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THE JPL/NASA/TAMU NICKEL-CADMIUM BATTERY MODEL DEVELOPMENT STATUS

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NASA BATTERY WORKSHOP
HUNTSVILLE, ALABAMA

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OUTLINE

CELL MODEL DEVELOPMENT

BATTERY MODEL DEVELOPMENT

JPL DEVELOPMENT GOALS

APPROACHES SELECTED

NEGATIVE ELECTRODE

POSITIVE ELECTRODE

ADDITIONAL WORK

SUMMARY

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CELL MODEL DEVELOPMENT

TEXAS A&M UNIVERSITY DEVELOPED FIRST PRINCIPLES NI-CD BATTERY MODEL

positive electrode

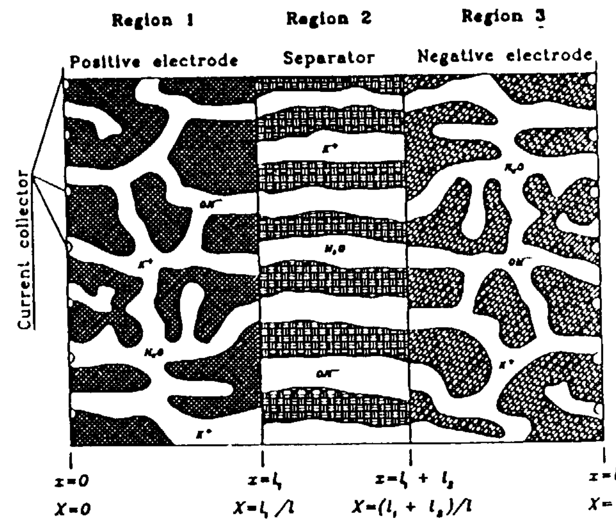
$$NiOOH + H_2O + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Ni(OH)_2 + OH^- \quad [1]$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} 2\,OH^- \quad [2]$$

negative electrode

$$Cd + 2\,OH^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Cd(OH)_2 + 2e^- \quad [3]$$

$$2\,OH^- \underset{charge}{\overset{discharge}{\longleftarrow}} \frac{1}{2}O_2 + H_2O + 2e^- \quad [4]$$



PUBLISHED RESULTS OF EFFORTS

1. D. Fan and R.E. White, "Mathematical Model of a Sealed Nickel-Cadmium Battery", J. Electrochemical Soc., Vol 138, No. 1, pp. 17, January 1991.

2. D. Fan and R.E. White, " Mathematical Modeling of a Nickel-Cadmium Battery: Effects of Intercalation and oxygen Reactions", Vol.138 No. 10, pp. 2952, October 1991.

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BATTERY MODEL DEVELOPMENT

THERMAL MODEL - USES FINITE DIFFENERNCE NODAL MODEL

BATTERY LEVEL MODEL - PROVIDES DESIGN AND CONTROL OPTIONS

CELL DESIGN DATABASE - ALLOWS ENGINEERING LEVEL CELL DESIGN INPUTS

REGIME CONTROL - PROVIDES BATTERY LEVEL REGIME SPECIFICATION

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APPROACHES SELECTED

- IMPROVED TREATMENT OF POSITIVE ELECTRODE
  - LINEARIZED PROTON DIFFUSION EQUATION IN OXIDE LAYER
  - ELECTRONIC CONDUCTIVITY OF OXIDE LAYER
- IMPROVE TREATMENT OF NEGATIVE ELECTRODE
  - MODIFIED KINETIC EXPRESSION AS PER Pb/PbSO
  - IMPROVED SOLID PHASE CONDUCTIVITY

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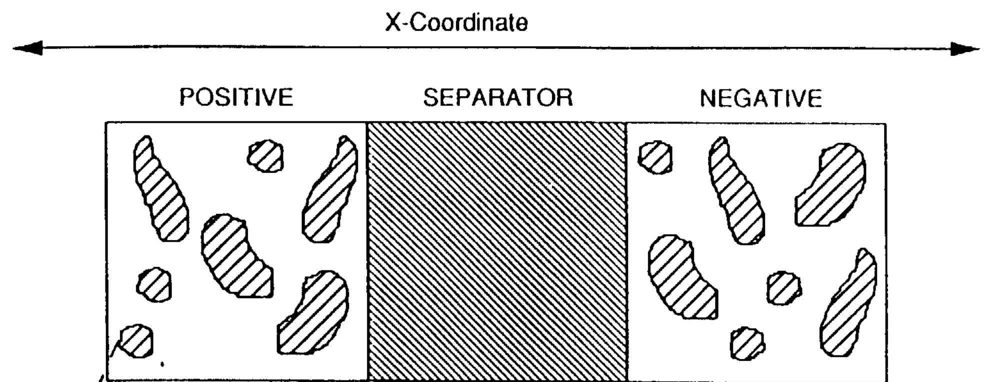
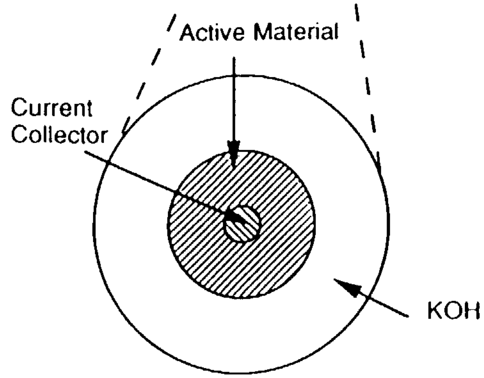
ADDITION OF OXIDE LAYER TO EXISTING MODEL



