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Mathematical Modeling of a Thermovoltaic Cell

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ABSTRACT

A Mathematical Model of a Copper Oxide/Copper "Vaporvolt" Cell. (August 1992)

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A new type of battery named "Vaporvolt"* cell is in the early stage of its development. A mathematical model of a CuO/Cu "Vaporvolt" cell is presented that can be used to predict the potential and the transport behavior of the cell during discharge. A sensitivity analysis of the various transport and electrokinetic parameters indicates which parameters have the most influence on the predicted energy and power density of the "Vaporvolt" cell. This information can be used to decide which parameters should be optimized or determined more accurately through further modeling or experimental studies. The optimal thicknesses of electrodes and separator, the concentration of the electrolyte, and the current density are determined by maximizing the power density. These parameter sensitivities and optimal design parameter values will help in the development of a better CuO/Cu "Vaporvolt" cell.

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* Product name of Energy Innovations, Inc.

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INTRODUCTION

Development of batteries with higher energy and power densities has been desired for many years. The traditional approach has been to employ more energetic reactions, which results in higher unit cell voltage, to achieve higher power and energy densities (1–13). Although stored energy and power densities have both increased by this approach (14), the specific stored energy and power densities are still relatively low. This is because of the additional weight required to contain these highly reactive materials and to maintain the mechanical strength of the battery. In addition, the energy densities of secondary batteries are much lower than that of primary batteries (15). Furthermore, there is a safety concern associated with using highly reactive chemicals such as lithium and thionyl chloride (16–18). Another approach to achieve higher specific energy and power densities is to minimize unnecessary weight and volume in existing systems.

"Vaporvolt" cells, which are currently being evaluated by Energy Innovations, Inc. for NASA as possible replacements for high power density primary lithium batteries, use this approach. Weight and volume are minimized by using thin laminations of metals and their oxides as the active materials of a battery (19). Reaction rates at the electrode surfaces of these batteries are low, resulting in minimal stress on the

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electrodes. High currents are obtained by using the high area per volume characteristic of thin laminations. Desired voltage can be obtained by bipolar construction. Electrochemical conversion is accomplished by displacing oxygen from one metal to the other. There are no side reactions that complicate the process and make unwanted by-products; and, in most cases, the energy conversion process is highly reversible.

In designing high performance "Vaporvolt" cells, there are various attributes that can significantly influence the system. Such attributes might be the thicknesses of the electrodes and the separator, KOH concentration, and the current density. A sensitivity analysis is performed on various parameters to determine which parameters are most influential in increasing or decreasing the energy and power densities. This information can indicate the direction one should take in order to design better "Vaporvolt" cells. The results of the sensitivity analysis can also suggest which parameters should be obtained with more accuracy through further modeling studies or experimentation.

To achieve high performance in the "Vaporvolt" cell, various design parameters can be optimized so that the cell will deliver the maximum attainable power density. The important parameters in the "Vaporvolt" cell are the thicknesses of the positive electrode (L_{pos}), negative electrode (L_{neg}) and separator (L_s), the concentration of KOH (c_{KOH}), and current density (i). The CuO/Cu system was selected in this investigation because the CuO/Cu "Vaporvolt" cells are the only successfully manufactured batteries at this time. By using a mathematical model of the CuO/Cu "Vaporvolt" cell, these parameters are investigated in order to determine if an optimal value exists for each parameter. The sensitivity of the model predictions to various parameters will then be examined followed by the determination of the optimal design parameters to maximize the power density of the "Vaporvolt" cell.

MODEL DEVELOPMENT

Electrochemical Reactions at Electrodes

The reactions occurring in the CuO/Cu "Vaporvolt" cell during discharge are the reduction of CuO at the cathode (positive electrode)

$$\text{Positive Electrode}: \qquad \mathrm{CuO} + \frac{1}{2}\mathrm{H_2O} + e^- \rightarrow \frac{1}{2}\mathrm{Cu_2O} + \mathrm{OH^-} \qquad [1]$$

$$U_{pos} = 0.669 - 0.0591\mathrm{pH} \quad \mathrm{V\ vs.\ NHE} \qquad [2]$$

and the oxidation of copper at the anode (negative electrode)

$$\text{Negative Electrode}: \qquad \mathrm{Cu} + \mathrm{OH^-} \rightarrow \frac{1}{2}\mathrm{Cu_2O} + \frac{1}{2}\mathrm{H_2O} + e^- \qquad [3]$$

$$U_{neg} = 0.471 - 0.0591\mathrm{pH} \quad \mathrm{V\ vs.\ NHE} \qquad [4]$$

where U_{pos} and U_{neg} are the open circuit potentials of the positive and negative electrodes, respectively. The electrochemical data in equations [2] and [4] are taken from reference (20), at 25 °C.

The overall reaction is the production of $\mathrm{Cu_2O}$ from CuO and Cu.

$$\text{Total}: \qquad \mathrm{CuO} + \mathrm{Cu} \rightarrow \mathrm{Cu_2O} \qquad [5]$$

Since the solubility of Cu_2O in basic solution is very low, solid Cu_2O is formed during discharge. The open circuit voltage of a CuO/Cu "Vaporvolt" cell, U_{cell} is obtained by subtracting equation [4] from equation [2].

$$U_{cell} = 0.198 \text{ V vs. NHE} \tag{6}$$

This open circuit voltage of CuO/Cu couple is not so high. It is easily predicted that if we employ a system with higher open circuit voltage, we can obtain higher energy and power density. However; CuO/Cu couple is the only successfully manufactured "Vaporvolt" cells at this time.

The objective of the present investigation is to develop a mathematical model that could be used to estimate the optimum values of transport and electrokinetic parameters, and to predict the maximum attainable energy and power densities of a CuO/Cu "Vaporvolt" cell.

Assumptions

The assumptions are as follows.

1. One dimensional model can describe the behavior of the cell.
2. Dilute solution theory (21), applies. Negligible interactions between the solutes are assumed.

3. The Nernst-Einstein equation, $D_i = u_i RT$, which is implicit in the dilute solution theory, applies.
4. The current density takes the form of the Butler-Volmer equation, which expresses the exponential dependence of the current on the overpotential.
5. The physical, transport, and electrokinetic parameters are constant throughout the solution.
6. The cell is isothermal.
7. No homogeneous chemical reactions occur in the electrolyte.
8. No electrolyte movement.
9. The electrochemical reactions occur at the surface of the electrodes.

Governing Equations

A schematic of a CuO/Cu "Vaporvolt" cell is shown in Fig. 1. During discharge of a CuO/Cu "Vaporvolt" cell, hydroxide ions are released from the positive electrode (see equation [1]), and consumed at the negative electrode (see equation [3]). Therefore, hydroxide ions must be transported in the electrolyte in the separator from the positive electrode to the negative electrode. Mass transport in this system is due to migration in an electric field and diffusion in a concentration gradient. Therefore, the flux expression for each species i can be written as

$$\mathbf{N}_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i \qquad [7]$$

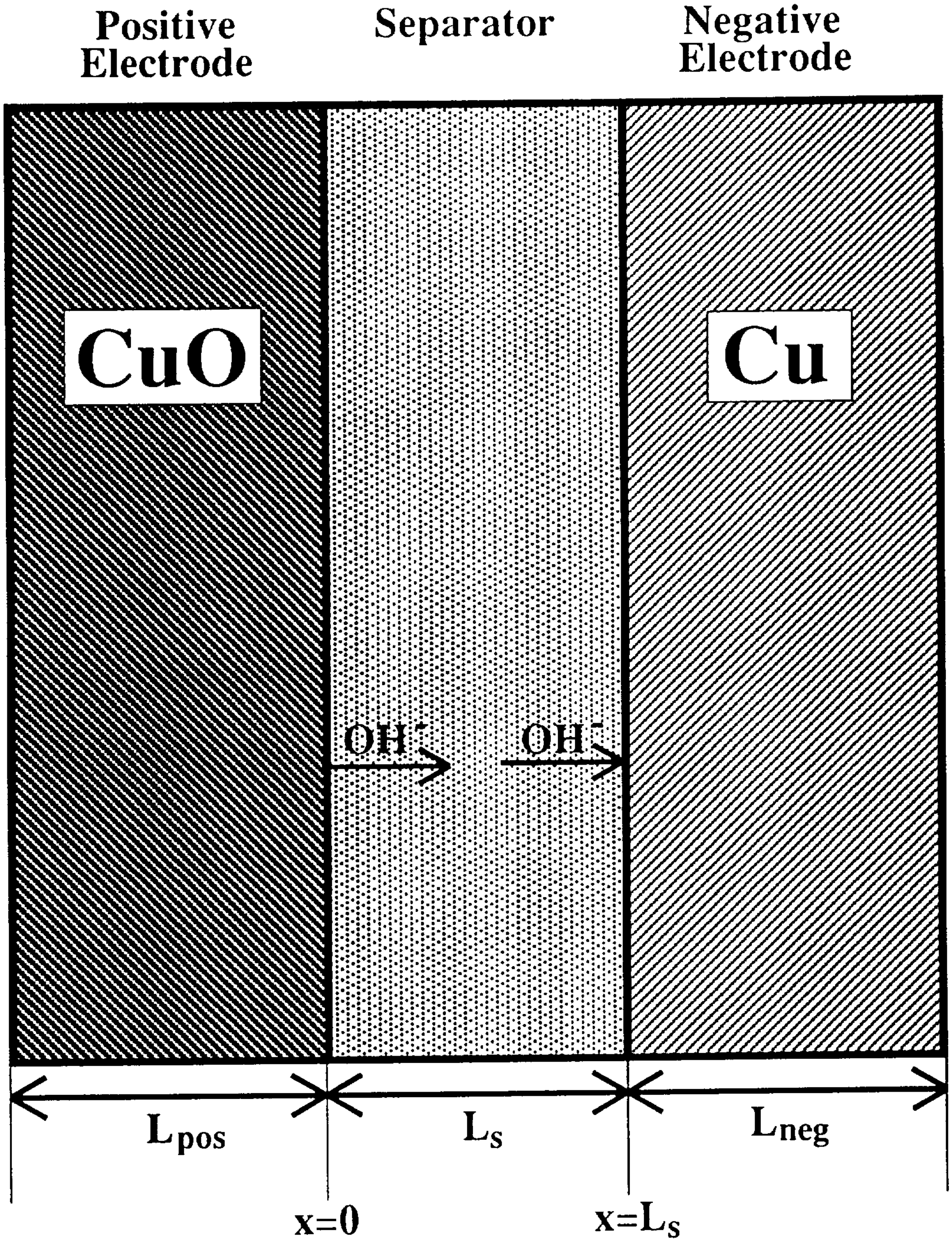

Figure 1. Schematic of a "Vaporvolt" cell.

where the ionic mobility, u_i, is assumed to be related to the diffusion coefficient D_i by the Nernst-Einstein equation

$$u_i = \frac{D_i}{RT} \qquad [8]$$

The first and the second terms of right side of equation [7] represent the mass transport in solution due to migration in an electric field and diffusion in a concentration gradient, respectively. The differential material balance equation for each species without homogeneous chemical reaction in the electrolyte is as follows

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathrm{N}_i \qquad [9]$$

By combining equations [7] and [9], we can obtain following equation

$$\frac{\partial c_i}{\partial t} = z_i u_i F\left(c_i \nabla^2 \Phi + \nabla c_i \nabla \Phi\right) + D_i \nabla^2 c_i \qquad [10]$$

Since the net charge in the bulk electrolyte is zero, the equation of electroneutrality

$$\sum_i z_i c_i = 0 \qquad [11]$$

must hold in the electrolyte.

The flow of charge is related to the current density **i** in the solution:

$$\mathbf{i} = F\sum_{\mathrm{i}} z_i \mathrm{N}_i \qquad [12]$$

Equations [7] and [12] can be combined and rearranged to get

$$\nabla\Phi = \frac{-\mathbf{i}}{\kappa} - \frac{F}{\kappa}\left(\sum_i z_i D_i \nabla c_i\right) \qquad [13]$$

where

$$\kappa = \frac{F^2}{RT}\sum_i z_i^2 D_i c_i \qquad [14]$$

Equations [10] and [13] for one spatial coordinate reduces to equations [15] and [16], respectively

$$\frac{\partial c_i}{\partial t} = z_i u_i F\left(c_i \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial c_i}{\partial x}\frac{\partial \Phi}{\partial x}\right) + D_i \frac{\partial^2 c_i}{\partial x^2} \qquad [15]$$

$$\frac{\partial \Phi}{\partial x} = \frac{-i}{\kappa} - \frac{F}{\kappa}\left(\sum_i z_i D_i \frac{\partial c_i}{\partial x}\right) \qquad [16]$$

There are three unknowns c_{K^+}, c_{OH^-} and Φ, so we need three governing equations.

