THERMO-CHEMICAL MODELING OF INTERNAL-REFORMING SOFCs
AT THE IDAHO NATIONAL ENGINEERING LABORATORY

Chester G. Motloch and Ralph G. Bennett
Idaho National Engineering Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-3815

ABSTRACT

The Idaho National Engineering Laboratory is performing research and
development of a cross-flow, internal-reforming SOFC. Part of the effort
entails development of a thermo-chemical computer model to execute
scoping, design, and performance studies of the INEL SOFC design. A
one-dimensional model is being completed and extensions to two- and
three-dimensions are planned. Mass, heat, electrochemical, and chemical
kinetic balance equations are presented along with preliminary simulation
results.

INTRODUCTION

This paper reports the development of an advanced thermo-chemical computer model
of an internal-reforming Solid Oxide Fuel Cell (SOFC) concept that is being developed at
the Idaho National Engineering Laboratory (INEL). The model is being developed to
address key questions about SOFC performance. These include the calculation of the
SOFC thermal distribution, fuel and electrical efficiency, and whether or not the SOFC
becomes thermally quenched. These depend on the rates of internal-reforming,
oxidation, and shift that occur. These in turn are dependent on the heat and mass transfer
and particularly the multi-region, multi-species diffusion in the porous media. A coupled
set of nonlinear second-order differential equations are being developed to calculate the
solution to this problem under representative material, geometric, boundary, and
operating conditions.

MODELING SCOPE

Our work is centered on two aspects. The first is to advance the state of SOFC
computer modeling, and the second is to characterize the INEL SOFC behavior using the
new model. A recent model by Achenbach (1) is one of the most sophisticated found in
the literature. The INEL SOFC model will include most features of Reference 1 (except
co-flow and counter-current flow because they are not relevant to the INEL SOFC), plus
it will include full multi-region, multi-species diffusion in porous media. In
Reference (1), Achenbach combines the four solid elements of a SOFC into a single

1133
lump. In contrast, the INEL SOFC model explicitly details each of the fuel cell regions, i.e., air and fuel channels, plus interconnect, anode, electrolyte, and cathode. This is necessary to more correctly model the reforming that occurs within the interconnect and anode in the INEL SOFC. That is, the reforming in our SOFC is a homogeneous phenomenon as opposed to the heterogeneous approximation made in Reference 1. This affects the rate determining steps and the evolution and distribution of product species and heat. Explicit modeling of each of the species is also important because the interactions between them affect their diffusivities which in turn affect the dynamic mass, energy, and electrochemical processes.

**INEL SOLID OXIDE FUEL CELL**

The INEL SOFC concept is depicted in Figure 1. It features a planar stack design with internal steam-reforming and cross-flow of the fuel and air. Working from the bottom up, the repeat unit is comprised of the interconnect, cathode, electrolyte, and anode.

The interconnect is made of intermetallic nickel aluminide, Ni-Al; the cathode is made of LaMnO$_3$; the electrolyte is made of ZrO$_2$; and the anode is made of NiO-ZrO$_2$. Selection of these materials is based on electrical, thermal, and mechanical properties, and low cost. Both the interconnect material (Ni-Al) and the anode material (NiO-ZrO$_2$) are catalytic to steam-reforming of methane. The technology for depositing the thin electrolyte is based upon a unique liquid injection plasma deposition (LIPD) system for producing high-density thin coatings. Patent applications have been submitted for both the choice of materials and fabrication technologies (2,3).

**SOFC OPERATION**

There are five chemical reactions involving six species that are of principal concern for internal-reforming SOFCs. These include three exothermic oxidation reactions for hydrogen, carbon monoxide, and methane that are respectively given by:

\[
H_2 + 0.5O_2 \leftrightarrow H_2O \quad [1]
\]

\[
CO + 0.5O_2 \leftrightarrow CO_2 \quad [2]
\]

\[
CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad [3]
\]

The remaining two important chemical reactions are the endothermic steam-reforming of methane and the exothermic shift of carbon monoxide. Each is respectively given by:
\[
CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad [4]
\]
\[
CO + H_2O \leftrightarrow CO_2 + H_2 \quad [5]
\]

For off-equilibrium conditions, chemical kinetics equations are required for the dominant rate processes. Until design specific information becomes available, the rate equation reported by Achenbach (1) for steam reforming in nickel cermets is used:

\[
\dot{r}_{CH_4} = r_0 e^{-\frac{E_A}{R_g T}} \Phi_{CH_4} \quad [6]
\]

The stoichiometric ideal fuel cell electrical potential is called the Gibbs voltage, \( U_G \), and is given by:

\[
U_G = \frac{-\Delta G}{n_F} \quad [7]
\]

For off-equilibrium concentrations, the Gibbs voltage is modified to yield a cell potential called the Nemst voltage. Three other electrochemical losses (commonly referred to as polarizations) are also relevant (4). One is the activation polarization, the second is the concentration polarizations at the anode and cathode, and the third is the resistance polarization.

