Studies of the Codeposition of Cobalt Hydroxide and Nickel Hydroxide

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S14-44

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

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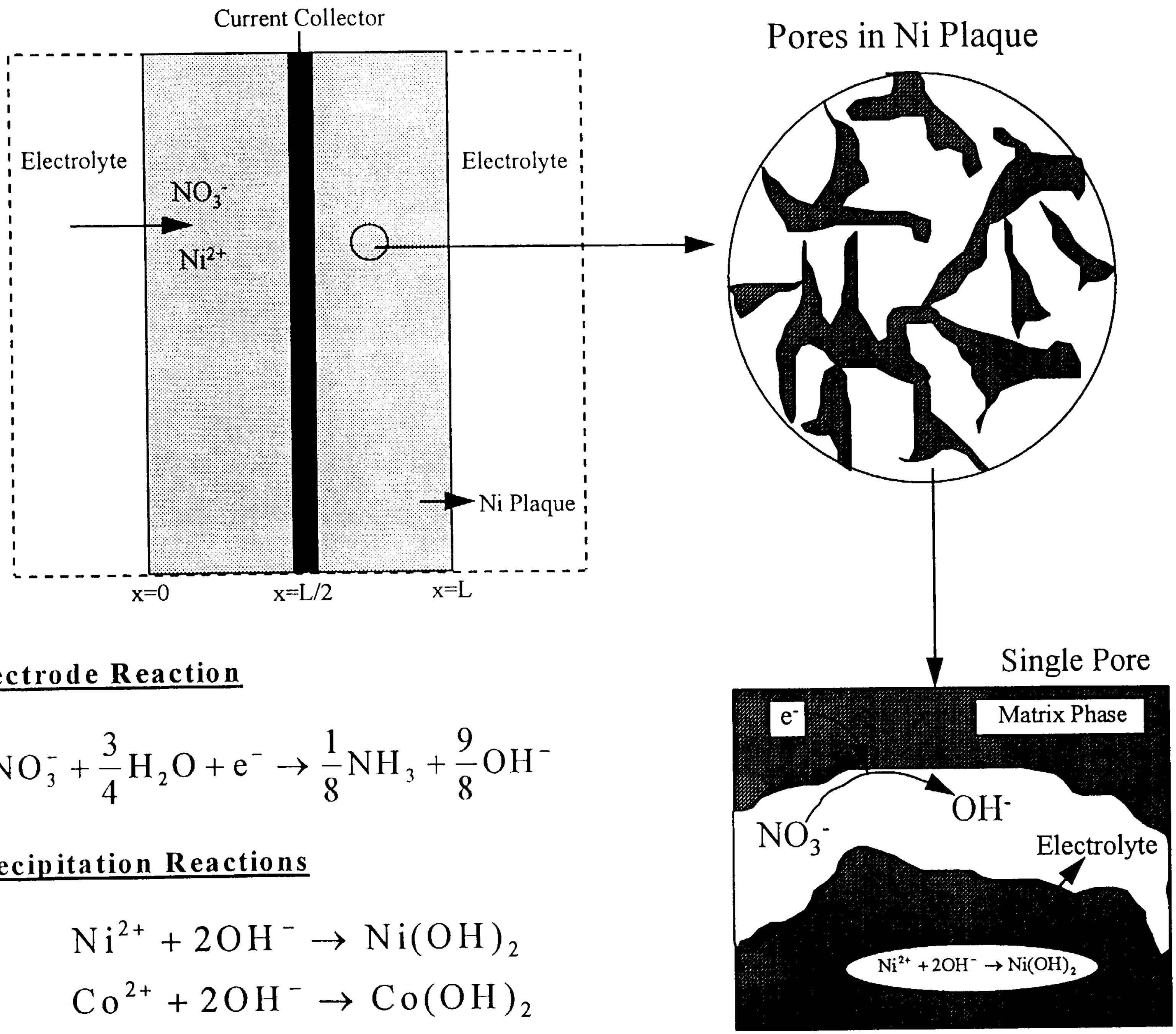

Electrode Reaction

$$\frac{1}{8}NO_3^- + \frac{3}{4}H_2O + e^- \rightarrow \frac{1}{8}NH_3 + \frac{9}{8}OH^-$$

Precipitation Reactions

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$$

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2$$

Nickel Chemistry

- Dilute Solutions ($Ni^{2+} < 0.1$ M, pH < 7)

$$Ni^{2+} + H_2O \Leftrightarrow NiOH^{+} + H^{+}$$

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

$$4Ni^{2+} + 4H_2O \Leftrightarrow Ni_4OH_4^{4+} + 4H^{+}$$

References: Baes & Mesmer (1976), Kawai et al. (1973), Burkov et al. (1965), Kolski et al. (1969)

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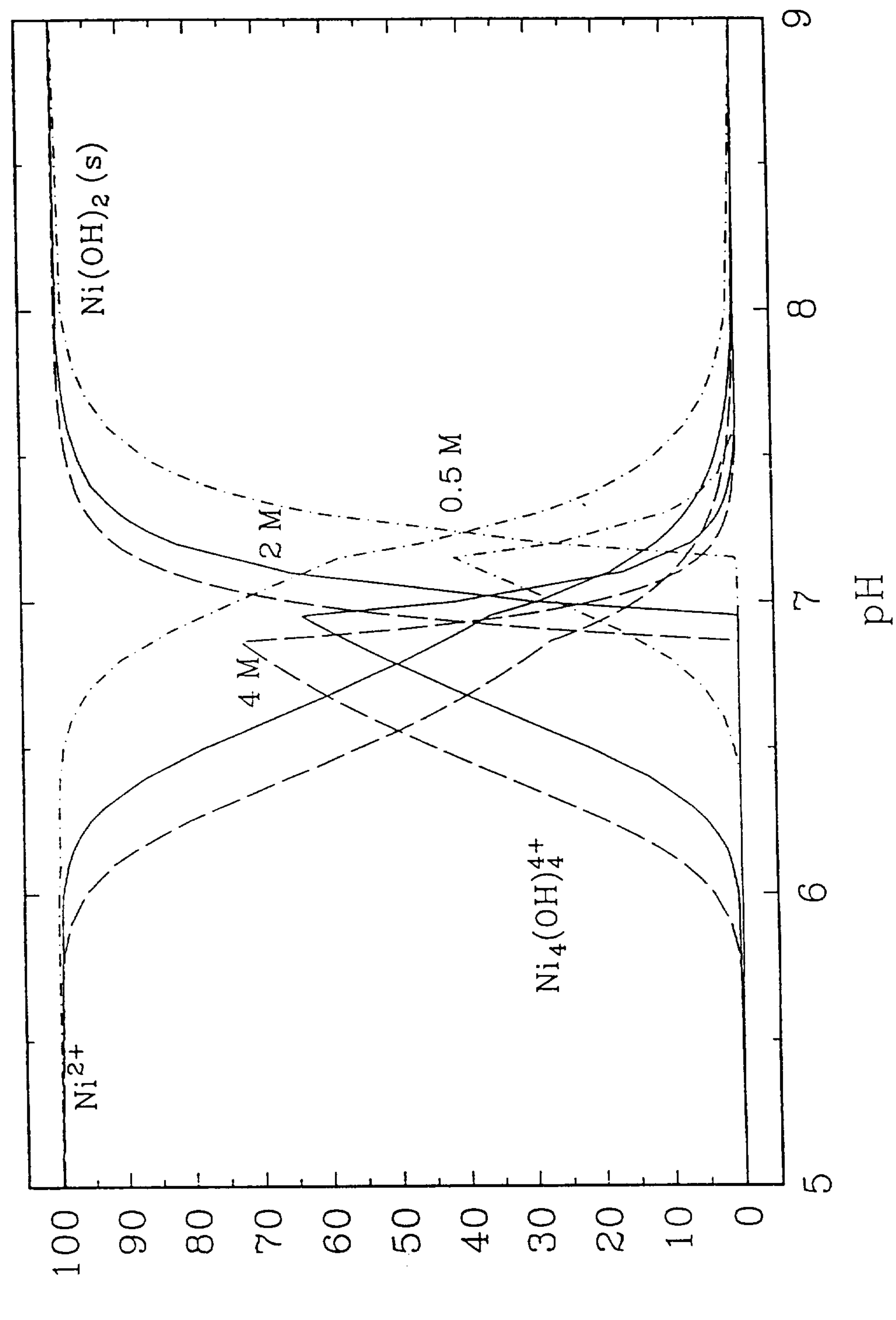
Equilibrium Concentration of Ni^{2+}, $Ni(OH)_2$, and $Ni_4(OH)_4^{4+}$ Species



Cobalt Chemistry

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

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

- Concentrated solutions ($Co^{2+} > 0.1$ M, 5 < 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

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Equilibrium Chemical Reactions

- Two Step Deposition Mechanism *(Streinz et al. 1995)*

$$Ni^{2+} + OH^- \Leftrightarrow \frac{1}{4} Ni_4(OH)_4^{4+}$$

$$\frac{1}{4} Ni_4(OH)_4^{4+} + OH^- \Leftrightarrow Ni(OH)_2 \downarrow$$

- Cobalt Deposition Mechanism (*Baes and Mesmer 1976*)

$$Co^{2+} + OH^- \Leftrightarrow \frac{1}{4} Co_4(OH)_4^{4+}$$

$$\frac{1}{4} Co_4(OH)_4^{4+} + OH^- \Leftrightarrow Co(OH)_2 \downarrow$$

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Equilibrium Chemical Reactions(Contd.)

