DOE/ET/11322--T4 TR-181

MR 2083
8-1

MASTER

ET 11322

AC03-78ET11322

PHYSICAL SCIENCES INC.

30 COMMERCE WAY, WOBURN, MASS. 01801

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PERFORMANCE MODEL FOR MOLTEN-
CARBONATE FUEL CELLS

Quarterly Report for
5 January 1979 through 5 April 1979

Prepared for
U. S. DEPARTMENT OF ENERGY
San Francisco Operations Office

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PERFORMANCE MODEL FOR MOLTEN-
CARBONATE FUEL CELLS

Quarterly Report for

6 January 1979 through 5 April 1979

G. Wilemski, T. Wolf, D. Bloomfield,
M. L. Finson, E. R. Pugh, and K. L. Wray

Physical Sciences Inc.
30 Commerce Way
Woburn, MA 01801

Prepared for

U. S. DEPARTMENT OF ENERGY
San Francisco Operations Office

Under Contract No. DE-AC-03-79ET11322

ABSTRACT

Progress on the development of a performance model for molten carbonate fuel cells is reported. Key physical and chemical phenomena being modeled include mass transport, ohmic losses, electrode kinetics, fuel and oxidant utilization, gas phase convective heat transfer and in-plane heat conduction through cell hardware. Numerical schemes have been developed and programmed to calculate overpotential versus current density curves for individual electrodes, the cell current density distribution, and the cell temperature distribution.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
SUMMARY	v
1. INTRODUCTION	1
2. DIFFERENTIAL CELL MODEL	2
2.1 Initial Slope of Polarization Curve	2
2.2 Numerical Calculations of Electrode Polarization Curves	14
2.3 Effects of Finite Electrical Conductivity of Electrodes	27
3. INTEGRAL CELL MODEL	31
3.1 Introduction	31
3.2 Potential Balance Equation	32
3.3 Mass Balance Equations	33
3.4 Stack Heat Transfer	35
3.5 Effect of Finite Hardware Conductivity	35
3.6 Hardware Energy Balance with Inplane Conduction	42
3.7 Energy Addition to Gas Streams	44
3.8 Numerical Solution	45
3.9 Arbitrary Flow Geometries	49
3.10 Results	50
4. REFERENCES	56

LIST OF ILLUSTRATIONS

<u>Figure No.</u>		<u>Page</u>
1.	Fitted values of i_o versus film length for anodes.	9
2.	Qualitative sketch of Z' vs. i_o .	11
3.	Picture of anode implied by parametric fits of thin film model to low overpotential data.	13
4.	IR free polarization curves for cathodes.	19
5.	IR free polarization curves for anodes.	22
6.	Ohmic losses (Ω) versus pore current density j and IR free polarization curves for cathodes.	24
7.	Decomposition of anode IR free polarization curves (1 and 4) into activation (A) and concentration (C) overpotential versus current density j .	25
8.	a) Repeating stack elements, b) Analogous thermal network for a point in the cell plane.	36
9.	Local heat addition to gas streams based on actual and infinite hardware thermal conductivity.	41
10.	Flowchart for numerical scheme.	48
11.	Performance curves for isothermal cell with constant inlet gas flow rates.	52
12.	Net anode utilizations for isothermal cell with constant inlet gas flow rates.	53

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
1.	Parameter values used with Eq. (2. 20).	8
2.	Gas compositions and slopes of polarization curves.	10
3.	Parameter values used in calculations for Figures 4 and 6.	18
4.	Parameter values used in calculations for Figures 5 and 7.	21
5.	Numerical values for cell hardware heat transfer parameters.	39
6.	Conditions for calculated results presented in Figures 9 and 11.	50
7.	Sample calculation of isothermal current density and utilization distributions for full CO and CH ₄ equilibria.	55

SUMMARY

This report is a description of work performed under U. S. Department of Energy Contract No. DE-AC-03-79ET11322 directed towards the development of a performance model for molten carbonate fuel cells. In this quarter we continued development of the physical and chemical concepts and numerical techniques for both the differential cell model (DCM) and the integral cell model (ICM). The key physical and chemical phenomena that are presently treated include: mass transport of reactants and products between the electrode surfaces and the bulk gas streams, ohmic losses in the electrolyte within the pores, electrochemical reaction kinetics via a Butler-Volmer equation with provision for different reaction mechanisms, utilization in the oxidant and fuel gas streams including the effects of water-gas shift and methanation equilibria, heat transfer from the cell hardware to the flowing gas streams, and inplane heat conduction through the cell hardware. The basic pore geometry being used is that of the cylindrical thin film model employed previously.

Emphasis this quarter for the DCM fell in three main areas: We developed an exact analytical expression for the initial slope of the polarization curve for the thin film model. This equation is used to determine the range of values for parameters used in the model by fitting to experimental porous electrode data. Secondly, we studied the effects of different reaction mechanisms on electrode performance and we continued our assessment of the dependence of electrode performance on the other model parameters. The calculations were performed using the full non-linear equations for the transfer current density that result when reaction mechanisms are considered. Finally, because cathodes oxidize in situ to NiO we developed the capability to treat ohmic losses in an electrode with finite electrical conductivity.

The analysis for the ICM this quarter was extended to include cell stacking effects and in-plane heat conduction, in contrast with the earlier version of this model that dealt with just a single adiabatic cell with no in-plane conduction. The current, more realistic treatment utilizes an implicit numerical scheme to integrate the elliptic differential equations that arise when in-plane heat conduction is included. The capability to handle methane utilization in the full equilibrium limit was also added to the numerical scheme.

1. INTRODUCTION

The objective of this program is the development of a molten carbonate fuel cell model that describes cell performance (current density versus voltage) as a function of inlet gas compositions, temperatures, flow rates and pressure. In addition, the model should provide a clear picture of the temperature and current density distributions over the electrode faces. The model can be conveniently discussed in terms of its two main components: a differential cell model (DCM) and an integral cell model, (ICM).

In the DCM, cell performance is described on a local basis by incorporating phenomenological treatments of electrokinetics, mass transport, and porous electrode structure. The primary output of this model is the current density as a function of local gas conditions, temperature and voltage. The other principal output of this model is the local heat release rate which is easily determined once the local current density is known.

In the ICM cell behavior is treated on an overall basis, accounting for fuel and oxidant utilization and heat transfer within the cell. The output of the DCM is combined with treatment of gas phase mass balance and convective heat transfer and in-plane heat conduction through cell hardware in order to calculate current density and temperature distributions in the cell.

2. DIFFERENTIAL CELL MODEL

2.1 Initial Slope of Polarization Curve

At low overpotentials η (and low current densities j) electrode polarization curves are often sufficiently linear to be well described by the equation:

$$\eta = Zj \quad (2.1)$$

where the impedance or polarization resistance is defined as:

$$Z = \left(\frac{\partial \eta}{\partial j} \right)_{j=0} \quad (2.2)$$

For non-porous electrodes Riddiford¹ has elegantly derived a very general expression for Z which reads:

$$Z = \frac{RT}{nF} \left[\sum_s \frac{\mu_s}{i_{o,s}} - \sum_k \frac{v_k}{i_{lim,k}} \right] \quad (2.3)$$

Here, μ_s is the stoichiometric coefficient of the s^{th} unit step appearing in the overall electrode reaction mechanism, v_k is the stoichiometric coefficient of species k in the overall stoichiometric equation for the electrode reaction, $i_{o,s}$ is the exchange current density of the s^{th} unit step and $i_{lim,k}$ is the limiting current associated with species k .

Despite its generality, Eq. (2.3) is still limited to non-porous electrodes. This restriction is not difficult to relax, as will be shown.

The result of the analysis is an algebraic expression for the initial slope of the polarization curve for the cylindrical thin film model. The expression has an explicit dependence on all of the chemical and physical parameters of the model, and for this reason it should be useful in correlating low overpotential-low current density measurements on porous electrodes with internal electrode-electrolyte structure.

We outline the derivation for an electrode with negligible electrical resistivity. Finite resistivity requires certain modifications that will be discussed in detail in the final report. Some work on this problem is reported in Section 2.3.

The total overpotential η is defined as

$$\eta = \eta_S + \eta_C \quad (2.4a)$$

where η_C is the concentration overpotential and η_S is the "surface" overpotential and is equal to the sum of the activation overpotential η_A and the ohmic losses in the film η_Ω :

$$\eta_S = \eta_A + \eta_\Omega \quad (2.4b)$$

From Eq. (2.2) the required derivative is:

$$Z = \left(\frac{d\eta_S}{dj} \right)_{j=0} + \left(\frac{d\eta_C}{dj} \right)_{j=0} \quad (2.5)$$

In an earlier report² (with slightly different notation for η_S) we showed that

$$j = Z_S^{-1} \eta_S \quad (2.6)$$

where

$$Z_S = \left[2\pi R_p N_p \delta'' \kappa K \tan(K\ell) \right]^{-1} \quad (2.7)$$

Here, N_p is the number of pores per unit electrode surface area, κ is the electrolyte conductivity, ℓ is the length of the electrolyte film covering the pore, R_p is the pore radius, and

$$K = \left(\frac{i_o nF}{\kappa \delta'' RT} \right)^{\frac{1}{2}} \quad (2.8)$$

$$\delta'' = \delta \left(1 - \delta / 2 R_p \right)$$

where i_o is the exchange current and density and n is the number of moles of electrons transferred, and δ is the film thickness.