ONE DIMENSIONAL MACRO - HOMOGENEOUS MODEL



- OXIDE LAYER TREATMENT
    - CREATES HETROGENEOUS SOLID PHASE
    - ALLOWS SPECIES TRANSPORT ACROSS OXIDE LAYER
    - MAINTAINS SIMPLICITY OF ONE DIMENSIONAL APPROACH
    - INDEPENDENT OF INTERNAL ELECTRODE GEOMETRY

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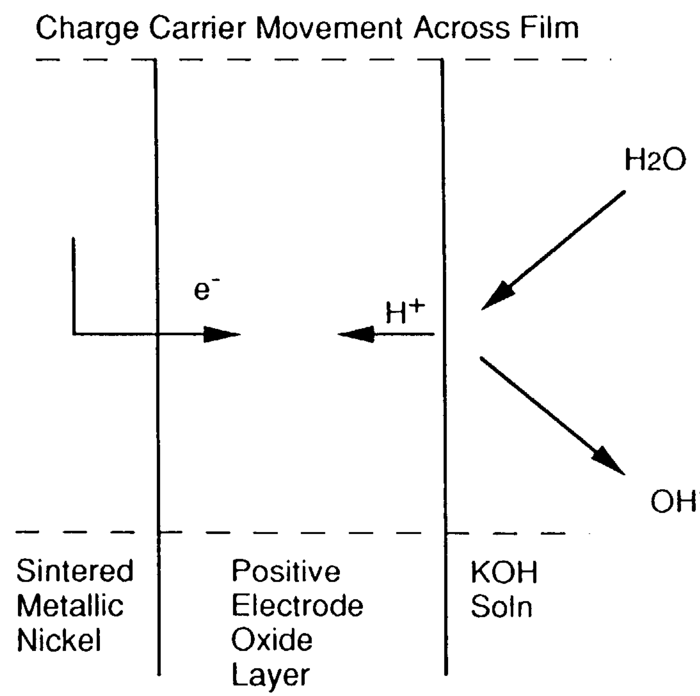
NICKEL OXIDE LAYER CHEMISTRY



- OVERALL REACTION $NiOOH + H_2O + e^- \Leftrightarrow Ni(OH)_2 + OH^-$

- SURFACE REACTION $H_2O \Leftrightarrow OH^- + H^+$

- BULK REACTION $NiOOH + H^+ + e^- \Leftrightarrow Ni(OH)_2$

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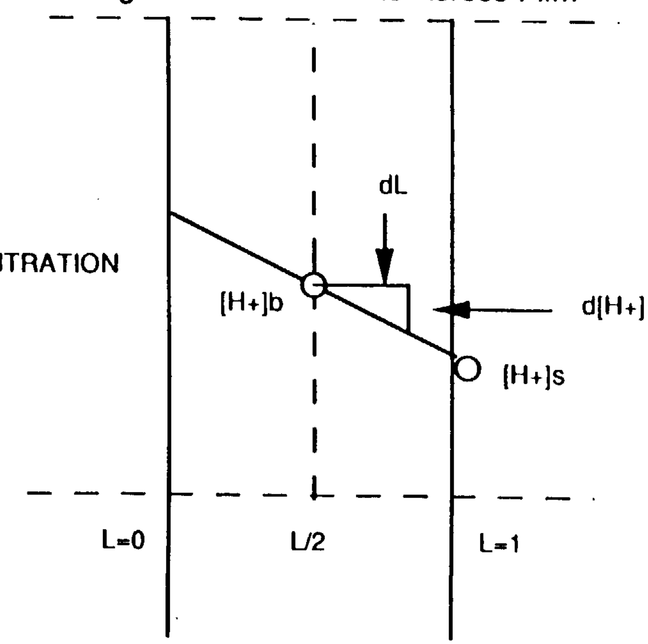
LINEARIZED PROTON DIFFUSION GRADIENT DIAGRAM



$$[H^+]_S = [H^+]_b - d[H^+] / dL$$

$$d[H^+]/dL = J_{ni} * AL / 2FD$$

Where:
- D is Diffusion Coefficient
- $[H^+]_S$ is Surface Proton Concentration
- $[H^+]_B$ is Bulk Proton Concentration
- L is Film Thickness
- Jni is Reaction Current Density
- A is the Specific Surface Area

