circ \), the total pressure in the gas channel, is fixed at the exit of the cathode gas channel by the use of a back-pressure regulator.

Flooding will occur when the partial pressure of water at \( x = 0 \) is greater than the saturated vapor pressure of water at the temperature \( T_{GDL} \) with a correction for pore condensation:

\[
P_{H_2O}(0,z) \geq P_{H_2O}^{sat}(T_{GDL}) \exp\left( -\frac{\Pi V_i^{GDL}}{RT_{GDL}} \right), \tag{24}
\]

\[
\Pi = \frac{2\gamma_{H_2O} \rho(i)}{r_{pore}}. \tag{25}
\]

3.4. Model Results

Microsoft Excel was used to integrate \([22]\) and \([23]\) with different inlet conditions. The results are taken to be qualitative in nature, since the assumptions needed to make the problem tractable are of uncertain validity. However, the model still provides insight into the effect that different physical, geometrical, and operating parameters have on the current density at which cathode flooding can be expected to occur.

The partial pressure of water in the cathode at the active layer (\( x = 0 \)) is monitored as the model is stepped down the gas channel. Once the partial pressure of water at the active layer reaches the saturated vapor pressure of water, flooding is assumed to have occurred.

The factors which appear to influence most heavily the maximum current density for which flooding would be predicted not to occur were the oxygen flow rate, initial water-vapor mole fraction, and the width of the gas channel. Of these parameters, only the width of the gas channel cannot be manipulated by altering process conditions. Because of this, it is important to select an appropriately sized gas channel in order to provide for good cathode performance.

Thinner gas channels provide better resistance to flooding due to increased gas velocity, and hence increased mass-transfer coefficient at the gas channel – gas-diffusion layer interface. An example of model results for which flooding is predicted to occur is given in Figure 5. The oxygen flow rate was chosen to be close to the stoichiometric flow rate for the current density used in the simulation.
Distance along flow channel / cm

Figure 5. Example of operating parameters for which the cathode heat- and mass-transfer model predicts flooding to occur. \( i = 1.2 \text{ A/cm}^2, y_\text{water}^0 = 0.8 \), \( T_{\text{inlet}} = 90^\circ \text{C}, \text{O}_2 \text{ flow} = 66 \text{ sccm}, w = 1.6 \text{ mm} \)

The solid line in Figure 5 is the predicted water partial pressure in the gas channel. The dashed line is the water partial pressure in the gas channel that would correspond to a partial pressure of water at the active layer which would exceed that of the saturated vapor pressure of water and, hence, induce flooding.

When applying this model to the design of a fuel cell experiment, one must be careful to recall that the assumption that all of the water and heat generated at the active layer of the cathode must exit through the cathode gas channel is of uncertain validity. However, if one were to include electroosmotic drag of water from the anode to the cathode and the diffusion of water within the polymer electrolyte membrane, then one would essentially have to duplicate this model at the anode. This would introduce several more variables into the solution of the problem. The model here has also neglected the conduction of heat through the polymer electrolyte. Inclusion of these effects would dramatically increase the effort needed to describe the processes involved in such a system.

Fuller has developed a model approaching this level of complexity, but that model treats the fuel cell as either isothermal, or as a “black-box” with an overall heat-transfer coefficient to the surrounding environment (6). As such, the model considers only the overall heat generation of the complete fuel cell reaction, and no consideration of the relative proportion of the heat generated at the anode and cathode is presented.

The usefulness of the model presented here is limited to qualitative predictions of the sensitivity of performance to geometric and operating parameters. However, it has been successfully applied to the selection of fuel cell designs that are resistant to flooding at high current densities.
4. MEA POTENTIAL DISTRIBUTION

When attempts are made to measure the electrochemical behavior of materials in liquid-phase systems, there are rules of thumb to guide the experimentalist in the selection of the geometric layout of the test system. One of these rules of thumb regards the placement of the reference electrode in a system. It is generally accepted that one should place the reference electrode as close to the working electrode as is possible provided that this does not interfere with mass transfer to and from the working electrode surface, or the electric field distribution.

