PERFORMANCE MODEL FOR MOLTEN
CARBONATE FUEL CELLS

MASTER

Quarterly Report for

5 October 1978 through 5 January 1979

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

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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, and convective heat transfer. 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, neglecting the effects of in-plane heat conduction.

SUMMARY

This report is a description of work performed under U. S. Department of Energy Contract No. ET-78-C-03-2083 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 equilibrium, and heat transfer from the cell hardware to the flowing gas streams. The basic pore geometry being used is that of the cylindrical thin film model employed previously.

For the DCM, emphasis this quarter was placed on combining the various phenomenological equations in such a way as to enhance mathematical tractability without sacrificing the essential physical description embodied in the equations. Two approaches were initiated this quarter.

The first, which occupied most of the work on the DCM, focused on developing numerical solutions to the set of equations obtained by the justifiable neglect of gas phase diffusion in the pore and by linearizing the terms depending on liquid phase concentrations. This latter approximation also appears well justified for most circumstances, but will receive additional future assessment. The numerical integration of the derived equation proceeds with ease and speed insofar as generating single electrode polarization curves for given conditions is concerned.

Because of the large number of times that the DCM's output will probably have to be computed when performing an integral cell calculation of current and temperature distribution, faster numerical analysis will likely be required for the DCM. A semi-analytic approach that we have also begun to investigate has produced encouraging preliminary results with respect to accuracy. The speed of this approach remains to be investigated.

Regarding the ICM, a quantitative heat transfer scheme was devised, programmed and combined with our earlier mass balance scheme in order to simultaneously calculate the cell current density and temperature distributions. The scheme accounts for heat transferred conductively (and radiatively, if necessary) into the anode and cathode gas streams and for the thermal effects of the addition of mass at the electrode temperature to the gas streams at different temperatures. Presently, the cell temperature distribution is calculated while neglecting the effects of in-plane heat conduction through the cell hardware. That effect will be considered in the next quarter of the program.

As an indicator of the internal consistency of the present energy transfer scheme, conservation of energy is checked on a total cell basis. The results obtained demonstrate energy conservation identically.

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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 three main components: a differential cell model (DCM) and two integral cell models, (ICM-I and ICM-II).

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.

The integral cell models treat cell behavior on an overall basis, accounting for fuel and oxidant utilization and heat transfer within the cell. In the ICM-I the output of the DCM is combined with treatment of gas phase mass balance and convective heat transfer in order to calculate current density and temperature distributions in the cell. Heat conduction in the plane of the cell is not included in the ICM-I. This effect will be incorporated in the ICM-II which is otherwise essentially identical with ICM-I.

2. DIFFERENTIAL CELL MODEL

2.1 Summary of Basic Equations

This quarter we continued the mathematical analysis of the thin film model of a porous electrode presented in our last Quarterly Report.¹ Before presenting the necessary equations, it may be helpful to recall the basic geometry of the model.

In Fig. 1, a sketch of the thin film model of an electrode pore is presented. The pore is taken to be a cylinder of radius R_p and is covered by a thin film of thickness δ for a length ℓ along the pore wall. The axial coordinate along the pore is z and r is the radial coordinate.

Fig. 1 Thin Film Model of an Electrode Pore

Now, for an assumed electrode half-reaction mechanism (one will be discussed shortly), a Butler-Volmer type equation can be derived that will relate the transfer current density i at a point on the pore surface to the total local overpotential η_T and local concentrations of reactants and products "at" the electrode surface. Using the various equilibrium relationships that hold in the melt, this equation for i can be expressed in terms of concentrations of dissolved neutral gas species. As an example, for the cathode, the equation will have the following form:

$$i = i_o \left[f(C_{O_2}, C_{CO_2}) \exp(\alpha_c \eta_T F/RT) - g(C_{O_2}, C_{CO_2}) \exp(-\alpha_a \eta_T F/RT) \right] \quad (1)$$

where i_o is the exchange current, F is the Faraday, R is the gas constant and T is the temperature; f and g are functions of the concentrations C of the dissolved gases whose particular form depends on the assumed reaction mechanism. The same is true of the effective transfer coefficients α_c and α_a .

The "surface" concentrations C can, in turn, be expressed in terms of concentrations in the melt at the gas/electrolyte interface by integrating the simple equation governing diffusion of reactants and products in the melt:

$$n F r D \frac{dC}{dr} = \gamma R_p i \quad (2)$$

where $\gamma = -1$ for reactants and $\gamma = +1$ for reaction products, D is a liquid phase diffusion coefficient and n is the number of moles of electrons transferred per mole of reactant destroyed or product created.

We next integrate Eq. (2) from the gas/electrolyte interface ($r = R_p - \delta$, $C(R_p - \delta) = C'$) to electrode/electrolyte interface ($r = R_p$, $C(R_p) = C$). Upon solving for C we find

$$\frac{C}{C'} = 1 + \frac{\gamma \delta' i}{n F D C'} \quad (3)$$

where

$$\delta' = -R_p \ln \left(1 - \frac{\delta}{R_p} \right) \quad (4)$$

The parameter δ' , which may be considered to be an effective film thickness, reduces to δ for $\delta/R_p \ll 1$ and is only slightly larger than δ in the range where it still makes sense to talk about a thin film, say $\delta/R_p \leq 0.2$.

As we will show in the next section, the effects of diffusion in the gas phase are negligibly small, and so it remains only to consider the effects of ohmic resistance in the pore. Assuming that the conductivity of the electrode is much higher than that of the electrolyte, we should write, in the one-dimensional approximation, for the variation of the total overpotential in the electrolyte film,

$$d\eta_T(z) = (2\tau R_p \delta \kappa)^{-1} I(z) dz + d\eta_C(z) \quad (5)$$

Here κ is the film conductivity, η_T and I are the total overpotential and current at point z in the pore and η_C is the overpotential arising from changes in concentration of the dissolved reactants and products. The necessity for including $d\eta_C$ in Eq. (1) becomes clear when we consider that for electrolytes with very high conductivities there may still be a potential drop in the film arising from changes in the concentration overpotential along the pore. This concentration overpotential can be calculated in the usual fashion using the Nernst equation.¹ Because of the low solubilities of the dissolved gas species, the assumption of ideal solution behavior (made because of ignorance of the real solution behavior) may be quite good. Thus we have

$$\eta_C = \frac{RT}{nF} \ln \left[\prod_p \left(\frac{C_p}{C_p^o} \right)^{\nu_p} \right] \left[\prod_r \left(\frac{C_r}{C_r^o} \right)^{\nu_r} \right] \quad (6)$$

where the ν 's are the signed stoichiometric coefficients of the products (p) and reactants (r) for the half reaction in which n moles of electrons are transferred. The superscript o in Eq. (6) designates open circuit values of the concentrations "at" the electrode surface. Because, as will be shown, gas phase diffusion in the pore is very rapid and dissolution (and evaporation) of gas in the electrolyte should be equally fast, it should be reasonable to suppose that the concentration of each dissolved gas species at the gas/electrolyte interface remains at its open circuit value. We may thus identify C' in Eq. (3) with C^o in Eq. (6) and use Eq. (3) to express η_C in terms of i .

This explicit accounting of η_C will prove worthwhile. For one, it will help to simplify the differential equation we need to solve. It will also enable us to calculate explicitly the contribution of η_C to η_T , and we will see from the numerical results presented later that this contribution can at times be substantial.

Explicitly, then, we have the equation

$$\eta_T = \eta + \eta_C \quad (7)$$

where η is the sum of the activation overpotential in the pore and the overpotential arising from ohmic losses in the pore. To see this more clearly, substitute Eq. (7) into Eq. (5) to obtain

$$\frac{d\eta}{dz} = (2\pi R_p \delta \kappa)^{-1} I(z) \quad (8)$$

which we may integrate formally to obtain

$$\eta(z) = \eta(0) + \int_0^z (2\pi R_p \delta \kappa)^{-1} I(z') dz' \quad (9)$$

We may interpret $\eta(0)$ as the activation overpotential in the pore in the absence of the ohmic losses represented by the integral.

To complete our set of equations we must relate $I(z)$ to i :

$$\frac{dI}{dz} = 2\pi R_p i. \quad (10)$$

Equations (8) and (10) then yield

$$\frac{d^2 \eta}{dz^2} = \frac{i}{\kappa \delta} \quad (11)$$

which must be solved using Eqs. (1), (3), (6) and (7). We will outline this procedure in Section 2.3. First, we briefly discuss gas phase diffusion in the pores.

2.2 Gas Phase Diffusion in the Pores

From mass balance considerations in the gas phase of the pore (neglecting radial diffusion) we can derive the equation

$$n F D_g R_p \frac{d^2 C_g}{dz^2} = 2i \quad (12)$$

for a reactant whose concentration and diffusion constant are denoted C_g and D_g . For the purposes of our argument we can express the z dependence of i as

$$i = i' (z/\ell)^m \quad (13)$$

where i' is a constant. The precise form of $i(z)$ as well as the value of $m (= 1, 2, 3, \dots)$ are immaterial. Equation (13) is close enough to the truth for our present purposes. Using Eq. (13), we next integrate Eqs. (10) and (12) with the result that

$$\Delta C_g \equiv C_g(\ell) - C_g(0) = - \left(\frac{m+1}{m+2} \right) \frac{\ell j}{\eta F D_g} \quad (14)$$

where the apparent current density j of the pore is defined as

$$j \approx \frac{I(\ell)}{\pi R_p^2}$$

and

$$I(\ell) = \frac{2\pi R_p \ell}{m+1} i'$$

To gauge the effect of diffusion on the gas phase concentrations in the pore, we can estimate the value of $\Delta C_g / C_g(0)$ for typical conditions. Assuming that the gas concentration at the beginning of the pore has its bulk stream value, we can put

$$C_g(0) = P/RT$$

where P is the partial pressure in the bulk stream. For a 30% CO_2 ,

70% air mixture at 1 atm and 923°K, we estimate³ for O₂, $D \simeq 1.5 \text{ cm}^2/\text{sec}$ and for CO₂, $D \simeq 2 \text{ cm}^2/\text{sec}$. With $\ell = 5 \times 10^{-2} \text{ cm}$ for $j = 300 \text{ mA/cm}^2$, we then find

$$\frac{\Delta C_g}{C_g(0)} \approx \frac{j\ell RT}{nFDp} \approx 1 \times 10^{-2}$$

for both O₂ and CO₂. These are very small concentration changes, especially considering the magnitude of j . We conclude that it is very reasonable to assume a uniform gas composition throughout the pore and ignore the further mathematical complications that a full treatment of gas phase diffusion would entail. The situation is even better at the anode where the gas diffusion coefficients are higher.

