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A Mathematical Model of the Self-Discharge of a Ni-H$_2$ Battery

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ABSTRACT

A simple mathematical model is presented and used to characterize the self-discharge of a nickel oxyhydroxide (NiOOH) electrode in a hydrogen environment. This model includes diffusion of dissolved hydrogen in an electrolyte film which covers a flooded electrode, electrochemical oxidation of hydrogen, reduction of nickel oxyhydroxide, and changes of surface area and of porosity of the electrode during the self-discharge process. Although the self-discharge process is complicated, the predictions of the model are consistent with experimental results reported in the literature, which include linear relationships between the logarithm of hydrogen pressure and time and between the logarithm of the capacity and continued film growth.

It is a commonly known that the self-discharge rate of a Ni-H$_2$ battery is many times higher than that of other batteries which use a NiOOH/Ni(OH)$_2$ electrode as the positive electrode, such as Ni-Cd, Ni-Fe, Ni-Zn, etc. This high self-discharge has imposed limits on applications of this battery, a problem which needs to be overcome. Previous investigations (1-5) into this area have contributed significantly to understanding of the self-discharge process, but discrepancies in interpretation of the phenomena exist from different experiments. Markin and Dell (3) reported that the diffusion of dissolved hydrogen has a significant effect on the self-discharge rate. They demonstrated that the self-discharge rate was substantially decreased when the nickel electrode was fully immersed in the electrolyte. The microcalorimetric measurements by Mao et al. (6) also showed such an effect of the electrolyte. However, Holleck (1) suggested that some kind of an interface reaction is the controlling step, because his theoretical calculation indicated that the self-discharge rate under diffusion control would be two orders of magnitude higher than that experimentally measured. Holleck's view on the self-discharge process was shared by many researchers in the Ni-H$_2$ battery community. That is, the self-discharge is a kinetically controlled process. However, the mechanism of hydrogen oxidation is far from being well understood. There are few investigations reported on this subject.

$^*$ Electrochemical Society Active Member.
of undischarged NiOOH in the battery, with little attention being paid to the mechanism. By measuring the heat generation rate of β-NiOOH powder as well as a mixture of β-NiOOH and pure nickel powders in a hydrogen environment, Lim et al. (4) concluded that the mechanism of hydrogen oxidation is direct chemical reaction between hydrogen and nickel oxide material. More work is needed to characterize the self-discharge of a nickel electrode in hydrogen environment and to determine the mechanism. In this work, a simple mathematical model is presented to simulate the self-discharge process. The objective of this work is to gain a better understanding of the process so that an effective means can be taken to reduce the self-discharge rate.

Since the self-discharge always results in a corresponding drop of the hydrogen pressure in the cell, the overall reaction may be written as

\[
H_2 + 2\text{NiOOH} \rightarrow 2\text{Ni(OH)}_2
\]

This reaction involves the transfer of two moles of electrons from \(H_2\) to two moles of \(Ni^{2+}\). It is possible that this reaction occurs via two electrochemical reactions as follows:

\[
\begin{align*}
H_2 + 2 OH^- - 2e^- & \rightarrow 2H_2O \\
2\text{NiOOH} + 2H_2O + 2e^- & \rightarrow 2\text{Ni(OH)}_2 + 2OH^- 
\end{align*}
\]

According to reaction [3], the reduction of nickel oxyhydroxide will occur regardless of the presence of hydrogen if the electrode potential is below the equilibrium potential of \(\text{NiOOH}/\text{Ni(OH)}_2\). According to reaction [2], the oxidation of hydrogen does not depend on the availability of NiOOH if the electrode potential is high enough for hydrogen oxidation.

If the self-discharge process is due to a chemical reaction between hydrogen and NiOOH as shown in reaction [1], the local reaction rate in the nickel electrode would depend on the local hydrogen concentration and the local amount of NiOOH. The electrode potential would not affect the reaction rate, even though the potential of the electrode would change with the ratio of the amount of NiOOH to Ni(OH)_2 in the electrode. This chemical mechanism would be limited only to direct reaction between hydrogen and nickel oxyhydroxide; consequently, the local hydrogen oxidation rate would be exactly equal to the local reduction rate of nickel oxyhydroxide. If the self-discharge occurs electrochemically as shown by reactions [2] and [3], the local reaction rates of reactions [2] and [3] would depend on the local dissolved hydrogen concentration, the state of charge of the nickel electrode, and the electrode potential. The measured potential of the nickel oxyhydroxide electrode would be a mixed potential balanced by the polarizations of reactions [2] and [3] under the constraint of zero total current, depending on state of charge, self-discharge rate, and the reversibility of reaction [2] and [3]. In this work, the electrochemical mechanism is assumed to apply.