Equation [11] is used for c_{K^+}, equation [15] is used for c_{OH^-}, and equation [16] is used for Φ.

The initial and the boundary conditions for these dependent variables are as follows.

At t=0, the concentration of the species are their initial values

$$For\ all\ x\ at\ t = 0 \qquad c_i(t = 0, x) = c_i^{\circ} \qquad [17]$$

since c_i° must obey $\sum_i z_i c_i^{\circ} = 0$.

At x=0 (positive electrode surface), the change in the concentration of OH^- is related to the current density since the number of OH^- ions released at the positive electrode surface is proportional to the number of the electrons received at the electrode, that is, current density (see equation [1]).

$$For\ all\ t,\ t > 0 \qquad \frac{\partial c_{OH^-}}{\partial x}|_{x=0} = \frac{i}{n_1 F D_{OH^-}} \qquad [18]$$

where n_1 is the number of the electrons transferred in equation [1].

At $x=L_s$ (negative electrode surface), the change in the concentration of OH^- is also related to the current density (see equation [3]).

$$For\ all\ t,\ t > 0 \qquad \frac{\partial c_{OH^-}}{\partial x}|_{x=L_s} = \frac{i}{n_3 F D_{OH^-}} \qquad [19]$$

where n_3 is the number of the electrons transferred in equation [3].

Since we cannot measure the absolute potential, we need to fix a potential at $x = 0$:

$$For\ all\ t\ at\ x = 0 \qquad \Phi(t, x = 0) = 0 \tag{20}$$

Cell Voltage

The relation between the current density, *i*, and the overpotential, η, is expressed by the Butler-Volmer electrochemical rate expression

$$i = i^{\circ}\frac{A^*}{A}\left[\prod_i\left(\frac{c_i}{c_i^r}\right)^{p_i}\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \prod_i\left(\frac{c_i}{c_i^r}\right)^{q_i}\exp\left(\frac{-\alpha_c F}{RT}\eta\right)\right] \tag{21}$$

where A^* and A are the active surface area of the electrode and the geometric surface area of the electrode, respectively. Active surface area of the electrodes decreases with the discharge of the cell since Cu_2O, that has very low electric conductivity, is formed on the electrodes during discharge. The active surface area of each electrode is assumed to change according to the following equation

$$A^* = A\frac{m}{m^{\circ}} \tag{22}$$

where *m* is the amount of active material (CuO for positive electrode, Cu for negative electrode) in an electrode at time t, and m° is the initial amount of active material in the electrode. The initial amount of active material, m°, is simply expressed by the following equation

$$m^\circ = L_j d_j \tag{23}$$

where L_j is the thickness of the electrode and d_j is the density of the electrode. For a constant current density discharge, the amount of active material, m, changes with time according to following equation

$$m = m^\circ - \frac{M_j\, i\, t}{n_j F} \tag{24}$$

where M_j is a molecular weight of an electrode j.

By combining equations [21] through [24], we can obtain following relation between the current density i and the overpotential η

$$i = i^\circ\left(1 - \frac{M_j\, i\, t}{L_j d_j n_j F}\right)\left[\prod_i \left(\frac{c_i}{c_i^r}\right)^{p_i} \exp\left(\frac{\alpha_a F}{RT}\eta\right) - \prod_i \left(\frac{c_i}{c_i^r}\right)^{q_i} \exp\left(\frac{-\alpha_c F}{RT}\eta\right)\right] \tag{25}$$

Note that CuO, Cu_2O and Cu exist as solids because of their low solubility in a basic solution, so the values of $\left(\frac{c_i}{c_i^r}\right)^{p_i}$ and $\left(\frac{c_i}{c_i^r}\right)^{q_i}$ for CuO, Cu_2O and Cu in equation

[25] remain constant.

In addition, the anodic and cathodic transfer coefficients are assumed to sum to the number of electrons transferred (i.e., $\alpha_a + \alpha_c = n_j$), and the reaction order coefficients are assumed to be simply related to s_i

$$\begin{array}{lll} p_i = s_i & q_i = 0 & \text{if } s_i > 0 \\ p_i = 0 & q_i = -s_i & \text{if } s_i < 0 \end{array} \qquad [26]$$

And the electrode potentials, E_{pos} and E_{neg}, are expressed by

$$E_{pos} = U_{pos} + \Phi(t, x = 0) + \eta_{pos} \qquad [27]$$

$$E_{neg} = U_{neg} + \Phi(t, x = L_s) + \eta_{neg} \qquad [28]$$

The potential of a "Vaporvolt" cell, E_{cell}, is the difference between the potentials of the positive electrode and the negative electrode. By subtracting equation [28] from equation [27],

$$\begin{aligned} E_{cell} &= E_{pos} - E_{neg} \\ &= U_{cell} - \Phi(t, x = L_s) + \eta_{pos} - \eta_{neg} \end{aligned} \qquad [29]$$

$$U_{cell} = U_{pos} - U_{neg} \qquad [30]$$

where U_{cell} is the open circuit potential of the "Vaporvolt" cell.

Note that an overpotential takes a negative value at the positive electrode, and takes a positive value at the negative electrode, and $\Phi(t, x = L_s)$ is always positive during discharge because negatively charged particle (OH^-) must transport from the positive electrode ($x = 0$) to the negative electrode ($x = L_s$). Therefore, the potential of a "Vaporvolt" cell, E_{cell}, is always smaller than the open circuit potential of the "Vaporvolt" cell, U_{cell}.

Equations [7] – [16] represent the basic governing equations necessary to describe the behavior in the electrolyte of a "Vaporvolt" cell. It should be noted that these equations are solved numerically by setting the cell current density, i, and calculating the potential of the "Vaporvolt" cell, E_{cell}, or the power density, P ($= iE_{cell}$). BAND(J), a finite difference numerical technique developed by Newman (21), was used to solve the equations. The computer program used for this investigation is listed in Appendix. The model parameters associated with these equations are shown in Table I.

Table I. Base case parameter values for the CuO/Cu "Vaporvolt" cell simulation.

Structural parameters:	
Thickness of positive electrode (CuO) (L_{pos})	0.00254 cm
Thickness of negative electrode (Cu) (L_{neg})	0.00254 cm
Separator thickness (L_s)	0.00254 cm
Open circuit potential (U_{cell})	198 mV
Current density (i)	0.001 A/cm^2
Anodic and cathodic exchange current densities (i°)	0.001 A/cm^2
Anodic transfer coefficient for Cu oxidation ($\alpha_{a,\mathrm{Cu}}$)	0.5
Cathodic transfer coefficient for CuO reduction ($\alpha_{c,\mathrm{CuO}}$)	0.5
Electrolyte concentration (c_{KOH})	8.3878 M
Initial K$^+$ concentration ($c^\circ_{K^+}$)	8.3878 M
Initial OH$^-$ concentration ($c^\circ_{OH^-}$)	8.3878 M
Reference K$^+$ concentration ($c^r_{K^+}$)	1.0000M
Reference OH$^-$ concentration ($c^r_{OH^-}$)	1.0000M
Temperature (T)	298 K

RESULTS AND DISCUSSION

The Effects of the Separator Thickness

It is assumed that the electrochemical reaction occurs only at the surface of the active material, however; actual reaction layer moves into the inside of the active material as the cell discharges. Therefore, the thickness of the mass transport region of the cell increases as the cell discharges. To check the validity of this assumption, the cell performances with different separator thicknesses are predicted and compared. First, the cell performance is predicted with the parameter values listed in Table I, and then, the thickness of the separator is doubled, and the cell performance is predicted again. The result is shown in Table II. The predicted performances of "Vaporvolt" cells with different separator thicknesses are almost the same. This result indicates that the movement of the reaction layer in the cell has little effect on the performance of the cell. Therefore, the assumption that the electrochemical reaction occurs only at the surface of the active material is valid in this model.

Table II. Comparison of the performances of the "Vaporvolt" cells with different separator thicknesses.

Separator thickness	0.00254 cm	0.00508 cm
Cell capacity	17.82711 C/cm^2	17.82711 C/cm^2
Energy density	1.88573 Ws/cm^2	1.88569 Ws/cm^2
Power density	0.10637 mW/cm^2	0.10636 mW/cm^2

The Effects of Current Density

Fig. 2 shows the cell voltage change during the discharge with the parameter values listed in Table I, at various current densities. The cell voltage drop due to the increases in the overpotentials at the positive and the negative electrodes as we increase the current density during discharge. Therefore, the capacity and the energy density of the cell decrease with increasing current density of the cell during discharge, as shown in Figs. 3 and 4. However, the power density of the "Vaporvolt" cell is not a monotonic function of the current density. As shown in Fig. 5, the power density of the cell first increases and then decreases as the current density increases. So there exists a maximum power density value at a current density.

Sensitivity Analysis

In order to determine the relative importance of the design feature of the cell (thickness of the electrode, e.g.) and the transport and kinetic parameters on the "Vaporvolt" cell's performance, a sensitivity analysis was done. The sensitivity analysis can indicate which parameters have the largest influence on the predicted performance of the "Vaporvolt" cell. If a small perturbation in a parameter does not significantly change the predicted capacity, energy density or the power density of the "Vaporvolt" cell, then that parameter could assume a large range of values, all of which will give the same performance. The sensitivity coefficient can be defined as the dimensionless change in the predicted capacity, energy density, and the power density

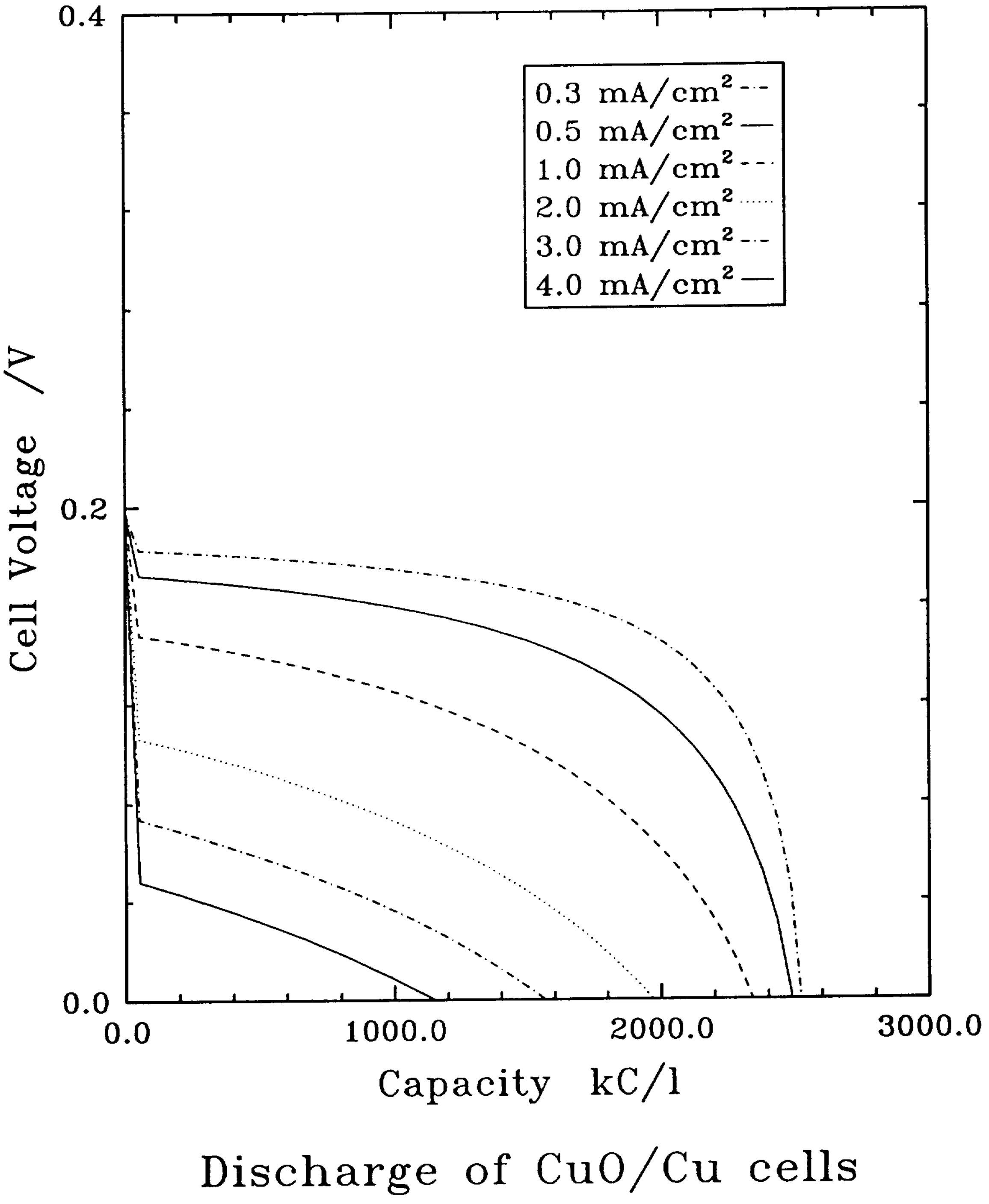

Figure 2. Cell voltage vs. capacity delivered.

