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Mathematical Modeling of a Nickel-Cadmium Cell: Proton Diffusion in the Nickel Electrode

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ABSTRACT

In this paper we present a mathematical model of a sealed nickel-cadmium cell that includes proton diffusion and ohmic drop through the active material in the nickel electrode. The model is used to calculate sensitivity coefficients for various parameters in the model. These calculations show that the discharge voltage of the cell is affected mostly by the kinetics of the nickel reaction. Toward the end of discharge, proton diffusion also becomes important, because the proton diffusion process affects the active material utilization significantly. During charge, the cell voltage is mainly affected by the kinetics of the nickel reaction until the oxygen evolution reaction begins, after which time the kinetics of the oxygen evolution has the largest effect. The oxygen evolution reaction is also the most influencing factor on the actual charge uptake of the cell by the end of a charge operation (charge efficiency). Compared to the rates of reaction and proton diffusion, the ohmic drop in the active material of the nickel electrode and the mass transport and ohmic drop in the electrolyte have negligible effect on the behavior of the cell studied here.

Introduction

Many researchers and manufacturers are interested in the charge and discharge performance of the nickel-cadmium battery (Ni-Cd). It is well known that the battery performance is the result of complex chemical and physical phenomena that take place inside the battery. A mathematical model of an Ni-Cd cell can be used to help understand these phenomena.

Fan and White developed a one-dimensional (1D) model for the charge and discharge operations of a nickel-cadmium cell, which is similar to a model for a nickel-zinc cell presented by Choi and Yao. Fan and White included the oxygen reaction in both electrodes and used a non-Nernst expression for the equilibrium potential in the nickel electrode. They used this model to predict the experimental observation that the oxygen reaction is important toward the end of charge and during overcharge because it reduces the utilization of the active material. For low rates of discharge, Fan and White found that the model predictions were in fair agreement with the experimental data for moderate rates of discharge. However, for high discharge rates the predictions deviated from the experimental observations. Specifically, their model does not predict the decrease of active material utilization as the rate of discharge is increased, as discussed by Timmerman et al.

Contrary to Choi and Yao, Fan and White found that the mass transport in the electrolyte phase has little effect on the electrode behavior. They concluded that the charge and discharge behavior of the nickel-cadmium cell is under kinetic control.

Some researchers have proposed that the proton diffusion in the active material of the nickel electrode controls the performance of the cell. Bouet et al. developed a pseudo 2D model for the discharge operation of the nickel electrode that incorporates this proton diffusion process. Their model simulations are in excellent agreement with their experimental data. The nickel electrode discharge predictions obtained by Bouet et al. exhibit a significant improvement in simulating experimental observations over those from models that do not include the proton diffusion process. Their simulations show that the active material utilization is affected by the proton diffusion process. Miao et al. reached the same conclusion with a model for the discharge of a nickel-hydrogen cell that includes the proton diffusion in the nickel electrode.

Some studies indicate that the ohmic drop through the active material of the nickel electrode also may affect the behavior of the electrode. Experimental results reported by Zimmermann and Effa showed that the proton diffusion process controls most of the discharge of the nickel electrode. They also found that, as the electrode is being discharged, the conductivity of the active material decreases until the proton diffusion no longer controls the discharge and mixed control becomes evident. Further discharge results in the formation of a semiconductor layer that controls the last portion of the discharge.

Proton diffusion and the ohmic drop in the active material of the nickel electrode have been identified as possible important factors in the behavior of the nickel electrode. However, these factors have not been included in a model for the nickel-cadmium battery. Our purpose here is to present a mathematical model of a sealed nickel-cadmium cell that includes proton diffusion and ohmic drop through the active material in the nickel electrode and to evaluate the effect of these phenomena on the predicted behavior of the cell during charge and discharge. This was done by conducting a sensitivity analysis of various model parameters on the voltage of the cell over time and the charge utilization for discharge and charge operation. We found that the kinetic parameters of the nickel electrode reaction have the largest effect on the predicted cell voltage during discharge. Also, the proton diffusion coefficient becomes important toward the end of discharge because it has the largest effect on the active material utilization. During charge, the kinetic parameters of the main reactions of both electrodes are the most important parameters until the oxygen evolution reaction begins on the nickel electrode. Then, the kinetic parameters for oxygen evolution become the most important parameters affecting the cell voltage and the actual charge uptake of the cell by the end of a charge operation. The parameters involved in the mass transfer of electrolyte, the ohmic drop in the electrolyte, and the ohmic drop in the active material of the nickel electrode have a negligible effect on the predicted cell voltage and charge utilization in the cell.

The model presented here can be used to predict the performance of the Ni-Cd cell during charge and discharge. Therefore, it can assist battery designers and engineers in studying the effect of various design parameters on battery performance.

Model Development

Figure 1 shows a schematic diagram of the cross-sectional view of the nickel-cadmium cell and the idealization...
Fig. 1. A schematic diagram of the representation of the nickel-cadmium cell in the model.

of the cell as it is represented in the mathematical model. The nickel-cadmium cell consists of three regions: the positive electrode (porous nickel oxyhydroxide), the separator, and the negative electrode (porous cadmium). The electrolyte is a concentrated KOH aqueous solution. The electrochemical reactions included in the model are

Positive electrode

\[ \text{NiOOH} + \text{H}_2\text{O} + e^- \xrightarrow{\text{discharge}} \text{Ni(OH)}_2 + \text{OH}^- \]  \[1\]

\[ \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \xrightarrow{\text{charge}} 2 \text{OH}^- \]  \[2\]

Negative electrode

\[ \text{Cd} + 2 \text{OH}^- \xrightarrow{\text{discharge}} \text{Cd(OH)}_2 + 2e^- \]  \[3\]

\[ 2 \text{OH}^- \xrightarrow{\text{charge}} \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \]  \[4\]

In the following paragraphs we present the model equations. The equations are formulated separately for the nickel electrode, the separator, and the cadmium electrode.

**Positive electrode.**—We use a pseudo-2D approach to treat the mass transfer and ohmic losses in the nickel electrode. This representation is the same as the one we use in the model for a nickel/hydrogen cell. In this pseudo-2D model, the \( x \) dimension is defined across the electrode, and the pseudo-\( y \) dimension is defined inside the layer of active material from the nickel substrate to the interface with the electrolyte, as shown in Fig. 1. In our representation of the nickel electrode, the current collector (nickel screen) is placed in the center of the electrode, which corresponds to \( x = 0 \). Thus, the total thickness of the electrode is \( 2l_e \). The surface of the nickel electrode which is in contact with the separator corresponds to \( x = l_e \). The governing equations were derived using the theory for concentrated electrolytes and the theory for porous electrodes.

