A Mathematical Model for the Galvanostatic Deposition of Nickel Hydroxide

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ABSTRACT

A mathematical model is presented for the galvanostatic deposition of Ni(OH)₂ films in stagnant Ni(NO₃)₂ solutions. The objective is to quantify the anomalous deposition behavior reported previously in which the utilization of the electrochemically generated OH⁻ species decreases drastically as the concentration of Ni(NO₃)₂ increases beyond 0.1 M. For example, as the Ni(NO₃)₂ concentration increased from 0.1 to 2.0 M, the deposition rate decreased by a factor of ten at 2.5 mA/cm². At this high ratio of concentration to current density, a comparison with Faraday's law indicates that only 10% of the OH⁻ species generated at the surface led to deposition. It has been proposed that the inefficient use of electrochemically generated OH⁻ species is due to the presence of Ni(OH)₄⁺ as an intermediate in the deposition process. As the bulk Ni(NO₃)₂ concentration increases, the concentration of Ni(OH)₄⁺ at the electrode surface increases. A high concentration of the intermediate results in an increase in the diffusion rate of the species away from the electrode surface and thus a decrease in the deposition rate. Here, this hypothesis is tested by developing a model which includes the generation of OH⁻ from the electrochemical reduction of nitrate to ammonia and the diffusion and migration of Ni²⁺, NO₃⁻, OH⁻, H⁺, and Ni(OH)₄⁺. The model predictions agree well with previously reported mass deposition data collected using an electrochemical quartz crystal microbalance at different currents and over a range of Ni(NO₃)₂ concentrations. The present work confirms the role that Ni(OH)₄⁺ plays in the deposition process and provides a fundamental framework for understanding the electrochemical impregnation of nickel electrodes.

Introduction

Electrochemical impregnation is one of the main processes for the production of nickel hydroxide electrodes, because it yields superior electrodes with longer life.¹ This process involves the electrochemical reduction of NO₃⁻ within a porous nickel sinter and the subsequent generation of OH⁻. Although any or all of reactions 1-1 through 1-5 shown in Table I could be involved, the primary result is the production of OH⁻, which may react further with Ni²⁺ species to form Ni(OH)₂, according to reaction 1-6. Recently, Streinz et al.² reported the anomalous deposition behavior of Ni(OH)₂ wherein they observed a drastic decrease in deposition rates as Ni(NO₃)₂ concentration increased from 0.1 to 2.0 M. They measured deposition rates for different currents and Ni(NO₃)₂ concentrations using an electrochemical quartz crystal microbalance (EQCM). In 2.0 M Ni(NO₃)₂ solutions, they observed only 10% utilization of the electrochemically generated OH⁻ species, as compared to almost 100% utilization in 0.1 M solutions at 2.5 mA/cm². They concluded that the diffusion of an intermediate, Ni(OH)₄⁺ species was responsible for this inefficiency. Baes and Mesmer³ also mention that for high Ni²⁺ concentrations (C_Ni²⁺ > 0.1 M), the Ni(OH)₂ species is formed predominantly. Based on these observations, Streinz et al.² postulated a two-step deposition mechanism shown by reactions 1-7 and 1-8. The deposition occurs at the surface of the electrode which is saturated in hydroxyl ions and where the pH is between 6.5 and 8. The pH at which deposition begins is a strong function of Ni(NO₃)₂ concentration, as shown in Fig. 1a.

Table I. Electrochemical and chemical reactions considered in the model. (All values correspond to standard conditions at 25°C.)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemical Equation</th>
<th>Standard Free Energy Change (kJ/mol)</th>
<th>Standard Entropy Change (J/kmol-K)</th>
<th>Standard Entropy Change (kJ/kmol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>NO₃⁻ + H₂O + 2e⁻ → NO₂⁻ + 2 OH⁻</td>
<td>-368.4</td>
<td>184.6</td>
<td>3.36</td>
</tr>
<tr>
<td>1-2</td>
<td>NO₃⁻ + 5H₂O + 6e⁻ → NH₄⁺ + 7 OH⁻</td>
<td>-1304.1</td>
<td>439.6</td>
<td>8.88</td>
</tr>
<tr>
<td>1-3</td>
<td>NO₃⁻ + H₂O + 2e⁻ → NH₃ + 4 OH⁻</td>
<td>-128.9</td>
<td>184.6</td>
<td>3.36</td>
</tr>
<tr>
<td>1-4</td>
<td>2NO₃⁻ + 3H₂O + 4e⁻ → NO₂⁻ + 6 OH⁻</td>
<td>-685.1</td>
<td>543.1</td>
<td>10.86</td>
</tr>
<tr>
<td>1-5</td>
<td>Ni²⁺ + OH⁻ → 1/4 Ni(OH)₄⁺</td>
<td>-48.4</td>
<td>-27.3</td>
<td>0.54</td>
</tr>
<tr>
<td>1-6</td>
<td>1/4 Ni(OH)₄⁺ + OH⁻ → Ni(OH)₂</td>
<td>-424.2</td>
<td>184.6</td>
<td>3.36</td>
</tr>
<tr>
<td>1-7</td>
<td>Ni(OH)₂ + OH⁻ + H⁺ → Ni(OH)₃⁺ + H₂O</td>
<td>-145.4</td>
<td>184.6</td>
<td>3.36</td>
</tr>
<tr>
<td>1-8</td>
<td>Ni(OH)₄⁺ + H₂O + Ni(OH)₂</td>
<td>-48.4</td>
<td>-27.3</td>
<td>0.54</td>
</tr>
<tr>
<td>1-9</td>
<td>K_p = 1.6 x 10⁻²² (mol/cm³)² (see Ref. 12)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1-10</td>
<td>K_p = 2.6 x 10⁻¹² (mol/cm³)²</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1-11</td>
<td>K_p = 3.3 x 10⁻¹¹ (mol/cm³)²</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1-12</td>
<td>K_p = 3.3 x 10⁻¹¹ (mol/cm³)²</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1-13</td>
<td>K_p = 1.38 x 10⁻¹⁰ mol/cm³</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1-14</td>
<td>K_p = 1.38 x 10⁻¹³ mol/cm³</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