**Mathematical Model**

In the model presented here, the self-discharge process consists of the following steps (see Fig. 1). Hydrogen gas dissolves into the electrolyte and diffuses to the nickel electrode, where it is oxidized to form \(H_2O\) with \(OH^-\). The nickel electrode is flooded and covered by a layer of electrolyte. Since the electrolyte is highly concentrated with potassium hydroxide (about 26-31 weight percent KOH), the solubility of hydrogen gas is small (about \(10^{-4} M/\text{atm}\)). On the other hand, the self-discharge rate is also known to be small, which should not cause an appreciable change in KOH concentration. Therefore, the transport of dissolved hydrogen can be considered to be simple diffusion according to Fick's law

\[
\frac{\partial C_{H_2}}{\partial t} = \frac{D_{H_2}}{\varepsilon} \frac{\partial}{\partial x} \left( \varepsilon \frac{\partial C_{H_2}}{\partial x} \right)
\]

where \(\varepsilon\) is the porosity of this electrolyte region which could represent the separator of the battery, and \(D_{H_2}\) is the diffusion coefficient of dissolved hydrogen in the electrolyte. This dissolved hydrogen is consumed by reaction [2] within the electrode. By measuring the short-circuit currents between the \(\text{NiOOH}/\text{Ni(OH)}_2\) electrode and various other electrodes in hydrogen and argon environments, respectively, Lim concluded that the hydrogen oxidation occurs predominantly on the \(\text{NiOOH}/\text{Ni(OH)}_2\) material. Mao and White (8) measured hydrogen oxidation currents at a \(\text{NiOOH}/\text{Ni(OH)}_2\) electrode and a bare Ni sinter electrode at constant potentials, and found that the hydrogen oxidation current on a bare nickel electrode is much smaller than that on the \(\text{NiOOH}/\text{Ni(OH)}_2\) electrode. Therefore, it seems reasonable to assume that the hydrogen oxidation process occurs in the nickel electrode on the \(\text{NiOOH}/\text{Ni(OH)}_2\). A mass balance for the dissolved hydrogen in the electrode is given by

\[
\frac{\partial C_{H_2}}{\partial t} = \frac{\partial}{\partial x} \left( \varepsilon D_{H_2} \frac{\partial C_{H_2}}{\partial x} - \frac{i_1}{2F} \right)
\]

where \(i_1\) is the transfer current per unit volume of the electrode due to reaction [5], and can be expressed by

\[
i_1 = i_{t_1} \alpha_1 \left( \frac{C_{H_2}}{C_{\text{NiOOH}}} \right)^{\frac{\rho}{\varepsilon}} \exp \left[ \frac{\alpha_1 F}{R T} (E - E_{t_1}) \right]
\]

where \(i_{t_1}\) is the exchange current density for reaction [2], and \(E_{t_1}\) is the equilibrium potential of reaction [2] at a reference condition (e.g., at the initial hydrogen pressure). Since the electrode potential deviates far from the hydrogen equilibrium potential, the cathodic part of reaction [2] has been neglected.

Because nickel oxyhydroxide is continuously converted into less dense nickel hydroxide, the electrode becomes less porous, and consequently, the path for hydrogen diffusion in the electrode becomes narrower. The rate of change in the local porosity of the electrode can be calculated from the change in the material densities and the local self-discharge rate

\[
\frac{\partial \varepsilon}{\partial t} = i_{t_2} \left( \frac{M_{\text{NiOOH}}}{\rho_{\text{NiOOH}}} - \frac{M_{\text{Ni(OH)}_2}}{\rho_{\text{Ni(OH)}_2}} \right)
\]

where \(M_{\text{NiOOH}}, M_{\text{Ni(OH)}_2}, \rho_{\text{NiOOH}}\), and \(\rho_{\text{Ni(OH)}_2}\) are the molecular weights and the densities of nickel hydroxide and nickel oxyhydroxide, respectively. The symbol \(i_{t_2}\) is the local transfer current per unit volume of the electrode due to reaction [3], and can be expressed by a modified Butler-Volmer equation (9).
i_2 = i_{o2}a_{\text{max}}x_{\text{NiOOH}}^{1-x_{\text{NiOOH}}} \exp \left[ \frac{\beta F}{RT} (E - E_{2,\text{s}}) \right] \\
- \exp \left[ - \frac{\beta F}{RT} (E - E_{2,\text{s}}) \right] \right] \tag{8}