When the electrochemical behavior of an electrode in a solid-phase system is investigated as it is done in the present work, it becomes difficult, if not impossible, to apply traditional rules of thumb regarding the experimental geometry. However, this does not obviate the need to be concerned with the portion of the uncompensated iR drop that is included in the measurement of the working-electrode potential.

4.1. Approach

The approach taken here is to solve for the potential distribution in the polymer electrolyte membrane with different placements of the electrodes in the system. The anode and cathode are necessarily placed opposite each other while the reference electrode is constrained to the same plane as the anode, but separated by a distance on the order of 3 mm.

It should be noted that other investigators have considered the potential distribution in similar systems. This model is, in one sense, a particular application of potential theory. Newman provides several references to works in the general area including that of Newman and of Moulton (7-9). West and Newman discuss the effects of a nonuniform potential distribution on measured kinetic data for a disk electrode and a channel flow cell (10,11). More recently, Chan et al. have discussed similar issues as discussed here for solid-oxide fuel cells, but their work was conducted independently of the work presented here (12). The effects of electrode misalignment on impedance studies on thin-film electrolyte systems are discussed by Adler (13).

Nafion\textsuperscript®-117, a popular PEM, is only 0.178 mm thick in the dry state. Due to this small thickness, the reference electrode can be considered to be a large distance from the anode and cathode. This leads to the simplification of the model needing only to find the potential distribution at distances very far away from the anode and cathode. That is not to say that “end-effects” can be neglected, but only to say that the exact location of the reference electrode is immaterial and not included in the model.

4.2. Assumptions

The assumptions made in developing this model are:

- The reference electrode is placed far away from the anode and cathode.
• Polarization effects due to kinetic polarization are neglected, giving the so-called primary potential distribution.
• Electroneutrality holds within the electrolyte, which implies that electrolyte can be treated as being macroscopically neutral.

4.3. Governing Equations

In this work we consider only the so-called primary potential distribution. We begin with Laplace’s equation for the electrolyte:

$$\nabla^2 \phi = 0.$$ \[26\]

The boundary conditions for \[26\] for the primary potential distribution are:

$$\nabla \phi = 0 \text{ at insulating boundaries},$$ \[27\]

$$\phi = \phi_{\text{anode}} \text{ at the anode},$$ \[28\]

$$\phi = \phi_{\text{cathode}} \text{ at the cathode}.$$ \[29\]

Since no current flows through the reference electrode, the electrostatic potential in the electrolyte adjacent to the reference electrode is determined by the electrostatic potential in the electrolyte adjacent to the anode and to the cathode as well as the placement of the anode and cathode relative to each other and the reference electrode.

4.4. Model Results

4.4.1. Numerical Solution. The electrolyte domain was divided into a mesh with a spacing of 13 cells for the thickness of the membrane (this spacing was deemed sufficient to observe the potential distribution, but also computationally tractable). Laplace’s equation [26] was solved subject to the boundary conditions [27] through [29] using Microsoft Excel in iterative mode, and the values for \(\phi_{\text{anode}}\) and \(\phi_{\text{cathode}}\) were chosen to be 0 and 1000, respectively to avoid round-off errors. The iteration was set to achieve a maximum change of \(10^{-7}\) (on this 0 to 1000 scale) at convergence. The effect of another combination of anode and cathode potentials can be determined from these results by utilizing \(\phi\) as the appropriate dimensionless electrostatic potential.

The small thickness of the electrolyte membrane requires the relocation of the reference electrode to a more practical location. One such location is one located in the same plane as the working electrode as illustrated in Figure 6.
This arrangement of electrodes allows for easy contact and gas supply to the electrodes, including the reference electrode, but results in a geometry where a small misalignment of the anode and cathode can result in a very large deviation of the potential distribution as compared to that for the case where the anode and cathode are perfectly aligned.