2.3 Treatment of Concentration Terms in Butler-Volmer Equation

As mentioned, the precise form of the functions f and g in Eq. (1) will depend on the reaction mechanism being modeled. An explicit example is probably worthwhile to present. Let us consider a mechanism proposed by Appleby and Nicholson^{4,5} to account for the cathode kinetics.

At open circuit, considerations of detailed balance would lead us to believe that reaction (ii) is the RDS for the reverse reaction and that reactions (iii) and (iv) are also in equilibrium. In analyzing this mechanism we will assume that those considerations remain valid away from open circuit conditions. Upon expressing the rates of the forward and reverse reactions in terms of the concentrations of O_2 and CO_2 we find the expression

$$i = i_o \left\{ \left(\frac{C_{O_2}}{C_{O_2}^o} \right)^a \left(\frac{C_{CO_2}}{C_{CO_2}^o} \right)^b \exp(\alpha_c \eta_T F/RT) - \left(\frac{C_{O_2}}{C_{O_2}^o} \right)^e \left(\frac{C_{CO_2}}{C_{CO_2}^o} \right)^d \exp(-\alpha_a \eta_T F/RT) \right\} \quad (15)$$

where $a = 1/2$, $b = -1$, $e = 0$, $d = -2$, $\alpha_c = \alpha$, $\alpha_a = 2 - \alpha$, and α is the transfer coefficient for the RDS. For the present mechanism the exchange current can be shown to be

$$i_o = (\text{const}) \left(\frac{C_{O_2}}{C_{O_2}^o} \right)^{(2-\alpha)/4} \left(\frac{C_{CO_2}}{C_{CO_2}^o} \right)^{-(2+\alpha)/2}$$

We next want to explicitly eliminate η_c from Eq. (15) using Eq. (7) and Eq. (6), which appears as

$$\eta_c = -\frac{RT}{2F} \ln \left(\frac{C_{O_2}}{C_{O_2}^o} \right)^{1/2} \left(\frac{C_{CO_2}}{C_{CO_2}^o} \right) \quad (16)$$

when evaluated for the O_2 , CO_2 half reaction (v). Substituting Eqs. (7) and (16) into Eq. (15), we obtain

$$i = i_o \left(\frac{C_{O_2}}{C_{O_2}^o} \right)^\sigma \left(\frac{C_{CO_2}}{C_{CO_2}^o} \right)^\tau S(\eta) \quad (17)$$

$$S(\eta) = e^{\alpha_c \eta F/RT} - e^{-\alpha_a \eta F/RT} \quad (18)$$

The pleasingly simple appearance of Eq. (17) results from the identities

$$\begin{aligned} \sigma &= a - \frac{\alpha_c}{4} = e + \frac{\alpha_a}{4} \\ \tau &= b - \frac{\alpha_c}{2} = d + \frac{\alpha_a}{2} \end{aligned} \quad (19)$$

that are exact consequences of our invoking of detailed balancing in analyzing the reaction mechanism. Equation (17) is thus a general result for low overpotentials (small deviations from open circuit "equilibrium"). It is probably adequate at high overpotentials too (presuming the same forward mechanism still holds) because of the decreasing importance of the reverse reaction at high overpotentials:

$$e^{\alpha_c \eta_T F/RT} \gg e^{-\alpha_a \eta_T F/RT}$$

As discussed in Section 2.1., we can use Eq. (3) to evaluate the concentration ratios appearing in Eq. (17), which then becomes, in general, a non-linear equation for i . This difficulty, however, can be obviated to a large extent by taking advantage of the relative smallness of the exponents σ and τ and of $i\delta'/nFDC^o$ in order to linearize the concentration terms in Eq. (17).

Note, first, that in Eq. (3) the quantity $\delta'i/(nFDC^o)$ is the ratio of the actual local transfer current density to its limiting value i_l ,

$$i_l = \frac{nFDC^o}{\delta'} \quad (20)$$

Each species has a characteristic limiting current calculable from Eq. (20) for the pertinent local conditions. It is obvious that i can never exceed the smallest of these i_l values (and will normally be much smaller than it), so we expect to find generally that $i/i_l \ll 1$. It is possible that for a product species, say H_2O or CO_2 at the anode, that i/i_l could exceed 1. This would only arise when very high cell current densities were called for, and a different solution procedure than that to be proposed here would be required.

The smallness of the exponents σ and τ has also been noted. For example, Appleby and Nicholson found, for the cited mechanism, that $\alpha \approx 1/2$. For this value, the exponents σ and τ then equal $3/8$ and $-5/4$. These values are typical (in magnitude) of those that occur for other possible reaction mechanisms not examined here. Similar values are also found for anode mechanisms.

Based on the above discussion, we conclude that a promising simplification of Eq. (17) can be accomplished by expanding the concentration ratios and retaining only terms linear in i . We then find that Eq. (17) can be solved for i as

$$i = i_o S(\eta) / (1 + i_o A S(\eta)) \quad (21)$$

where

$$A = \frac{\sigma}{i_{l, O_2}} + \frac{\tau}{i_{l, CO_2}} \quad (22)$$

We have numerically integrated Eq. (11) using Eq. (21) for a range of values of the key parameters appearing in these equations. These preliminary results will be discussed in Section 2.5. Here, we just remark that each computation requires 3 to 5 seconds of computer time. The result of each computation is one pair of (η_T, I) values where the pore current is

$$I = 2\pi R_p \delta \kappa \left. \frac{d\eta}{dz} \right|_{z=l} \quad (23)$$

The required output of the DCM is the total electrode overpotential $\eta_{T,a} + \eta_{T,c}$ and current I such that the relationship for the cell and local Nernst voltages V and E

$$E - V = \eta_{T,a} + \eta_{T,c} + IR \quad (24)$$

is satisfied at each point in the cell. Even assuming orthogonal current flow between electrodes, finding the correct pairs $(\eta_{T,a}, I)$ and $(\eta_{T,c}, I)$ that satisfy Eq. (24) may require numerically integrating Eq. (11) at least several times for each electrode. Thus, for current density calculations on even a small 20×20 mesh, the time spent on just this aspect of the calculation could easily run into hours. To alleviate this difficulty we plan to investigate alternative and potentially faster numerical methods of solving Eq. (11). We have also undertaken a promising semi-analytic approach, described in the next section, that may help speed up matters.

Integration of Eq. (11) with the non-linearized Eq. (17) has not yet been attempted. These calculations will be pursued during the next quarter in order to fully assess the range of validity of the "linearized concentration" approximation.

2.4 Semi-analytic Solution Procedure

A further simplification in our solution strategy arises if we linearize $S(\eta)$ to obtain from Eq. (21)

$$i = y_o \eta / (1 + \Lambda \eta), \quad (25)$$

where

$$y_o = \frac{i_o F}{RT} (\alpha_c + \alpha_a),$$

and

$$\Lambda = y_o A.$$

Eq. (11) can then be analytically integrated once giving

$$\Lambda^2 \left(\frac{d\eta}{dz} \right)^2 = 2K_o^2 \left\{ \ln \left(\frac{1 + \Lambda \eta_0}{1 + \Lambda \eta} \right) + \Lambda (\eta - \eta_0) \right\} \quad (26)$$

where

$$K_o^2 = \gamma_o (\kappa \delta)^{-1}, \text{ and } \eta_0 = \eta(0).$$

Eq. (26) can then be integrated numerically in the form

$$\Lambda \int_{\eta_0}^{\eta_l} \frac{d\eta}{\left(\ln \left(\frac{1 + \Lambda \eta_0}{1 + \Lambda \eta} \right) + \Lambda (\eta - \eta_0) \right)^{1/2}} = 2^{1/2} K_o l, \quad (27)$$

where $\eta_l = \eta(l)$, by varying η_l (for a particular η_0) until equality is obtained. The current can then be computed from Eqs. (23) and (26). Preliminary results from Eq. (26) agree very well with those obtained from Eqs. (11) and (21). For example, with the parameter values listed in Table 1

TABLE 1

PARAMETERS USED FOR CALCULATIONS REPORTED IN TABLE 2.

l	$= 5 \times 10^{-2} \text{ cm}$	D_{O_2}	$= D_{CO_2} = 10^{-5} \text{ cm}^2/\text{sec}$
δ	$= 5 \times 10^{-5} \text{ cm}$	C_{O_2}	$= 6 \times 10^{-8} \text{ moles/cm}^3$
R_p	$= 2.5 \times 10^{-4} \text{ cm}$	C_{CO_2}	$= 3.6 \times 10^{-6} \text{ moles/cm}^3$
κ	$= 1 \text{ (ohm}^{-1} \text{) (cm}^{-1} \text{)}$	T	$= 923^\circ \text{K}$
i_o	$= 1 \text{ mA/cm}^2$	$\sigma = \tau$	$= 1$
		$\alpha_c = \alpha_a$	$= 1$

we find the following results:

TABLE 2

Comparison of values of $d\eta/dz$ calculated using Eq. (26) and Eqs. (11) and (21). The concentrations correspond to the partial pressures $P_{O_2} = 0.15$ atm, $P_{CO_2} = 0.3$ atm using the solubilities reported in Ref. 3. (See Section 2.5.)