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ELECTRONIC CONDUCTIVITY OF OXIDE LAYER

$$\left(J_{Ni} + J_{O_2}\right) = -\sigma_{ox} \frac{\partial \phi_{ox}}{\partial y}$$

$$\phi_{ox} = \phi_s - A \int_0^L \frac{\left(J_{Ni} + J_{O_2}\right)}{\sigma_{ox}} \, dy$$

WHERE

- ϕ_{ox} **IS POTENTIAL IN THE OXIDE PHASE AT THE ELECTROLYTE INTERFACE**
- ϕ_s **IS THE POTENTIAL IN THE SOLID MATRIX**
- **L IS THE OXIDE LAYER THICKNESS**
- **A IS THE SPECIFIC AREA**

CONDUCTIVITY OF SOLID OXIDE LAYER IS EXPRESSED AS A SEMICONDUCTOR

$$\sigma_{ox} = \sigma_{max} \, e^{-b\,(1-\theta)^c} \qquad \textit{DISCHARGE}$$

$$\sigma_{ox} = \sigma_{max} \qquad \textit{CHARGE}$$

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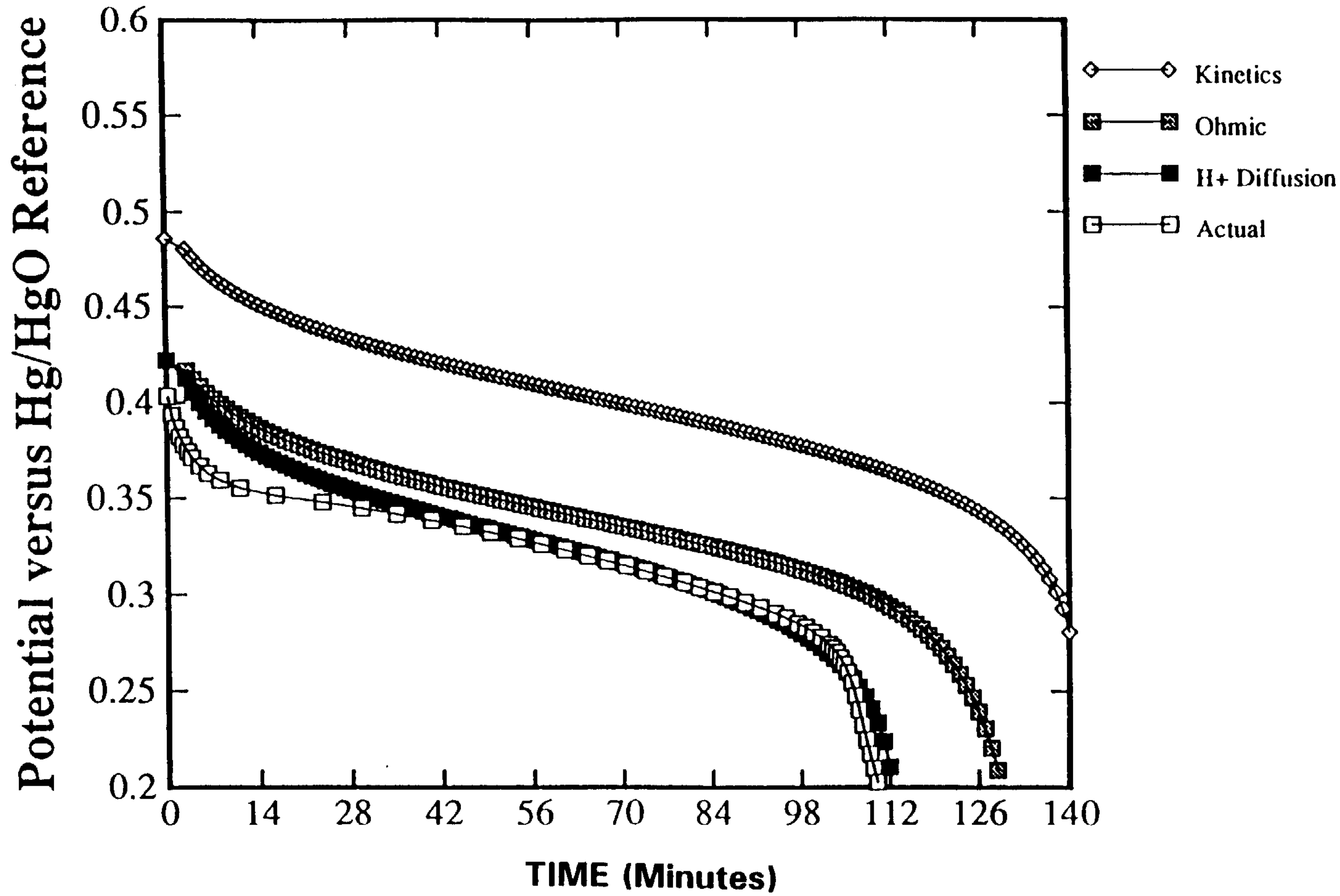
Predicted Positive Potentials for Disharge