where \(a_{\text{max}}\) is the nickel oxyhydroxide specific surface area when the electrode is fully charged, and \(E_{2,\text{s}}\) is the equilibrium potential for reaction [3]. The mixing reaction between NiOOH and Ni(OH)\(_2\) via proton diffusion is probably much faster than the self-discharge; consequently, the solid NiOOH/Ni(OH)\(_2\) in the electrode is treated here as a homogeneous solid solution. That is, the equilibrium electrode potential for reaction [3] is given by the Nernst equation (10, 11)

\[ E_{2,\text{o}} = E_{2,\text{s}} + \frac{RT}{F} \ln \left( \frac{x_{\text{NiOOH}}}{x_{\text{Ni(OH)2}}} \right) \tag{9} \]

where \(x_{\text{NiOOH}}\) and \(x_{\text{Ni(OH)2}}\) represent the mole fractions of NiOOH and Ni(OH)\(_2\), respectively, in the solid solution of the nickel electrode; \(E_{2,\text{s}}\) = \(E_{\text{f}} - (RT/F) \ln [\text{OH}^-]\) with [OH\(^-\)] assumed to be constant during the self-discharge (8 M here); \(Q\) represents the discharged capacity per unit volume of the electrode; and \(Q_{\text{max}}\) is the total capacity per unit volume. To maintain a charge balance, the rate of a change in the local discharged capacity must be equal to the local transfer current due to reaction [3]

\[ \sigma \frac{dQ}{dt} = -i_2 \tag{10} \]

When the local transfer currents, \(i_1\) and \(i_2\), differ in magnitude from each other, there must be a current flow in the solid phase along the electrode. Ohm's law governs such a current flow

\[ \sigma \frac{dE}{dx} = -l \tag{11} \]

The rate of a change of the current density \(l\) with position must be equal to the sum of the local transfer currents, which yields

\[ -\sigma \frac{d^2E}{dx^2} = i_1 + i_2 \tag{12} \]

**Boundary conditions.**—Hydrogen gas is assumed to be in equilibrium with dissolved hydrogen at the interface between the electrolyte and the gas phase \( (x = 0) \). The dissolved hydrogen diffuses into the bulk electrolyte and into the nickel electrode. The dissolution rate from the gas is equal to the diffusion rate in the electrolyte at the interface. Under these conditions, the concentration of dissolved hydrogen satisfies the following equation at this boundary \( (x = 0) \), see Appendix for the derivation

\[ \frac{LQ_{\text{max}}}{2PF_{\text{H}_2}H} \frac{\partial C_{\text{H}_2}}{\partial t} \bigg|_{x = 0} = -D_{\text{H}_2} \frac{\partial C_{\text{H}_2}}{\partial x} \bigg|_{x = 0} \tag{13} \]

where \(L\) is the thickness of the electrode, \(P_{\text{H}_2}\) is the initial hydrogen pressure, \(H\) represents Henry's constant, and \(e\) is the fraction of excess hydrogen in the cell.

At the interface between the electrolyte and the electrode \( (x = x_i) \), the flux of dissolved hydrogen must be continuous. That is, the flux evaluated from the electrolyte side should be equal to that from the electrode side

\[ D_{\text{H}_2} \frac{\partial C_{\text{H}_2}}{\partial x} \bigg|_{x = 0} = D_{\text{H}_2} \frac{\partial C_{\text{H}_2}}{\partial x} \bigg|_{x = x_i} \tag{14} \]

Since electrical current in the electrode solid phase does not flow into the electrolyte layer near the electrode \( (0 \leq x \leq x_i) \), the derivative of the electrode potential must be zero at this interface