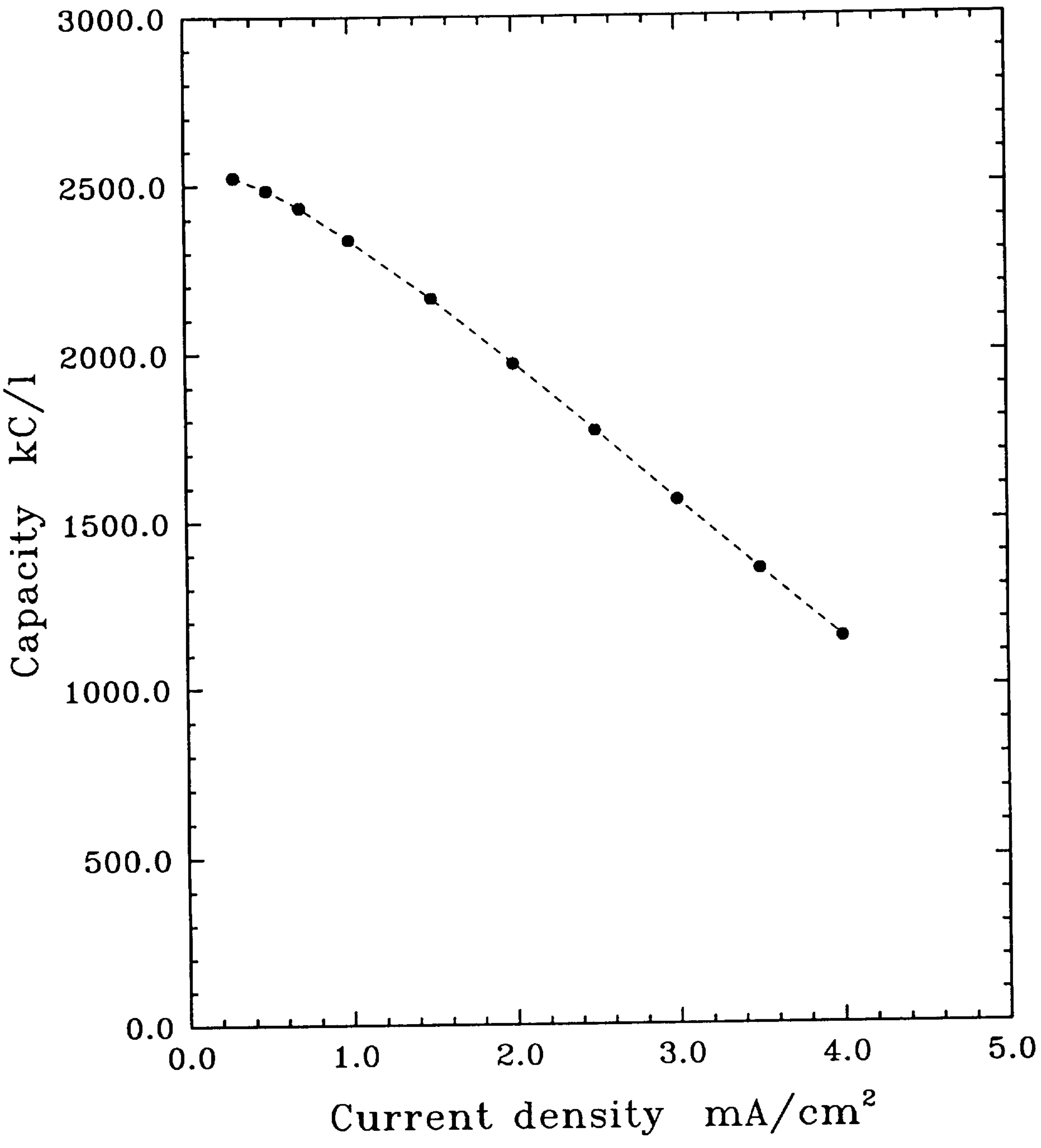

Figure 3. The effects of current density on capacity of "Vaporvolt" cells.

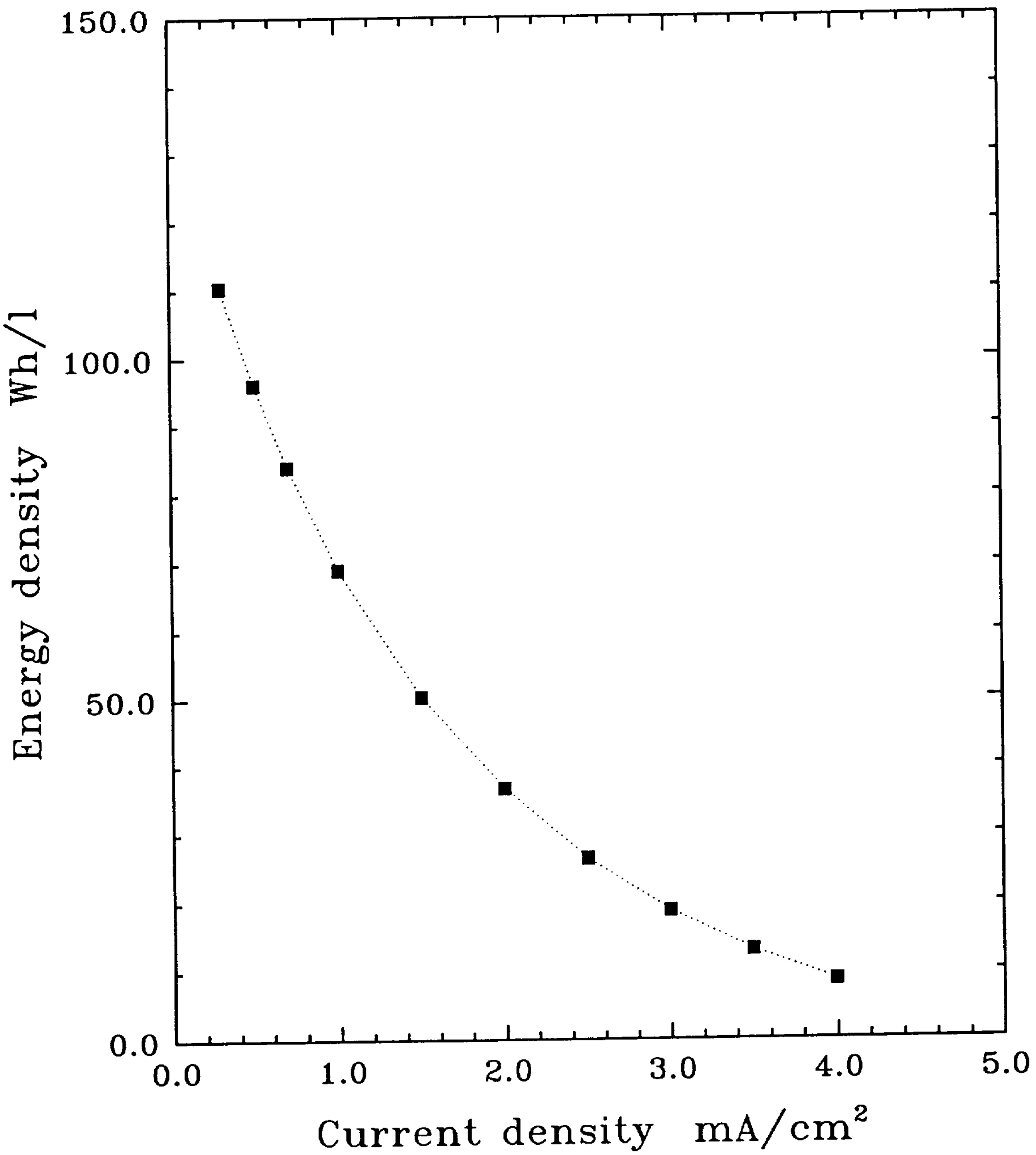

Figure 4. The effects of current density on energy density of "Vaporvolt" cells.

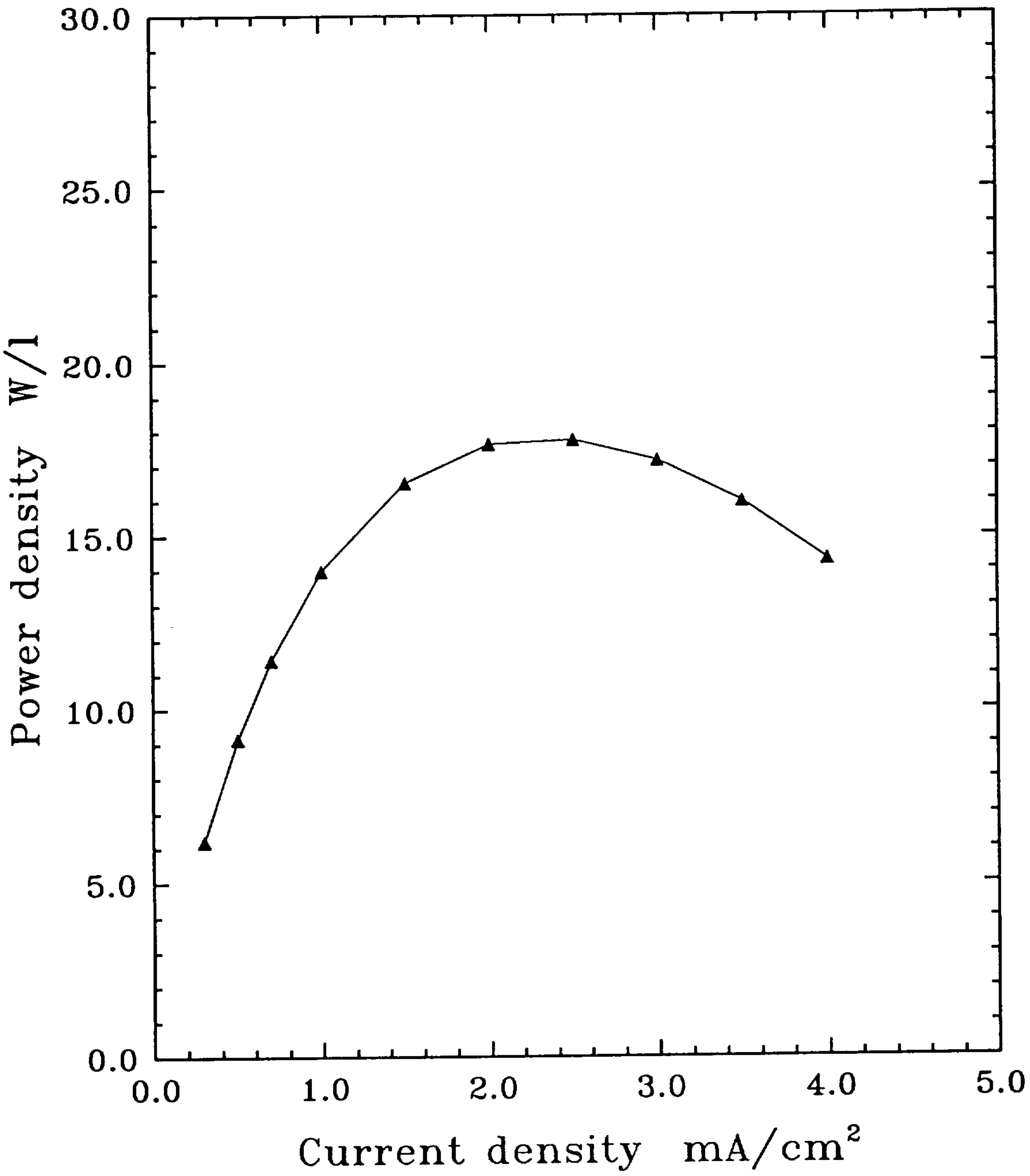

Figure 5. The effects of current density on power density of "Vaporvolt" cells.

of the cell for a small dimensionless perturbation in a parameter *j*, while holding all other parameters constant (22):

$$Sensitivity = \frac{\partial G/G}{\partial \theta_j/\theta_j} \qquad [31]$$

where θ_j is the parameter and G is the capacity, the energy density, or the power density of the cell.

