Modeling the Behavior of Zn-AgO Batteries During High Rates of Discharge

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Outline

- Objectives
- Electrode Reactions
- Prototype Battery
- Model Development
- Model Predictions
  - Concentration Distributions
  - Heat Generation Rates

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Long-Term Model-Objectives

- Determine Local Heat Generation Rates
  - function of x,y,z in a cell
  - function of plate position
  - function of time & discharge rate
  - function of cycle
  - function of charge rate
- For Heat Removal:
  - Consider Alternate Grid Designs
  - External Cooling

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Electrode Reactions

- Positive Electrode

$$Ag_2O + H_2O + 2e^- \xrightarrow{\text{discharge}} 2Ag + OH^- \quad U^{\Theta} = 0.342\ V$$

$$2AgO + H_2O + 2e^- \xrightarrow{\text{discharge}} Ag_2O + OH^- \quad U^{\Theta} = 0.642\ V$$

- Negative Electrode

$$Zn(OH)_4^{-2} \longleftrightarrow ZnO + 2(OH)^- \quad K_{eq} = 0.003$$

$$ZnO + H_2O + 2e^- \xleftarrow{\text{discharge}} Zn + 2\ OH^- \quad U^{\Theta} = -1.35\ V$$

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Prototype Battery

- 135 A-h Capacity
- 12-25 knots
- 50 -250 Amps   10 -100 mA/cm^2
- 250 V
- 168 cells ÷ 24 cells/case = 7 cases
- 15 in^2
- Nylon, Cellophane, FRSC = 0.130 in.
- AgO, Zn thick. = 0.039, 0.060 in.

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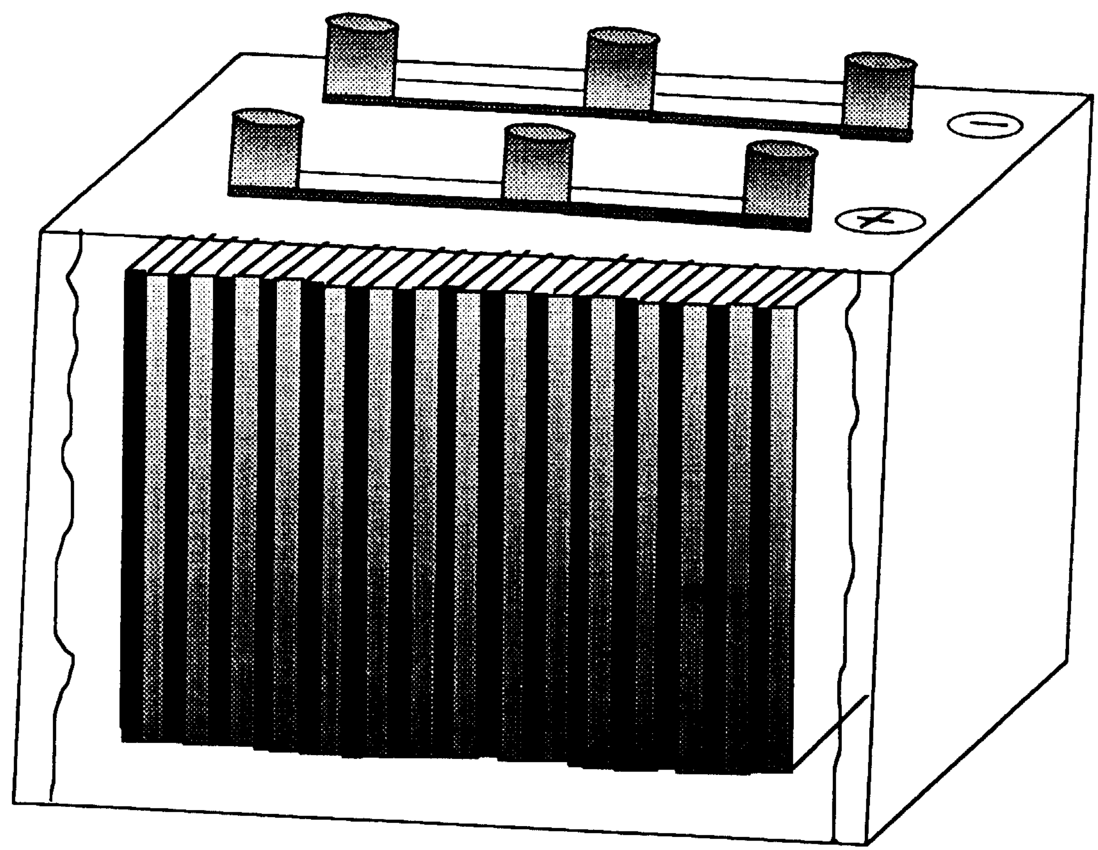
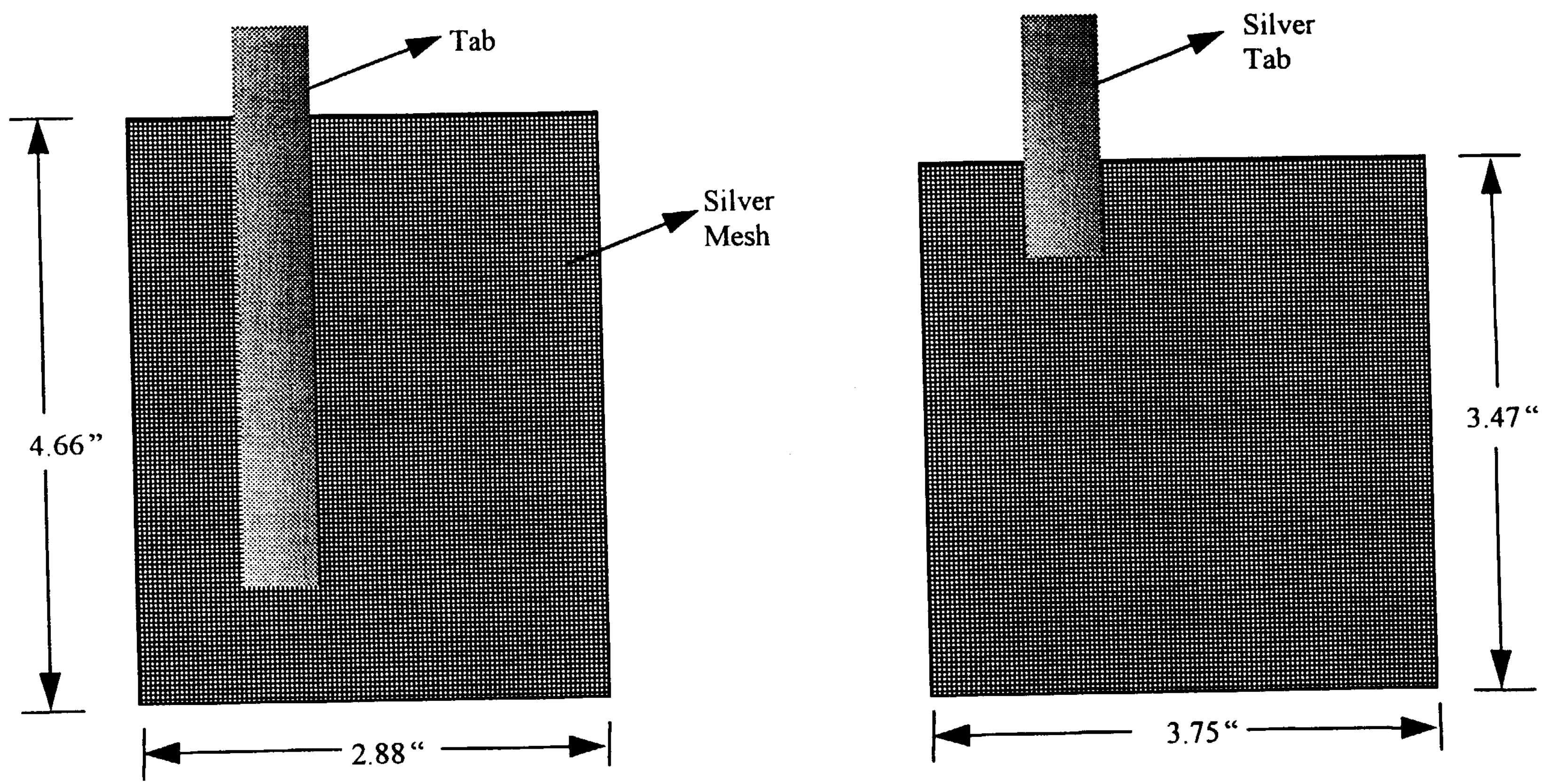
Schematic of a 135 A-hr Zn/AgO Battery

(Only 15 of the 24 positive (Ag) and 25 negative (Zn) plates are shown
separators not shown



Alternate Electrode Designs



Present Assumptions

- \- One-Dimensional Transport.
- \- No Convection in the Porous Electrode.
- \- Dilute Solution Theory.
- \- Constant Porosity.
- \- Large Matrix Conductivity

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One-dimensional flux expression

$$\frac{N_i}{\varepsilon} = -\frac{D_i}{\tau}\frac{\partial C_i}{\partial x} - \frac{F z_i D_i C_i}{\tau R T}\frac{\partial \phi_2}{\partial x}$$

