Mathematical Modeling of Ni/H_2 and Li-Ion Batteries

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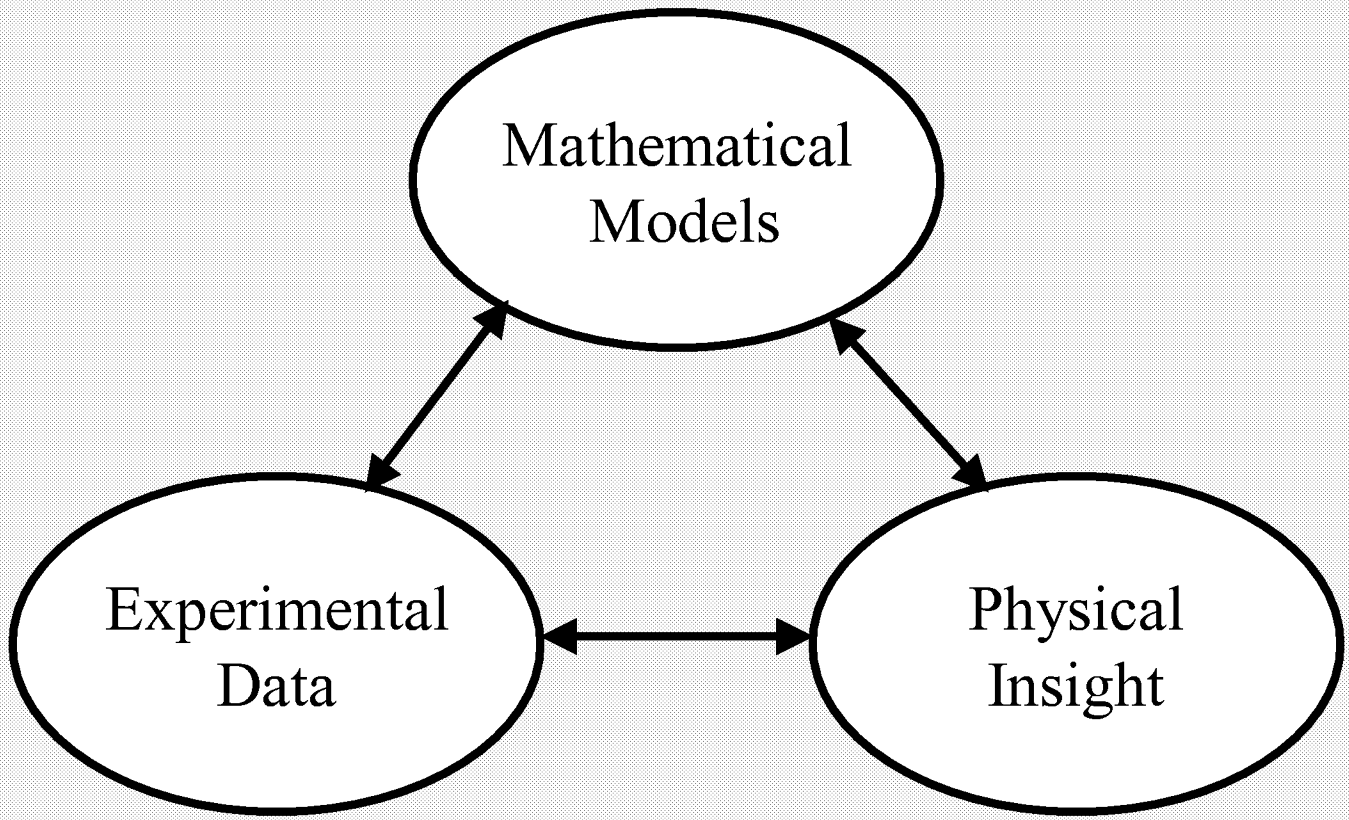
Analysis of Battery Systems



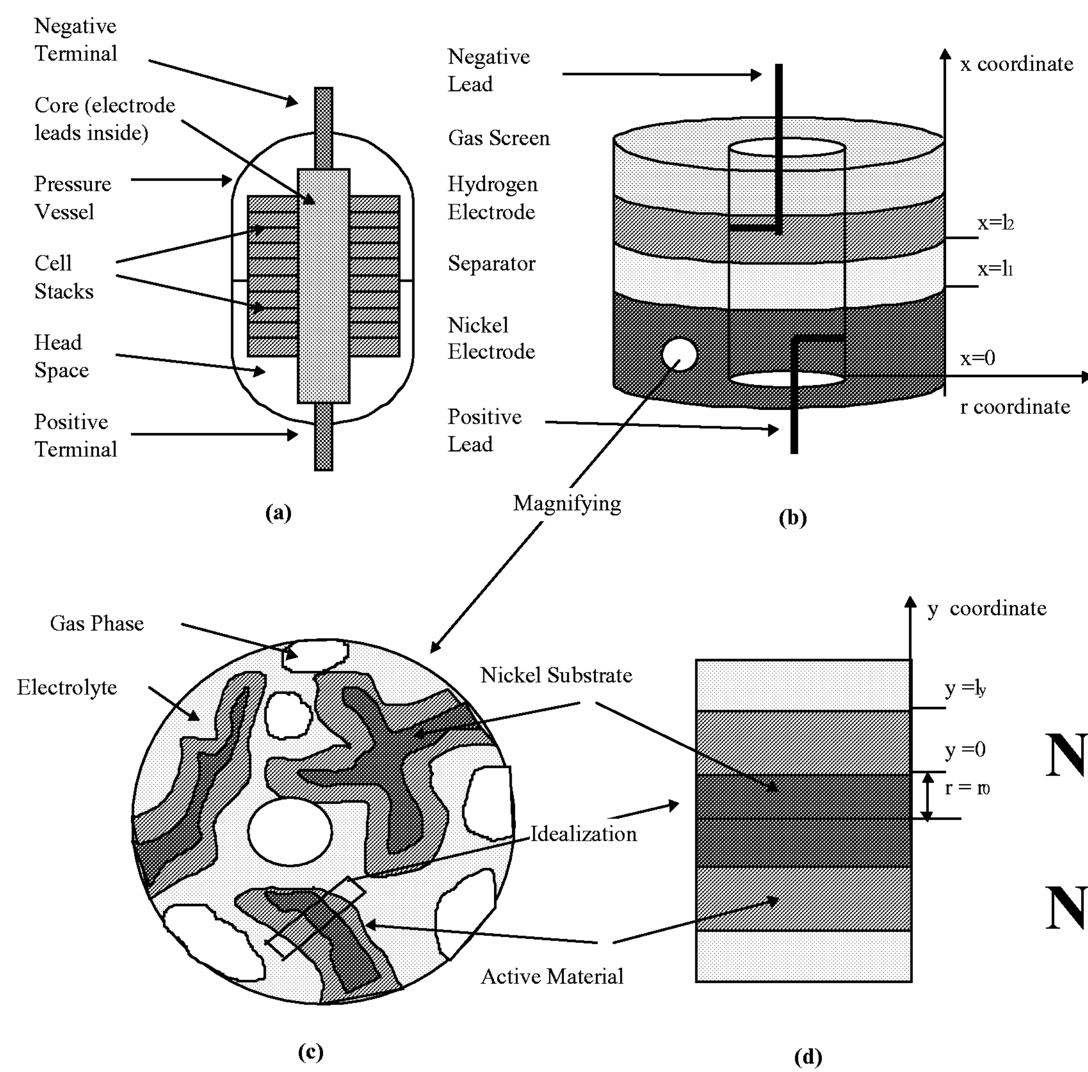
Modeling Effort

- Electrochemical Deposition of Nickel Hydroxide
  - Deposition rates of thin films
  - Impregnation of porous electrodes
- Experimental Characterization of Nickel Hydroxide
  - Diffusion coefficients of protons
  - Self-discharge rates (*i.e.*, oxygen-evolution kinetics)
  - Hysteresis between charge and discharge
  - Capacity loss on cycling

Modeling Effort

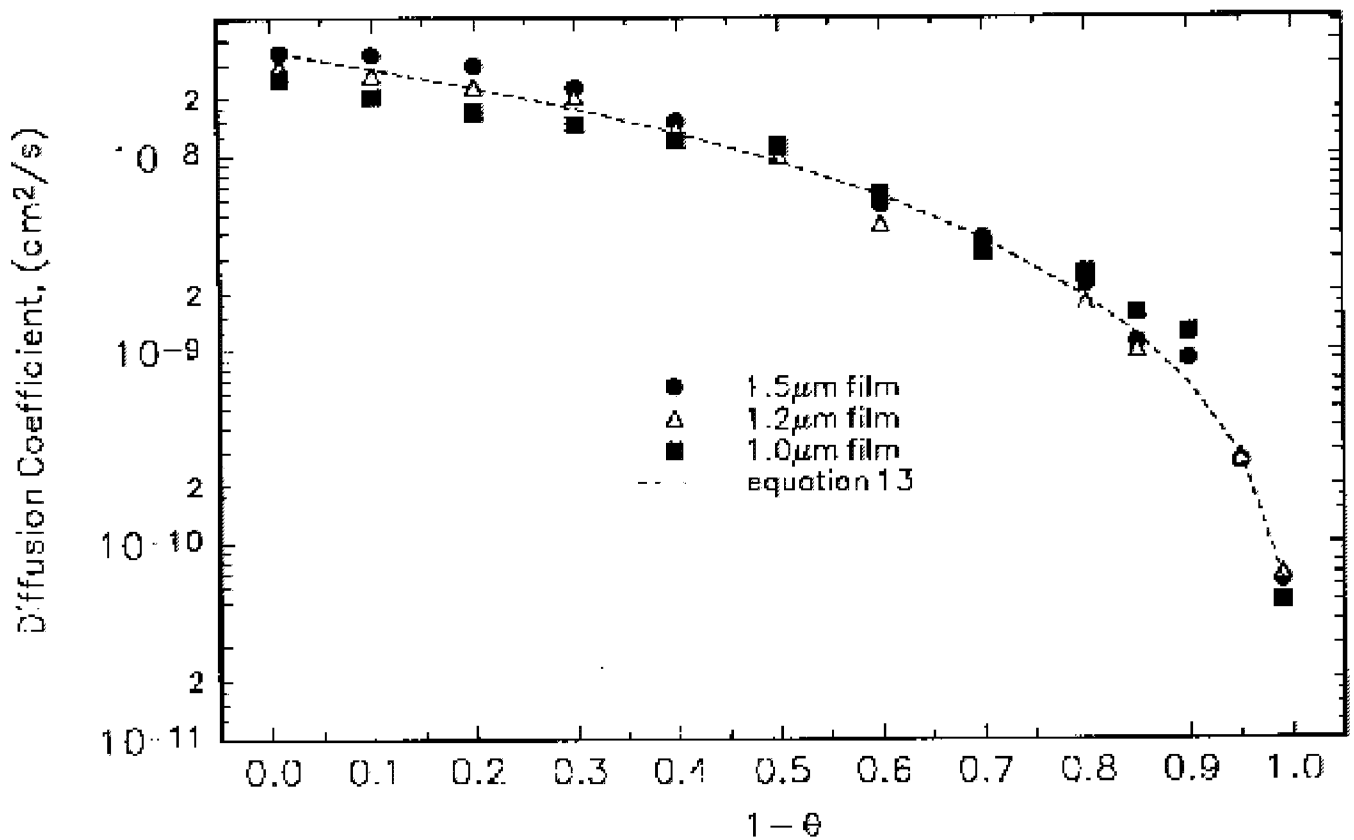
- Mathematical Modeling of Ni/H_2 Batteries
- Experimental Verification of the Ni/H_2 Battery Model
- Mathematical Modeling Li-Ion Batteries
- Experimental Verification of the Li-Ion Battery Model
- Integrated Power System Models for Satellites
- Experimental Verification of Integrated-Systems Model