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Footnotes:
¹ Equation 1-3 used in the model is a combination of 1-1 and 1-2.
² Calculated using K_p and reported value of log K_p = -27.32 from Ref. 9.
³ Calculated using K_p and K_1.

Figure 1a shows that pH affects the equilibrium distribution of nickel species for reactions 1-7 through 1-11. (The calculations used for this figure are discussed in Appendix A.) The pH at which Ni(OH)₂ forms decreases from 7.2 for 0.5 M Ni(NO₃)₂ to 6.8 for 4.0 M solutions. Figure 1a also shows that, in 4 M solutions, about 75% of the nickel exists as Ni(OH)₄⁺ prior to the deposition of Ni(OH)₂. This maximum occurs at pH 5.6, as shown in Fig. 1b. Figure 1a shows that at a pH less than 5.0 all the nickel exists as its divalent ion. These calculations are consistent with our measurements of the pH for various temperatures and concentrations of Ni(NO₃)₂ shown in Fig. 1b. (See Appendix B for a discussion of the experimental technique.)

Figure 1b shows that the pH of Ni(NO₃)₂ solutions drops from 3.75 for 0.5 M to 1.2 for 4.0 M at 25°C. A similar trend is also observed at higher temperatures. The change in pH is attributed to the generation of H⁺ mainly due to the formation of hydrolysis products like NiOH⁺ according to reaction 1-11. We calculate that, for 4.0 M solutions, about 2% of Ni²⁺ is bound to OH⁻ generated from the water equilibrium reaction, and this results in a pH of 1.2. However, this value is difficult to see on the scale in Fig. 1a. Note that a comparison of the equilibrium constants for reactions 1-10 and 1-7 indicates that the concentration of Ni(OH)₂ is small in the region where Ni(OH)₄⁺ exists.

The purpose of this paper is to test the hypothesis of Streinz et al.² by developing a model and comparing the predictions with their experimental results. Other workers have deposited films on planar electrodes but made no attempt to quantify the deposition process over a range of deposition conditions. For example, Cordoba-Torresi...
bulk can occur before deposition. A growing diffusion face with the growing film. The flux of the Ni\textsuperscript{4+} (OH)\textsuperscript{4+} predictions agree well with the mass-deposition data of paper considers the diffusion and migration of Ni\textsuperscript{2+}, NO\textsubscript{3}, chemical production of HNO\textsubscript{2}. The model developed in this single-step deposition of reaction I-6 and the electro-nitrate reduction using a rotating-disk assembly and films. Bernardi, et al. on the other hand, studied the kinetics of MacArthur postulated that proton diffusion was the rate-dominating process during the oxidation and reduction of films. Bernardi, on the other hand, studied the kinetics of nitrate reduction using a rotating-disk assembly and developed a model for Ni(OH)\textsubscript{2} film formation based on the single-step deposition of reaction 1-6 and the electrochemical production of HNO\textsubscript{2}. The model developed in this paper considers the diffusion and migration of Ni\textsuperscript{2+}, NO\textsubscript{3}, OH\textsuperscript{-}, H\textsuperscript{+}, and Ni\textsubscript{4+}(OH)\textsuperscript{4+} at a planar electrode. The model predictions agree well with the mass-deposition data of Streinz et al. for a range of current densities and Ni(NO\textsubscript{3})\textsubscript{2} concentrations.