Hence, large sensitivity coefficients mean that the parameter of interest significantly influences the cell performances. If the sensitivity coefficients for a parameter is large, the parameters should be obtained with more accuracy through further modeling or experimental studies. That is, if the value for a parameter is not accurately known and the parameter has a large sensitivity coefficient, then that parameter value should be ascertained more accurately to gain confidence in the model predictions.

All sensitivity coefficients calculated for this work were accomplished by increasing the parameter of interest by 5% over the base case value (shown in Table I) and calculating the resulting change in the capacity, energy density, and power density of the cell from the base case values. The sensitivity coefficients for various parameters are shown in Figs. 6 through 10. As shown in Fig. 6, the model predictions are most sensitive to the current density.

The model predictions show little sensitivity to small perturbations in the KOH concentration as shown in Fig. 7. This is because the IR drop due to the resistance

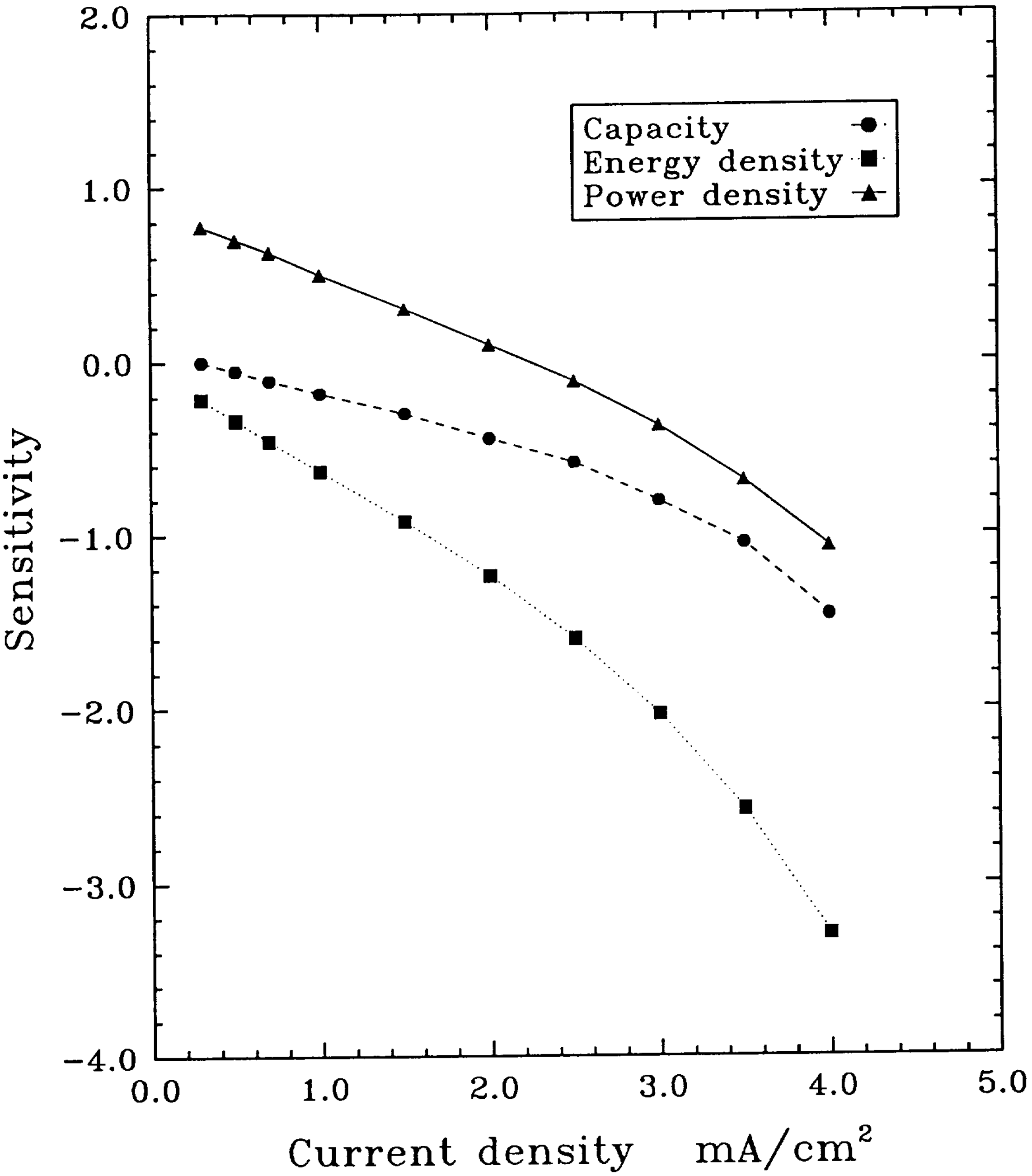

Figure 6. Sensitivity of the model predictions to the changes in the current density.

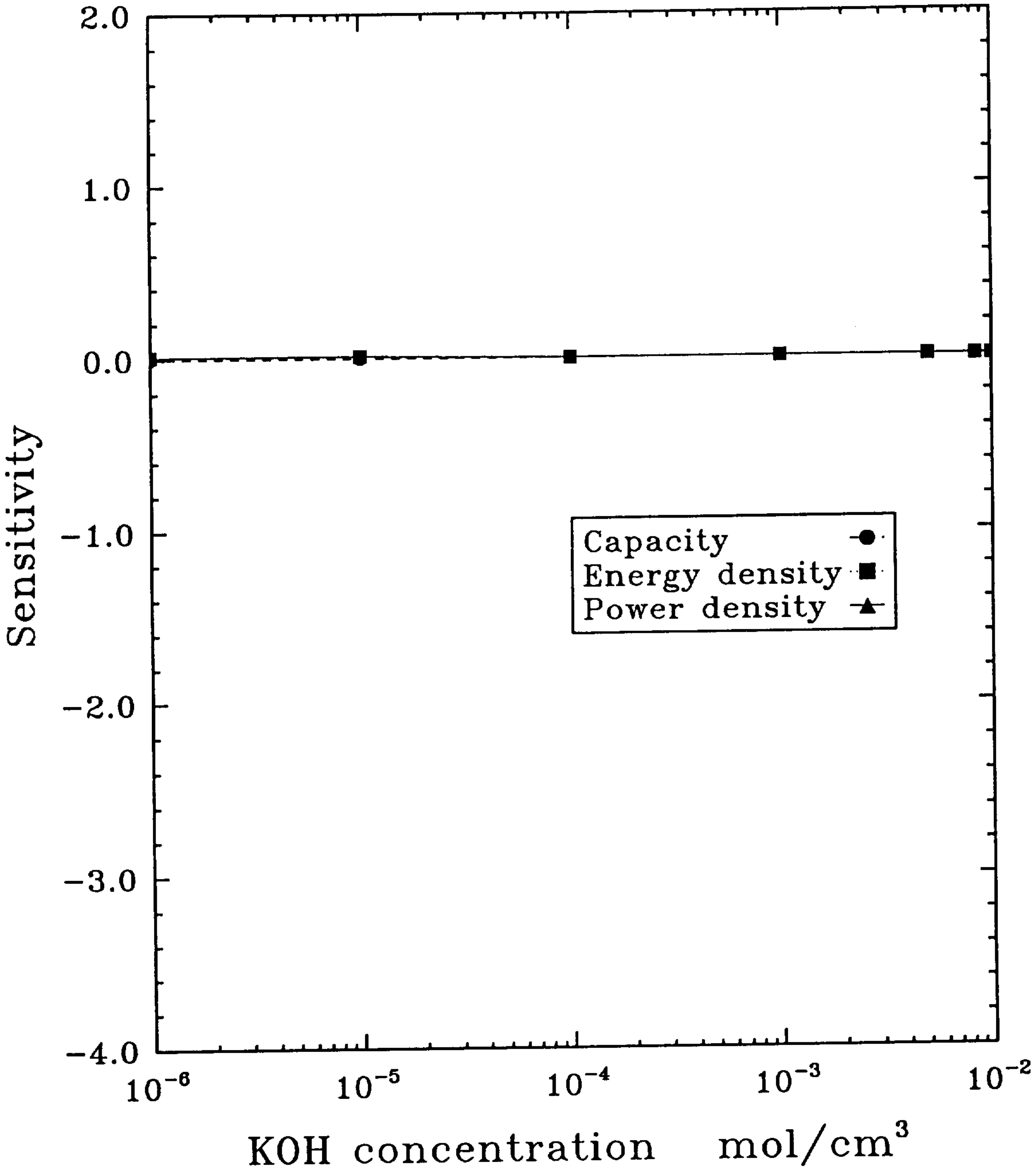

Figure 7. Sensitivity of the model predictions to the changes in the concentration of KOH.

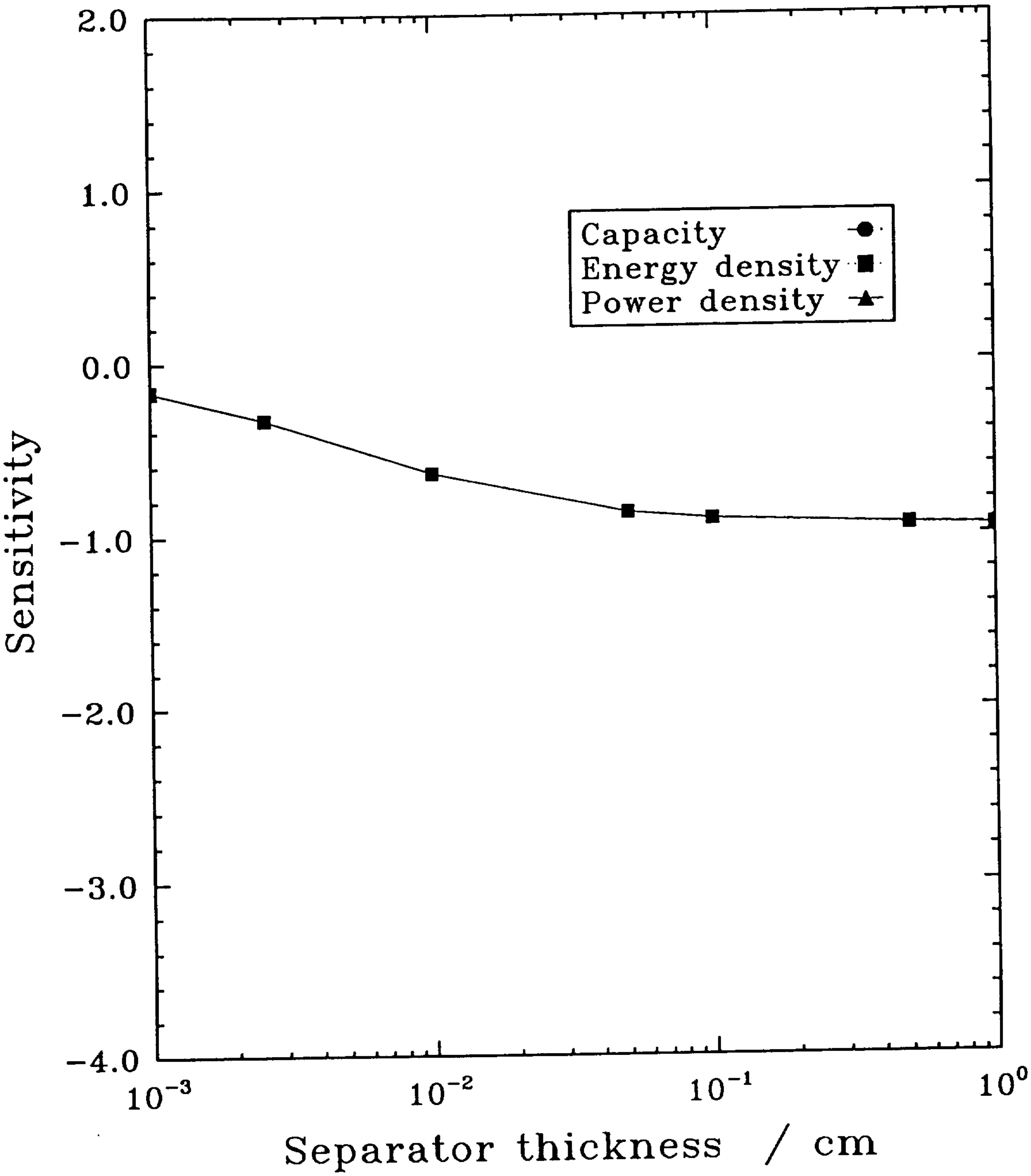

Figure 8. Sensitivity of the model predictions to the changes in the thickness of the separator.