Schematic of Ni/H_2 Battery



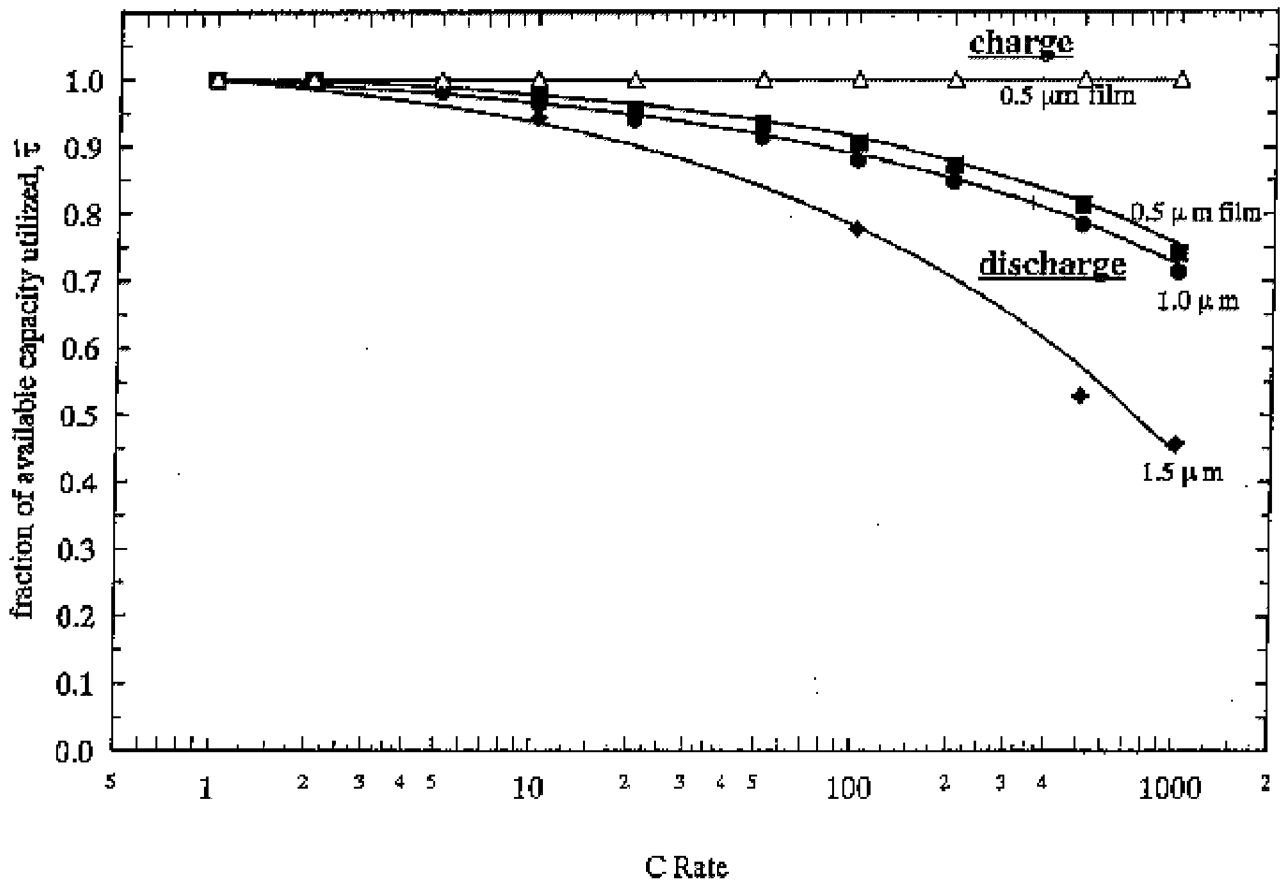
$$Ni(OH)_2 \leftrightarrow NiOOH$$

Proton Diffusion Coefficient



S. Motupally, C. C. Streinz, and J. W. Weidner, *J. Electrochem. Soc.*, **142**, 1401-1408 (1995).

Utilization of the NiOOH



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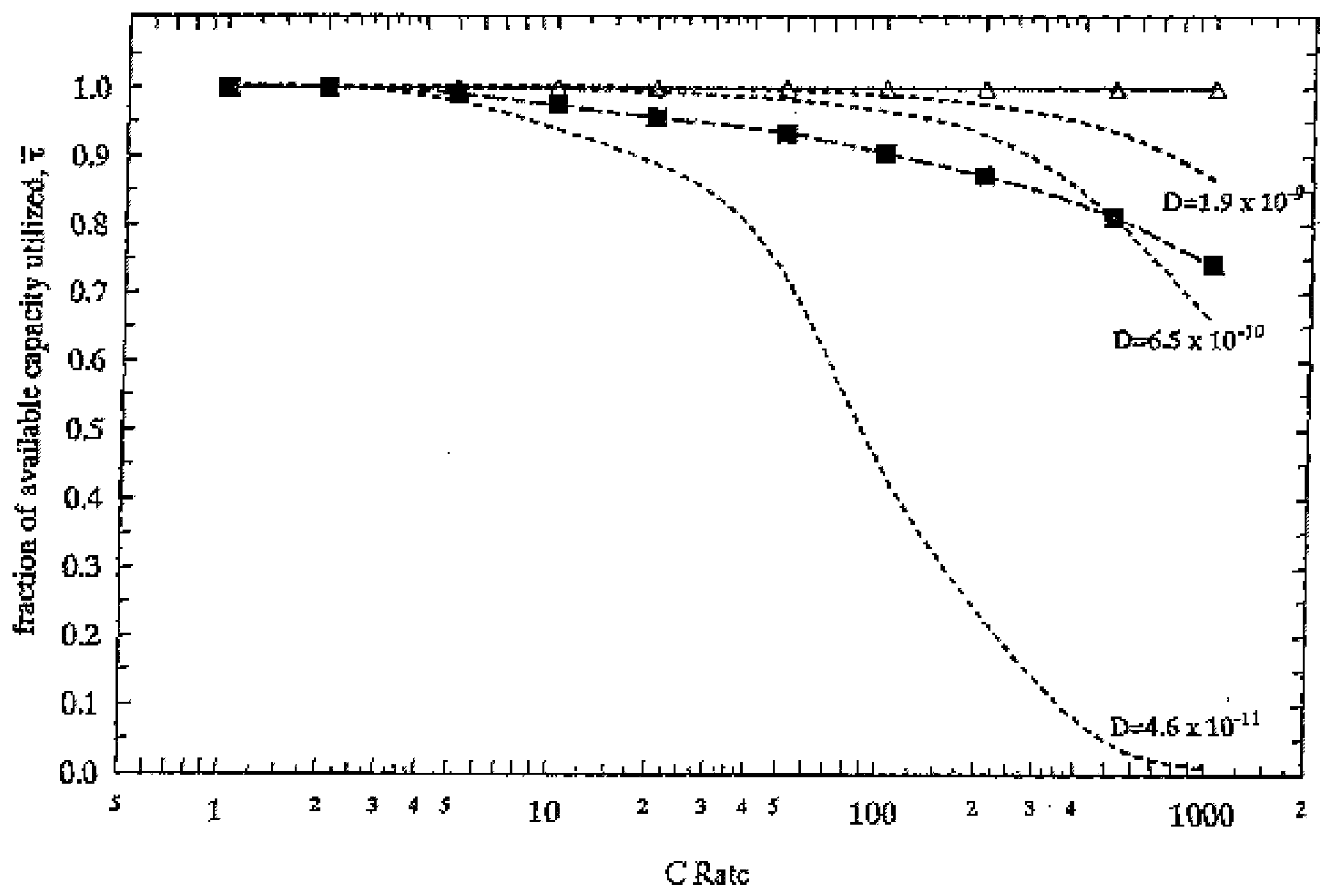
Utilization of the NiOOH



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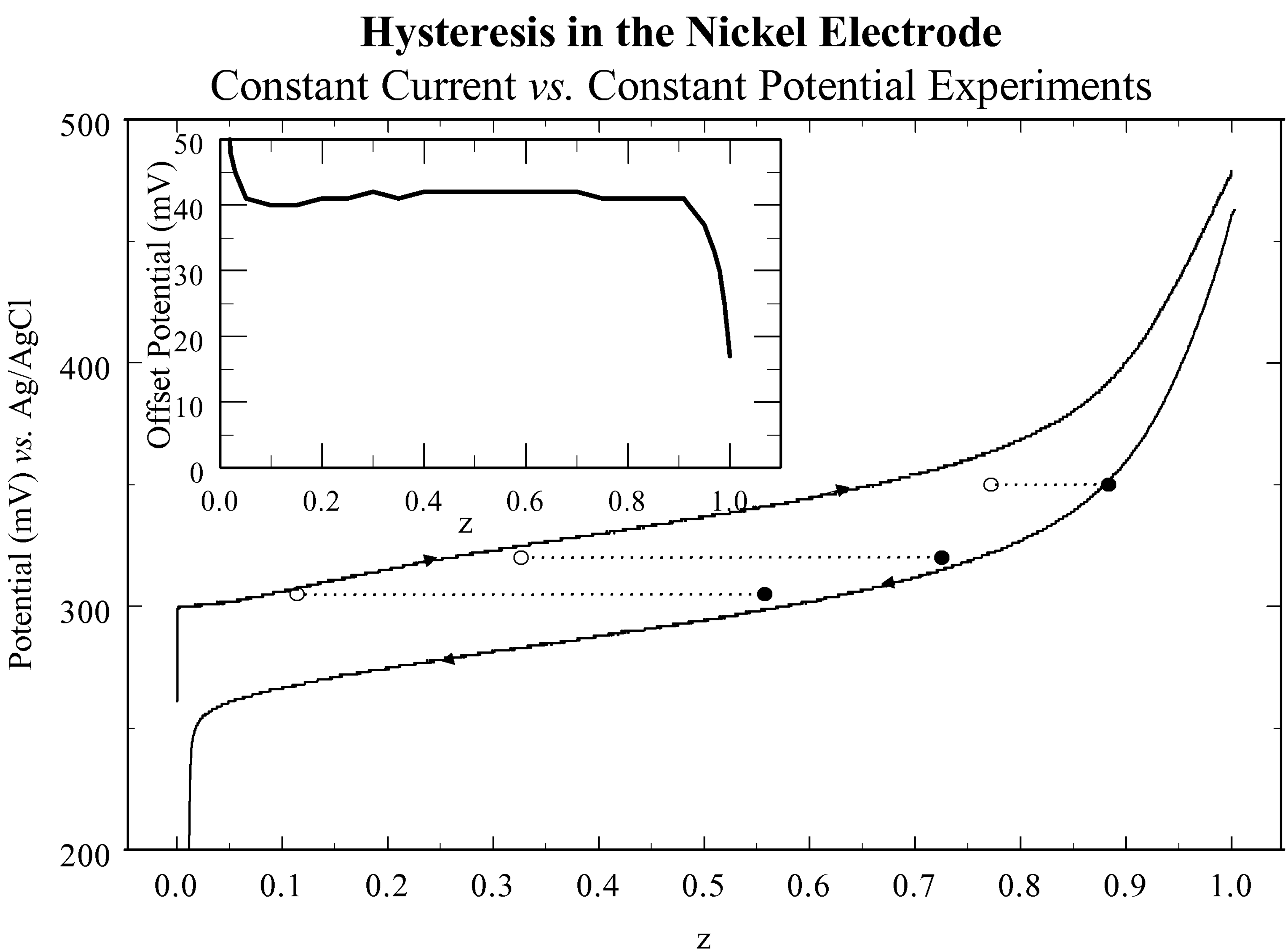
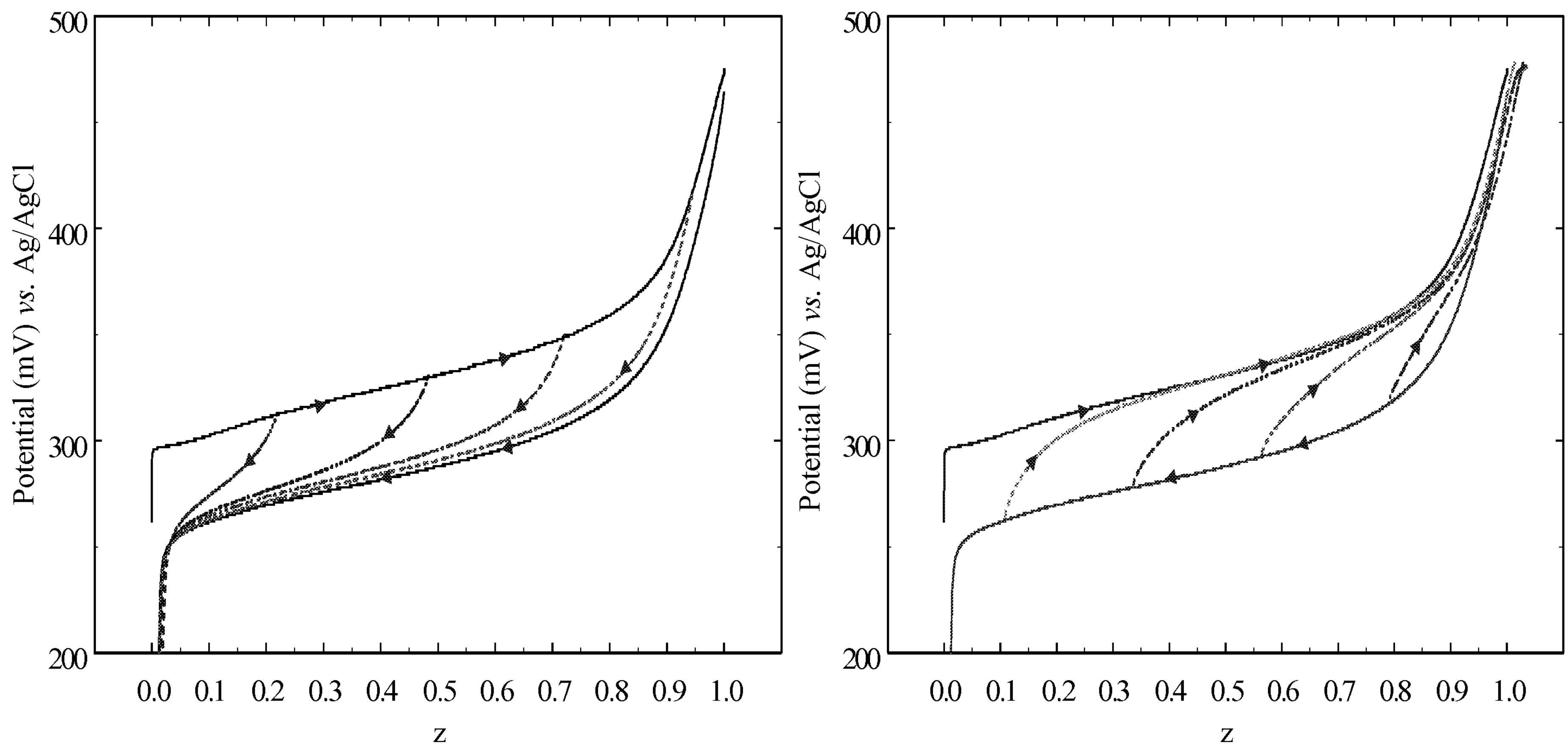
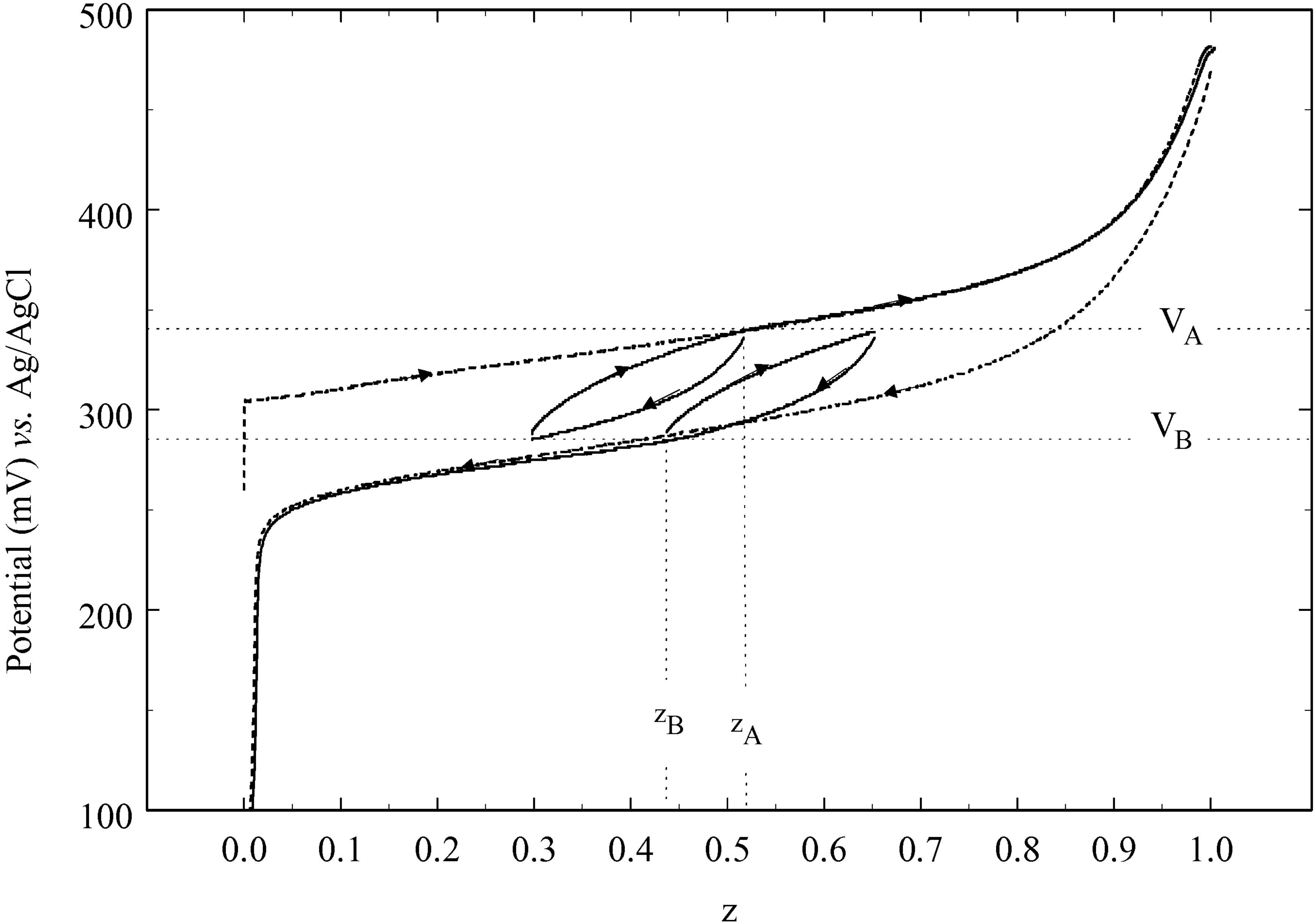


Hysteresis in the Nickel Electrode
Constant Current *vs.* Constant Potential Experiments
Potential (mV) *vs.* Ag/AgCl
500
400
300
200
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
z
Offset Potential (mV)
50
40
30
20
10
0
0.0
0.2
0.4
0.6
0.8
1.0
z