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Governing Equations- in Zn electrode

$$\varepsilon_{Zn} \frac{\partial C_{K^+}}{\partial t} = -\nabla \cdot N_{K^+}$$

$$\varepsilon_{Zn} \frac{\partial C_{OH^-}}{\partial t} = -\frac{as_{OH^-} i_n}{nF} - \nabla \cdot N_{OH^-} + 2R$$

$$\varepsilon_{Zn} \frac{\partial C_{Zn(OH)_4^{-2}}}{\partial t} = -\frac{as_{Zn(OH)_4^{-2}} \cdot i_n}{nF} - \nabla \cdot N_{Zn(OH)_4^{-2}} - R$$

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Governing Equations- in Zn electrode (cont.)

$$\frac{\partial M_{ZnO}}{\partial t} = -\frac{A_s i_n s_{ZnO}}{nF}$$

$$\sum z_i C_i = 0$$

$$\frac{\partial i_2}{\partial x} = a i_n$$

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Butler-Volmer Equation

$$i_n = i_o \left\{ y \left(\frac{C_{OH^-}}{C_{OH^-,ref}} \right)^2 \exp\left(\frac{F\alpha_a}{RT}\eta_a\right) - (1 - y) \exp\left(-\frac{F\alpha_c}{RT}\eta_c\right) \right\}$$