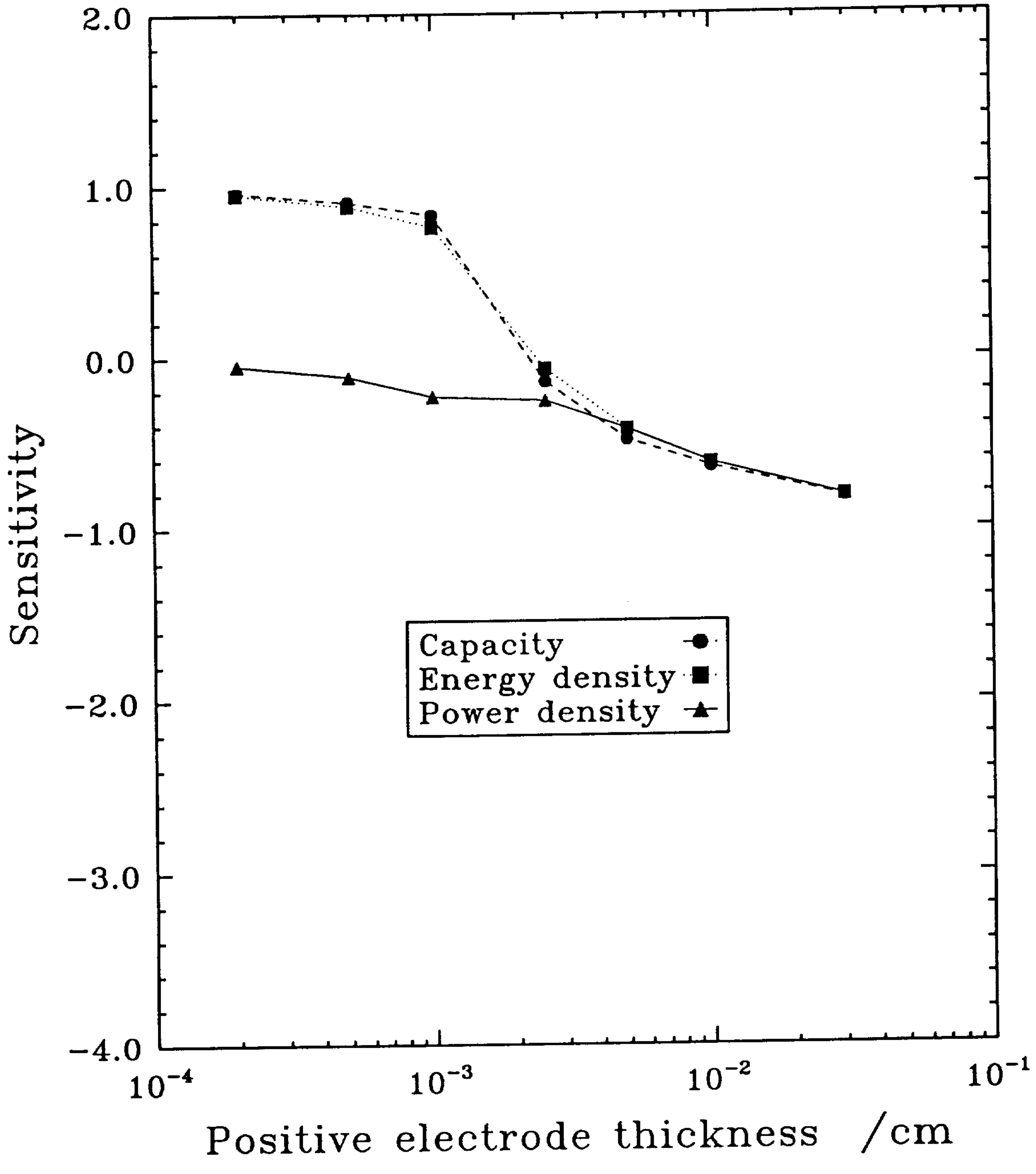

Figure 9. Sensitivity of the model predictions to the changes in the thickness of the positive electrode.

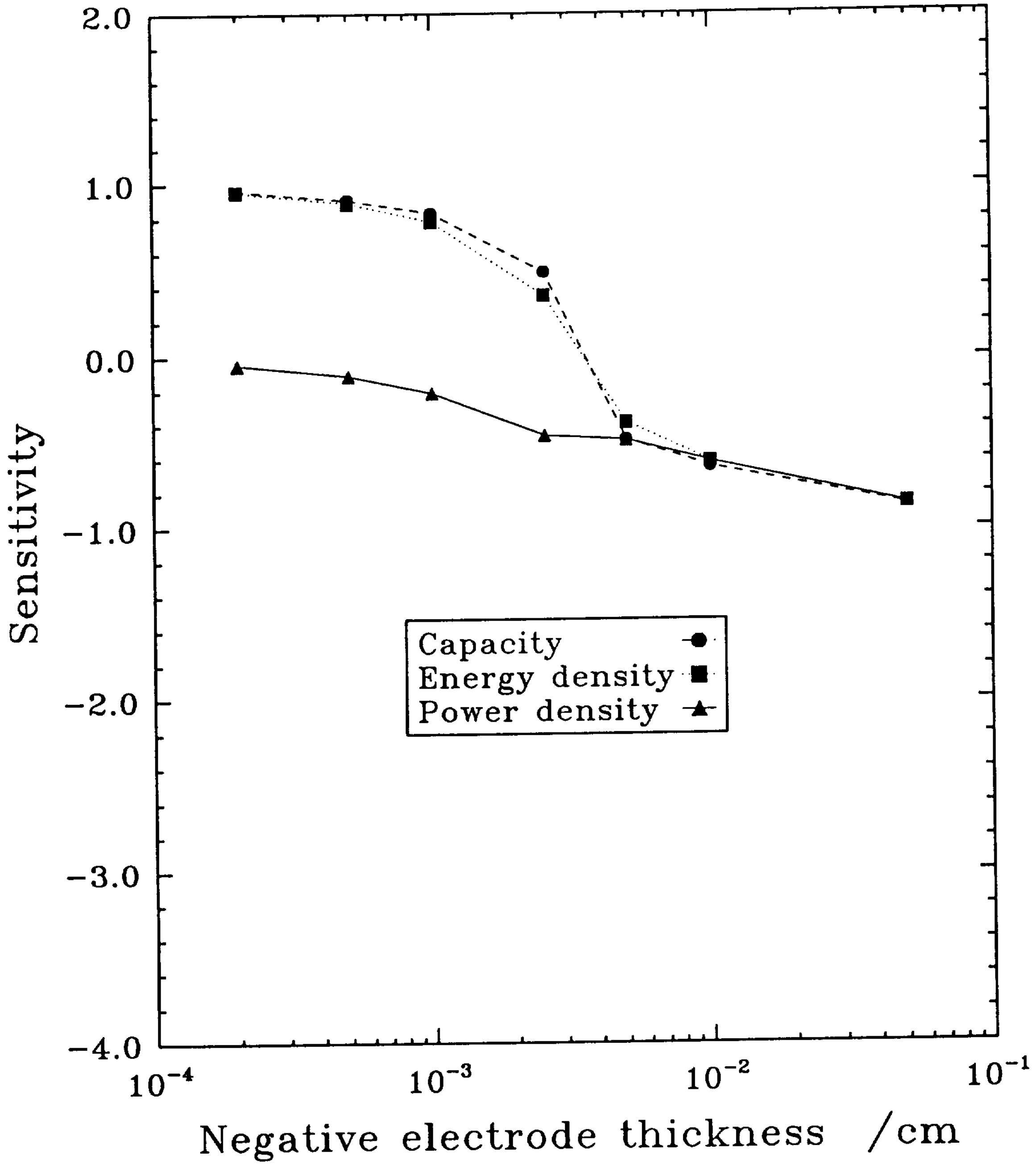

Figure 10. Sensitivity of the model predictions to the changes in the thickness of the negative electrode.

of the electrolyte is negligible since the thickness of the separator is very small. The concentration of KOH in this region has very small effect on the capacity, the energy density, and the power density of the cell.

The effects of the "Vaporvolt" cell separator thickness on the predicted performance are shown in Fig. 8. The sensitivity coefficients for the capacity, the energy density, and the power density of the cell decrease similarly and monotonically with the increase of the separator thickness. Therefore, the thickness of the separator should be as thin as possible, however; to avoid shortening of the cell, the thickness of the separator should be about 0.001 cm.

Figs. 9 and 10 show the effects of "Vaporvolt" cell positive and negative electrodes thickness on the predicted performances. The capacity and the energy density of the "Vaporvolt" cell increase as we increase the electrode thicknesses up to 0.002 cm since the sensitivity coefficients for the capacity and the energy density are positive in this region, but the capacity and the energy density decrease as we increase the electrode thicknesses when the thicknesses are above 0.002 cm. Therefore, the capacity and energy density become their maximum when the electrode thicknesses are about 0.002 cm. The sensitivity coefficient for the power density of the cell is always negative, as shown in Figs. 9 and 10, so a small electrode thickness is favorable to get a larger power density. However; employing electrodes that are less than 0.001 cm could results in shortening of the cell. A thickness of 0.001 cm is favorable for the positive and negative electrodes of a "Vaporvolt" cell to obtain maximum power density.

Optimization

The maximum power density can be obtained when we employ 0.001 cm as the thicknesses of the separator, the positive electrode, and the negative electrode, and current density 2.5 mA/cm^2. As shown in Table III, the maximum power density obtained is 45.1 W/l, and the capacity is 1768 kC/l and the energy density is 26.5 Wh/l at these parameter values. These values are lower than that of the high energy density primary cells, such as Li/SOCl$_2$ cells, which highest power density is approximately 80 W/l and its energy density is about 150 Wh/l when the highest power density is obtained (14), however; the maximum attainable power density of a CuO/Cu "Vaporvolt" cell is much higher than that of Li/CF$_x$ or Li/MnO$_2$ cells, which highest power density is approximately 15 W/l and the energy density is about 50 Wh/l when the highest power density is obtained (14). This is summarized in Table IV. If stable electrodes with thickness less than 0.001 cm could be developed in the future, much larger power density could be obtained. For example, if we could make

Table III. The result of the optimization.

Starting Values	Optimized Values
Current density = 0.001 A/cm^2	Current density = 0.0025 A/cm^2
Cell capacity = 2336 kC/l	Cell capacity = 1768 kC/l
Energy density = 69.1 Wh/l	Energy density = 26.5 Wh/l
Power density = 14.0 W/l	Power density = 45.1 W/l

electrodes and separators with thicknesses of 0.0005 cm, the maximum power density is 90.3 W/l, as shown in Fig. 11; and the capacity and the energy density will be 1768 kC/l and 26.5 Wh/l, respectively.

Table IV. Comparison of the "Vaporvolt" cell performances with lithium batteries.

	CuO/Cu "Vaporvolt"	Li/$SOCl_2$	Li/MnO_2
Power density, W/l	45.1	80*	15*
Energy density, Wh/l	26.5	150*	50*
Unit cell open circuit voltage , V	0.198	3.67*	3.5*

* These values are taken from ref. [14].