From Eq. (2.6) it is transparent that

$$\left(\frac{d\eta_S}{dj} \right)_{j=0} = Z_S \quad (2.9)$$

The other derivative is obtained by applying the chain rule after recognizing that:

$$\eta_C = \frac{RT}{nF} \sum_k \nu_k \ln \left(C_k / C_k^o \right) \quad , \quad (2.10)$$

$$\frac{C_k}{C_k^o} = 1 - \frac{i}{i_{\text{lim},k}} \quad , \quad (2.11)$$

where C_k^o is the open circuit concentration of species k at the electrode, and that in this limiting regime

$$i = i_o \frac{nF}{RT} \eta_S$$

We find

$$\left(\frac{d\eta_C}{dj} \right)_{j=0} = - \left(i_o Z_S \right) \sum \left(v_k / i_{lim,k} \right) \quad (2.12)$$

Equations (2.5), (2.9) and (2.12) yield the desired result:

$$Z = Z_S \left(1 - i_o \sum_k \left(v_k / i_{lim,k} \right) \right) \quad (2.13)$$

For the cylindrical thin film model we have

$$i_{lim,k} = \frac{-n D_k C_k^o}{v_k \delta'} \quad (2.14)$$

where

$$\delta' = R_p \ln \left(1 - \delta / R_p \right) \quad (2.15)$$

and the negative sign used to insure that i_{lim} is positive for reactants ($v_k \leq 0$) and negative for products ($v_k \geq 0$). Equation (2.14) is presumed to hold for a dissolved gas species with diffusion coefficient D_k and carbonate ions are not considered as a possible limiting species. We then have

$$Z = Z_S \left(1 + i_o \delta' \sum_k v_k^2 / \left(n D_k C_k^o \right) \right) \quad (2.16)$$

It is interesting to note that for $K\ell \ll 1$ we have

$$Z_S = 2\pi R_p \ell N_p (nF/RT) i_o \quad (2.17)$$

and Eq. (2.13) reduces to essentially Riddiford's expression corrected for the internal area of the porous electrode.

More generally, we see that Eq. (2.13) displays a coupling of activation (i_o), ohmic (κ) and mass transport (i_{lim}) factors with the pore-electrolyte geometric parameters (R_p, l, δ) to give rise to the overall initial behavior of the electrode.

Polarization curves are usually reported on an IR free basis, so Eq. (2.13) must be corrected for the ohmic losses in the pore. In the present case, we have²:

$$\begin{aligned}\eta_{\Omega} &= \eta_S - \eta_A = \eta_A \left[\cosh(Kl) - 1 \right] \\ &= Z_S \left[1 - \operatorname{sech}(Kl) \right] j\end{aligned}\quad (2.18)$$

with the aid of Eq. (2.6). If we designate η' as the IR free, "total" overpotential, we find with the aid of Eqs. (2.13) and (2.18),

$$\eta' = \eta - \eta_{\Omega} = Z'j \quad (2.19)$$

where

$$\begin{aligned}Z' &= Z - Z_S [1 - \operatorname{sech}(Kl)] \\ &= Z_S \left[\operatorname{sech}(Kl) - i_o \sum_k \left(v_k / i_{lim,k} \right) \right]\end{aligned}\quad (2.20)$$

Even though Eq. (2.20) represents the initial slope of an IR free polarization curve, it still contains a significant dependence on κ . Only when $Kl \ll 1$ does this dependence vanish. Otherwise, the effects of the ohmic losses in making the pore current distribution nonlinear within the pore are contained in Eq. (2.20).

We used Eq. (2.20) in a series of attempts to reproduce the linear polarization curves reported in a recent IGT Quarterly Report³ for low overpotentials and low current densities. Our procedure in fitting this equation was as follows.

We fitted the values reported/estimated in earlier IGT reports^{4,5} for diffusion constants, electrical conductivities and Henry's Law solubility constants to expressions of an Arrhenius form:

$$q = q' \exp(-E/RT)$$

which we then used to calculate values at 923K. The electrode and electrolyte geometric parameters were specified within the following ranges: l , the film length could be no longer than the electrode thickness 0.05 cm, but could be as short as 5×10^{-4} cm. The pore radius R_p was perhaps most reasonably estimated as 2.5×10^{-4} cm using the above electrode thickness, the typical internal/external area ratio of 320 and by assuming closest packing; R_p was also allowed to equal 1.25×10^{-4} cm and 7.5×10^{-4} cm. In these cases, the pore density N_p was adjusted using the result of the closest packing model:

$$N_p = \frac{1}{4 R_p^2} \quad (2.21)$$

The film thickness δ was allowed to range over the three values: 5×10^{-5} cm, 1×10^{-5} cm, and 5×10^{-6} cm. Finally, given values for all of the above mentioned parameters, Eq. (2.20) was solved for the value of i_o that would give agreement with the reported measurement for the case under consideration.

In Figure 1, values of i_o calculated as described above are plotted versus the film length l for two values of R_p and two values of δ . The calculations were made using the parameter values listed in Table 1, and were designed to be representative of behavior at an anode. Dissolved gas concentrations were calculated from the equation

$$C^o = S^o P$$

where P is the partial pressure of the gas species. In Table 2, we list the gas compositions used in the experiments. In the computations we used compositions in shift equilibrium that were derived from the reported initial compositions. The slopes of the polarization curves are also listed in Table 2. These were inferred from the reported numerical results and they agree well with the inset figures plotted in the IGT report.³ The case A1 listed in the table is an average of IGT runs 1, 4, 5, and 6 which were performed with identical fuel mixtures.

TABLE 1 Parameter Values used with Eq. (2.20)

D_{H_2}	$1.58 \times 10^{-5} \text{ cm}^2/\text{sec}$	$T = 923 \text{ K}$
D_{H_2O}	$1.33 \times 10^{-5} \text{ cm}^2/\text{sec}$	$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$
D_{CO_2}	$9.40 \times 10^{-6} \text{ cm}^2/\text{sec}$	$F = 96,485 \text{ C mol}^{-1}$
$S^o_{H_2}$	$5.79 \times 10^{-6} \text{ moles/cm}^3\text{-atm}$	$\kappa = 1.4 \text{ ohm}^{-1} \text{ cm}^{-1}$
$S^o_{H_2O}$	$5.79 \times 10^{-6} \text{ moles/cm}^3\text{-atm}$	
$S^o_{CO_2}$	$1.166 \times 10^{-5} \text{ moles/cm}^3\text{-atm}$	

TABLE 2 Gas Compositions and Slopes of Polarization Curves

Case	Initial Gas Comp.	Shifted Gas Comp.	Slope (mV/mA cm ⁻²)
	mole % H ₂ / CO ₂ / N ₂	mole % H ₂ / H ₂ O / CO ₂ / N ₂	
A1	80 / 20 / 0	66 / 14 / 6 / 0	0.88
A2	40 / 20 / 40	29 / 11 / 9 / 40	0.69
A3	20 / 20 / 60	12 / 8 / 12 / 60	0.65

There are several features of Fig. 1 that are worth noting. The variation of i_o with R_p and l can be understood by using the equation:

$$(i_o)_{app} = i_o (2\pi R_p l) N_p$$

for an apparent exchange current density of the total electrode. This equation is actually exact when $Kl \ll 1$ (see Eq. (2.17) and is approximately true otherwise. From Eq. (2.21), we get

$$i_o = (\text{constant}) \frac{R_p}{l}$$

So we see either from this equation or from Fig. 1 that in order to satisfy Eq. (2.20) i_o must be increased when either R_p is increased or l is decreased.

As far as the dependence of i_o on δ is concerned, we see from the curves A3 for $\delta = 1 \times 10^{-5}$ cm and $\delta = 5 \times 10^{-5}$ cm that at large l the fitted value of i_o is quite insensitive to the value of δ specified. However, as l is decreased we see an increasing divergence of these two curves.

Fig. 1.. Fitted values of i_o versus film length for anodes.

What's happening is that as ℓ decreases, i_o must increase to compensate for the loss of active, wetted area. For the thicker film ($\delta = 5 \times 10^{-5}$ cm) mass transport limitations start to be significant sooner than for the thinner film ($\delta = 1 \times 10^{-5}$ cm). Eventually, a point is reached beyond which further increases in i_o lead to larger values of Z' because of enhanced mass transport limitations. Consult Eq. (2.20) to see this more clearly. Increasing i_o (for given values of all other parameters) does diminish Z_S and, hence, Z' , initially, but further increases in i_o lead eventually to domination by the second, mass transport, term of Eq. (2.20). Qualitatively we have the situation sketched in Figure 2.

Figure 2 - Qualitative Sketch of Z' -vs- i_o

The actual value of the minimum in the above curve depends, of course, on the chosen values of δ , R_p , and ℓ . So it is entirely possible that an inappropriate choice for these parameters makes it impossible to sufficiently minimize Z' by varying i_o . Such a situation occurs in Fig. 1,

for curve A3 with $\delta = 5.0 \times 10^{-5}$ cm. At $l \approx 1.01 \times 10^{-3}$ cm, we have $i_o \approx 149.4 \text{ mA/cm}^2$. For any l value smaller than this, no solution for i_o can be found for the equation $Z' = 0.65$ (see Table 2). This is a general feature of this equation, and it shows up in many of our calculations. It does not show up in any of the other six curves presented in Figure 1 because these calculations were arbitrarily stopped at $l = 5 \times 10^{-4}$ cm, a relatively small value for l . For the reasons just stated, it would be unwise to extrapolate these curves much beyond their termini at $l = 5 \times 10^{-4}$ cm.