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

$$Ni^{2+} + NO_3^- \Leftrightarrow Ni(NO_3)^+$$

$$Ni^{2+} + 2NO_3^- \Leftrightarrow Ni(NO_3)_2 \text{ (aq)}$$

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

$$Co^{2+} + NO_3^- \Leftrightarrow Co(NO_3)^+$$

$$Co^{2+} + 2NO_3^- \Leftrightarrow Co(NO_3)_2 \text{ (aq)}$$

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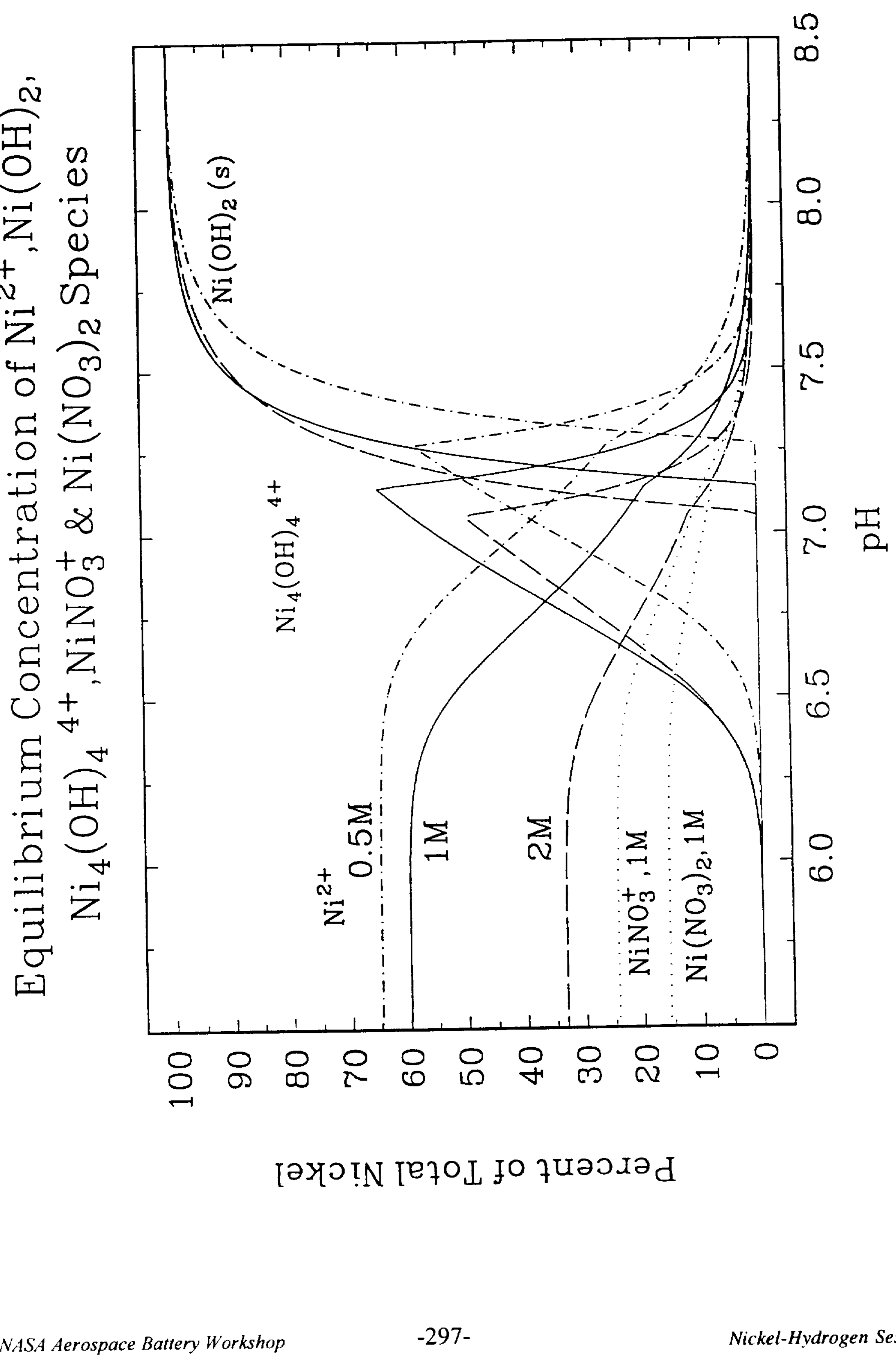
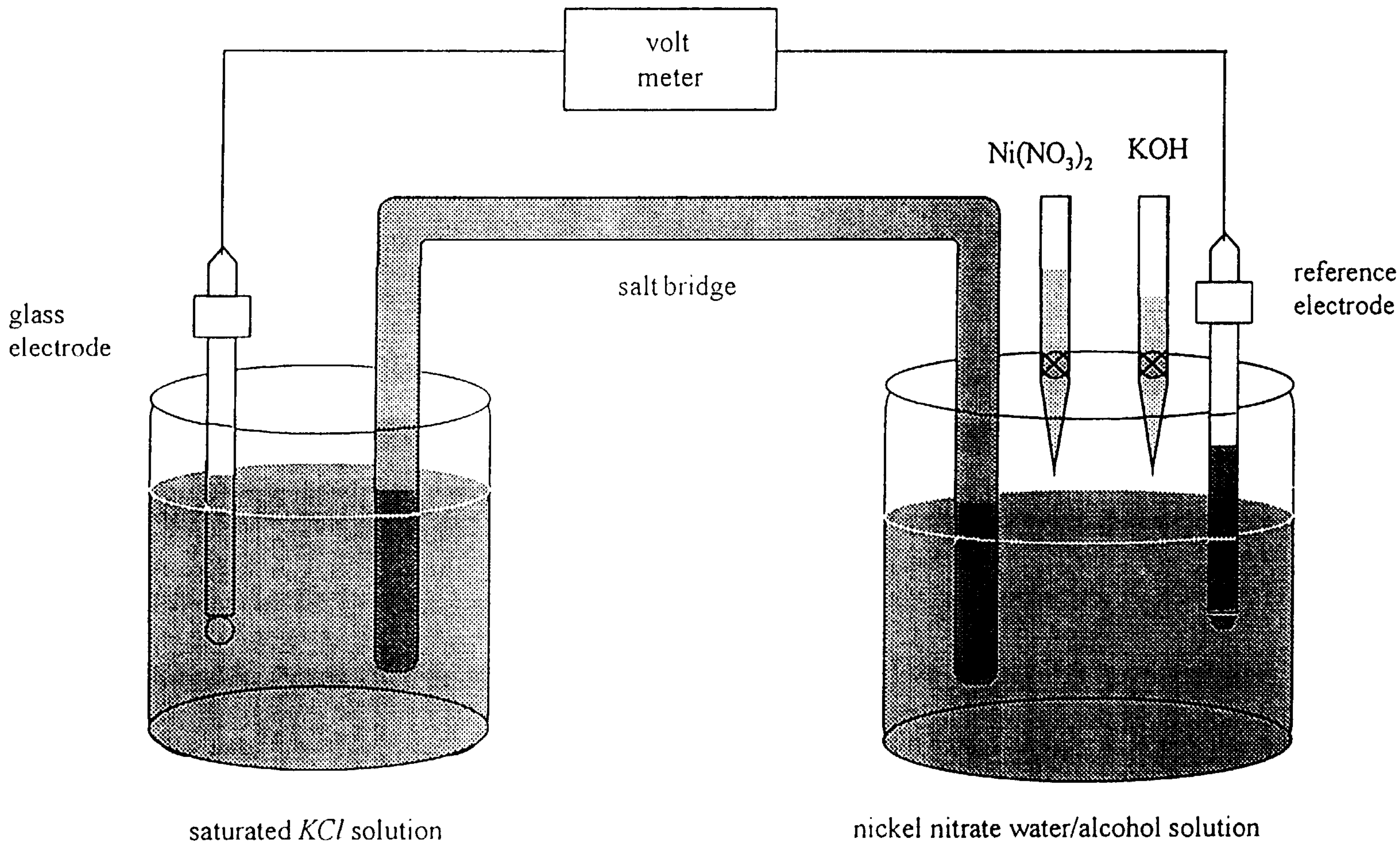


Equilibrium Concentration of Ni2+, Ni(OH)2, Ni4(OH)4 4+, NiNO3+ & Ni(NO3)2 Species
Percent of Total Nickel
pH
Ni2+
0.5M
1M
2M
NiNO3+, 1M
Ni(NO3)2, 1M
Ni4(OH)4 4+
Ni(OH)2 (s)
100
90
80
70
60
50
40
30
20
10
0
6.0
6.5
7.0
7.5
8.0
8.5



Schematic Diagram for Nonaqueous pH Measurement

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Experimental Measurement

- Hydrolytic reaction

$$qNi^{2+} + pH_2O = Ni_q(OH)_p^{(2q-p)+} + pH^+$$

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

- Material Balance

$$B° = B^N + B + b$$

$$[(B+b)]\,Z = h - H + K_W h^{-1}$$

$$= (Q_{1,1}bh^{-1} + 4Q_{4,4}b^4h^{-4} + Q_{1,2}b^2h^{-1})$$

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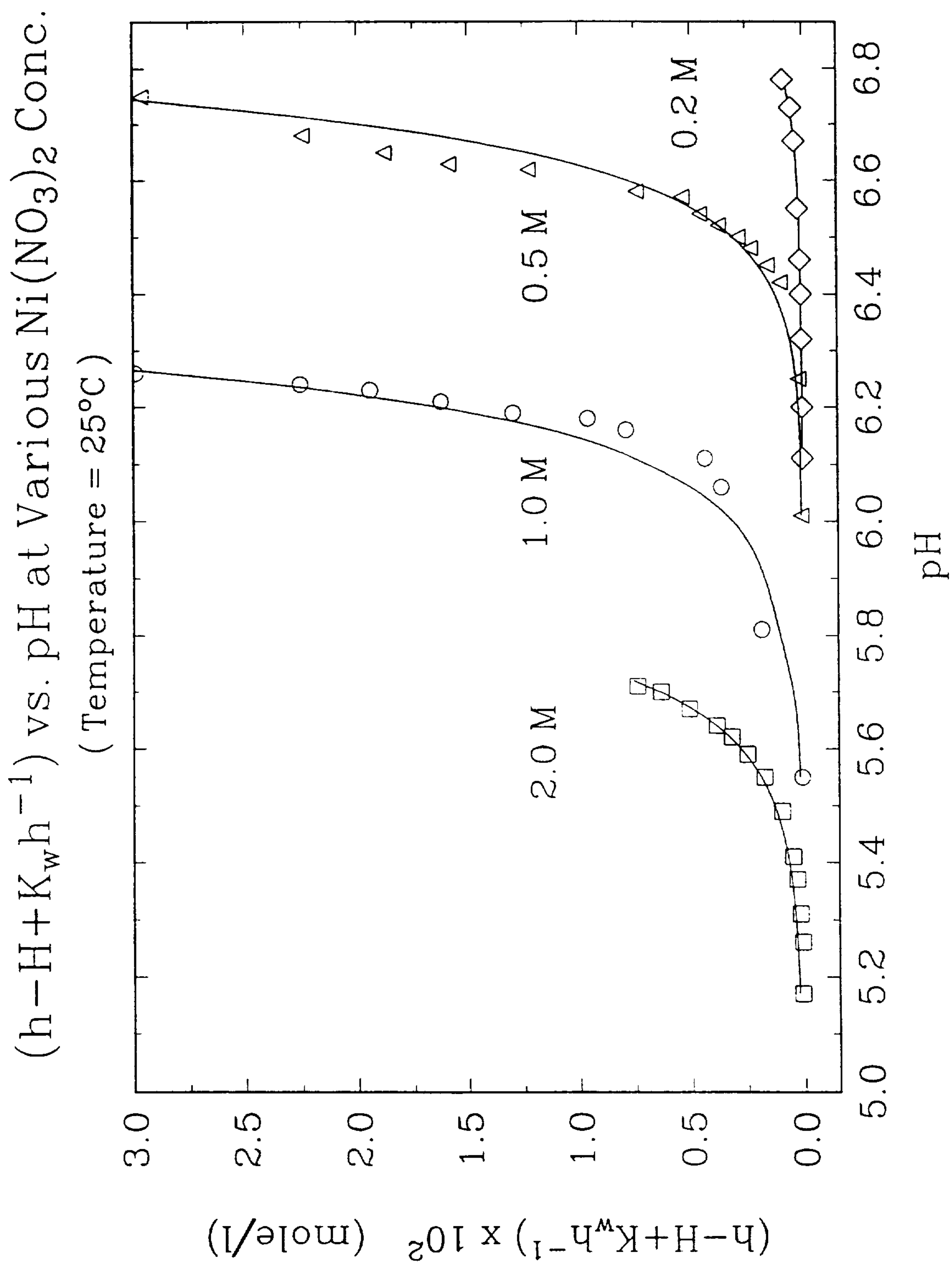
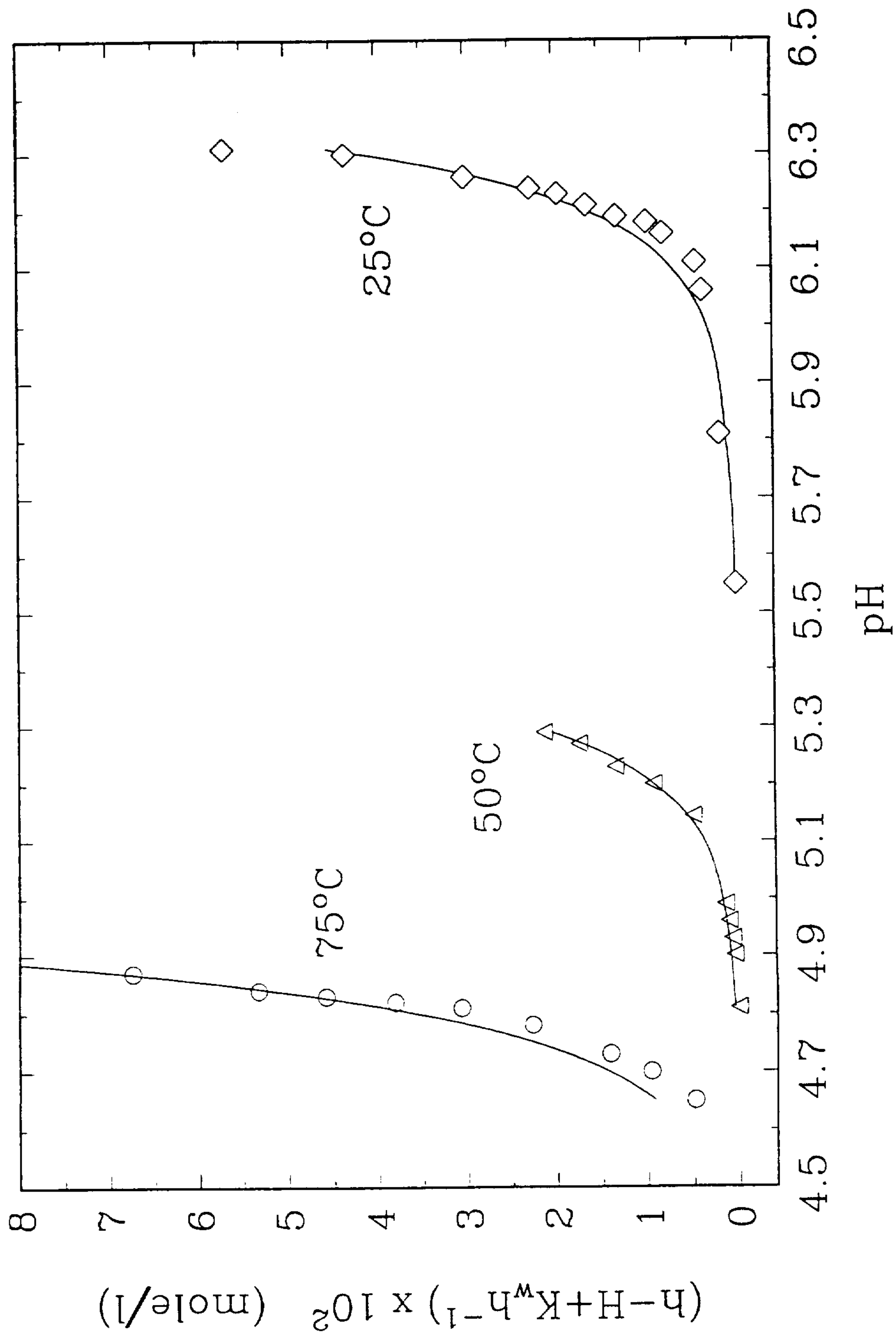
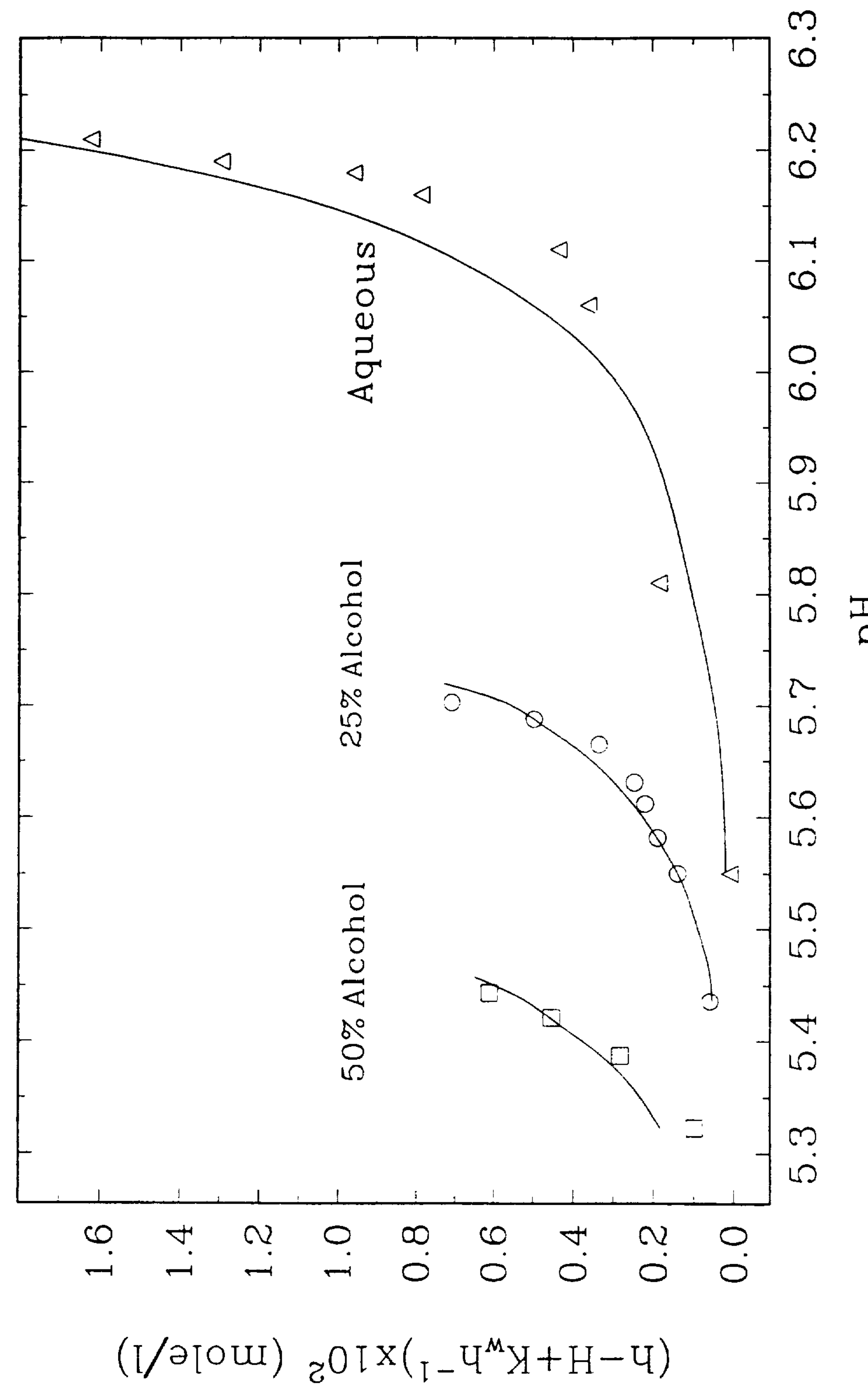