When an external load is applied to the fuel cell, it will develop a current density, \( j \), related to the molar flux of oxygen ions, \( N_O \). Faraday's law gives \( j \) as:

\[
j = n_F N_O \quad [8]
\]

CONSERVATION EQUATIONS

Conservation equations are being developed for the flowing chemistry, electrochemistry, mass, and energy balances relevant to the INEL SOFC concept. The important chemical processes include reforming, shift, oxidation, reduction, and the associated chemical kinetics. These relationships are the bases for the mass and energy balance equations. The electrochemical relations provide another set that help close the balance equations. These generally provide the source terms in the energy equations.
The SOFC stack can be mathematically represented by a matrix of unit cells. A typical unit cell is shown in Figure 2. For each unit cell, energy balance equations are formulated for each species in each material region. For example, the two-dimensional finite-difference unit cell energy balance in the interconnect is given by:

\[
\begin{align*}
&k_I A_{Ix} \frac{(T_{Iy}(k,l) - T_{Iy}(k,l-1))}{\Delta x_I} + k_I A_{Iy} \frac{(T_{Iy}(k,l) - T_{Iy}(k,l+1))}{\Delta y_I} \\
&+ k_I A_{Ia} \frac{(T_{Ia}(k,l) - T_{Ia}(k-1,l))}{\Delta y_I} + k_I A_{Ia} \frac{(T_{Ia}(k,l) - T_{Ia}(k+1,l))}{\Delta y_I} \\
&+ \left(\frac{T_{Ia} - T_{If}}{R_{If}}\right)(k,l) + \left(\frac{T_{Ia} - T_{If}}{R_{If}}\right)(k,l) \\
&= \left(\frac{h_{Ia} A_{Ia} (T_{Ia} - T_a)}{R_{If}}\right)(k,l) + \left(\frac{h_{If} A_{If} (T_{If} - T_f)}{R_{If}}\right)(k,l) \\
&+ (N_{If}^{CH4} A_{If} c_p^{CH4} T_f)(k,l) + (N_{If}^{H2O} A_{If} c_p^{H2O} T_f)(k,l) \\
&- (N_{If}^{CO2} A_{If} c_p^{CO2} T_f)(k,l) + (q_l)(k,l)
\end{align*}
\]

If the interconnect geometry is approximated as an equivalent slab, the interconnect average temperature in the z direction in each unit cell is given by:

\[
\bar{T}_I = \frac{q_l \Delta z_I}{12 k_I A_{If}} + \frac{T_{Ia} + T_{If}}{2}
\]

The unit cell mass balance equation for the fuel channel is given by:

\[
[N_j^{If} A_{If}](k,l) + [N_j^{If} A_{If}](k,l+1) = [N_j^{If} A_{If}](k,l) + [N_j^{If} A_{If}](k,l)
\]

Because of the multi-species nature of the model, the Stefan-Maxwell equation is required to develop the mass balance equations in the solid regions (5):

\[
\frac{dx_j}{dz} = \sum_{j=1}^{n} \frac{1}{cD_{ij}}(x_i N_j - x_j N_i)
\]
Based upon stoichiometric relationships for specific chemical reactions involving gas species $i, j, k, l,$ and $m$, an effective diffusivity is defined, $D_i$. For the steam-reforming reaction, $D_j$ is given by:

$$[D_i]^{-1} = \left( \frac{1}{D_{ij}} - \frac{3}{D_{ik}} - \frac{1}{D_{il}} \right) x_i - \left( \frac{1}{D_{ij}} \right) x_j$$

$$- \left( \frac{1}{D_{ik}} \right) x_k - \left( \frac{1}{D_{il}} \right) x_l - \left( \frac{1}{D_{im}} \right) x_m$$  \[13\]

When $D_A$ is used in Fick's first law of diffusion and in turn substituted into the mass balance equation and with $r^w$ defined as the volumetric rate constant, we find:

$$\frac{dN_i}{dz} = \frac{\partial}{\partial z (cD_i \frac{dx_i}{dz})} = -r^w c x_i$$  \[14\]

Both the interconnect and the anode mass balances have homogeneous steam-reforming source terms. In addition, the anode mass balance has two heterogeneous kinetic terms resulting from the oxidation of the carbon monoxide and hydrogen at the anode/electrolyte interface.

