Modeling the Polymer-Electrolyte Fuel-Cell Catalyst Layer

Adam Z. Weber and John Newman

Department of Chemical Engineering,
University of California
Berkeley, CA 94720-1462

In this paper, three different catalyst-layer models are presented and fit to experimental data. The model that considers both porous-electrode- and agglomerate-scale effects shows the best agreement with experimental data. Analysis of the results reveals that such a model can predict the expected low effectiveness factors and nonuniform reaction-rate distributions at low cell potentials. The model also predicts the optimum in power with respect to membrane loading. Discussion demonstrates that the catalyst layer is a key component in polymer-electrolyte fuel-cell water management at all cell potentials, and a correct model is crucial in understanding and predicting fuel-cell performance and the limiting phenomena and behavior

INTRODUCTION

It is well known that for optimal performance of polymer-electrolyte fuel cells (PEFCs), the design of the catalyst layers (CLs) is critical. In many respects, making CLs is a black art, where the exact microstructure and effects are unknown. Through modeling, it is possible to ascertain the important phenomena occurring in the CLs, which leads to improved performance and understanding.

Previous work by us involved developing models for transport in a membrane (1) and for two-phase flow in PEFC gas-diffusion layers (GDLs) (2). Both models are based on physical principles and observations from a variety of literature sources. In this work, these models are used in a PEFC sandwich model as well as in the appropriate phases in the CLs, where all of the various phases, gas, liquid, solid, and membrane exist. In addition, there are platinum electrocatalyst particles where the charge-transfer reactions take place. An accurate model of a CL requires that all of these phases and their various interactions be modeled rigorously. Such an approach ensures that the relevant changes in cell performance due to variables and models within the CL are applied correctly.

There have been various models proposed for CLs over the last few decades (3). Of these models, there are different approaches with different levels of complexity. The simplest are interfacial models that treat a CL as an interface and use a polarization equation to determine the relevant variables. While these models are sometimes useful, they do not provide much information about the CL itself. More complicated models assume that the CL can be treated as a thin film or as an agglomerate slab. Unfortunately, both of these approaches assume that at least some properties remain constant, such as gas concentration in the former case and electrode potential in the latter.
Comparisons between these two models have been previously examined in the literature (4,5), with the agglomerate one showing better agreement with experimental data. However, a CL model should calculate and allow for variations among the various parameters and phases, as well as the existence of phenomena such as flooding, in order to mimic better what is actually occurring in a PEFC. For this reason, we focus on models that utilize porous-electrode theory (6). In this approach, a CL is effectively discretized into separate phases that all have their own governing equations and exist at all points within the layer (i.e., the model is macrohomogeneous).

In this work, we examine three different models and fit them to experimental polarization-curve data. Such an exercise allows for a determination and explanation of the most suitable model for the CLs. The three models try to account for the physical structure of the CL, shown schematically in Fig. 1. In the figure, the first length scale involves changes that occur over the length of the CL, \( L \), which mainly include changes in gas-phase concentrations and ionic- and electronic-phase potentials; and the second length scale involves changes that occur locally where the reaction occurs. In our first test model, only the porous-electrode scale is considered. In the second test model, a film of membrane is considered to be covering the reaction particle, and thus gas must diffuse through it to react. In the final test model, a film is not used, but the reaction particle is assumed to be an agglomerate made up of pores, supported catalyst, and membrane. The different governing equations are discussed below.

![Figure 1](image)

**Figure 1.** Schematic showing the two different length scales in the cathode catalyst layer, the porous electrode and the local reaction sites, which are either composed of an agglomerate (no film) or a film covering the carbon/platinum particle. The light grey is the membrane, the black is the electrocatalyst, the white is the gas, and the dark grey is the carbon support.

### MODEL DESCRIPTIONS

As mentioned, all of the different phases in a PEFC occur within the CLs. These are modeled using our previously discussed modeling methodology and equations (1,2,7), and are only briefly mentioned. In this section, we mainly focus on the three test models.

A schematic of the FC sandwich is given in Fig. 2. There are seven main layers to the modeling domain, the membrane and anode and cathode gas channels (GCs), CLs, and GDLs. The GDLs and pore properties of the CLs are taken to be symmetric for simplicity. Also shown in the figures are the dominant water fluxes in the system. Water can flow in liquid form away from the membrane and either to or from the membrane in the vapor phase. Furthermore, there are two different types of water fluxes in the...
membrane, one each for the vapor- and liquid-equilibrated transport modes, as well as the total net flux. Both of the transport mode fluxes are in principle made up of an electroosmotic flux and a back-gradient flux.