η_0 (mv)	η_ℓ (mv)	$\frac{F\ell}{RT} \left(\frac{d\eta}{dZ} \right)_{Z=\ell}$ (Eq. (11))	$\frac{F\ell}{RT} \left(\frac{d\eta}{dZ} \right)_{Z=\ell}$ (Eq. (26))
10	16.6	0.180	0.179
25	40.2	0.413	0.408
50	77.8	0.749	0.720

This good agreement persists over a wide range of parameter values, so it will be advantageous to pursue ways of solving Eq. (27) quickly and efficiently, provided the "linearized concentration" approximation discussed in Section 2.3 proves to be as good as we believe it to be. If this approach does prove to be accurate, it will yield one other simplification that may have a bearing on substantially speeding up the analysis. If we introduce the dimensionless variables

$$v = \eta/\eta_0 \quad (28)$$

and

$$Z = z/\ell$$

into Eqs. (11) and (17), we find four dimensionless groupings of parameters upon which all solutions depend: $i_0 A$, $\eta_0 F/RT$, $\alpha \eta_0 F/RT$ and $\ell^2 i_0 F/(\kappa \delta RT)$. Even if we always use $\alpha = 1/2$, there are three parameters with respect to which the solutions must be indexed. On the other hand, if we introduce v and

$$\Gamma = A\eta_0 \quad (29)$$

into Eq. (27) we obtain

$$\Gamma \int_1^{v_\ell} \frac{dv}{\left(\ln \left(\frac{1+\Gamma}{1+\Gamma v} \right) + \Gamma(v-1) \right)^{1/2}} = 2^{1/2} K_o \ell \quad (30)$$

Although this equation also depends on three parameters, we see that the left-hand-side is only a function of two of them, $F(\Gamma, v_\ell)$. It should thus be possible to tabulate values of F in advance in order to search them rapidly to determine the correct value of v_ℓ for given values of Γ and $K_o \ell$. This approach will also be pursued next quarter.

2.5 Results of Numerical Integration

We have performed numerical integrations of Eqs. (11) and (21) for several combinations of values of i_o and C_{O_2} , C_{CO_2} . These were the only parameters varied during these preliminary calculations; the remaining parameter values were identical to those listed in Table 1. For a chosen value of $\eta(0) = \eta_0$ we calculated $\eta (= \eta_0 + \eta_\Omega)$, η_C , η_T , i and I as functions of position (z) in the pore. (The ohmic loss in the pore η_Ω is defined by the integral in Eq. (9).) The apparent electrode current density j was obtained from

$$j = N_p I$$

where N_p is the number density (pores/cm²) of pores estimated for a square array of closest-packed circular pore mouths of radius R_p . ($N_p = (4R_p^2)^{-1}$).

For the R_p value, 2.5×10^{-4} cm, used in our calculations, we have $N_p = 4 \times 10^6$ pores/cm². For the i_o values (in mA/cm²) of 0.01, 0.4 and 1.0 the gas concentrations $C_{O_2}^o$ and $C_{CO_2}^o$ were chosen to correspond to mixtures in which the partial pressures of O_2 and CO_2 were

$$P_{O_2} = 0.15 \text{ atm}, \quad P_{CO_2} = 0.3 \text{ atm},$$

in the first case, and

$$P_{O_2} = 0.03 \text{ atm} , \quad P_{CO_2} = 0.06 \text{ atm}$$

in the second. The first set approximates closely the partial pressures in a standard 30% CO_2 , 70% air mixture at 1 atm total pressure; the second set corresponds to the mixture resulting from 88% utilization of the mixture represented by the first set. The 88% utilization probably represents an extreme condition for a cathode mixture, but one that will be useful in studying the effects of utilization on cathode performance. The actual concentrations C^o were computed from the equation

$$C^o = s^o P \quad (31)$$

where we estimated the solubility s^o (moles/cm³-atm) of each species at 923°K, as

$$s_{O}^o = 4.0 \times 10^{-7} \text{ moles}/(\text{cm}^3\text{-atm})$$

$$s_{CO_2}^o = 1.2 \times 10^{-5} \text{ moles}/(\text{cm}^3\text{-atm})$$

from the values afforded in Ref. 3.

a) Results for $i_o = 0.01 \text{ mA}/\text{cm}^2$

These results were neither very surprising nor interesting. The total overpotential for the pore received only very tiny contributions ($\approx 1\%$) from the concentration overpotential and the ohmic loss in the pore. As a result the overpotential throughout the pore was essentially constant and equal to its initial (pure activation) value (see Eq. (9)). The current I was, therefore,

linear in z in the pore. Because of the small value of i_o only very small values of j were generated. For example, at $\eta_T \approx 100$ mV we calculated that $j \approx 10$ mA/cm². Changing the partial pressures, as indicated above, produced only small changes in the results. Evidently the smallness of i_o is the dominating factor in these calculations.

b) Results for $i_o = 0.4$ and 1.0 mA/cm².

These results display several interesting differences from those for $i_o = 0.01$ mA/cm². We note first, in Fig. 2, the greatly increased current densities produced for relatively low overpotentials ($\eta_T \leq 100$ mV). Also apparent in Fig. 1 is the sizeable effect that raising the partial pressures by a factor of 5 has on the performance curves. Curves 1 and 3 show clear tendencies to steepen, in contrast to the flatter curves labeled 2 and 4. Thus, the low partial pressure curves, 1 and 3, display an earlier onset of mass transport limitations than do the high partial pressure curves, 2 and 4. Curves 3 and 4 ($i_o = 1$ mA/cm²) also show the expected increase in current density at constant overpotential, when compared to curves 1 and 2 ($i_o = 0.4$ mA/cm²) because of the increased exchange current density i_o .

As shown in Fig. 3 for $i_o = 1$ mA/cm² and low partial pressures, the concentration overpotential η_C and the ohmic loss in the pore η_Ω make important contributions to the total overpotential η_T in this parameter range. For the low pressure case we found $\eta_C > \eta_\Omega$, while for the high pressure case we found $\eta_\Omega > \eta_C$, but the total contribution $\eta_\Omega + \eta_C$ to the total overpotential remained appreciable.

One other feature of the results computed for these low i_o cases is the relatively uniform variation in η_T , i and I that occurs with changing position within the pore (not illustrated).

Fig. 2 Total overpotential η_T versus current density j in the cylindrical thin film model for parameter values in Table 1 and listed values of exchange current and oxygen and carbon dioxide partial pressures.

Fig. 3 Contributions of ohmic losses η_Ω , concentration overpotential η_C and activation overpotential η_0 to the total overpotential η_T for $i_o = 1.0$ mA/cm; $P_{O_2} = 0.03$ atm and $P_{CO_2} = 0.06$ atm.

c) Results for $i_0 = 40 \text{ mA/cm}^2$.

For this calculation we used Eq. (31) with s^0 and partial pressures characteristic of H_2 and H_2O at the anode in order to roughly simulate that electrode. (High exchange current densities for the anode are currently being suggested.) We used a partial pressure of 0.5 atm for O_2 (" H_2 ") and of 0.1 atm for CO_2 (" H_2O ") and estimated for both H_2 and H_2O from Ref. 3 that $s^0 = 5.8 \times 10^{-6} \text{ moles/(cm}^3\text{-atm)}$. No other changes in the equations or parameter values were made for this test case.

The most obvious feature of the results for these parameter values is the extremely large current densities that are produced for relatively low total overpotentials. For example, at $\eta_T = 14.5 \text{ mV}$ we already calculated $j = 226 \text{ mA/cm}^2$, but at $\eta_T = 72.9 \text{ mV}$, j had increased to 1120 mA/cm^2 !

It is also important to note that the total overpotential in the pore η_T is almost entirely equal to the sum of the concentration overpotential η_C and the ohmic loss in the pore η_Ω . The "pure" activation overpotential η_0 (Eq. (9)) contributes almost nothing to η_T . (It can't be zero, because there would then be no current generated whatsoever.) One other significant feature of these results is visible in Fig. 4, where we have logarithmically plotted I , i , η_T , η_C and η_Ω as functions of position in the pore. What we see is that over 90% of the overpotential η_T and the current I arises in the last 40% of the length of the pore. We may be tempted to infer from this result that the pore is roughly double the length it needs to be, but we will resist drawing this conclusion until we consider more carefully how the current scales with the pore length. This non-uniform variation of these quantities in the pore contrasts with the behavior exhibited earlier for the smaller i_0 cases.

On the basis of the results and discussion presented in b) and c), it is clear that a satisfactory accounting of both the concentration overpotential and the ohmic losses in pores is required in order to generate an adequate porous electrode model.

Fig. 4 Current I , exchange current density i , total overpotential η_T , concentration overpotential η_C , and ohmic loss η_Ω as a function of position z/l in pore for $i_0 = 40 \text{ mA}/\text{cm}^2$ and "anode-like" concentrations (see text).

3. INTEGRAL CELL MODEL

3.1 Introduction

The integral cell model incorporates the local current-overpotential relation obtained from the DCM to treat the cell as a whole. A local potential balance expression and differential relations based on conservation of mass and energy are developed, and form the basis of a numerical integration scheme that computes distributions of current density and cell temperature for a given set of operating conditions (cell voltage, inlet gas compositions and temperatures, pressure). The interdependence of current density and temperature is handled by local iteration; at each point in the cell an assumed local temperature gives rise to a local current density, which is used to estimate an updated temperature, and so on to convergence. The calculation proceeds in stepwise fashion with temperature and current density at each point based on the upstream history of the gas flows.

At present the numerical scheme is operational for a single cell with crossflow geometry in the absence of in-plane heat conduction. For reasons of simplicity and consistency with previous work,¹ we make use of a linear current-overpotential relation to perform the calculation.

3.2 Basic Equations

a. Potential Balance Equation

We assume, as in our previous quarterly report,¹ 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 . We had defined local anode and cathode utilization parameters

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

$$\mu = \frac{\dot{n}_{\text{CO}_2}^{\circ} - \dot{n}_{\text{CO}_2}}{\dot{n}_{\text{CO}_2}^{\circ}}$$

Where $\dot{n}_i$ is the molar flow rate (per unit channel width) of species i , and superscript $^{\circ}$ denotes an inlet quantity.