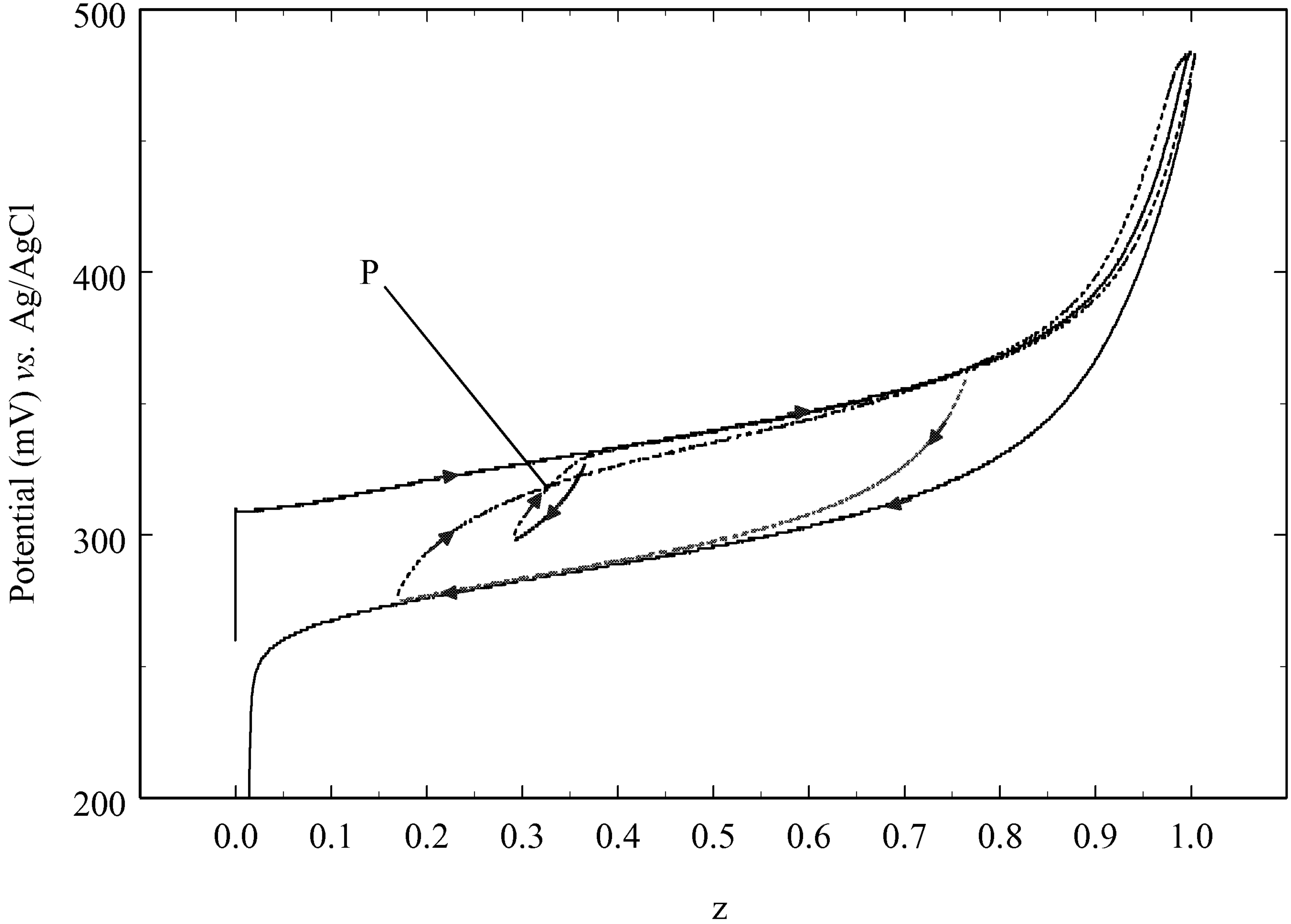
Boundary and Scanning Curves During Proton Intercalation/Extraction



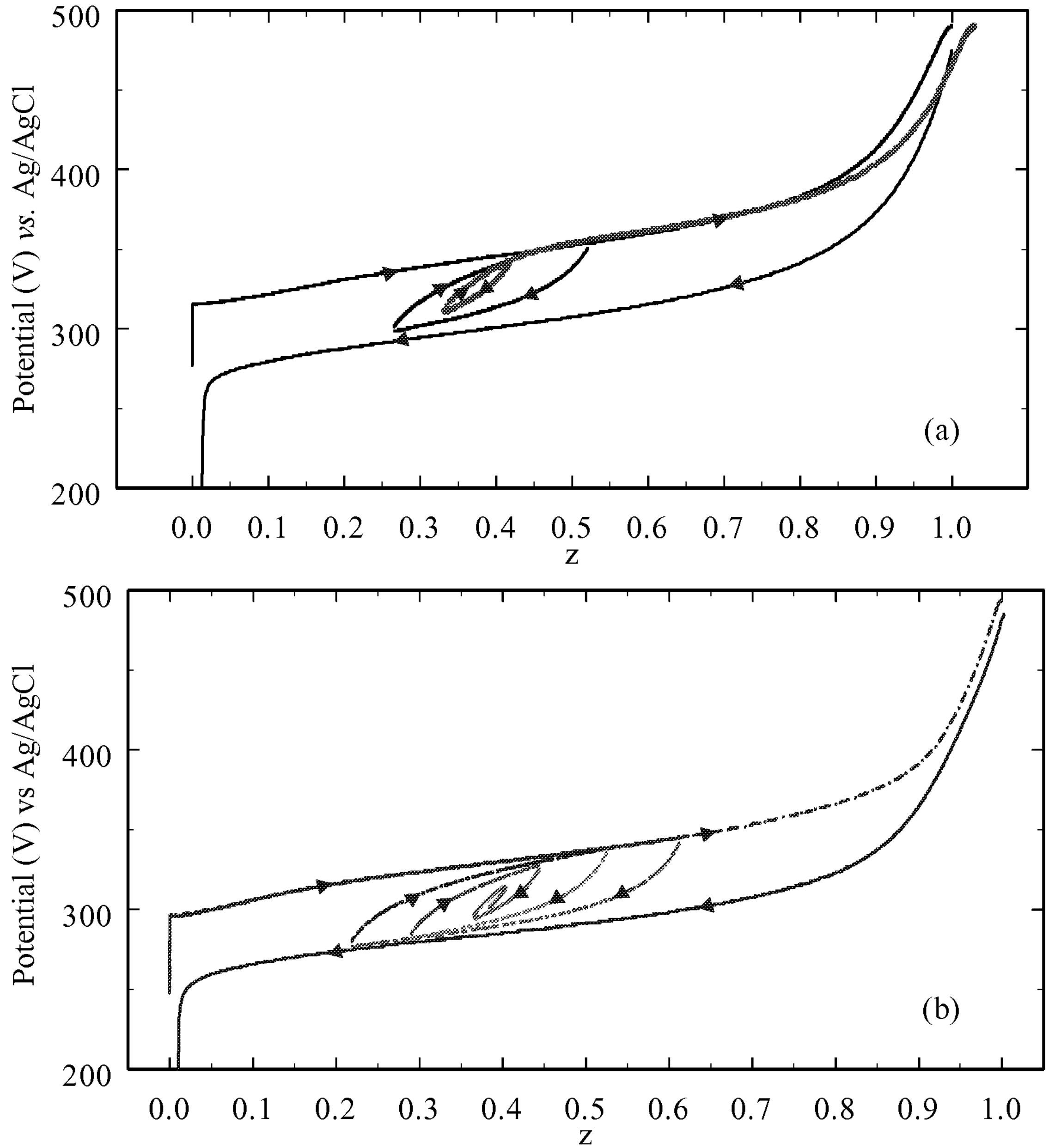
“Wiping-out” Property of Systems Exhibiting Hysteresis



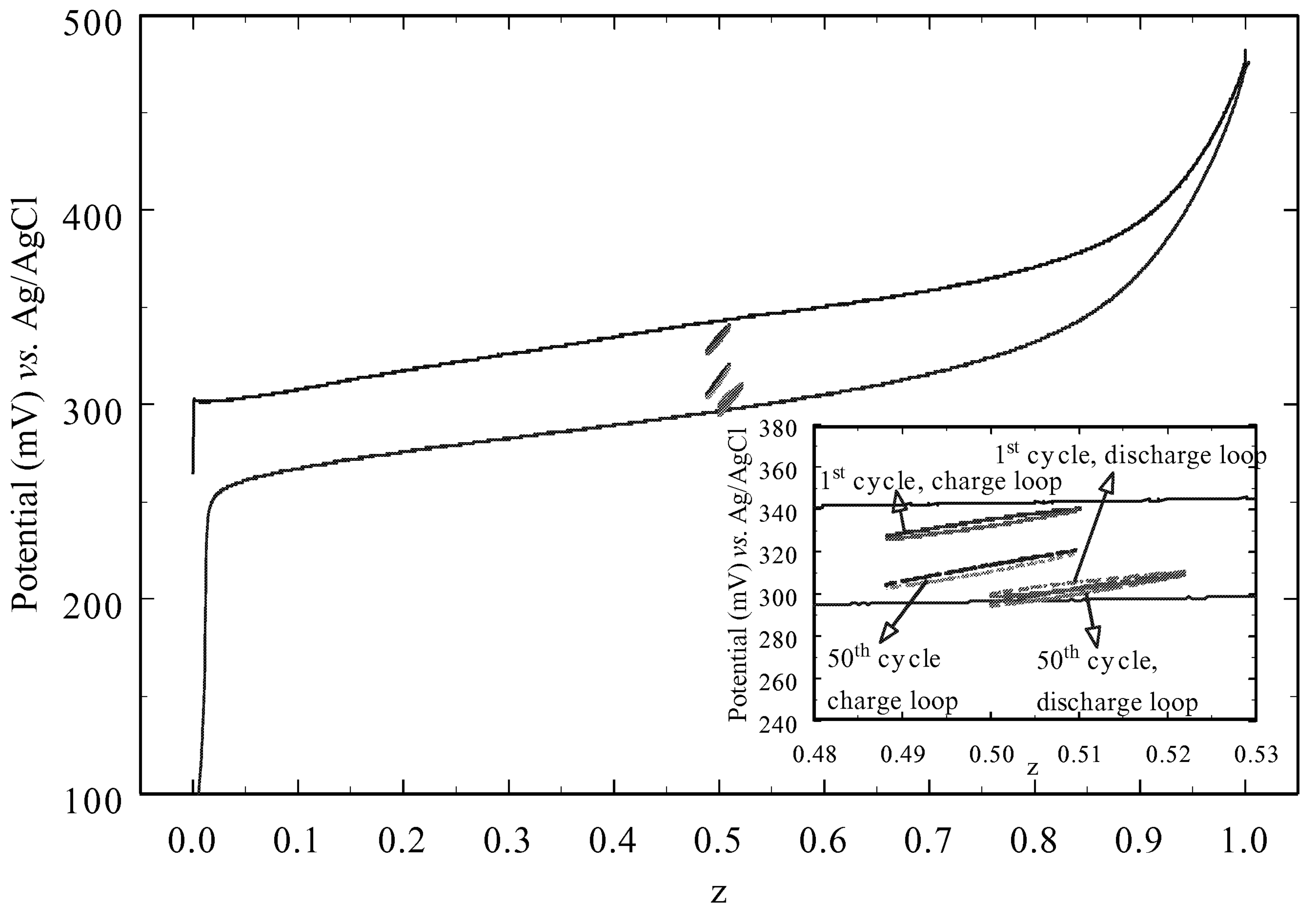
The History-Dependent Path of the Ni Electrode



Internal Hysteresis Loops in The Ni Electrode

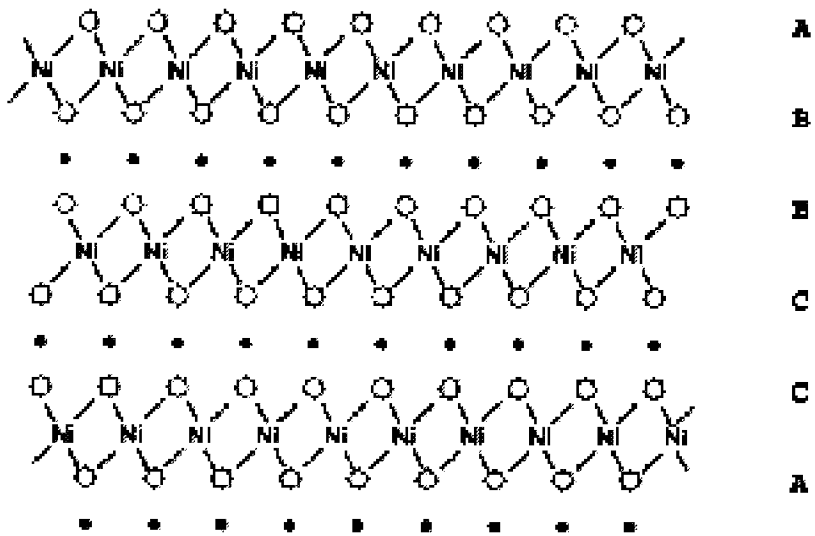


Path of the System During Continuous Cycling Over Small Z

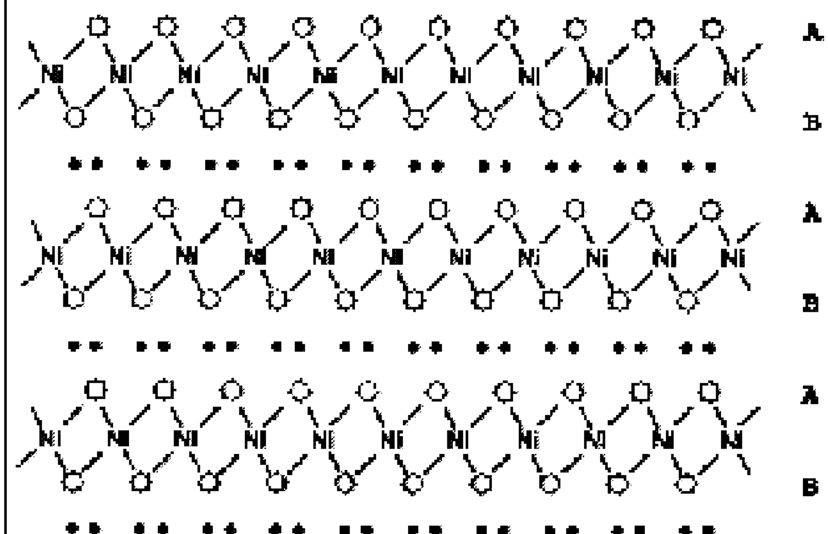


Crystal Structures for Nickel Hydroxide

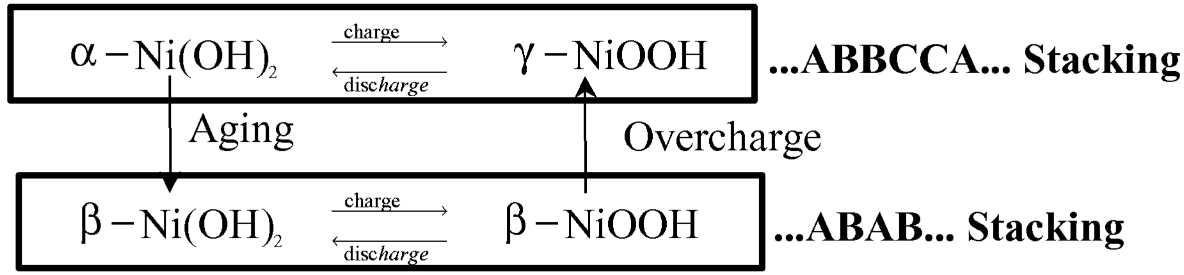
ABBCCA Structure: NiOOH



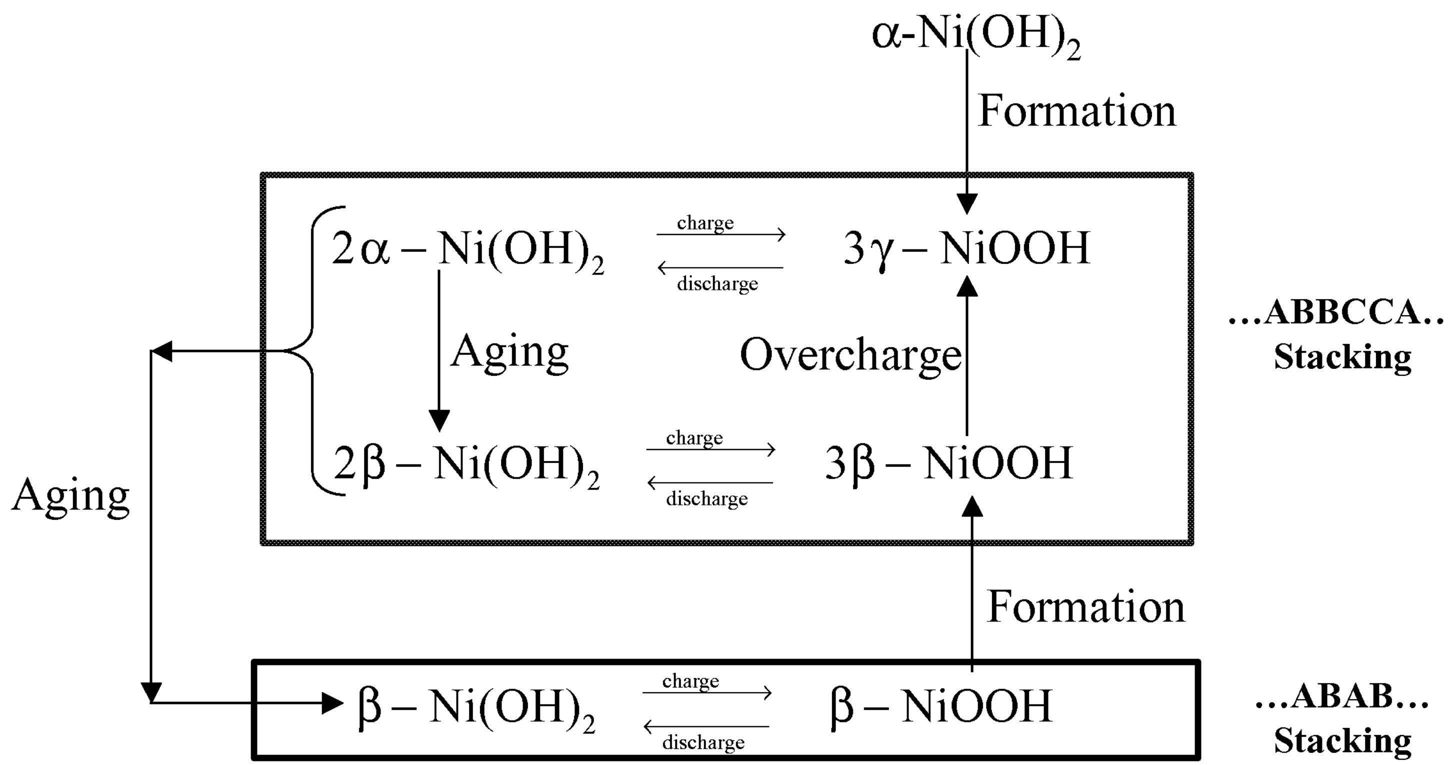
ABAB Structure: $Ni(OH)_2$



Bode Diagram



Modified Bode Diagram



Defect Representation of the Nickel Hydroxide Electrode

$$\boxed{\left[Ni_{1-x}(K_i)_y(H_i)_{x-y}\right]OOH_{2-z}\cdot X_w H_2O}$$

$$x = \frac{\text{number of Ni vacancies}}{\text{total number of Ni lattice sites}}$$

$$y = \frac{\text{number of Ni vacancies occupied by } K^+}{\text{total number of Ni lattice sites}}$$

$$n = \frac{\text{number of } H^+}{\text{number of Ni vacancies not occupied by } K^+}$$

$$X_w = \frac{\text{number of water molecules}}{\text{total number of Ni lattice sites}}$$

$$2 - z = \frac{\text{number of interlamellar protons}}{\text{total number of Ni lattice sites}}$$