Figure 2. Schematic of the modeling sandwich showing the various water fluxes and PEFC layers.

General Modeling Equations

In this section, those equations that apply for all of the test cases are discussed. For the membrane, there are four governing equations and four unknowns, the electrical potential, the superficial current density, the superficial flux density of water in the membrane, and the chemical potential of water in the membrane. The four equations contain three transport properties, the ionic conductivity of the membrane and the electroosmotic and transport coefficients. All of the transport properties are functions of temperature and water content (1). There are two transport modes in the membrane, the vapor- and liquid-equilibrated. In the vapor-equilibrated transport mode, the gradient flux is caused by water moving by diffusion down its chemical-potential gradient, while in the liquid-equilibrated mode it is caused by water moving by convection down its hydraulic-pressure gradient. Between these extremes, the fraction of expanded channels is used to partition the overall water flux, and local equilibrium is assumed between the two modes.

For the GDLs and the pores in the CLs, a porous-medium model is used wherein the gases are treated as ideal, and their transport is governed by the Stefan-Maxwell multicomponent diffusion equations with consideration of Knudsen diffusion. The model also calculates a saturation, \( S \), which is the volume fraction of pores filled by liquid. This saturation depends on the capillary pressure and the properties of the medium such as contact angle and pore-size distribution. Each layer is assumed to be composed of both a hydrophilic and hydrophobic pore-size distribution. For transport of liquid water, Darcy’s law is used with an effective permeability, whose deviation from the saturated-permeability value is calculated in a similar fashion to the saturation. Transport of electrons through all of the GDLs and CLs is governed by Ohm’s law with a Bruggeman correction for the conductivity. For evaporation and condensation of water, a rate constant and the effective interfacial area are used, and Faraday’s law is used with the reaction transfer current to calculate water production and hydrogen and oxygen consumption. Large mass-transfer coefficients are also used between liquid and the liquid-equilibrated mode and vapor and the vapor-equilibrated mode, since an order-of-magnitude analysis shows that any film resistance should not be large, although the vapor rate constant is about 50 times lower than the liquid one.
Test model 1: Porous Electrode (PE)

In this model, only the typical porous-electrode equations are used. Flow in the pores of the CLs and the membrane are treated as above. For the reaction rates in the CLs, the following expressions are used for the oxygen-reduction reaction (ORR) and hydrogen-oxidation reaction (HOR), respectively:

\[ i_{\text{ORR}} = -i_{\text{ORR}} \left( \frac{P_{O_2}}{P_{O_2}^{\text{ref}}} \right) \exp \left( -\frac{\alpha_a F}{RT} (\Phi_1 - \Phi_2 - U_0^0) \right) \text{ and} \]

\[ i_{\text{HOR}} = i_{\text{HOR}} \left( \frac{P_{H_2}}{P_{H_2}^{\text{ref}}} \right) \exp \left( \frac{\alpha_a F}{RT} (\Phi_1 - \Phi_2) \right) - \exp \left( -\frac{\alpha_c F}{RT} (\Phi_1 - \Phi_2) \right) \]

By conservation of charge, the transfer current is related to the divergence of the electronic (subscript 1) and ionic (subscript 2) currents by

\[ \nabla \cdot i_1 = -\nabla \cdot i_2 = a_{i,2} \left( 1 - S \right) j_b \]

where \( a_{i,2} \) is the interfacial area per unit volume between the ionically and electronically conducting phases without any water coverage, and is taken as a fitting parameter. The other fitting parameter is the permeability at saturation of the GDLs, \( k_{\text{sat, GDL}} \). The saturation comes into the above equation in that it is assumed that, if liquid water exists, it can cover the reaction sites and effectively shut down the reaction there.