Mathematical Model

Figure 2 shows the scheme of the EQCM electrode surface with the growing film. The flux of the Ni\textsubscript{4+}(OH)\textsuperscript{4+} species is directed away from the electrode surface, indicating that diffusion or migration of this species into the bulk can occur before deposition. A growing diffusion layer is characteristic of this experimental system, and this diffusion layer is approximately 100 times larger than the thickness of the deposit.

The equations that describe the deposition mechanism of nickel hydroxide are derived by considering Fig. 2 and the dilute-solution theory described by Newman. The dependent variables of interest are the five ionic species, numbered 1 to 5: Ni\textsuperscript{2+}, NO\textsubscript{3}, H\textsuperscript{+}, OH\textsuperscript{-}, and Ni\textsubscript{4+}(OH)\textsuperscript{4+}, and the solution potential, \( \Phi \). The assumptions used to model the conditions during EQCM experiments concerned with the growth of Ni(OH)\textsubscript{2} films are:

1. One-dimensional transport is considered in the direction normal to the surface of the electrode.
2. Dilute-solution theory applies.
3. The electrolyte is stagnant during deposition. Therefore, the flux of all species is purely due to diffusion and migration.
4. Isothermal conditions exist.
5. The thickness of the film is much smaller than that of the diffusion layer. Therefore, there is no spatial difference between the electrode surface where OH\textsuperscript{-} is produced and the front of the film where Ni(OH)\textsubscript{2} is deposited. The film is slightly porous to allow OH\textsuperscript{-} transport from the electrode to the deposition site.
6. The volume of the deposition bath is large relative to the electrode area so that the concentration of Ni(NO\textsubscript{3})\textsubscript{2} is assumed to remain constant during deposition.
7. The electrochemical reaction of nitrate reduction occurs according to the stoichiometry of reaction 1-3 and without nitrite or nitrous acid intermediates.
8. Deposition of Ni(OH)\textsubscript{2} occurs only at the electrode surface with no bulk precipitation. The film is assumed to be composed of pure Ni(OH)\textsubscript{2}.
9. The vertical length of the EQCM electrode is small so that natural convection is negligible.
10. Activity coefficient corrections to the equilibrium and solubility product constants are negligible.
11. The concentration of NH\textsubscript{3} is small, and NH\textsubscript{4} and nickel-ammonia complexes are not important.

The concentration of each ionic species is governed by the following material-balance equation

\[
\frac{\partial C_i}{\partial t} = -V \cdot N_i + R_i \quad (i = 1, 2, 3, 4, 5)
\]

where \( R_i \) denotes the net homogenous production of species \( i \) from all reactions. Therefore, \( R_i = 2r_i \) (i-species, j-reaction) where \( r_i \) refers to the homogenous production rate of species \( i \) in individual reactions. The flux of each species is given by

\[
N_i = -D_i \frac{\partial C_i}{\partial x} - \frac{\varepsilon_i D_i F C_i}{RT} \frac{\partial \Phi}{\partial x}
\]

and contains contributions from diffusion and migration only. The potential in the solution varies according to the electroneutrality condition

\[
\Sigma \varepsilon_i C_i = 0
\]
The homogenous reaction rate can be written explicitly for each species according to Eq. 4. The numbered subscripts in Eq. 4 refer to the specific reaction number in Table I.

\[
R_1 = r_{1,1} \quad R_2 = 0 \quad R_3 = r_{3,3} \quad R_4 = r_{4,1} + r_{4,5} \quad R_5 = r_{5,1}
\]

[4]

Equation 1 with \( i = 1 \) to 5 results in five material-balance expressions with species 1, 3, 4, and 5 each containing a homogenous reaction term. The unknown rates can be eliminated by combining the expressions in Eq. 1, suitably resulting in three equations. These three equations and two equilibrium expressions (Eq. 1-7 and 1-9) form the governing equations listed in Table II.A as Eq. II-7 through II-11.

Boundary conditions at the diffusion layer-electrolyte interface.—The boundary conditions far from the surface correspond to bulk conditions where the equilibrium relations are valid. Therefore, as shown in Eq. II-1 through II-6 of Table II.A, at \( x = \infty \). The initial conditions are

\[
C_{N2}^0 = C_{N2} \quad [II-1]
\]

\[
C_{NO3} = C_{NO3}^0 \quad [II-2]
\]

\[
C_{HI} = C_{HI}^0 \quad [II-3]
\]

\[
C_{OH} = C_{OH}^0 \quad [II-4]
\]

\[
K_{eq}C_{N2}C_{OH} = C_{NH4OH}^{1/4} \quad [II-5]
\]

\[
\phi = 0 \quad [II-6]
\]

where \( C_{N2}^0 \) is the bulk concentration of \( NO_2^- \) species and \( C_{HI}^0 \) is the concentration of \( H^+ \) corresponding to the experimentally measured pH at the specified bulk \( NO_3^- \) concentration.

