Studies of the Codeposition of Cobalt Hydroxide and Nickel Hydroxide

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Outline

- Chemistry
- Experimental Measurements
- Planar Film Model Development
- Impregnation Model Development
- Results & Conclusions
  - Effect of Ni$_4$(OH)$_4$$^{4+}$
  - Effect of Cobalt Concentration on Deposition / Loading
  - Effect of Current Density on Loading Distribution
- Acknowledgment
**Electrode Reaction**

\[
\frac{1}{8} \text{NO}_3^- + \frac{3}{4} \text{H}_2\text{O} + e^- \rightarrow \frac{1}{8} \text{NH}_3 + \frac{9}{8} \text{OH}^- 
\]

**Precipitation Reactions**

\[
\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \\
\text{Co}^{2+} + 2\text{OH}^- \rightarrow \text{Co(OH)}_2 
\]
Nickel Chemistry

- Dilute Solutions \((\text{Ni}^{2+} < 0.1 \text{ M, pH } < 7)\)
  \[
  \text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+
  \]

- Concentrated solutions \((\text{Ni}^{2+} > 0.1 \text{ M, } 5 < \text{pH } < 7)\)
  \[
  4\text{Ni}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Ni}_4\text{OH}_4^{4+} + 4\text{H}^+
  \]

References: Baes & Mesmer (1976), Kawai et al. (1973), Burkov et al. (1965), Kolski et al. (1969)
Equilibrium Concentration of Ni$^{2+}$, Ni(OH)$_2$, and Ni$_4$(OH)$_4$$^{4+}$ Species

Percent of Total Nickel

pH

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Cobalt Chemistry

- Dilute solutions ($Co^{2+} < 0.1 \text{ M}, \text{pH} < 7$)

$$Co^{2+} + H_2O \Leftrightarrow CoOH^+ + H^+$$

- Concentrated solutions ($Co^{2+} > 0.1 \text{ M}, 5 < \text{pH} < 7$)

$$4Co^{2+} + 4H_2O \Leftrightarrow Co_4(OH)_4^{4+} + 4H^+$$

- Cobalt $K_{eq} \approx 0.1 \ K_{eq}$ of nickel species

Reference: Baes & Mesmer (1976)

- Ionic strength important
Equilibrium Chemical Reactions

- Two Step Deposition Mechanism (Streinz et al. 1995)
  \[ \text{Ni}^{2+} + \text{OH}^- \leftrightharpoons \frac{1}{4} \text{Ni}_4(\text{OH})_4^{4+} \]
  
  \[ \frac{1}{4} \text{Ni}_4(\text{OH})_4^{4+} + \text{OH}^- \leftrightharpoons \text{Ni(OH)}_2 \downarrow \]

- Cobalt Deposition Mechanism (Baes and Mesmer 1976)
  \[ \text{Co}^{2+} + \text{OH}^- \leftrightharpoons \frac{1}{4} \text{Co}_4(\text{OH})_4^{4+} \]
  
  \[ \frac{1}{4} \text{Co}_4(\text{OH})_4^{4+} + \text{OH}^- \leftrightharpoons \text{Co(OH)}_2 \downarrow \]
Equilibrium Chemical Reactions (Contd.)

Reactions for Nickel Nitrate Complexes (Fedorov et al. 1976)

\[
\begin{align*}
Ni^{2+} + NO_3^- & \rightleftharpoons Ni(NO_3)_2^+ \\
Ni^{2+} + 2NO_3^- & \rightleftharpoons Ni(NO_3)_2^{aq}
\end{align*}
\]

Reactions for Cobalt Nitrate Complexes (Fedorov et al. 1976)

\[
\begin{align*}
Co^{2+} + NO_3^- & \rightleftharpoons Co(NO_3)_2^+ \\
Co^{2+} + 2NO_3^- & \rightleftharpoons Co(NO_3)_2^{aq}
\end{align*}
\]