Test model 2: Porous Electrode with Film (PEF)

In this model, the same reaction expressions as above are used except that there is an extra film of membrane that the reactant gases must diffuse through in order to react. Doing the math results in an expression for the reaction rate of

\[ \nabla \cdot i_1 = 4Fp_{O_2}^{\text{bulk}} \left( \frac{1}{\delta_{\text{film}}} + \frac{1}{a_{i,2} \psi_{O_2} k_{\text{ORR}}} \right) \text{ and} \]

\[ \nabla \cdot i_1 = -2F \left( \frac{p_{H_2}^{\text{bulk}} - \exp \left( -\left( \alpha_a + \alpha_c \right) \frac{F}{RT} (\Phi_1 - \Phi_2) \right)}{\delta_{\text{film}}} + \frac{1}{a_{i,2} \psi_{H_2} k_{\text{HOR}}} \right) \]

for the ORR and HOR, respectively, where

\[ k_{\text{ORR}} = \frac{a_{i,2} i_{\text{ORR}}^{\text{ref}}}{4FP_{O_2}^{\text{ref}}} \exp \left( -\frac{\alpha_a F}{RT} (\Phi_1 - \Phi_2 - U_0^0) \right) \text{ and} \]

\[ k_{\text{HOR}} = \frac{a_{i,2} i_{\text{HOR}}^{\text{ref}}}{2FP_{H_2}^{\text{ref}}} \exp \left( \frac{\alpha_a F}{RT} (\Phi_1 - \Phi_2) \right) \]
In the above expressions, all of the parameters are known (i.e., taken from literature sources) except for the film thickness, $\delta_{\text{film}}$, specific interfacial area, $a_{1,2}^0$, and saturated permeability of the GDLs, $k_{\text{sat,GDL}}$, which are used as fitting parameters.

Test model 3: Porous Electrode with Agglomerate (PEA)

In this model, the same porous-electrode equations are used as in the PE model except that it is assumed that the reaction site is composed not of a single site, but a spherical agglomerate. In this situation, there is both gas diffusion and reaction occurring throughout the agglomerate. In order to simplify and yield an analytic expression, the agglomerate is assumed to be at a uniform potential, although different agglomerates will be at different potentials depending on their location within the CL. This case of reaction and diffusion has been treated in porous catalyst particles (8) and yields the following expression for the reaction rate

$$\nabla \cdot \mathbf{i}_2 = -\nabla \cdot \mathbf{i}_1 = a_{1,2}^0 (1 - S) \dot{i}_h E$$

where $E$ is the effectiveness factor

$$E = \frac{1}{3\phi^2} (3\phi \coth(3\phi) - 1)$$

where $\phi$ is the Thiele modulus for the system

$$\phi = \sqrt{\frac{R^2 k'}{\Psi_{\text{agg}}}} = \sqrt{\phi_{m} k'}$$

where $\phi_m$ is the mass-transfer portion of the Thiele modulus and $k'$ is the kinetic portion of the Thiele modulus and is given by equations 6 and 7 for the ORR and HOR, respectively. For this model, $\phi_m$, $k_{\text{sat,GDL}}$, and $a_{1,2}^0$ are taken to be the fitting parameters, and the values of $\phi_m$ for hydrogen and oxygen are assumed to have the same ratio as their permeation in Nafion (i.e., the oxygen value is fit and the hydrogen one is calculated).

Boundary Conditions

At all internal boundaries, the superficial fluxes and interstitial concentrations are taken to be continuous. In the gas channels, the gas-phase pressure and composition are set. For the simulations in this paper, a log-normal average is used for all feed gases and they are assumed to be fully humidified. If the liquid-water pressure at the GC/DM interface is greater than the gas pressure, a boundary condition of zero capillary pressure (gas and liquid pressures are equal) is used, if not, then a zero liquid-water flux condition is used. For the current density and electrical potential, an arbitrary zero of potential is set at the aGC/aGDL interface, and the potential at the cGDL/cGC interface is set to the operating potential. In terms of numerical implementation, a discretization of 20 mesh points is used for each layer besides the membrane, where it is 50. The operation is isothermal and steady, with uniform total gas pressure and temperature.
RESULTS AND DISCUSSION

Model Agreement with Experimental Data

As noted, all of the parameters for all of the layers are taken from experimental data as discussed in previous publications (1,2,7), with the exception of the fitting parameters and operating conditions. The fitting parameters are $a_{i,2}$ and $k_{in,GDL}$ for all three models and additionally $\delta_{film}$ and $\phi_{mf}$ for the PEF and PEA models, respectively. The models were run and fit to three separate sources of data as shown in Figure 3. The values of the relevant operating conditions are given in the figure caption, and the fitting-parameter values are given in Table I.