Boundary conditions at the electrode surface.—The boundary conditions at the electrode surface depend on pH and whether deposition of \( Ni(OH)_2 \) occurs, as shown in Table II.B. Common to both sets are the equations corresponding to the \( NO_3^- \) flux and the acid/base and tetramer equilibria. The stoichiometry of Eq. 1-3 relates the flux of nitrate to the applied current. Similarly, the two equilibria...
where $A$ is the area of the electrode used in the experiments (see Ref. 2), $M_{Ni(OH)_{2}}$ refers to the molecular weight of nickel hydroxide, and $t$ refers to the time from the start of the experiment. The efficiency of the deposition process $e_{OH^-}$ (based on the utilization of $OH^-$ ions) can be calculated based on the ratio of the average deposition rate (left side of Eq. 8) to the rate calculated from Faraday’s law as

$$W_{Ni(OH)_{2}} = \frac{\int_{t}^{t'} e_{OH^-} A M_{Ni(OH)_{2}} \, dt}{16F}$$

It should be noted that the $9/16$ depends on assumption 7 and that a different, albeit similar, ratio exists if a reaction other than reaction I-3 occurs. This assumption is discussed in Ref. 2.

Initial conditions and physical property data.—Before the start of the experiment, it is assumed that bulk conditions exist throughout the diffusion layer. The initial conditions are the same as Eq. 5. Also, the model predictions require knowledge of physical properties of all species, and these have been summarized in Table III. Note that the solubility product was equaled, the second set of integration was restarted using Eq. 11-13 through 11-18. Once the solubility product was equaled, the second set of boundary conditions was used to recompute the variables. The accuracy was checked with 1001 points. The accuracy of the predictions was found to be in the third decimal place.

During the first time step, the technique used the set of boundary conditions which is valid for conditions prior to precipitation. The converged values of the concentrations were then used to check the solubility product criterion stated in Eq. 6. If the solubility product criterion was exceeded during the first time step, a smaller time step was used. Typically, the initial time step size was decreased by a factor of ten until the concentrations were less than those required for precipitation. Then the integration was restarted using Eq. 11 through 11-18. Once the solubility product was equaled, the second set of boundary conditions was used to recompute the variables. Therefore, at each time step, Eq. 6 was checked, and the appropriate set of conditions was used in the program.

Results and Discussion

The model was used to simulate the deposition conditions reported by Streinz et al. In contrast to the predictions and data shown in Fig. 1, their electrolyte consisted of various concentrations of $Ni(NO_{3})_{2}$ in a 50 v/o of ethanol and water. Their depositions were performed at constant current and at room temperature (23 to 25°C) on an EQCM. The electrode area was 0.2 cm², and the volume of the electrolyte was approximately 20 cm³. Thus, assumption 6 was valid even at 0.1 $M$ Ni(NO$_3$)$_2$, since only 0.87 $\mu$mol of Ni$^{2+}$ would be deposited in 300 s at 2.5 mA/cm² (assuming the
stochiometry of reaction 1-3 and 100% deposition efficiency. Likewise, the bulk concentration of H° would decrease by only 0.87 μmol after 300 s at 2.5 mA/cm², even if the deposition efficiency were 50%. Thus, even at the relatively high pH shown by 0.1 M Ni(NO₃)₂, the bulk pH of 3.5 remains almost constant. We present first the comparison of the model predictions with the experimental data, and then we use the model to explain the fundamental phenomena occurring during the experiments. As shown below, the model predictions are consistent with the observations in Ref. 2 and show that Ni^{2+} concentration has a pronounced effect on the deposition efficiencies at their reported current densities. It is shown that the deposition efficiency depends on the interaction of the electrochemical generation of OH°, the flux of OH° and Ni{OH}°, and the values of the equilibrium constant and solubility products.

Figure 3 shows that, at a low concentration of Ni(NO₃)₂ of 0.2 M, the rate of deposition (i.e., the slope of the mass gain vs. time) is constant and approximately proportional to the current density at all times. Note that the deposition efficiency for 0.2 M solutions determined using Eq. 8 is greater than 70% for all three current densities and that at this concentration the maximum Ni(OH)° concentration is only 0.013 M [i.e., 26% of the total nickel is in the form of Ni(OH)°]. It was observed that the deposition rate is not very sensitive to the value of the equilibrium constants and diffusion coefficients at these low concentrations and these relatively high current densities. Higher current densities increase deposition efficiency due to greater OH° generation, which causes precipitation to occur before the Ni(OH)° species can diffuse away from the surface.