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Equilibrium Concentration of Ni$^{2+}$, Ni(OH)$_2$, Ni$_4$(OH)$_4$$^{4+}$, NiNO$_3^+$ & Ni(NO$_3$)$_2$ Species

Percent of Total Nickel
Schematic Diagram for Nonaqueous pH Measurement

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Experimental Measurement

- Hydrolytic reaction

\[ qNi^{2+} + pH_2O = Ni_q(OH)_{(2q-p)^+} + pH^+ \]

\[ Q_{p,q} = \frac{[Ni_q(OH)_{(2q-p)^+}][H^+]^p}{b^q} \]

- Material Balance

\[ B^o = B^N + B + b \]

\[ [(B + b)] Z = h - H + K Wh^{-1} \]

\[ = (Q_{1,1}bh^{-1} + 4Q_{4,4}b^4h^{-4} + Q_{1,2}b^2h^{-1}) \]
\[(h - H + K_{\text{wh}}^{-1}) \text{ vs. } pH \text{ at Various Ni(NO}_3\text{)}_2 \text{ Conc.}
\]
(Temperature = 25°C)
(h−H+Kw h⁻¹) vs. pH at Various Temperatures

(1.0 M Ni(NO₃)₂ solution)
(h - H + K_w h^{-1}) v.s. pH in 1.0 M Ni(NO_3)_2 solutions

(Temperature = 25°C)
Effect of Ionic Strength

- Equilibrium reaction

\[ 4\text{Ni}^{2+} + 4\text{H}_2\text{O} = \text{Ni}_4(\text{OH})_{4}^{4+} + 4\text{H}^+ \]

\[ Q_{eq} = \frac{[\text{Ni}_4(\text{OH})_{4}^{4+}]}{[\text{Ni}^{2+}]^4} \left[ \frac{[\text{H}^+]}{4} \right]^4 \]

- Effect of ionic strength

\[ \log Q_{eq} = \log K_{eq} + \frac{aI^{1/2}}{1 + I^{1/12}} + bm_x \]
Effect of Ionic Strength on the Equilibrium Quotient of Nickel Complex
\((-R \ln K_{p,q})\) vs. \(1/T\) for hydrolytic reactions of

\(\text{Ni}_4(\text{OH})_4^{4+}\) and \(\text{Ni}(\text{OH})^+\)

\[\Delta H^o = 46.7 \pm 2.9 \text{ kcal/mole (43, Arnek)}\]

\[\Delta H^o = 12.4 \text{ Kcal/mole (11.8, Arnek)}\]
Schematic of an Electrochemical Quartz Crystal Microbalance

EQCM

Potentiostat

SCE RE

Platinum CE

Nickel Nitrate Bath

Gold WE

Quartz Crystal

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Nickel-Hydrogen Session
Schematic of the Deposition Process on Planar Electrodes
Governing Equations for Planar Film Model

- Mass balances for species: \( \text{Ni}^{2+}, \text{Co}^{2+}, \text{NO}_3^-, \text{OH}^- \)

\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot \text{Ni} + R_i
\]

- Equilibrium reactions for remaining species, \( \text{H}^+, \text{NiNO}_3^+, \text{Ni(NO}_3)_2, \text{CoNO}_3^+, \text{Co(NO}_3)_2, \text{Ni}_4(\text{OH})_4^{4+}, \) and \( \text{Co}_4(\text{OH})_4^{4+} \)

- Electroneutrality for solution potential, \( \phi \)

- Eleven concentrations and \( \phi \)
Boundary Conditions for Planar Film Model

- Diffusion layer-electrolyte interface
  \[ C_i = C_{i,b} \]
  \[ \phi = 0 \]

- Electrode surface
  - flux balances
  - equilibrium reactions
  - electroneutrality
Effect of Ni(NO₃)₂ on EQCM Mass Gain
Ref: Streinz et al., JES, 147, 1084 (1995)

\[ i = 2.5 \text{ mA/cm}^2 \]