(h−H+K_wh^−1) vs. pH at Various Ni(NO3)2 Conc.
(Temperature = 25°C)
(h−H+K_wh^−1) x 10^2 (mole/l)
pH
0.2 M
0.5 M
1.0 M
2.0 M
0.0
0.5
1.0
1.5
2.0
2.5
3.0
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8



$(h-H+K_wh^{-1})$ vs. pH at Various Temperatures

(1.0 M $Ni(NO_3)_2$ 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

$$4Ni^{2+} + 4H_2O = Ni_4(OH)_4^{4+} + 4H^+$$

$$Q_{eq} = \frac{\left[Ni_4(OH)_4^{4+}\right]\left[H^+\right]^4}{\left[Ni^{2+}\right]^4}$$

- Effect of ionic strength

$$\log\ Q_{eq} = \log\ K_{eq} + \frac{a\,I^{1/2}}{1 + I^{1/12}} + bm_X$$

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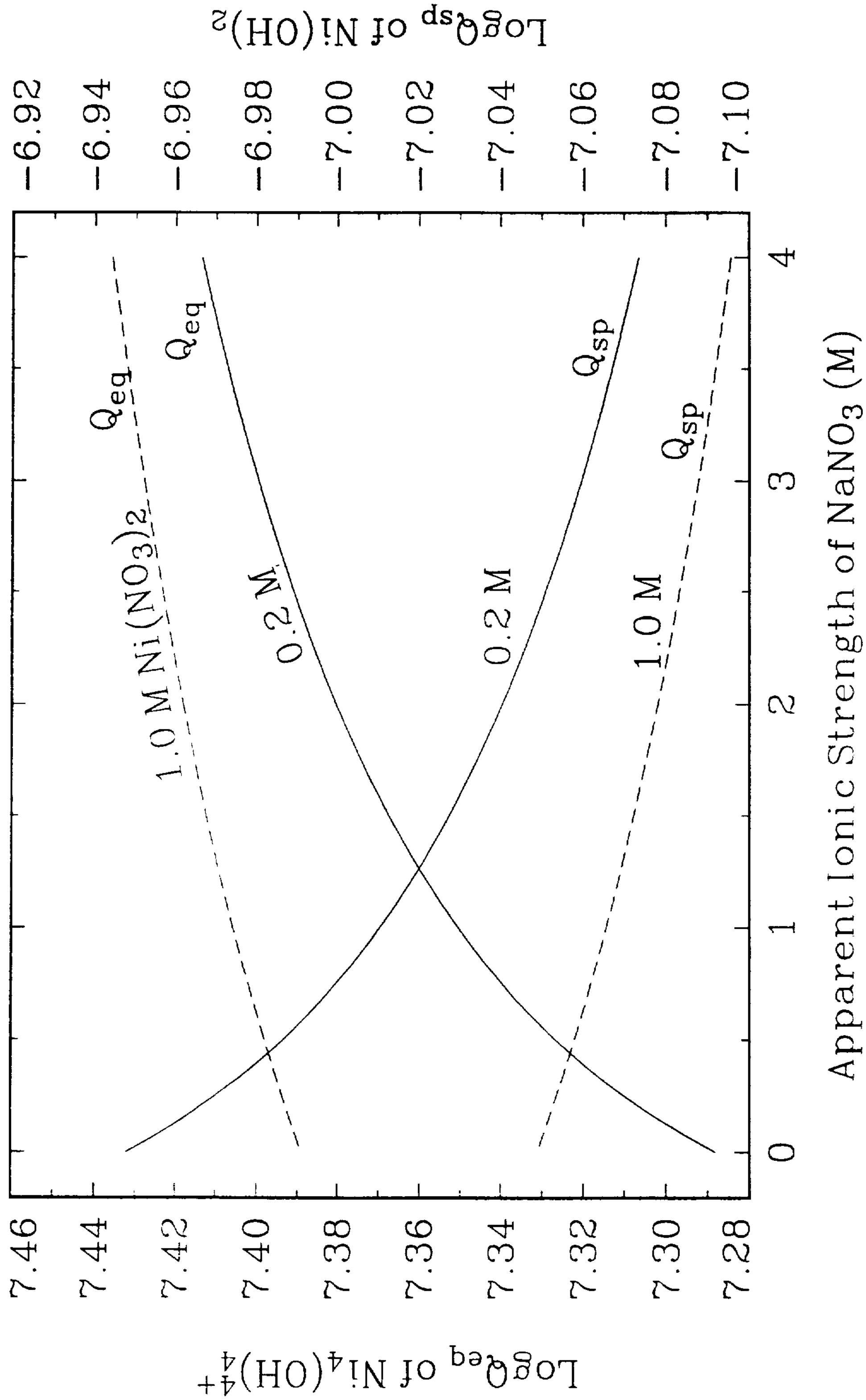
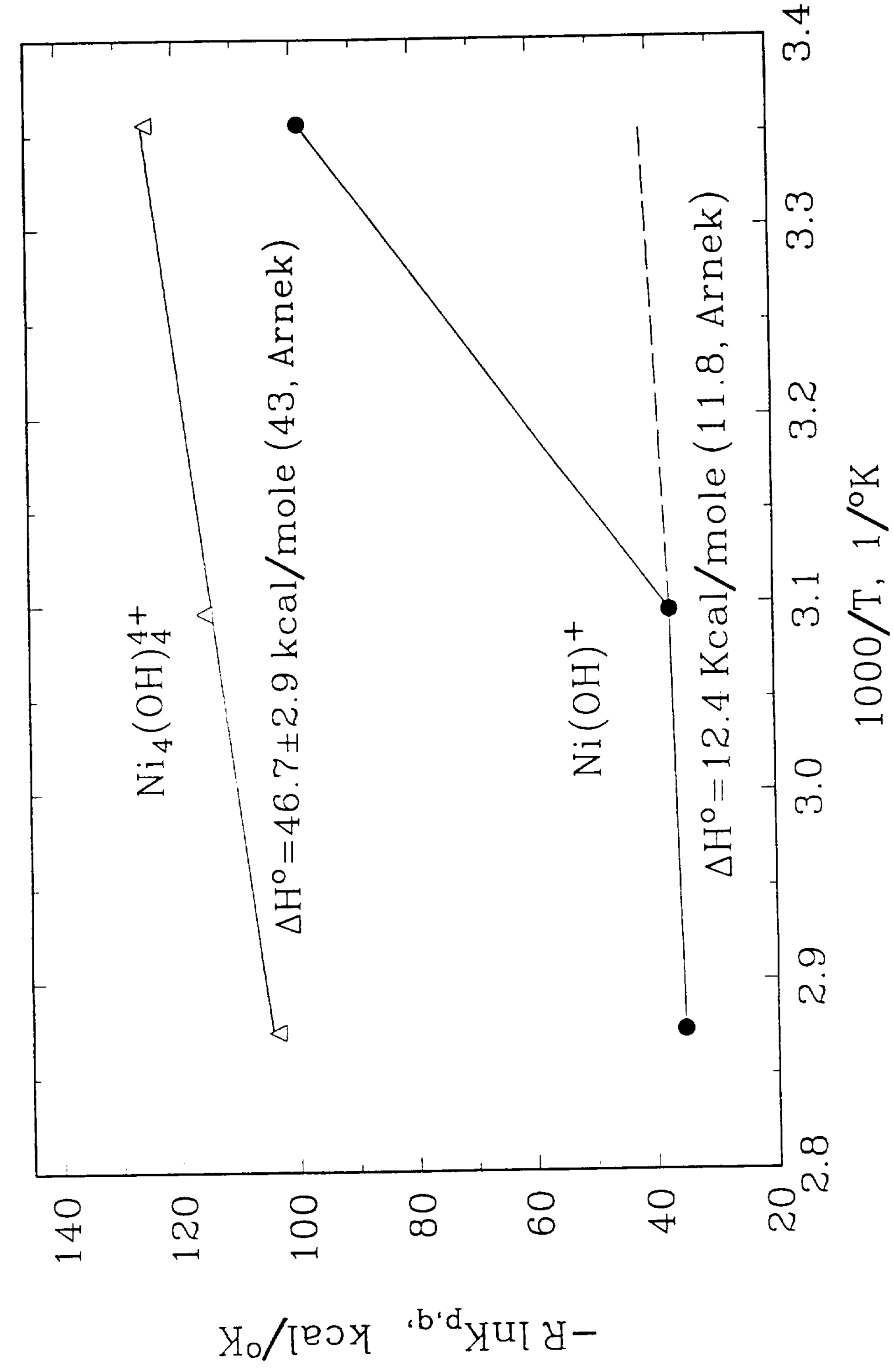
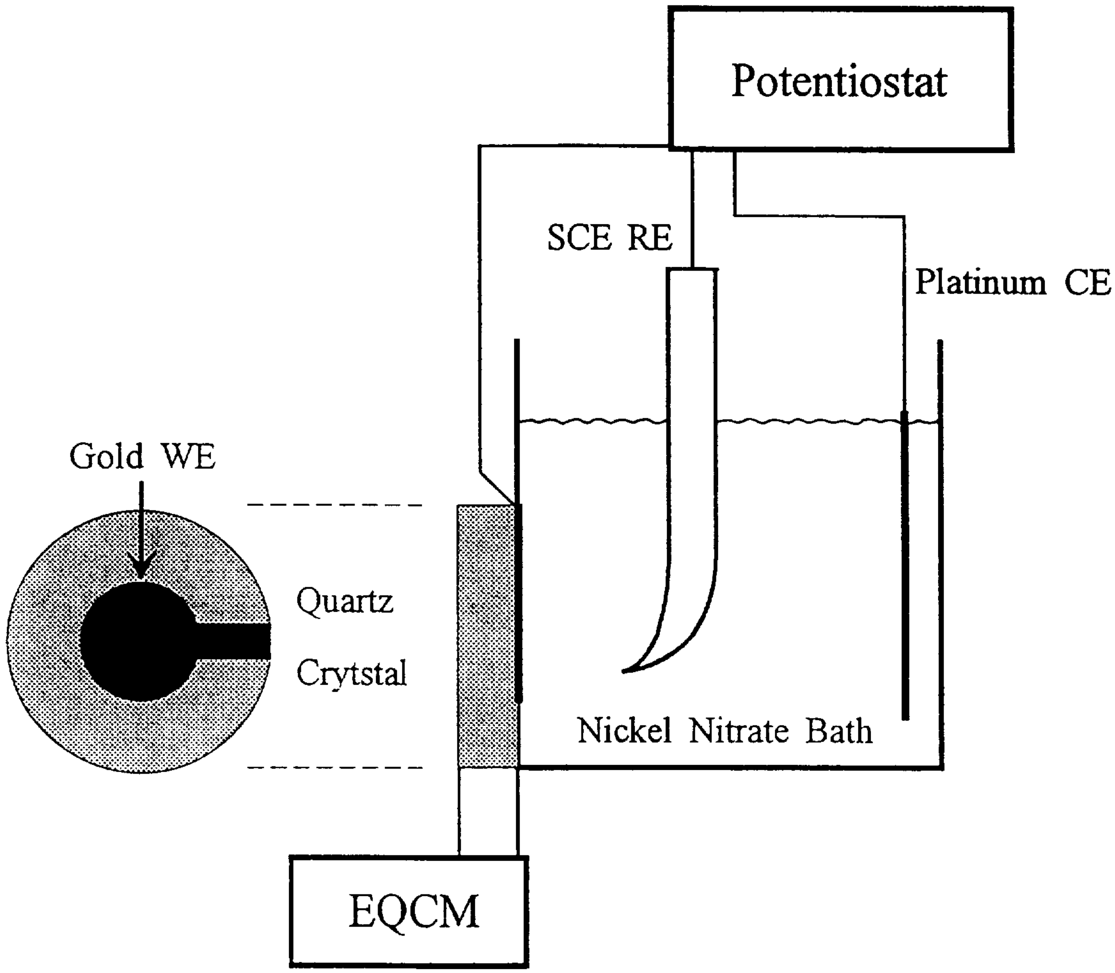
Effect of Ionic Strength on the Equilibrium Quotient of Nickel Complex