If we assume uniform composition across the channel depth (justified in Section 3.8), the composition terms of the Nernst equation may be written in terms of λ and μ to give the potential balance equation, Eq. (24), which can be solved for current density j , as

$$j(\lambda, \mu, T_o) = \left(\frac{RT_o}{2F} \ln \left(\frac{K_c}{K_a} \right) + \frac{RT_o}{4F} \ln P - V \right) \left\{ \frac{1}{z_{\text{TOT}}} \right\} \quad (32)$$

where

$$K_a = K_a(\lambda, \dot{n}_{ia}) = \frac{(\dot{n}_{\text{H}_2\text{O}}^{\circ} + \dot{n}_{\text{H}_2}^{\circ} \lambda) (\dot{n}_{\text{CO}_2}^{\circ} + \dot{n}_{\text{H}_2}^{\circ} \lambda)}{\dot{n}_{\text{H}_2}^{\circ} (1 - \lambda)} \left(\frac{1}{\dot{n}_a^{\circ} + \dot{n}_{\text{H}_2}^{\circ} \lambda} \right)$$

$$K_c = K_c(\mu, \dot{n}_{ic}) = \left(\dot{n}_{\text{O}_2}^{\circ} - \frac{1}{2} \dot{n}_{\text{CO}_2}^{\circ} \mu \right)^{1/2} (\dot{n}_{\text{CO}_2}^{\circ} (1 - \mu)) \left(\frac{1}{\dot{n}_c^{\circ} - \frac{3}{2} \dot{n}_{\text{CO}_2}^{\circ} \mu} \right)^{3/2}$$

where $\dot{n}_a = (\sum \dot{n}_i)_{\text{anode}}$, $\dot{n}_c = (\sum \dot{n}_i)_{\text{cathode}}$, and the summations are taken over all species present in the anode and cathode streams. For consistency with previous work, the total overpotential is taken to be linear in current density and the dependence of the total impedance z_{TOT} on local conditions is ignored. Relaxation of this restriction should pose no additional numerical problems.

b. Mass Balance Equations

From mass balance considerations we had developed the local relations

(33)

$$\dot{n}_{H_2}^o \frac{\partial \lambda}{\partial x} = \frac{j}{2F} \quad (33)$$

$$\dot{n}_{CO_2}^o \frac{\partial \mu}{\partial y} = \frac{j}{2F} \quad (34)$$

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

c. Local Heat Release

The local heat release per unit cell area is related to the current density by the relation

$$\dot{q} = -j \left(\frac{\Delta H(T_o)}{2F} + V \right) \quad (35)$$

where $\Delta H(T_o)$ is the heat of formation of H_2O at the local cell temperature T_o . Two important points should be made here:

(i) Gas phase reactions are presumed not to occur in the bulk streams, so that the heat release of Eq. (35) is evolved entirely within the electrode-tile sandwich. The model need not be sensitive to whether heat release/absorption occurs at the anode or cathode separately; because of sufficiently high tile conductivity account is taken only of the total heat release evolved per unit cell area.

(ii) The heat release of Eq. (35) is the residual heat generated by chemical reaction at the cell temperature T_o , and is transferred by conduction (or radiation) to the gas streams. Energy exchange associated with mass transfer as the reacting species enter or leave the gas streams must be taken account of separately in the calculation of the bulk stream temperatures. Neglecting radiation, then, we have

$$\dot{q} = \dot{q}_{ka} + \dot{q}_{kc} \quad (36-1)$$

where $\dot{q}_{ka}$, $\dot{q}_{kc}$ are the conductive heat fluxes entering the anode and cathode streams.

d. Conductive Heat Transfer

We are primarily interested in computing only the distribution of average local cell temperatures in the plane of the electrolyte tile, and the distribution of mean gas temperatures in the anode and cathode streams.

These considerations suggest a simplified "heat exchanger" type analysis, in which the conductive heat flux $\dot{q}_k$ into either gas stream is taken to have the form

$$\dot{q}_k = h^*(T_o - T_m) \text{ (watts/cm}^2\text{)}$$

where

T_o = local tile temperature

T_m = local mean gas temperature

h^* = unit surface conductance coefficient

Values for h^* are tabulated for a variety of channel geometries in the form of the nondimensional Nusselt modulus Nu, where

$$Nu = \frac{h^* L}{k}$$

and

k = gas thermal conductivity

L = a characteristic length, e. g. channel depth.

Strictly speaking, Nu is constant in the limiting case of

- (1) Fully developed velocity and temperature profiles
- (2) Constant fluid properties (hence no concentration gradients)
- (3) Rate of heat addition constant in the streamwise direction.

We will use a constant value for Nu, consistent with the approximation that the above restrictions hold on a local basis. We are assuming that streamwise changes are sufficiently gradual to allow distributions of velocity,

temperature, and composition to relax instantaneously to fully developed profiles at each station. We also assume that mass fluxes at the gas/electrode interface are small, allowing us to assume that the fully developed composition profile is simply that of uniform composition across the channel depth. We demonstrate the validity of these assumptions for the present case in Section 3.8.

Equation (36-1) from the previous section is now written as

$$\dot{q} = h_a^* (T_o - T_{ma}) + h_c^* (T_o - T_{mc}) \quad (36-2)$$

Solving for T_o we obtain

$$T_o = \frac{\dot{q} + h_a^* T_{ma} + h_c^* T_{mc}}{h_a^* + h_c^*}$$

e. Energy Balance

As discussed previously, thermal energy exchange between the cell and either gas stream is due to the combined effect of conductive and radiative heat transfer, and a mass transfer contribution associated with exchange of reacting species at the cell temperature. An expression relating the mean gas temperature to these heat and mass fluxes can be derived.

Consider a multicomponent gas stream flowing in the x-direction at local mean temperature T_m , with mass added at temperature T_o . We denote $\dot{n}_i$ the molar flow rate (per unit channel width) and C_{pi} the molar heat capacity of species i. Over a distance Δx , let ΔT_m be the change in the mean gas temperature and $\Delta \dot{n}_i$ be the corresponding change in $\dot{n}_i$ due to mass addition. The conductive heat flux (per unit area) $\dot{q}_k$ heats the initial bulk stream from T_m to $T_m + \Delta T$, while the additional mass changes temperature from T_o to $T_m + \Delta T$:

$$\sum_i \dot{n}_i \int_{T_m}^{T_m + \Delta T} C_{p_i} dT + \sum_i \Delta \dot{n}_i \int_{T_o}^{T_m + \Delta T} C_{p_i} dT = \int_x^{x + \Delta x} \dot{q}_k dx$$

As $\Delta T \rightarrow 0$, and $\Delta x \rightarrow 0$, we can write $\Delta T = \frac{dT}{dx} dx$,

$$\text{and } \Delta \dot{n}_i = \frac{d\dot{n}_i}{dx} dx = g_i dx$$

where g_i is the molar flux of species i entering the stream.

We then obtain the following differo-integral relation for the energy balance

$$\sum_i \dot{n}_i C_{p_i} \frac{dT_m}{dx} + \sum_i g_i \int_{T_o}^{T_m} C_{p_i} dT = \dot{q}_k$$

If we treat C_{p_i} as constant (a good assumption for the temperature range of interest) and introduce the bulk heat capacity

$$C_p = \dot{n}^{-1} \sum_i \dot{n}_i C_{p_i}$$

we then have

$$\dot{n} C_p \frac{dT_m}{dx} + \sum_i (g_i C_{p_i}) (T_m - T_o) = \dot{q}_k \quad (37-1)$$

It is possible to derive the relation

$$\frac{d}{dx} (\dot{n} C_p T_m) = \dot{n} C_p \frac{dT_m}{dx} + \sum_i g_i C_{p_i} T_m$$

which can be used to rewrite Eq. (37-1) in the form

$$\frac{d}{dx} (\dot{n}_p C_p T_m) = h^*(T_o - T_m) + \sum (g_i C_{pi}) T_o \quad (37-2)$$

where we have substituted $\dot{q}_k = h^*(T_o - T_m)$.

3.3 First Order Numerical Scheme

A first order numerical scheme is used to integrate the required set of partial differential equations.

The equations are summarized below

$$j = \left(\frac{RT_o}{2F} \ln \left(\frac{K_c}{K_a} \right) + \frac{RT_o}{4F} \ln P - V \right) \left\{ \frac{1}{z_{TOT}} \right\} = f_1(\lambda, \mu, T_o)$$

$$\frac{\partial \lambda}{\partial x} = \frac{1}{\dot{n}_{H_2}} \frac{j}{2F} = f_2(j)$$

$$\frac{\partial \mu}{\partial y} = \frac{1}{\dot{n}_{CO_2}} \frac{j}{2F} = f_3(j)$$

$$\frac{\partial}{\partial x} (\dot{n}_p C_p T_m)_a = h_a^*(T_o - T_{ma}) + \sum (g_i C_{pi})_a T_o = f_4(j, \lambda, T_{ma}, T_o)$$

$$\frac{\partial}{\partial y} (\dot{n}_p C_p T_m)_c = h_c^*(T_o - T_{mc}) + \sum (g_i C_{pi})_c T_o = f_5(j, \mu, T_{mc}, T_o)$$

$$T_o = \frac{-j \left(\frac{\Delta H(T_{ref}) - T_{ref} \Delta C_p}{2F} + V \right) + h_a^* T_{ma} + h_c^* T_{mc}}{h_a^* + h_c^* + \frac{j}{2F} \Delta C_p} = f_6(j, \lambda, \mu, T_{ma}, T_{mc})$$

and we note that $\dot{n}_a$, C_{pa} , h_a^* are functions of λ , that $\dot{n}_c$, C_{pc} and h_c^* are functions of μ and the g_i are functions of j .

The final equation was obtained by substituting Eq. (35) into Eq. (36-2). The heat of formation of H_2O has been referenced to T_{ref} by way of

$$\Delta H(T_o) = \Delta H(T_{ref}) + \int_{T_{ref}}^{T_o} \Delta C_p dt$$

where $\Delta C_p \left(= C_{pH_2O} - C_{pH_2} - \frac{1}{2} C_{pO_2} \right)$ is taken as a constant over the temperature range of interest.

The boundary conditions are given as

$$\lambda(0, y) = 0 \quad T_{ma}(0, y) = T_{ma}^0$$

$$\mu(x, 0) = 0 \quad T_{mc}(x, 0) = T_{mc}^0$$

and V , P , z_{TOT} and inlet molar flow rates $\dot{n}_{i_a}^o$, $\dot{n}_{i_c}^o$ must also be specified.