- 0.1 M Ni(NO₃)₂
- 0.2 M Ni(NO₃)₂
- 1 M Ni(NO₃)₂
- 2 M Ni(NO₃)₂

Mass (μg) vs. Time (s)
Efficiency of Utilization vs Inverse Concentration
Comparison of Model and Experimental Data

Efficiency, ε_{OH} -

Deposition Rate (μg/min)

Inverse Concentration (1/mol)

Ni(OH)₂

Co(OH)₂

Efficiency = 1
Determination of $K_{eq}$ and $K_{sp}$ from Film Experiments

- Determine least square error between experimentally measured mass and model predictions.

$$E = \sum_{i=1}^{q} (m_{I_1}^{exp} - m_{I_1}^{pred.})^2 + \sum_{i=1}^{q} (m_{I_2}^{exp} - m_{I_2}^{pred.})^2$$

where $m = f(K_{eq}, K_{sp})$ and $K_{eq}$, $K_{sp}$ correspond to zero ionic strength

$$E = E_1 + E_2$$

$m$: mass gain of Ni(OH)$_2$

$I_1$, $I_2$: Ionic strength of medium

$q$: number of experimental data
Percentage Co in Ni(OH)$_2$ Film with Time
1 M Ni(NO$_3$)$_2$ with Varying Co Concentrations

Time (min)

Percentage Co in Film

0 10 20 30 40 50 60 70 80 90 100

0.05 M Co
0.1 M Co
0.2 M Co
0.25 M Co

i = 0.5 mA
Electrochemical Impregnation System

Nickel Plaque

Anodes

Impregnation Cell

Pump

aqueous Ni(NO₃)₂ + Ethanol

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CURRENT COLLECTOR & TAB

POROUS NICKEL PLAQUE

COUNTER ELECTRODE

COUNTER ELECTRODE

v, C_{i,b}

\( x = 0 \)

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Governing Equations for Impregnation Model

- Mass balances for species: $\text{Ni}^{2+}, \text{Co}^{2+}, \text{NO}_3^-, \text{OH}^-$

\[
\frac{\partial \epsilon C_i}{\partial t} = - \frac{s_i}{nF} \frac{\partial i_2}{\partial x} - \frac{\partial N_i}{\partial x} + R_i
\]

- Flux: Diffusion and migration only

- Equilibrium equations for: $H^+$, $\text{Ni}_4(\text{OH})_4^{4+}$, $\text{Co}_4(\text{OH})_4^{4+}$, $\text{Ni(NO}_3)^+$, $\text{Ni(NO}_3)_2$, $\text{Co(NO}_3)^+$, $\text{Co(NO}_3)_2$

- $\phi_2$ is governed by electroneutrality
Governing Equations (Cont.)

◆ The rates of precipitation are related to $Q_{sp}$ of the hydroxides. ($r_{ppt1}$, $r_{ppt2}$)

◆ Solution current: \[ \frac{\partial i_2}{\partial x} = a \ j_n \]

◆ Porosity:

\[ \frac{\partial \varepsilon}{\partial t} = - r_{ppt1} \left( \frac{M}{\rho} \right)_{Ni(OH)_2} - r_{ppt2} \left( \frac{M}{\rho} \right)_{Co(OH)_2} \]
Concentration Profile of Ni$_4$(OH)$_4$ in Ni Plaque

$(a_{i_0} = 10^{-3} \text{A/cm}^2, \eta_{x_0} = -375 \text{mV}, \tau = 1.6, \varepsilon^0 = 0.8, L = 0.1 \text{cm})$
Effect of Alcohol Volume % on Loading Distribution in Ni Pla

\( a_{i_0} = 10^{-3} \text{A/cm}^3, \eta|_{x=0} = -375 \text{mV}, \tau = 1.6, \text{time} = 30 \text{min}, L = 0.1 \text{cm} \)

\[ H_2O, i = -48.1 \text{mA/cm}^2, W_{avg} = 0.872 \text{g/cm}^3 \]

\[ 50\% \text{ EtOH}, i = -43.9 \text{mA/cm}^2, W_{avg} = 0.929 \text{g/cm}^3 \]

\[ 100\% \text{ EtOH}, i = -43.1 \text{mA/cm}^2, W_{avg} = 0.989 \text{g/cm}^3 \]
Non-Uniformity vs. Current Density at Various Solutions