**Equations in the \( x \)-direction.**—The equations are written for four dependent variables: the electrolyte concentration, \( c \); the oxygen concentration, \( c_{\text{O}_2} \); the potential in the liquid phase, \( \phi \); and the current density in the liquid phase, \( i_e \). The equations that describe the behavior of the positive electrode are

Material balance on electrolyte (KOH)

\[
\epsilon_1 \frac{\partial c}{\partial t} = \epsilon_1 \left( D_{\text{eff}} \frac{\partial^2 c}{\partial x^2} + \left( \frac{t_{\text{OH}}}{F} - 1 \right) \frac{\partial \phi}{\partial x} \right)
\]  \[5\]
Material balance on oxygen

\[ \frac{\partial c_\text{O}_2}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{O}_2} \frac{\partial c_\text{O}_2}{\partial x} + \frac{1}{4} \frac{F \eta}{J} \right) \]  

[6]

Modified Ohm's law for the liquid phase

\[ \frac{v_\text{elec}}{k_e} = -\frac{\partial \phi}{\partial x} \frac{2RT}{cF} \left( 1 - t^* \right) + \frac{c}{2c_\text{O}_2} \frac{\partial c}{\partial x} \]  

[7]

Transfer current

\[ \frac{\partial \phi}{\partial x} = j_1 + j_2 \]  

[8]

In the above equations \( \epsilon_1 \) is the porosity of the positive electrode, \( \gamma_1 \) is the tortuosity factor associated with the porosity, \( t^* \) is the transference number of the anion \( \text{OH}^- \) with respect to the solvent velocity, \( D_{\text{O}_2} \) is the diffusion coefficient of KOH, \( D_{\text{H}_2} \) is the apparent diffusion coefficient of oxygen, \( j_1 \) and \( j_2 \) are the nickel and oxygen transfer currents per unit volume of electrode, and \( k \) is the conductivity of the electrolyte.

The mass transfer of electrolyte (Eq. 5) is considered to be caused only by diffusion and migration; that is, convection has been neglected as suggested by Sinha\(^3\) and Fan and White.\(^4\) The oxygen is treated in the same way as Fan and White\(^4\) did in their model for a nickel/cadmium cell. The mass transfer of oxygen (Eq. 6) is represented using an effective oxygen concentration, \( c_{\text{O}_2}\). The effective oxygen concentration accounts for the oxygen in the gas phase and that dissolved in the liquid phase. Equation 7 states that the current density at a given position in the electrolyte inside the electrode results from a gradient in the electrolyte's electric potential and a gradient in electrolyte concentration. Theelectrochemical reactions that occur in the electrolyte produce a gradient in the current density in the electrolyte; this is represented by Eq. 8.

During charge and discharge the porosity of the positive electrode, \( \epsilon_1 \), varies as the active material changes back and forth from NiOOH to Ni(OH)\(_2\). However, the variation in porosity is small,\(^4\) and thus the porosity in the nickel electrode is considered to be a constant.

The Butler-Volmer equations is used to express the reaction rates for the nickel and oxygen reactions. The equations are

\[ j_1 = a_{i1,\text{cell}} \left\{ \left( \frac{c_{\text{Ni}^{2+}}}{c_{\text{Ni}^{2+}}} \right) \exp \left[ \frac{\alpha_{i1} F}{RT} \eta_1 \right] - \left( \frac{c_{\text{Ni}^{2+\text{max}}}}{c_{\text{Ni}^{2+}}} \right) \exp \left[ \frac{-\alpha_{i1} F}{RT} \eta_1 \right] \right\} \]  

[9]

\[ j_2 = a_{i2,\text{cell}} \left\{ \left( \frac{c_{\text{Ni}^{2+}}}{c_{\text{Ni}^{2+}}} \right) \exp \left[ \frac{\alpha_{i2} F}{RT} \eta_2 \right] - \left( \frac{c_{\text{Ni}^{2+\text{max}}}}{c_{\text{Ni}^{2+}}} \right) \exp \left[ \frac{-\alpha_{i2} F}{RT} \eta_2 \right] \right\} \]  

[10]

in which \( a_{i1,\text{cell}} \) and \( a_{i2,\text{cell}} \) are the exchange current densities of the nickel and oxygen reactions evaluated at reference conditions, and \( c_{\text{Ni}^{2+}} \) is the proton concentration in the active material. The reference concentrations are indicated by the subscript ref. When the active material is completely discharged, the proton concentration takes its maximum value, \( c_{\text{Ni}^{2+\text{max}}} \). The overpotentials in Eqs. 9 and 10 are

\[ \eta_1 = \phi_1 - \phi_2 - U_{1,\text{ref}} \]  

[11]

\[ \eta_2 = \phi_1 - \phi_2 - U_{2,\text{ref}} \]  

[12]

in which \( \phi_1 \) is the potential in the solid phase and \( U_{1,\text{ref}} \) and \( U_{2,\text{ref}} \) are the equilibrium potentials at the reference conditions for reactions 1 and 2, respectively. The equilibrium potentials are expressed with respect to an Hg/HgO reference electrode. Assuming that the reference electrode is at the same conditions as the working electrode, the equilibrium potentials for reactions 1 and 2 evaluated at reference conditions are given by

\[ U_{1,\text{ref}} = U^0_1 - U_{\text{H}_2} - \frac{RT}{F} \ln \left( \frac{c_{\text{H}_2\text{O}}}{c_{\text{H}_2\text{O}}} \right) \]  

[13]

\[ U_{2,\text{ref}} = U^0_2 - U_{\text{H}_2} + \frac{RT}{F} \ln P_{\text{O}_2,\text{ref}} \]  

[14]

where \( U^0_1 \) and \( U^0_2 \) are the standard potentials for reactions 1 and 2, \( U_{\text{H}_2} \) is the standard potential for the Hg/HgO reaction in alkaline media, and \( P_{\text{O}_2,\text{ref}} \) is the reference oxygen pressure.

In Eq. 9 and 10 we assume that the orders of reaction for NiOOH and \( \text{OH}^- \) are consistent with the stoichiometry of reactions 1 and 2. The stoichiometry of reaction 2 would predict an order of reaction of 1/2 for \( \text{O}_2 \) to be used in Eq. 10; however, we assume an order of reaction of 1.0 because there is experimental evidence that the rate of oxygen reduction varies linearly with oxygen pressure.\(^2\) Similar assumptions are made for the kinetics of the reactions taking place in the cadmium electrode, where the oxygen reduction is relevant.

At the center of the positive electrode (\( x = 0 \)) the boundary conditions are

\[ \frac{\partial c}{\partial x} \bigg|_{x=0} = 0 \]  

[15]

\[ \frac{\partial c_{\text{H}_2\text{O}}}{\partial x} \bigg|_{x=0} = 0 \]  

[16]

\[ \frac{\partial \phi}{\partial x} \bigg|_{x=0} = 0 \]  

[17]

\[ i_1 \bigg|_{x=0} = 0 \]  

[18]

Equations 15 and 16 represent the condition of zero flux of electrolyte and oxygen. Equations 17 and 18 indicate that all the current density goes through the solid phase (current collector), thus the potential gradient and the current density in the electrolyte are both equal to zero.