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CADMIUM ELECTRODE KINETICS

MODIFIED AS PER NYUGEN Pb-PbS04 KINETICS

$$j_{Cd} = i_{0,ref}\, a_{Cd} \left(\frac{\varepsilon_3 - \varepsilon_{03}}{\varepsilon_{max3} - \varepsilon_{03}} \right)^{\zeta 3} \left\{ \left(\frac{C}{C_{ref}} \right)^{\gamma_3} \exp\left[\frac{\alpha_a F}{RT} \eta_3 \right] - \left(\frac{\varepsilon_{max3} - \varepsilon_3}{\varepsilon_{max3} - \varepsilon_{03}} \right) \exp\left[\frac{-\alpha_c F}{RT} \eta_3 \right] \right\} \quad (5)$$

PRE-EXPONENTIAL AREA TERM INCREASES OVERPOTENTIAL AT LOW STATES-OF-CHARGE

CATHODIC TERM GIVES HIGHER OVERPOTENTIAL AT END-OF-CHARGE

IMPROVES BEGINNING OF LIFE PREDICTIONS

ADDS DEGRADATION / CAPACITY UTILIZATION FUNCTION

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CADMIUM ELECTRODE OHMIC DROP IN X-AXIS

ADDED STATE-OF-CHARGE DEPENDANCE TO OHM'S LAW IN SOLID PHASE

$$\sigma = A * \mathbf{exp}^{-B * (1 - \theta)^{C}}$$

WHERE σ IS THE CONDUCTIVITY, A,B, AND C ARE CONSTANTS, AND θ IS SOC

$$i_2 - \sigma_{Cd}\, \epsilon^{exm3} \left(\frac{d\Phi_{1,Cd}}{dx} \right) = i_{cell}$$

WHERE i_2 IS CURRENT THROUGH ELECTROLYTE,
i_{cell} IS TOTAL CURRENT FLUX,
exm1 IS THE TORTUOSITY PARAMETER,
ρ_1 IS THE POTENTIAL IN THE SOLID