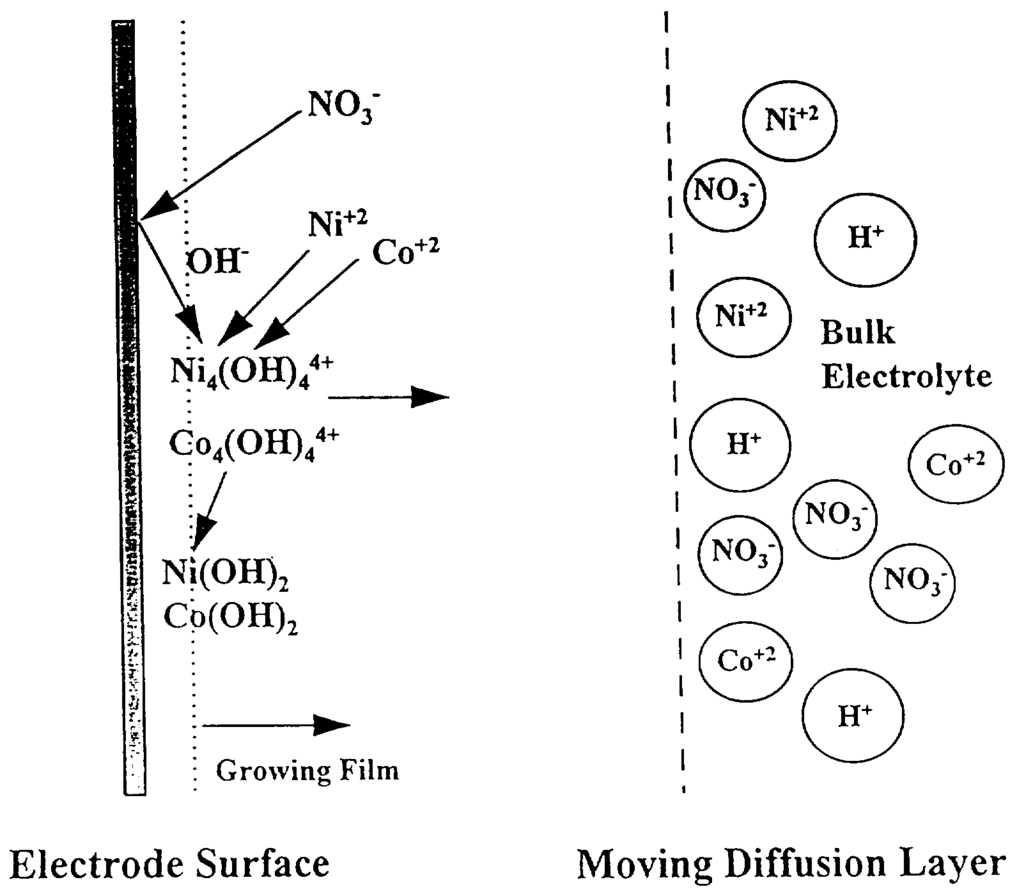


$(-R \ln K_{p,q})$ vs. $1/T$ for hydrolytic reactions of $Ni_4(OH)_4^{4+}$ and $Ni(OH)^+$



Schematic of an Electrochemical Quartz Crystal Microbalance





Schematic of the Deposition Process on Planar Electrodes

Governing Equations for Planar Film Model

- Mass balances for species: Ni^{2+}, Co^{2+}, NO_3^-, OH^-

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot Ni + R_i$$

- Equilibrium reactions for remaining species, H^+, $NiNO_3^+$, $Ni(NO_3)_2$, $CoNO_3^+$, $Co(NO_3)_2$, $Ni_4(OH)_4^{4+}$, and $Co_4(OH)_4^{4+}$

- Electroneutrality for solution potential, ϕ

- Eleven concentrations and ϕ

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Boundary Conditions for Planar Film Model

- Diffusion layer-electrolyte interface

$$C_i = C_{i,b}$$

$$\phi = 0$$

- Electrode surface
  - flux balances
  - equilibrium reactions
  - electroneutrality

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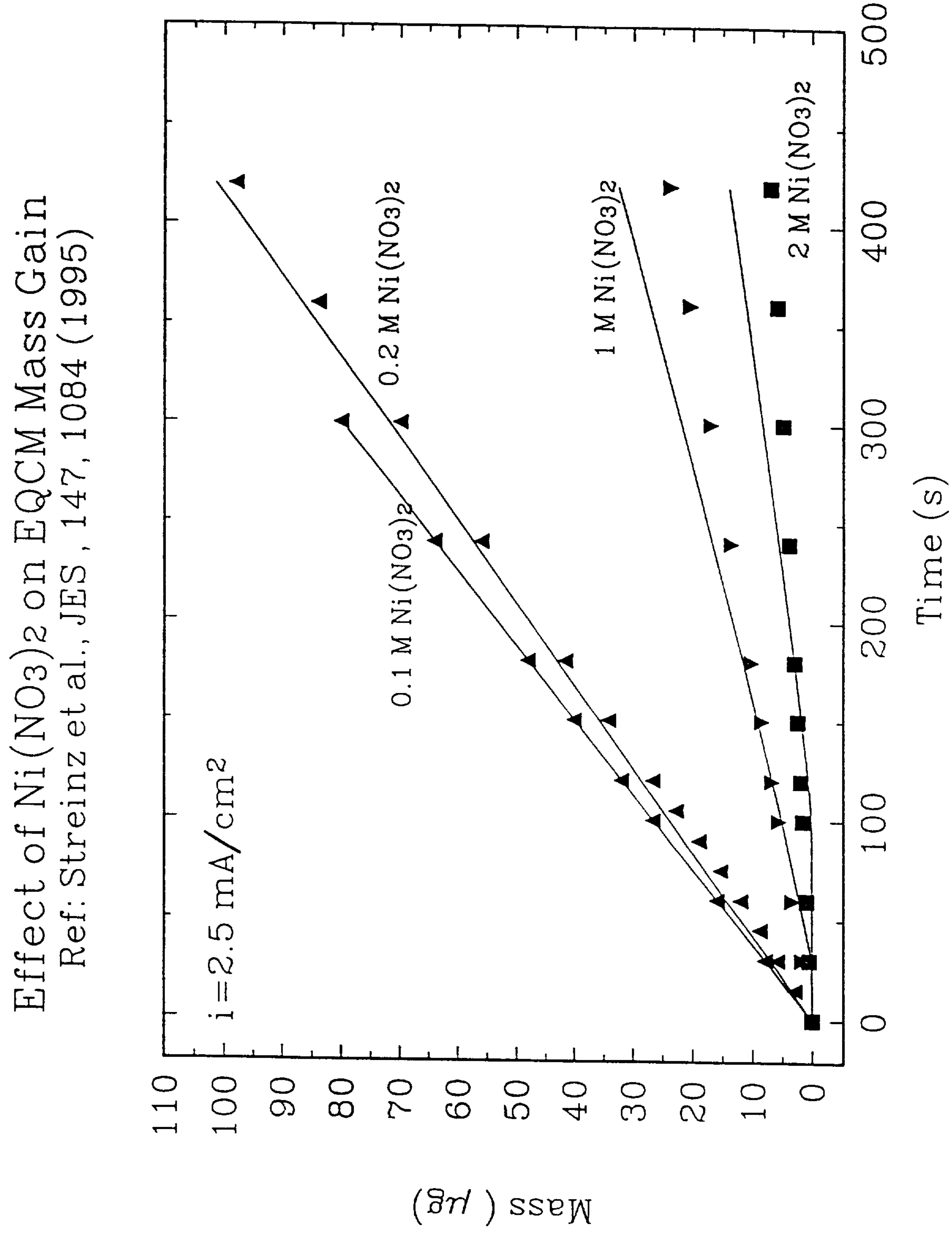
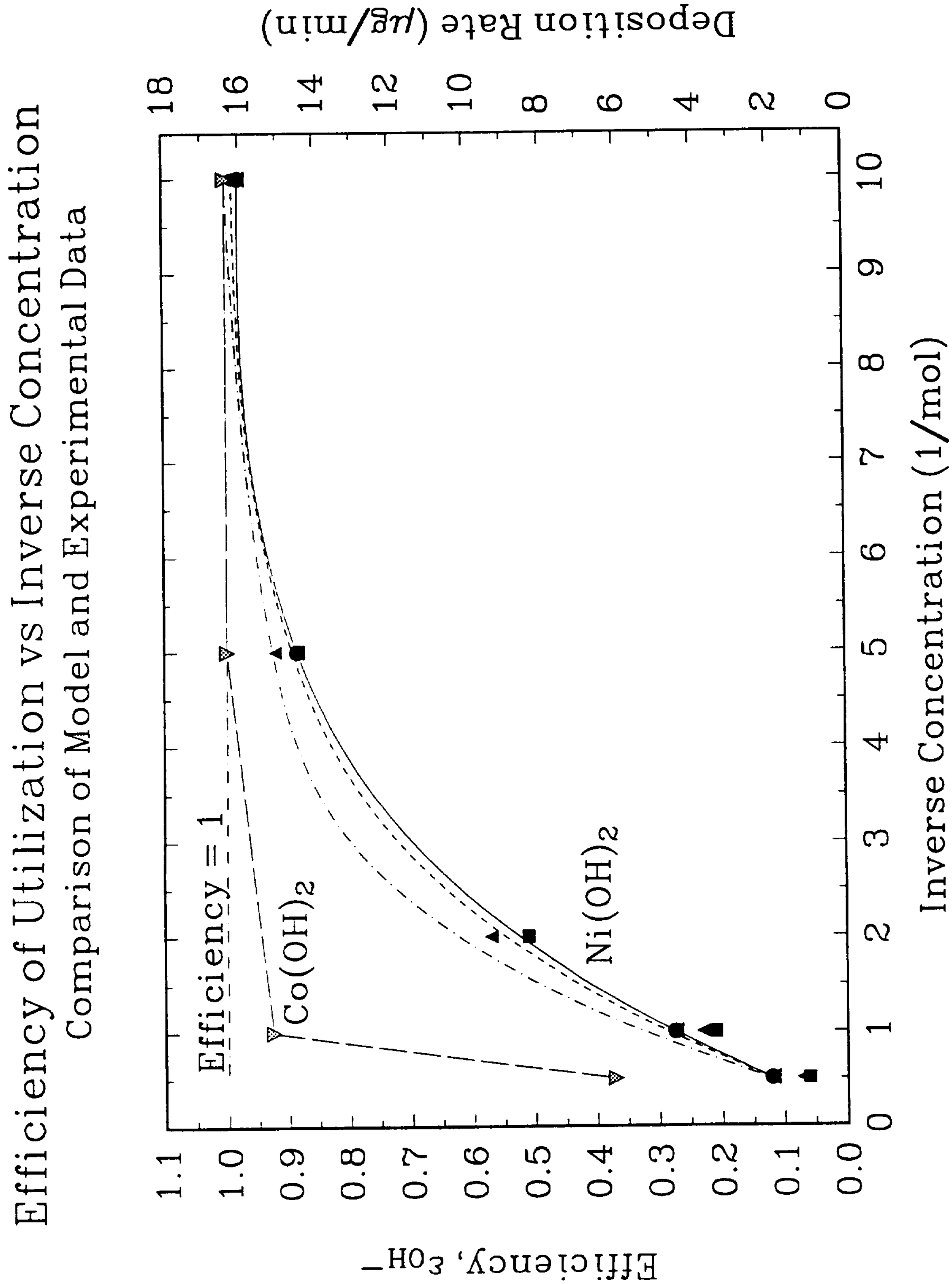

Effect of Ni(NO3)2 on EQCM Mass Gain
Ref: Streinz et al., JES, 147, 1084 (1995)
i=2.5 mA/cm2
0.1 M Ni(NO3)2
0.2 M Ni(NO3)2
1 M Ni(NO3)2
2 M Ni(NO3)2
Mass (μg)
Time (s)
0
10
20
30
40
50
60
70
80
90
100
110
0
100
200
300
400
500


Efficiency of Utilization vs Inverse Concentration
Comparison of Model and Experimental Data
Efficiency = 1
Co(OH)2
Ni(OH)2
Efficiency, εOH−
Deposition Rate (μg/min)
Inverse Concentration (1/mol)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
0
2
4
6
8
10
12
14
16
18
0
1
2
3
4
5
6
7
8
9
10