Figure 4 shows a comparison of model predictions and EQCM data for various concentrations of Ni(NO₃)₂ at an applied current density of 2.5 mA/cm². As before, the model predicts a linear increase in mass at low concentrations. However, the rate of deposition is strongly dependent on the Ni(NO₃)₂ concentration and decreases with increasing Ni(NO₃)₂ concentration. The rates of deposition are in good agreement with the experimental values at low concentrations where efficiencies are high [100% for 0.1 M Ni(NO₃)₂], however, the model overpredicts the mass gain for 1 and 2 M Ni(NO₃)₂ concentrations for the parameters of Table III. With these parameters for 1.0 and 2.0 M solutions, the model predicts no deposition until 35 and 95 s, respectively. This delay is a result of an equilibrium concentration of the nickel tetramer species which is almost equal to 50% of the total nickel in solution (see Fig. 1a) prior to deposition. This relatively large tetramer concentration causes the model predictions to be very sensitive to the value of K°. For example, the predicted deposition rate in 1 M Ni(NO₃)₂ solutions could be changed from the 4.5 μg/min of Fig. 4 to 3.06 μg/min if K° was increased by 10% from that listed in Table III. Similarly, the predicted rate would increase from 4.5 μg/min to 4.62 μg/min if K° was decreased by 10% with the K° fixed at the value in Table III.

It must be noted that the diffusion coefficients, solubility product, and equilibrium constants in ethanol solutions are not available in the literature. Second, the effect of ethanol in the precipitation mechanism is not well understood. For these reasons, the equilibrium constant values were adjusted from those reported in the literature to those shown in Table III. This adjustment was done by comparing the model predictions and the data at 2.0 M and 2.5 mA/cm² without the aid of parameter-estimation techniques. Note that the predictions are very sensitive to changes in K values at these conditions. It must also be noted that these values have been obtained by assuming the diffusion coefficients of all species to be independent of solution concentration and equal to their dilute-solution values. The agreement can be considered adequate, since the primary objective of this paper is to explain the observable inefficiency based on the formation of this complex species.

Figure 5 shows the model predictions of the instantaneous rate of precipitation of Ni(OH)₂ at 2.5 mA/cm² for the concentrations of Fig. 4. For dilute solutions (0.2 M), deposition begins immediately, and the rate attains a constant value from the start of the experiment. For 1 M solutions, the rate is zero initially and then undergoes a step change, increases, and reaches a constant value in about 35 s. For the 2 M solutions, the step change occurs after about 95 s. The delay in the onset of precipitation is a result of the time required for the concentration of OH° at the surface to change from the bulk pH to that consistent with the K°. It should be noted that the boundary conditions at the electrode surface are changed at these times as we have described.

Figure 6a shows this delay and the model predictions of the pH change for a bulk concentration of 1 M Ni(NO₃)₂ at 2.5 mA/cm². From an initial value of 1.9, the pH at the electrode rises until it equals the required value for deposition. The pH corresponding to deposition of Ni(OH)₂ in 50 v/o ethanol is 7.35 for 1 M Ni(NO₃)₂ and occurs at 27 s, as shown in Fig. 6a. This figure also shows that the neutralization plane moves away from the electrode surface at a rate which decreases with time from an initial value of approximately 7 × 10⁻⁴ cm/s after 30 s. Note that for the case where a complexation reaction does not exist, the diffusion layer thickness should grow at a faster rate,
were obtained in 1 M Ni(NO₃)₂ at a current density of 2.5 mA/cm². Decreasing the Ni(NO₃)₂ concentration from 2 to 0.2 M causes a threefold increase in the rate. In dilute Ni(NO₃)₂, precipitation begins immediately, and the rate attains a constant value. In concentrated Ni(NO₃)₂, the rate is zero initially, then increases quickly, and finally attains a steady value.

This is a result of two competing phenomena: First, the steep concentration gradient for the movement of this intermediate species. Second, the bulk pH of 0.2 M Ni(NO₃)₂ is higher than that of 1 M Ni(NO₃)₂ (i.e., compare 3.5 vs. 1.9, as shown in Table III).

Figure 7 further illustrates the model predictions at 2.5 mA/cm² for two concentrations by comparing the values of \( N₁ \times 10^8 \), \( N₂ \times 4 \times 10^8 \), and \( r₄₉₅ \times 10^9 \) at \( x = 0 \). At 1 M Ni(NO₃)₂, the fluxes of Ni²⁺, Ni₄(OH)⁴⁺, and the rate of precipitation, \( rₚₚ \), are zero until about 13 s. At short times (\( t < 13 \) s), the electrochemically generated OH⁻ neutralizes the acidity of the solution, which raises the local pH as discussed previously. At 13 s, the fluxes become infinite and then quickly become stoichiometrically equal and opposite at \( \pm 3 \) mol/cm²-s until 27 s. Comparison with Fig. 6a shows that 13 s is the time after which the surface pH is constant and the time when the neutralization front begins to move away from the surface. Comparison of Fig. 7 and 6b shows that for 0.2 M Ni(NO₃)₂, the acidity is neutralized in less than 0.5 s. This short time corresponds to the nearly instantaneous start of deposition for 0.2 M.