where $y = M_{Zn} / M^o_{ZnO}$ and $1 - y = M_{ZnO} / M^o_{ZnO}$

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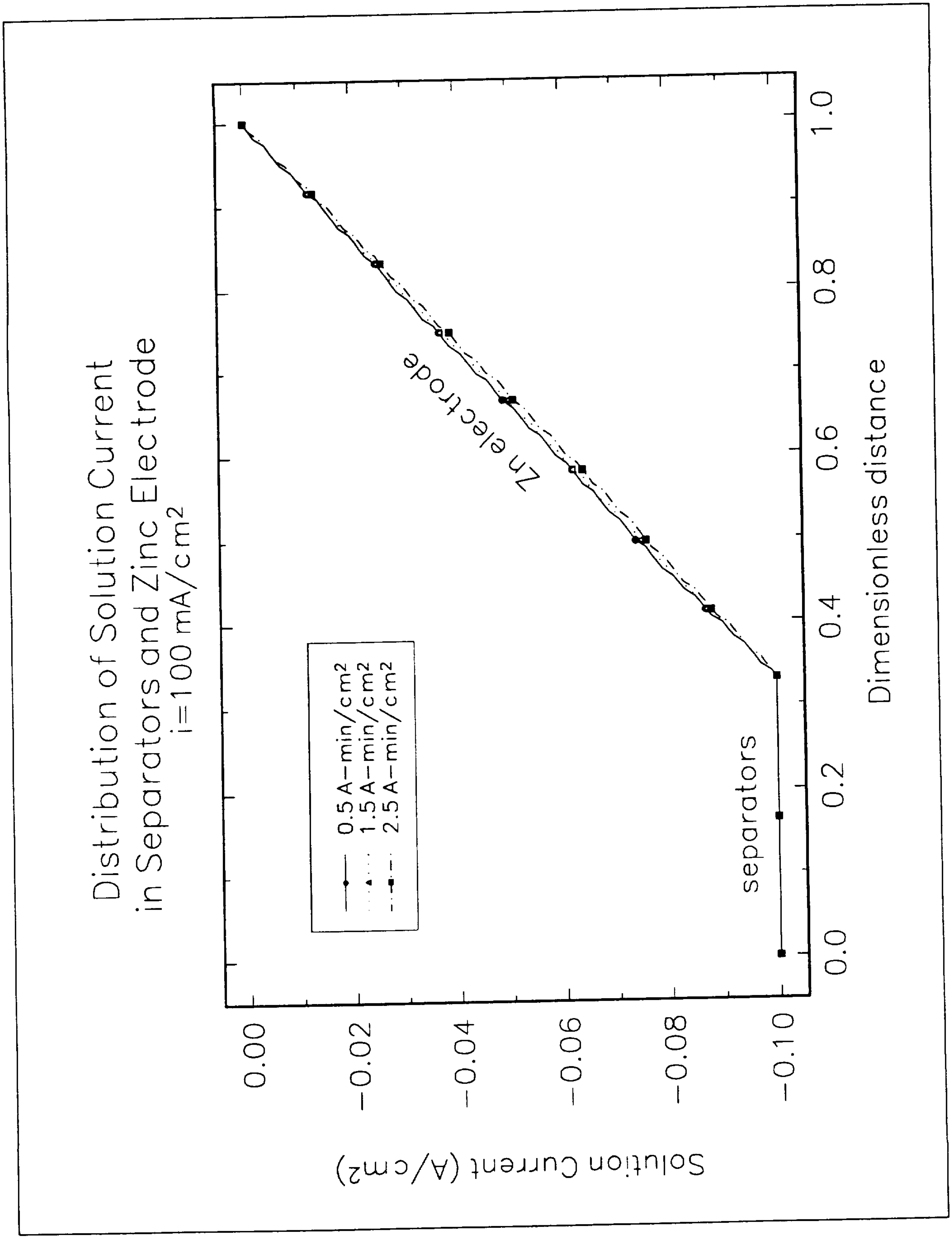
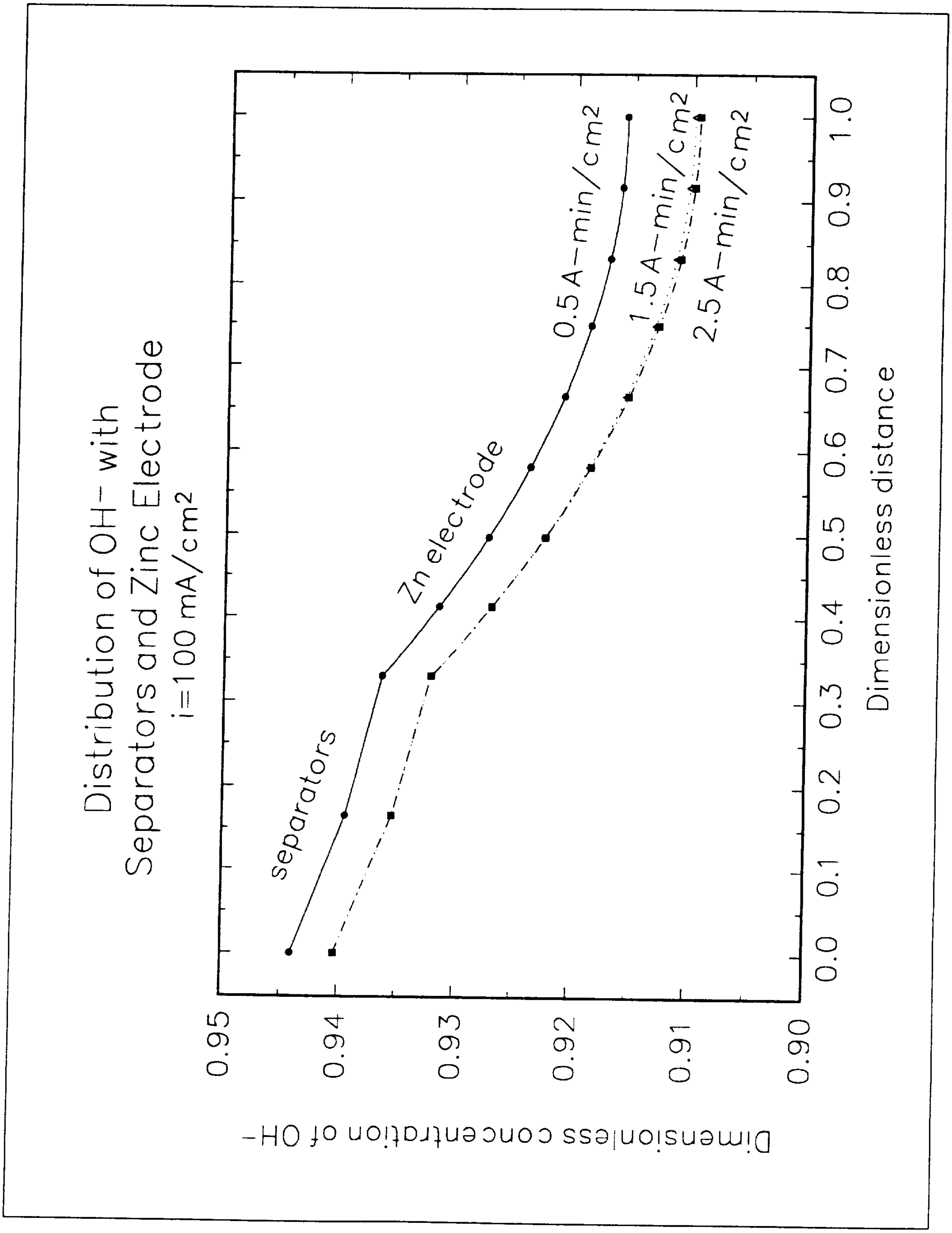
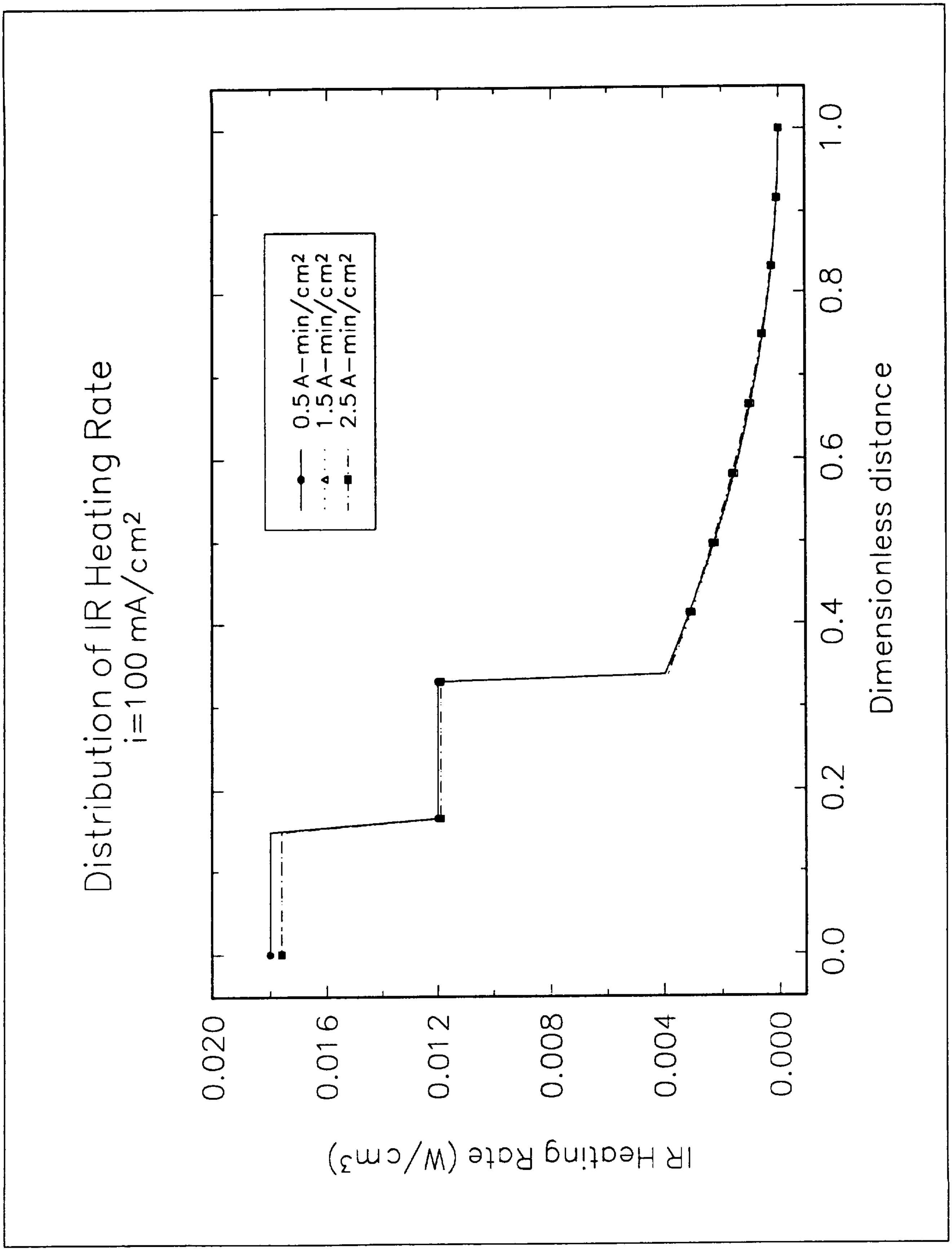
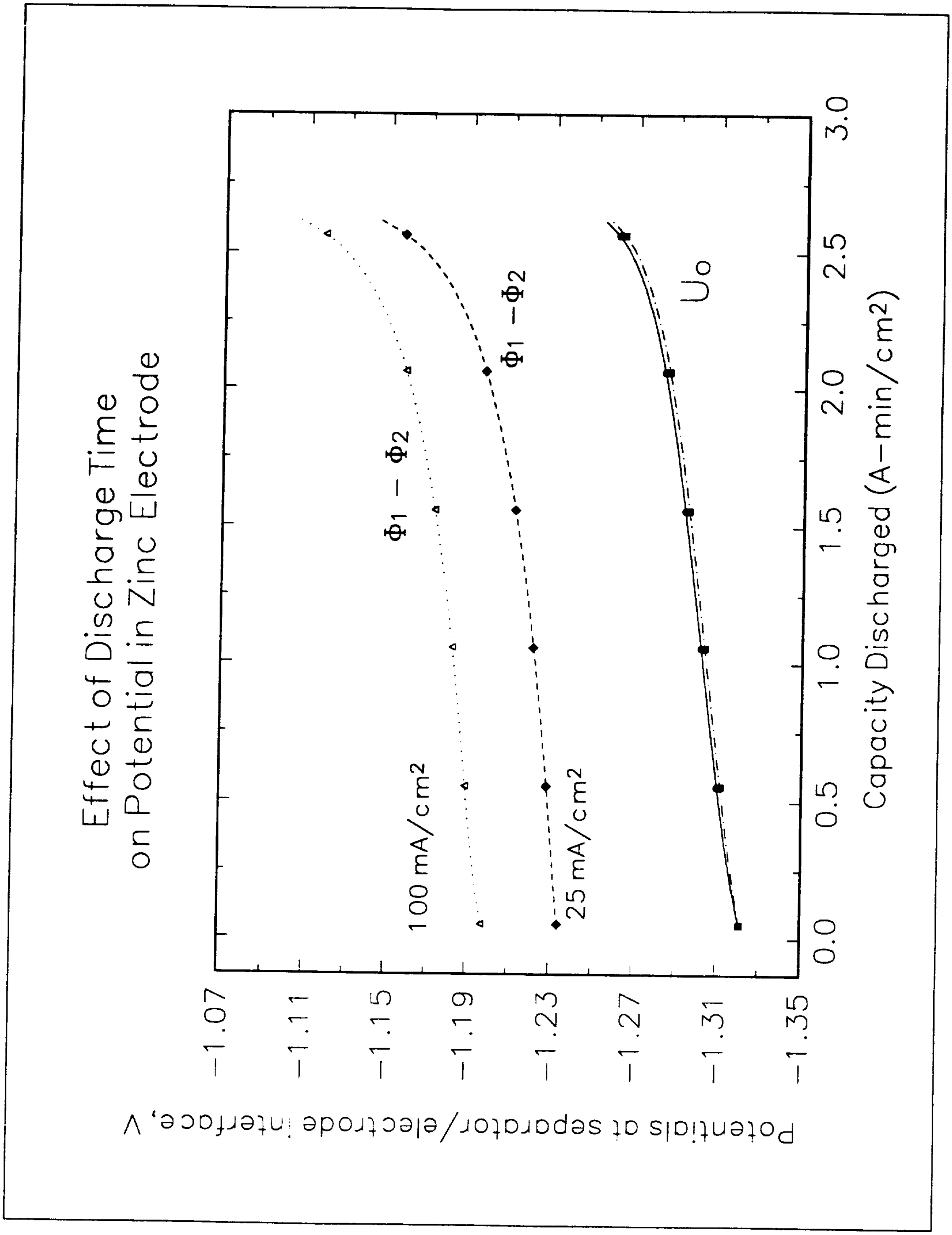
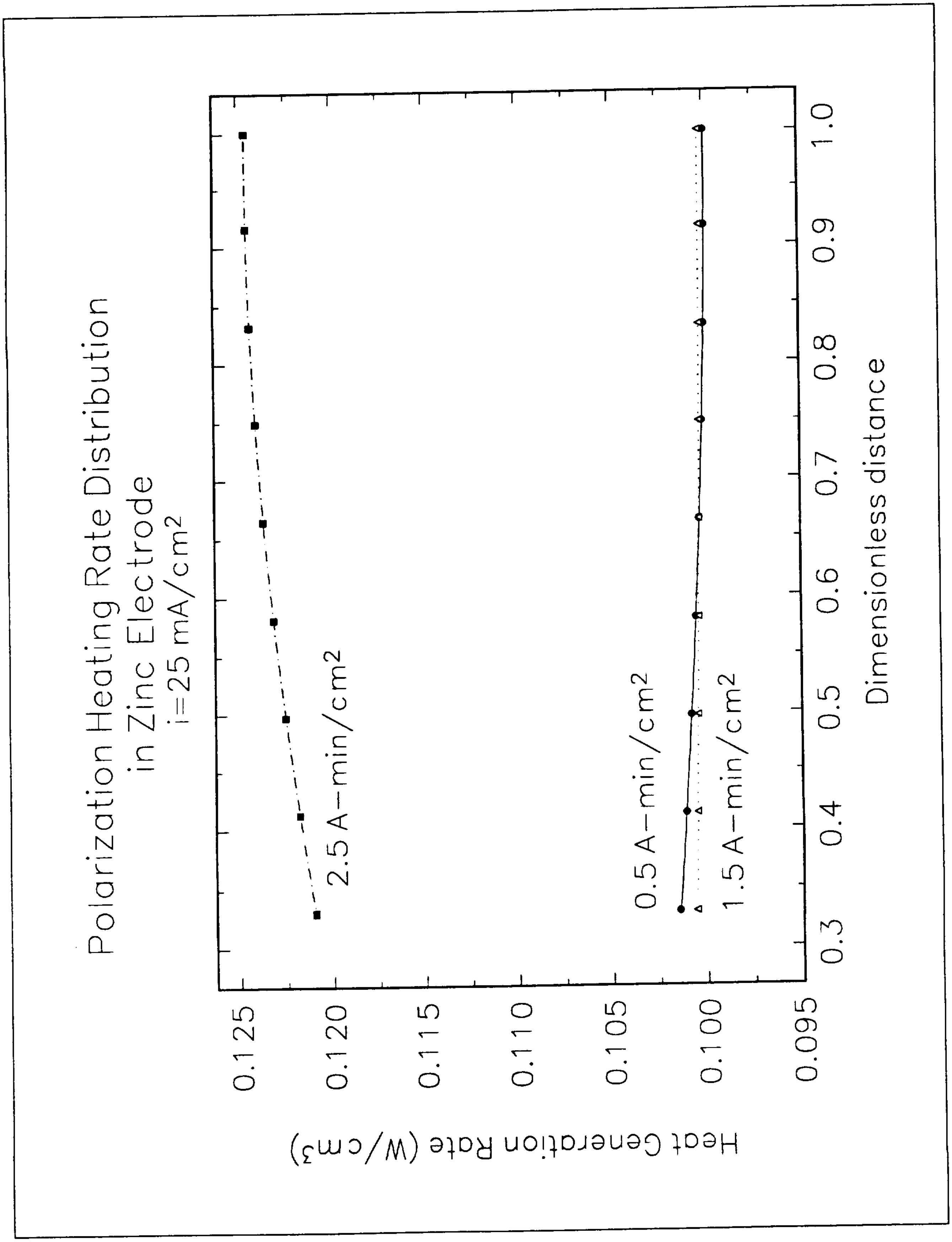