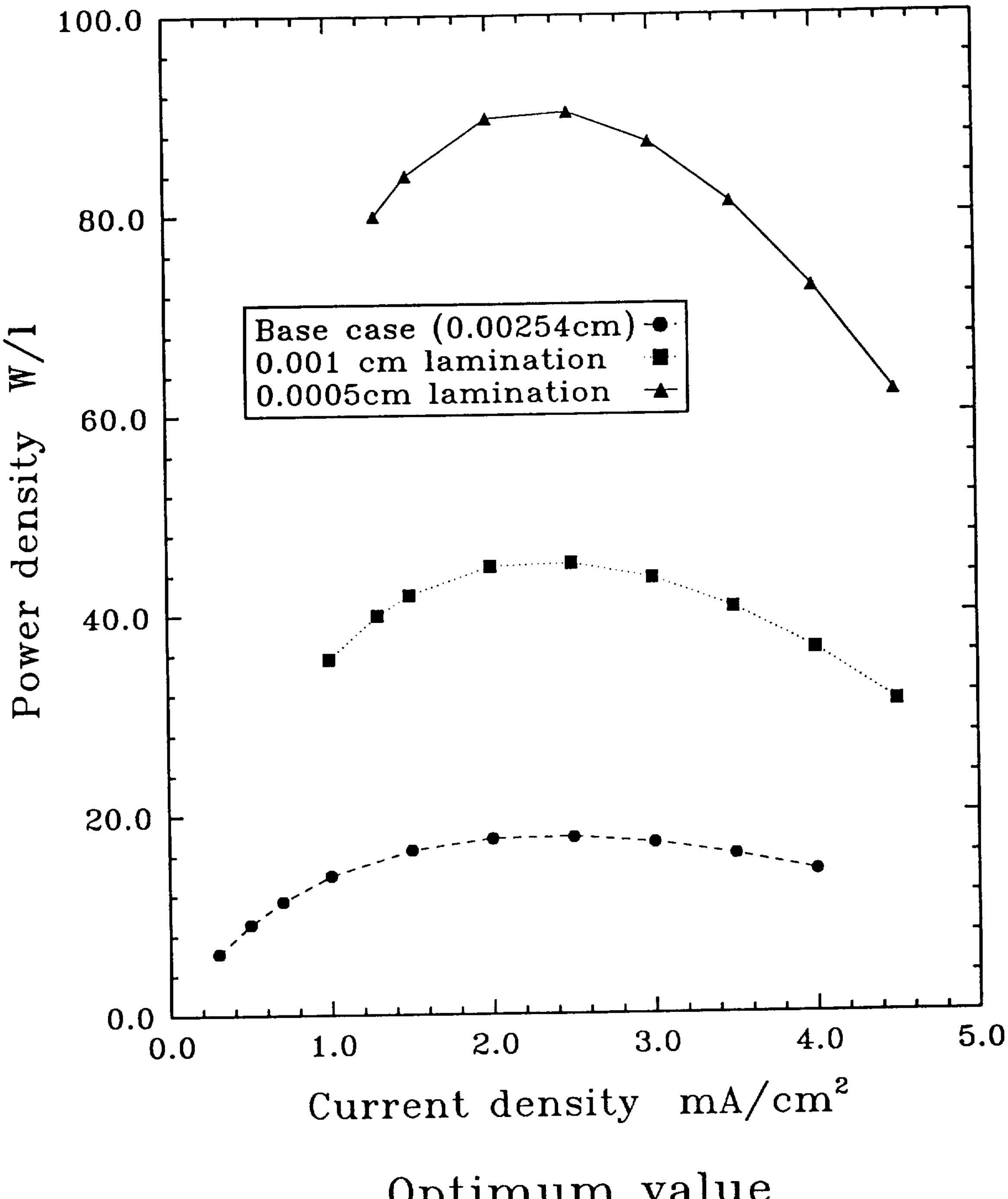

Figure 11. The effects of current density on power density of the cell when thicknesses of the electrodes and separator are optimized.

SUMMARY

A mathematical model of a CuO/Cu "Vaporvolt" cell is presented to predict the potential and the transport behavior of the cell during discharge. A sensitivity analysis of a CuO/Cu "Vaporvolt" cell model indicates that several parameters can significantly influence the performance of the system. In particular, current density has been found to influence significantly the performance. The effect of various design parameters have been investigated to determine if optimal values exist for the parameters. The model has shown that the thicknesses of the electrodes and separator, and current density can be optimized to give the maximum attainable power density. The model has also shown that the power density can be significantly improved if we could make thinner electrodes and separators could be made.

NOMENCLATURE

Roman Symbols

A^*	Active surface area of the electrode, cm^2
A	Surface area of the electrode, cm^2
c_i	Concentration of species i, mol/cm^3
c_i°	Initial concentration of species i, mol/cm^3
c_i^r	Reference concentration of species i, mol/cm^3
D_i	Diffusion coefficient for species i, cm^2/s
d_j	Density of electrode j, g/cm^3
E	Electrode potential, V
F	Faraday's constant, 96487 C/mol
G	Capacity, Energy density, or Power density
$\mathbf{i}$	Current density vector, A/cm^2
i	Current density, A/cm^2
i°	Exchange current density, A/cm^2
L	Thickness, cm
M_j	Molecular weight of electrode j, g/mole
m	Amount of active material at time t, g/cm^2
m°	Initial amount of active material, g/cm^2
n_j	Number of electrons transferred in reaction j
$\mathbf{N}_i$	Flux vector of species i, $mol/(cm^2\text{-}s)$
P	Power density, W/l
p_i	Anodic reaction order for species i
q_i	Cathodic reaction order for species i
R	Gas constant, 8.3143 J/(mol-K) or 82.057 $cm^3atm/(mol\text{-}K)$
R_i	Production rate of species i, $mol/(cm^3\text{-}s)$
s_i	Stoichiometric coefficient of species i
T	Temperature, K

U	Open circuit potential, V
u_i	Mobility of species *i*, mol-cm^2/(J-s)
$\mathbf{v}$	Electrolyte velocity vector, cm/s
z_i	Charge number of species *i*

Greek Symbols

α_a	Anodic transfer coefficient
α_c	Cathodic transfer coefficient
κ	conductivity of a solution, S/cm
η	Overpotential, V
Φ	Solution phase potential, V
θ_j	Parameter *j*

Superscripts and Subscripts

a	Anode
c	Cathode
i	Species *i*
j	Reaction *j* or electrode *j*
neg	Negative electrode
pos	Positive electrode
r	Reference condition
s	Separator layer

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APPENDIX

Computer Program Data File

```
ishow                  0       ishow=1 for monitor output of
                               iterations

jmax                 100       Max program iterations
nj                   101       Number of meshpoints
nt                   400       Number of timesteps
ntpr                  40       Print every ntpr timesteps
nc                     6       Number of current steps
area      4.00000000d+00       Area of the separator, sq.cm
cio       8.38780000d-03       Initial KOH concentration, mol/cc
ecur(1)   1.00000000d-03       Exchange current density
                               (positive electrode), A/cm2

ecur(2)   1.00000000d-03       Exchange current density
                               (negative electrode), A/cm2

aa(1)     0.50000000d+00       Anodic transfer coefficient (pos)
ac(1)     0.50000000d+00       Cathodic transfer coefficient
                               (pos)

aa(2)     0.50000000d+00       Anodic transfer coefficient (neg)
ac(2)     0.50000000d+00       Cathodic transfer coefficient
                               (neg)

ocv       198.000000d-03       Open circuit voltage, V
delta     2.54000000d-03       Separator thickness, cm
dpos      2.54000000d-03       Positive electrode thickness, cm
dneg      2.54000000d-03       Negative electrode thickness, cm
denp      6.40000000d+00       Positive electrode density, g/cm3
denn      8.92000000d+00       Negative electrode density, g/cm3
denpd     6.00000000d+00       Positive electrode density
                               after discharge, g/cm3

dennd     6.00000000d+00       Negative electrode density
                               after discharge, g/cm3

atomp     79.5454000d+00       Atomic weight of positive
                               active material, g/mole

atomn     63.5460000d+00       Atomic weight of negative
                               active material, g/mole

atompd    71.5430000d+00       Atomic weight of p.a.m.
                               after discharge, g/mole

atomnd    71.5430000d+00       Atomic weight of n.a.m.
                               after discharge, g/mole

epos      1.00000000d+00       Number of electron transfer
```

		(positive electrode)
eneg	1.00000000d+00	Number of electron transfer (negative electrode)
diff(1)	2.19000000d-05	Anion diff. coeff., sq.cm/sec
diff(2)	2.19000000d-05	Cation diff. coeff., sq.cm/sec
temp	298.000000d+00	Temperature, K
toler	1.00000000d-05	Relative error tolerance
zi(1)	-1.00000000d+00	Anion (OH-) charge number
zi(2)	1.00000000d+00	Cation (K+) charge number
cur(1)	1.00000000d-03	Current density(1), A/cm2
cur(2)	2.00000000d-03	Current density(2), A/cm2
cur(3)	3.00000000d-03	Current density(3), A/cm2
cur(4)	4.00000000d-03	Current density(4), A/cm2
cur(5)	5.00000000d-03	Current density(5), A/cm2
cur(6)	6.00000000d-03	Current density(5), A/cm2