At the interface between the positive electrode and the separator (\( x = L \)) the boundary conditions are

\[ \frac{\partial c_{\text{Ni}^{2+}}}{\partial x} \bigg|_{x=L} = \frac{\partial c_\text{O}_2}{\partial x} \bigg|_{x=L} = 0 \]  

[19]

\[ \frac{\partial \phi}{\partial x} \bigg|_{x=L} = \frac{\partial \phi_2}{\partial x} \bigg|_{x=L} = 0 \]  

[20]

\[ i_1 \bigg|_{x=L} = i_{\text{cell}} \]  

[22]

in which \( \epsilon_2 \) is the porosity of the separator, \( \gamma_2 \) is the tortuosity factor associated with the porosity of the separator, and \( i_{\text{cell}} \) is the applied current density.

Equations 19 and 20 represent the continuity of electrolyte and oxygen flux. Equation 21 represents the continuity of current density in the electrolyte. The current density in the electrolyte is equal to the set current density through the cell, \( i_{\text{cell}} \) (Eq. 22).

Equations in the y-direction.—The solid particles in the positive electrode are modeled as cylindrical particles that have the substrate along the central axes of the cylinders. The portion filled with substrate has an average radius of \( y_\text{p} \). The active material surrounds the substrate, and its thickness is considered to be equal to the average thickness of active material in the original particles, \( t_\text{p} \). The proton diffusion in the active material is considered only in the radial direction, \( y_\text{p} \), and is represented by

\[ \frac{\partial c_{\text{H}_2\text{O}}}{\partial t} = \frac{D_{\text{H}_2\text{O}}}{(y_\text{p} + y_\text{p})} \frac{\partial^2 c_{\text{H}_2\text{O}}}{\partial y^2} \]  

[23]

which is Fick's law in cylindrical coordinates.

Proton diffusion and electron transfer in the active material are assumed to occur simultaneously. Therefore, the current flows only in the radial direction, \( y_\text{p} \), and there is no current flow in the \( x \)-direction in the active material. This
results in no generation or consumption of net charge inside the active material. The conservation of charge reduces to the divergence of the current density being equal to zero
\[
\frac{\partial \sigma_N}{\partial y} \frac{\partial j_y}{\partial y} + \sigma_N \left( \frac{\partial^2 j_y}{\partial y^2} + \frac{1}{y+y_i} \frac{\partial j_y}{\partial y} \right) = 0 \tag{24}
\]

The conductivity of the active material, \(\sigma_N\), is considered as a function of the state of charge of the electrode. In the model, we use the correlation found by Antonenko et al., \(^9\) which reads
\[
\sigma_N = 0.1185 \exp \left( -9.4590 \eta \right) \tag{25}
\]
where the state of charge of the nickel electrode, \(\eta\), is expressed in terms of the proton concentration as
\[
\eta = \frac{c_{H^+}}{c_{H^+\text{max}}} \tag{26}
\]
The boundary conditions at the interface of the electrolyte and the active material (\(y = L\)) are
\[
-\sigma_N \frac{\partial j_y}{\partial y} \bigg|_{y=L} = \frac{j_1 + j_2}{\sigma_N} \tag{27}
\]
\[
-FD_{H^+} \frac{\partial c_{H^+}}{\partial y} \bigg|_{y=L} = \frac{j_1}{\sigma_N} \tag{28}
\]

Equation 27 was obtained assuming that the potential in the active material obeys Ohm’s law. Equation 28 indicates that the flux of protons into the active material from the electrolyte is equal to the nickel reaction rate.

The boundary conditions at the interface of the active material and the nickel substrate (\(y = 0\)) are
\[
-\sigma_N \frac{\partial j_y}{\partial y} \bigg|_{y=0} = 0 \tag{29}
\]
\[
\phi_1 \bigg|_{y=0} = \phi_{\text{sub}} \tag{30}
\]

Equation 29 indicates that the flux of protons into the substrate must be zero. At this interface, the potential of the active material must be equal to that of the nickel substrate (Eq. 30).

**Separator.**—The separator is modeled in one space dimension, \(x\). The governing equations are basically the same as those posed for the positive electrode in the \(x\)-direction, but here there are no electrochemical reactions

**Material balance of electrolyte (KOH)**
\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_{OH} \frac{\partial c}{\partial x} \right) \tag{31}
\]

**Material balance on oxygen**
\[
\frac{\partial c_{O_2}}{\partial t} = \frac{\partial}{\partial x} \left( D_{O_2} \frac{\partial c_{O_2}}{\partial x} \right) \tag{32}
\]

**Modified Ohm’s law for the liquid phase**
\[
\frac{\partial j_2}{\partial x} = \frac{1}{cF} \left( 1 - t^* + \frac{c}{2c_{O_2}} \right) \frac{\partial c}{\partial x} \tag{33}
\]

**Potential in the solid phase**
\[
\phi_1 = 0 \tag{34}
\]

**Current in the electrolyte**
\[
j_2 = \dot{i}_{\text{cell}} \tag{35}
\]

Equations 31 and 32 represent the mass transfer of electrolyte and oxygen in the absence of electrochemical reactions. The current density in the liquid phase is equal to the cell’s current density (Eq. 33), because the solid material in the separator is an electrical insulator (Eq. 34). As in the positive electrode, the current density, the potential, and the concentration of electrolyte in the liquid phase are related by Ohm’s law (Eq. 33).

**Material balance of electrolyte (KOH)**
\[
\frac{\partial (c_{OH})}{\partial t} = \frac{\partial}{\partial x} \left( D_{OH} \frac{\partial c_{OH}}{\partial x} + \frac{1}{F} \frac{\partial i_2}{\partial x} \right) \tag{36}
\]

**Material balance of oxygen**
\[
\frac{\partial (c_{O_2})}{\partial t} = \frac{\partial}{\partial x} \left( D_{O_2} \frac{\partial c_{O_2}}{\partial x} + \frac{1}{F} \frac{\partial j_2}{\partial x} \right) \tag{37}
\]

**Modified Ohm’s law for the liquid phase**
\[
\frac{\partial j_2}{\partial x} = \frac{1}{cF} \left( 1 - t^* + \frac{c}{2c_{O_2}} \right) \frac{\partial c}{\partial x} \tag{38}
\]

**Conservation of charge**
\[
j_2 = \sigma_N \frac{\partial \phi_1}{\partial x} = \dot{i}_{\text{cell}} \tag{39}
\]

**Transfer current**
\[
\frac{\partial \dot{i}_2}{\partial x} = j_1 + j_2 \tag{40}
\]

**Porosity variation**
\[
\frac{\partial \psi}{\partial t} = 1 \left( \frac{M_{CD}}{\rho} - \frac{M_{CD}(OH)}{\rho} \right) \frac{\partial \psi}{\partial x} \tag{41}
\]

In these equations \(\psi\) is the porosity of the negative electrode, \(\gamma_i\) is the tortuosity factor associated to the porosity of the electrode, \(\sigma_{cd}\) is the conductivity of the solid material in the electrode, \(\theta_1\) is the state of charge of the negative electrode (see below), \(\beta\) is the tortuosity factor associated to the porosity of the solid material in the cadmium electrode, \(j_3\) and \(j_4\) are the cadmium and oxygen reaction currents per unit of volume, \(M_i\) is the molecular weight of species \(i\), and \(\rho\) is the density of species \(i\).