Using the indices M , L to correspond to the x , y directions respectively, the derivatives are expressed as first order forward difference operators to give

$$j_{L,M} = f_1(\lambda, \mu, T_o^n)_{L,M}$$

$$\frac{\lambda_{L,M} - \lambda_{L,M-1}}{\Delta x} = f_2(j)_{L,M-1}$$

$$\frac{\mu_{L,M} - \mu_{L,M-1}}{\Delta y} = f_3(j)_{L-1,M}$$

$$\frac{(\dot{n}_c T)_{p, mL, M} - (\dot{n}_c T)_{p, mL, M-1}}{\Delta x} = f_4(j, \lambda, T_{ma}, T_o^n)_{L, M-1}$$

$$\frac{(\dot{n}C_p T_m)_{L,M} - (\dot{n}C_p T_m)_{L-1,M}}{\Delta y} = f_5(j, \mu, T_{mc}, T_o^n)_{L-1,M}$$

$$T_o^{n+1}_{L,M} = f_6(j, \lambda, \mu, T_{ma}, T_{mc})_{L,M}$$

The difference equations are solved for values at station (L, M) in terms of previously computed values at (L, M-1) and (L-1, M). Values at (L, M) are initially computed subject to an estimated T_o^n , and substituted into $f_6(j, \lambda, \mu, T_{ma}, T_{mc})$ to give an updated estimate T_o^{n+1} . The procedure is iterated to convergence. A marching forward scheme is appropriate, the calculation proceeding row by row in the positive x and y directions so that all upstream quantities have been previously computed as each point is encountered.

We note that for the case of the simple linear current-overpotential relation used here, T_o can be obtained as an explicit function of $\lambda, \mu, T_{ma}, T_{mc}$, thereby eliminating the need for iteration. Program structure has been deliberately kept general in order to accomodate the more complex expression to be obtained from the refined differential cell model.

3.4 Program Validation

Some useful checks on the internal consistency of the calculation scheme can be found from the requirement that the cell conserve mass and energy on an overall basis.

a. Mass Conservation

Mass fluxes entering and leaving the cell must of course be equal and opposite to maintain steady operation, or

$$\left[\int_a (\sum \dot{n}_i M_i) dy + \int_c (\sum \dot{n}_i M_i) dx \right]_{\text{inlet}} = \left[\int_a (\sum \dot{n}_i M_i) dy + \int_c (\sum \dot{n}_i M_i) dx \right]_{\text{outlet}} \quad (38)$$

where $\dot{n}_i$ is the molar flow rate (per unit channel width) and M_i is the molecular weight of species i , the integrals are taken across the anode and cathode inlets, and anode and cathode outlets respectively.

We also have from stoichiometry that 1 mole of reactants is consumed for every four moles of electrons transferred. Applying this equality to the cell as a whole gives

$$\left[\int_a (\sum \dot{n}_i) dy + \int_c (\sum \dot{n}_i) dx \right]_{\text{inlet}} - \left[\int_a (\sum \dot{n}_i) dy + \int_c (\sum \dot{n}_i) dx \right]_{\text{outlet}} = \frac{1}{4F} \int_{\text{cell area}} j dx dy \quad (39)$$

b. Energy Conservation

The chemical energy extracted from the gas streams must appear either as electrical work, or as waste heat which is assumed to be carried off by thermal convection. The overall energy balance is then

$\Delta(\text{enthalpy of the gas streams}) = \text{electrical work of cell, or}$

$$\left[\int_a (\sum \dot{n}_i \bar{H}_i) dy + \int_c (\sum \dot{n}_i \bar{H}_i) dx \right]_{\text{inlet}} - \left[\int_a (\sum \dot{n}_i \bar{H}_i) dy + \int_c (\sum \dot{n}_i \bar{H}_i) dx \right]_{\text{outlet}} = V \int_{\text{cell area}} j dx dy \quad (40)$$

where $\bar{H}_i$ is the partial molar enthalpy of species i . A computationally useful form of this equation is obtained by noting that the left hand side can also be identified as the variation in the enthalpy change required to convert all components in the gas streams at the inlet and outlet temperatures into elements at some reference temperature T_{ref} .

This statement can be expressed mathematically by simply replacing each summation $\sum_i \bar{H}_i(T_m)$ in Eq. (40) by the expression

$$\sum_k \dot{n}_k \Delta H_{fk}(T_m) + \sum_l \int_{T_{ref}}^{T_m} \dot{n}_l C_{pl} dT$$

where k and l are summation indices for compounds and elements, respectively and $\Delta H_{fk}(T_m)$ is the heat of formation of compound k at the mean gas temperature T_m . Equations (38), (39), and (40) have been calculated numerically and are identically satisfied by our computational scheme.

3.5 Sample Calculation

A sample calculation of the cell temperature and current density distributions was performed for the conditions listed in Table 3. The results are presented in Table 4.

TABLE 3

CONDITIONS FOR CALCULATED RESULTS PRESENTED IN TABLE 4

	<u>Anode Stream</u>	<u>Cathode Stream</u>
Inlet gas Composition	64% H ₂ , 10% H ₂ O 6% CO ₂ , 20% CO	20% CO ₂ , 20% O ₂ 60% N ₂
Inlet molar flow rates	3×10^{-4} moles/sec	3×10^{-3} moles/sec
Inlet mean gas temperatures	850°K	850°K
Cell voltage = .75V, P = 1 atm, $z_{TOT} = 1.025 \text{ ohm-cm}^2$, $Nu = h^* L/k = 2$		
Cell dimensions: 10 x 10 cm		

For this preliminary calculation a linear current-overpotential relation was used, and the effects of in-plane heat conduction and CO utilization were not considered. Because we are neglecting any temperature dependence

TABLE 4

MAPS OF CURRENT DENSITY AND TEMPERATURE FOR A 10 X 10 cm CELL WITH OPERATING CONDITIONS LISTED IN TABLE 3. ANODE STREAM FLOWS LEFT TO RIGHT, CATHODE STREAM DOWN THE PAGE.

CURRENT DENSITY, AMP/CM²

0.325	0.287	0.263	0.245	0.231	0.218	0.208	0.198	0.189	0.181	0.172
0.324	0.287	0.262	0.244	0.230	0.218	0.207	0.197	0.188	0.180	0.172
0.324	0.287	0.262	0.244	0.229	0.217	0.206	0.196	0.187	0.179	0.171
0.323	0.287	0.262	0.243	0.228	0.216	0.205	0.195	0.187	0.178	0.170
0.322	0.286	0.261	0.242	0.228	0.215	0.204	0.195	0.186	0.177	0.169
0.321	0.286	0.261	0.242	0.227	0.215	0.204	0.194	0.185	0.176	0.168
0.320	0.286	0.260	0.241	0.226	0.214	0.203	0.193	0.184	0.176	0.167
0.319	0.285	0.259	0.240	0.225	0.213	0.202	0.192	0.183	0.175	0.167
0.318	0.285	0.259	0.240	0.225	0.212	0.201	0.191	0.182	0.174	0.166
0.317	0.284	0.258	0.239	0.224	0.211	0.200	0.190	0.181	0.173	0.165
0.316	0.283	0.258	0.238	0.223	0.210	0.199	0.189	0.180	0.172	0.164

CELL TEMPERATURE, DEG K

857.5	880.1	877.7	875.8	874.3	873.0	871.8	870.8	869.9	869.0	868.1
858.1	893.1	890.6	887.7	885.4	883.5	881.9	880.4	879.0	877.7	876.5
858.5	905.6	903.5	899.8	896.7	894.2	892.0	890.0	888.2	886.5	884.9
859.8	917.5	916.6	912.0	909.2	905.0	902.2	899.7	897.5	895.3	893.3
859.0	928.7	929.7	924.5	919.8	915.9	912.5	909.6	906.8	904.3	901.9
859.1	939.1	942.8	937.0	931.6	927.0	923.0	919.5	916.3	913.3	910.5
859.2	948.6	955.6	949.8	943.5	938.2	933.6	929.5	925.8	922.4	919.2
859.3	957.3	968.7	962.6	955.6	949.5	944.3	939.7	935.5	931.6	927.9
859.3	965.1	981.4	975.6	967.8	961.0	955.1	949.9	945.2	940.9	936.0
859.3	972.1	993.8	988.6	980.2	972.6	966.0	960.3	955.0	950.2	945.7
859.3	978.2	1005.8	1001.7	992.8	984.4	977.1	970.7	965.0	959.7	954.7

ANODE MEAN GAS TEMPERATURE, DEG K

850.0	880.2	877.9	876.0	874.4	873.1	872.0	871.0	870.0	869.2	868.3
850.0	893.0	890.8	888.0	885.7	883.7	882.1	880.6	879.2	877.9	876.7
850.0	905.3	903.0	900.1	897.0	894.5	892.3	890.3	888.5	886.8	885.2
850.0	916.8	916.9	912.5	908.6	905.4	902.6	900.1	897.8	895.7	893.7
850.0	927.5	930.1	925.0	920.3	916.4	913.0	910.0	907.3	904.7	902.3
850.0	937.4	943.2	937.6	932.1	927.5	923.5	920.0	916.8	913.8	911.0
850.0	946.4	956.1	950.4	944.2	938.8	934.2	930.1	926.4	923.0	919.8
850.0	954.5	968.9	963.3	956.3	950.2	945.0	940.3	935.1	932.3	928.6
850.0	961.6	981.4	976.4	968.7	961.8	955.9	950.7	946.0	941.6	937.6
850.0	968.0	993.6	989.4	981.1	973.5	966.9	961.1	955.9	951.1	946.6
850.0	973.5	1005.3	1002.5	993.8	985.4	978.1	971.7	965.9	960.6	955.6

CATHODE MEAN GAS TEMPERATURE, DEG K

850.0	850.0	850.0	850.0	850.0	850.0	850.0	850.0	850.0	850.0	850.0
852.9	863.5	862.6	861.7	861.0	860.4	859.9	859.5	859.0	858.6	858.3
854.9	876.0	875.4	873.6	872.2	871.0	870.0	869.0	868.2	867.4	866.6
856.3	889.0	888.4	885.7	883.5	881.7	880.1	878.7	877.4	876.2	875.0
857.3	902.4	901.5	897.9	895.0	892.5	890.4	888.4	886.7	885.0	883.5
858.0	914.4	914.7	910.4	906.6	903.4	900.7	898.3	896.1	894.0	892.0
858.4	925.7	927.9	923.0	918.4	914.5	911.2	908.2	905.6	903.0	900.7
858.7	936.2	941.1	935.7	930.3	925.7	921.8	918.3	915.1	912.2	909.4
859.9	946.0	954.3	948.6	942.4	937.1	932.5	928.5	924.8	921.4	918.2
859.1	954.9	967.3	961.6	954.7	948.6	943.3	938.7	934.5	930.7	927.0
859.2	962.9	980.1	974.8	967.1	960.2	954.3	949.1	944.4	940.1	936.0

of the overpotential, this current density distribution is only slightly modified from that corresponding to an isothermal cell at 923K. Current density is seen to be largest at anode and cathode inlet where the gas streams are richest in fuel and oxidant content, and smallest at outlet due to depletion of the gas streams. Nonisothermal operation may affect current density appreciably when a realistic current-overpotential relation is used.