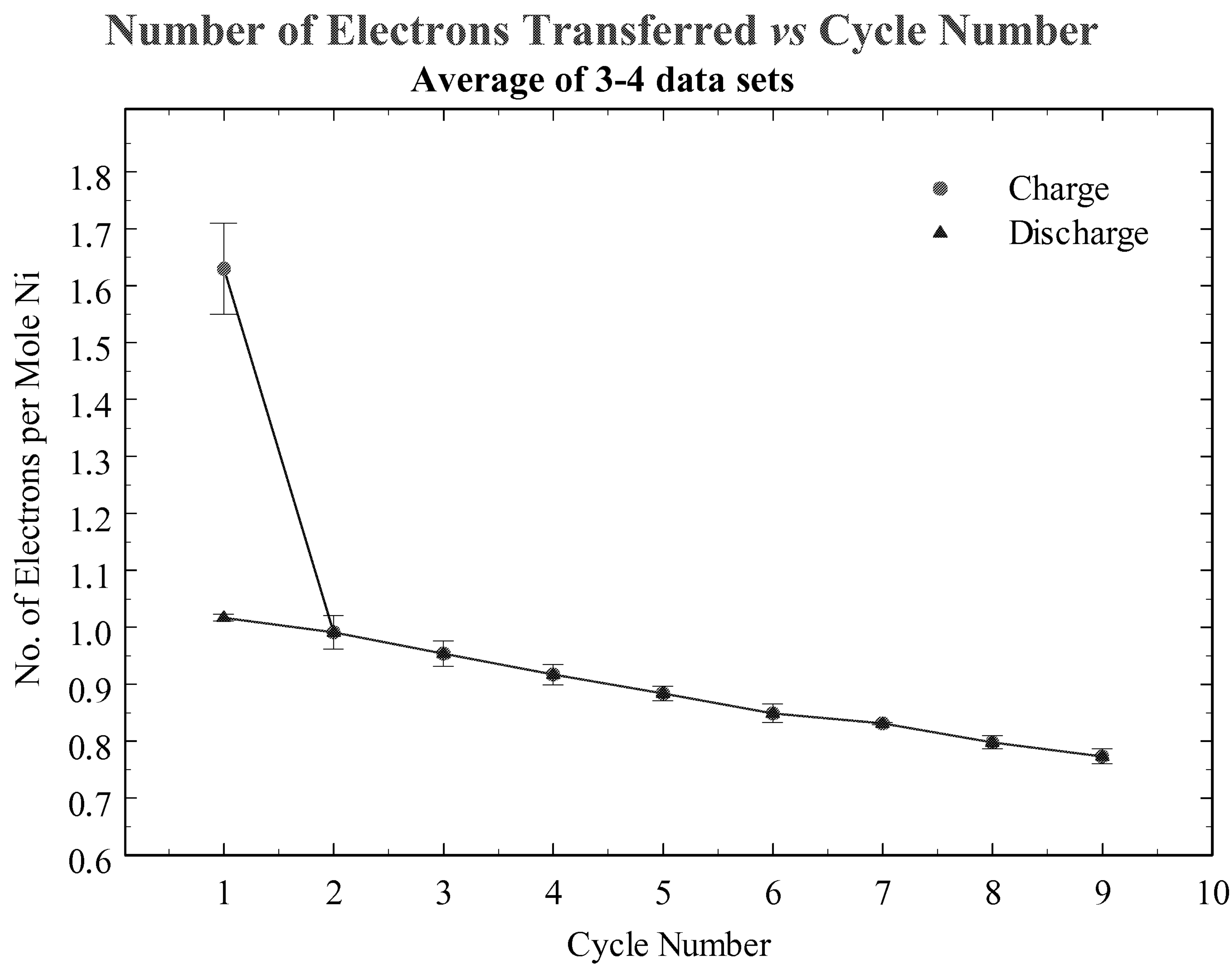
Nickel Hydroxide Redox Reaction

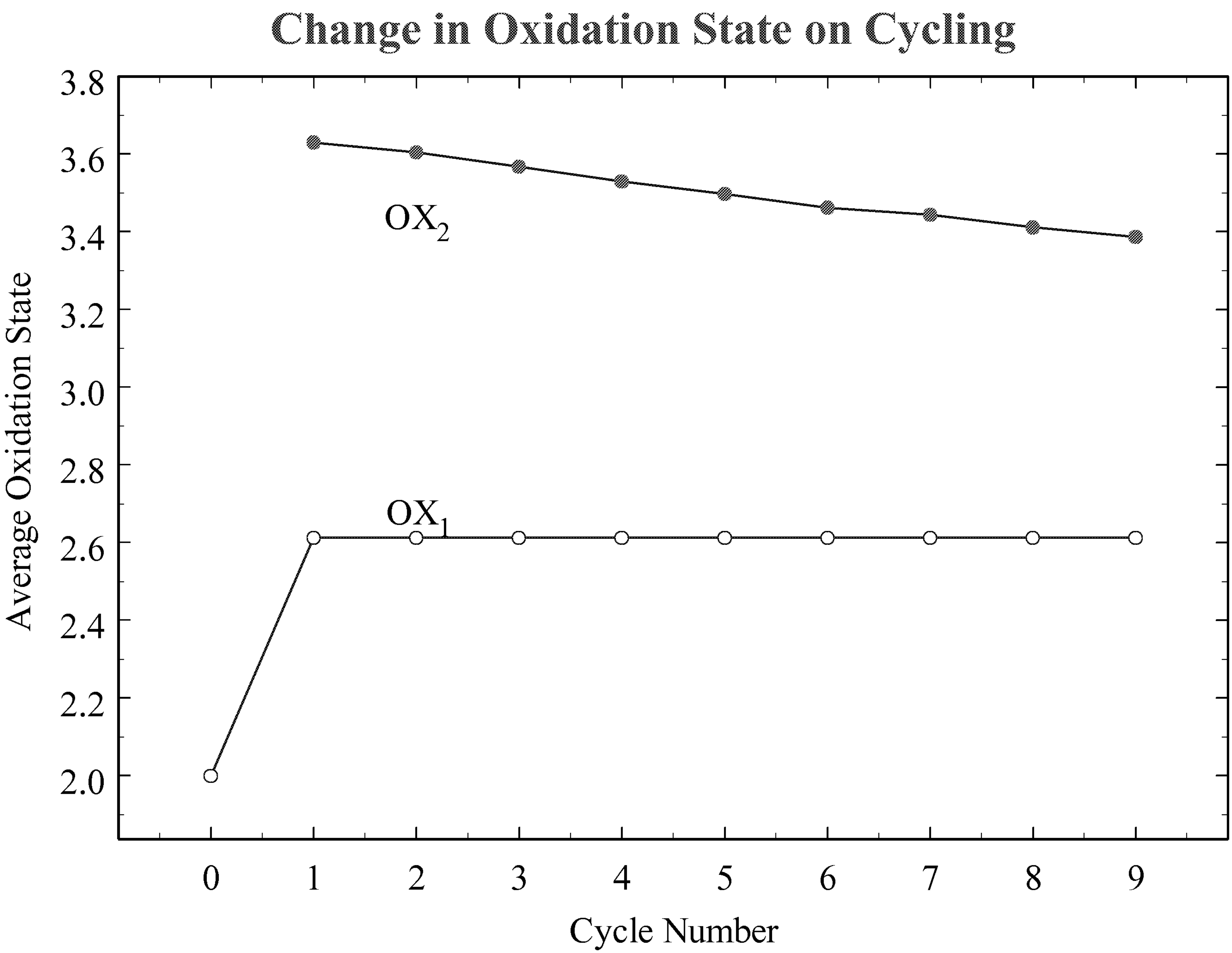
$$\left[\mathrm{Ni}\ (\mathrm{K})_{\frac{y_1}{(1-x_1)}}(n_1\mathrm{H})_{\frac{x_1-y_1}{1-x_1}}\right]\mathrm{O}_{\frac{2}{1-x_1}}\mathrm{H}_{\frac{2}{1-x_1}}\cdot X_{w_1}\mathrm{H_2O}+\lambda_1\mathrm{OH^-}+\lambda_2\mathrm{K^+}$$

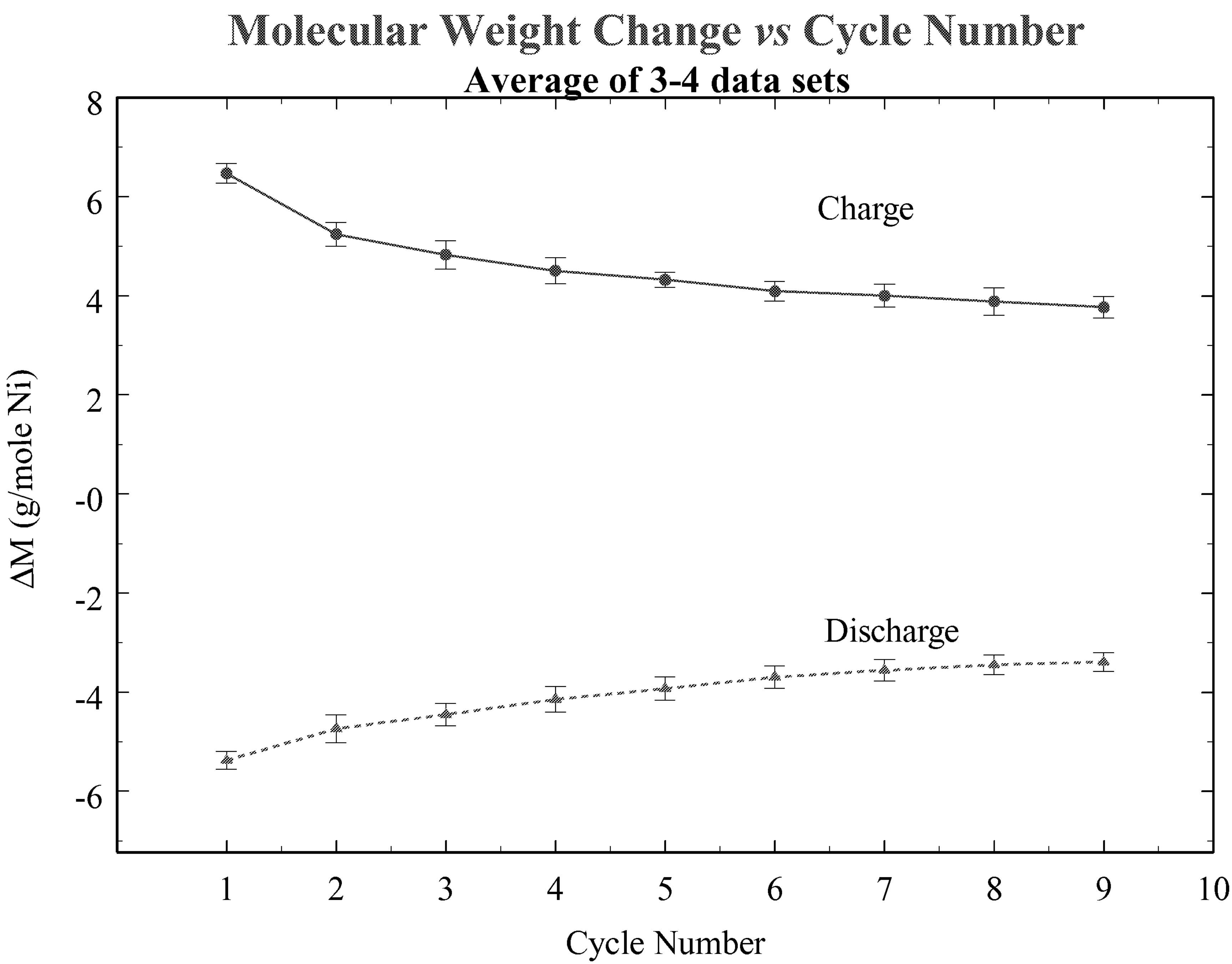
$$\underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}}\left[\mathrm{Ni}\ (\mathrm{K})_{\frac{y_2}{(1-x_2)}}(n_2\mathrm{H})_{\frac{x_2-y_2}{1-x_2}}\right]\mathrm{O}_{\frac{2}{1-x_2}}\mathrm{H}_{\frac{1}{1-x_2}}\cdot X_{w_2}\mathrm{H_2O}+\lambda_3\mathrm{H_2O}+\lambda_4 e^-$$