The conservation of charge is represented by Ohm’s law in the solid phase (Eq. 39). The porosity of the negative electrode varies as the solid material changes from Cd to Cd(OH). Therefore, the rate at which the porosity changes is considered to be proportional to the rate of the cadmium reaction (Eq. 41).

**The kinetic expressions for the cadmium and oxygen reactions** are
\[
j_3 = a_{Ca} \theta_1 \exp \left( \frac{\alpha_{Ca} F}{RT} \eta_1 \right) - \exp \left( -\frac{\alpha_{Ca} F}{RT} \eta_1 \right) \tag{42}
\]
\[
j_4 = a_{Ca} \theta_1 \exp \left( \frac{\alpha_{Ca} F}{RT} \eta_1 \right) - \exp \left( -\frac{\alpha_{Ca} F}{RT} \eta_1 \right) \tag{43}
\]

**The local state of charge of the negative electrode, \(\theta_3\), can be expressed as a function of electrode porosity**
\[
\theta_3 = \frac{\psi - \psi_{\text{min}}}{\psi_{\text{max}} - \psi_{\text{min}}} \tag{44}
\]

The porosity of the electrode takes its maximum value, \(\psi_{\text{max}}\), when the electrode is completely charged. When the electrode is completely discharged the porosity takes its minimum value, \(\psi_{\text{min}}\). The overpotentials in Eq. 42 and 43 are
\[
\eta_1 = \phi_2 - \phi_3 - U_{eq,1} \tag{45}
\]
\[
\eta_4 = \phi_3 - \phi_2 - U_{eq,4} \tag{46}
\]

In which \(U_{eq,1}\) and \(U_{eq,4}\) are the equilibrium potentials at reference conditions for reactions 3 and 4, respectively. The equilibrium potentials are expressed with respect to an Hg/
Porosity of the nickel electrode

\[ Q_{\text{max}} = \frac{P_{\text{Ni(OH)2}}}{M_{\text{Ni(OH)2}}} \]  

[61]

Maximum proton concentration

\[ C_{\text{H2O}} \]

[60]

Porosity of the nickel electrode

\[ \varepsilon = \varepsilon_{\text{p}} - \frac{Q_{\text{max}}}{F C_{\text{H2O}} l_i} \]  

[62]

Radius of the nickel substrate in cylindrical shape

\[ l = y_e \sqrt{1 + \frac{2(Q_{\text{p}} - \varepsilon)}{Q_{\text{p}}}} - y_0 \]  

[63]

Thickness of the active material

\[ y_e = \frac{2(1 - \varepsilon_{\text{p}})}{\varepsilon} \]  

[64]

Specific active surface area of the nickel electrode

\[ \alpha_{\text{Ni}} = \alpha \sqrt{1 - \varepsilon_{\text{p}}} \]  

[65]

Minimum porosity of the cadmium electrode

\[ \varepsilon_{\text{Ni(OH)2}} \]

Table I. Value of the model parameters used in the simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{\text{H2O}} )</td>
<td>7.044 \times 10^{-26} \text{ mol cm}^{-3}</td>
<td>Eq. 61</td>
</tr>
<tr>
<td>( \rho )</td>
<td>2.6 \times 10^{-8} \text{ S cm}^{-1}</td>
<td>Eq. 47 (Ref. 22)</td>
</tr>
<tr>
<td>( l_i )</td>
<td>1.3 \times 10^{-14} \text{ A cm}^{-2}</td>
<td>Ref. 19</td>
</tr>
<tr>
<td>( \varepsilon_{\text{Ni(OH)2}} )</td>
<td>0.401 \text{ V}</td>
<td>Ref. 22</td>
</tr>
<tr>
<td>( \varepsilon_{\text{Cd}} )</td>
<td>0.401 \text{ V}</td>
<td>Ref. 22</td>
</tr>
<tr>
<td>( \varepsilon_{\text{Cd(OH)2}} )</td>
<td>0.401 \text{ V}</td>
<td>Ref. 22</td>
</tr>
<tr>
<td>( \varepsilon_{\text{Cd(OH)3}} )</td>
<td>0.401 \text{ V}</td>
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</tr>
</tbody>
</table>

* Solubility of oxygen in a 35% weight KOH electrolyte solution in equilibrium with an oxygen atmosphere at 1 atm.

* Conductivity of pure cadmium.
Diffusion coefficient, $D_{\text{OH}}$
Using experimental data reported for the integral diffusion coefficients at 25°C for electrolyte concentrations in the range 0.103 to 13.719 × 10^{-3} \text{ mol cm}^{-3}, we obtained

$$D_{\text{OH}} = \exp (-10.467 - 8.1607 c^{1/2} + 286.2 c - 2539.8 c^{3/2} + 7207.5 c^2)$$

The regression had an average relative error of 0.36%. The differential diffusion coefficient, $D_{\text{OH}}$, which is the one we need in Eq. 5, 31, and 36, is given by

$$D_{\text{OH}} = D_{\text{OH}} \left( c \frac{d \rho_{\text{OH}}}{dc} + 1 \right) = D_{\text{OH}} (1.0 - 4.0804 c^{1/2} + 286.2 c - 3809.7 c^{3/2} + 14415.0 c^2)$$

Specific conductivity, $\kappa$
The following expression was obtained for the specific conductivity of the free-electrolyte using experimental data for the equivalent conductance at 25°C for electrolyte concentrations in the range 0.06081 to 10.611 × 10^{-3} \text{ mol cm}^{-3}, 2

$$\kappa = c \exp (5.5657 - 6.1538 c^{1/2} + 286.2 c - 3809.7 c^{3/2} + 14415.0 c^2)$$

The regression had an average relative error of 1.67%. The experimental data used for the regression is for electrolyte concentrations in the range 0.3617 to 13.449 × 10^{-3} \text{ mol cm}^{-3}. The regression had an average relative error of 0.36%. The differential diffusion coefficient, which is the one we need in Eq. 5, 31, and 36, is given by

$$D_{\text{OH}} = D_{\text{OH}} \left( c \frac{d \rho_{\text{OH}}}{dc} + 1 \right) = D_{\text{OH}} (1.0 - 4.0804 c^{1/2} + 286.2 c - 3809.7 c^{3/2} + 14415.0 c^2)$$

The ratio of electrolyte concentration to water concentration, $c/c_w$
Using experimental data for the density of the electrolyte at 25°C, 7 we obtained the following expression for $c/c_w$

$$c/c_w = \exp (-6.8818 + 118.75 c^{1/2} - 1030.5 c + 4004.7 c^2)$$

The experimental data used for the regression is for electrolyte concentrations in the range 0.3617 to 13.449 × 10^{-3} \text{ mol cm}^{-3}. The regression had an average relative error of 0.16%.