Distribution of Solution Current
in Separators and Zinc Electrode
i=100 mA/cm2
0.5 A-min/cm2
1.5 A-min/cm2
2.5 A-min/cm2
Zn electrode
separators
Solution Current (A/cm2)
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
Dimensionless distance
0.0
0.2
0.4
0.6
0.8
1.0

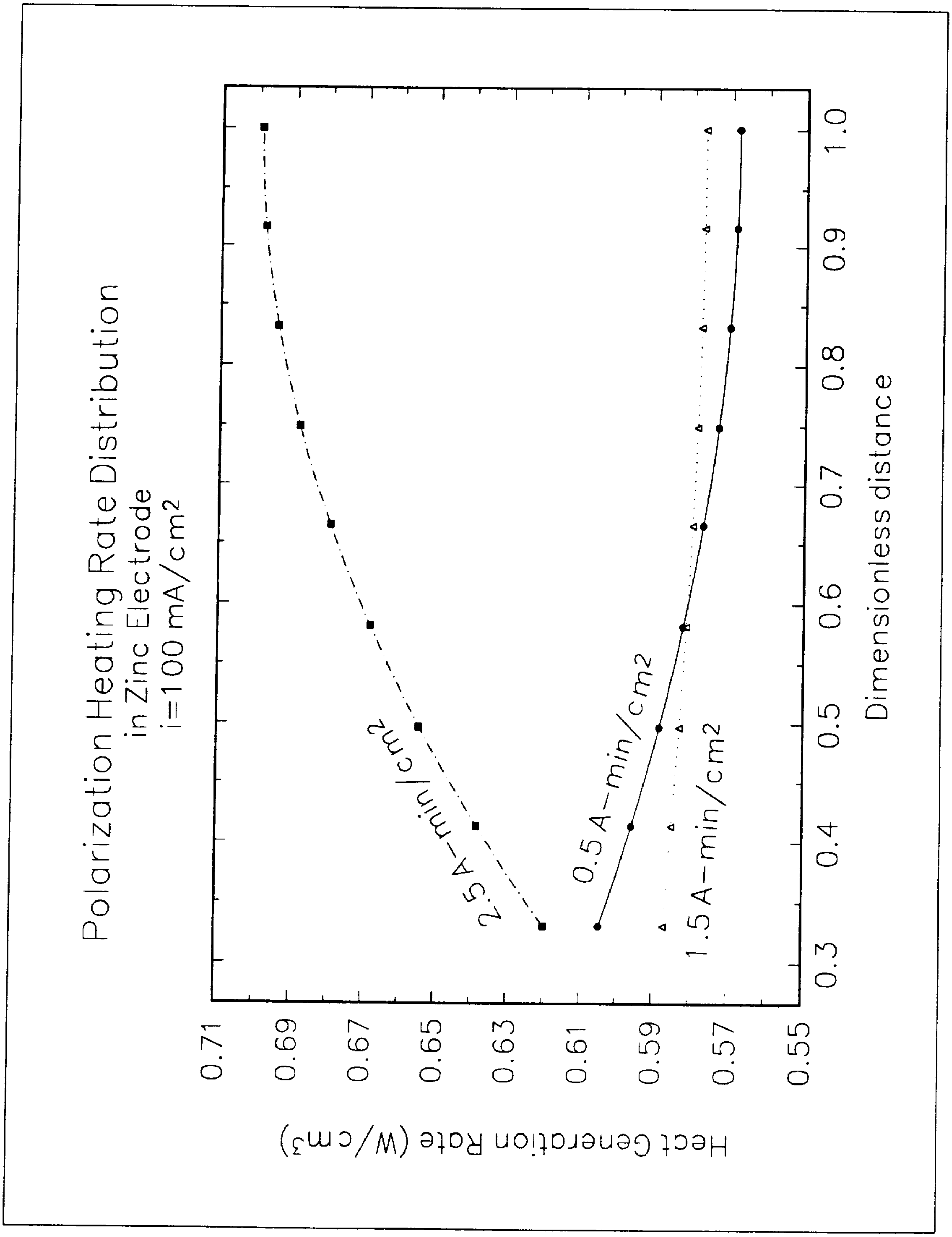

Distribution of OH− with
Separators and Zinc Electrode
i=100 mA/cm2
Separators
Zn electrode
0.5 A−min/cm2
1.5 A−min/cm2
2.5 A−min/cm2
Dimensionless concentration of OH−
Dimensionless distance
0.95
0.94
0.93
0.92
0.91
0.90
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Distribution of IR Heating Rate
i=100 mA/cm2
0.5 A−min/cm2
1.5 A−min/cm2
2.5 A−min/cm2
IR Heating Rate (W/cm3)
0.020
0.016
0.012
0.008
0.004
0.000
0.0
0.2
0.4
0.6
0.8
1.0
Dimensionless distance



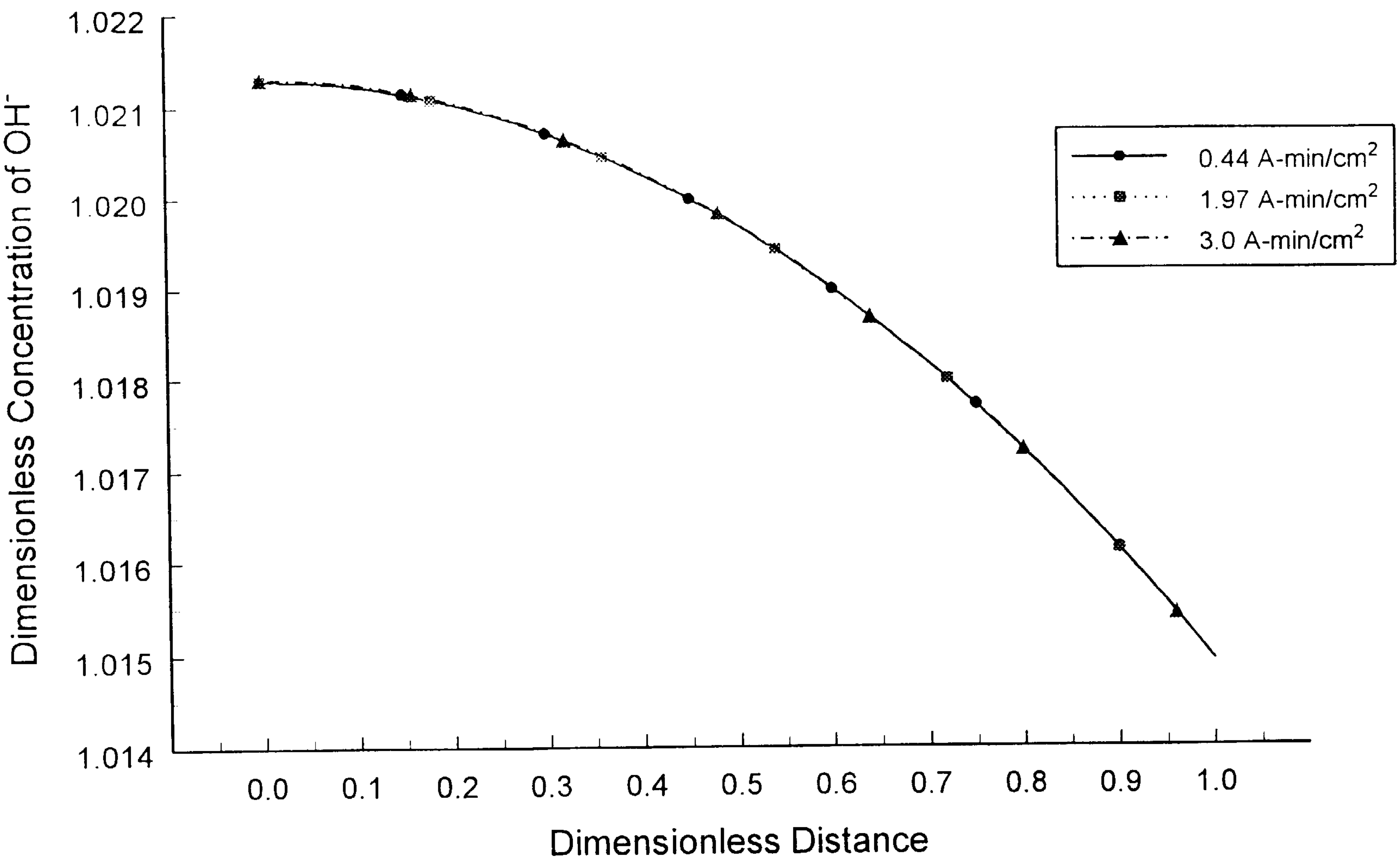
Effect of Discharge Time
on Potential in Zinc Electrode
Potentials at separator/electrode interface, V
Capacity Discharged (A−min/cm²)
100 mA/cm²
25 mA/cm²
Φ1 − Φ2
Φ1 − Φ2
U0
−1.07
−1.11
−1.15
−1.19
−1.23
−1.27
−1.31
−1.35
0.0
0.5
1.0
1.5
2.0
2.5
3.0