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

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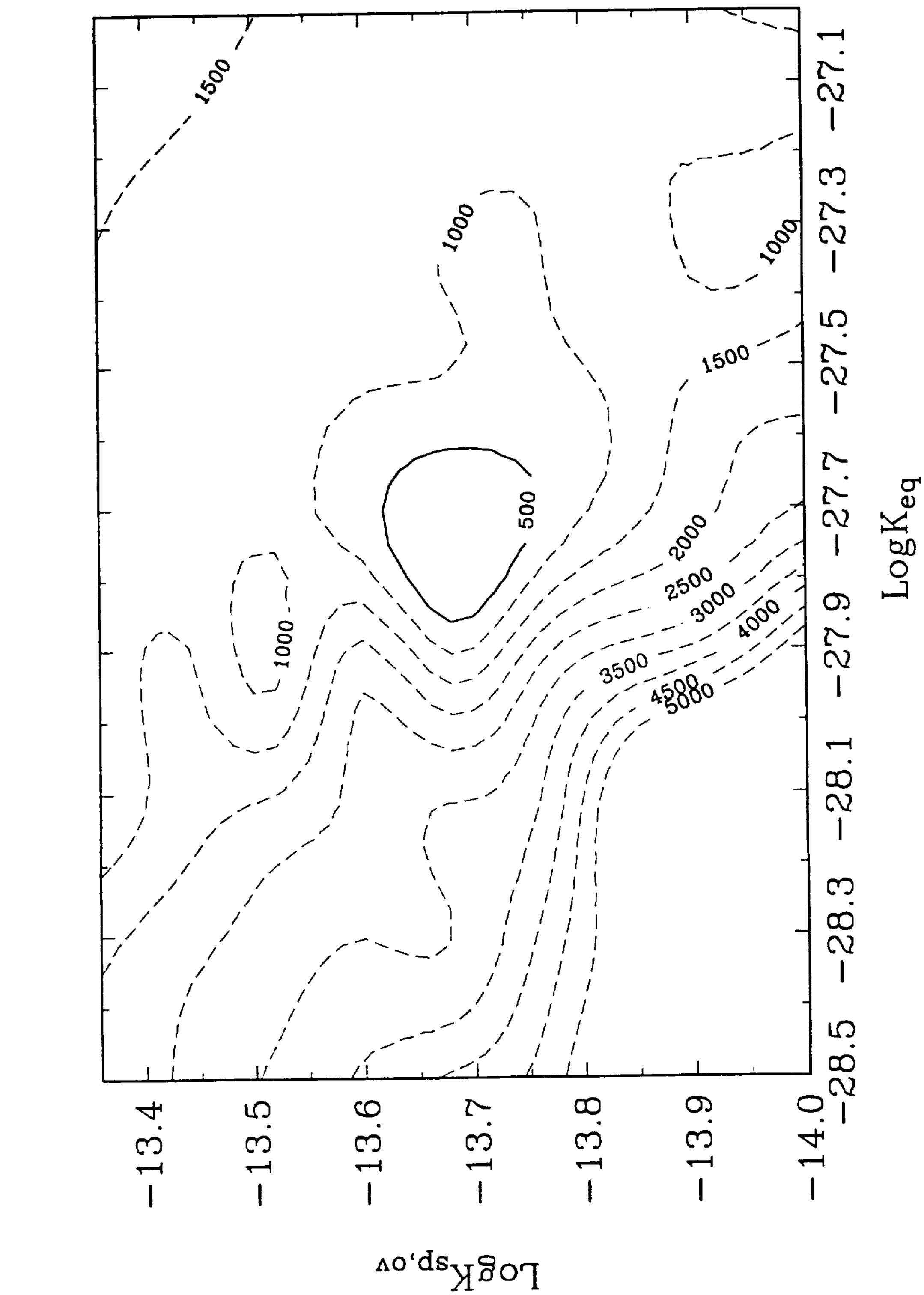
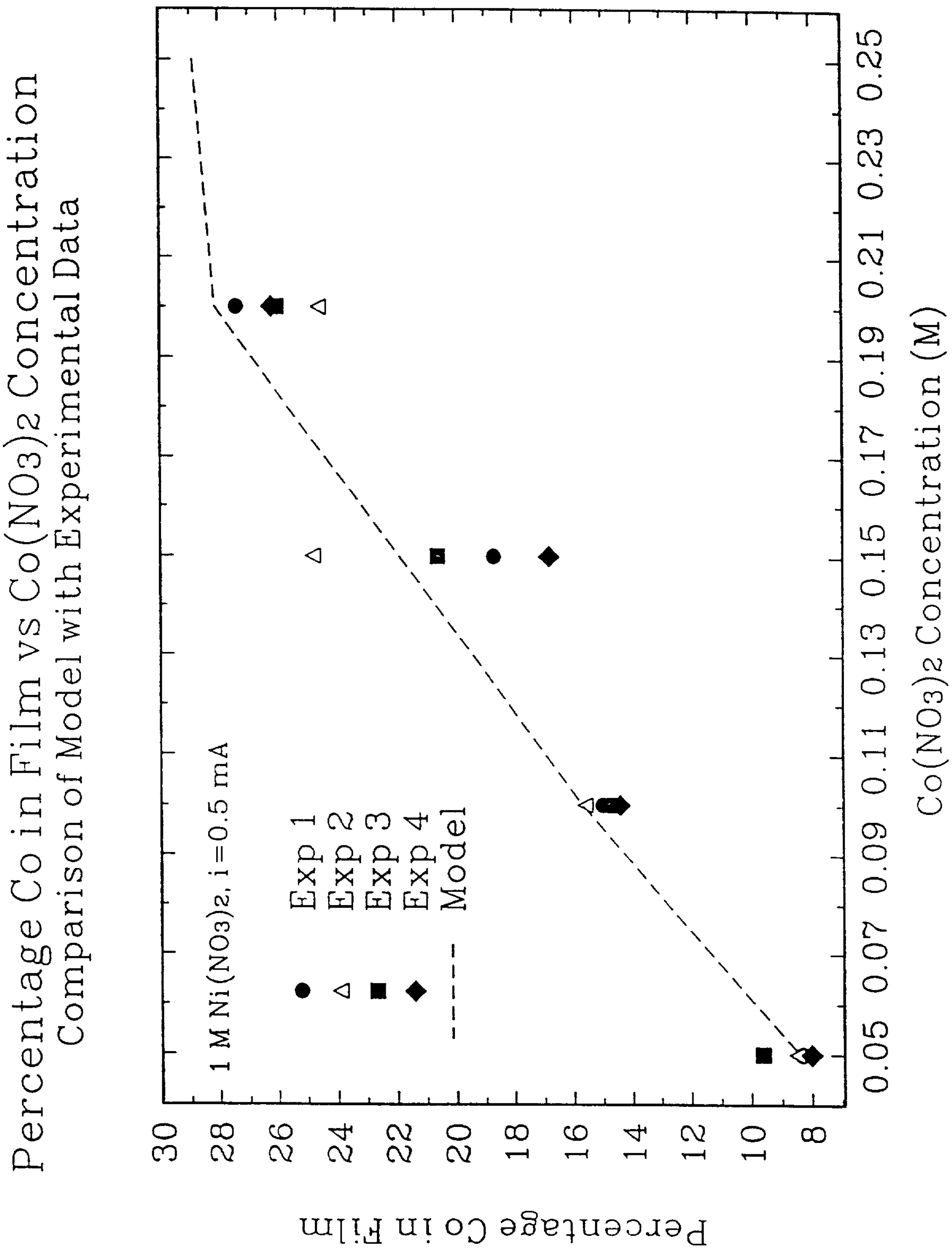
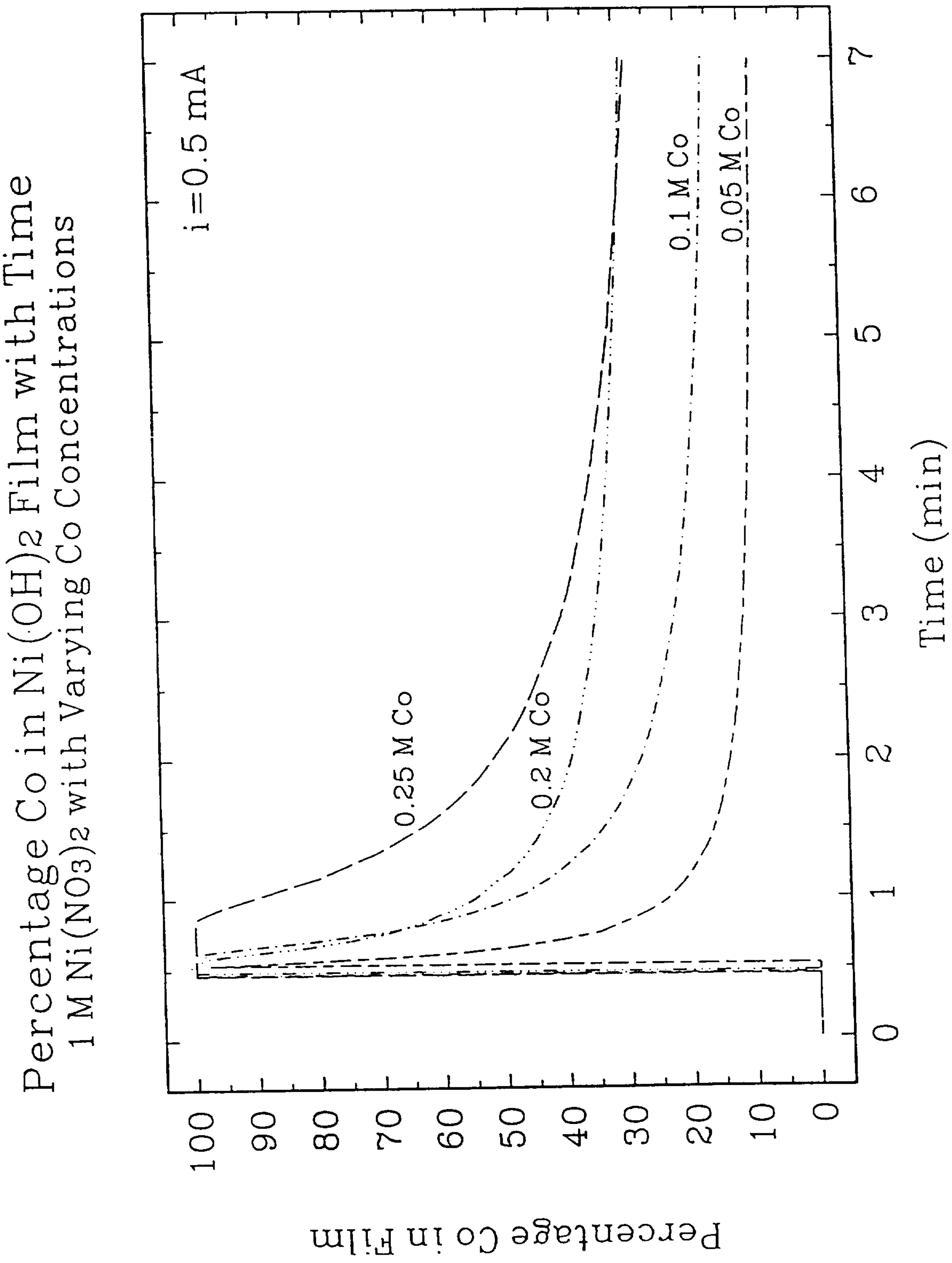
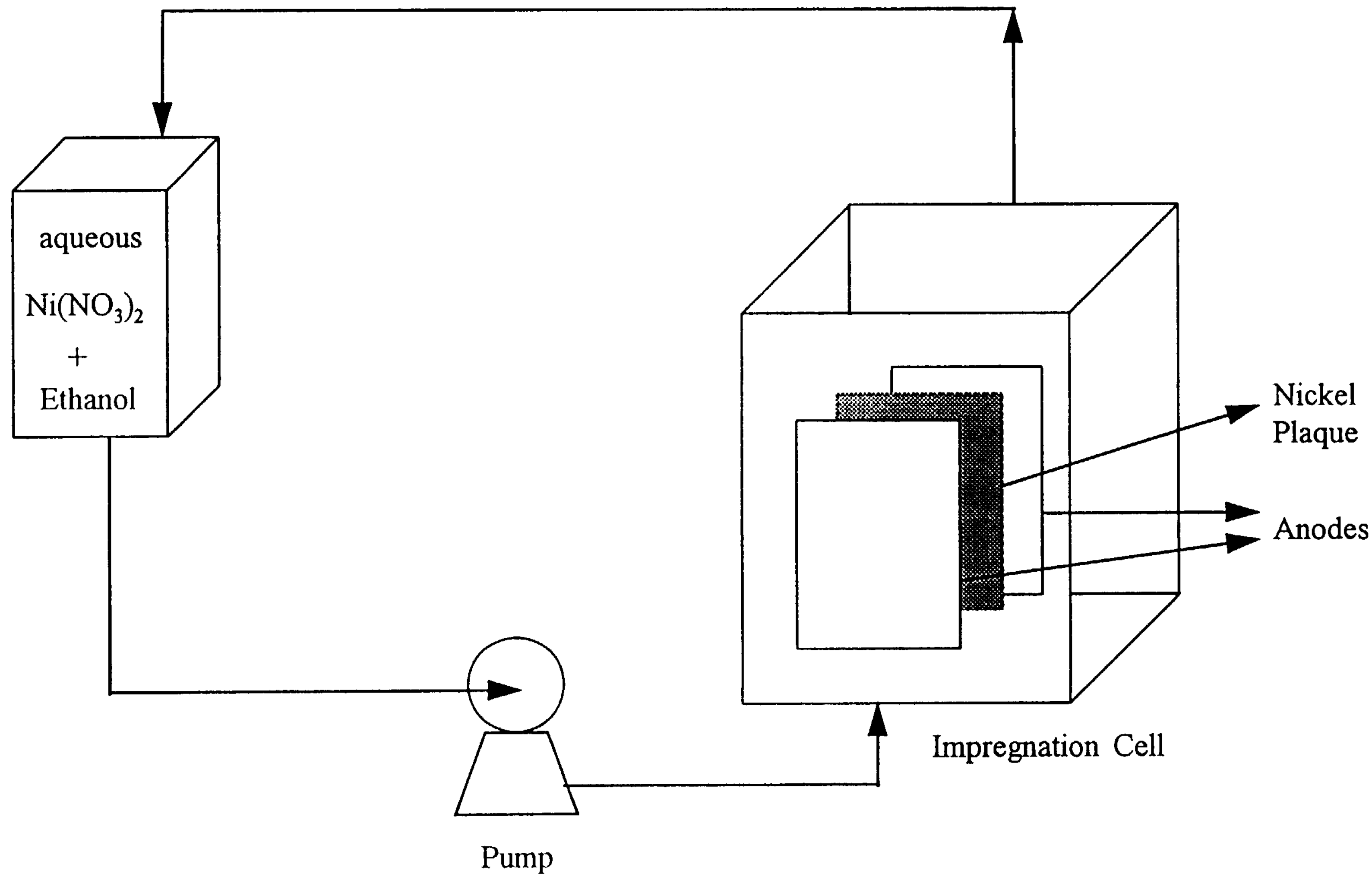
Contour Plot for E