UTILIZATION ON DISCHARGE NOW DECREASES WITH INCREASED RATE

STRONG EFFECT ON LOCAL CURRENT DENSITY DISTRIBUTION

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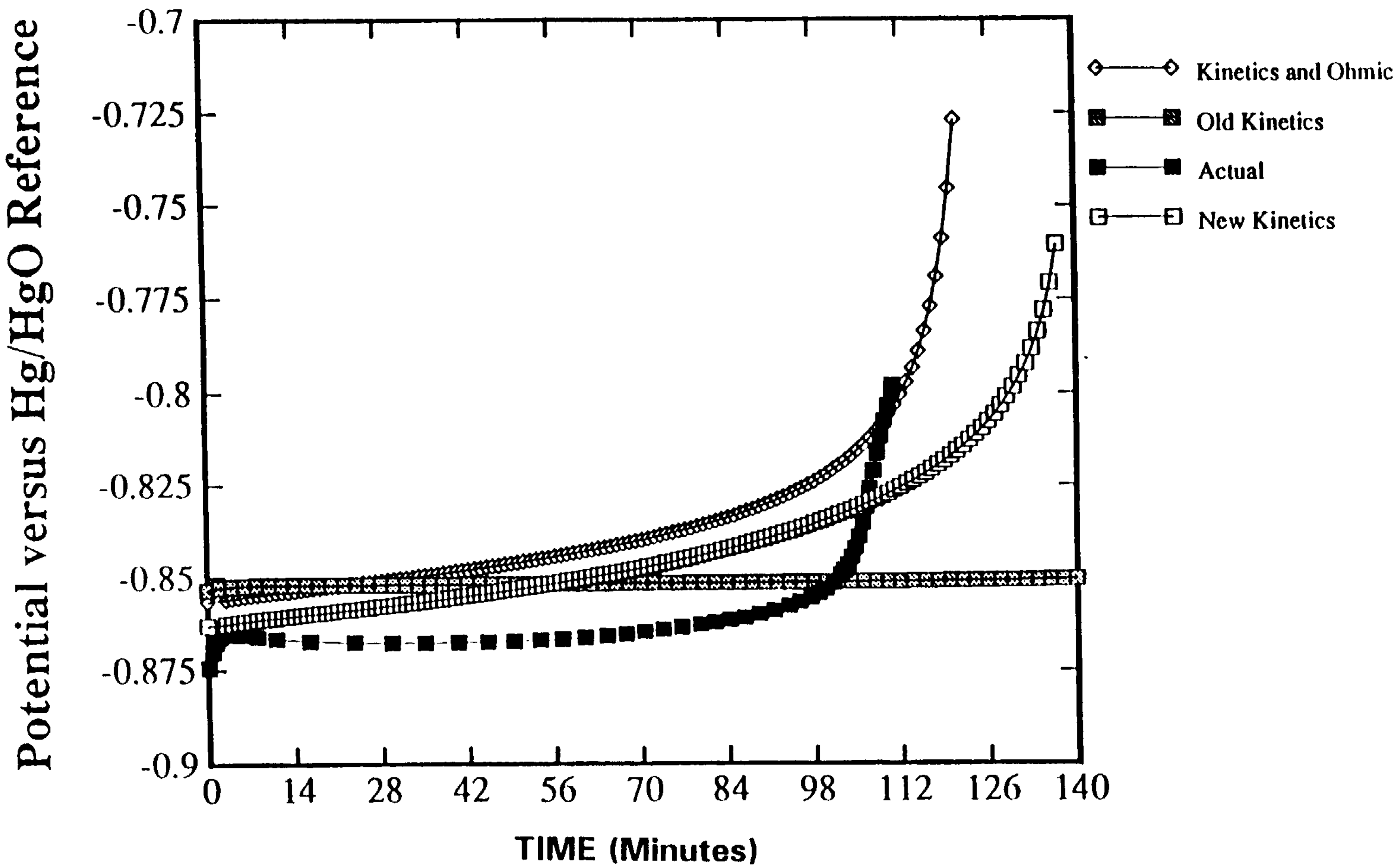
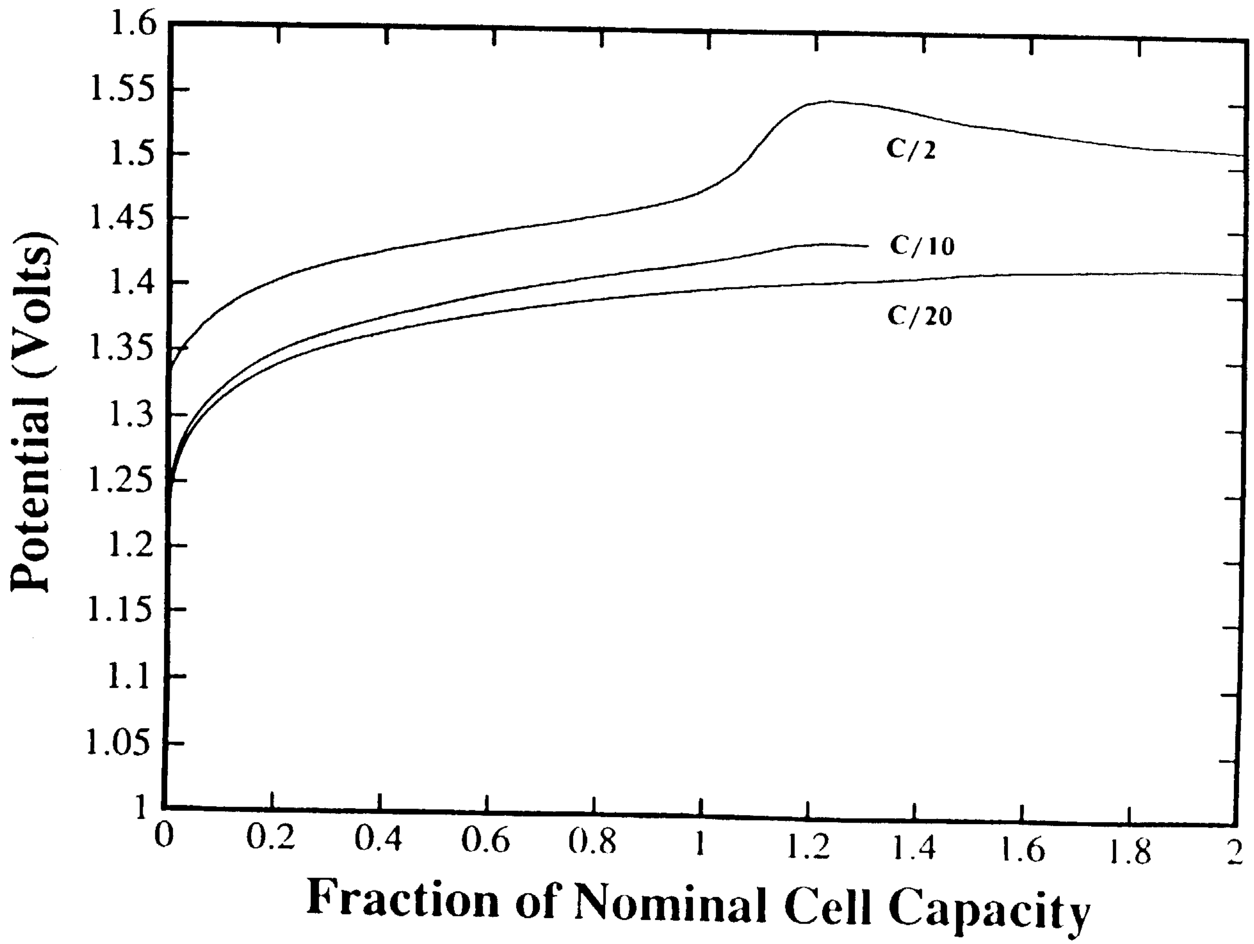
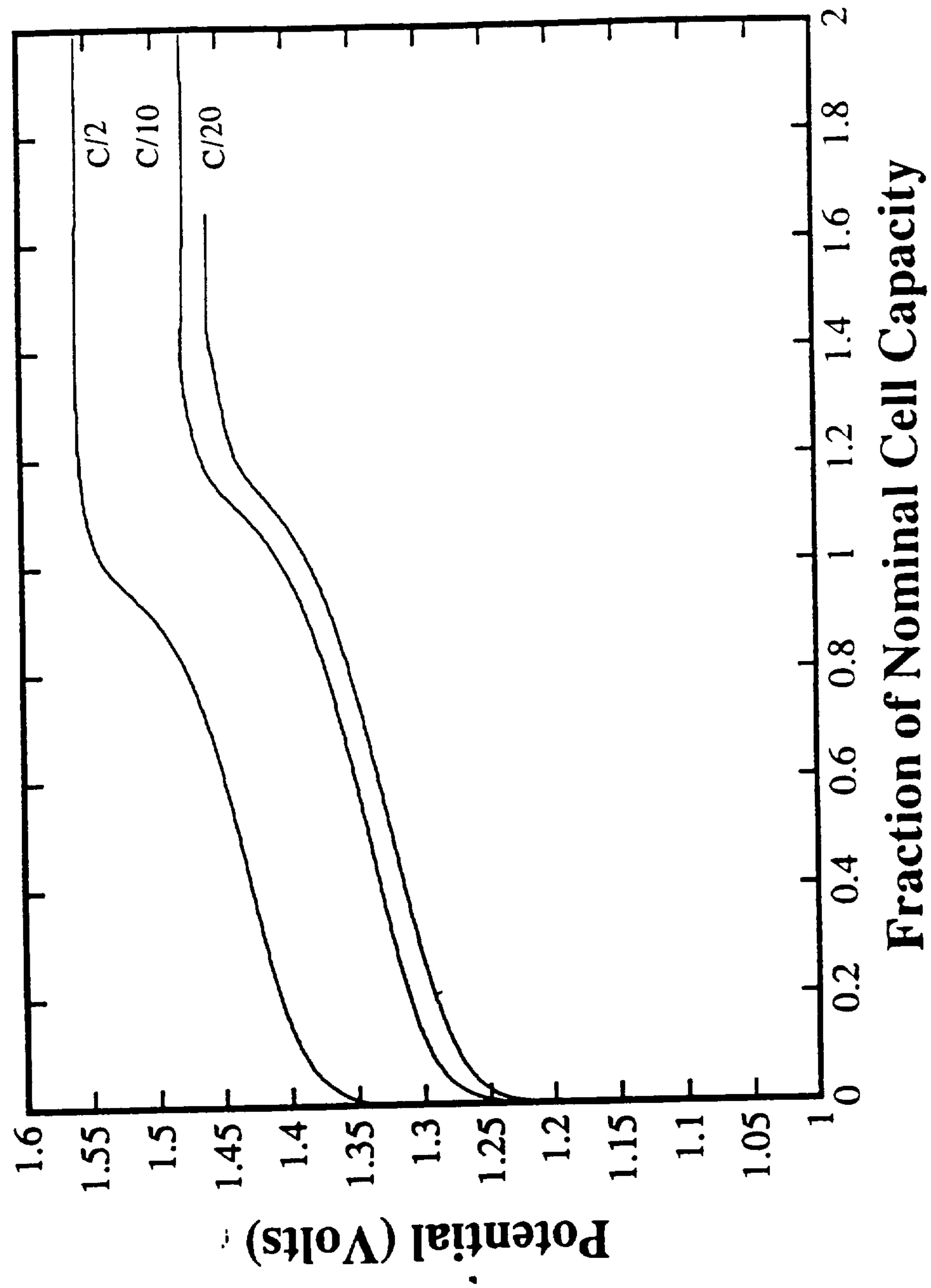
Predicted Negative Potentials for Discharge