Not shown in Fig. 7 is the relative contribution of diffusion and migration to the flux of Ni₄(OH)⁴⁺. For 0.2 M Ni(NO₃)₂, the migration term was observed to be relatively constant at \( 8 \times 10^{-11} \) mol/cm²-s, but the diffusion term decreased by a factor of 20 from approximately \( -4.3 \times 10^{-9} \) mol/cm²-s during the first 150 s of deposition. On the other hand, at 1 M Ni(NO₃)₂, the diffusion flux decreased by a factor of three from approximately \( -3 \times 10^{-8} \) mol/cm²-s between 15 and 150 s. The migration term increased from \( 1.9 \times 10^{-9} \) mol/cm²-s to \( 3.5 \times 10^{-9} \) mol/cm²-s during the same period. Thus, migration is not important for the concentrations of Fig. 7.

Figure 8a shows that the delay in the rate of precipitation between 15 and 21 s is greater for the tetramer concentration than that of Ni(OH)₂. This is a result of two competing phenomena: First, the tetramer concentration gradient is very steep, its flux drops faster than that of Ni²⁺. This can be seen in Fig. 8a, which shows that within short distances from the electrode surface, the Ni₄(OH)⁴⁺ concentration steeply falls to \( 10^{-30} \) M where the pH is low. This steep gradient causes the Ni₄(OH)⁴⁺ species to diffuse into the bulk. Therefore, the concentrations of all nickel species at the electrode surface are decreasing. At long times, the changes in the fluxes become very small, and the rate of precipitation becomes nearly a constant. Figure 8b shows the tetramer concentration profiles in the diffusion layer for 0.2 M Ni(NO₃)₂ solutions. A comparison with Fig. 8a shows that the surface concentration of Ni₄(OH)⁴⁺ is almost 100 times lower than in 1 M solution.
The local pH exceeds 6.5. Therefore, the acidity of the electrolyte adjacent to the electrode is first neutralized during the initial stages of the experiment.

Due to the loss of 4 moles of hydroxyl ions for every mole of the tetramer species, the utilization of the OH\(^-\) ions is greatly reduced. This efficiency, as explained in Eq. 8, cannot be calculated for any deposition current based on the predicted rate. Figure 10 shows the rate of deposition for a current density of 2.5 mA/cm\(^2\) and \(\epsilon_{OH^-}\) at 2.5 and 5.0 mA/cm\(^2\) plotted as a function of inverse Ni(NO\(_3\))\(_2\) concentration. The theoretical deposition rate, as calculated from Eq. 8, predicts a rate of 16.2 \(\mu\)g/min which is independent of solution concentration. This rate is observable only in 0.1 M solutions. In 2 M Ni(NO\(_3\))\(_2\), the deposition rate drops to 2 \(\mu\)g/min. The model predictions have been compared with the experimental data (see Ref. 2) obtained under these conditions. The variation of \(\epsilon_{OH^-}\) is also inversely related to the solution concentration. At very dilute concentrations [0.1 M Ni(NO\(_3\))\(_2\)], \(\epsilon_{OH^-}\) is nearly equal to 1 and agrees well with the value predicted by Faraday's law. At high concentrations [2 M Ni(NO\(_3\))\(_2\)], \(\epsilon_{OH^-}\) drops to less than 10\%, and in this range the value is very sensitive to solution concentration.

**Conclusions**

A mathematical model that predicts the experimentally observed inefficiencies in the deposition rates of nickel hydroxide on planar electrodes has been developed. The inefficiency in the deposition rate at high nickel concentrations (C\(_{Ni(OH)_4} > 0.1\) M) is explained quantitatively by the formation of an intermediate Ni\(_4\)(OH)\(_{4}\)\(^{4-}\) species. A two-step precipitation mechanism involving this species and proposed by Steinzer et al.\(^{1}\) has been found to be suitable in explaining the observable inefficiency. This species forms at the pH when deposition begins and diffuses into the bulk prior to deposition. The model predicts a linear increase in mass with time, as seen in the experiments for a low ratio of bulk concentration and current density. At higher ratios, the efficiency of utilization of the generated OH\(^-\) drops from 100\% for 0.1 M Ni(NO\(_3\))\(_2\) to less than 10\% for 2 M Ni(NO\(_3\))\(_2\). Based on the agreement with experimental data, the model has been used to explain the competing phenomena occurring during the experiments. Predictions for higher temperatures and differing ethanol concentrations such as those reported recently by Steinzer et al.\(^{11}\) will require values of diffusion coefficients and equilibrium constants other than those shown in Table III.

Our model could be used to estimate equilibrium and solubility product constants by fitting their deposition data. As an alternative, experiments in our laboratory focus on
independent measurement of these constants. This fundamental understanding of the chemistry of the deposition process will help develop better mathematical models for the impregnation of nickel electrodes.