![Figure 3](image_url)

**Figure 3.** Comparisons of the three test models, PE (dashed), PEF (dotted), and PEA (solid), to experimental data (squares). Case (a) is from Ticianelli et al. (9) at 50°C with air and Nafion 117; case (b) is from Gloaguen et al. (4) at 50°C with oxygen and Nafion 112, and the inset is the Tafel plot; and case (c) is from Qi and Kaufman (10) at 60°C and 75°C with air and Nafion 112.
As is readily apparent, the PEA model fits the experimental data much better than the other ones. This is in agreement with previous analysis, although here the PE model is more comprehensive. Although not shown, it is the cCL that dominates the effects and the differences between the different models, which is expected. For case (b), mass-transfer effects never become truly limiting, and all of the curves fit the data well. This can also be seen in that the fit parameters are very similar for the three models for that case. Thus, for just kinetically and ohmically controlled curves, the models are similar and do not distinguish themselves greatly. However, as cases (a) and (c) show, the three models do not fit the mass-transfer limitation part of the curves equally well. This is important because when comparing different models and data for CLs, it is common to examine only the kinetic part of the curve, which can lead to inaccurate conclusions. Thus, the whole curve must be examined because the CLs affect the water balance and subsequently all portions of the polarization curve. However, since the saturated permeability of the GDL was also fit, this does play a dominant role in water management and flooding, although the fit values are relatively close to one another.

Table I. Values for the fitting parameters for the three simulation cases given in Fig. 3.

| Case | PE Parameter | PEF Parameter | PEA Parameter |
|------|--------------|---------------|---------------|
|      | $a_{1,2}^O$ | $k_{\text{sat,GDL}}$ | $\delta_{\text{film}}$ | $\phi_{\text{int,O}_2}$ |
|      | (cm$^{-1}$) | (cm$^{-3}$) | (cm$^{-1}$) | (cm$^{-3}$) | (nm) | (bar cm$^3$ s/mol) |
| a   | 1500         | 0.5×10$^{-12}$ | 2000         | 0.6×10$^{-12}$ | 0.4   | 10000         | 0.6×10$^{-12}$ | 6×10$^4$       |
| b   | 500          | 3×10$^{-12}$   | 550          | 3.3×10$^{-12}$ | 1.8   | 500           | 3.5×10$^{-12}$ | 2.7×10$^3$       |
| c   | 10000        | 2×10$^{-12}$   | 40000        | 2.3×10$^{-12}$ | 26    | 100000        | 2.1×10$^{-12}$ | 5×10$^3$       |

The values for case (c) were fit to the 60°C data

For case (c), the model parameters in Table I correspond to the fit at 60°C. The temperature was then raised in the model, with all of its associated effects, to 75°C, and then compared to data at that temperature. The only fitting parameters that depend directly on temperature are $\phi_{\text{int}}$ for each gas, and it was assumed that their dependence was the same as in bulk Nation. In agreement with the results at 60°C, the PEA model still fits the best at 75°C, while the PEF model fits better and the PE model fits worse than at 60°C (see Fig. 3). This clearly shows that some kind of temperature-dependent mass-transfer process (e.g., diffusion) occurs within the CL and needs to be considered.

It is noteworthy that the fit specific interfacial area is higher for the PEA model than the other ones, even though its performance is usually lower. This indicates that the effectiveness factor (and catalyst utilization) is not as high as it could be. Thus, mass-transport limitations in the CLs can be almost as important as those in the GDLs, and should be optimized over. To put the fit mass-transfer Thiele values into some perspective, if one assumes that permeation through the agglomerate is the same as permeation through Nation, then the three cases result in agglomerate radii of 11, 2.8, and 2.3 μm, respectively. These values are in line with those seen in the literature (5).

For the three cases in Fig. 3, the PEF model mainly follows the PE model in terms of fitting the curve. This can be seen in the thinness of the layer as shown in Table I. The only possible exception is case (c), where the PEF model results in a better fit and has a thicker layer. However, the general shapes of the curves from this model are similar to
the PE ones, *i.e.*, they have a pronounced "knee" in the mass-transfer portion of the curve. Thus, one can surmise that the added fitting parameter and diffusion resistance provided by the PEF model has only a minimal impact. Therefore, a single barrier to oxygen transport is not limiting, and one needs combined reaction and diffusion.

**PEA Model Attributes**

To understand why the PEA model is better, various parameters from the PE and PEA models for case (a) are compared in Fig. 4. The ohmic resistances predicted by the two models are basically identical until currents close to the limiting current are obtained. When this occurs, the more uniform reaction distribution with the PEA model predicts a lower ohmic resistance, which results in a slower approach to the limiting current. More important than the ohmic resistance is the limitation of oxygen through the cGDL.