Polarization Heating Rate Distribution
in Zinc Electrode
i=25 mA/cm2
2.5 A-min/cm2
0.5 A-min/cm2
1.5 A-min/cm2
Heat Generation Rate (W/cm3)
Dimensionless distance
0.125
0.120
0.115
0.110
0.105
0.100
0.095
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Polarization Heating Rate Distribution
in Zinc Electrode
i=100 mA/cm2
2.5 A-min/cm2
0.5 A-min/cm2
1.5 A-min/cm2
Heat Generation Rate (W/cm3)
0.71
0.69
0.67
0.65
0.63
0.61
0.59
0.57
0.55
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Dimensionless distance

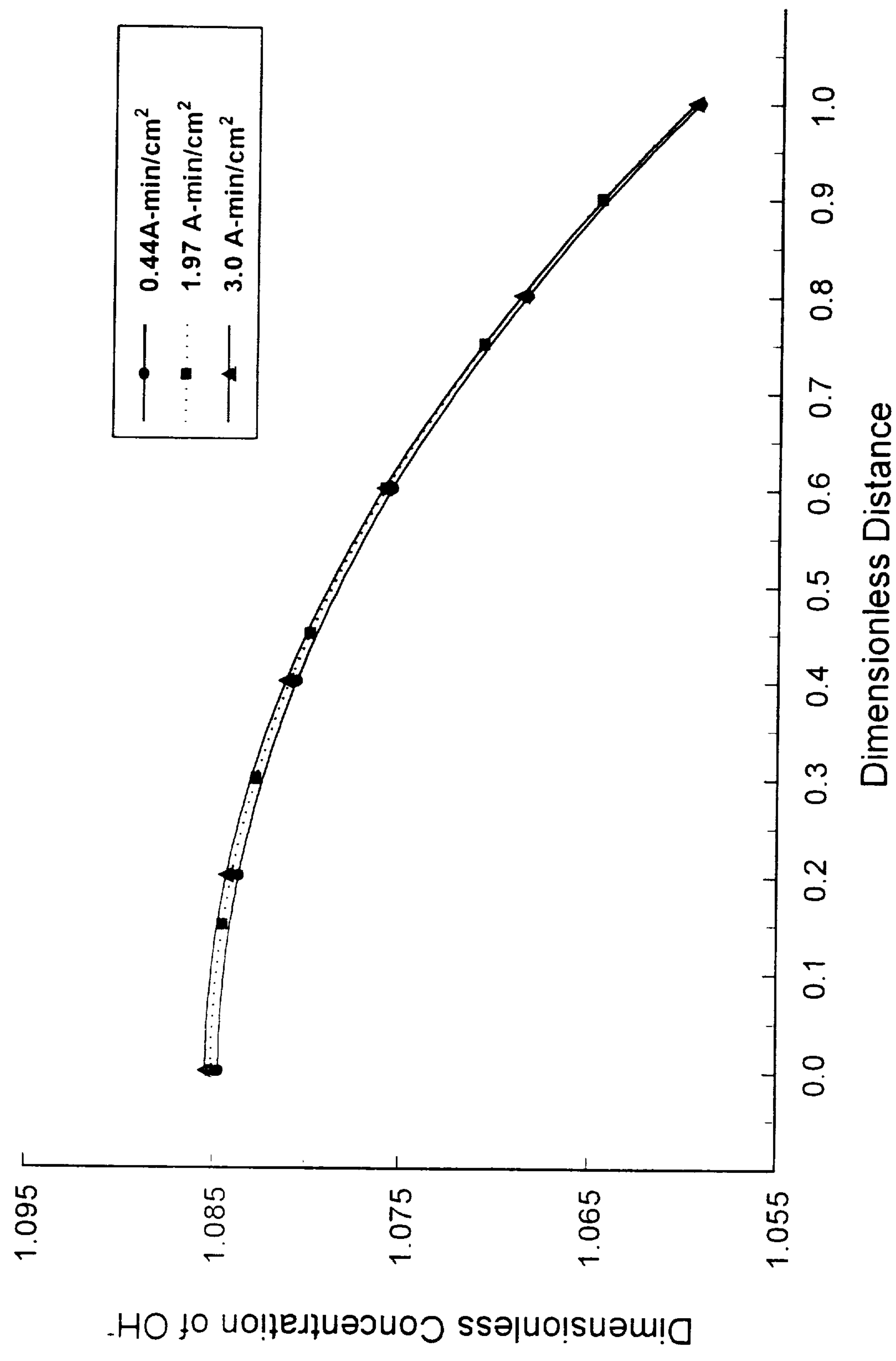
Distribution of OH^- Concentration

Silver electrode (i=25 mA/cm^2)



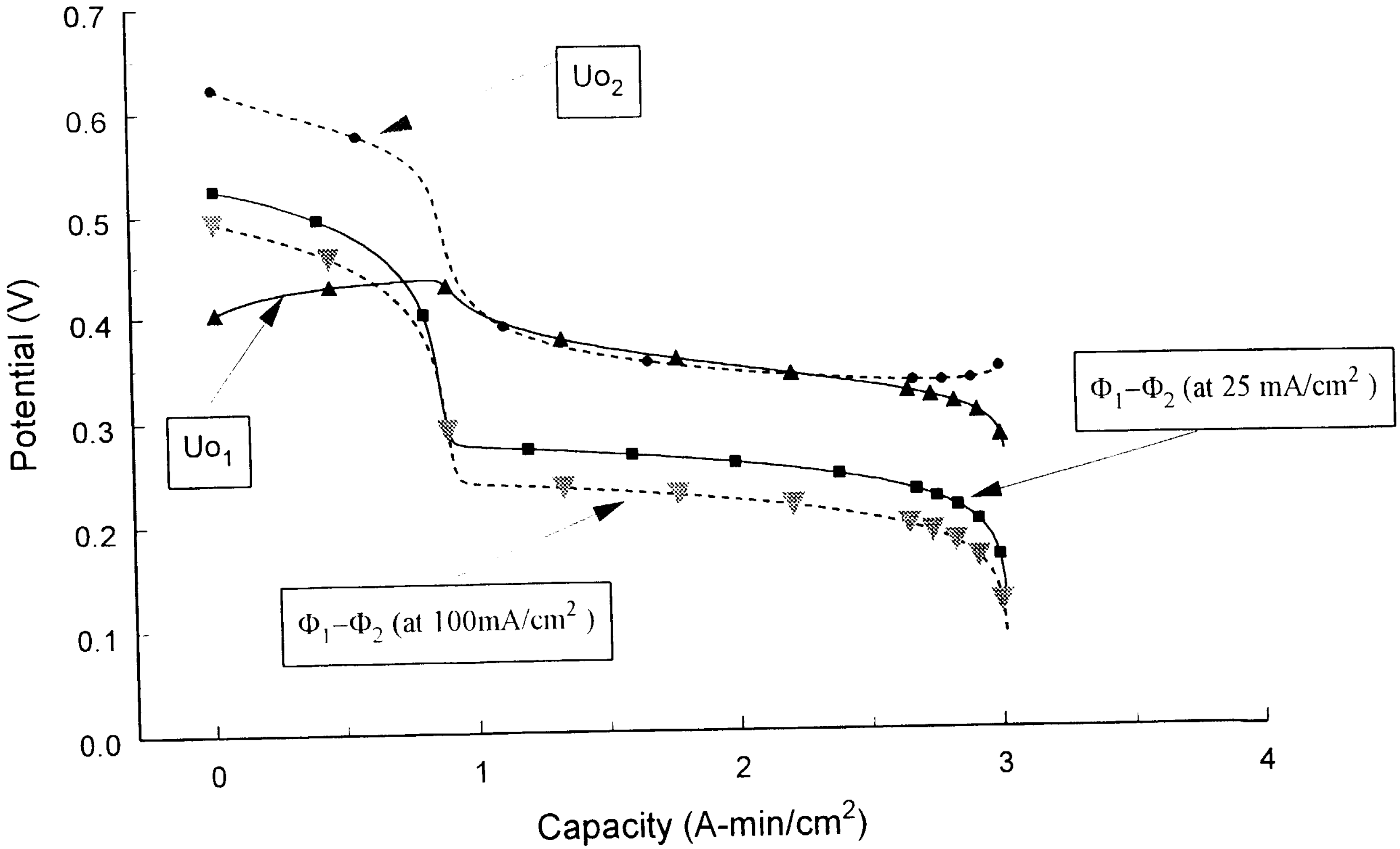
Distribution of OH^- Concentration

Silver electrode (i=100 mA/cm^2)