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APPENDIX A

Necessary Equations for Developing Fig. 1a

In this section, we describe the equilibrium equations that were solved to obtain the fraction of the total nickel that exists as NiSO4, Ni(OH)2, and Ni(OH)4 as a function of pH. It should be noted that the predictions of Fig. 1a neglect activity-coefficient corrections to the concentration and solubility-product constants. The precipitation pH divides the plot into two regions, and therefore, two sets of equations are needed.

Case I: Prior to Ni(OH)2 precipitation.—We first make a mass balance on the total nickel in solution. All the nickel in solution exists either as its divalent ion, Ni2+ (x) or as the Ni(OH)2+ (y) species. If c denotes the concentration of Ni(NO3)2, we can write the following mass balance

\[
c = x + 4y \quad \text{[A-1]}\]

Then we have the two equilibrium relations given by reactions 1-7 and 1-9, and the four unknowns are the concentrations of Ni2+, H+, OH−, and Ni(OH)2+. By fixing the pH, the other three unknowns can be determined. It must be noted that pH can be varied until a value corresponding to the precipitation pH is obtained. This value is a function of the total Ni(NO3)2 concentration, c.

Case II: During Ni(OH)2 precipitation.—Once the precipitation pH is reached, nickel can also exist as Ni(OH)2. Instead of Eq. A-1, we have Eq. 6 of the main section, which involves the solubility product, Ksp. Then Eq. 6 and the two equilibrium relations mentioned can be solved simultaneously by once again fixing the pH to determine the amounts of nickel present as Ni2+, Ni(OH)2+, and Ni(OH)4−. The values of ksp and K2 used for Fig. 1a are 2.6 × 10−12 (mol/cm5)−1 and 1.2 × 10−16 (mol/cm5)−3, respectively.

APPENDIX B

Procedure for Measurement of pH of Aqueous Ni(NO3)2 Solutions

Fresh solutions of aqueous Ni(NO3)2 (Malinckrodt, analytical reagent grade) of concentrations ranging from 0.5 M to 4.0 M were prepared. A water bath was used to maintain the solutions at the desired temperature during pH measurements. The pH electrode (ROSS® type from Orion Research) was initially calibrated in standard buffer solutions of pH 4, 7, and 10. For measurements at higher concentrations of Ni(NO3)2, we can write the following mass balance

\[
c = x + 4y \quad \text{[A-1]}\]

Then we have the two equilibrium relations given by reactions 1-7 and 1-9, and the four unknowns are the concentrations of Ni2+, H+, OH−, and Ni(OH)2+. By fixing the pH, the other three unknowns can be determined. It must be noted that pH can be varied until a value corresponding to the precipitation pH is obtained. This value is a function of the total Ni(NO3)2 concentration, c.

Case II: During Ni(OH)2 precipitation.—Once the precipitation pH is reached, nickel can also exist as Ni(OH)2. Instead of Eq. A-1, we have Eq. 6 of the main section, which involves the solubility product, Ksp. Then Eq. 6 and the two equilibrium relations mentioned can be solved simultaneously by once again fixing the pH to determine the amounts of nickel present as Ni2+, Ni(OH)2+, and Ni(OH)4−. The values of ksp and K2 used for Fig. 1a are 2.6 × 10−12 (mol/cm5)−1 and 1.2 × 10−16 (mol/cm5)−3, respectively.

APPENDIX C

Development of Model Equations at the Electrode Surface

This section discusses the development of model equations at the electrode surface which have been listed in Table II of the main section.

Case I: Prior to Ni(OH)2 precipitation.—We first make a mole balance for each of the five species [i.e., Ni2+, NO3−, H+, OH−, and Ni(OH)2+] considering reactions I-3, I-7, and I-9 listed in Table I. The numbered subscripts, j, denote reactions I-7 and I-9 in Table I. The rates of homogenous reactions (rj) are written now in terms of per unit surface area of the electrode.

Species & Mole balance at x = 0

\[
\begin{align*}
\text{Ni}^{2+} & : N_{\text{Ni}^{2+}} - r_{i,j} = 0 \\
\text{NO}_3^- & : N_{\text{NO}_3^-} = - \frac{g_{\text{Ni}^{2+}}}{nF} \\
\text{H}^+ & : N_{\text{H}^+} - r_{i,j} = 0 \\
\text{OH}^- & : N_{\text{OH}^-} - r_{i,j} - r_{i,9} + \frac{g_{\text{Ni}^{2+}}}{nF} = 0 \\
\text{Ni(OH)}_2^+ & : N_{\text{Ni(OH)}_2^+} - \frac{g_{\text{Ni}^{2+}}}{nF} = 0 \\
\text{Ni(OH)}_4^- & : N_{\text{Ni(OH)}_4^-} = 0
\end{align*}
\]