Ideally, it would be nice to be able to infer something about the nature of the electrolyte film in the porous electrode from the values of δ and l (for given R_p) needed to find i_o values that are comparable with those found experimentally on smooth electrodes. For anodes, values of i_o in the range $15\text{-}70 \text{ mA/cm}^2$ have been reported for recent experiments on wire electrodes at IGT⁶. What we see from Fig. 1 is that in order to get i_o values in this range, we must let l lie roughly in the range 1.1×10^{-3} cm to 1.4×10^{-3} cm when $\delta = 5 \times 10^{-5}$ cm (a relatively thick film) or l must vary from 5×10^{-4} cm to 7×10^{-4} cm when $\delta = 1 \times 10^{-5}$ cm or less. (Calculations for $\delta = 5 \times 10^{-6}$ cm are not shown, but they do not differ substantially from those with $\delta = 1 \times 10^{-5}$ cm). Consistent use of the thin film model demands that these particular groupings of parameter values be used in the calculation of the full polarization curves. These results imply a picture (see Fig. 3) of an anode pore that is more or less flooded with a thin film extending beyond the flooded portion for a distance of only two to six times the pore radius.

Figure 3. Picture of anode implied by parametric fits of thin film model to low overpotential data.

It, of course, remains to be seen whether this much faith can be put into the predictions of the simple thin film model. Much additional experimentation and theoretical work needs to be done.

A similar set of calculations was performed for cathode conditions. Qualitatively similar results were obtained. It was found that for $R_p = 2.5 \times 10^{-4}$ cm, it was necessary to put $\ell = 5 \times 10^{-2}$ cm, which is the approximate electrode thickness, in order to find values for i_o in the range 0.2 to 0.4 mA/cm² currently being suggested as appropriate for molten carbonate cathodes. These results showed very little sensitivity to δ , as could be inferred from Fig. 1, for the value of ℓ quoted. These latter results do come, however, with a large caveat. . These fits were made with the neglect of finite electrical conductivity of the NiO cathode material. Lately, we have come to believe that this effect may be important to include in the analysis. Our preliminary considerations are reported in Sec. 2.3. A full accounting will be made in the final report.

2.2 Numerical Calculations of Electrode Polarization Curves

a) Effect of Different Choices for Reaction Mechanism

We have shown previously that by assuming equilibrium for all steps in the reaction mechanism save for the rate determining step (RDS) (the quasi-equilibrium assumption) and because of detailed balancing that the general expression for the transfer current density i could be written as:

$$i = i_o \left[\prod_{j=1}^N (C_j / C_j^o)^{m_j} \right] S(\eta_S) \quad (2.22)$$

$$S(\eta_S) = \exp(\alpha_f \eta_S F/RT) - \exp(-\alpha_r \eta_S F/RT)$$

where the exchange current density is given by the equation:

$$i_o = (\text{const}) \prod_j (C_j^o)^{m_j} \quad (2.23)$$

Here C_j and C_j^o are the concentrations of species j "at" the electrode surface under load and at open circuit, and η_S is the "surface" overpotential, that is, the total overpotential η across the double layer minus the concentration overpotential η_C ; as defined previously in Eq. (2.4a):

$$\eta_S = \eta - \eta_C$$

(Once again note the difference in notation from our earlier reports^{2,7}).

The effective transfer coefficients for the overall forward (f) and reverse (r) reactions are designated α_f and α_r . They, of course, must sum to the total number (n) of moles of electrons transferred in the overall reaction scheme:

$$\alpha_f + \alpha_r = n$$

Next, recall from Section 2.1 that we can write:

$$\frac{C_i}{C_j} = 1 - \frac{i}{i_{\text{lim},j}} \quad (2.24)$$

where $i_{\text{lim},j}$ is the limiting current for species j. Upon combining Eqs. (2.22) and (2.24), we obtain the following non-linear equation for i:

$$i = i_o \cdot \left[\prod_j (1 - i/i_{\text{lim},j})^{m_j} \right] S(\eta_S) \quad (2.25)$$

From Eqs. (2.23) and (2.25) it is apparent that reaction mechanisms that give rise to different sets of (m_j , α_f and α_r) will affect predicted electrode performance in two ways:

- The gas partial pressure dependence of i_o will vary with the mechanism selected. Thus, for a given gas composition, different values of i_o may arise for different mechanisms. As seen in Section 2.1, the value of i_o plays a large role in determining the initial slope of the polarization curve. Hence, this effect could play a major role in

influencing predicted performance. An indication of the quantitative importance of this effect can be gotten by referring to an earlier report,⁷ where calculations using different values of i_o were reported.

- The precise mathematical dependence of i on η_S (and hence on η) will change with the reaction mechanism selected. This can have a large influence on the predicted performance. Examples of this type of behavior are illustrated in Figures 4 and 5.

As described in earlier reports, the calculations are performed by numerically integrating the equation

$$\frac{d^2 \eta_S}{dz^2} = \frac{1}{\kappa \delta''} i \quad (2.26)$$

where $\delta'' = \delta(1 - \delta/2R_p)$ using Eq. (2.25) for i . Because no current leaves the film at $z=0$, we have the initial condition:

$$\left. \frac{d\eta_S}{dz} \right|_{z=0} = 0 \quad (2.27)$$

and the other initial condition can be chosen arbitrarily:

$$\eta_S(0) = \eta_A \quad (2.28)$$

where η_A is the activation overpotential for the pore in the absence of ohmic losses. Because we assume very large electrode conductivity,

the measurable total overpotential is the value of η at $z=l$:

$$\eta(l) = \eta_A + \eta_\Omega(l) + \eta_C(l) = \eta_S(l) + \eta_C(l) .$$

Generally, IR free polarization curves are reported, so we plot the apparent electrode current density j against η' where

$$\eta' = \eta(l) - \eta_\Omega = \eta_A + \eta_C(l) \quad (2.29)$$

and

$$j = N_p I .$$

The total current I is, of course, a result of the numerical integration of Eq. (2.26):

$$I = 2\pi R_p \int_0^l i dz \quad (2.30a)$$

$$= 2\pi R_p \kappa \delta'' (d\eta_S / dz)_{z=l} \quad (2.30b)$$

In Figure 4, performance curves characteristics of cathodes are presented. The calculations were made using the parameter values listed in Table 3. Species 1 was taken to be O_2 and species 2 to be CO_2 . Gas solubility was assumed to be linear in the partial pressure.

TABLE 3. Parameter values used in calculations for
Figures 4 and 6.

κ	$= 1.4 \text{ ohm}^{-1} \text{ cm}^{-1}$	T	$= 923 \text{ K}$
l	$= 5.0 \times 10^{-2} \text{ cm}$	D_{O_2}	$= 1.11 \times 10^{-5} \text{ cm}^2/\text{sec}$
R_p	$= 2.5 \times 10^{-4} \text{ cm}$	D_{CO_2}	$= 9.4 \times 10^{-6} \text{ cm}^2/\text{sec}$
P_{O_2}	$= 0.15 \text{ atm}$	$S_{\text{O}_2}^0$	$= 3.97 \times 10^{-7} \text{ mol cm}^{-3} \text{ atm}^{-1}$
P_{CO_2}	$= 0.30 \text{ atm}$	$S_{\text{CO}_2}^0$	$= 1.166 \times 10^{-5} \text{ mol cm}^{-3} \text{ atm}^{-1}$

Parameter	Curve	1	2	3	4	5
$\delta (\mu\text{m})$		0.5	0.5	0.5	0.5	0.1
$i_o (\text{mA}/\text{cm}^2)$		0.22	0.33	0.33	0.33	0.33
$m_1(\text{O}_2)$		5/8	3/8	1	1	3/8
$m_2(\text{CO}_2)$		-3/4	-5/4	1	1	-5/4
α_f		1/2	1/2	1/2	3/2	1/2
α_r		5/2	3/2	3/2	1/2	3/2

Figure 4. IR free polarization curves for cathodes. Curves are identified in Table 3.

The exponents used for curves 1, 2, and 5 correspond to the two cathode mechanisms proposed by Appleby and Nicholson.⁸ The exponents for curves 3 and 4 were selected arbitrarily for purposes of comparison. The value of ni_o was also arbitrarily set equal to $0.66 \text{ mA/cm}^2\text{-mol}$, a representative cathode value. This gives $i_o = 0.33 \text{ mA/cm}^2$ for curves 2 - 5, and $i_o = 0.22 \text{ mA/cm}^2$ for curve 1.

In Figure 5, performance curves for anodes are presented. The parameter values used in these calculations are listed in Table 4. The exponents used for curve 1 correspond to the mechanism that best accounts for experimental data obtained at IGT.⁶ The exponents used for curve 2 were arbitrarily chosen for comparative purposes. Both curves will eventually approach limiting current asymptotes at about 650 mA/cm^2 . This relatively low limiting current derives partly from the low H_2 partial pressure used, but mainly from the small active area of the pore ($2\pi R_p l$) for the parameter values used. At higher hydrogen partial pressures, the overpotential at a particular current density would be decreased somewhat and the limiting current density would be increased.