A line of maximum cell temperatures is observed a few centimeters downstream of the anode inlet with the peak temperature occurring at the cathode outlet side. This maximum is due to the following effects:

1. Near the anode inlet, the thermal conductivity of the fresh (hydrogen rich) anode gas is high and its effective heat capacity is low, resulting in a rapid increase in anode stream temperature in this region. The cell and the anode stream cannot differ substantially in temperature in this region due to the high conductivity of the anode gas, so the cell temperature also rises dramatically.
2. The cathode gas in the vicinity of the anode inlet is heated substantially as it traverses the region of high current density/heat release, giving the peak temperatures at the cathode outlet side.
3. Cell temperature is decreased farther from the anode inlet as the cell and the anode stream lose heat to the substantially cooler cathode stream.

The inclusion of in-plane heat conduction will undoubtedly moderate the severity of this temperature maximum. Temperature gradients in this region may still appear somewhat unrealistic unless the anode stream is allowed to heat up before entering the cell. In a real cell heat conduction

through inlet manifolding and upstream in the gas would most certainly have this pre-heating effect.

3.6 Effect of CO Utilization

The equations governing cell performance with simultaneous utilization of H_2 and CO in the anode stream were developed in our previous report¹. Briefly, even if direct electrochemical reaction of CO is slow, the water gas shift equilibrium

does seem to be preserved throughout the anode gas stream. Thus CO utilization can occur indirectly via the shift reaction as H_2 is consumed electrochemically.

Using our earlier definition of H_2 utilization λ and providing a similar definition for the net CO utilization ρ

$$\rho = \frac{\dot{n}_{CO}^o - \dot{n}_{CO}}{\dot{n}_{CO}^o}$$

the mass balance equation for the anode stream becomes

$$\frac{\partial}{\partial x} (\dot{n}_{CO}^o \rho + \dot{n}_{H_2}^o \lambda) = \frac{j}{2F} \quad (41)$$

We next introduce the shift equilibrium constant

$$K_s = \frac{x_{H_2} x_{CO_2}}{x_{H_2O} x_{CO}} \quad (42)$$

The relation between λ and ρ can then be deduced from stoichiometric considerations as

$$1 - \rho = \frac{(1 - \lambda) \left(1 + \lambda \frac{x_{H_2}^o}{x_{CO_2}^o} + 2 \frac{x_{CO}^o}{x_{CO_2}^o} \right)}{\frac{K_s}{K_s^o} \left(1 + \lambda \frac{x_{H_2}^o}{x_{H_2O}^o} \right) + (1 + \lambda) \left(2 \frac{x_{CO}^o}{x_{CO_2}^o} \right)} \quad (43)$$

where K_s^o is evaluated at the inlet temperature. The inlet mole fractions must satisfy equilibrium in this expression.

Numerical solution is accomplished through integration of Eq. (41) with ρ eliminated by way of Eq. (43); λ is thus obtained as a root of a quadratic equation.

In Tables 6 - 9 we present maps of current density and fuel (H_2 and CO) and oxidant utilizations for the conditions listed in Table 5, along with results for inert CO. The calculations were performed for an isothermal case to facilitate direct comparison of the results.

CO utilization replenishes the supply of available H_2 in the anode stream, hence fuel is depleted less rapidly and current density does not fall off as sharply downstream as for the case of inert CO. This effect is small where the inlet anode stream is rich in hydrogen, as in case 1 (Tables 6 and 7) where less than 20% of the inlet CO is converted, giving rise to a 3% increase in current density at anode outlet and less than a 1% increase in total cell current. The effect is more pronounced in case 2 (Tables 8 and 9) where the anode stream is hydrogen lean, and nearly 35% of the inlet CO is converted to give a 20% increase in current density at anode outlet and a 6% increase in total cell current.

We note that the shift reaction can be driven toward net CO production as in the anode inlet region for case 1. This condition occurs because at inlet X_{H_2} is large and X_{CO_2} is small; electrochemical production of CO_2

TABLE 5

CONDITIONS FOR CALCULATIONS DEMONSTRATING EFFECT OF
CO UTILIZATION SHOWN IN TABLES 6 - 9

<u>Case 1</u>	<u>Anode Stream</u>	<u>Cathode Stream</u>
Inlet gas composition	64.2% H ₂ , 9.8% H ₂ O, 6.2% CO ₂ , 19.8% CO	20% CO ₂ , 20% O ₂ , 60% N ₂
Inlet molar flow rate	3×10^{-4} moles/sec	3×10^{-3} moles/sec
 <u>Case 2</u>		
Inlet gas composition	19.1% H ₂ , 4.4% H ₂ O, 8.6% CO ₂ , 17.9 % CO, 50% N ₂	20% CO ₂ , 20% O ₂ , 60% N ₂
Inlet molar flow rate	8×10^{-4} moles/sec	3×10^{-3} moles/sec

For both cases: cell voltage = .75V, $p = 1$ atm, $z_{TOT} = 1.025 \text{ ohm-cm}^2$
 cell temperature = 923°K
 cell dimensions: 10 x 10 cm
 K_s at 923°K = 2.06

TABLE 6

(CASE I) CURRENT DENSITY AND FUEL AND OXIDANT UTILIZATION
FOR AN ISOTHERMAL CELL, WITH WATER-GAS SHIFT
EQUILIBRIUM ASSUMED IN THE ANODE STREAM.
OPERATING CONDITIONS ARE LISTED IN TABLE 5.

CURRENT DENSITY, AMP/CM ²										
0.331	0.289	0.264	0.246	0.231	0.219	0.208	0.199	0.191	0.183	0.176
0.330	0.269	0.263	0.245	0.231	0.218	0.208	0.199	0.190	0.183	0.176
0.320	0.268	0.263	0.245	0.230	0.218	0.208	0.198	0.190	0.183	0.175
0.328	0.267	0.262	0.244	0.230	0.218	0.207	0.198	0.190	0.182	0.175
0.327	0.267	0.262	0.243	0.229	0.217	0.207	0.198	0.189	0.182	0.175
0.326	0.286	0.261	0.243	0.229	0.217	0.206	0.197	0.189	0.182	0.175
0.325	0.285	0.260	0.242	0.228	0.216	0.206	0.197	0.189	0.181	0.174
0.324	0.284	0.260	0.242	0.228	0.216	0.206	0.197	0.188	0.181	0.174
0.323	0.284	0.259	0.241	0.227	0.215	0.205	0.196	0.188	0.181	0.174
0.322	0.283	0.258	0.241	0.227	0.215	0.205	0.196	0.188	0.180	0.173
0.321	0.282	0.258	0.240	0.226	0.214	0.204	0.195	0.187	0.180	0.173
ANODE H ₂ CONVERSIONS										
0.000	0.089	0.162	0.225	0.281	0.332	0.379	0.422	0.452	0.499	0.534
0.000	0.058	0.161	0.224	0.281	0.331	0.378	0.421	0.461	0.498	0.533
0.000	0.088	0.161	0.224	0.280	0.331	0.377	0.420	0.460	0.497	0.532
0.000	0.088	0.161	0.223	0.279	0.330	0.377	0.419	0.459	0.497	0.531
0.000	0.088	0.160	0.223	0.279	0.329	0.376	0.419	0.458	0.496	0.531
0.000	0.088	0.160	0.222	0.278	0.329	0.375	0.418	0.457	0.495	0.530
0.000	0.087	0.159	0.222	0.278	0.328	0.374	0.417	0.457	0.494	0.529
0.000	0.087	0.159	0.221	0.277	0.327	0.373	0.416	0.456	0.493	0.528
0.000	0.087	0.159	0.221	0.276	0.326	0.372	0.415	0.455	0.492	0.526
0.000	0.087	0.158	0.220	0.275	0.326	0.372	0.414	0.454	0.491	0.525
0.000	0.086	0.158	0.220	0.275	0.325	0.371	0.413	0.453	0.490	0.524
ANODE CO CONVERSIONS										
0.000	-0.023	-0.025	-0.014	0.004	0.028	0.057	0.088	0.122	0.158	0.195
0.000	-0.023	-0.025	-0.014	0.004	0.028	0.056	0.088	0.122	0.157	0.194
0.000	-0.023	-0.025	-0.015	0.004	0.028	0.056	0.087	0.121	0.156	0.193
0.000	-0.023	-0.025	-0.015	0.003	0.027	0.055	0.087	0.120	0.155	0.192
0.000	-0.022	-0.025	-0.015	0.003	0.027	0.055	0.086	0.119	0.154	0.191
0.000	-0.022	-0.025	-0.015	0.003	0.027	0.054	0.085	0.119	0.154	0.190
0.000	-0.022	-0.025	-0.015	0.003	0.026	0.054	0.085	0.118	0.153	0.189
0.000	-0.022	-0.025	-0.015	0.002	0.026	0.053	0.084	0.117	0.152	0.188
0.000	-0.022	-0.025	-0.015	0.002	0.025	0.053	0.083	0.116	0.151	0.187
0.000	-0.022	-0.025	-0.016	0.002	0.025	0.052	0.082	0.115	0.150	0.185
0.000	-0.022	-0.025	-0.016	0.002	0.024	0.052	0.082	0.114	0.149	0.184
CATHODE CO ₂ CONVERSIONS										
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.027	0.024	0.022	0.020	0.019	0.018	0.017	0.016	0.016	0.015	0.014
0.054	0.048	0.043	0.040	0.038	0.036	0.034	0.033	0.031	0.030	0.029
0.091	0.071	0.065	0.060	0.057	0.054	0.051	0.049	0.047	0.045	0.043
0.108	0.095	0.087	0.081	0.076	0.072	0.068	0.065	0.063	0.060	0.058
0.135	0.118	0.103	0.101	0.095	0.090	0.085	0.082	0.078	0.075	0.072
0.162	0.142	0.129	0.120	0.113	0.107	0.102	0.098	0.094	0.090	0.086
0.189	0.165	0.151	0.140	0.132	0.125	0.119	0.114	0.109	0.105	0.101
0.216	0.189	0.172	0.160	0.151	0.143	0.136	0.130	0.125	0.120	0.115
0.242	0.212	0.194	0.180	0.169	0.161	0.153	0.146	0.140	0.135	0.129
0.269	0.235	0.215	0.200	0.188	0.179	0.170	0.162	0.156	0.149	0.144

TABLE 7

(CASE I) - CURRENT DENSITY AND FUEL AND OXIDENT UTILIZATION FOR AN ISOTHERMAL CELL WITH ANODE CO ASSUMED TO BE INERT. OPERATING CONDITIONS ARE LISTED IN TABLE 5.