Sensitivity Analysis
We performed a sensitivity analysis to determine the effect of the various parameters included in the model on the simulated cell behavior. The processes associated with those parameters with the largest sensitivities are the most influential in predicting cell behavior. We have used this method to evaluate the impact of including the proton diffusion and ohmic drop in the active material of the nickel electrode in a model for an Ni-Cd cell.

First, we need to define what we call the behavior of a cell. The model can be used to simulate several responses of an Ni-Cd cell, such as, concentration, potential, and current profiles inside the cell. We choose two responses of the cell that can be simulated with the model and that are of practical interest, the predicted cell voltage as a function of the state-of-charge during a charge and discharge operation and at a given time during overcharge. To compute the sensitivity coefficients, we use the following approximations

$$S_{p} = \frac{\Delta Q/Q_{\text{max}}}{\Delta p/p}$$

in which $Q$ is the amount of charge in the nickel electrode and is calculated as

$$Q = \frac{(1 - \varepsilon_i F)}{\pi (y + y_i)} \int_{y_i}^{y_f} \int_{y_j}^{y_f} dy \, dx \left( \frac{C}{\text{cm}^3 \text{of electrode}} \right)$$

The coefficient $S_{p}$ is computed at the cutoff voltage of 0.9 V for the discharge operation and at a given time during overcharge. The resulting correlations are presented in Table II. The initial conditions used for charge and discharge simulations are listed in Table III.

Results and Discussion
Several of the plots presented here are given as a function of the state-of-discharge and state-of-charge of the Ni-Cd cell, which we define as follows

State-of-discharge during a discharge operation

$$\text{SOD} = -\frac{i_{\text{cell}}}{Q_{\text{max}}} \text{ with } i_{\text{cell}} < 0$$

State-of-charge during a charge operation

$$\text{SOC} = \frac{i_{\text{cell}}}{Q_{\text{max}}} \text{ with } i_{\text{cell}} > 0$$

The results of these analyses are presented in Table II. The initial conditions used for charge and discharge simulations are listed in Table III.
In Eq. 75, the first term is the potential in the nickel substrate at the center of the nickel electrode and the second term is the potential in the solid phase at the center of the cadmium electrode.

**Discharge characteristics.**—Figure 2 presents curves for the predicted cell voltage during discharge for three discharge rates. The curves are consistent with the real behavior of a cell during discharge in regard to the decrease of the discharge potential as the discharge rate is increased. Figure 3 shows the same discharge curves as a function of the SOD of the cell. These curves show the characteristic decrease in the SOD at the end of the discharge operation (cutoff voltage of 0.9 V) as the discharge rate is increased. This behavior is caused by a slow proton diffusion process relative to the electrochemical reaction (Eq. 1) that takes place on the surface of the active material in the nickel electrode. During discharge, the proton concentration at the surface of the active material increases because of the main electrochemical reaction (Eq. 1). As the proton concentration increases, the potential of the nickel electrode increases causing the cell potential to decrease, and when it reaches the maximum proton concentration, $c_{\text{max}}$, the cell potential drops sharply. The accumulation of protons at the surface of the active material increases because of the main electrochemical reaction and the proton diffusion into the bulk of the active material. As the discharge rate is increased, the electrochemical reaction rate (j) increases, the proton concentration at the surface of the active material reaches $c_{\text{max}}$ sooner, and a sharp drop in the potential of the cell occurs earlier. Thus, increasingly more active material is left unreacted in the nickel electrode as the discharge rate is increased.

Figure 4 shows the sensitivity coefficient of various parameters on the predicted cell voltage as defined by Eq. 71. The sensitivity coefficients are given as a function of the SOD for a discharge operation at C/2.1 rate ($-10$ mA cm$^{-2}$). In this plot we show only the results for the parameters that have the largest sensitivities. At the beginning of discharge the largest sensitivity is that of the exchange current density of the main reaction in the nickel electrode, $i_{\text{cat}}$. As the discharge proceeds, the sensitivity coefficient of the transfer coefficient, $\alpha_{\text{cat}}$, increases until it becomes the largest. Therefore, the kinetic parameters of the main reaction of the nickel electrode (Eq. 1) has the largest effect on the discharge voltage during almost the entire operation. However, toward the end of discharge ($\text{SOD} = 0.95$) the sensitivity of the proton diffusion coefficient becomes important also, and the predicted cell voltage is affected by both the kinetics of the nickel reaction and proton diffusion into the active material. If the cell is discharged at a higher rate (C/0.7), the sensitivity coefficients for the various parameters exhibit a similar behavior as those for a C/2.1 rate. In Fig. 5 we can see the results for the largest sensitivity coefficients for both rates, and these are those for $i_{\text{cat}}$, $\alpha_{\text{cat}}$, and $D_p$. As the rate of discharge is increased, the sensitivity coefficients become larger, but the most important parameters are the same for both rates. However, the sharp increase in the sensitivity coefficient for the proton diffusion coefficient takes place at a smaller SOD for the C/0.7 rate (SOD = 0.9). This means that the portion of the discharge operation during which the proton diffusion affects the cell voltage widens as the rate of discharge is increased.