Boilerplate Cell Potentials for Charge



Predicted Cell Potentials for Charge



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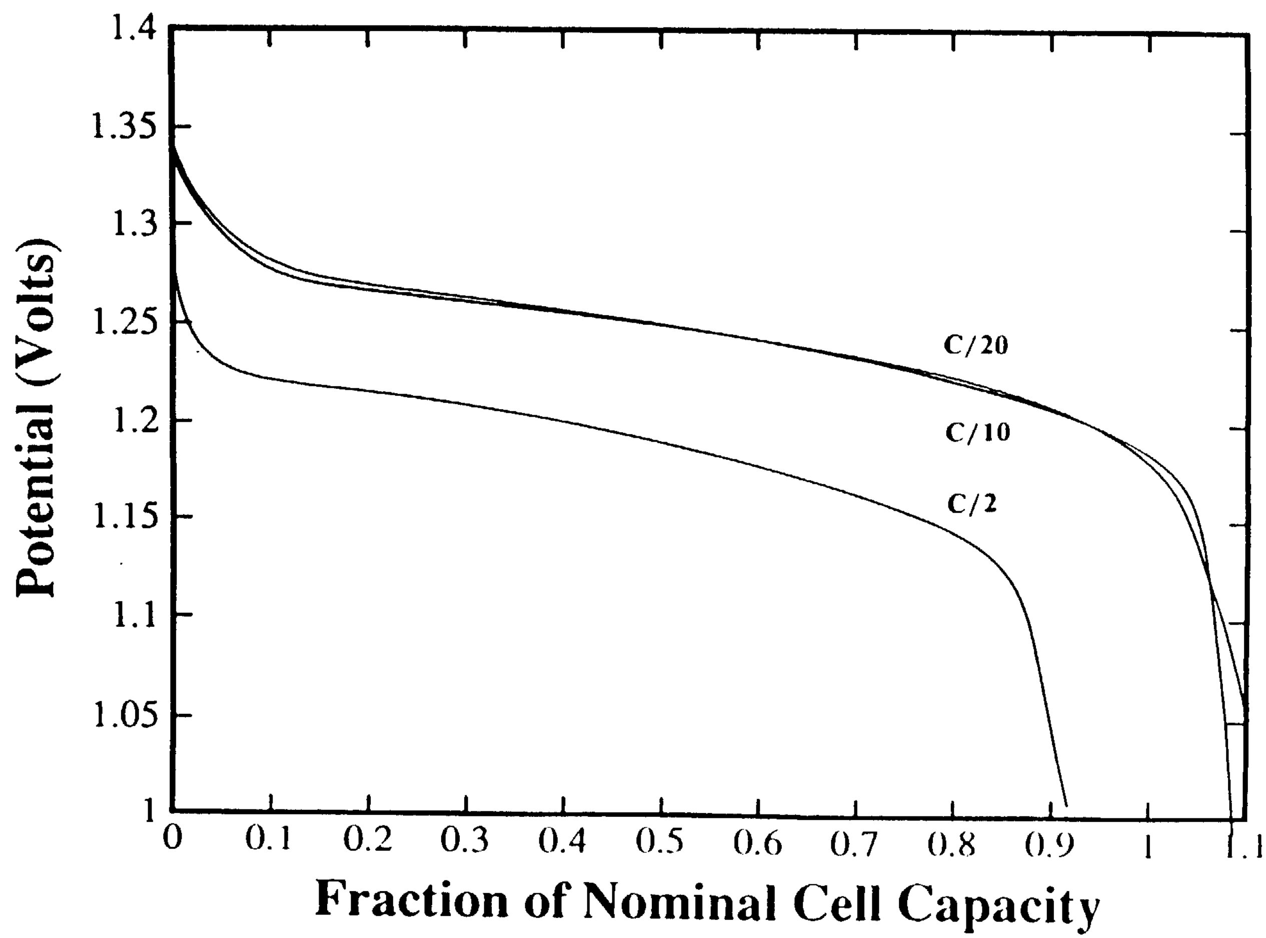
Boilerplate Cell Potentials for Discharge