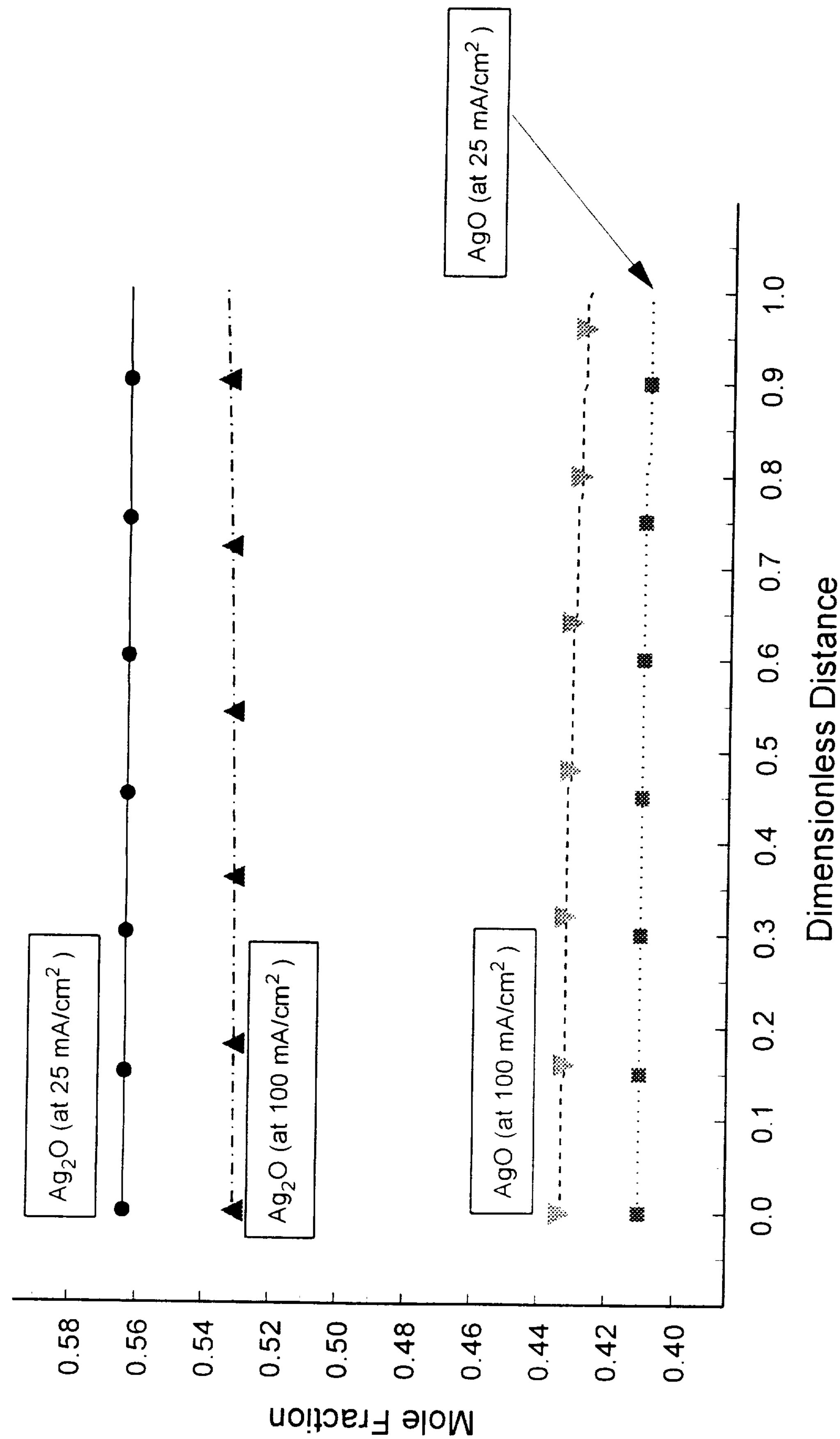


The Effect of Capacity on Potential

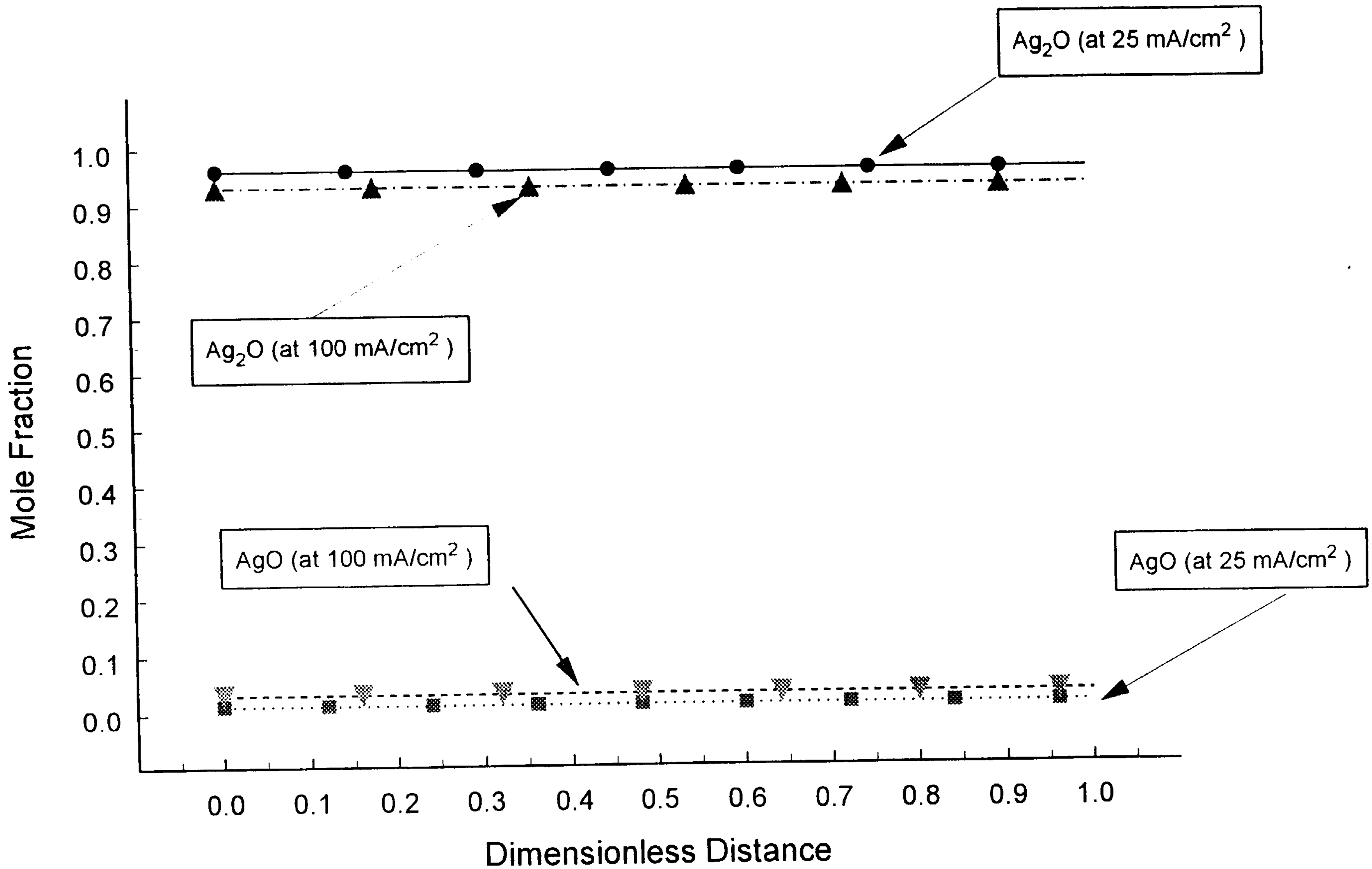
Silver electrode (at x=1.0)