![Figure 4. Comparison of the saturation, oxygen partial pressure at the cCL / cGDL interface, and total cell ohmic resistance for the PE and PEA models of case (a) of Fig. 3.](image)

It can be seen that the lower value of the saturated permeability for the PE model results in higher saturations and a lower partial pressure of oxygen in the cCL (*i.e.*, larger pressure drop of oxygen in the cGDL). This lower concentration is trying to mimic the poor performance of the PEFC as shown in Fig. 3a. However, even with this and a smaller specific interfacial area, the model still overpredicts the actual performance until severe flooding is reached at the limiting current. In accordance with the "knee" and limiting current in Fig. 3a, the oxygen partial pressure approaches zero at high current densities. Unlike this profile, the PEA model shows a more gradual decrease in the oxygen partial pressure. This type of profile results in a lower cell potential at a given current density due to the larger overpotential required to obtain the given reaction rate, which is solely a function of current density. The gradual decrease and lower potentials result from a decrease in the effectiveness factors, as shown in Fig. 5.

Examination of Fig. 5 shows that at low current densities, the effectiveness factor for the anode is lower than for the cathode because of the facile kinetics of the HOR, but is higher at higher current densities due to the higher hydrogen concentration in the aCL and faster hydrogen...
diffusion in the agglomerate. However, it is the cCL and its effectiveness factor that is limiting in all cases.

![Figure 5. Anode and cathode effectiveness factors as a function of current density for case (a) using the PEA model.](image)

The above analysis contains many variables that were taken to be constant. These average values from the literature may not accurately reflect those in each of the cases, but it is noteworthy that the polarization curves could be fit by using only three parameters. The above also highlights the importance of understanding water management in predicting and optimizing PEFC performance.

An example of the optimization is of the loading of Nafion in the CLs, as show in Fig. 6, where the PEA model was used with the case (a) parameters.

![Figure 6. Effect of Nafion loading on power density at 0.5 V. The model and conditions are those of case (a), where the loading changes the agglomerate radius and various volume fractions.](image)
Experimentally, the above optimum has been witnessed with respect to Nafion loading (11-15). The optimum is due to the interplay between higher reaction rates with Nafion loading due to better membrane connectivity and properties (i.e., Bruggeman relation), and lower reaction rates due to lower effectiveness factors caused by the increasing radius of the agglomerate. However, one should be aware that the experimental optima are normally in terms of loading or weight percentage (and can be functions of the platinum loading (16,17)), which must be directly related to the parameters in the model. To do this, we assumed that the thickness of the prepared CL remained constant and the extra Nafion loading causes a change in the various volume fractions. Thus, the Nafion loading was converted to a volume fraction and the porosity and solid-phase volume fraction were reduced proportionally. In addition, the agglomerate radius or mass-transfer portion of the Thiele modulus was altered by assuming that the Nafion volume fraction thickens the agglomerate uniformly. While the above is a consistent treatment, another one would be to keep the volume fractions constant and increase the thickness of the CL. Both treatments have some validity, and more data (such as CL thickness) are needed to justify one over the other. The true situation is probably a combination of the two.

Finally, as discussed above, rough values for the agglomerate radii can be as large as half of the CL thickness. Thus, one might wonder if it is better to just use a slab or cylindrical agglomerate model for the entire CL, as has been done in the literature (3). The reason for doing this is the possibility of analytic solutions, much less computational cost, and easier convergence. However, this kind of treatment has various drawbacks. First, changes in membrane hydration and ionic and electronic potentials cannot be easily calculated, and often other uniform values are assumed; these changes are not negligible in typical PEFC CLs. To examine this, the reaction-rate distributions are shown in Fig. 7 for case (a) for both the anode and cathode.

![Figure 8. Reaction-rate distribution for both the aCL and cCL for case (a). The lines go from a cell potential of 0.1 to 1 V in 0.1 V increments. No other fuel-cell layers are shown.](image)
From the figure, the anode reaction rate at high current densities (low potentials) becomes more and more nonuniform with the highest rate next to the membrane surface. The reason is that ionic transport is limiting, especially since the membrane is only vapor-equilibrated. This type of profile is not normally obtainable with a simple agglomerate model since it typically only accounts for reactant diffusion and reaction. On average, the profile for the cCL is more uniform than for the aCL at the same potential because of the much more sluggish ORR kinetics. As the current density increases, the oxygen concentration drops substantially (see Fig. 4), and this causes the distribution to have higher rates farther from the membrane, which can be seen in the 0.1 V curve. At slightly higher potentials, ionic and oxygen transport are both controlling.