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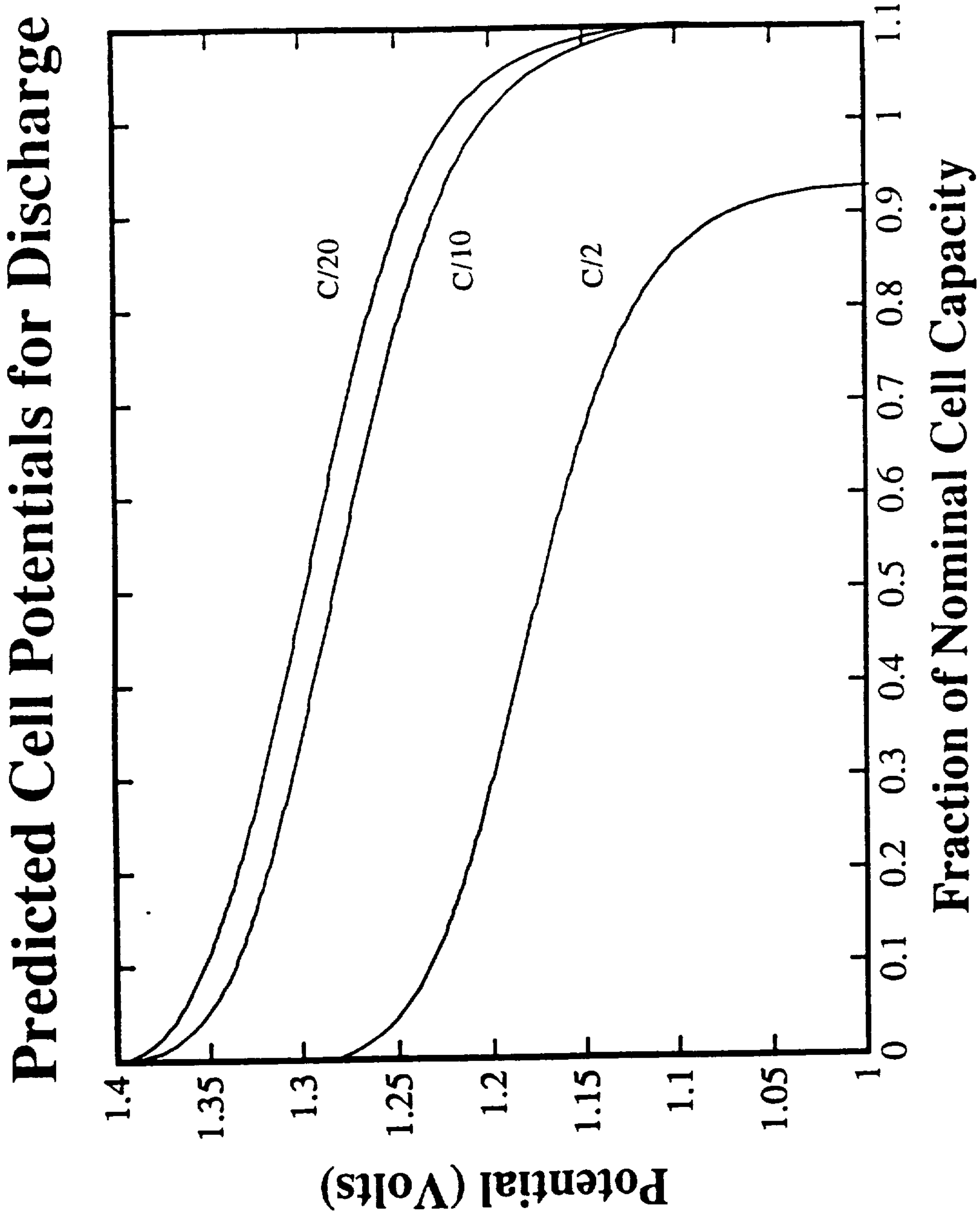
Predicted Cell Potentials for Discharge
Potential (Volts)
Fraction of Nominal Cell Capacity
C/20
C/10
C/2
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1

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SUMMARY

- FUNDAMENTAL CELL MODEL DEVELOPMENT CONTINUED
- NICKEL OXIDE LAYER DESCRIBED
  - ELECTRONIC CONDUCTIVITY OF OXIDE LAYER
  - PROTON DIFFUSION THOUGH OXIDE LAYER
- CADMIUM ELECTRODE IMPROVED
  - IMPROVED KINETIC EXPRESSION
  - IMPROVED CONDUCTIVITY EXPRESSION
- PERFORMANCE PREDICTIONS ARE SIGNIFICANTLY IMPROVED

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