From these results, it is apparent that the reaction mechanism (s) selected to describe the electrochemistry at an electrode will play a significant role in determining the predicted performance for that electrode. In particular, judging from Figs. 4 and 5, the value of α_f , the effective transfer coefficient for the overall forward reaction, will exert the greatest influence of all the exponents (barring exceptional cases) in determining electrode performance at intermediate current densities.

TABLE 4. Parameter values used in calculations for
Figures 5 and 7.

κ	$= 1.4 \text{ ohm}^{-1} \text{ cm}^{-1}$	D_{H_2}	$= 1.58 \times 10^{-5} \text{ cm}^2/\text{sec}$
T	$= 923 \text{ K}$	D_{CO_2}	$= 9.4 \times 10^{-6} \text{ cm}^2/\text{sec}$
P_{H_2}	$= 0.12 \text{ atm}$	$D_{\text{H}_2\text{O}}$	$= 1.33 \times 10^{-5} \text{ cm}^2/\text{sec}$
P_{CO_2}	$= 0.12 \text{ atm}$	$S_{\text{H}_2}^{\circ} = S_{\text{H}_2\text{O}}^{\circ}$	$= 5.79 \times 10^{-6} \text{ mol cm}^{-3} \text{ atm}^{-1}$
$P_{\text{H}_2\text{O}}$	$= 0.08 \text{ atm}$	$S_{\text{CO}_2}^{\circ}$	$= 1.166 \times 10^{-5} \text{ mol cm}^{-3} \text{ atm}^{-1}$

Parameter	Curve	1	2	3	4
$\delta \text{ (}\mu\text{m)}$		0.1	0.1	0.1	0.5
$R_p \text{ (}\mu\text{m)}$		2.5	2.5	2.5	2.5
$l \text{ (}\mu\text{m)}$		5	5	5	12.5
$i_o \text{ (mA/cm}^2\text{)}$		30	30	30	30
$m_1 \text{ (H}_2\text{)}$		1/4	1	1	1/4
$m_2 \text{ (CO}_2\text{)}$		1/4	1	1	1/4
$m_3 \text{ (H}_2\text{O)}$		1/4	1	1	1/4
α_f		1/2	1/2	3/2	1/2
α_r		3/2	3/2	1/2	3/2

Figure 5. IR free polarization curves for anodes. Curves are identified in Table 4.

b) Effect of Film-geometry Parameters

As we saw in Sec. 2.1, fitting the low polarization data to the analytical expression for the initial slope of the polarization curve did not result in a unique determination of all of the parameters used in the model. In Figures 6 and 7, we present some of the consequences of this non-uniqueness.

In Figure 6, curve 2 is identical to that in Fig. 4, and curve 5 has been calculated for the same set of parameters as curve 2 except that $\delta = 1 \times 10^{-5}$ cm, a five-fold decrease in δ . The curves labeled 2_{Ω} and 5_{Ω} represent the ohmic losses in the pore as a function of pore current density j . We see that although there is a modest increase in IR-free performance with decreased δ , there is also a significant increase in the film ohmic losses (curve 5_{Ω}). Thus, the net effect of reducing δ in this case would be a drastic decrease in predicted performance even though on an IR free basis both curves have nearly the same initial slope. Parenthetically, we remark that curves 2 and 5 are essentially due solely to activation overpotential; concentration overpotential accounts, generally, for less than 3% and 1% of the IR free overpotential for the respective curves.

In Figure 7, an analogous situation is plotted for anode-like conditions. The difference between curves 1 and 4 lies in the values chosen for δ and l as shown in Table 4. As discussed in Sec. 2.1 and as evident from the figure, both sets of values give the same initial slope for the IR free polarization curves. Because of the short length of the films in these calculations, ohmic losses are completely negligible. Curves 1 and 4 represent therefore, not just the IR free overpotential, but the total overpotential, activation plus concentration.

Figure 6. Ohmic losses (Ω) versus pore current density j and IR free polarization curves for cathodes. Curves are identified in Table 3.

Figure 7. Decomposition of anode IR free polarization curves (1 and 4) into activation (A) and concentration (C) overpotential versus current density j . Curves 1 and 4 are identified in Table 4.

The curves labeled with the subscripts A and C are the activation and concentration overpotentials plotted against current density j . The dramatic difference between curves 1A, 1C and 4A, 4C can be understood by calculating the limiting current densities j_{lim} for these cases. We know that j_{lim} will be proportional to the area covered by the thin film, $2\pi R\rho\ell$, and inversely proportional to the film thickness, δ . Thus:

$$\frac{j_{\text{lim},4}}{j_{\text{lim},1}} = \frac{\ell_4 \delta_1}{\ell_1 \delta_4} = \frac{1}{2}$$

Earlier, we remarked that

$$j_{\text{lim},1} = 650 \text{ mA/cm}^2,$$

so what we see in Figure 7 is just the rapid approach of curve 4 to its limiting asymptote at about 325 mA/cm^2 . Despite this much earlier onset of limiting behavior, curve 4, displays lower total polarization than curve 1 at given values of the current density below 260 mA/cm^2 . These results are a good example of the disparate types of behavior resulting from different film geometries which nevertheless produce identical initial performance.

2.3 Effects of Finite Electrical Conductivity of Electrodes

Because cathodes oxidize in situ to NiO, it may be necessary to account for the effects of finite electrode conductivity κ_E on the current and overpotential distribution in the pore. We designate the electrical potentials in the electrode (E) and in the electrolyte (liquid - L) as φ_E and φ_L . At each point z along the pore the potential drop across the double layer $\Delta\varphi$ can be written as:

$$\Delta\varphi = \varphi_E - \varphi_L = \Delta\varphi^0 - \eta \quad (2.31)$$

where $\Delta\varphi^0$ is the open circuit potential drop across the double layer and η is the total overpotential. In the one dimensional approximation to compute the variation in $\Delta\varphi$ with distance z along the pore we recognize first that φ_E and φ_L will both vary because of ohmic losses:

$$\left(\frac{d\varphi_E}{dz}\right)_\Omega = \frac{I_E}{\kappa_E a_E} \quad (2.32)$$

$$\left(\frac{d\varphi_L}{dz}\right)_\Omega = \frac{I_L}{\kappa_L a_L} \quad (2.33)$$

Here, I_E and I_L are the total currents in the electrode and in the electrolyte at point z along the pore axis, κ_E and κ_L are the electrode and electrolyte conductivities, and a_E and a_L are the cross sectional areas through which electrons and ions must flow. (The minus sign usually found in Ohm's Law is absent in Eqs. (2.32) and (2.33) because in our coordinate system current flows in the direction of decreasing z ; I_E and I_L are positive, scalar quantities.)

Because of the ohmic losses, the transfer current density i will vary along the pore. This in turn causes variations in the concentration overpotential which also contribute to the change in $\Delta\phi$ with z . We thus find

$$\frac{d\Delta\phi}{dz} = \frac{I_E}{\kappa_E a_E} - \frac{I_L}{\kappa_L a_L} - \frac{d\eta_C}{dz}, \quad (2.34)$$

but from Eq. (2.31) we also have

$$\frac{d\Delta\phi}{dz} = - \frac{d\eta}{dz} \quad (2.35)$$

We next obtain from Eqs. (2.4a), (2.34) and (2.35), the result

$$\frac{d\eta_S}{dz} = \frac{I_L}{\kappa_L a_L} - \frac{I_E}{\kappa_E a_E} \quad (2.36)$$

Now, from mass balance we see that

$$I_L + I_E = I = \text{constant} \quad (2.37)$$

and

$$\frac{dI_L}{dz} = 2\pi R_p i \quad (2.38)$$

where R_p is the pore radius.

Thus, Eqs. (2.36) and (2.38) give:

$$\frac{d^2 \eta_S}{dz^2} = 2\pi R_p \left(\frac{1}{\kappa_L a_L} + \frac{1}{\kappa_E a_E} \right) i. \quad (2.39)$$

In order to integrate Eq. (2.39), we note the following boundary conditions:

$$\left. \frac{d \eta_S}{dz} \right|_{z=0} = - \frac{I}{\kappa_E a_E}$$

$$\left. \frac{d \eta_S}{dz} \right|_{z=\ell} = \frac{I}{\kappa_L a_L}$$

where I is given by Eq. (2.30a). We are thus left, in general, with a somewhat different numerical problem than the one outlined in the previous section. We do note from Eq. (2.36) that there is an intermediate value of z for which

$$\left. \frac{d \eta_S}{dz} \right|_{z=\ell'} = 0 \quad (2.40)$$

Then from Eqs. (2.36) and (2.37) we see that

$$I_L(\ell') = \left(\frac{\kappa_L a_L}{\kappa_L a_L + \kappa_E a_E} \right) I.$$

If then we have the condition,

$$\frac{\kappa_E a_E}{\kappa_L a_L} \ll 1,$$

we will probably find $l' \approx l$, so that we can use Eq. (2.40) for an alternative boundary condition, thus formally reducing the problem to the one previously considered. Quantitative evaluation of this problem awaits a reliable estimate of κ_E . Further details will be provided in the final report.

3. INTEGRAL CELL MODEL

3.1 Introduction

In the integral cell model distributions of current density and cell temperature are computed for a given set of operating conditions (cell voltage, inlet gas compositions and temperatures, pressure). The current-overpotential relation of the DCM is applied on a local basis, and the cell treated as a whole through numerical integration. The model was developed in a previous report for the case of a single adiabatic cell with no inplane heat conduction. In the present study the analysis is extended to include cell stacking effects and inplane conduction.