...
these equations subjected to the specific boundary and initial conditions are obtained, other variables such as the capacity remaining (C.R.), self-discharge rate (R~), and hydrogen pressure (P_{H_2}) in the battery can be calculated using the following equations

\[ P_{H_2} = C_{H_2}(0, t)/H \]  
\[ Q_{\text{max}} = \frac{1}{x_{\text{s}} - x_{\text{L}}} \int_{x_{\text{L}}}^{x_{\text{s}}} Q dx \]  
\[ \text{C.R.} = \left( \frac{Q_x}{Q_{\text{max}}} \right) \times 100 \]  
\[ R_{\text{H}_2} = - \int_{x_{\text{L}}}^{x_{\text{s}}} i dx = \int_{x_{\text{L}}}^{x_{\text{s}}} \left( \frac{\partial C_{H_2}}{\partial x} \right)_{x_{\text{s}}} dx \]

After some preliminary computations, it was found that the concentration profile of dissolved hydrogen in the electrolyte layer is essentially linear. To simplify the computation and save computer time, Eq. [4] can be dropped by using a linear relation for \( C_2 \) in the electrolyte layer and modifying the boundary condition at \( x = x_{\text{s}} \) (see Appendix A).

\[ -D_{H_2} e^{-\frac{1}{x_{\text{s}} - x_{\text{L}}} [C_{H_2}(x, t) - C_{H_2}(0, t - \Delta t)]} = -D_{H_2} e^{-\frac{\partial C_{H_2}}{\partial x}} \]

The governing equations and those for the boundary conditions were written in finite difference form using central and implicit backward differences in the spatial and time coordinates, respectively, and solved using the algorithm developed by Newman (12).

**Model Predictions and Discussion**

Predicted electrode potentials as a function of time are presented in Fig. 2 for different values of the exchange current density for hydrogen oxidation. As expected, the electrode potential changes rapidly in an early stage of the self-discharge, decreases slowly for a certain period, and finally, drops sharply when the electrode has almost lost all its capacity. The value of the exchange current density for hydrogen oxidation has a significant effect on the predicted electrode potential. For example, by increasing the exchange current density by one order of magnitude, the time for the loss of total capacity is reduced by about 200 h, and the electrode potential is lowered significantly. In an actual battery, hydrogen oxidation is a slow process which may consist of many steps and the exchange current density may be close to that for the slowest case in Fig. 2. A typical value of the self-discharge rate for a Ni-H\(_2\) battery was reported to be about 10% of its capacity per day (4), which is equivalent to 0.1 mA/cm\(^2\) for an electrode with a capacity of 24 mAh/cm\(^2\). Assuming that the electrode thickness is 0.08 cm and the concentration of dissolved hydrogen is the same in the electrode as that at the interface between the electrolyte and the gas phase, the exchange current density is estimated to be \(2.17 \times 10^{-10}\) A/cm\(^2\) by using the parameters in Table I and solving Eq. [22] for \( i_{\text{t1}} \) at an electrode potential of 0.4 V

\[ I = \frac{L}{i_{\text{t1}}} \]

where \( I \) represents the self-discharge rate in A/cm\(^2\), \( L \) is the thickness of the electrode, and \( i_{\text{t1}} \) is the transfer current for the reduction of nickel oxyhydroxide and the capacity remaining is complicated in the mathematical model, the predicted self-discharge rate varies apparently linearly with the capacity remaining for certain portions of the curves, giving a first-order reaction with respect to the capacity remaining, a typical behavior of the self-discharge process as reported in literature (5, 14). The predicted hydrogen pressures as a function of time for various excess amounts of hydrogen are presented in Fig. 4(a)-(c), which are plotted in the same way as those previously reported for experimental results (1, 13). Visual inspection of Fig. 4(a) reveals that the logarithm of hydrogen pressure does not depend linearly on time. However, when the residual pressure (see List of Symbols for its definition) is subtracted from the total pressure, a plot of the logarithm of the hydrogen pressure difference vs. time shows a straight line for a certain period of time [see Fig. 4(b)]. Therefore, the linearity in the relationship between the logarithm of hydrogen pressure and time depends on the residual pressure. The self-discharge behavior is often characterized by the feature that the hydrogen pressure decreases linearly with the square root of time for approximately the first 50 h (13). Figure 4(c) shows such a linear behavior, except for late stages of the self-discharge and for the first few hours. The initial deviation from the linear behavior was observed by Lim (7). Figure 4(b) indicates that the more excess hydrogen is present, the faster the hydrogen pressure drops. This is because the self-discharge rate is higher when a large amount of hydrogen is present.