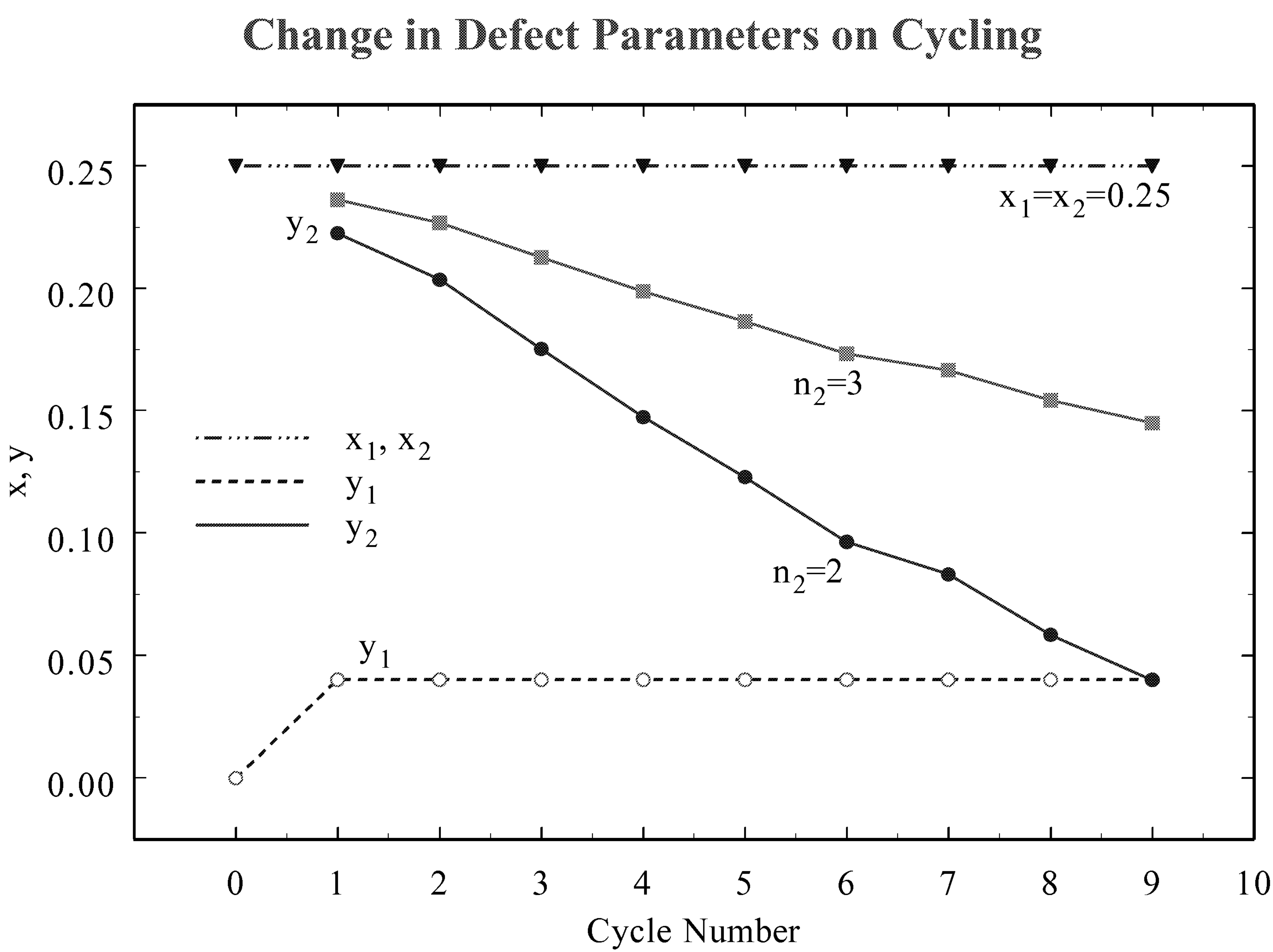
$$\lambda_1=\left[\frac{n_1(x_1-y_1)-2}{(1-x_1)}-\frac{n_2(x_2-y_2)-3}{(1-x_2)}\right]\qquad \lambda_3=\left[\frac{n_1(x_1-y_1)}{(1-x_1)}-\frac{n_2(x_2-y_2)-1}{(1-x_2)}\right]+X_{w_1}-X_{w_2}$$

$$\lambda_2=\left[\frac{y_2}{(1-x_2)}-\frac{y_1}{(1-x_1)}\right]\qquad \lambda_4=\left[\frac{3-y_2-n_2(x_2-y_2)}{(1-x_2)}-\frac{2-y_1-n_1(x_1-y_1)}{(1-x_1)}\right]$$


Number of Electrons Transferred vs Cycle Number
Average of 3-4 data sets
No. of Electrons per Mole Ni
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
1
2
3
4
5
6
7
8
9
10
Cycle Number
Charge
Discharge


Change in Oxidation State on Cycling
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
Average Oxidation State
OX_2
OX_1
0
1
2
3
4
5
6
7
8
9
Cycle Number


Molecular Weight Change vs Cycle Number
Average of 3-4 data sets
ΔM (g/mole Ni)
8
6
4
2
-0
-2
-4
-6
Charge
Discharge
1
2
3
4
5
6
7
8
9
10
Cycle Number


Change in Defect Parameters on Cycling
x, y
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
7
8
9
10
Cycle Number
x_1, x_2
y_1
y_2
$x_1=x_2=0.25$
y_2
$n_2=3$
$n_2=2$
y_1

Redox Reactions In the Nickel Electrode as Described by the Defect Model

$x_1 = x_2 = y_2 = 0.25$, $n_1 = 0$ and $y_1 = 0$

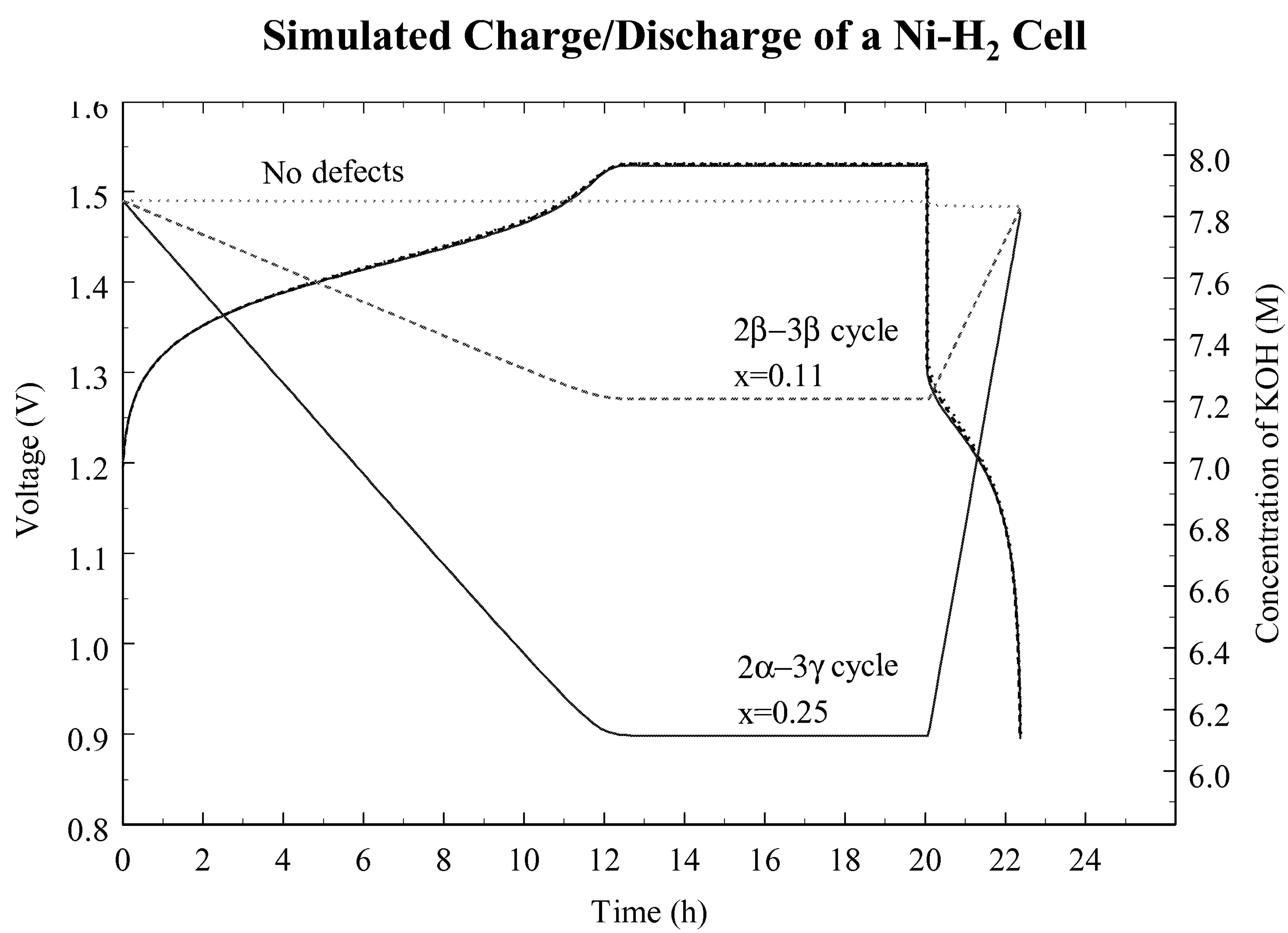
$$2\alpha-\left[Ni^{2.67}(V_{Ni})_{0.33}\right]O_{2.67}H_{2.67} + 1.33OH^- + 0.33K^+ \underset{discharge}{\overset{charge}{\rightleftarrows}} 3\gamma-\left[Ni^{3.67}(K)_{0.33}\right]O_{2.67}H_{1.33} + 1.33\,H_2O + 1\,e^-$$

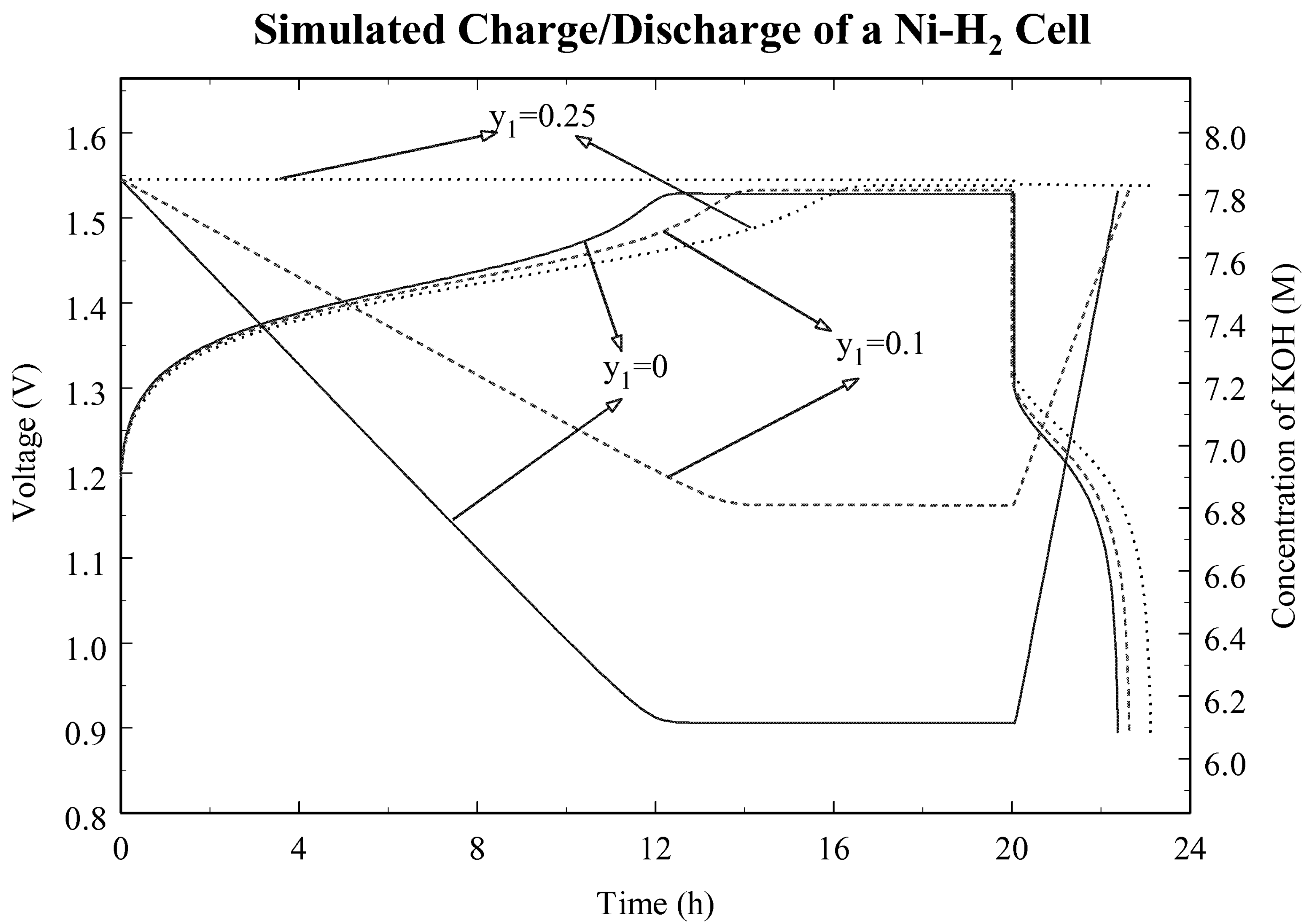
$x_1 = x_2 = 0.11$, $n_1 = 0$, $y_1 = y_2 = 0$ and $n_2 = 1$

$$2\beta-\left[Ni^{2.25}(V_{Ni})_{0.12}\right]O_{2.25}H_{2.25} + OH^- \underset{discharge}{\overset{charge}{\rightleftarrows}} 3\beta-\left[Ni^{3.25}(H)_{0.12}\right]O_{2.25}H_{1.12} + H_2O + 1e^-$$

$x_1 = x_2 = y_2 = 0.25$, $n_1 = 2$ and $y_1 = 0$

$$\alpha-\left[Ni^{2.0}(2H)_{0.33}\right]O_{2.67}H_{2.67} + 2OH^- + 0.33K^+ \xrightarrow{Formation} 3\gamma-\left[Ni^{3.67}(K)_{0.33}\right]O_{2.67}H_{1.33} + 2\,H_2O + 1.67\,e^-$$

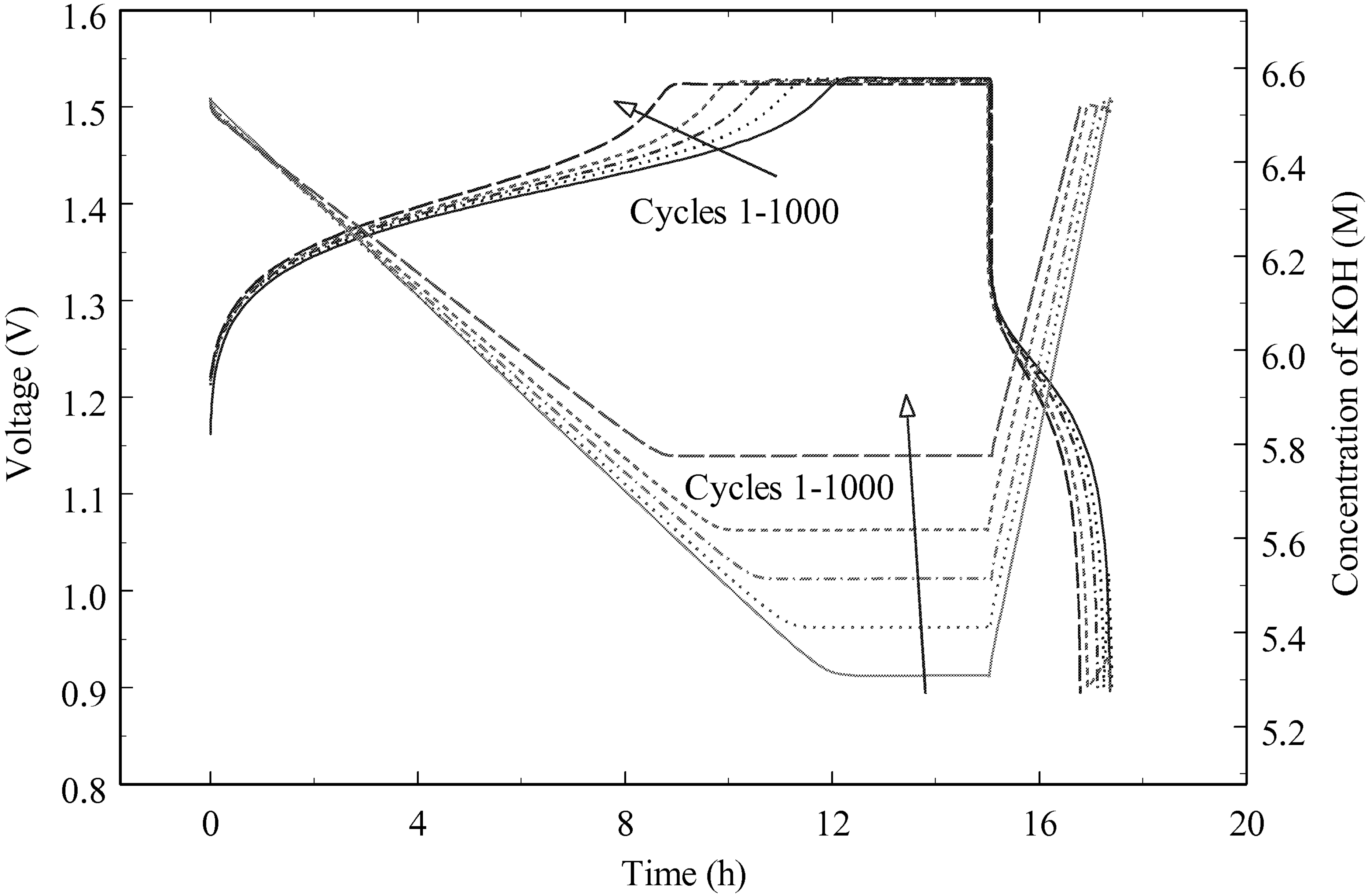

Simulated Charge/Discharge of a Ni-H2 Cell
No defects
2β–3β cycle
x=0.11
2α–3γ cycle
x=0.25
Voltage (V)
Concentration of KOH (M)
Time (h)
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
0
2
4
6
8
10
12
14
16
18
20
22
24