Other drawbacks of the simple and not embedded agglomerate models include the fact that it is hard to assess the impact of flooding and liquid-water blockage of the reaction sites. This is because the pore structure is lost due to the assumption of only agglomerates. In a similar fashion, the interactions between gas, liquid, and membrane are no longer as interconnected as one expects from the physical picture of the CL. In other words, oxygen and water have only single paths that they can travel within the CL. Overall, the PEA model using porous-electrode theory with embedded agglomerates at the reaction sites is the best CL model to use due to its ability to best mimic the actual physical structure and operation.

CONCLUSIONS

An appropriate catalyst-layer model is crucial in understanding water management and predicting fuel-cell performance. To this end, three different models were considered for the catalyst layers in a polymer-electrolyte fuel cell. All of the models were derived from porous-electrode theory with the first having no additions, the second having a film over the catalyst particle, and the third treating the catalyst particle as an agglomerate. The relevant equations for the cases were given and each model was fit to various sets of polarization-curve data. The model using the agglomerate (PEA model) demonstrated the best fit because it allows for the observed gradual decrease in cell potential with respect to current density. The other models failed to do this and predicted a much more abrupt change in the potential due to flooding. The ability of the agglomerate model to make a gradual transition through the different polarization regimes is due to its consideration of both diffusion and reaction simultaneously within not only the larger porous electrode scale, but also on the local reaction scale. It is the consideration of both of these effects that is required to obtain the complex reaction-rate distributions and correctly model the various phenomena that are occurring such as flooding and gas, ionic, and electronic transport, to name a few. The model contained three fitting parameters. The agglomerate radius allowed the calculation and tradeoff of mass-transfer and reaction (i.e., effectiveness factor) at the reaction or agglomerate scale. The value of the saturated permeability of the gas-diffusion layer was the critical parameter in determining the limiting current, but could not accurately model the other parts of the polarization curve. The value of the specific interfacial area was shown to affect the kinetic regime as well as the rest of the curve through water production and oxygen consumption. Overall, the PEA model is probably the best representation of the physical situation inside the catalyst layer.
ACKNOWLEDGEMENTS

This research has been supported by UTC Fuel Cells, LLC, and by an EPA STAR graduate fellowship (91601301-0).

REFERENCES

1. A. Z. Weber and J. Newman, J. Electrochem. Soc., 151, A311 (2004).
2. A. Z. Weber, R. M. Darling, and J. Newman, J. Electrochem. Soc., in press (2004).
3. A. Z. Weber and J. Newman, Chem. Rev., (2004).
4. F. Gloaguen, P. Convert, S. Gamburzev, O. A. Velev, and S. Srinivasan, Electrochim. Acta, 43, 3767 (1998).
5. K. Broka and P. Ekduinge, J. Appl. Electrochem., 27, 281 (1997).
6. A. Z. Weber and J. Newman, J. Electrochem. Soc., submitted (2004).
7. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena 2nd ed., John Wiley & Sons, Inc., New York (2002).
9. E. A. Ticianelli, C. R. Derouin, A. Redondo, and S. Srinivasan, J. Electrochem. Soc., 135, 2209 (1988).
10. Z. G. Qi and A. Kaufman, J. Power Sources, 109, 38 (2002).
11. E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, and L. Giorgi, Electrochim. Acta, 46, 799 (2001).
12. S. Litster and G. McLean, J. Power Sources, 130, 61 (2004).
13. S. J. Lee, S. Mukerjee, J. McBreen, Y. W. Rho, Y. T. Kho, and T. H. Lee, Electrochim. Acta, 43, 3693 (1998).
14. M. Uchida, Y. Aoyama, N. Eda, and A. Ohta, J. Electrochem. Soc., 142, 4143 (1995).
15. G. Li and P. P. Pickup, J. Electrochem. Soc., 150, C745 (2003).
16. G. Sasikumar, J. W. Ihm, and H. Ryu, J. Power Sources, 132, 11 (2004).
17. E. A. Ticianelli, J. G. Beery, and S. Srinivasan, J. Appl. Electrochem., 21, 597 (1991).