(Temp = 25°C, τ = 1.6, ε₀ = 0.8)

- 1M Ni(NO₃)₂
- 2M Ni(NO₃)₂
- 1M Ni(NO₃)₂ (without tetramer)

Percent Non-Uniformity (%)

Current Density (mA/cm²)

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Cobalt Content of the Active Material in Ni Plaque

\[(T=25^\circ C, i=-60mA/cm^2, \varepsilon=0.8, 1M \text{ Ni(NO}_3\text{)}_2)\]

\begin{figure}
\centering
\includegraphics[width=\textwidth]{chart.png}
\end{figure}

- 0.2M Co(NO\textsubscript{3})\textsubscript{2} \quad t=24\text{min} \quad W_{avg}=1.08 \text{ g/cm}^3
- 0.1M \quad W_{avg}=1.01 \text{ g/cm}^3
- 0.05M \quad W_{avg}=0.95 \text{ g/cm}^3
Loading Distributions of Co(OH)$_2$ in Porous Nickel Plaque

(1.0 M Ni(NO$_3$)$_2$, 0.1 M Co(NO$_3$)$_2$, i = -60 mA/cm$^2$)

Local Loading Level (g/m$^2$ void volume)

Dimensionless Distance $\xi$

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

2 min
4 min
10 min
20 min
Distributions of Ni(OH)$_2$ & Co(OH)$_2$ in Nickel Plaque

(1.0M Ni(NO$_3$)$_2$, i=-60mA/cm$^2$, W$_{avg}$=0.85gm/cm$^3$)

Local Loading Level (g/void volume) vs. Dimensionless Distance $\xi$
Effect of Co(NO₃)₂ Conc. on the Porosity Distribution

(ε⁰ = 0.8, 1.0M Ni(NO₃)₂, i = -60mA/cm², W_avg = 0.85 g/cm³)
Loading Distributions of Ni(OH)$_2$ & Co(OH)$_2$ in Nickel Plaque

(1.0M Ni(NO$_3$)$_2$, 0.1M Co(NO$_3$)$_2$, T=25°C, W$_{avg}$=0.75 g/cm$^3$)
Summary

◆ Titration Experiments Determine $Q_{sp}$, and $Q_{eq}$
  ■ $f(T, \text{Alcohol}, [\text{Ni(NO}_3\text{)}_2])$
◆ Raman Spectra Identifies $\text{Ni}_4(\text{OH})_4^{4+}$
  ■ Absorbance is $f(\text{pH})$
◆ EQCN Experiments and Film Model
  ■ Confirm Values of $K_{eq}$, $K_{sp}$, and Ionic Strength Equations
◆ Porous Electrode Model
  ■ Agree with $\text{Ni(OH)}_2$ Distribution Measurements
◆ Porous Electrode Model Predicts Ni/Co Distributions
Conclusions

♦ For Uniform Total Deposit

■ Decrease Effect of Tetramer
  • Lower pH for deposition (decrease $Q_{sp}$)
  • Decrease formation constant ($Q_{eq}$)
  • Lower [Ni(NO$_3$)$_2$] for fixed $Q_{sp}$ and $Q_{eq}$
  • Optimum current density (low)

■ Decrease Current Density

♦ Quantify the Amount of Change
Conclusions (Cont.)

- Factors Affecting $Q_{sp}$ and $Q_{eq}$
  - Increase in $T$ yields decrease in $Q_{sp}$ and increase in $Q_{eq}$
  - Increase in Alcohol conc. yields same as $T$
  - Increase ionic strength yields same as $T$

- $\text{Co(OH)}_2$ and $\text{Ni(OH)}_2$ depends on $[\text{Co(NO}_3\text{)}_2]$, Ionic Strength, $[\text{Ni(NO}_3\text{)}_2]$, $T$, and Alcohol Concentration
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