The influence of inplane conduction was found to be too significant to be treated as an iterative correction to our existing numerical scheme. Instead, an implicit scheme is required to integrate the set of elliptic differential equations that arise with the inclusion of inplane heat conduction. Results are, of course, consistent with those obtained previously if the thermal conductivity in the plane of the cell is set equal to zero.

As in our previous report, we continue for reasons of simplicity to present numerical results based on a linear current-overpotential relation. No additional numerical problems are anticipated with inclusion of the refined DCM, and in fact some preliminary investigations have already been conducted using a current-overpotential relation that depends on local cell conditions.

3.2 Potential Balance Equation

We assume, as in our previous quarterly report, that the gas streams are constrained to flow in narrow channels, and that the anode and cathode are locally at the same temperature T_o (see Section 3.5). In the anode stream, we define fuel utilization parameters:

$$u_{H_2} = \frac{\dot{n}_{H_2}^o - \dot{n}_{H_2}}{\dot{n}_{H_2}^o}$$

$$u_{CO} = \frac{\dot{n}_{CO}^o - \dot{n}_{CO}}{\dot{n}_{CO}^o} \quad (\text{anode})$$

$$u_{CH_4} = \frac{\dot{n}_{CH_4}^o - \dot{n}_{CH_4}}{\dot{n}_{CH_4}^o}$$

Similarly in the cathode stream, we define an oxidant utilization parameter:

$$v_{CO_2} = \frac{\dot{n}_{CO_2}^o - \dot{n}_{CO_2}}{\dot{n}_{CO_2}^o} \quad (\text{cathode})$$

In these expressions $\dot{n}_i$ is the molar flow rate (per unit channel width) of species i ; and superscript 'o' denotes an inlet quantity.

If we assume uniform composition across the channel depth (see Ref. (7)), the composition terms of the Nernst equation (evaluated at the electrode surfaces) may be written in terms of the bulk gas stream utilizations. This gives a potential balance equation, Eq. (3.1), which can be solved for current density j as:

$$j = \left(V^{\ominus} + \frac{RT_o}{2F} \ln \left(\frac{K_c}{K_a} \right) + \frac{RT_o}{4F} \ln P - V \right) \left| 1/Z_{\text{tot}} \left(u_{H_2}, u_{CO}, u_{CH_4}, v_{CO_2}, T_o \right) \right| \quad (3.1)$$

where

$$K_a(u_{H_2}, u_{CO}, u_{CH_4}) = \left(\frac{x_{H_2O} x_{CO_2}}{x_{H_2}} \right)_a, \quad K_c(v_{CO_2}) = \left(\frac{1/2}{x_{O_2} x_{CO_2}} \right)_c$$

$V^{\ominus}$ and V are the standard state cell voltage and the actual cell voltage. The total impedance Z_{tot} is seen to be a function of local gas compositions and cell temperature, with this dependence determined from the differential cell model.

3.3 Mass Balance Equations

Although only H_2 is considered to undergo direct electrochemical conversion, anode CO and CH_4 act as fuels by supplying H_2 via the water-gas shift and methanation reactions, that is

We define a net fuel utilization parameter u_F as

$$u_F = \frac{1}{\dot{n}_{H_2}^o} \left(\dot{n}_{H_2}^o u_{H_2} + \dot{n}_{CO}^o u_{CO} + 4 \dot{n}_{CH_4}^o u_{CH_4} \right) \quad (3.4)$$

u_F represents the total number of moles of H_2 that are converted electrochemically, normalized by the number of moles of H_2 available at inlet. Note that the value of u_F can exceed unity if a sufficient quantity of H_2 is manufactured via reactions (3.2) and (3.3).

From mass balance considerations we can write the local relations

$$\frac{\partial u_F}{\partial x} = \frac{1}{2F\dot{n}_{H_2}^o} j \quad (\text{anode}) \quad (3.5)$$

$$\frac{\partial v_{CO_2}}{\partial y} = \frac{1}{2F\dot{n}_{CO_2}^o} j \quad (\text{cathode}) \quad (3.6)$$

where x and y are the anode and cathode flow directions, respectively.

If reactions (3.2) and (3.3) are in equilibrium in the anode stream, we have the equilibrium constraints

$$K_s = \frac{x_{H_2} x_{CO_2}}{x_{H_2O} x_{CO}} = K_s \left(u_{H_2}, u_{CO}, u_{CH_4}, \dot{n}_i^o \right) \quad (3.7)$$

$$K_m = \frac{x_{CO_2}^4 x_{H_2}^2 P^2}{x_{CH_4}^2 x_{H_2O}^2} = K_m(u_{H_2}, u_{CO}, u_{CH_4}, \dot{n}_i^o) \quad (3.8)$$

As indicated, the equilibrium expressions can be written in terms of the anode utilizations and the inlet molar flow rates of the constituents $\dot{n}_i^o$ (the inlet flow rates must satisfy equilibrium). Given K_s, K_m , with u_F obtained from integration of Eq. (3.5), Eqs. (3.4), (3.7) and (3.8) can be solved for the anode utilizations $u_{H_2}, u_{CO}, u_{CH_4}$.

3.4 Stack Heat Transfer

Cell performance in a stack is influenced by heat transfer between adjacent cells. We will consider the case of a single cell operating in an infinitely large stack of identical cells, for which symmetry conditions dictate that the net heat exchange between a given cell and neighboring cells is zero. Stacking effects will be incorporated into the analysis by treating the connective hardware between adjacent cells as a crossflow heat exchanger with negligible thermal resistance normal to the gas flows, thereby assuming that all of the cell hardware is locally at the same temperature. The validity of this assumption is demonstrated in the following section.

3.5 Effect of Finite Hardware Conductivity

Figures 8a, b depict the arrangement of repeating stack elements and the analogous thermal network representing a given location in the plane of the cell. Account is taken only of heat flow normal to the stack (in the z-direction) for purposes of the following approximate calculation.

Figure 8. a) Repeating stack elements,
b) Analogous thermal network
for a point in the cell plane.

Here U is a hardware unit surface conductance coefficient, h^* a gas/hardware interface unit surface conductance coefficient, both with units $\text{watts/cm}^2 \text{K}$. The subscripts in Figure 8b correspond to elements of stack hardware as follows:

U_{sand} - electrode/tile sandwich conductance, equal to $1 / \left(\frac{1}{U_a} + \frac{1}{U_c} + \frac{1}{U_t} \right)$ with U_a, U_c, U_t the anode, cathode, and electrolyte tile conductances, respectively

U_{sp}	-	separator plate conductance
U_{ka}, U_{kc}	-	anode, cathode current collector conductances
h_a^*, h_c^*	-	" " gas/hardware surface conductances
$\dot{Q}_a, \dot{Q}_c$	-	anode, cathode heat releases (have opposite signs)
T_{oa}, T_{oc}	-	" " gas/electrode interface temperatures
T_{spa}, T_{spc}	-	" " gas/separator plate interface temperatures
T_{ma}, T_{mc}	-	" " mean gas temperatures
$\bar{A}_a, \bar{A}_c$	-	" " ratios of gas/hardware interface area to cell area (The factors of 1/2 appear because we assume, somewhat crudely, that 50% of the interface is at the electrode temperature, 50% at the separator plate temperature)

It is obvious that if all of the hardware conductances become infinitely large, then the stack hardware will assume a uniform local temperature (making this approximation, if justified, will considerably simplify the analysis). Our strategy in examining the importance of finite hardware conductivity is to solve the network of Figure 8b based on realistic values of hardware geometry and conductivity, and to compare the results thus obtained with those based on infinite hardware conductivity, over a range of gas stream temperatures.

The equations governing $T_{oa}, T_{oc}, T_{spa}, T_{spc}$ are conveniently written in matrix form as:

$$\underline{U} \underline{T} = \underline{\hat{Q}} \quad (3.9a)$$

where

$$\tilde{U} = \begin{pmatrix} U_{sand} + U_{ka} + \frac{1}{2} \bar{A}_{aa} h_a^* & -U_{sand} & -U_{ka} & 0 \\ -U_{sand} & U_{sand} + U_{kc} + \frac{1}{2} \bar{A}_{aa} h_a^* & 0 & -U_{kc} \\ -U_{ka} & 0 & U_{sp} + U_{ka} + \frac{1}{2} \bar{A}_{aa} h_a^* & -U_{sp} \\ 0 & -U_{kc} & -U_{sp} & U_{sp} + U_{kc} + \frac{1}{2} \bar{A}_{cc} h_c^* \end{pmatrix} \quad (3.9b)$$

$$\tilde{T} = \begin{pmatrix} T_{oa} \\ T_{oc} \\ T_{spa} \\ T_{spc} \end{pmatrix} \quad (3.9c)$$

$$\hat{\tilde{Q}} = \begin{pmatrix} Q_a + \frac{1}{2} \bar{A}_{aa} h_a^* T_{ma} \\ Q_c + \frac{1}{2} \bar{A}_{cc} h_c^* T_{mc} \\ \frac{1}{2} \bar{A}_{aa} h_a^* T_{ma} \\ \frac{1}{2} \bar{A}_{cc} h_c^* T_{mc} \end{pmatrix} \quad (3.9d)$$

In the limit of infinite hardware conductance, this system reduces to a single equation for the hardware temperature T_o :

$$T_o = \frac{\dot{Q}_a + \dot{Q}_c + \bar{A}_a h_a^* T_{ma} + \bar{A}_c h_c^* T_{mc}}{\bar{A}_a h_a^* + \bar{A}_c h_c^*} \quad (3.10)$$

Denoting thermal conductivity λ and thickness (in the z-direction) L for each component, with subscripts as above, we have:

$$U_{sp} = \frac{\lambda_{sp}}{L_{sp}}, \quad U_{ka} = \frac{1}{2} \frac{\lambda_{ka}}{L_{ka}}, \quad U_{kc} = \frac{1}{2} \frac{\lambda_{kc}}{L_{kc}}, \quad U_{sand} = \left(\frac{L_a}{\lambda_a} + \frac{L_c}{\lambda_c} + \frac{L_k}{\lambda_k} \right)^{-1}$$

where the factor of $\frac{1}{2}$ in U_{ka} , U_{kc} is based on a 50% electrode/current collector and separator plate/current collector contact area.