In addition to the predicted cell voltage during discharge, we considered the amount of charge left in the nickel electrode at the end of discharge as a response of interest, because it reflects the discharge efficiency. The sensitivity coefficient of a parameter on this response is given by Eq. 72. Figure 6 shows the results for the largest sensitivity coefficients for discharge rates of C/2.1 and C/0.7. The most important parameter is the proton diffusion coefficient, $\alpha_{\text{cat}}$, followed by the anodic transfer coefficient of the nickel reaction, $\alpha_{\text{cat}}$. This means that the discharge efficiency is mostly affected by the proton diffusion process and the kinetics of the nickel reaction with the proton diffusion having the largest effect. Both processes affect the discharge efficiency of the cell, and their relative importance varies with operating conditions. For example, in Fig. 6 we can see that the sensitivity of $D_p$ for a discharge rate of C/0.7 is approximately 2.5 times that for a C/2.1 rate; however, the sensitivity of $\alpha_{\text{cat}}$ for C/0.7 is approximately five times that for C/2.1 rate. Thus, the relative effect of $D_p$ and $\alpha_{\text{cat}}$ on the discharge efficiency changes with

## Table III. Initial conditions used in the simulations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Positive electrode charge/discharge</th>
<th>Separator charge/discharge</th>
<th>Negative electrode charge/discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>$7.1 \times 10^{-2}$</td>
<td>$7.1 \times 10^{-2}$</td>
<td>$7.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>$10^{20}/10^{-20}$ mol cm$^{-3}$</td>
<td>$10^{20}/10^{-20}$ mol cm$^{-3}$</td>
<td>$10^{20}/10^{-20}$ mol cm$^{-3}$</td>
</tr>
<tr>
<td>$q_D$</td>
<td>$0/0$</td>
<td>$0/0$</td>
<td>$0/0$</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>solve Eq. 9 for $j_i = 0$</td>
<td>solve Eq. 9 for $j_i = 0$</td>
<td>solve Eq. 9 for $j_i = 0$</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>same $\phi_1$ as in positive</td>
<td>same $\phi_2$ as in positive</td>
<td>same $\phi_2$ as in positive</td>
</tr>
<tr>
<td>$\phi_3$</td>
<td>$0/0$</td>
<td>$0/0$</td>
<td>$0/0$</td>
</tr>
<tr>
<td>$a$</td>
<td>$5.156 \times 10^{-7}$</td>
<td>$1.0418 \times 10^{-7}$</td>
<td>$0.47/0.64$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>$7.1 \times 10^{-3}$ tool cm$^{-3}$</td>
<td>$7.1 \times 10^{-3}$ tool cm$^{-3}$</td>
<td>$7.1 \times 10^{-3}$ tool cm$^{-3}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$0.01$</td>
<td>$0.01$</td>
<td>$0.01$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>$0.01$</td>
<td>$0.01$</td>
<td>$0.01$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$1.0418 \times 10^{-7}$ mol cm$^{-3}$</td>
<td>$1.0418 \times 10^{-7}$ mol cm$^{-3}$</td>
<td>$1.0418 \times 10^{-7}$ mol cm$^{-3}$</td>
</tr>
</tbody>
</table>

## Table IV. Model parameters used in the sensitivity analysis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel reaction in the positive electrode</td>
<td>$i_{\text{cat}}$, $\alpha_{\text{cat}}$, $\sigma_{\text{cat}}$</td>
</tr>
<tr>
<td>Oxygen reaction in the positive electrode</td>
<td>$\alpha_{\text{cat}}$, $\sigma_{\text{cat}}$</td>
</tr>
<tr>
<td>Cadmium reaction in the negative electrode</td>
<td>$i_{\text{cat}}$, $\alpha_{\text{cat}}$, $\sigma_{\text{cat}}$</td>
</tr>
<tr>
<td>Oxygen reaction in the negative electrode</td>
<td>$\alpha_{\text{cat}}$, $\sigma_{\text{cat}}$</td>
</tr>
<tr>
<td>Proton diffusion</td>
<td>$D_p$</td>
</tr>
<tr>
<td>Ohmic drop in the active material in the nickel electrode</td>
<td>$\kappa$ and $\tau$</td>
</tr>
<tr>
<td>Ohmic drop in the electrolyte</td>
<td>$D_\text{el}$ and $\tau$</td>
</tr>
<tr>
<td>Mass transfer of electrolyte</td>
<td>$D_\text{el}$</td>
</tr>
<tr>
<td>Mass transfer of oxygen</td>
<td>$D_\text{el}$</td>
</tr>
</tbody>
</table>

![Fig. 2. Predicted cell voltage as a function of time during a discharge operation for three discharge rates (C rate = 20.6 mA cm$^{-2}$).](image-url)
the discharge rate, and the effect of $D_H$ is larger at the higher discharge rate. The sign of the sensitivity coefficients indicates that the amount of charge left in the nickel electrode at the end of discharge decreases as $D_H$ increases and it increases as $\alpha_{i_3}$ increases. There is more charge drained from the cell if the proton diffusion process is faster relative to the rest of the processes, especially relative to the rate of the nickel reaction.

In summary, the kinetic parameters of the main reactions in both electrodes and the proton diffusion coefficient are the most important parameters affecting the predicted cell voltage and efficiency during discharge. The kinetics of the main reaction in the nickel electrode is the leading factor in predicting the cell voltage during discharge, with the proton diffusion having a smaller effect limited to the very last portion of the discharge process. However, the proton diffusion is the main factor influencing the predictions for discharge efficiency, that is, the total charge drained from the cell during discharge.

Charge characteristics.—Simulations of the charge operation are readily obtained using the same model and changing the sign of the applied current density. Figure 7 shows predicted charge curves for three different rates. The curves exhibit the characteristic overcharge plateau toward the end of the charge process due to the oxygen evolution at the nickel electrode and reduction at the cadmium electrode. As the charge rate increases, the cell potential rises more sharply, and the overcharge voltage increases.

Also, the roll-over of the voltage curve at the beginning of overcharge becomes apparent as the charge rate increases. This is caused by the large overpotentials of the oxygen evolution at the nickel electrode and that of the oxygen reduction at the cadmium electrode right after reactions 2 and 4 begin. As the electrochemical reduction of oxygen proceeds in the cadmium electrode, the oxygen concentration decreases, and the overpotential decreases (see Eq. 43); thus, the cell voltage is reduced.

We computed the sensitivity coefficients for the same parameters and responses as for the discharge operation. Figure 8 shows the results for the parameters that have the largest sensitivity coefficients on the cell voltage during charge at C/2.1 rate. Before the oxygen evolution reaction begins (SOC ~ 0.9), the voltage of the cell is mostly affected by the kinetics of the nickel and cadmium reactions, as shown in Fig. 8. When the oxygen evolution reaction begins (SOC > 0.9) the sensitivity of the transfer coefficient for oxygen evolution ($\alpha_{i_3}$) increases rapidly as the other sensitivity coefficients tend to zero. Thus, the predicted cell voltage during overcharge is affected almost exclusively by the oxygen reaction. For a larger rate of charge of C/0.7, the largest sensitivity coefficients correspond to the same set of parameters as for C/2.1, as shown in Fig. 9.