Next, since the rates of reaction are unknown values, they should be eliminated. That is, since \( r_{i,j} = -4r_{i,9} \), adding Eq. C-1 and C-5 gives the total balance for nickel in solution (see Eq. II-13 in Table III)

\[
N_{\text{Ni}^{2+}} + 4N_{\text{Ni(OH)}_2^+} = 0
\]

Similarly, since \( r_{i,j} = r_{i,j} + r_{i,9} \), the expression can be obtained for OH− by combining Eq. C-1, C-3, and C-4 to obtain Eq. II-16

\[
N_{\text{OH}^-} - N_{\text{H}^+} - N_{\text{Ni}^{2+}} + \frac{g_{\text{Ni}^{2+}}}{nF} = 0
\]

The two equilibrium expressions corresponding to reactions 1-7 and 1-9, the electroneutrality relation given by Eq. II-18, and Eq. C-2 complete the set of six equations for the boundary conditions prior to precipitation.

Case II: During Ni(OH)2 precipitation.—When the concentrations of Ni2+, Ni(OH)2+, and Ni(OH)4− equal or exceed those corresponding to the solubility product of reaction 1-8, precipitation conditions exist. Then, Eq. C-4 and C-5 need to be modified to include the precipitation rates, \( r_{i,9} \). These flux expressions for the OH− and Ni(OH)2+ species are rewritten in Eq. C-8 and C-9

\[
\begin{align*}
\text{Species} & \quad \text{Mole balance at x = 0} \\
\text{OH}^- & : N_{\text{OH}^-} - r_{i,j} - r_{i,9} + \frac{g_{\text{Ni}^{2+}}}{nF} = 0 \\
\text{Ni(OH)}_2^+ & : N_{\text{Ni(OH)}_2^+} - \frac{g_{\text{Ni}^{2+}}}{nF} = 0
\end{align*}
\]

Equation C-1 and C-9 can be combined to give

\[
N_{\text{Ni}^{2+}} + 4N_{\text{Ni(OH)}_2^+} = -r_{i,9}
\]

Also, Eq. C-1, C-3, and C-8 can be combined to give

\[
N_{\text{OH}^-} - N_{\text{H}^+} - N_{\text{Ni}^{2+}} + \frac{g_{\text{Ni}^{2+}}}{nF} = -r_{i,9}
\]

The rate of precipitation can be eliminated by subtracting Eq. C-10 from C-11, which results in Eq. II-19 in Table II. The set of six equations required for the six unknowns is completed by using three equilibrium expressions corresponding to reactions 1-7 through I-9, Eq. C-2, and the electroneutrality expression for the solution potential, Eq. II-24.

LIST OF SYMBOLS

A

area of the EQCM electrode, 0.2 cm²

C

congcentration of species i, mol/cm³

C

bulk or initial concentration, mol/cm³

D

diffusion coefficient of species i, cm²/s

F

Faraday’s constant, 96,487 C/mol

i

applied cathodic current density, A/cm²

K

ionic product for water equilibrium, (mol/cm³)−2

K

equilibrium constant for reaction I-7, (mol/cm³)−2/3

K

equilibrium constant for reaction I-10, cm/mol

K

equilibrium constant for reaction I-11, mol/cm³

K

solubility product for Ni(OH)₂ precipitation for reaction I-8, (mol/cm³)−1
$K_w$ solubility product for Ni(OH)$_2$ precipitation for reaction 1-8, (mol/cm$^3$)$^{0.4}$

$M_{Ni(OH)_2}$ molecular weight of Ni(OH)$_2$, 92.7 g/mol

$N_i$ flux of species $i$, mol/cm$^2$-s

$n$ number of electrons in reaction 1-3

$R$ gas constant, 8.314 J/mol K

$R_i$ net homogenous production of species $i$ from all the reactions, mol/cm$^3$-s

$r_{i,j}$ rate of production of species $i$ from reaction $j$, mol/cm$^2$-s

$r_{i,j}^*$ rate of production of species $i$ at the electrode surface from reaction $j$, mol/cm$^2$-s

$r_{p,i,j}$ rate of precipitation of Ni(OH)$_2$ at the electrode surface, mol/cm$^2$-s

$s_i$ stochiometric coefficient of species $i$

$T$ temperature, K

$t$ time, s

$\Phi$ standard potential for reactions 1-1 through 1-5, V

$W_{Ni(OH)_2}$ mass of Ni(OH)$_2$, deposited, g

$x$ spatial distance normal to the electrode surface, cm

Greek

$\eta$ efficiency of OH$^-$ utilization

$\Phi$ solution potential, V

Subscripts

$i$ species involved in the various reactions (1, 2, 3, 4, and 5)

$1$ Ni$^{2+}$

$2$ NO$_3^-$

$3$ H$^+$

$4$ OH$^-$

$5$ Ni$_4$(OH)$_3^+$

REFERENCES