The logarithm of the predicted capacity remaining also has an approximately linear relationship with time, as shown in Fig. 5, which is qualitatively consistent with the experimental results reported by Stockel (14). However, it should be noted that this behavior of the self-discharge does not agree with the linear relationship between the logarithm of absolute hydrogen pressure and time reported by Holleck (1). According to the linear relation in Fig. 5, the self-discharge rate can be expressed simply by
where \( Q_{\text{max}} - Q \) represents the undischarged capacity, and \( k \) is the slope of the curve. Assuming an ideal gas for hydrogen, the capacity remaining can be expressed in terms of the hydrogen pressure

\[
\frac{\partial}{\partial t} (Q_{\text{max}} - Q) = k(Q_{\text{max}} - Q) \tag{23}
\]

where \( P_{\text{max}} - P_{\text{res}} \) is the residual pressure, and \( A \) is a proportional constant. Substitution of Eq. (24) into (23) yields

\[
\frac{\partial P_{\text{H}_2}}{\partial t} = k(P_{\text{H}_2} - P_{\text{res}}) \tag{25}
\]

Obviously, the logarithm of absolute hydrogen pressure is not linearly proportional to time, but the logarithm of the pressure difference between the absolute value and the residual pressure has a linear behavior. Figure 5 also indicates that the transport property of dissolved hydrogen has a significant effect on the self-discharge rate. The capacity remaining decreases more slowly for the smaller diffusion coefficient.

Figure 6 presents the predicted self-discharge rate as a function of time for different thicknesses of the electrolyte layer on the electrode. As expected, the logarithm of the self-discharge rate decreases linearly with time. The thickness of the electrolyte layer slightly affects the self-discharge rate. The self-discharge rate decreases more rapidly for a thin electrolyte layer than a thick electrolyte layer, because the former enables dissolved hydrogen to diffuse quickly to the electrode, resulting in a higher self-discharge rate initially. However, when the self-discharge rate becomes small, the reaction becomes more kinetically controlled, and consequently, the self-discharge rate becomes smaller for the thin electrolyte layer than for a thick electrolyte layer, because in the latter there is more hydrogen present in the cell.

The self-discharge rate for a nickel electrode can be directly determined by measuring the heat generation rate of the electrode in a hydrogen environment. Mao et al. (6) did
such measurements with a microcalorimeter under constant hydrogen pressures, and found that the self-discharge rate can be fitted with a simple equation

$$R_t = a + b \exp(kt)$$

where $a$, $b$, and $k$ are constant, and their values depend on experimental conditions such as constant hydrogen pressure and electrode immersion state in the electrolyte. To determine whether the model presented in this work can predict the self-discharge behavior as observed in the microcalorimetric experiments, the flux boundary condition (Eq. [13]) was changed to a fixed boundary condition. That is

$$C_{H_2,x=0} = H P_{H_2}$$

The curves predicted from the model presented here and that given by Eq. [26] are presented in Fig. 7, where $a = 0.1439$ mA/cm$^2$-s, $b = 0.0939$ mA/cm$^2$-s, and $k = 0.2009$ h$^{-1}$. It can be seen that these two curves match well with each other. This means that the self-discharge rate as a function of time as measured by a microcalorimeter is of the same shape as that predicted by the model presented here.

It is often thought that the concentration gradient of dissolved hydrogen is minimal, and that the diffusion of dissolved hydrogen would affect the self-discharge rate because the self-discharge rate is small. However, the predicted concentration profile for dissolved hydrogen reveals a profound gradient, as shown in Fig. 8(a). This result is directly attributed to a small solubility of hydrogen gas in the concentrated alkaline solution and a small diffusion coefficient of dissolved hydrogen. Under hydrogen diffusion control, the maximum diffusion rate across an electrolyte layer of 0.01 cm is estimated to be 0.182 mA/cm$^2$ at a hydrogen pressure of 50 atm. This value is higher by one order of magnitude less than that corresponding to 10% capacity loss per day. Therefore, the diffusion of dissolved hydrogen still controls partially the self-discharge rate, particularly at early stages of the self-discharge process. Although Fig. 8(a) also shows that the concentration profile comes almost flat when the electrode looses nearly the entire capacity, the self-discharge rate is very small at this state of charge and does not represent the overall self-discharge rate. Contrary to the concentration profile of dissolved hydrogen, the porosity distribution is uniform throughout the electrode, as shown in Fig. 8(b). Since a uniform initial porosity was assumed, and the electrode is highly conductive, the driving force for the reduction of nickel oxyhydroxide remains constant along the electrode, resulting in a uniform transfer current for the reaction.