Realistic values for these quantities are listed in Table 5.

Table 5. Numerical values for cell hardware heat transfer parameters.

<u>Component</u>	<u>Material</u>	<u>λ (watt/cmK)</u>	<u>L(cm)</u>
separator plate	stainless steel	.22	.03
anode current collector	"	.22	.2
cathode current collector	"	.22	.2
anode	Ni	.78	.08
cathode	NiO	.009	.04
tile	molten salt & LiAlO ₂ matrix	.02	.18

In addition, we choose as typical values:

$$\bar{A}_a = \bar{A}_c = 2$$

$$\dot{Q}_a = -.15 \frac{\text{watt}}{\text{cm}^2}$$

$$\dot{Q}_c = +.2 \frac{\text{watt}}{\text{cm}^2} \text{ based on a local current density of } 200\text{mA/cm}^2$$

$$h_a^* = .05 \frac{\text{watt}}{\text{cm}^2 \text{ } ^\circ\text{K}}$$

$$h_c^* = .02 \frac{\text{watt}}{\text{cm}^2 \text{ } ^\circ\text{K}} \text{ based on typical gas stream compositions, Nusselt modulus based on channel depth } = 4$$

As a basis for comparison we choose the heat fluxes absorbed by the gas streams, that is

$$\dot{q}_a = \frac{1}{2} \bar{A}_a h_a^* (T_{oa} - T_{ma}) + \frac{1}{2} \bar{A}_a h_a^* (T_{spa} - T_{ma})$$

$$\dot{q}_c = \frac{1}{2} \bar{A}_c h_c^* (T_{oc} - T_{mc}) + \frac{1}{2} \bar{A}_c h_c^* (T_{spc} - T_{mc})$$

Figure 9 shows these heat fluxes as computed using Eqs. (3.9) (solid lines) and using Eq. (3.10) (dashed lines), with numerical parameters and conditions listed in Table 5, and using $T_{ma} = 1000\text{K}$ while varying T_{mc} between 800 and 1200K. The approximate results are no more than 3% in error except in the immediate vicinity of $T_{ma} = T_{mc}$, where the magnitudes of the heat fluxes are of the order of the heat release terms. There are negligible compared with the heat flux exchanged between the gas streams when they differ by more than a few degrees (a condition that

Figure 9. Local heat addition to gas streams based on actual and infinite hardware thermal conductivity.

prevails nearly everywhere in the cell). In fact, it is a lucky coincidence that the curves intersect in the region for which T_{ma} is about 30K higher than T_{mc} , which is approximately the case over much of the cell for all of the cases investigated thus far.

These results indicate that neglecting the thermal resistance of the stack hardware normal to the gas flows introduces no significant error, so that we are justified in using a uniform local hardware temperature T_o .

3.6 Hardware Energy Balance with Inplane Conduction

With the inclusion of heat conduction in the plane of the stack hardware, the magnitude of the heat flux transferred locally to the gas streams is equal to the sum of the local heat release and the net heat flow convergent on a given point due to inplane conduction. The equation governing the local hardware temperature T_o is then:

$$\dot{Q} + \dot{Q}_{ip} = \bar{A}_a h_a^* (T_o - T_{ma}) + \bar{A}_c h_c^* (T_o - T_{mc}) \quad (3.11)$$

Where $\dot{Q} = \dot{Q}_a + \dot{Q}_c$ is the net heat release per unit cell area (see below).

Eq. (3.6) is identical to Eq. (3.10), except for the addition of the inplane conduction term $\dot{Q}_{ip}$, given by

$$\dot{Q}_{ip} = \Sigma (L_n \lambda_n) \nabla^2 T_o \quad (3.12)$$

The summation is over all hardware components to give an effective hardware inplane thermal conductivity, that is:

$$\Sigma (L_n \lambda_n) = L_a \lambda_a + L_c \lambda_c + L_t \lambda_t + L_{sp} \lambda_{sp} + \gamma_{ka} L_{ka} \lambda_{ka} + \gamma_{kc} L_{kc} \lambda_{kc}$$

with subscripts defined as in Section 3.5. γ_{ka} , γ_{kc} are fractional ratios that depend on current collector geometry, chosen such that the last two terms represent effective current collector inplane thermal conductivities.

The net heat release $\dot{Q}$ includes the net electrochemical heat release (subscript 'e') and the net heat release due to chemical reaction (subscript 'r') in the anode stream, so that

$$\dot{Q} = \dot{Q}_{ae} + \dot{Q}_{ce} + \dot{Q}_{ar} = \dot{Q}_e + \dot{Q}_{ar} \quad (3.13)$$

$\dot{Q}_e$ is related to the current density j by

$$\dot{Q}_e = -j \left(\frac{\Delta H_{H_2O}(T_o)}{2F} + V \right) \quad (3.14)$$

$\dot{Q}_{ar}$ is proportional to the rate at which reactants are used up in the anode stream, or

$$\dot{Q}_{ar} = \frac{d\dot{n}_{CO}}{dx} \Delta H_s(T_o) + \frac{d\dot{n}_{CH_4}}{dx} \Delta H_m(T_o) \quad (3.15)$$

with ΔH_{H_2O} the heat of formation of H_2O , ΔH_s and ΔH_m the enthalpy changes (per mole CO , CH_4) associated with the water-gas shift and methanation reactions (Eqs. (3.2) and (3.3)). Because gas phase reactions are presumably catalyzed by the Ni electrode surface, the heat is evolved at the local hardware temperature T_o .

3.7 Energy Addition to Gas Streams

In a previous report we had developed a relation governing the change in the mean temperature of a flowing gas mixture as heat and mass are added at a boundary, assuming heat capacity of each component to be independent of temperature. Applying this result to the anode and cathode gas streams yields the equations:

$$\frac{\partial T_{ma}}{\partial x} = \frac{1}{\dot{n}_a c_{pa}} \left\{ \bar{A}_a h_a^* + \sum (g_i c_{pi})_a \right\} (T_o - T_{ma}) \quad (3.16)$$

$$\frac{\partial T_{mc}}{\partial y} = \frac{1}{\dot{n}_c c_{pc}} \left\{ \bar{A}_c h_c^* + \sum (g_i c_{pi})_c \right\} (T_o - T_{mc}) \quad (3.17)$$

The g_i are molar fluxes (moles per unit cell area) of transferred species i with heat capacity c_{pi} , assumed to enter the gas streams at the hardware temperature T_o . The unit surface conductance coefficients h_a^* , h_c^* are normalized with respect to gas/hardware interface area, and must therefore be multiplied by the area ratios $\bar{A}_a$, $\bar{A}_c$ (ratio of interface area/cell area). $\dot{n}$ and c_p are molar flow rate and heat capacity for the bulk streams.

We note that the molar fluxes g_i result (in either stream) from mass transfer due to chemical reaction at the electrode surfaces, but that in the anode stream there is an additional contribution due to heterogeneous chemistry associated with the water-gas shift and methanation reactions.

3.8 Numerical Solution

We outline here the numerical scheme used to integrate the required set of partial differential equations.