Figure 7a illustrates the case where the anode and cathode are perfectly aligned. It is clear that, many membrane thicknesses away from the working electrode and counterelectrode, the electrostatic potential has dropped to a potential representing one-half of the total potential drop between the working electrode and counterelectrode. Therefore, the potential difference between the working and reference electrode includes exactly half of the potential drop between the anode and cathode.

However, if the electrodes are misaligned by only 0.019 cm as in Figure 7b, the measurement of the electrochemical potential difference between an electrode and the
reference electrode includes either 87.7% of the electrostatic potential drop between the anode and cathode or 12.3% of the electrostatic potential drop depending on the which electrode (anode or cathode) is shifted towards the reference electrode. If the electrodes are even further misaligned, then the situation presented in Figure 7c applies. In this figure, the electrodes are misaligned to such an extent that one electrode extends past the portion of the solution domain which is presented in this figure. The entire solution domain is about five times larger than the portion that is presented in these figures.

4.4.2. Analytic Solution. An analytical solution can be found through the use of conformal-mapping techniques. The conformal mapping

\[ w = f(z) = \ln[\sin(z) - L]; \quad |L| \leq 1 \]  \[30\]

maps the infinite strip \(-\pi/2 \leq \text{Re}(z) \leq \pi/2\) onto the \(w\)-plane with the lines \(\text{Re}(z) = -\pi/2\) mapped onto the rays \(\text{Im}(w) = \pm \pi/2\); \(\text{Re}(w) \geq 0\) and \(\text{Re}(z) = \pi/2\) onto the ray \(\text{Im}(w) = 0\); \(\text{Re}(w) \geq -\ln(1 - L)\). This transformation represents the geometry of electrodes misaligned by a distance \(\ln(1 - L)\).

Setting up the boundary conditions for Laplace’s equation in the \(z\)-plane of \(\phi(z) = \pm \pi/2\) at \(\text{Re}(z) = \pm \pi/2\) yields the solution \(\phi = \text{Re}(z)\). The corresponding solution in the transformed system can be found through the inverse mapping:

\[ z = f^{-1}(w) = \sin^{-1}(e^w + L); \quad |L| \leq 1 \]  \[31\]

The potential distribution can be found by plotting contours of \(\text{Re}(z)\). Figure 8 illustrates the results obtained for electrodes perfectly aligned, slightly misaligned, and grossly misaligned.

Figure 8. The potential distribution as determined by the use of conformal mapping. a) electrodes perfectly aligned, b) electrodes slightly misaligned, and c) electrodes grossly misaligned.
The important result of this model is that small misalignments of the anode and cathode on the MEA result in large variations of the electric field within the electrolyte outside the edges of the main electrodes. These variations in turn cause variations in the fraction of the electrostatic potential drop between the anode and cathode introduced into the measurement of the anode potential relative to the reference electrode. Fortunately, this phenomenon can be utilized to eliminate almost all of the electrostatic potential drop from the measurement of the working-electrode potential by purposely misaligning the electrodes so that the edge of the working electrode closest to the reference electrode is about 1.5 mm closer to the reference electrode than the corresponding edge of the counter electrode.

It should be noted that since this model considers only the primary potential distribution, large current densities are predicted at the edges of the electrodes. However, if one were to include the effects of electrode kinetics in this model to obtain the secondary potential distribution, one would likely see smaller current densities in these regions.

5. CONCLUSIONS

The operation of a fuel cell in such a manner that one can measure the kinetic parameters of the anode electrocatalyst is a nontrivial task. There are many factors that need to be taken into account in order to ensure that the measured performance is not limited by other electrodes, other processes within the anode, or offset by uncompensated iR-drop.

The modeling efforts undertaken in this work were aimed at elucidating the interplay of these various effects and confirming that the electrical performance of the fuel cell is indeed a measure of anode-electrocatalyst performance.

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