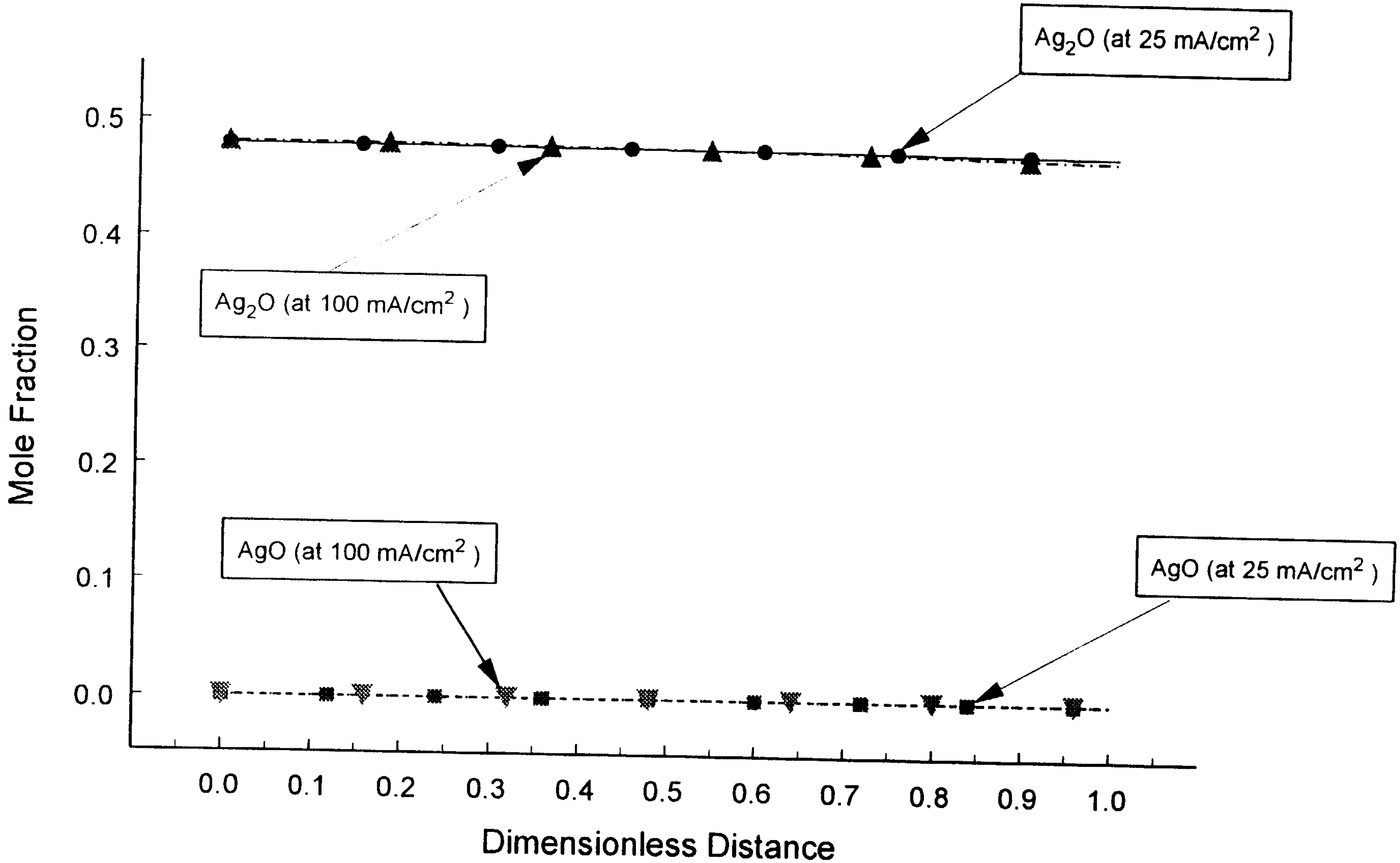
Effect of Current Density on Silver Mole Fractions at 0.44 A-min/cm^2 of Discharge



Effect of Current Density on Silver Mole Fractions at 0.88 A-min/cm^2 of Discharge

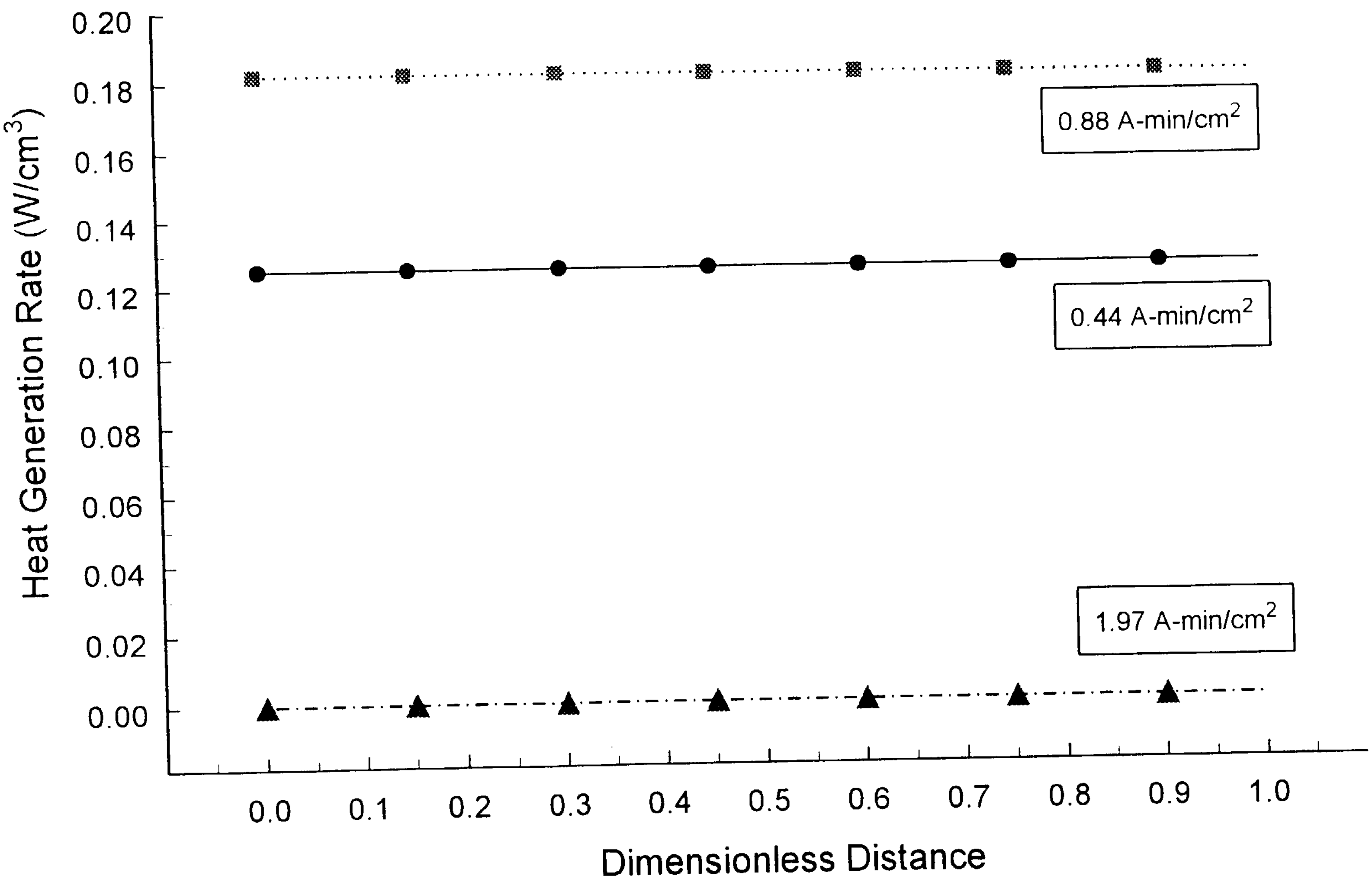


Effect of Current Density on Silver Mole Fractions at 1.97 A-min/cm² of Discharge



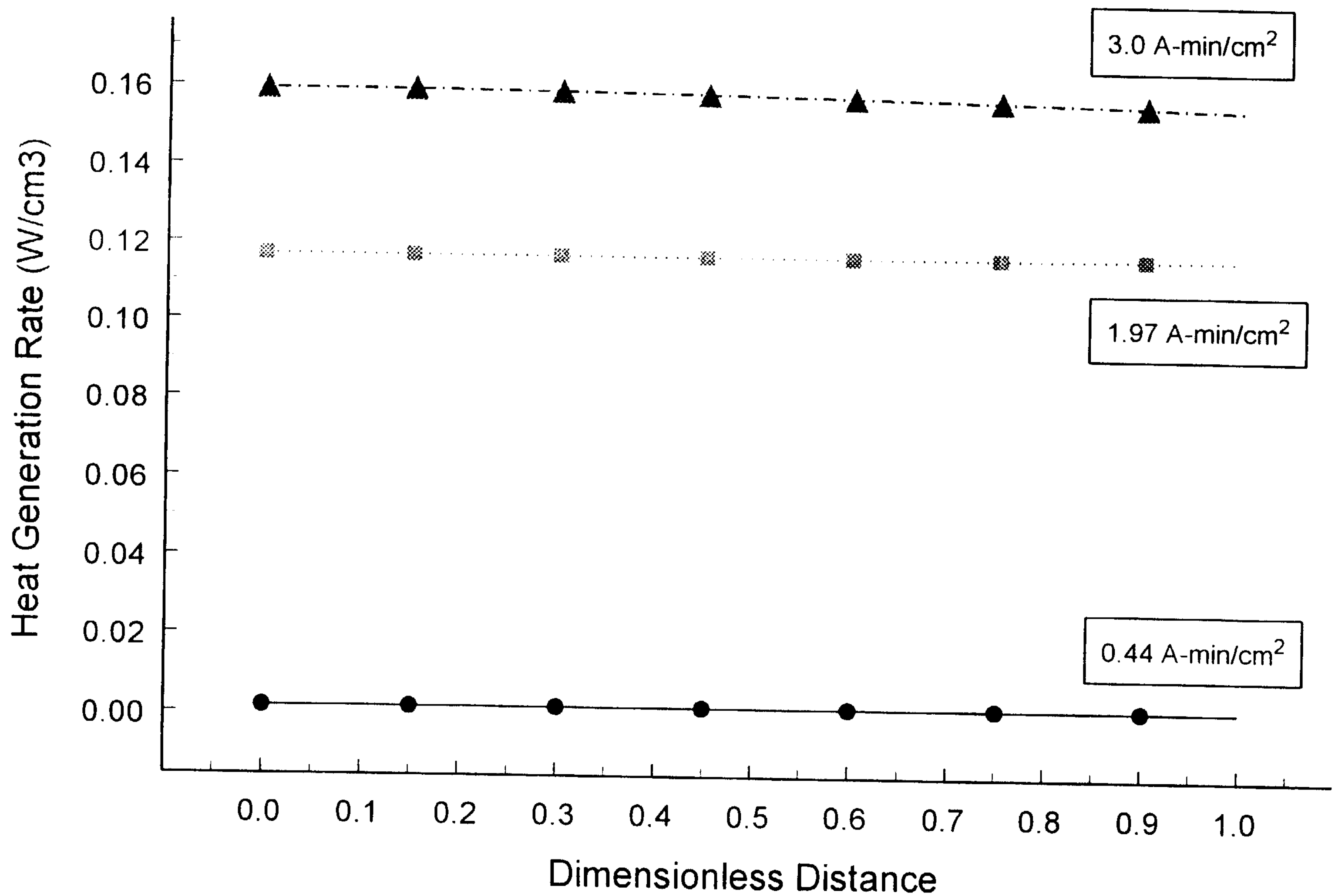
Heating Rate from Reaction 2 Polarization