CURRENT DENSITY, AMP/CM²

0.331	0.289	0.264	0.246	0.231	0.218	0.207	0.197	0.188	0.179	0.171
0.330	0.289	0.264	0.245	0.230	0.218	0.207	0.197	0.188	0.179	0.171
0.329	0.288	0.263	0.245	0.230	0.218	0.207	0.197	0.188	0.179	0.171
0.328	0.287	0.262	0.244	0.230	0.217	0.206	0.196	0.187	0.179	0.170
0.327	0.287	0.262	0.244	0.229	0.217	0.206	0.196	0.187	0.178	0.170
0.326	0.286	0.261	0.243	0.229	0.216	0.205	0.196	0.187	0.178	0.170
0.325	0.285	0.260	0.243	0.228	0.216	0.205	0.195	0.186	0.178	0.170
0.324	0.284	0.260	0.242	0.228	0.215	0.205	0.195	0.186	0.178	0.170
0.323	0.283	0.259	0.241	0.227	0.215	0.204	0.195	0.186	0.177	0.169
0.322	0.283	0.258	0.241	0.227	0.214	0.204	0.194	0.185	0.177	0.169
0.321	0.282	0.258	0.240	0.226	0.214	0.203	0.194	0.185	0.177	0.169

ANODE H₂ CONVERSIONS

0.000	0.082	0.154	0.221	0.282	0.341	0.396	0.449	0.499	0.546	0.592
0.000	0.082	0.154	0.220	0.282	0.340	0.395	0.448	0.498	0.545	0.590
0.000	0.081	0.153	0.219	0.281	0.339	0.394	0.447	0.496	0.544	0.589
0.000	0.081	0.153	0.219	0.281	0.339	0.393	0.446	0.495	0.543	0.588
0.000	0.081	0.153	0.218	0.280	0.338	0.393	0.445	0.494	0.542	0.587
0.000	0.081	0.152	0.218	0.279	0.337	0.392	0.444	0.493	0.540	0.586
0.000	0.080	0.152	0.217	0.278	0.336	0.391	0.443	0.492	0.539	0.584
0.000	0.080	0.151	0.217	0.278	0.335	0.390	0.441	0.491	0.538	0.583
0.000	0.080	0.151	0.216	0.277	0.334	0.389	0.440	0.490	0.537	0.582
0.000	0.080	0.150	0.215	0.276	0.333	0.388	0.439	0.488	0.535	0.580
0.000	0.079	0.150	0.215	0.275	0.332	0.386	0.438	0.487	0.534	0.579

ANODE CO CONVERSIONS

0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

CATHODE CO₂ CONVERSIONS

0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.027	0.024	0.022	0.020	0.019	0.018	0.017	0.016	0.015	0.015	0.014
0.054	0.049	0.043	0.040	0.038	0.036	0.034	0.032	0.031	0.029	0.028
0.081	0.071	0.065	0.060	0.057	0.054	0.051	0.049	0.046	0.044	0.042
0.108	0.095	0.087	0.081	0.076	0.072	0.068	0.065	0.062	0.059	0.056
0.135	0.118	0.108	0.101	0.095	0.089	0.085	0.081	0.077	0.074	0.070
0.162	0.142	0.130	0.121	0.113	0.107	0.102	0.097	0.092	0.088	0.084
0.189	0.165	0.151	0.140	0.132	0.125	0.119	0.113	0.108	0.103	0.098
0.216	0.189	0.172	0.160	0.151	0.143	0.136	0.129	0.123	0.117	0.112
0.242	0.212	0.194	0.180	0.169	0.160	0.152	0.145	0.138	0.132	0.126
0.269	0.235	0.215	0.200	0.188	0.178	0.169	0.161	0.154	0.147	0.140

TABLE 8

(CASE II) CURRENT DENSITY AND FUEL AND OXIDANT UTILIZATION
FOR AN ISOTHERMAL CELL WITH WATER-GAS SHIFT
EQUILIBRIUM ASSUMED IN THE ANODE STREAM.
OPERATING CONDITIONS ARE LISTED IN TABLE 5.

CURRENT DENSITY, AMP/CM²

0.302	0.282	0.266	0.253	0.242	0.232	0.223	0.215	0.208	0.201	0.195
0.302	0.281	0.265	0.252	0.241	0.231	0.223	0.215	0.208	0.201	0.195
0.301	0.280	0.265	0.252	0.241	0.231	0.222	0.215	0.207	0.201	0.194
0.300	0.280	0.264	0.251	0.240	0.231	0.222	0.214	0.207	0.200	0.194
0.299	0.279	0.263	0.250	0.240	0.230	0.221	0.214	0.207	0.200	0.194
0.298	0.278	0.263	0.250	0.239	0.229	0.221	0.213	0.206	0.199	0.193
0.297	0.277	0.262	0.249	0.238	0.229	0.220	0.213	0.206	0.199	0.193
0.296	0.277	0.261	0.249	0.238	0.228	0.220	0.212	0.205	0.199	0.192
0.295	0.276	0.260	0.248	0.237	0.228	0.219	0.212	0.205	0.198	0.192
0.294	0.275	0.260	0.247	0.237	0.227	0.219	0.211	0.204	0.198	0.192
0.293	0.274	0.259	0.247	0.236	0.227	0.218	0.211	0.204	0.197	0.191

ANODE H₂ CONVERSIONS

0.000	0.060	0.115	0.166	0.213	0.257	0.299	0.339	0.376	0.412	0.446
0.000	0.060	0.115	0.165	0.213	0.257	0.298	0.338	0.375	0.411	0.445
0.000	0.060	0.115	0.165	0.212	0.256	0.298	0.337	0.375	0.410	0.444
0.000	0.060	0.114	0.165	0.212	0.256	0.297	0.336	0.374	0.409	0.443
0.000	0.060	0.114	0.164	0.211	0.255	0.296	0.336	0.373	0.409	0.443
0.000	0.060	0.114	0.164	0.211	0.254	0.296	0.335	0.372	0.408	0.442
0.000	0.059	0.113	0.163	0.210	0.254	0.295	0.334	0.371	0.407	0.441
0.000	0.059	0.113	0.163	0.209	0.253	0.294	0.333	0.370	0.406	0.440
0.000	0.059	0.113	0.162	0.209	0.252	0.293	0.332	0.369	0.405	0.439
0.000	0.059	0.112	0.162	0.208	0.252	0.293	0.332	0.369	0.404	0.438
0.000	0.059	0.112	0.161	0.208	0.251	0.292	0.331	0.368	0.403	0.436

ANODE CO CONVERSIONS

0.000	0.038	0.075	0.111	0.147	0.182	0.217	0.251	0.285	0.317	0.350
0.000	0.038	0.075	0.111	0.147	0.182	0.216	0.250	0.284	0.317	0.349
0.000	0.038	0.075	0.111	0.146	0.181	0.216	0.250	0.283	0.316	0.348
0.000	0.038	0.074	0.111	0.146	0.181	0.215	0.249	0.282	0.315	0.347
0.000	0.038	0.074	0.110	0.146	0.180	0.215	0.248	0.282	0.314	0.346
0.000	0.037	0.074	0.110	0.145	0.180	0.214	0.248	0.281	0.313	0.345
0.000	0.037	0.074	0.110	0.145	0.179	0.214	0.247	0.280	0.313	0.345
0.000	0.037	0.074	0.109	0.144	0.179	0.213	0.246	0.279	0.312	0.344
0.000	0.037	0.073	0.109	0.144	0.178	0.212	0.246	0.278	0.311	0.343
0.000	0.037	0.073	0.109	0.143	0.178	0.212	0.245	0.278	0.310	0.342
0.000	0.037	0.073	0.108	0.143	0.177	0.211	0.244	0.277	0.309	0.341

CATHODE CO₂ CONVERSIONS

0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.025	0.023	0.022	0.021	0.020	0.019	0.018	0.018	0.017	0.017	0.016
0.050	0.046	0.044	0.042	0.040	0.038	0.037	0.035	0.034	0.033	0.032
0.074	0.069	0.065	0.062	0.059	0.057	0.055	0.053	0.051	0.050	0.049
0.099	0.092	0.087	0.083	0.079	0.076	0.073	0.071	0.068	0.066	0.064
0.124	0.115	0.109	0.103	0.099	0.095	0.091	0.088	0.085	0.082	0.080
0.149	0.138	0.130	0.124	0.119	0.114	0.110	0.105	0.102	0.099	0.096
0.173	0.161	0.152	0.144	0.138	0.133	0.128	0.123	0.119	0.115	0.112
0.197	0.184	0.173	0.165	0.158	0.151	0.146	0.141	0.136	0.132	0.127
0.221	0.206	0.195	0.185	0.177	0.170	0.164	0.158	0.153	0.148	0.143
0.245	0.229	0.216	0.206	0.197	0.189	0.182	0.175	0.170	0.164	0.159

TABLE 9

(CASE II) CURRENT DENSITY AND FUEL AND OXIDANT UTILIZATION FOR AN ISOTHERMAL CELL, WITH ANODE CO ASSUMED TO BE INERT. OPERATING CONDITIONS ARE LISTED IN TABLE 5.