The equations are summarized below:

$$\frac{\partial u_F}{\partial x} = \frac{1}{2F\dot{n}_{H_2}} j \left(u_{H_2}, u_{CO}, u_{CH_4}, v_{CO_2}, T_o \right) \quad (3.5)$$

$$K_s(T_{ma}) = K_s(u_{H_2}, u_{CO}, u_{CH_4}) \quad (3.7)$$

$$K_m(T_{ma}) = K_m(u_{H_2}, u_{CO}, u_{CH_4}) \quad (3.8)$$

$$u_F = u_F(u_{H_2}, u_{CO}, u_{CH_4}) \quad (3.4)$$

$$\frac{\partial v_{CO_2}}{\partial y} = \frac{1}{2F\dot{n}_{CO_2}} j \left(u_{H_2}, u_{CO}, u_{CH_4}, v_{CO_2}, T_o \right) \quad (3.6)$$

$$\dot{Q} + \dot{Q}_{ip} = \bar{A} h_a^* (T_o - T_{ma}) + \bar{A} h_c^* (T_o - T_{mc}) \quad (3.11)$$

$$\dot{Q} = -j \left(\frac{\Delta H_{2O}(T_o)}{2F} + v \right) + \frac{d\dot{n}_{CO}}{dx} \Delta H_s(T_o) + \frac{d\dot{n}_{CH_4}}{dx} \Delta H_m(T_o) \quad (3.14-15)$$

$$\dot{Q}_{ip} = \sum (L_n \lambda_n) \nabla^2 T_o \quad (3.12)$$

$$\frac{\partial T_{ma}}{\partial x} = \frac{1}{\dot{n}_a C_{pa}} \left\{ \bar{A} h_a^* + \sum (g_i C_{pi})_a \right\} (T_o - T_{ma}) \quad (3.16)$$

$$\frac{\partial T_{mc}}{\partial y} = \frac{1}{\dot{n}_c C_{pc}} \left\{ \bar{A} h_c^* + \sum (g_i C_{pi})_c \right\} (T_o - T_{mc}) \quad (3.17)$$

with boundary conditions:

inlet gas conditions -

$$x = 0 : u_{H_2} = u_{CO} = u_{CH_4} = 0, T_{ma} = T_{ma}^0$$

$$y = 0 : v_{CO_2} = 0, T_{mc} = T_{mc}^0$$

edges of hardware insulated -

$$\frac{\partial T_o}{\partial x} = 0 \text{ at } x = 0, l$$

$$\frac{\partial T_o}{\partial y} = 0 \text{ at } y = 0, l$$

The equations are obviously nonlinear; h^* , $\dot{n}$, c_p are functions of gas stream composition, Q and the g_i are functions of composition, temperature, and local current density, and local current density is a nonlinear function of composition and temperature. Eq. (3.11) is elliptic due to the presence of the inplane conduction term.

In general, nonlinear elliptic equations cannot be integrated directly whereas if the equations are linear numerical solution is straightforward. Expression of linear elliptic equations in finite difference form yields a system of linear algebraic equations that are solved by inverting a (typically large) matrix. These considerations suggest an iterative scheme in which the nonlinear terms are replaced by numerical values, assumed initially but computed in subsequent iterations, thereby repeatedly solving a directly integrable set of linear differential equations. When we have relaxed to the correct solution these linear equations will represent the nonlinear system we ultimately wish to solve.

More specifically, the equations are written in finite difference form using backward difference operators for derivatives in the gas streams, centered difference operators for the ∇^2 terms, e.g.:

$$\left. \frac{\partial T_{ma}}{\partial x} \right|_{L,M} = \frac{T_{ma_{L,M}} - T_{ma_{L,M-1}}}{\Delta x}, \quad \frac{\partial T_{mc}}{\partial y} = \frac{T_{mc_{L,M}} - T_{mc_{L-1,M}}}{\Delta y}$$

$$\nabla^2 T_o = \frac{T_o_{L+1,M} + T_o_{L-1,M} - 2T_o_{L,M}}{\Delta x^2} + \frac{T_o_{L,M+1} + T_o_{L,M-1} - 2T_o_{L,M}}{\Delta y^2}$$

where the indices M & L correspond to the x & y directions, respectively.

In principle, if we represent the x-y plane of the stack with NxN mesh points, then the finite difference representations result in a system of $7N^2$ simultaneous equations (5 differential equations and 2 equilibrium constraints to be satisfied at each mesh point). Fortunately, computation can be simplified by exploiting the weakness of the temperature dependence of the mass balance equations (Eqs. (3.5), (3.6)) and solving them separately given a prescribed temperature distribution. Because the mass balance equations are not elliptic they can be solved using an explicit (marching) scheme. On the other hand, the temperature equations (Eqs. (3.11), (3.16), (3.17)) demand an implicit solution because Eq. (3.11) is elliptic, and it is strongly coupled with Eqs. (3.16), (3.17).

The foregoing ideas are incorporated into a numerical scheme summarized schematically in Fig. 10. The indices k, m identify inner and outer iteration loops, respectively. Calculation begins with assumed distribution of hardware temperature T_o and current density j. The mass balance equations (Eqs. (3.5), (3.6)) are then integrated by marching to give the anode and

Figure 10. Flowchart for numerical scheme.

cathode utilization parameters u_F , v_{CO_2} . At each mesh point the local anode utilizations u_{H_2} , u_{CO} , u_{CH_4} are computed (using a Newton-Raphson iteration) via Eqs. (3.4), (3.7), (3.8), with the equilibrium constants evaluated at the local anode stream temperature (assumed equal to the inlet temperature for the first iteration step). Using these distributions of utilization and assumed cell temperature, a new distribution of current density is computed from the potential balance relation. The procedure is iterated to convergence (iteration level k).

Given a computed distribution of current density and a prescribed temperature distribution, all of the nonlinear coefficients of the temperature equations (n , g_i , h^* , c_p , $\dot{Q}$) can be computed. The system of $3N^2$ linear algebraic equations corresponding to the finite difference representations of Eqs. (3.11), (3.16), (3.17) is then solved, using standard matrix techniques, to compute new distributions of T_o , T_{ma} , T_{mc} . The entire procedure iterated to convergence (iteration level m).

3.9 Arbitrary Flow Geometries

The numerical procedure discussed in the previous section is readily adapted to arbitrary flow geometries (e.g., counterflow, u-flow). The streamwise derivatives must be evaluated in the local flow directions, making for potentially more complex bookkeeping, but no additional computational problems.

3.10 Results

(1) With Heat Transfer

The numerical scheme has been completely assembled (using a linear current-overpotential relation), but at present numerical solution is only practical with the use of unreasonably coarse meshes. Temperature distributions obtained thus far with no inplane conduction are consistent with those computed using a different numerical procedure, presented in a previous report. The inclusion of inplane heat conduction is seen to result in more uniform temperature distributions, as would be expected. Results are not presented here because numerical integration error renders them too approximate to be physically realistic. Work is currently underway to upgrade the efficiency of our matrix inversion subroutine, which will allow much improved numerical accuracy.

Table 6. Conditions for calculated results presented in Figures 9, 11.

	<u>Anode Stream</u>	<u>Cathode Stream</u>
Inlet gas Composition	20% H ₂ , 6.2% H ₂ O, 10% CO ₂ , 17% CO, 46% N ₂ , 0.8% CH ₄	30% CO ₂ 15% O ₂ 55% N ₂
Inlet molar flow rates	.07 moles/sec	.15 moles/sec
T=923°K, P= 1 atm, z _{TOT} = 1.025 ohm/cm ²	Cell dimensions: 1 x 1 m ²	

(2) Without Heat Transfer

Isothermal cells are easily treated with the existing numerical scheme (no elliptic equations need be solved). Performance curves are presented in Fig. 11. for the case of a $1 \times 1 \text{ m}^2$ cell running at 923K, using an anode feed gas composition typically produced by a low BTU coal gasifier, cathode feed gas a 70-30% air CO_2 mixture, under operating conditions listed in Table 6. Calculations were performed with anode CO and CH_4 taken to be inert, with CO in equilibrium and CH_4 inert, and with CO and CH_4 in equilibrium. A linear current-overpotential relation was used throughout.

Figure 11. indicates an improvement in performance due to enrichment of anode H_2 via the water-gas shift and methane reformation reactions. Although the gains appear modest, the following points should be remembered in interpreting these results:

- The performance curves are all computed at the same inlet gas flow rates. As a result, utilizations vary widely among the cases investigated, as evidenced by Fig. 12. With CO and CH_4 frozen in the anode stream, the maximum attainable average current density (corresponding to 100% H_2 utilization) is less than 270 mA/cm^2 , whereas with CO and CH_4 in equilibrium 270 mA/cm^2 is achieved with 52% H_2 utilization; the equilibrium curve could have been extended to much higher current densities than indicated in Fig. 11. with conversion of this excess fuel.
- Although essentially all of the CH_4 is converted at average current densities above 200 mA/cm^2 , less than 1% CH_4 is present at inlet, so that the effect of CH_4 utilization is not likely to be pronounced. The maximum possible increase

Figure 11. Performance curves for isothermal cell with constant inlet gas flow rates.

Figure 12. Net anode utilizations for isothermal cell with constant inlet gas flow rates.

in average current density is 45 mA/cm^2 , based on 100% CH_4 conversion with all of the resultant H_2 converted electrochemically. Only 10% of this increase is realized because most of the H_2 produced is not converted.

Also included is a sample calculation of current density and utilization distributions (Table 7). As discussed in previous reports, maximum current densities are seen at the inlet corner where the gas streams are freshest, minimum current densities at the outlet corner where the fuel and oxidant have been depleted. Of interest in the equilibrium case shown is the rapidity with which CH_4 is consumed in the anode stream, due to the combined effect of H_2 depletion and H_2O production in driving the methanation reaction, Eq. (3.3), toward utilization of CH_4 .

TABLE 7. Sample calculation of isothermal current density and utilization distributions for full CO and CH₄ equilibria. Anode gas flows left to right, cathode gas down the page.