Silver electrode (i=25mA/cm^2)



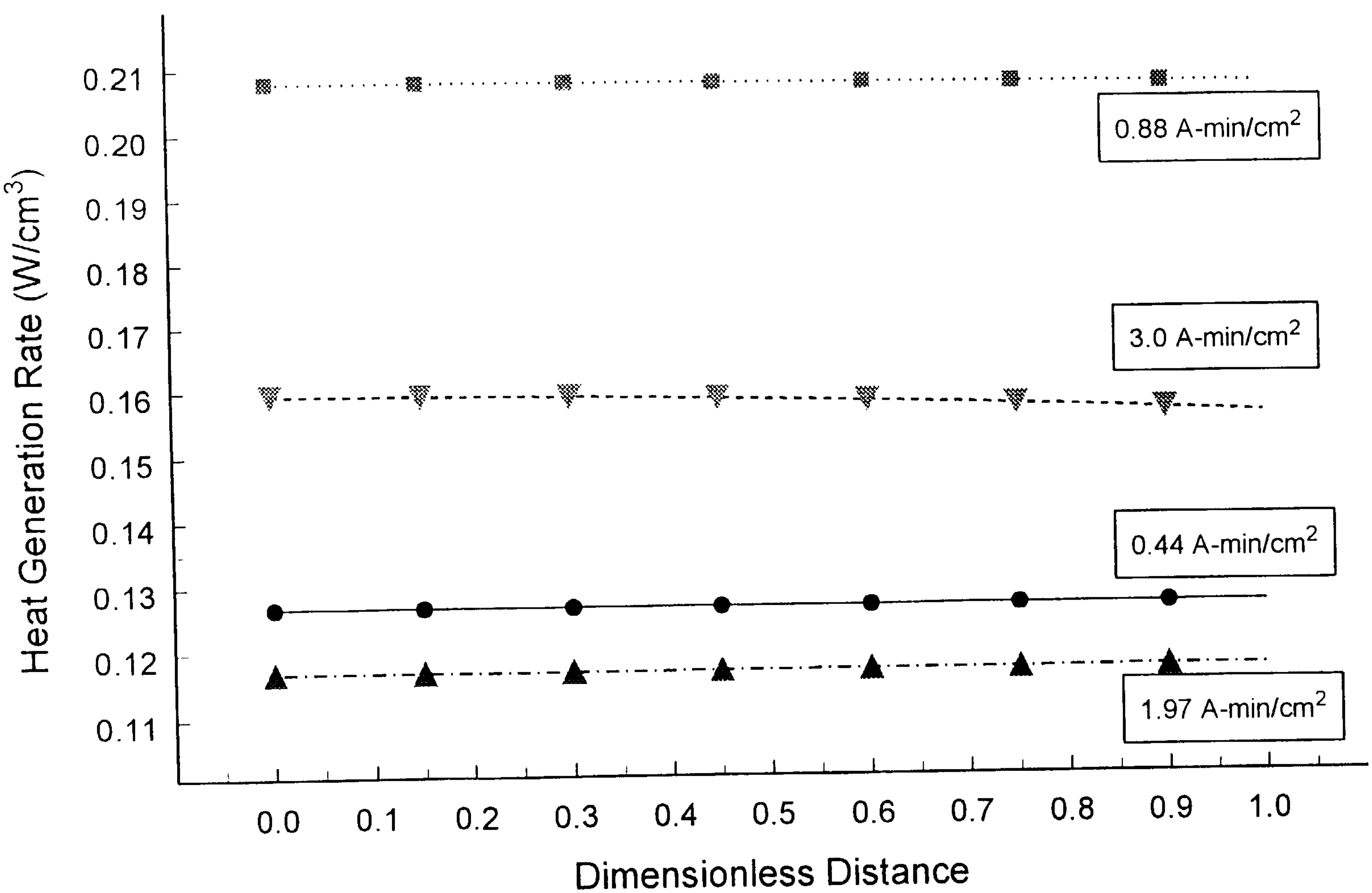
Heating Rate from Reaction 1 Polarization

Silver electrode (i=25 mA/cm^2)



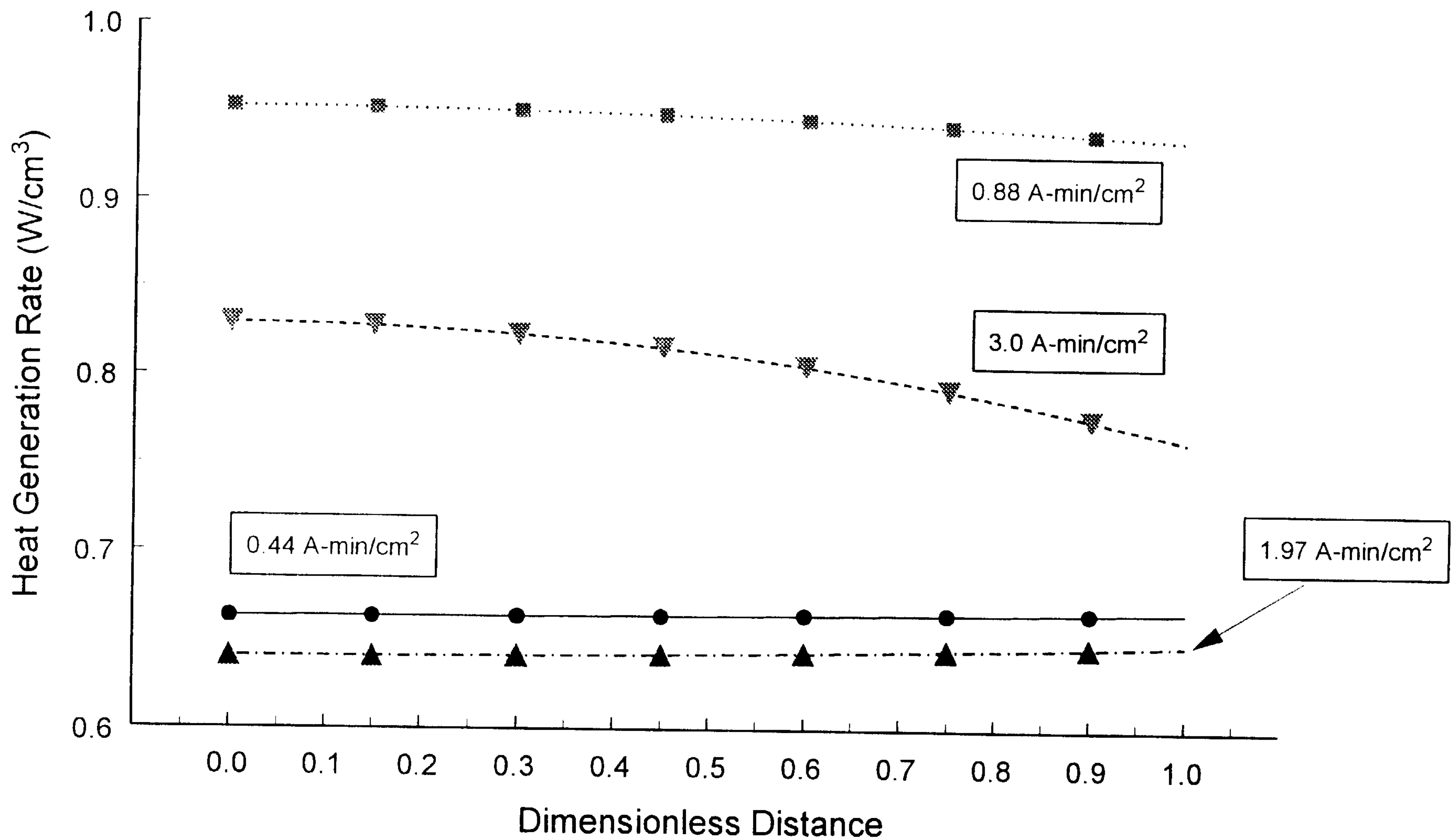
Total Heating Rate from Polarization

Silver electrode (i=25 mA/cm²)



Total Heating Rate from Polarization

Silver electrode (i=100 mA/cm²)



Summary & Future Work

- First Principles Model Developed
- Local Isothermal Heat Generation Predicted
- Include Temperature Feedback
  - Kinetics, conductivity, thermodynamics
- Extend to 3-D Current Distribution
- Solve 3-D Temperature Distribution

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