Figure 9 shows the distribution of the transfer current for hydrogen oxidation in the electrode. It can be seen that the oxidation of dissolved hydrogen takes place predominantly near the front side of the electrode, initially, and penetrates gradually into the electrode. The transfer current distribution becomes flat when the transfer current becomes small and the electrode has lost most of its capacity.

**Conclusions**

A simple mathematical model has been presented and used to predict the self-discharge behavior of a Ni-H$_2$ battery. The model predictions are consistent qualitatively with experimental results reported in the literature. These include linear relationships between time and the logarithm of the self-discharge rate, the logarithm of the capacity remaining, and the square root of hydrogen pressure. Since some parameters such as the thickness of the electrolyte layer ($x_e$) and the effective specific electrode sur-
face area are difficult to determine, no attempt was made to fit the model predictions to any experimental data. Comparisons between the model predictions and experimental data are limited to qualitative agreement.

The concentration gradient of dissolved hydrogen in the electrolyte layer and electrode is large, particularly at an early stage of the self-discharge process, even though the self-discharge rate is small, because the hydrogen solubility and the diffusion coefficient of dissolved hydrogen are small. The thickness of an electrolyte layer on the electrode does not significantly affect the overall self-discharge rate. Any means which can reduce the diffusion of dissolved hydrogen can reduce the self-discharge rate, particularly for electrodes at high states of charge. The dependence of the logarithm of hydrogen pressure on time is apparently not linear, but the logarithm of hydrogen pressure minus a residual pressure shows a linear relation with time. Such behavior is consistent with other features of the self-discharge process, such as the relation between the capacity remaining and time.

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APPENDIX

Derivation of the Boundary Conditions at \( x = 0 \) and \( x = x_s \)

Hydrogen gas dissolves into the electrolyte at the interface between the electrolyte and gas phase (at \( x = 0 \)), and the consumption rate of hydrogen gas must be equal to the hydrogen diffusion rate at the interface multiplied by the total area of the interface. Assuming that dissolved hydrogen is in equilibrium with hydrogen gas at this interface, and that the gas is ideal, the following equations are valid

\[
\begin{align*}
\frac{\partial n_{\text{H}_2}}{\partial t} &= -S \frac{V P_{\text{H}_2}}{R T} C_{\text{H}_2}(x_s, t) \\
\frac{\partial C_{\text{H}_2}}{\partial x} |_{x=0} &= 0
\end{align*}
\]

Substituting Eq. [A-3] and [A-2] into [A-1] to eliminate \( n_{\text{H}_2} \)

\[
\frac{V}{S} \frac{1}{R T} \frac{\partial C_{\text{H}_2}}{\partial t} = -D_{\text{H}_2} \frac{\partial C_{\text{H}_2}}{\partial x} \]

Although the actual volume of hydrogen gas is unknown, the ratio of \( V \) to \( S \) can be eliminated from Eq. [A-4] using the initial material balance as follows

\[
n_{\text{H}_2} = \frac{V P_{\text{H}_2}}{R T} = (1 + ex) S \frac{Q_{\text{max}} L}{2F} \]

where \( ex \) represents the fraction of the excess amount of hydrogen present in the cell. Substitution of Eq. [A-6] into [A-4] yields the boundary condition at \( x = 0 \)

\[
- \left[ (1 + ex) \frac{L Q_{\text{max}}}{2 F P_{\text{H}_2} H} \right] \frac{\partial C_{\text{H}_2}}{\partial t} |_{x=0} = -D_{\text{H}_2} \frac{\partial C_{\text{H}_2}}{\partial x} |_{x=0} \]

If the concentration profile is linear in the electrolyte region, and the derivative of the concentration with respect to time is expressed in backward difference form with a time step size of \( \delta_t \), one obtains the following equations

\[
\begin{align*}
\frac{\partial C_{\text{H}_2}(x_s, t) - C_{\text{H}_2}(0, t)}{\partial \delta_t} &= \frac{C_{\text{H}_2}(0, t) - C_{\text{H}_2}(0, t - \delta_t)}{\delta_t} \quad \text{[A-8]} \\
C_{\text{H}_2}(0, t) - C_{\text{H}_2}(0, t - \delta_t) &= \frac{\delta_t b_t}{x_s} (C_{\text{H}_2}(x_s, t) - C_{\text{H}_2}(0, t)) \\
\text{where} \\
b_t &= \frac{D_{\text{H}_2} \delta_t}{(1 + ex) \frac{L Q_{\text{max}}}{2 F P_{\text{H}_2} H}} \quad \text{[A-11]}
\end{align*}
\]