OPEN CIRCUIT VOLTAGE=1.072

FULL EQUILIBRIUM IN ANODE STREAM

CELL VOLTAGE=0.80

AVG CURRENT DENSITY(AMP/CM**2)=0.203

NET ANODE UTILIZATIONS- H2:0.385 CO:0.261 CH4:0.949

NET CATHODE UTILIZATIONS- CO2:0.234

CURRENT DENSITY, AMP/CM**2

0.249	0.236	0.225	0.216	0.207	0.199	0.192	0.185	0.179	0.173
0.248	0.236	0.225	0.215	0.206	0.199	0.191	0.185	0.178	0.173
0.247	0.235	0.224	0.214	0.206	0.198	0.191	0.194	0.178	0.172
0.246	0.234	0.223	0.214	0.205	0.197	0.190	0.184	0.177	0.172
0.245	0.233	0.222	0.213	0.204	0.197	0.190	0.183	0.177	0.171
0.244	0.232	0.221	0.212	0.204	0.196	0.189	0.182	0.176	0.171
0.243	0.231	0.220	0.211	0.203	0.195	0.188	0.182	0.176	0.170
0.242	0.230	0.219	0.210	0.202	0.195	0.190	0.181	0.175	0.170
0.241	0.229	0.219	0.209	0.201	0.194	0.197	0.181	0.175	0.169
0.239	0.228	0.217	0.209	0.200	0.193	0.196	0.180	0.174	0.168

ANODE H2 CONVERSIONS

0.037	0.077	0.119	0.161	0.202	0.243	0.282	0.320	0.355	0.391
0.036	0.077	0.118	0.160	0.202	0.242	0.281	0.319	0.355	0.390
0.036	0.076	0.118	0.160	0.201	0.241	0.280	0.318	0.354	0.389
0.036	0.076	0.117	0.159	0.200	0.240	0.279	0.316	0.353	0.387
0.036	0.076	0.117	0.158	0.199	0.239	0.278	0.315	0.351	0.386
0.036	0.075	0.116	0.158	0.198	0.238	0.277	0.314	0.350	0.385
0.036	0.075	0.116	0.157	0.197	0.237	0.275	0.313	0.348	0.383
0.035	0.075	0.115	0.156	0.196	0.236	0.274	0.311	0.347	0.381
0.035	0.074	0.115	0.155	0.195	0.235	0.273	0.310	0.345	0.380
0.035	0.074	0.114	0.154	0.194	0.233	0.271	0.308	0.344	0.379

ANODE CO CONVERSIONS

0.012	0.031	0.055	0.082	0.111	0.141	0.172	0.204	0.235	0.267
0.012	0.031	0.054	0.081	0.110	0.140	0.171	0.203	0.234	0.266
0.012	0.030	0.054	0.081	0.109	0.139	0.170	0.202	0.233	0.265
0.012	0.030	0.054	0.080	0.109	0.139	0.169	0.201	0.232	0.264
0.011	0.030	0.053	0.080	0.108	0.138	0.168	0.200	0.231	0.262
0.011	0.030	0.053	0.079	0.108	0.137	0.168	0.198	0.230	0.261
0.011	0.030	0.053	0.079	0.107	0.136	0.167	0.197	0.229	0.259
0.011	0.030	0.052	0.078	0.106	0.135	0.166	0.196	0.227	0.258
0.011	0.029	0.052	0.078	0.105	0.135	0.165	0.195	0.226	0.257
0.011	0.029	0.052	0.077	0.105	0.134	0.163	0.194	0.224	0.255

ANODE CH4 CONVERSIONS

0.292	0.490	0.629	0.727	0.797	0.849	0.907	0.915	0.935	0.952
0.291	0.489	0.627	0.726	0.796	0.848	0.906	0.914	0.935	0.951
0.290	0.488	0.626	0.724	0.795	0.847	0.905	0.913	0.935	0.951
0.289	0.486	0.625	0.723	0.794	0.846	0.904	0.913	0.934	0.950
0.288	0.485	0.623	0.721	0.793	0.845	0.903	0.912	0.933	0.949
0.287	0.483	0.621	0.720	0.791	0.844	0.902	0.911	0.933	0.949
0.286	0.482	0.620	0.718	0.790	0.842	0.901	0.910	0.932	0.948
0.284	0.480	0.618	0.717	0.788	0.841	0.900	0.909	0.931	0.947
0.283	0.479	0.616	0.715	0.787	0.840	0.899	0.908	0.930	0.947
0.282	0.477	0.615	0.713	0.785	0.838	0.898	0.907	0.929	0.946

CATHODE CO2 CONVERSIONS

0.029	0.027	0.026	0.025	0.024	0.023	0.022	0.021	0.021	0.020
0.057	0.054	0.052	0.050	0.048	0.046	0.044	0.043	0.041	0.040
0.086	0.081	0.079	0.074	0.071	0.069	0.066	0.064	0.062	0.060
0.114	0.108	0.103	0.099	0.095	0.091	0.088	0.085	0.082	0.080
0.142	0.135	0.129	0.123	0.119	0.114	0.110	0.106	0.103	0.099
0.170	0.162	0.154	0.148	0.142	0.137	0.132	0.127	0.123	0.119
0.198	0.188	0.180	0.172	0.165	0.159	0.154	0.148	0.143	0.139
0.226	0.215	0.205	0.196	0.189	0.182	0.175	0.169	0.164	0.158
0.254	0.241	0.230	0.221	0.212	0.204	0.197	0.190	0.184	0.178
0.282	0.267	0.255	0.245	0.235	0.226	0.218	0.211	0.204	0.197

4. REFERENCES

1. A. C. Riddiford, "Stationary Current-Voltage Curves for Complex Electrode Processes", J. Chem. Soc. (London) 1175 (1960)
2. Physical Sciences, Inc., "Performance Model for Molten Carbonate Fuel Cells", Quarterly Report for 5 July-5 October 1978, PSI TR-149a.
3. Institute for Gas Technology, "Fuel Cell Research on Second-Generation Molten-Carbonate Systems", Vol. II, Project 8984 Final Report for 1 July 1976-30 September 1977.
4. Institute for Gas Technology, "Fuel Cell Research on Second-Generation Molten-Carbonate Systems", Vol. II, Project 8984 Quarterly Report for 1 July-30 September, 1976.
5. Institute for Gas Technology, "Fuel Cell Research on Second-Generation Molten-Carbonate Systems", Project 8984 Quarterly Report for 1 January-31 March 1977.
6. P. Ang and A. F. Sammells, "Influence of Electrolyte Composition on Electrode Kinetics in the Molten Carbonate Fuel Cell", to appear in Proc. Second Intl. Symp. on Molten Salts, Electrochemical Society, Princeton, N. J. 1979, and A. F. Sammells and P. P. Ang, "Anode Electrochemistry in Selected Molten Carbonate Melts", paper presented at the Molten Carbonate Fuel Cell Workshop, Oak Ridge, TN, 1978.
7. Physical Sciences, Inc., "Performance Model for Molten Carbonate Fuel Cells", Quarterly Report for 5 October 1978-5 January 1979, PSI TR-163.
8. A. J. Appleby and S. Nicholson, "The Reduction of Oxygen in Molten Lithium Carbonate", J. Electroanal. Chem. 53, 105 (1974); "Reduction of Oxygen in Alkali Carbonate Melts", J. Electroanal. Chem. 83, 309 (1977).

Distribution List for Quarterly Report

Under Contract #DE-AC-03-79ET11322

Dr. John Ackerman
Argonne National Laboratory
Argonne, IL 60439

Dr. A. Borucka
Borucka Research Company
60 Chestnut Street
Livingston, NJ 07039

Professor E. Yeager
Case Western Reserve
Electrochemistry Laboratory
University Circle
Cleveland, OH 44106

Mr. J. Huff
DRDME-EC
Department of the Army
U.S. Army Mobility Equipment
Research and Development Command
Fort Belvoir, VA 22060

Mr. Gary E. Voelker
Department of Energy
20 Massachusetts Ave., NW
Washington, D. C. 20545

Mr. Martin Zlotnick
Department of Energy
20 Massachusetts Ave., NW
Washington, D. C. 20545

Mr. Arnold P. Fickett
Electric Power Research Institute
3412 Hillview Avenue
P. O. Box 10412
Palo Alto, CA 94304

Mr. E. Gillis
Electric Power Research Institute
3412 Hillview Avenue
P. O. Box 10412
Palo Alto, CA 94304

Dr. Theodore R. Beck
Electrochemical Technology Corp.
3935 Leary Way, N. W.
Seattle, WA 98107

Dr. Bernard S. Baker
Energy Research Corporation
3 Great Pasture Road
Danbury, CT 06810

Mr. J. W. Harrison
General Electric Company DECP
50 Fordham Road
Wilmington, MA 01887

Dr. D. Chatterji, Manager
Electrochemistry Branch
General Electric Research &
Development Center
P. O. Box 8
Bldg. K-1, Room 2A54
Schenectady, NY 12301

Dr. J. Giner, President
Giner, Inc.
14 Spring Street
Waltham, MA 02154

Mr. Leonard Marianowski
Institute of Gas Technology
3424 S. State Street
Chicago, IL 60616

Page 2 of Distribution List for Quarterly Report

Under Contract #DE AC 03-79ET11322

Mr. Ron Guidotti
Montana Energy and MHD Research
and Development Institute, Inc.
P. O. Box 3809
Butte, MT 59701

Mr. Joseph M. King
Program Manager
United Technologies Corporation
P. O. Box 109
South Windsor, CT 06074

Dr. J. J. Rasmussen
Montana Energy and MHD Research
and Development Institute, Inc.
P. O. Box 3809
Butte, MT 59701

Dr. D. L. Johnson
Technological Institute
Department of Materials Science
Northwestern University
Evanston, IL 60201

Mr. Leslie M. Ferris
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

Dr. Kurt Wray
Physical Sciences Inc.
30 Commerce Way
Woburn, MA 01801

Mr. Leonard Nanis
Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, CA 94025

Mr. R. D. Weaver
Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, CA 94205