Figure 10 shows the largest sensitivity coefficients of the parameters on the amount of charge at the end of charge. The end of charge was considered to be at $t = 2.52$ h for a
charge rate of C/2.1 and at \( t = 0.84 \) h for C/0.7; that is, an 
overcharge of 20% over the theoretical time that it would 
take to charge the nickel electrode fully. The results shown 
in Fig. 10 indicate that the transfer coefficient for the oxy-
gen reaction, \( \alpha_{a2} \), has the largest effect on the amount of 
charge present in the nickel electrode by the end of charge. 
The next most important parameter is the transfer coeffi-
cient of the nickel reaction, \( \alpha_{a1} \). Also, the sign of the sensi-
tivity coefficients indicates that the amount of charge de-
creases if \( \alpha_{a4} \) is increased and it increases if \( \alpha_{a3} \) is increased. 
The larger the rate of oxygen evolution the larger is the 
amount of current used in this reaction, and thus, the cur-
rent used in the main nickel reaction is smaller leading to 
less charge in the electrode.

**Conclusion**

The incorporation of proton diffusion in the nickel elec-
trode in the model for an Ni-Cd cell improves the simula-
tion capabilities of the model, particularly for the dis-
charge process. For the operating conditions considered in 
this work, the magnitude of the ohmic drop in the active 
material is small compared to the overall potential drop in 
the nickel electrode and was shown to have a negligible 
effect on cell behavior during charge and discharge opera-
tions. The most important factors affecting the discharge 
behavior are the kinetics of the nickel reaction and the 
proton diffusion process. The discharge efficiency (utiliza-
tion of active material) is mostly affected by proton diffu-
sion. For the charge operation, the kinetics of the nickel 
and cadmium reactions affect the predicted cell voltage 
almost equally. These two reactions are the most important 
factors in determining the cell voltage during charge before 
oxygen evolution begins at the nickel electrode; at which 
time the kinetics of the oxygen evolution become the only 
relevant process affecting the cell voltage. Likewise, the 
amount of charge that is input into the cell at the end of a 
charge operation (charge efficiency) is mostly affected by 
the oxygen evolution kinetics. The effect of mass transfer 
and ohmic drop in the electrolyte during charge and dis-
charge is considerably smaller than those just mentioned.

In view of these results, one may consider the option of 
neglecting the mass transfer and ohmic drop in the elec-
trolyte for an approximate and simpler mathematical 
model of an Ni-Cd cell. However, if one is interested in 
predicting the electrolyte concentration and potential dis-
tribution inside the cell, these processes must be included 
in a model of an Ni-Cd cell. From the results presented 
here, it appears evident that any modeling effort for an 
Ni-Cd cell benefits largely from any improvement in the 
representation of the electrode processes: main electro-
chemical reactions, oxygen evolution reaction, and proton 
diffusion.

The model presented here can be used to estimate the 
parameters that were shown to have the largest sensitivi-
ities.
ties on the cell behavior. The experimental data must be collected for conditions under which the parameters have their largest sensitivities. Also, this model can be used to predict battery performance during charge and discharge operations. Therefore, it can assist battery designers and engineers in studying the effect of various design parameters on battery performance.

**Acknowledgment**

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**LIST OF SYMBOLS**

\( \alpha_{Cd} \) specific active surface area in the cadmium (negative) electrode, \( \text{cm}^2 \) \( \text{cm}^{-3} \)

\( \alpha_{Ni} \) specific active surface area in the nickel (positive) electrode, \( \text{cm}^2 \) \( \text{cm}^{-3} \)

\( \alpha_o \) specific surface area of the nickel substrate in the positive electrode, \( \text{cm}^2 \) \( \text{cm}^{-3} \)

\( c \) concentration of the electrolyte, KOH, mol \( \text{cm}^{-3} \)

\( c_{O_2} \) reference concentration of the binary electrolyte, KOH, mol \( \text{cm}^{-3} \)

\( C_p \) proton concentration in the active material, mol cm \(^{-1} \)

\( C_{P_{max}} \) proton concentration in the active material at fully discharged state, mol cm \(^{-2} \)

\( C_{O_2} \) reference proton concentration in the active material, mol cm \(^{-2} \)

\( C_{O_2,ref} \) effective oxygen concentration, mol \( \text{cm}^{-3} \)

\( C_{O_2,ref} \) effective oxygen concentration, mol \( \text{cm}^{-3} \)

\( D_{eff} \) diffusion coefficient of protons, \( \text{cm}^2 \text{s}^{-1} \)

\( D_{H} \) diffusion coefficient of KOH, \( \text{cm}^2 \text{s}^{-1} \)

\( D_{O_2} \) apparent diffusion coefficient of oxygen, \( \text{cm}^2 \text{s}^{-1} \)

\( F \) Faraday's constant, 96,487 C \( \text{mol}^{-1} \)

\( j \) current density in the liquid phase based on the projected electrode area, \( \text{A cm}^{-2} \)

\( j_{act} \) applied current density, \( \text{A cm}^{-2} \)

\( j_{act,ref} \) exchange current density of the nickel reaction at reference conditions, \( \text{A cm}^{-2} \) of active surface area

\( j_{act,ref} \) exchange current density of the cadmium reaction at reference conditions, \( \text{A cm}^{-2} \) of active surface area

\( j_{act,ref} \) exchange current density of the oxygen reaction in the cadmium electrode at reference conditions, \( \text{A cm}^{-2} \) of active surface area

\( j_{r} \) nickel reaction current per unit volume of positive electrode, \( \text{A cm}^{-2} \)

\( j_{r} \) oxygen reaction current per unit volume of positive electrode, \( \text{A cm}^{-2} \)

\( j_{r} \) cadmium reaction current per unit volume of the negative electrode, \( \text{A cm}^{-2} \)

\( j_{r} \) oxygen reaction current per unit volume of negative electrode, \( \text{A cm}^{-2} \)

\( l \) total thickness of the cell unit, cm

\( l_1 \) half thickness of the nickel electrode, cm

\( l_2 \) thickness of the separator, cm

\( l_3 \) half thickness of the cadmium electrode, cm

\( l_4 \) average thickness of active material in the nickel electrode, cm

\( L_{charged} \) loading in the cadmium electrode, g of Cd(OH)\(_2\)\( \text{cm}^{-3} \) of void

\( M_i \) molecular weight of species \( i \), g \( \text{mol}^{-1} \)

\( P_{O_2,ref} \) reference oxygen pressure, atm

\( p \) parameter

\( Q_{max} \) maximum theoretical charge in the nickel electrode, C \( \text{cm}^{-2} \) of electrode

\( Q \) amount of charge present in the nickel electrode at the end of charge or discharge operations, C \( \text{cm}^{-2} \) of electrode

\( R \) universal gas constant, 8.3143 J \( \text{mol}^{-1} \text{K}^{-1} \)

\( S_{P} \) sensitivity coefficient of parameter \( p \) on the amount of charge \( Q \) present in the electrode at the end of a charge or discharge operation

\( S_{P}^* \) sensitivity coefficient of parameter \( p \) on the cell voltage \( V_{cell} \)

\( SOC \) state of charge defined in Eq. 74

\( SOD \) state of discharge defined in Eq. 73

\( T \) temperature, K

\( t \) time, s

\( t^* \) transference number of the anion \( \text{OH}^- \) with respect to the solvent velocity