Solving Eq. [A-10] for \( C_{\text{H}_2}(0, t) \) gives

\[
C_{\text{H}_2}(x_s, t) - C_{\text{H}_2}(0, t) = \frac{b_t}{x_s} (C_{\text{H}_2}(0, t) - C_{\text{H}_2}(x_s, t)) \\
\text{[A-12]}
\]

At the boundary, \( x = x_s \), Eq. [A-14] can be expressed as

\[
-D_{\text{H}_2} \frac{\partial C_{\text{H}_2}}{\partial x} |_{x=x_s} = \frac{1}{x_s + \delta_t b_t} (C(x_s, t) - C(0, t)) \]

\[
\text{[A-13]}
\]

Substituting of Eq. [A-12] into [A-13] yields the boundary condition at \( x = x_s \)

\[
-D_{\text{H}_2} \frac{\partial C_{\text{H}_2}}{\partial x} |_{x=x_s} = \frac{1}{x_s + \delta_t b_t} (C(x_s, t) - C(0, t)) \]

\[
\text{[A-14]}
\]

LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>constant, A/cm(^2)-s</td>
</tr>
<tr>
<td>( a_{\text{max}} )</td>
<td>maximum electrode surface area per unit volume of the nickel electrode for the nickel oxide reduction, cm(^2)/cm(^3)</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>electrode surface area per unit volume of the nickel electrode for the hydrogen oxidation, cm(^2)/cm(^3)</td>
</tr>
<tr>
<td>( a_0 )</td>
<td>constant, A/cm(^2)-s</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>exchange current density for the nickel electrode for a given electrolyte, A/cm(^2)</td>
</tr>
<tr>
<td>( b )</td>
<td>constant, A/cm(^3)-s</td>
</tr>
<tr>
<td>( b_e )</td>
<td>intercalation coefficient, V</td>
</tr>
<tr>
<td>( b_f )</td>
<td>intercalation coefficient, V/C</td>
</tr>
<tr>
<td>( b_{\text{NiOOH}} )</td>
<td>the concentration of dissolved hydrogen ions, mol/cm(^3)</td>
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<tr>
<td>( b_{\text{NiOOH}} )</td>
<td>reference concentration of dissolved hydrogen, mol/cm(^3)</td>
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<tr>
<td>( D_{\text{H}_2} )</td>
<td>diffusion coefficient of dissolved hydrogen, cm(^2)/s</td>
</tr>
<tr>
<td>( E )</td>
<td>electrode potential (potential of the solid phase relative to the potential in the adjacent solution phase), V</td>
</tr>
<tr>
<td>( E_{\text{e}} )</td>
<td>initial electrode potential, V</td>
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<td>( E_{\text{e}} )</td>
<td>equilibrium potential of hydrogen oxidation at the nickel electrode for a given electrolyte, V</td>
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<tr>
<td>( E_{\text{e}} )</td>
<td>the nickel electrode potential at a given state of charge, V</td>
</tr>
<tr>
<td>( E_{\text{e}} )</td>
<td>the equilibrium nickel electrode potential at the standard condition, V</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday's constant, 96,487 C/equivalent</td>
</tr>
<tr>
<td>( H )</td>
<td>Henry's constant, mol/cm(^3)-atm</td>
</tr>
<tr>
<td>( i_1 )</td>
<td>current density relative to the projected area of the electrode in the solid phase of the electrode, A/cm(^2)</td>
</tr>
<tr>
<td>( i_{\text{H}_2} )</td>
<td>exchange current density for hydrogen oxidation evaluated at a reference hydrogen concentration, A/cm(^2)</td>
</tr>
<tr>
<td>( i_{\text{H}_2} )</td>
<td>exchange current density for the nickel electrode reaction, A/cm(^2)</td>
</tr>
<tr>
<td>( i_{\text{H}_2} )</td>
<td>local transfer current per unit volume of the electrode for hydrogen oxidation, A/cm(^3)</td>
</tr>
<tr>
<td>( i_{\text{H}_2} )</td>
<td>local transfer current per unit volume of the electrode for the reduction of nickel oxhydroxide, A/cm(^3)</td>
</tr>
<tr>
<td>( k )</td>
<td>constant, s(^{-1}) (Eq. [23]), s(^{-1}) (Eq. [26])</td>
</tr>
<tr>
<td>( L_2 )</td>
<td>thickness of nickel oxhydroxide electrode</td>
</tr>
<tr>
<td>( M_{\text{NiOOH}} )</td>
<td>the molecular weight of NiOOH</td>
</tr>
<tr>
<td>( M_{\text{NiOOH}} )</td>
<td>the molecular weight of NiOOH</td>
</tr>
<tr>
<td>( n_{\text{H}_2} )</td>
<td>initial amount of hydrogen gas in the cell, mol</td>
</tr>
<tr>
<td>( p )</td>
<td>reaction order with respect to the concentration of dissolved hydrogen</td>
</tr>
</tbody>
</table>
Moreover, extremely complicated. Experimental evidence is given on strong interaction of I and I⁻-ions with the FeS² surface, via p → Fe: eg direct transition in pyrite can be used to determine precisely its flatband potential (VFB), even in the presence of EER and conventional electro- and photoelectrochemical techniques. The EER signal originating from the 3.13 eV bandgap states, probably associated with Fe³⁺S⁵⁻ lattice impurities, seem to determine the photovoltage limitations which shifts of about 50 mV toward negative potentials indicate that specific adsorption is stronger for I⁻ than for I- species. Complex formation with Fe²⁺ lattice ions generated by hole capture during anodic polarization or illumination. Small VFB also been able to show that dynamic VFB measurements are possible under situations where capacitance studies are ex-