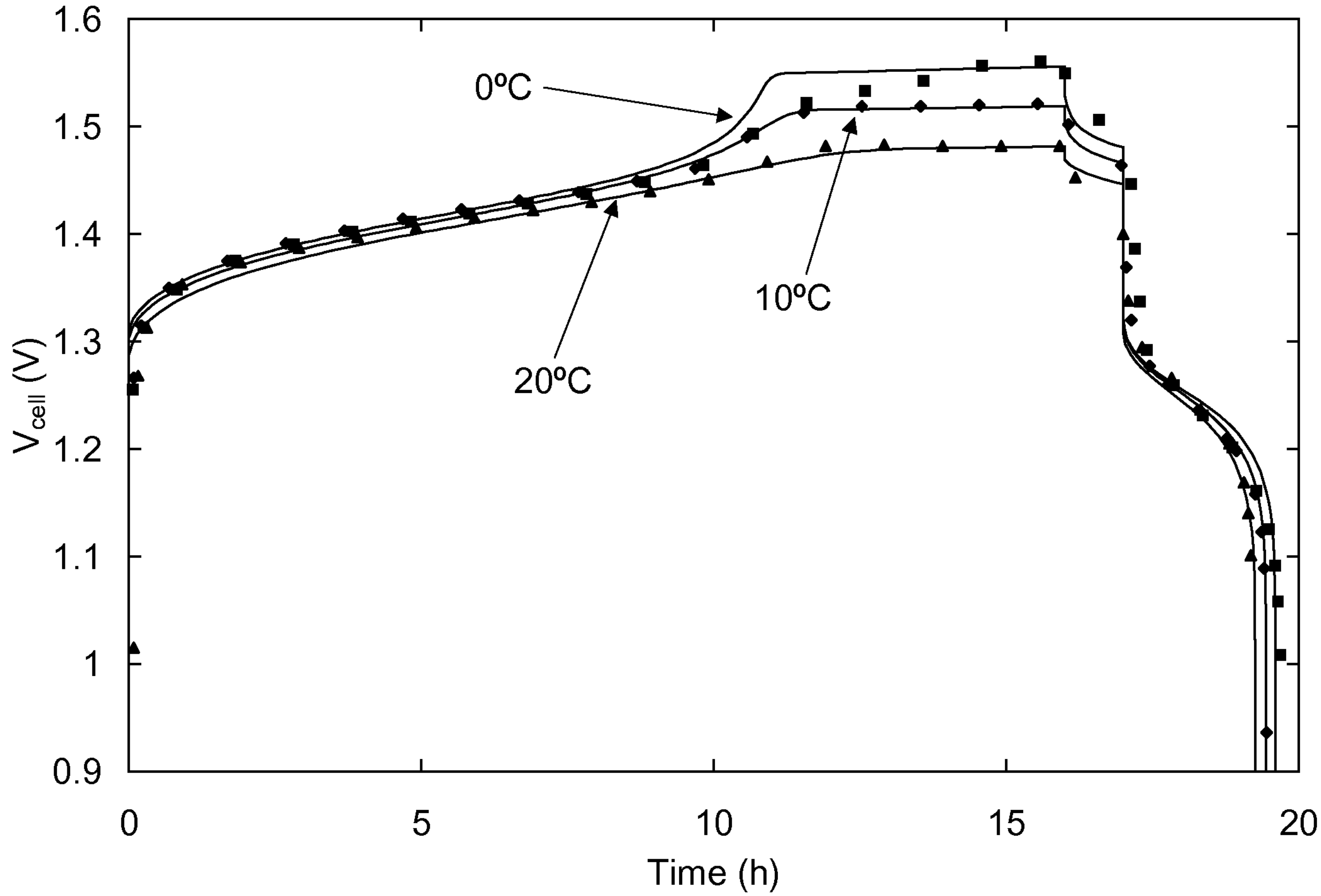
Simulated Charge/Discharge of a Ni-H2 Cell
y1=0.25
y1=0
y1=0.1
Voltage (V)
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
Concentration of KOH (M)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
Time (h)
0
4
8
12
16
20
24

Simulated Capacity and KOH Concentration on Cycling

y_2=0.25→0.11

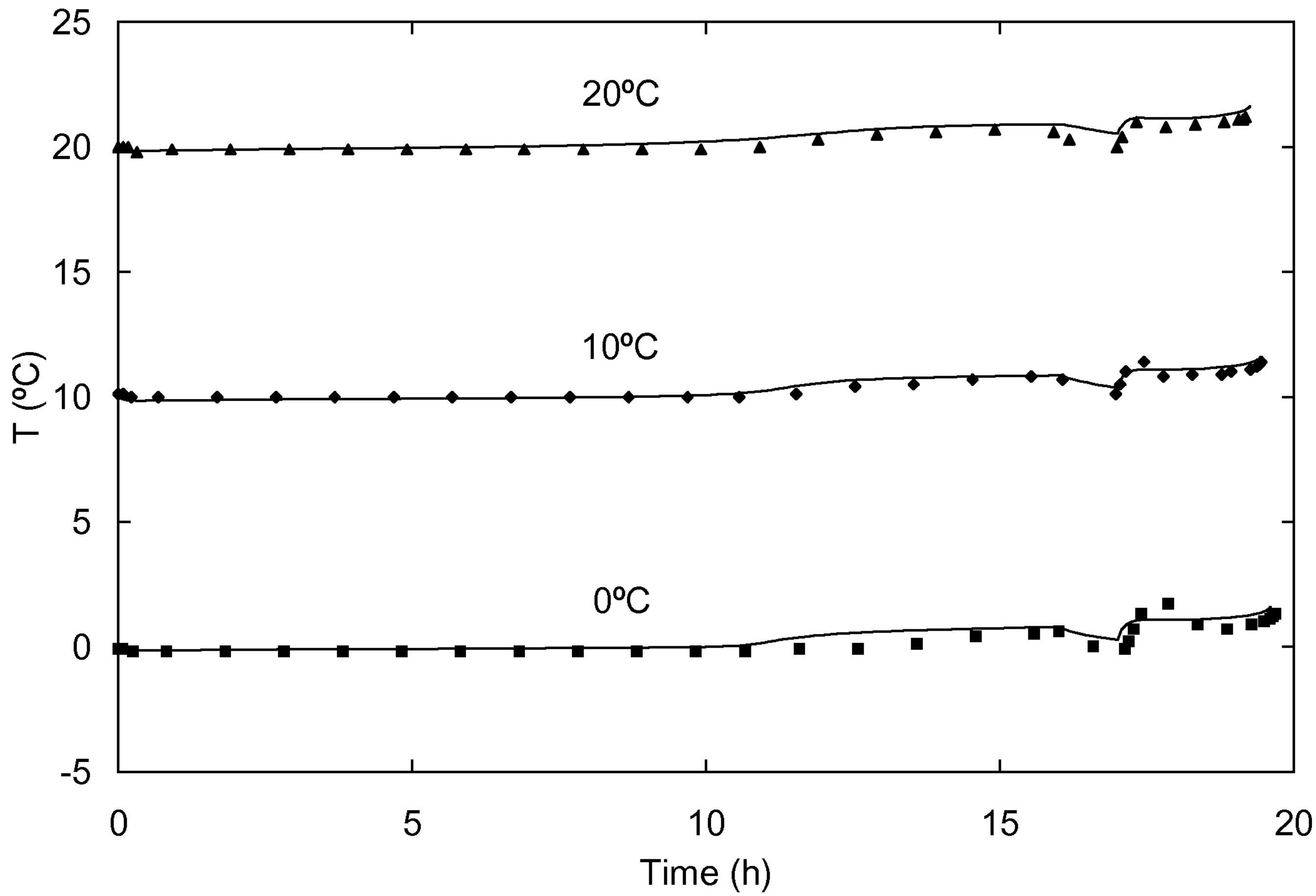


Comparison of Model Predicted Cell Potential with TRW Data



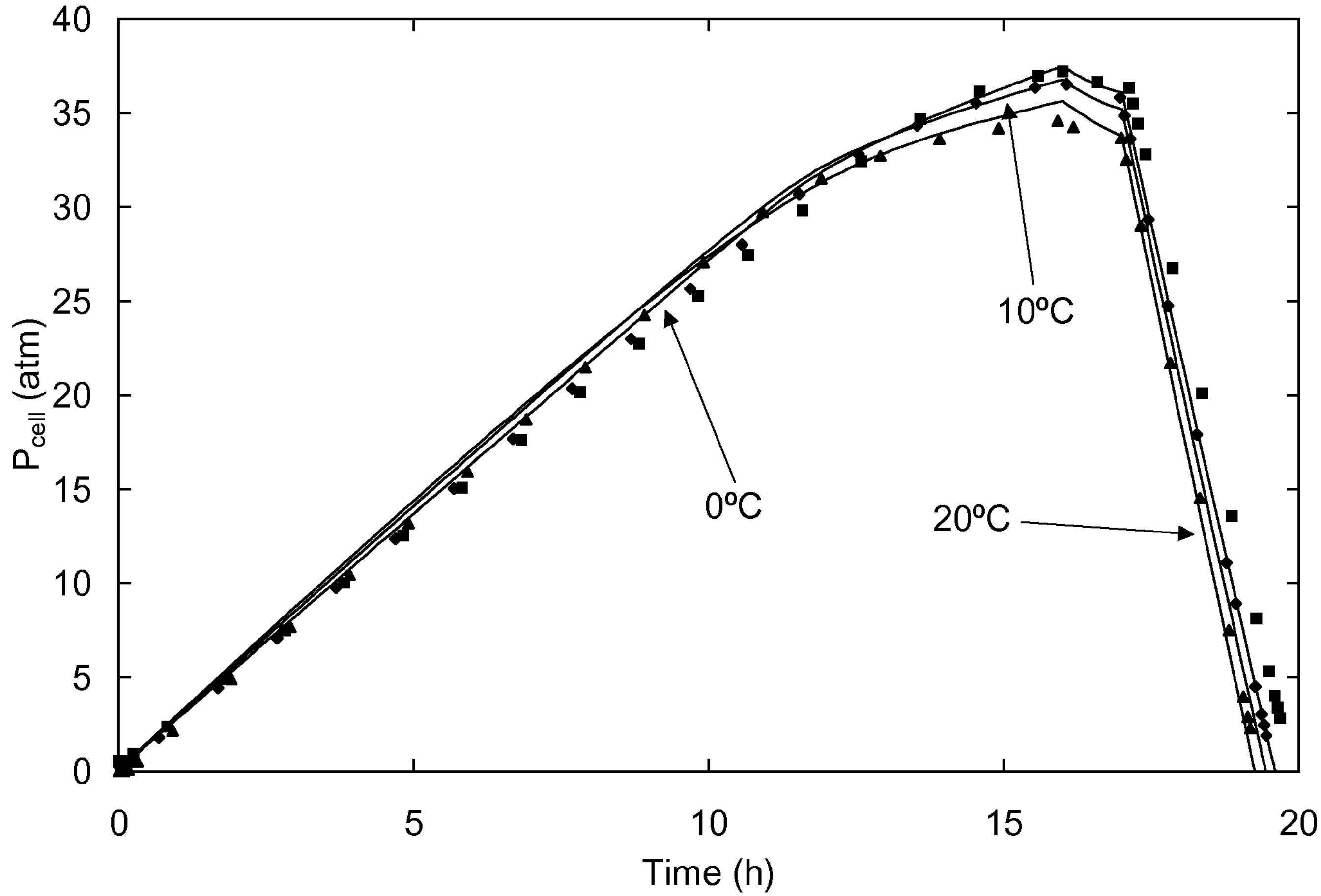
B. Wu and R. E. White, *J. Electrochem. Soc.*, in press (2000).

Comparison of Model Predicted Cell Temperature with TRW Data



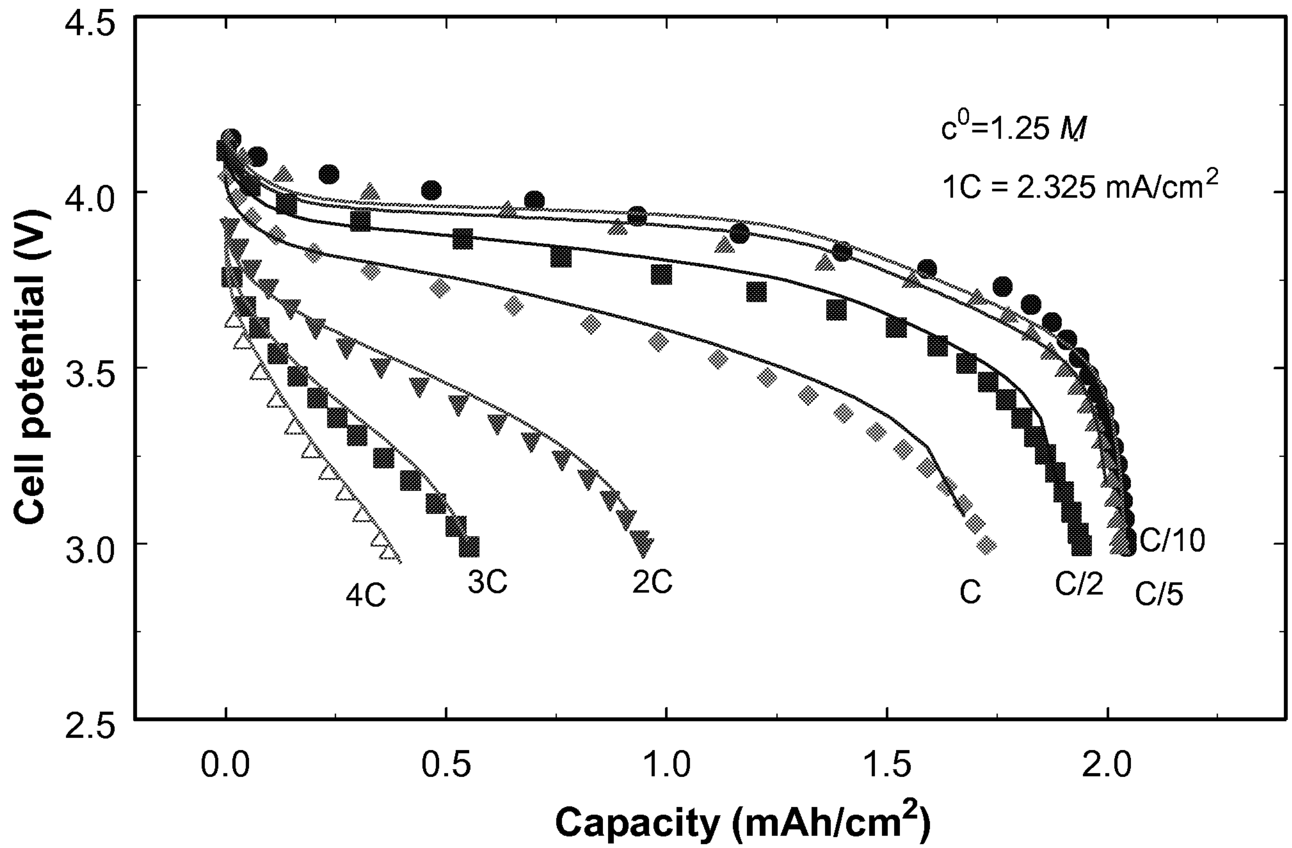
B. Wu and R. E. White, *J. Electrochem. Soc.*, in press (2000).