Percentage Co in Film vs Co(NO3)2 Concentration
Comparison of Model with Experimental Data
1 M Ni(NO3)2, i=0.5 mA
Exp 1
Exp 2
Exp 3
Exp 4
Model
Percentage Co in Film
30
28
26
24
22
20
18
16
14
12
10
8
0.05 0.07 0.09 0.11 0.13 0.15 0.17 0.19 0.21 0.23 0.25
Co(NO3)2 Concentration (M)


Percentage Co in Ni(OH)2 Film with Time
1 M Ni(NO3)2 with Varying Co Concentrations
i=0.5 mA
0.25 M Co
0.2 M Co
0.1 M Co
0.05 M Co
Time (min)
Percentage Co in Film
0
1
2
3
4
5
6
7
100
90
80
70
60
50
40
30
20
10
0



Electrochemical Impregnation System

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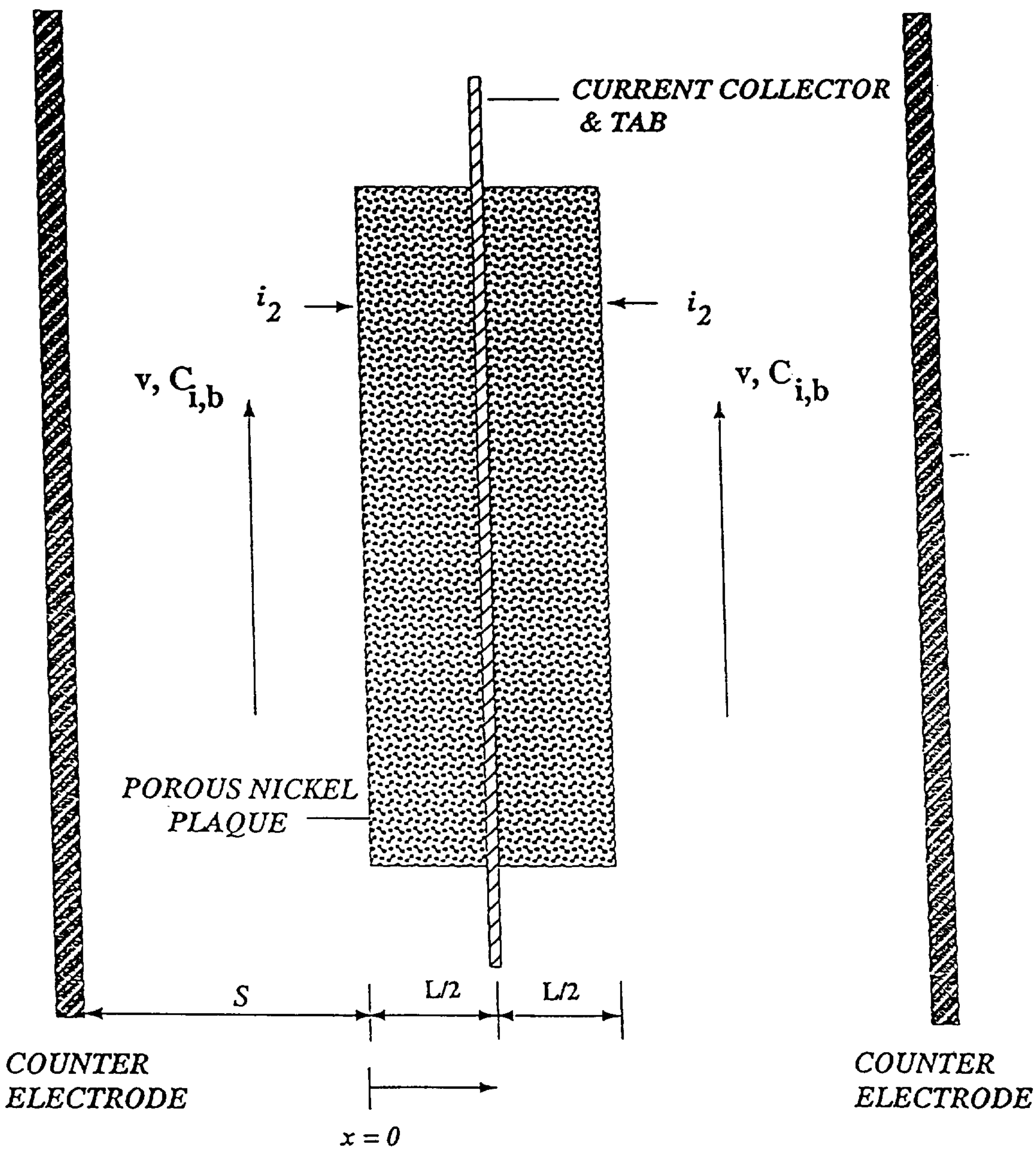
CURRENT COLLECTOR
& TAB
i2
i2
v, Ci,b
v, Ci,b
POROUS NICKEL
PLAQUE
S
L/2
L/2
COUNTER
ELECTRODE
COUNTER
ELECTRODE
x = 0

Governing Equations for Impregnation Model

- Mass balances for species: Ni^{2+}, Co^{2+}, NO_3^-, OH^-

$$\frac{\partial \varepsilon C_i}{\partial t} = -\frac{s_i}{nF}\frac{\partial i_2}{\partial x} - \frac{\partial N_i}{\partial x} + R_i$$

  - Flux: Diffusion and migration only

- Equilibrium equations for: H^+, $Ni_4(OH)_4^{4+}$, $Co_4(OH)_4^{4+}$, $Ni(NO_3)^+$, $Ni(NO_3)_2$, $Co(NO_3)^+$, $Co(NO_3)_2$
- ϕ_2 is governed by electroneutrality

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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:

$$\frac{\partial \varepsilon}{\partial t} = - r_{ppt1}\left(\frac{M}{\rho}\right)_{Ni(OH)_2} - r_{ppt2}\left(\frac{M}{\rho}\right)_{Co(OH)_2}$$

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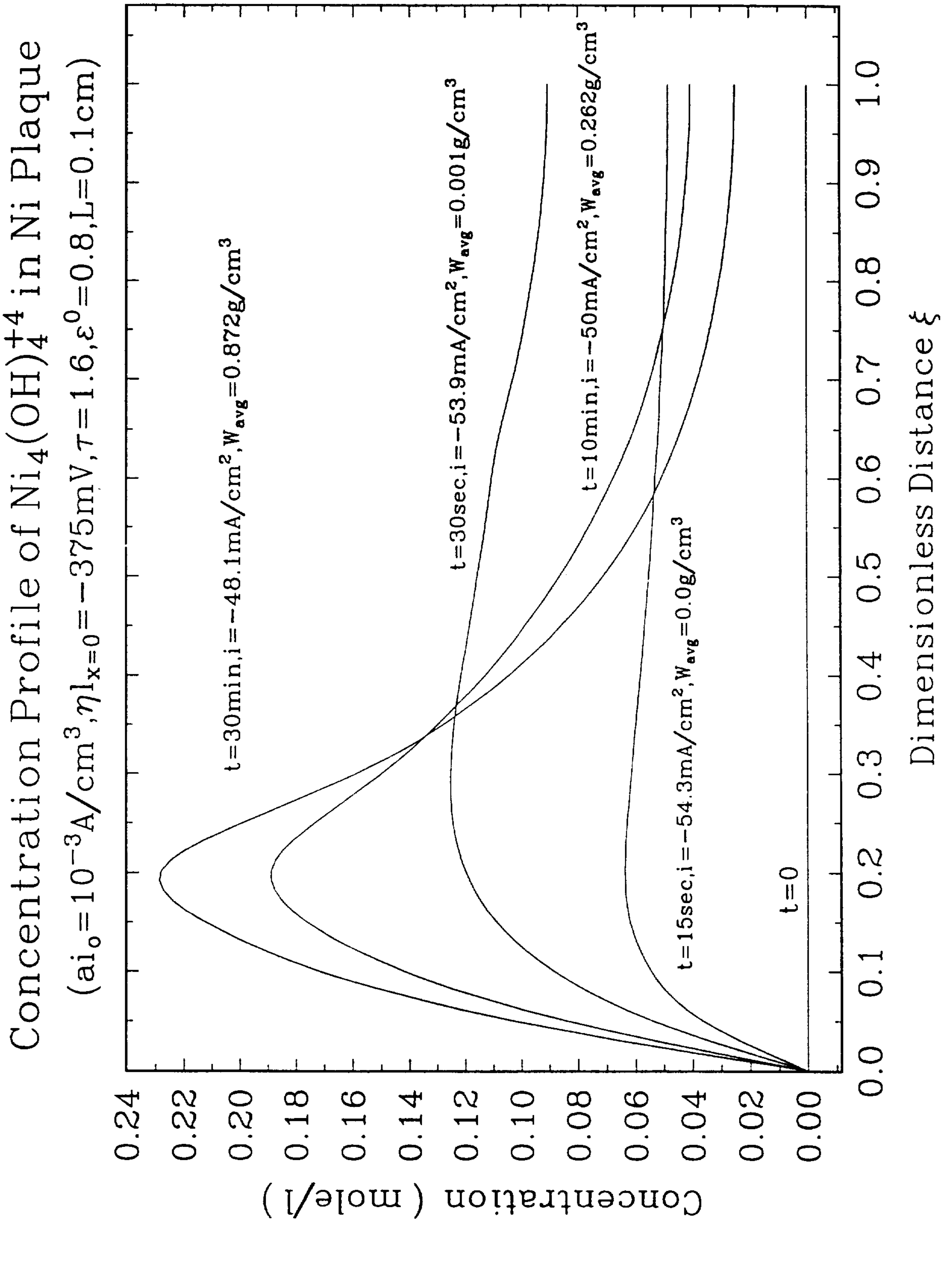
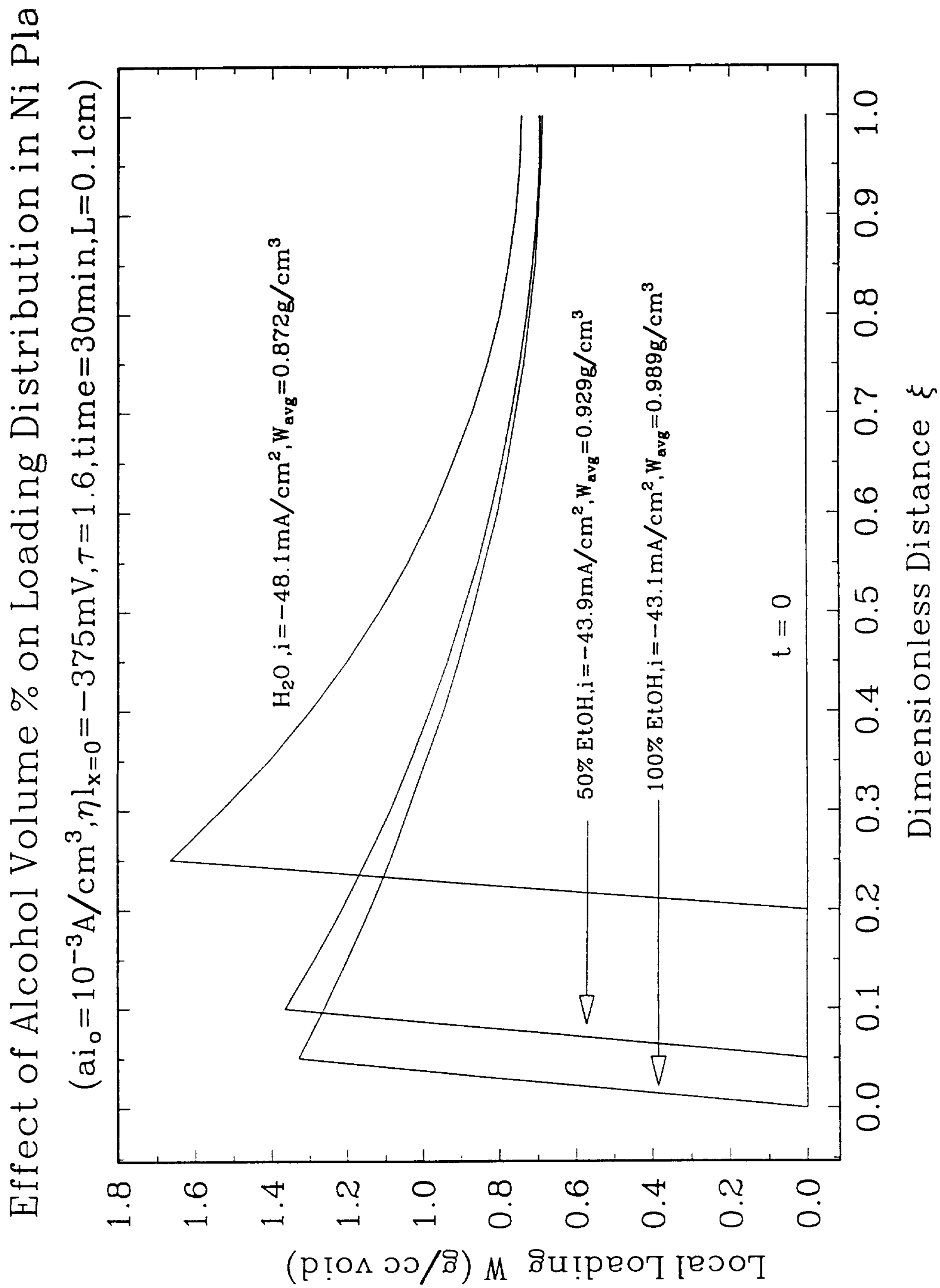
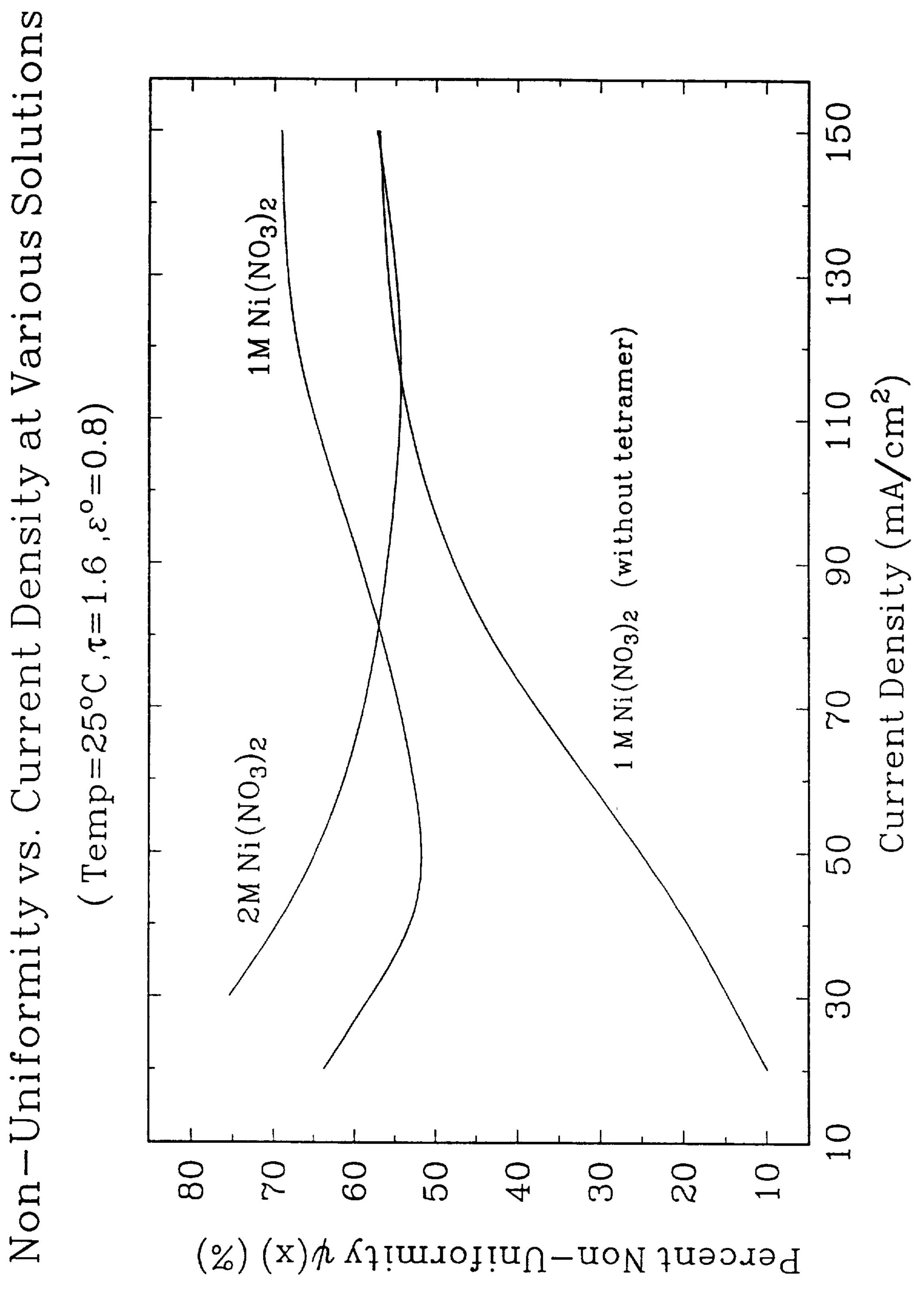