Greek Letters

- \( e_1 \): transfer coefficient for hydrogen oxidation at the nickel electrode
- \( \beta_1 \): anodic transfer coefficient for the nickel oxyhydroxide reduction
- \( \xi \): cathodic transfer coefficient for the nickel oxyhydroxide reduction
- \( \delta_\text{st} \): step size in the time coordinate, s
- \( \varepsilon_1 \): initial porosity of the nickel electrode
- \( \varepsilon_2 \): local porosity of the nickel electrode
- \( \varepsilon_3 \): porosity of the electrolyte layer
- \( \xi \): exponential term to correct properly an change in the electrode surface area
- \( \rho_{\text{Ni(OH)}} \): density of nickel hydroxide, g/cm³
- \( \rho_{\text{NiOOH}} \): density of nickel oxyhydroxide (NiOOH), g/cm³
- \( \sigma \): conductivity of the nickel electrode, S/cm
- \( \tau \): exponential term to correct the effective hydrogen diffusion coefficient

REFERENCES


Reaction Mechanisms at the \( n\)-FeS₂/I Interface

An Electrolyte Electroreflectance Study

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ABSTRACT

Monocrystalline \( n\)-FeS₂ (pyrite) in contact with the I/I⁻ redox couple was studied by electrolyte electroreflectance (EER) and complex electrochemical techniques. The EER signal originating from the 3.13 eV \( p \rightarrow Fe: e_\gamma \) direct transition in pyrite can be used to determine precisely its flatband potential (VFB), even in the presence of a high concentration of bandgap surface states, which is typical for this semiconducting transition metal sulfide. We have also been able to show that dynamic VFB measurements are possible under situations where capacitance studies are extremely complicated. Experimental evidence is given on strong interaction of I and I⁻-ions with the FeS₂ surface, via complex formation with Fe²⁺ lattice ions generated by hole capture during anodic polarization or illumination. Small VFB shifts of about 50 mV toward negative potentials indicate that specific adsorption is stronger for I⁻ than for I⁺ species. Moreover, VFB shifts of more than 1 V towards negative values can also be observed under cathodic polarization. This behavior is correlated to surface accumulation of electrons which accompanies FeS₂ electroreduction. A comprehensive model for surface photoreactions is proposed. This takes into account the catalytic role of the semiconductor surface in kinetics of charge transfer reactions in electrolyte. Both the very positive VFB (high electronic affinity) and the high density of bandgap states, probably associated with FeS₂ lattice impurities, seem to determine the photovoltage limitations which are inherent to the FeS₂/I⁺ system.

Transition metal chalcogenides with d-band character are known to be characterized by a high density of surface states (1). Accumulation of electric charge is found with each surface transition metal, which may lead to drastic shifts of the flatband potential. This property makes the application of conventional electrochemical techniques for flatband determination (Mott-Schottky plots) questionable and frequently impossible. Since the understanding...