Comparison of Model Predicted Cell Pressure with TRW Data



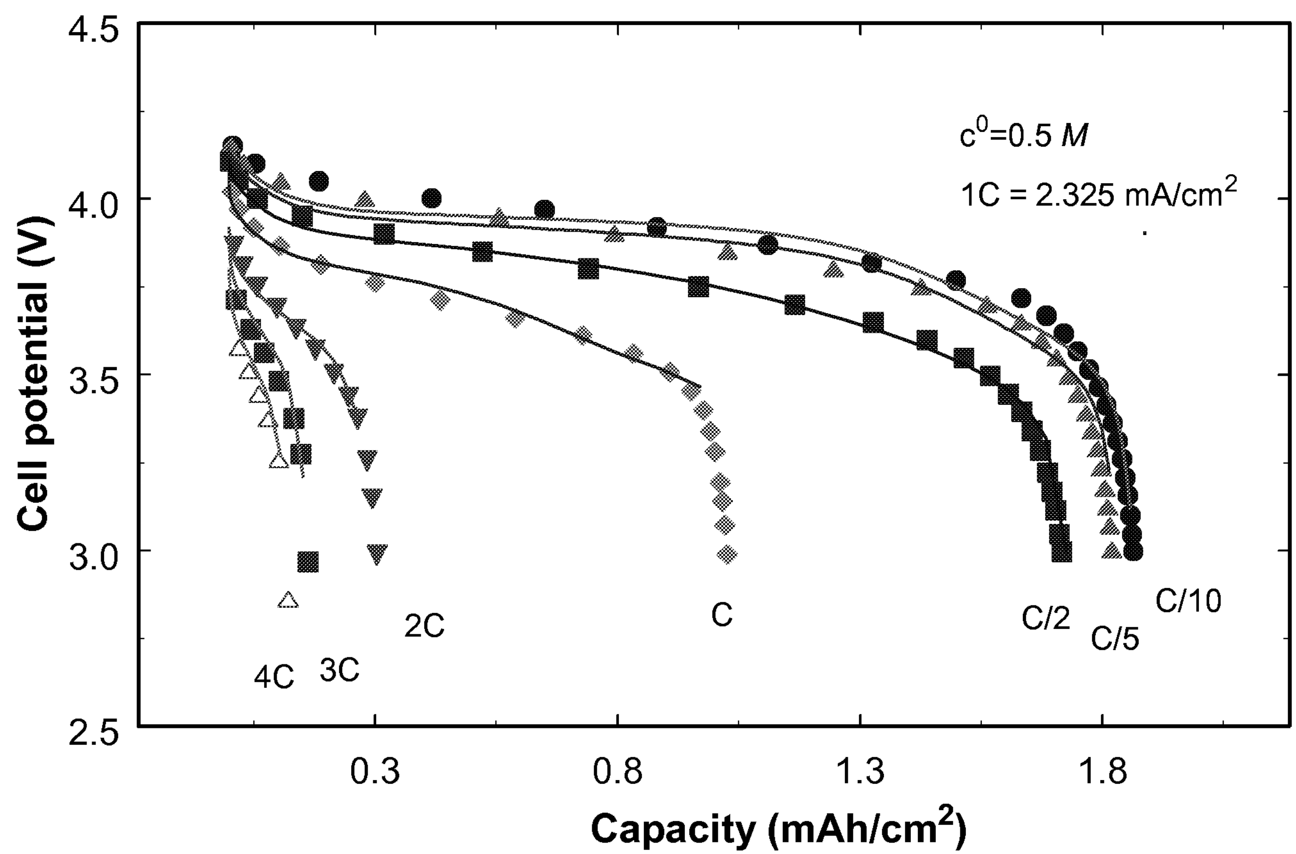
B. Wu and R. E. White, *J. Electrochem. Soc.*, in press (2000).

Experimental & Simulated Discharge Curves for a Li-Ion Cell with 1.25 M Initial Salt Concentration



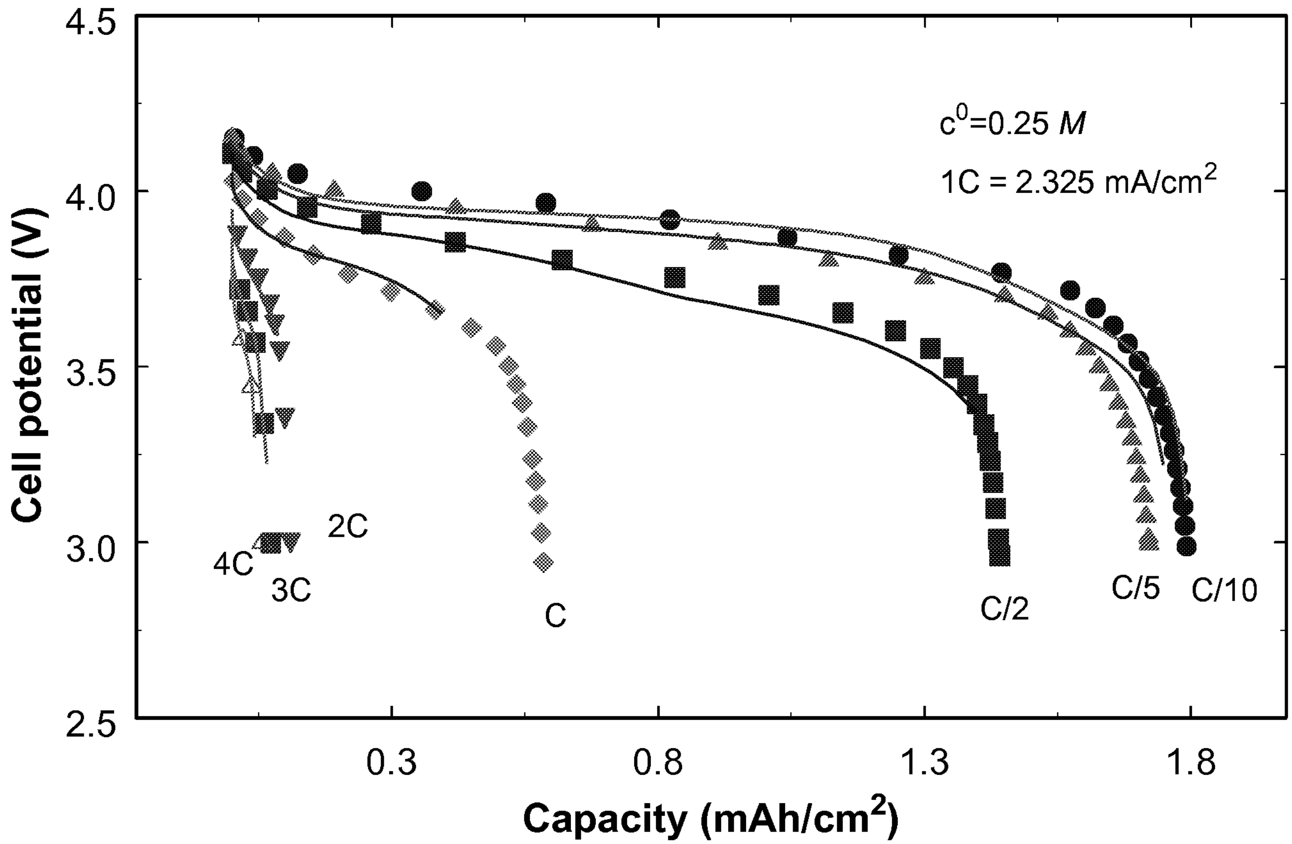
P. Arora, M. Doyle, A. S. Gozdz, R. E. White, and J. Newman, *J. Power Sources*., **88**, 219-231 (2000).

Experimental & Simulated Discharge Curves for a Li-Ion Cell with 0.5 M Initial Salt Concentration



P. Arora, M. Doyle, A. S. Gozdz, R. E. White, and J. Newman, *J. Power Sources*., **88**, 219-231 (2000).

Experimental & Simulated Discharge Curves for a Li-Ion Cell with 0.25 M Initial Salt Concentration



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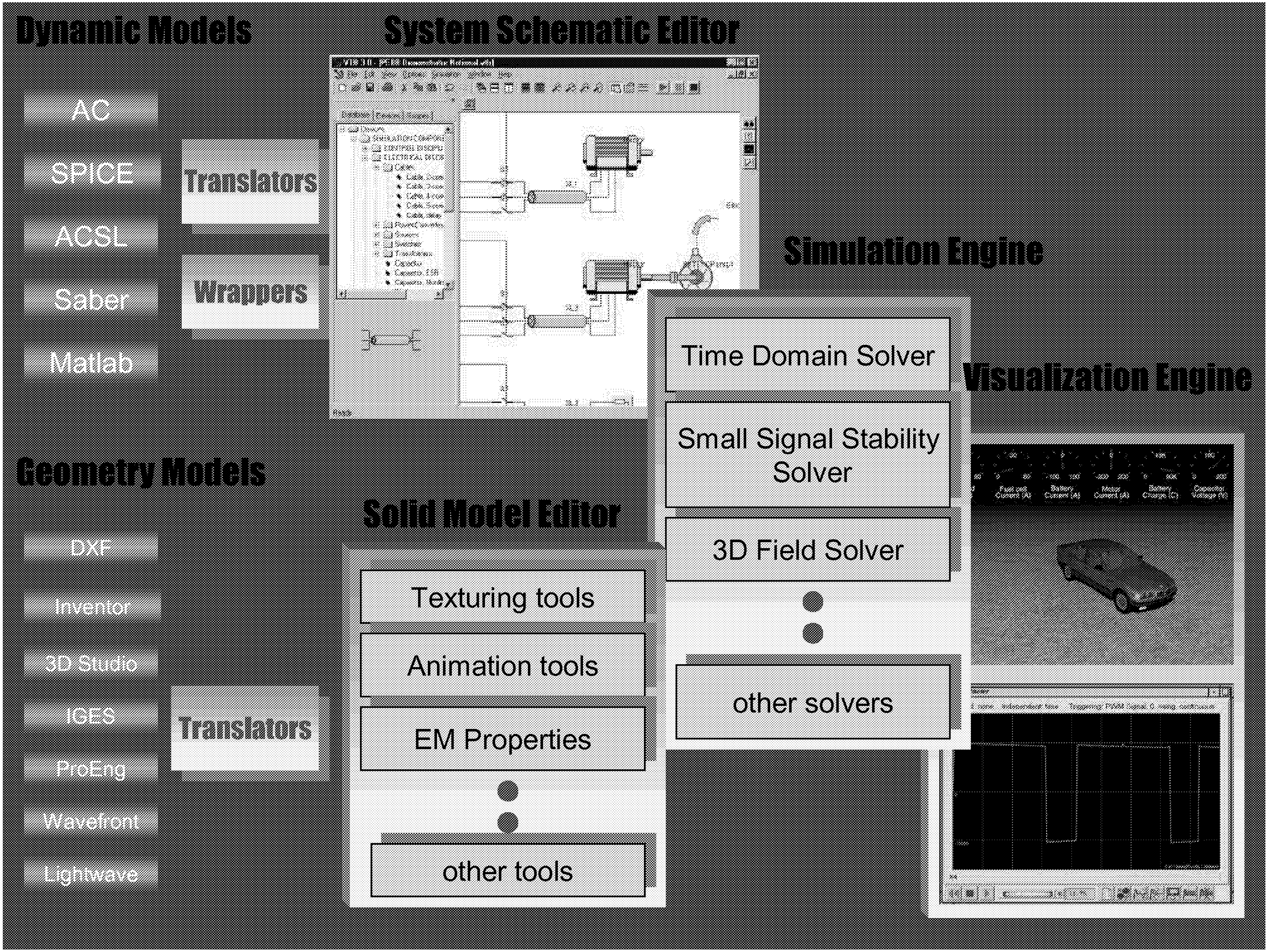
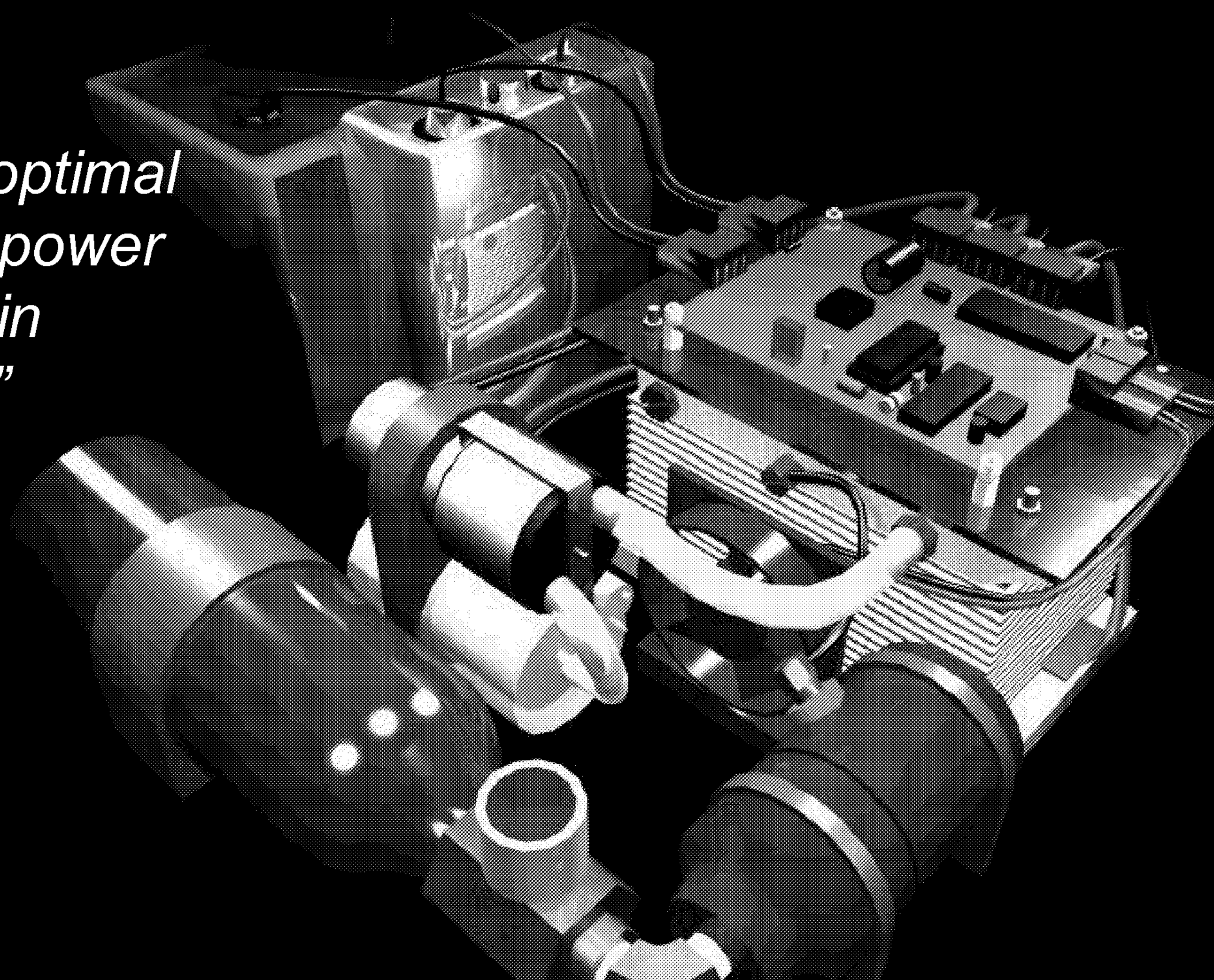
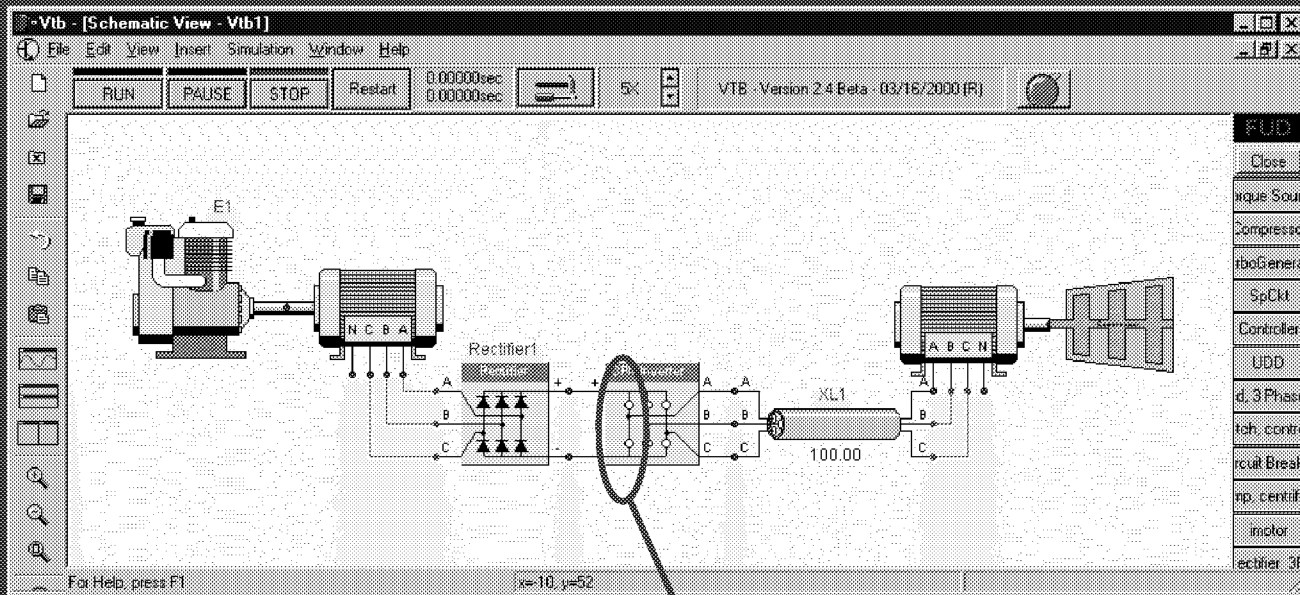