\( U_{ref} \) equilibrium potential for reaction \( i \) at reference conditions measured with respect to an \( \text{Hg/HgO} \) reference electrode, V

\( U^* \) standard potential for reaction \( i \), V

\( U_{ref}^* \) standard potential for the \( \text{Hg/HgO} \) reaction in alkaline media, V

\( U_{cell} \) cell voltage defined in Eq. 75, V

\( x \) spatial distance from the center of the positive electrode, cm

\( y \) spatial distance from the nickel substrate surface, cm

\( y_0 \) radius of the nickel substrate in cylindrical shape, cm

**Greek**

\( \alpha_{Cd} \) anodic transfer coefficient for reaction \( i \)

\( \alpha_{Cd} \) cathodic transfer coefficient for reaction \( i \)

\( \beta \) tortuosity factor associated to the porous solid material in the negative electrode

\( \epsilon_{Cd} \) porosity of the nickel substrate in the positive electrode

\( \epsilon_{Cd} \) porosity of the substrate in the negative electrode

\( \epsilon_{Cd} \) porosity of the positive electrode

\( \epsilon_{Cd} \) porosity of the separator with a 90% saturation level or wetability

\( \epsilon_{Cd} \) porosity of the negative electrode

\( \epsilon_{Cd,act} \) porosity of the negative at fully charged state

\( \epsilon_{Cd,ref} \) porosity of the negative at fully discharged state

\( \theta_{Cd} \) potential in the solid phase, V

\( \theta_{Cd} \) potential in the liquid phase, V

\( \theta_{Cd} \) potential in the nickel substrate, V

\( \eta \) tortuosity factor associated with the porous positive electrode

\( \eta \) tortuosity factor associated with the porous separator

\( \eta \) tortuosity factor associated to the porous negative electrode

\( \kappa \) electrolyte conductivity, S cm \(^{-1} \)

\( \kappa \) state of charge of the negative electrode

\( \rho \) density of species \( i \), g \( \text{cm}^{-3} \)

\( \sigma_{Cd} \) conductivity of the solid material in the negative electrode, S cm \(^{-1} \)

\( \sigma_{Cd} \) conductivity of the active material in the positive electrode, S cm \(^{-1} \)

\( \tau \) exponent for the local state of charge of the negative electrode included in the kinetic expressions defined in Eq. 42 and 43

**REFERENCES**


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Doped PrMnO₃ Perovskite Oxide as a New Cathode of Solid Oxide Fuel Cells for Low Temperature Operation

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Department of Applied Chemistry, Faculty of Engineering, Oita University, Dannoharu 700, Oita 870-11, Japan

ABSTRACT

Cathodic overpotentials of LnₓSrₙ₋ₓMnO₃ (Ln = La, Pr, Nd, Sm, Gd, Tb, and Y) were studied for a new cathode of solid oxide fuel cell (SOFC). Cathodic overpotentials as well as the electrical conductivity strongly depended on the rare earth cations used for the A sites of perovskite oxide. Strontium-doped PrMnO₃ exhibited the highest electrical conductivity among the examined perovskite oxide containing Mn for B sites. Moreover, overpotentials of Sr-doped PrMnO₃ cathode maintained low values in spite of decreasing the operating temperature. Consequently, almost the same power density of SOFC with La₀.₆Sr₀.₄MnO₃ cathode can be obtained at about 100 K lower operating temperature by using Sr-doped PrMnO₃ as the cathode. The overpotentials and electrical conductivity decreased and increased with increasing the amount of Sr dopant in PrMnO₃, respectively, and the lowest overpotential was attained at x = 0.4 in Pr₁₋ₓSrₓMnO₃. Comparing with La₀.₆Sr₀.₄MnO₃ oxide, the reactivity of Pr₁₋ₓSrₓMnO₃ with Y₂O₃-stabilized ZrO₂ is much less than that of La₀.₆Sr₀.₄MnO₃, and furthermore, the matching of thermal expansion of Pr₁₋ₓSrₓMnO₃ with Y₂O₃-ZrO₂ was satisfactorily high. Therefore, perovskite oxide of Pr₁₋ₓSrₓMnO₃ has a great possibility of the cathode materials for decreasing the operating temperature of solid oxide fuel cells.

Introduction

Solid oxide fuel cell (SOFC) is a new electric power generation system with less emission of pollutant, low noise, and high energy conversion efficiency. In particular, it is reported that the energy conversion efficiency is attained as high as 90% by combining with the heat recovery and steam turbine system. Furthermore, the steam reforming of fuels such as methane can directly proceed on the anode of SOFC, since the operating temperature is high. Decreases in the cost per unit electric power generated and the enhancement of reliability as a generation system are the current subjects for the practical application of SOFC. Although the operation of SOFC is generally studied at 1273 K, the advantages of SOFC listed are obtained by operating the temperature above 973 K and moreover, the rate of chemical reaction at the electrode decreases remarkably with decreasing operating temperature, and consequently, the overpotential of electrode becomes the main cause for the voltage drops of cell when the cell is operated in the low temperature range. On the other hand, the apparent activation energy of the La₀.₆Sr₀.₄MnO₃ cathode which was estimated from the temperature dependence of overpotential is 74 kJ/mol, which is larger than that of Ni anode, 64 kJ/mol. Therefore, it is expected that the decreases in the voltage drops due to the overpotentials of electrode, particularly, cathode are of importance for decreasing the operating temperature of SOFC without decreasing the power density. Perovskite type oxides of Sr-doped LaMnO₃ (M = Mn, Co, Cu, Fe) have been studied as cathode materials; however, these cathode oxides except for doped LaCoO₃ were examined at the operating temperature of 1273 K. The doped LaCoO₃ oxide is studied as a cathode material for SOFC operating at intermediate temperature, while there are many difficulties for the application of LaCoO₃ for the cathode of SOFC, such as high overpotentials for LaCoO₃ cathode. In our previous study, we investigated the effects of rare earth cations in the A site upon the cathodic overpotential of perovskite-type oxide containing Mn for B site cations, and it was found that A site cations have a great influence on the cathodic property of perovskite oxide. In the present study, the effects of A site cations as well as the dopant for A site on the cathodic property were studied in further detail for the development of a new cathode with low overpotential in a low temperature region.

Experimental

Perovskite-type oxide of LnₓSrₙ₋ₓMnO₃ (Ln = La, Pr, Nd, Sm, Gd, Tb, and Y) was prepared by the evaporation to dryness of the calculated amount of aqueous solutions of commercial Ln₂O₃ (99.99% pure), Sr(NO₃)₂, and Mn(CH₃COO)₂. The consequently obtained powders were calcined at 1473 K for 3 h and then applied to one face of YSZ disk (5 mm in diameter) as a cathode. YSZ disks...