Concentration Profile of $Ni_4(OH)_4^{+4}$ in Ni Plaque
($ai_o=10^{-3}A/cm^3, \eta|_{x=0}=-375mV, \tau=1.6, \varepsilon^0=0.8, L=0.1cm$)
t=30min,i=-48.1mA/cm², W_avg=0.872g/cm³
t=30sec,i=-53.9mA/cm², W_avg=0.001g/cm³
t=10min,i=-50mA/cm², W_avg=0.262g/cm³
t=15sec,i=-54.3mA/cm², W_avg=0.0g/cm³
t=0
Concentration (mole/l)
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Dimensionless Distance ξ

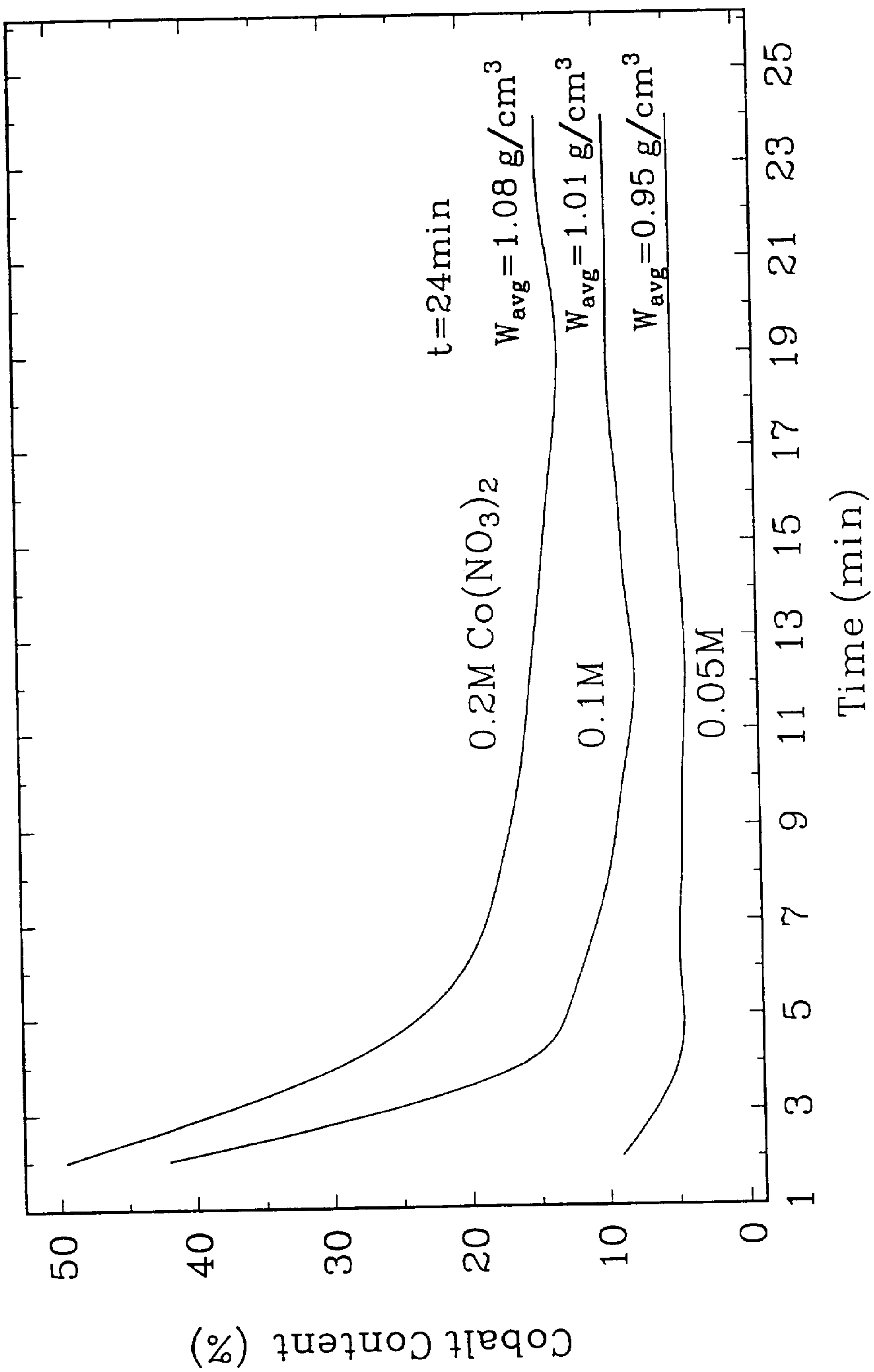


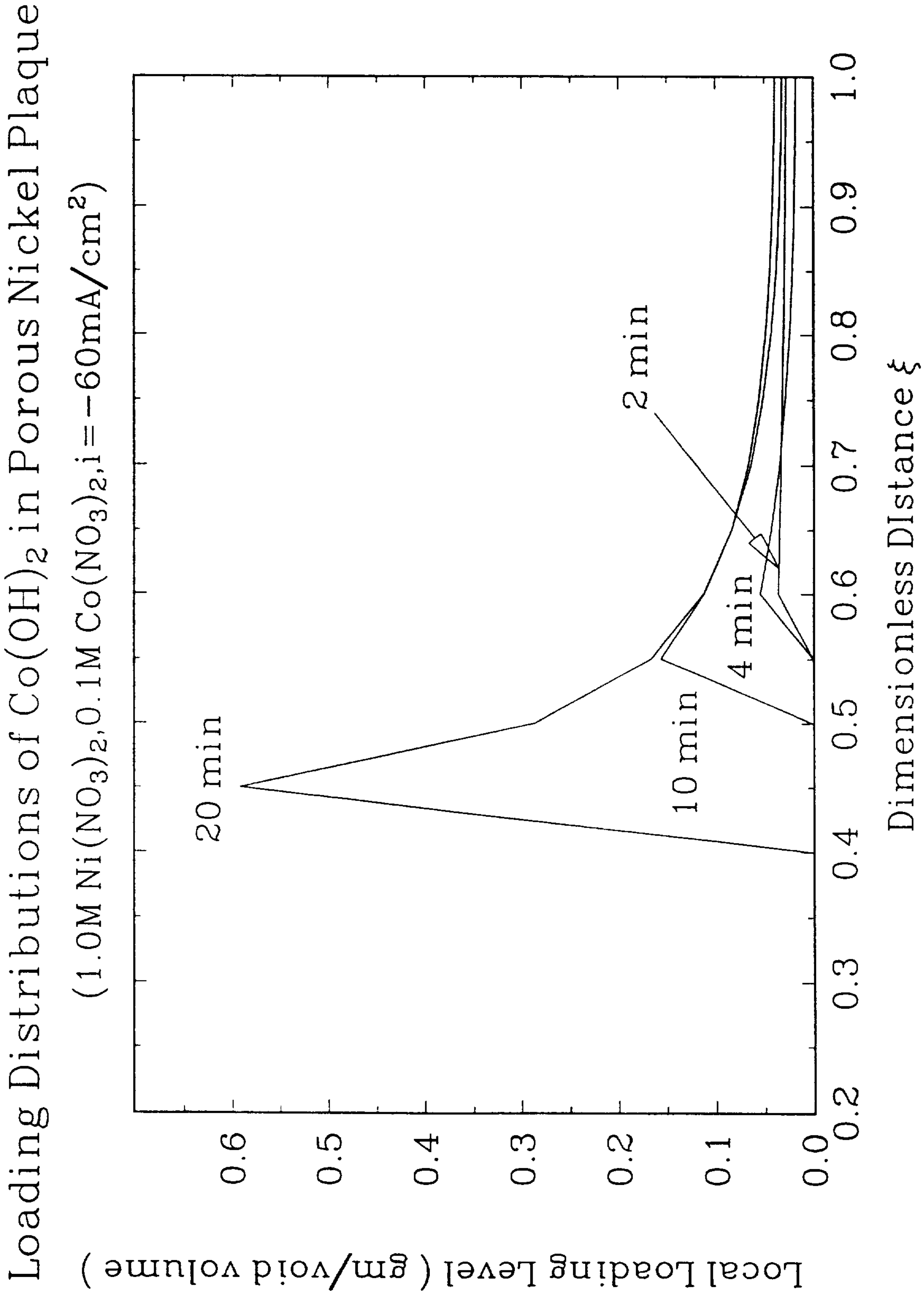
Effect of Alcohol Volume % on Loading Distribution in Ni Pla
(ai_o=10^{-3}A/cm^3,η|$_{x=0}$=−375mV,τ=1.6,time=30min,L=0.1cm)
H_2O ,i=−48.1mA/cm^2,W$_{avg}$=0.872g/cm^3
50% EtOH,i=−43.9mA/cm^2,W$_{avg}$=0.929g/cm^3
100% EtOH,i=−43.1mA/cm^2,W$_{avg}$=0.989g/cm^3
t = 0
Local Loading W (g/cc void)
Dimensionless Distance ξ
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.2
1.4
1.6
1.8