Computer Main Program File

```
c      model2.f
c      last edition May. 10, 1992

      implicit real*8 (a-h,o-z)
      dimensilpqon z(7,500),a(7,7),b(7,7),c(7,500),d(7,15),
     @          g(7),x(7,7),y(7,7),zk(500),zi(7),eta(2,500),
     &          pot(500),volt(500),actp(500),actn(500),ecur(2),
     &          aa(2),ac(2),aarea(2),diff(7),cur(7)
      common A,B,C,D,G,X,Y,N,NJ
      OPEN(1,FILE='model2.dat',STATUS='old')
      OPEN(2,FILE='model2.out',STATUS='unknown')
      OPEN(3,FILE='model2.outt',STATUS='unknown')

c    Model inputs.
      read(1,9911) ishow,jmax,nj,nt,ntpr,nc
9911  format(10x,i15)
      read(1,9912) area,cio,ecur(1),ecur(2),
     &             aa(1),ac(1),aa(2),ac(2),ocv,delta,
     &             dpos,dneg,
     &             denp,denn,denpd,dennd,atomp,atomn,atompd,
     &             atomnd,epos,eneg,diff(1),diff(2)
      read(1,9912) temp,toler,zi(1),zi(2)
      read(1,9912) (cur(jc),jc=1,nc)
9912  format(10x,d15.7)
      dposd=dpos*denp*atomp/atompd/denpd
      dnegd=dneg*denp*atomn/atomnd/dennd

c     Start current loop
      do 501 jc=1,nc
      write (6,721) jc,nc
721   format (//,10X,'Current loop  jc=',i3,'   nc=',i3,/)

      do 720 i=2,3
      write(i,9913) ishow,jmax,nj,nt,ntpr
      write(i,9914) cur(jc),area,cio,ecur(1),ecur(2),
     &              aa(1),ac(1),aa(2),ac(2),ocv,delta,
     &              dpos,dneg,dposd,dnegd
720   write(i,9915) denp,denn,denpd,dennd,atomp,atomn,atompd,
     &              atomnd,epos,eneg,diff(1),diff(2),
     &              temp,toler,zi(1),zi(2)
9913  format(1x,'MODEL INPUTS:'/
```

```
     @        1x,'ishow               ',i15/
     @        1x,'jmax                ',i15/
     @        1x,'nj                  ',i15/
     @        1x,'nt                  ',i15/
     @        1x,'ntpr                ',i15)
9914  format(1x,'cur                 ',f15.7/
     @        1x,'area                ',f15.7/
     @        1x,'cio                 ',f15.7/
     @        1x,'ecur(1)             ',f15.7/
     @        1x,'ecur(2)             ',f15.7/
     @        1x,'aa(1)               ',f15.7/
     @        1x,'ac(1)               ',f15.7/
     @        1x,'aa(2)               ',f15.7/
     @        1x,'ac(2)               ',f15.7/
     @        1x,'ocv                 ',f15.7/
     @        1x,'delta               ',f15.7/
     @        1x,'dpos                ',f15.7/
     @        1x,'dneg                ',f15.7/
     @        1x,'dposd               ',f15.7/
     @        1x,'dnegd               ',f15.7)
9915  format(1x,'denp                ',f15.7/
     @        1x,'denn                ',f15.7/
     @        1x,'denpd               ',f15.7/
     @        1x,'dennd               ',f15.7/
     @        1x,'atomp               ',f15.7/
     @        1x,'atomn               ',f15.7/
     @        1x,'atompd              ',f15.7/
     @        1x,'atomnd              ',f15.7/
     @        1x,'epos                ',f15.7/
     @        1x,'eneg                ',f15.7/
     @        1x,'diff(1)             ',e15.7/
     &        1x,'diff(2)             ',e15.7/
     &        1x,'temp                ',f15.7/
     @        1x,'toler               ',f15.7/
     @        1x,'zi(1)               ',f15.7/
     @        1x,'zi(2)               ',f15.7/
     @        1x,'OUTPUTS:'/)

c     c(1,j) is the OH- concentration in mol/cm3.
c     c(2,j) is the K+ concentration in mol/cm3.
c     c(nspl,j) is the electric potential.

      ns=2
      nspl=ns+1
```

```
      n=3
      del=delta/real(nj-1)
      two=2.d0
      twodel=del*two
      far=96487.d0
      frt=96487.d0/(8.314d0*temp)
c
c    INITIAL CONDITIONS:
      DO 1 J=1,NJ
      c(1,j)=cio
      c(2,j)=cio
      c(nspl,j)=0.d0
1     continue

      jcount=0
      jtd=0
      jtp=nt
      fmax=0.d0
      time=0.d0
      flux=0.d0
      fluxnj=0.d0

C    Calculate the initial amount of active material
      actp0=dpos*area*denp/atomp*epos*far
      actn0=dneg*area*denn/atomn*eneg*far
      actp(0) =actp0
      actn(0) =actn0
      tdel=dmin1(dpos*0.999d0*denp/atomp*epos,dneg*0.999d0*
     &      denn/atomn*eneg)*far/cur(jc)/real(nt)*(1.d0-1.d-6)
      aarea(1)=1.d0
      aarea(2)=1.d0

c    Print out initial conditions:
      write(2,293) jcount,ocv,eta(1,0),eta(2,0),
     &             aarea(1),aarea(2),cur(jc),time,actp0,actn0,
     &             actp(0)/actp0,actn(0)/actn0
      write(2,2941) (real(j-1)/real(nj-1),c(1,j),c(2,j),
     &             j=1,nj)
2941  format (3(1x,e11.5))

c    Start time loop:
      do 204 jt=1,nt
      write (6,722) jt,nt
722   format (10X,'Time step   jt=',i3,'   nt=',i3)
```

```
c    zk(jk) is used to time step the acid concentration.
      do 231 jk=1,nj
231   zk(jk)=c(1,jk)
      time=real(jt)*tdel

C    Calculate the amount of active material at t>0
      actp(jt)=actp(jt-1)-cur(jc)*area*tdel
      actn(jt)=actn(jt-1)-cur(jc)*area*tdel
      aarea(1)=1.d0-time*cur(jc)/dposd/denpd*atompd/epos/far
      aarea(2)=1.d0-time*cur(jc)/dnegd/dennd*atomnd/eneg/far
      if (aarea(1).le.0) go to 500
      if (aarea(2).le.0) go to 500

c    Find overpotential eta
      do 892 j=1,2
      eta0=-2.d1
      eta1=2.d1
891   eta(j,jt)=(eta0+eta1)/two
      tcur=ecur(j)*aarea(j)*(dexp(eta(j,jt)*frt*aa(j))-
     &     dexp(-eta(j,jt)*frt*ac(j)))
      if (abs(tcur-cur(jc))/cur(jc).le.toler) go to 892
      if (tcur.ge.cur(jc)) then
      eta1=eta(j,jt)
      go to 891
      endif
      if (tcur.le.cur(jc)) then
      eta0=eta(j,jt)
      goto 891
      endif
892   continue

c    Start boundary value problem:

24    JCOUNT=JCOUNT+1
      f1max=0.d0
      f2max=0.d0
      f3max=0.d0

c    Check number of program iterations:
      if (jcount .gt. jmax) then
      jtp=jt-1
      write (2,723) jt,nt
      write (3,723) jt,nt
      write (6,723) jt,nt
```

```
723   format (/,10X,'SOLUTION DOES NOT CONVERGE jt='
     &          ,i3,'   nt=',i3)
      GOTO 500

      endif
c    Print to monitor current variable values:
      if(ishow.eq.1) then
      write(*,724) jcount,time,cur(jc)

724   format(1x,'jcount= ',i15,'  time=',e15.7,
     &          '  cur=',e15.7/
     &          'zeta, c1, c2, c3,')
      write(*,725) (real(js-1)/real(nj-1),c(1,js),c(2,js),
     &               c(3,js),js=1,nj)
725   format(4(1x,e10.4))

      write(3,7241) jcount,time,cur(jc)

7241  format(1x,'jcount= ',i15,'  time=',e15.7,
     &          '  cur=',e15.7/
     &          'zeta, c1, c2, c3')
      write(3,7251) (real(js-1)/real(nj-1),c(1,js),c(2,js),
     &               c(3,js),js=1,nj)
7251  format(4(1x,e10.4))

      endif

      do 2 j=1,nj
      do 2 k=1,n
      if(jcount.eq.1) z(k,j)=c(k,j)
      z(k,j)=(1.d0-dp)*c(k,j)+dp*z(k,j)
2     continue

C    SET UP COEFFICIENT MATRIX

      J=0
      DO 31 I=1,N
      DO 31 K=1,N
      X(I,K)=0.0d0
31    Y(I,K)=0.0d0
16    J=J+1
      DO 32 I=1,N
      DO 32 K=1,N
      G(I)=0.0d0
```

```
      A(I,K)=0.0d0
      B(I,K)=0.0d0
32    D(I,K)=0.0d0
      IF (J .NE. 1) GO TO 18

C    FIRST MESH POINT
c    Material-balance equation:
      f1=(-z(1,3)+4.d0*z(1,2)-3.d0*z(1,1))/twodel+
     &          cur(jc)/zi(1)/far/diff(1)
      b(1,1)=-3.d0/twodel
      d(1,1)= 4.d0/twodel
      x(1,1)=-1.d0/twodel
      g(1)=-f1+b(1,1)*z(1,j)+d(1,1)*z(1,j+1)+
     &     x(1,1)*z(1,j+2)

c    Electroneutrality equation:
      f2=0.d0
      do 50 i=1,ns
      f2=f2+zi(i)*z(i,j)
   50 b(2,i)=zi(i)
      g(2)=-f2
      do 51 k=1,ns
   51 g(2)=g(2)+b(2,k)*z(k,j)

c    Potential equation:
      fnspl=z(nspl,j)
      b(nspl,nspl)=1.d0

      CALL BAND(J)
      GO TO 16
18    IF (J .EQ. NJ) GO TO 20

C    INNER MESH POINTS

      ck   =zk(j)
      c1   =z(1,j)
      dc1  =(z(1,j+1)-z(1,j-1))/twodel
      d2c1 =(z(1,j+1)+z(1,j-1)-two*z(1,j))/del**2
      c2   =z(2,j)
      dc2  =(z(2,j+1)-z(2,j-1))/twodel
      c3   =z(3,j)
      dc3  =(z(3,j+1)-z(3,j-1))/twodel
      d2c3 =(z(3,j+1)+z(3,j-1)-two*z(3,j))/del**2
```

```
c     Material-balance equation:
       f1=-(c1-ck)/tdel+zi(1)*frt*diff(1)*
     &    (c1*d2c3+dc1*dc3)+diff(1)*d2c1
       f1c1=-1.d0/tdel+zi(1)*frt*diff(1)*d2c3
       f1c1p=zi(1)*frt*diff(1)*dc3
       f1c1pp=diff(1)
       f1c3p=zi(1)*frt*diff(1)*dc1
       f1c3pp=zi(1)*frt*diff(1)*c1

c     Band coefficients:
       a(1,1)=f1c1p*(-1.d0/twodel) + f1c1pp*(1.d0/del**2)
       b(1,1)=f1c1 + f1c1pp*(-two/del**2)
       d(1,1)=f1c1p*( 1.d0/twodel) + f1c1pp*(1.d0/del**2)
       a(1,3)=f1c3p*(-1.d0/twodel) + f1c3pp*(1.d0/del**2)
       b(1,3)=f1c3pp*(-two/del**2)
       d(1,3)=f1c3p*( 1.d0/twodel) + f1c3pp*(1.d0/del**2)
       g(1)   =-f1+a(1,1)*z(1,j-1)+b(1,1)*z(1,j)+d(1,1)*z(1,j+1)+
     &          a(1,3)*z(3,j-1)+b(1,3)*z(3,j)+d(1,3)*z(3,j+1)

c     Electroneutrality equation:
       f2=0.d0
       do 52 i=1,ns
       f2=f2+zi(i)*z(i,j)
   52  b(2,i)=zi(i)
       g(2)=-f2
       do 53 k=1,ns
   53  g(2)=g(2)+b(2,k)*z(k,j)

c     Potential equation:
       f3 =dc3+(cur(jc)+far*(zi(2)*diff(2)*dc2+
     &          zi(1)*diff(1)*dc1))/
     &         (far*frt*(zi(2)**2*diff(2)*c2+
     &          zi(1)**2*diff(1)*c1))
       f3c1= -(cur(jc)+far*(zi(2)*diff(2)*dc2+
     &         zi(1)*diff(1)*dc1) )/

     &        (far*frt*(zi(2)**2*diff(2)*c2+
     &         zi(1)**2*diff(1)*c1)**2)*
     &         zi(1)**2*diff(1)
       f3c1p= zi(1)*diff(1)/
     &        (frt*(zi(2)**2*diff(2)*c2+zi(1)**2*diff(1)*c1))
       f3c2= -(cur(jc)+far*(zi(2)*diff(2)*dc2+
     &         zi(1)*diff(1)*dc1) )/
```

```
     &        (far*frt*(zi(2)**2*diff(2)*c2+
     &         zi(1)**2*diff(1)*c1)**2)*
     &         zi(2)**2*diff(2)
      f3c2p= zi(2)*diff(2)/
     &        (frt*(zi(2)**2*diff(2)*c2+zi(1)**2*diff(1)*c1))
      f3c3p= 1.d0
      a(3,1)=f3c1p*(-1.d0/twodel)
      b(3,1)=f3c1
      d(3,1)=f3c1p*( 1.d0/twodel)
      a(3,2)=f3c2p*(-1.d0/twodel)
      b(3,2)=f3c2
      d(3,2)=f3c2p*( 1.d0/twodel)
      a(3,3)=f3c3p*(-1.d0/twodel)