CURRENT DENSITY, AMP/CM²

0.302	0.278	0.260	0.244	0.231	0.219	0.207	0.196	0.186	0.175	0.164
0.302	0.278	0.259	0.244	0.231	0.218	0.207	0.196	0.185	0.175	0.164
0.301	0.277	0.259	0.243	0.230	0.218	0.207	0.196	0.185	0.174	0.163
0.300	0.276	0.259	0.243	0.230	0.218	0.206	0.195	0.185	0.174	0.163
0.299	0.275	0.257	0.242	0.229	0.217	0.206	0.195	0.185	0.174	0.163
0.298	0.275	0.257	0.242	0.229	0.217	0.205	0.195	0.184	0.174	0.163
0.297	0.274	0.256	0.241	0.228	0.216	0.205	0.194	0.184	0.174	0.163
0.296	0.273	0.255	0.241	0.228	0.216	0.205	0.194	0.184	0.173	0.163
0.295	0.272	0.255	0.240	0.227	0.215	0.204	0.194	0.183	0.173	0.163
0.294	0.272	0.254	0.239	0.226	0.215	0.204	0.193	0.183	0.173	0.163
0.293	0.271	0.253	0.239	0.226	0.214	0.203	0.193	0.183	0.173	0.162

ANODE H₂ CONVERSIONS

0.000	0.096	0.184	0.266	0.344	0.418	0.486	0.554	0.616	0.675	0.731
0.000	0.095	0.183	0.266	0.344	0.417	0.487	0.553	0.615	0.674	0.729
0.000	0.095	0.183	0.265	0.343	0.416	0.485	0.551	0.614	0.673	0.728
0.000	0.095	0.182	0.265	0.342	0.415	0.484	0.550	0.612	0.671	0.727
0.000	0.095	0.182	0.264	0.341	0.414	0.483	0.549	0.611	0.670	0.725
0.000	0.094	0.181	0.263	0.340	0.413	0.482	0.547	0.610	0.668	0.724
0.000	0.094	0.181	0.262	0.339	0.412	0.481	0.546	0.608	0.667	0.722
0.000	0.094	0.180	0.262	0.338	0.411	0.480	0.545	0.607	0.665	0.720
0.000	0.093	0.180	0.261	0.337	0.410	0.478	0.543	0.605	0.664	0.719
0.000	0.093	0.179	0.260	0.336	0.409	0.477	0.542	0.604	0.662	0.717
0.000	0.093	0.179	0.259	0.335	0.407	0.476	0.540	0.602	0.660	0.715

ANODE CO CONVERSIONS

0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

CATHODE CO₂ CONVERSIONS

0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.025	0.023	0.021	0.020	0.019	0.018	0.017	0.016	0.015	0.014	0.013
0.050	0.046	0.043	0.040	0.038	0.036	0.034	0.032	0.030	0.029	0.027
0.074	0.068	0.064	0.060	0.057	0.054	0.051	0.048	0.045	0.043	0.040
0.099	0.091	0.085	0.080	0.076	0.072	0.068	0.064	0.061	0.057	0.054
0.124	0.114	0.106	0.100	0.095	0.090	0.085	0.080	0.076	0.072	0.067
0.148	0.136	0.127	0.120	0.113	0.107	0.102	0.096	0.091	0.086	0.081
0.173	0.159	0.148	0.140	0.132	0.125	0.119	0.112	0.106	0.100	0.094
0.197	0.181	0.169	0.159	0.151	0.143	0.136	0.128	0.121	0.115	0.107
0.221	0.204	0.190	0.179	0.169	0.161	0.152	0.144	0.137	0.129	0.121
0.245	0.226	0.211	0.199	0.188	0.178	0.169	0.160	0.152	0.143	0.134

then leads to a sufficient percentage increase in X_{CO_2} to increase X_{CO} as can be seen from Eq. (42). After X_{CO_2} has increased, further production of H_2O and utilization of H_2 drive the shift reaction back toward net CO utilization.

It is also worth mentioning that the anode stream will not deposit carbon for either case investigated.

3.7 Counterflow Geometry

The preceding calculation procedure can be adapted to the case of counterflow geometry without extensive modification. The important simplification for this case is that the problem is one-dimensional, so that only one pair of counterflowing channels need be considered.

Defining anode and cathode utilization parameters λ , μ as before, with anode flow in the positive x-direction, cathode flow in the negative x-direction, we have

$$\frac{d\lambda}{dx} = \frac{j}{2F\dot{n}_{H_2}^o} \quad (\text{anode})$$

$$\frac{d\mu}{dx} = \frac{-j}{2F\dot{n}_{CO_2}^o} \quad (\text{cathode})$$

Solving for j gives

$$-\frac{d\mu}{dx} = \frac{\dot{n}_{H_2}^o}{\dot{n}_{CO_2}^o} \frac{d\lambda}{dx} \quad (44)$$

We take the anode inlet (and cathode outlet) to be at $x = 0$, cathode inlet (anode outlet) at $x = L$. Integrating Eq. (44) from $x = 0$ gives the relation between λ and μ as

$$\mu(x) = \mu(0) - (\dot{n}_{H_2}^o / \dot{n}_{CO_2}^o) \lambda(x),$$

reducing by one the number of variables required for this case.

The temperature relations appear as before, with derivatives taken with respect to x .

$$\frac{d}{dx} (\dot{n} C_p T_m)_a = h_a^* (T_o - T_{ma}) + \Sigma (g_i C_{pi})_a T_o \quad (\text{anode})$$

$$\frac{d}{dx} (\dot{n} C_p T_m)_c = h_c^* (T_o - T_{mc}) + \Sigma (g_i C_{pi})_c T_o \quad (\text{cathode})$$

The difficulty here is that the boundary conditions are specified at two different locations, i. e., at the anode and cathode inlets. If we choose to march in the positive x -direction, we are lacking all the necessary information at $x = 0$. An obvious approach to the problem is to assume values for the initially unknown quantities, then march the length of the channel to compute the "given" boundary conditions. The procedure can be iterated until satisfactory agreement is obtained between assumed and prescribed boundary conditions.

To summarize, we are given $\lambda(0)$, $T_{ma}(0)$, $\mu(L)$, $T_{mc}(L)$. To march in the positive x -direction, we must assume values for $\mu(0)$, $T_{mc}(0)$ such that the computed values of $\mu(L)$, $T_{mc}(L)$ match the prescribed values.

We note that numerical instabilities sometimes encountered in classical two-point boundary value problems are not anticipated here. These instabilities are associated with computing non-physical solutions subject to assumed boundary conditions, whereas in the present case every assumed boundary condition generates a solution to a real problem. The difficulty lies in identifying a solution that solves the problem of interest.

3.8 Justification of Assumptions

In the preceding analysis we have made use of the assumption that the velocity, temperature, and composition profiles are fully developed in the gas streams. These assumptions can be justified by examining the growth rates of the velocity, temperature, and composition boundary layers for the flow conditions of interest.

Boundary Layer Argument

Fully developed profiles exhibit streamwise similarity; we can always identify a nondimensional profile relation that is invariant in the flow direction. We can define fully developed velocity (u), temperature, and composition profiles respectively by the relations

$$\frac{\partial}{\partial x} \left(\frac{u}{u_m} \right) = \frac{\partial}{\partial x} \left(\frac{T_o - T}{T_o - T_m} \right) = \frac{\partial}{\partial x} \left(\frac{C_o - C}{C_o - C_m} \right) = 0$$

where the subscript 'o' denotes a value at a surface, subscript 'm' a mean value, and x is the flow direction.

If we consider the velocity profile as it develops in the inlet region of a smooth walled channel (Fig. 5), we see that the extent of the region of fluid retarded in the vicinity of the wall (the "boundary layer") grows in the streamwise direction. A fully developed profile is attained when the boundary layers merge some "entry length" downstream of the channel inlet. This entry length is then a measure of the capacity of the velocity profile to re-establish full development following a perturbation. (In this case, the perturbation is the abrupt imposition of the condition $u_{\text{wall}} = 0$.) If, for a given set of flow conditions, we find that the entry length is small compared with the overall streamwise dimensions, we can assume that the flow remains approximately fully developed on a local basis.

Figure 5

Development of the velocity profile in the hydrodynamic entry region of a channel.

From boundary layer theory⁶ we have the relation

$$\frac{\delta_v}{h} = 5 \left(\frac{x}{h \text{Re}_h} \right)^{1/2}$$

for the boundary layer thickness δ_v in terms of the Reynolds number Re_h ,

$$\text{Re}_h = \frac{uh}{\nu}$$

where h is the channel depth, x is the streamwise coordinate and ν is the kinematic viscosity (cm^2/sec). It follows that δ_v is then of the order of the channel depth for $x/h \sim \text{Re}/25$. For the worst case of $\text{Re}_h = 300$ (the highest value anticipated at either electrode), we compute $x_{\text{fully developed}} \sim 12h$.

Using as a typical aspect ratio for the channel $h/L \sim 0.001$, we have the entry length

$$x_{\text{fully developed}} \sim 1\% \text{ of the channel length.}$$

This is sufficiently small to support our assumptions that the velocity profile remains locally fully developed.

As far as the thermal profile is concerned, we quote the result from boundary layer theory⁶ that if the Prandtl number, defined by

$$Pr = \frac{vc_p}{\rho k} ,$$

where c_p is the specific heat, k is the thermal conductivity and ρ is the mass density, is unity, then the thickness of the thermal boundary layer will be of the same order as that of the velocity boundary layer.

Likewise, the species composition and thermal boundary layer will be of the same order if the Lewis number of each species i involved, defined by

$$Le_i = \left(\frac{\rho D}{k} \right)_i c_p ,$$

where D is a diffusion coefficient, is unity.

For the gas streams in molten carbonate cells, $Pr \sim Le_i \sim 1$ is approximately satisfied, allowing us to base assumption of fully developed temperature and composition profiles on our assumed fully developed velocity profile.

Finally, denoting molar flow rate per unit channel width $\dot{n}$, and molar flux across the gas/electrode interface g_w , we have

$$g_w \ll \frac{\dot{n}}{h} ,$$

permitting the assumption of constant composition across the channel depth.

4. REFERENCES

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