Dynamic Models
AC
SPICE
ACSL
Saber
Matlab
Translators
Wrappers
System Schematic Editor
Simulation Engine
Time Domain Solver
Small Signal Stability Solver
3D Field Solver
other solvers
Visualization Engine
Geometry Models
DXF
Inventor
3D Studio
IGES
ProEng
Wavefront
Lightwave
Translators
Solid Model Editor
Texturing tools
Animation tools
EM Properties
other tools

Project Objectives

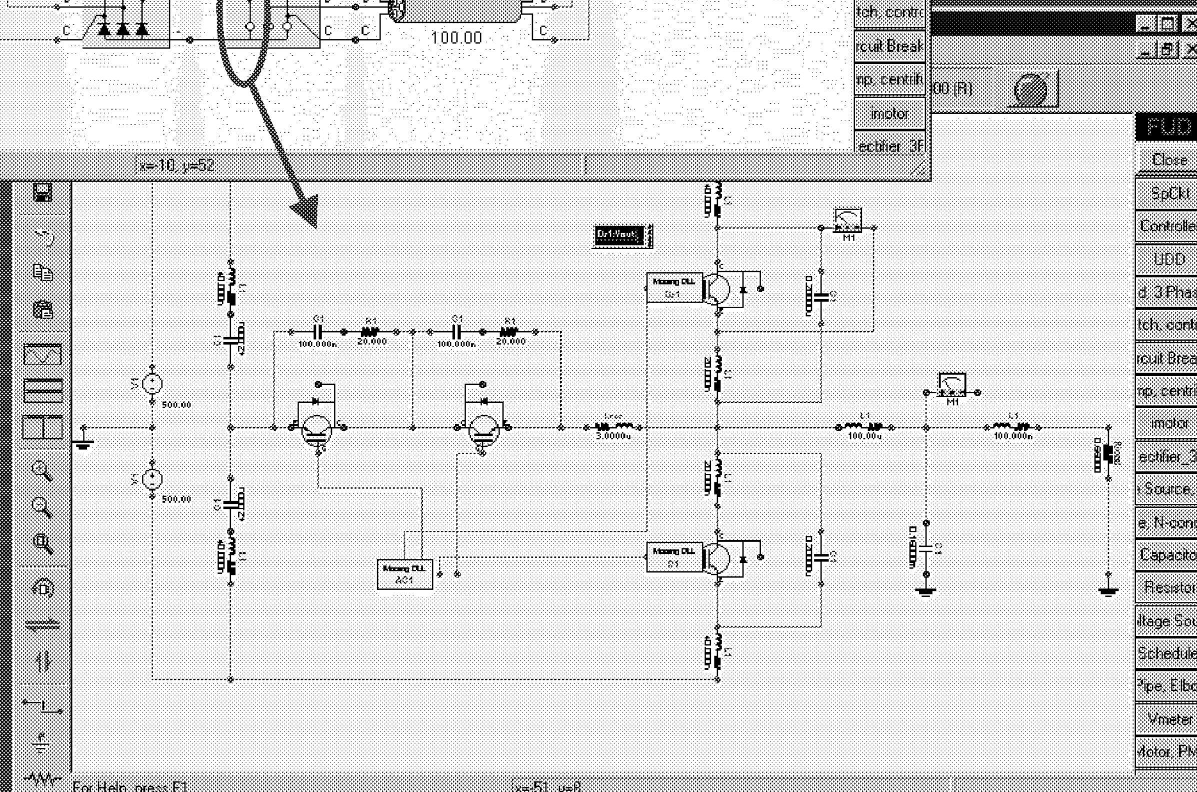
“Investigate the optimal design of hybrid power systems for use in mobile systems.”



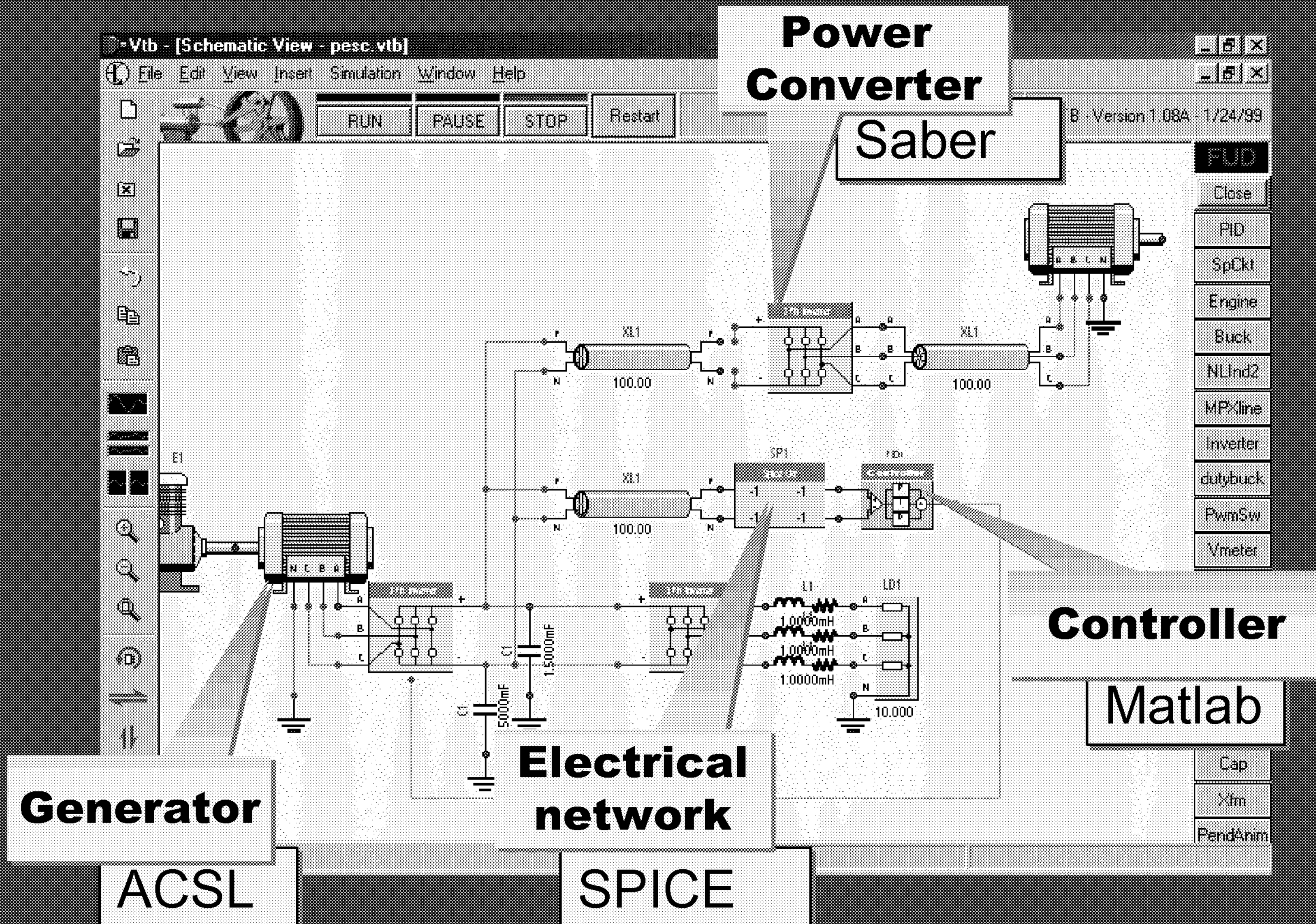
VTB supports analysis at the system level

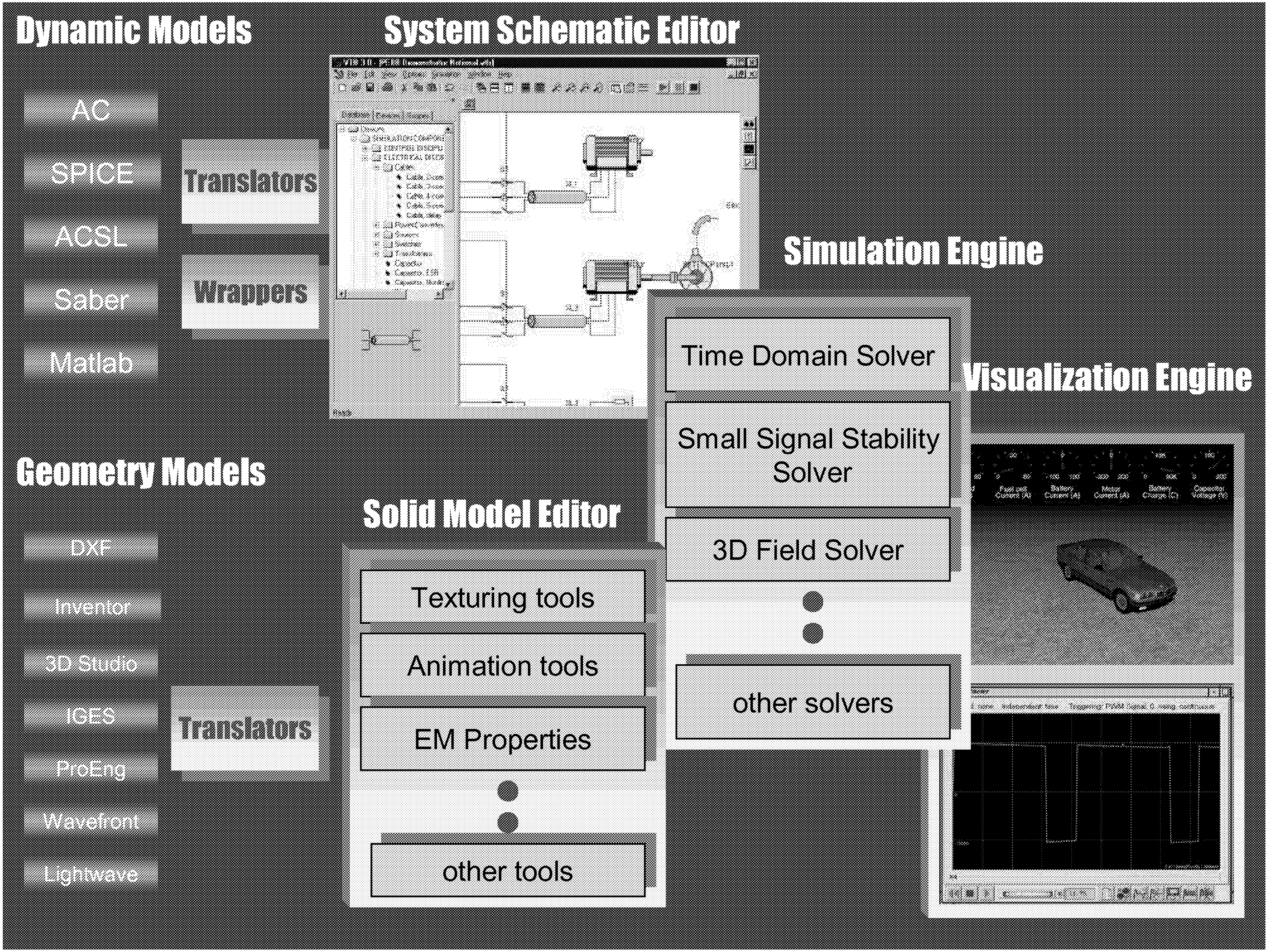


And at a detail level



The VTB is a highly interactive environment for collaborative design and virtual prototyping of advanced power systems.




Dynamic Models
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ProEng
Wavefront
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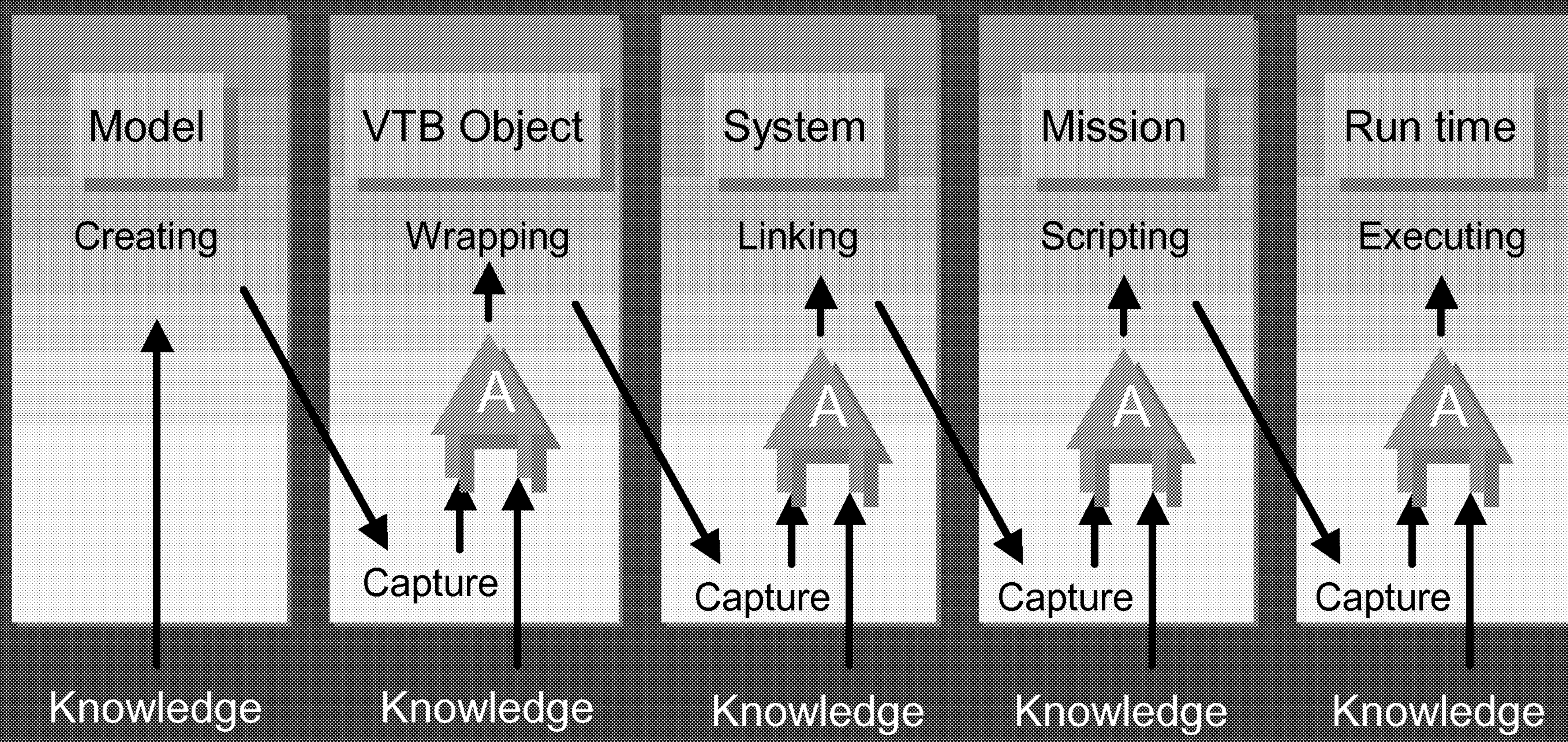
Translators
Solid Model Editor
Texturing tools
Animation tools
EM Properties
other tools

VTB facilitates interdisciplinary and distributed team work (and eliminates stovepipe work threading) by capturing and amplifying user knowledge at every step



Collaborators

- Pankaj Arora
- Bahne Cornilsen
- Roger A. Dougal
- Marc Doyle
- Antoni S. Gozdz
- Sathya Motupally
- John Newman
- Venkat Srinivasan
- Christopher Streinz
- John W. Van Zee
- John W. Weidner
- Ralph E. White
- Bin Wu