Non−Uniformity vs. Current Density at Various Solutions
(Temp=25°C ,τ=1.6 ,ε°=0.8)
1M Ni(NO3)2
2M Ni(NO3)2
1 M Ni(NO3)2 (without tetramer)
Percent Non−Uniformity ψ(x) (%)
Current Density (mA/cm2)
80
70
60
50
40
30
20
10
10
30
50
70
90
110
130
150

Cobalt Content of the Active Material in Ni Plaque

(T=25°C, $i=-60 mA/cm^2$, $\varepsilon=0.8$, 1M $Ni(NO_3)_2$)

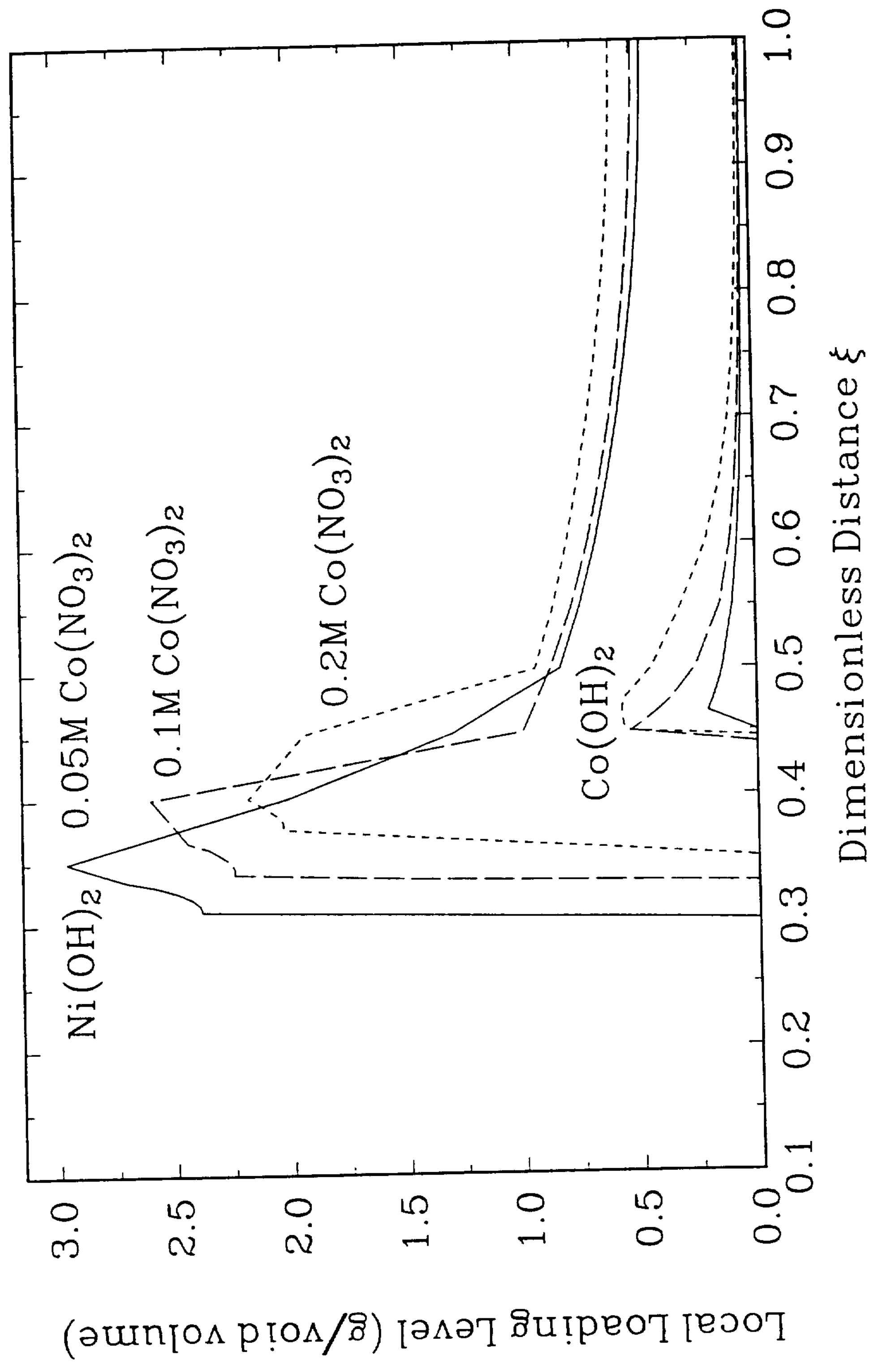


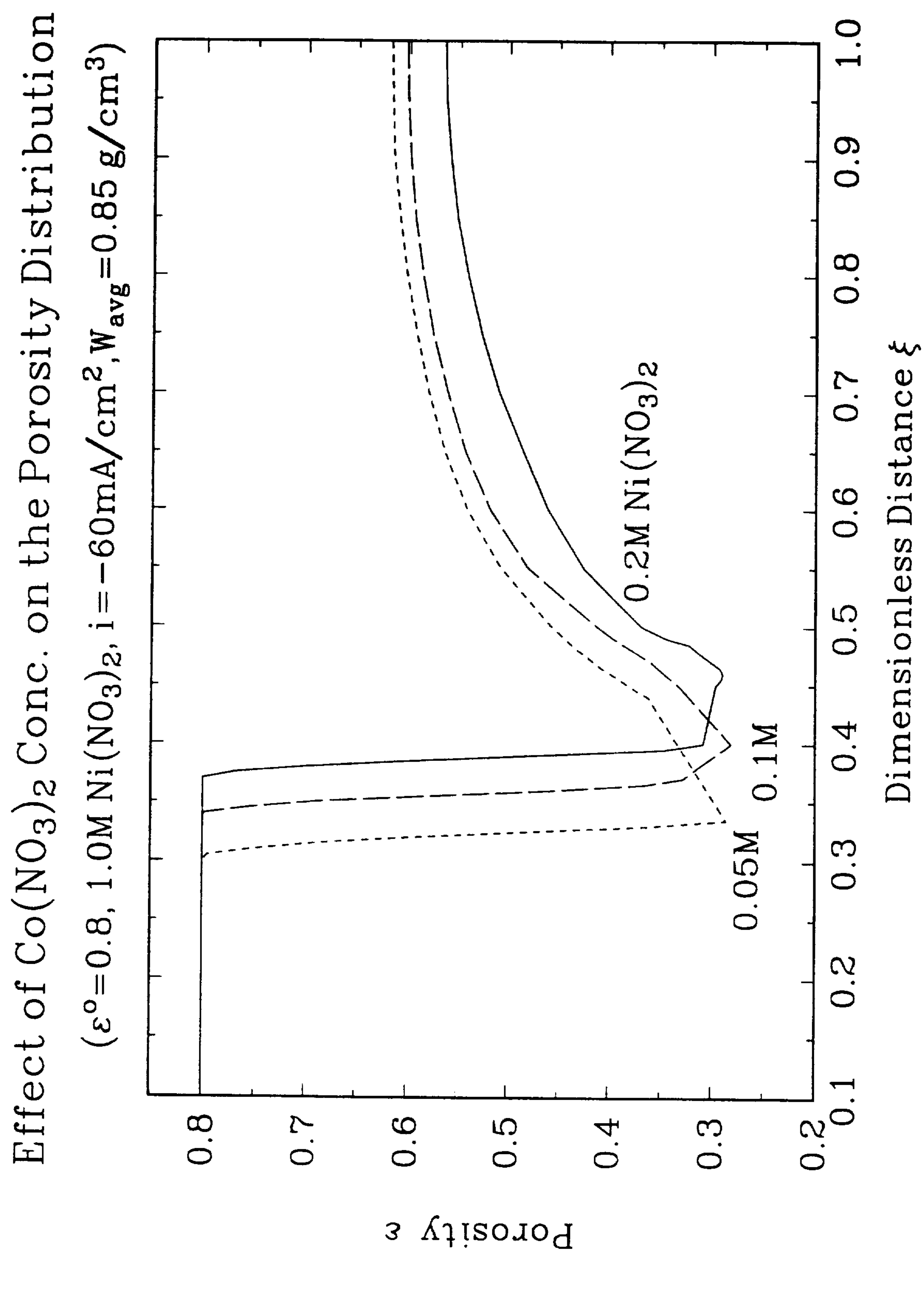


Loading Distributions of $Co(OH)_2$ in Porous Nickel Plaque
($1.0M\ Ni(NO_3)_2, 0.1M\ Co(NO_3)_2, i = -60mA/cm^2$)
Local Loading Level (gm/void volume)
Dimensionless DIstance ξ
20 min
10 min
4 min
2 min
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Distributions of $Ni(OH)_2$ & $Co(OH)_2$ in Nickel Plaque

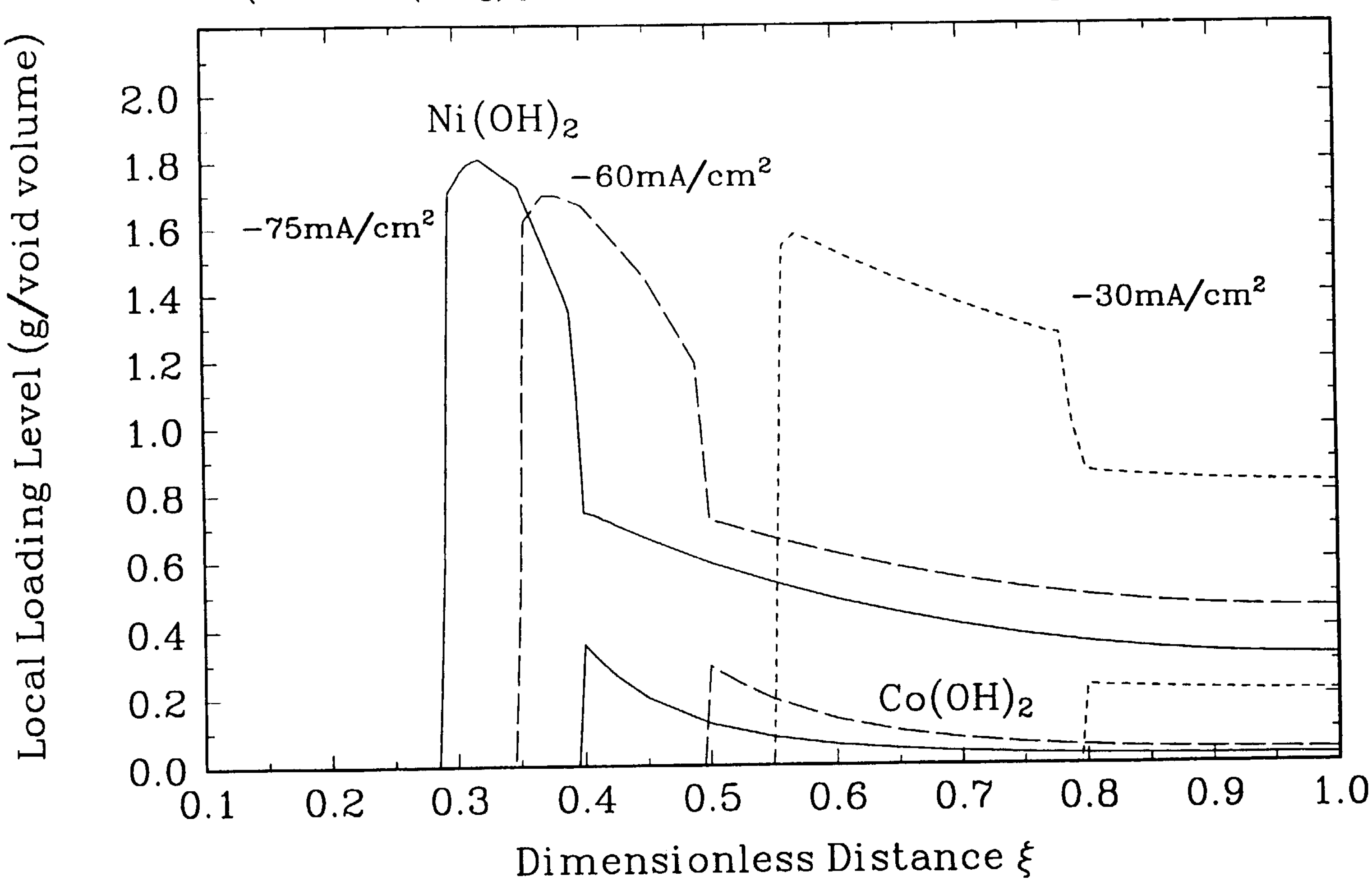
($1.0M\ Ni(NO_3)_2$, $i=-60mA/cm^2$, $W_{avg}=0.85gm/cm^3$)




Effect of $Co(NO_3)_2$ Conc. on the Porosity Distribution
(ε^o=0.8, 1.0M $Ni(NO_3)_2$, i=−60mA/cm^2, W_{avg}=0.85 g/cm^3)
0.2M $Ni(NO_3)_2$
0.1M
0.05M
Porosity ε
Dimensionless Distance ξ
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

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, Alcohol, [$Ni(NO_3)_2$])
- Raman Spectra Identifies $Ni_4(OH)_4^{4+}$
  - Absorbance is f(pH)
- EQCN Experiments and Film Model
  - Confirm Values of K_{eq}, K_{sp} ,and Ionic Strength Equations
- Porous Electrode Model
  - Agree with $Ni(OH)_2$ Distribution Measurements
- Porous Electrode Model Predicts Ni/Co Distributions

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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

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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

- $Co(OH)_2$ and $Ni(OH)_2$ depends on $[Co(NO_3)_2]$, Ionic Strength, $[Ni(NO_3)_2]$, T, and Alcohol Concentration

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