      d(3,3)=f3c3p*( 1.d0/twodel)
      g(3)   =-f3+a(3,1)*z(1,j-1)+b(3,1)*z(1,j)+d(3,1)*z(1,j+1)+
     &            a(3,2)*z(2,j-1)+b(3,2)*z(2,j)+d(3,2)*z(2,j+1)+
     &            a(3,3)*z(3,j-1)                 +d(3,3)*z(3,j+1)

c     Check on max f1,f2,f3,f4,f5:
       f1max=dmax1(abs(f1max),abs(f1))
       f2max=dmax1(abs(f2max),abs(f2))
       f3max=dmax1(abs(f3max),abs(f3))

       CALL BAND(J)
       GO TO 16

C     LAST MESH POINT

20     c1    =z(1,j)
       dc1   =(z(1,j-2)-4.d0*z(1,j-1)+3.d0*z(1,j))/twodel
       c2    =z(2,j)
       dc2   =(z(2,j-2)-4.d0*z(2,j-1)+3.d0*z(2,j))/twodel
       c3    =z(3,j)
       dc3   =(z(3,j-2)-4.d0*z(3,j-1)+3.d0*z(3,j))/twodel

c     Material-balance equation:
       f1 =  dc1+ cur(jc)/zi(1)/far/diff(1)
       y(1,1)= 1.d0/twodel
       a(1,1)=-4.d0/twodel
       b(1,1)= 3.d0/twodel
       g(1)=-f1+y(1,1)*z(1,j-2)+a(1,1)*z(1,j-1)+b(1,1)*z(1,j)


c     Electroneutrality equation:
```

```
      f2=0.d0
      do 55 i=1,ns
      f2=f2+zi(i)*z(i,j)
   55 b(2,i)=zi(i)
      g(2)=-f2
      do 56 k=1,n
   56 g(2)=g(2)+b(2,k)*z(k,j)


c     Potential equation:
      f3 =dc3+(cur(jc)+far*(zi(2)*diff(2)*dc2+
     &          zi(1)*diff(1)*dc1))/
     &         (far*frt*(zi(2)**2*diff(2)*c2+
     &          zi(1)**2*diff(1)*c1))
      f3c1= -(cur(jc)+far*(zi(2)*diff(2)*dc2+
     &         zi(1)*diff(1)*dc1) )/

     &         (far*frt*(zi(2)**2*diff(2)*c2+
     &          zi(1)**2*diff(1)*c1)**2)*
     &          zi(1)**2*diff(1)
      f3c1p= zi(1)*diff(1)/
     &         (frt*(zi(2)**2*diff(2)*c2+zi(1)**2*diff(1)*c1))
      f3c2= -(cur(jc)+far*(zi(2)*diff(2)*dc2+
     &          zi(1)*diff(1)*dc1) )/

     &         (far*frt*(zi(2)**2*diff(2)*c2+
     &          zi(1)**2*diff(1)*c1)**2)*
     &         zi(2)**2*diff(2)
      f3c2p= zi(2)*diff(2)/
     &         (frt*(zi(2)**2*diff(2)*c2+zi(1)**2*diff(1)*c1))
      f3c3p= 1.d0


      y(3,1)=f3c1p*(1.d0/twodel)
      a(3,1)=f3c1p*(-two/del)
      b(3,1)=f3c1+f3c1p*(3.d0/twodel)
      y(3,2)=f3c2p*(1.d0/twodel)
      a(3,2)=f3c2p*(-two/del)
      b(3,2)=f3c2+f3c2p*(3.d0/twodel)
      y(3,3)=f3c3p*(1.d0/twodel)
      a(3,3)=f3c3p*(-two/del)
      b(3,3)=f3c3p*(3.d0/twodel)
      g(3)   =-f3+y(3,1)*z(1,j-2)+a(3,1)*z(1,j-1)+b(3,1)*z(1,j)+
     &            y(3,2)*z(2,j-2)+a(3,2)*z(2,j-1)+b(3,2)*z(2,j)+
```

```
     &           y(3,3)*z(3,j-2)+a(3,3)*z(3,j-1)+b(3,3)*z(3,j)


c    Check on max f1,f2,f3:
      f1max=dmax1(abs(f1max),abs(f1))
      f2max=dmax1(abs(f2max),abs(f2))
      f3max=dmax1(abs(f3max),abs(f3))



      CALL BAND(J)


C    TEST FOR CONVERGENCE


      do 30 i=1,1
      do 30 j=1,nj
      if(z(i,j).ne.0.d0) change= dabs((c(i,j)-z(i,j))/z(i,j))
      if(c(i,j).ne.0.d0) change= dabs((c(i,j)-z(i,j))/c(i,j))
      if(c(i,j).eq.z(i,j)) change=0.d0
      if(change.ge.toler) go to 24

30    continue

c    List transient quantities:
c    Flux at j=1:
c    (The minimum of the coion or counterion flux determines
c    the acid or salt flux.)
      dc1=(-3.d0*c(1,1)+4.d0*c(1,2)-c(1,3))/twodel
      dc2=(-3.d0*c(2,1)+4.d0*c(2,2)-c(2,3))/twodel
      dc3=(-3.d0*c(3,1)+4.d0*c(3,2)-c(3,3))/twodel
      flux1=-zi(1)*frt*diff(1)*c(1,1)*dc3-diff(1)*dc1
      flux2=-zi(2)*frt*diff(2)*c(2,1)*dc3-diff(2)*dc2
      flux=dmin1(flux1,flux2)
c      if (flux1+flux2.le.0) flux=dmax1(flux1,flux2)

c    Flux at j=nj:
      dc1=-(-3.d0*c(1,nj)+4.d0*c(1,nj-1)-c(1,nj-2))/twodel
      dc2=-(-3.d0*c(2,nj)+4.d0*c(2,nj-1)-c(2,nj-2))/twodel
      dc3=-(-3.d0*c(3,nj)+4.d0*c(3,nj-1)-c(3,nj-2))/twodel
      fluxnj1=-zi(1)*frt*diff(1)*c(1,nj)*dc3-diff(1)*dc1
      fluxnj2=-zi(2)*frt*diff(2)*c(2,nj)*dc3-diff(2)*dc2
      fluxnj=dmin1(fluxnj1,fluxnj2)
```

```
c      if (fluxnj1+fluxnj2.le.0) fluxnj=dmax1(fluxnj1,fluxnj2)


      fmax=dmax1(abs(f1max),abs(f2max),abs(f3max),abs(f4max),
     &           abs(f5max))
c    Potential at nj is the potential drop through membrane:
      pot(jt)=c(3,nj)
      volt(jt)=ocv-eta(1,jt)-eta(2,jt)+pot(jt)
      if (volt(jt).ge.0.d0) then
           if (actp(jt).ge.0.d0) then
                 if (actn(jt).ge.0.d0) jtd=jt
           endif
      endif
c    Write results:
      if(amod(real(jt),real(ntpr)).lt.1.d-9) then
      write(2,286) dc1,dc2,dc3,flux,fluxnj,pot(jt)

286   format( 1x,'        ',/
     @        1x,' dc1:    ',e12.5,'   dc2:    ',e12.5,
     @           '  dc3:  ',e12.5/
     @        1x,' flux:   ',e12.5,'   fluxnj:',e12.5/
     @        1X,' IR DROP:',E12.5)

      write(2,293) jcount,volt(jt),
     &             eta(1,jt),eta(2,jt),aarea(1),aarea(2),
     &             cur(jc),time,actp(jt),
     &             actn(jt),actp(jt)/actp0, actn(jt)/actn0
293   format( 1x,'jcount                  ',i15/
     &        1x,'volt                    ',f15.5/
     &        1x,'eta(pos)                ',f15.5/
     &        1x,'eta(neg)                ',f15.5/
     &        1x,'aarea(pos)              ',f15.5/
     &        1x,'aarea(neg)              ',f15.5/
     &        1x,'cur(jc)                 ',f15.5/
     &        1x,'time                    ',f15.5/
     &        1x,'actp(jt)                ',f15.5/
     &        1x,'actn(jt)                ',f15.5/
     &        1x,'actp/actp0              ',f15.5/
     &        1x,'actn/actn0              ',f15.5/
     &        1x,'                        ',/
     &        1x,'j/nj, c1, c2, c3')
      write(2,294) (real(j-1)/real(nj-1),c(1,j),c(2,j),
     &              c(3,j),j=1,nj)
294   format(4(1x,e11.5))
```

```
        endif
 204    continue

c     Write results of transient quantities:
 500    power=volt(0)/two
        do 522 j=1,jtd
 522    power=power+volt(j)
        power=power*cur(jc)/real(jtd)/(delta+dpos+dneg)*1.0d3
        energy=power*tdel*real(jtd)/3.6d3
        cap  =cur(jc)*tdel*(real(jtd)+0.5d0)/(delta+dpos+dneg)
        power1=power*(delta+dpos+dneg)
        energy1=power1*tdel*real(jtd)/1000.0d0
        cap1  =cur(jc)*tdel*(real(jtd)+0.5d0)

        write(2,2041),cur(jc)*1.0d3,cap,energy,power,
     &                cap1,energy1,power1
        write(3,2041),cur(jc)*1.0d3,cap,energy,power,
     &                cap1,energy1,power1
        write(6,2041),cur(jc)*1.0d3,cap,energy,power,
     &                cap1,energy1,power1
 2041   format(/1x,'Results of transient quantities:'/
     @         1x,'current density :',f15.5,' mA/cm2'/
     @         1x,'capacity        :',f15.5,' kC/l'/
     @         1x,'energy density  :',f15.5,' Wh/l'/
     @         1x,'power  density  :',f15.5,' W /l'/
     @         1x,'capacity        :',f15.5,' C /cm2'/
     @         1x,'energy density  :',f15.5,' Ws/cm2'/
     @         1x,'power  density  :',f15.5,' mW/cm2'/
     @         1x,'capacity, potential')
 526    do 527 j=2,3
        write(j,2042) 0.d0,ocv
        write(j,2042) (cap*real(jt)/real(jtd),
     &                 volt(jt),jt=ntpr,jtp,ntpr)
 527    write(j,2043)
        write(6,2042) 0.d0,ocv
        write(6,2042) (cap*real(jt)/real(jtd),
     &                 volt(jt),jt=ntpr,jtp,ntpr)
 2042   format(2(1x,e10.4))
 2043   format(//)
   501 CONTINUE
   502 CONTINUE
   503 CONTINUE
   504 CONTINUE
   505 CONTINUE
```

```
      stop
      end


      SUBROUTINE MATINV(N,M,DETERM)
      implicit double precision (a-h,o-z)
      COMMON A(7,7),B(7,7),C(7,500),D(7,15)
      DIMENSION ID(7)
      DETERM=1.0
      DO 1 I=1,N
    1 ID(I)=0
      DO 18 NN=1,N
      BMAX=1.1
      DO 6 I=1,N
      IF(ID(I).NE.0) GOTO 6
      BNEXT=0.0
      BTRY=0.0
      DO 5 J=1,N
      IF(ID(J).NE.0) GOTO 5
      IF(dabs(B(I,J)).LE.BNEXT) GOTO 5
      BNEXT=dabs(B(I,J))
      IF(BNEXT.LE.BTRY) GOTO 5
      BNEXT=BTRY
      BTRY=dabs(B(I,J))
      JC=J
    5 CONTINUE
      IF(BNEXT.GE.BMAX*BTRY) GOTO 6
      BMAX=BNEXT/BTRY
      IROW=I
      JCOL=JC
    6 CONTINUE
      IF(ID(JC).EQ.0) GOTO 8
      DETERM=0.0
      RETURN
    8 ID(JCOL)=1
      IF(JCOL.EQ.IROW) GOTO 12
      DO 10 J=1,N
      SAVE=B(IROW,J)
      B(IROW,J)=B(JCOL,J)
   10 B(JCOL,J)=SAVE
      DO 11 K=1,M
      SAVE=D(IROW,K)
      D(IROW,K)=D(JCOL,K)
```

```
   11   D(JCOL,K)=SAVE
   12   F=1.0D0/B(JCOL,JCOL)
        DO 13 J=1,N
   13   B(JCOL,J)=B(JCOL,J)*F
        DO 14 K=1,M
   14   D(JCOL,K)=D(JCOL,K)*F
        DO 18 I=1,N
        IF(I.EQ.JCOL) GO TO 18
        F=B(I,JCOL)
        DO 16 J=1,N
   16   B(I,J)=B(I,J)-F*B(JCOL,J)
        DO 17 K=1,M
   17   D(I,K)=D(I,K)-F*D(JCOL,K)
   18   CONTINUE
        RETURN
        END
C
C
C
        SUBROUTINE BAND(J)
        implicit double precision (a-h,o-z)
        DIMENSION E(7,8,500)
        COMMON A(7,7),B(7,7),C(7,500),D(7,15),
     &        G(7),X(7,7),Y(7,7),N,NJ
  101   FORMAT (15H DETERM=0 AT J=,I4)
        IF (J-2)  1,6,8
    1   NP1 = N + 1
        DO 2 I=1,N
        D(I,2*N+1) = G(I)
        DO 2 L=1,N
        LPN = L + N
    2   D(I,LPN) = X(I,L)
        CALL MATINV(N,2*N+1,DETERM)
        IF (DETERM)  4,3,4
    3   write (3,101) J
    4   DO 5 K=1,N
        E(K,NP1,1) = D(K,2*N+1)
        DO 5 L=1,N
        E(K,L,1) = - D(K,L)
        LPN = L + N
    5   X(K,L) = - D(K,LPN)
        RETURN
    6   DO 7 I=1,N
        DO 7 K=1,N
```

```
   DO 7 L=1,N
 7 D(I,K) = D(I,K) + A(I,L)*X(L,K)
 8 IF (J-NJ)  11,9,9
 9 DO 10 I=1,N
   DO 10 L=1,N
   G(I) = G(I) - Y(I,L)*E(L,NP1,J-2)
   DO 10 M=1,N
10 A(I,L) = A(I,L) + Y(I,M)*E(M,L,J-2)
11 DO 12 I=1,N
   D(I,NP1) = - G(I)
   DO 12 L=1,N
   D(I,NP1) = D(I,NP1) + A(I,L)*E(L,NP1,J-1)
   DO 12 K=1,N
12 B(I,K) = B(I,K) + A(I,L)*E(L,K,J-1)
   CALL MATINV(N,NP1,DETERM)
   IF (DETERM)  14,13,14
13 write (3,101) J
14 DO 15 K=1,N
   DO 15 M=1,NP1
15 E(K,M,J) = - D(K,M)
   IF (J-NJ)  20,16,16
16 DO 17 K=1,N
17 C(K,J) = E(K,NP1,J)
   DO 18 JJ=2,NJ
   M = NJ - JJ + 1
   DO 18 K=1,N
   C(K,M) = E(K,NP1,M)
   DO 18 L=1,N
18 C(K,M) = C(K,M) + E(K,L,M)*C(L,M+1)
   DO 19 L=1,N
   DO 19 K=1,N
19 C(K,1) = C(K,1) + X(K,L)*C(L,3)
20 RETURN
   END
```

VITA

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