Once the molar fluxes are known from the mass balance, the electric current can be calculated using Faraday's law given in Equation [8]. Then the electrochemical polarizations and the associated heat source terms can be calculated.

Thus for each unit cell, energy, mass, and electric balance equations are formulated for the species in each region. Five species are present in the fuel channel, interconnect, and anode; two are present in the air channel; and one is present in the electrolyte. In the cathode, nitrogen plus oxygen atoms and oxygen ions are present, but the oxygen species are proportional to each other. This yields 20 mass balance equations. Further, one energy equation is required for each of the 6 regions, and one electric current equation is required for each of the four electrically conducting regions. Thus for each cell, a total of 30 balance equations is required. This distribution and the unknowns are shown in Table I.

**NODALIZATION**

The INEL SOFC stack model is divided into $(n \times n \times m)$ unit cells which results in $(n \times n \times m) \times 30$ unknowns. Approximate values for $n$ and $m$ for a $(15 \text{ cm} \times 15 \text{ cm} \times 13 \text{ cm})$, 5 kWe INEL SOFC stack are 38 and 42, respectively. Further, some of the equations may require additional discretization in the $z$ direction, orthogonal to the air and fuel channels.
Flows in the air and fuel channels are approximated as plug flow using a one-dimensional representation. This is justified by examining the relevant nondimensional parameters including the Prandtl number, Peclet number, Schmidt number, and Lewis number. The values for the gases found in the fuel channel are all near 1.0 and the values in the air channel range from about 1 to 10. This shows that all of the mass and heat transfer process are in relative balance including the inertial forces, viscous forces, thermal conduction, and mass diffusion.

Equivalent thermal resistances calculated for the unit cell are used to formulate a thermal network for modeling purposes. Nondimensional analysis has been performed to determine the suitability of the nodalization. For example, the Biot number determines the appropriate lumping of the unit cell. Preliminary calculations indicate that the Biot number is in the range of 0.1 to 0.4 for the interconnect and 1 to 5 for the anode/electrolyte/cathode structure. White (6) shows that for irregular shapes, the criteria for lumping is that the Biot number be less than 0.1. Thus, the interconnect is relatively lumpable, whereas the anode, electrolyte, and cathode structures are not. Hence, the anode, electrolyte, and cathode are explicitly modeled without lumping.

OPERATING CONDITIONS

The expected operating conditions are representative of high temperature SOFCs. The temperatures will range from about 900 K to 1500 K and the operating pressure will be near atmospheric. Initially, adiabatic surfaces are assumed but these are planned to be replaced with radiative and convective boundary conditions. The flow rate in the fuel channel has been calculated to range from 0.2 m/sec to 1.0 m/sec, and in the air channel it ranges from 0.6 m/sec to 2.9 m/sec. The corresponding Reynolds numbers in the fuel channel are 1.3 to 4.6, and in the air channel are 4.6 to 14.3. Thus, all Reynolds numbers are laminar.

The model requires a number of physical parameters and relations that include diffusivity, porosity, tortuosity, density, thermal conductivity, and electronic and ionic conductivity. Catalytic methane steam-reforming information will be obtained through bench top experiments performed by Wright (7) at INEL.

NUMERICAL APPROACH

To make the problem manageable, the solution scheme uses three nested loops. The inner loop calculates the mass and energy terms within each individual unit cell using a Newton-Raphson solver for nonlinear systems of equations with an LU decomposition routine. The next loop calculates the heat conduction in the interconnect in the x and y directions from one unit cell to another using the method of Successive Overrelaxation (8). The outer loop updates the current densities. The solution is iterated until acceptable convergence is obtained.
Figure 3 shows results from a very simple preliminary scoping model. The model calculates the fuel channel bulk gas temperature, molar concentrations of five species in the fuel channel, and the shift and reforming fractions based on equilibrium chemical kinetics. This preliminary model assumes a single homogeneous equilibrium mixture region and does not calculate any other processes such as mass or energy transfer. Scoping studies performed with the model demonstrate that most of the methane-reforming occurs near the SOFC entrance region and that some degree of exhaust recycle is required to prevent quenching.

CONCLUSION

To summarize, the INEL SOFC model is an extension of other models and will include multi-region, multi-species, mass diffusion and convection, and energy balances with both homogeneous and heterogeneous electrochemical kinetics. The INEL SOFC model will allow performance calculations to be done with increased sophistication. Analysis results will yield SOFC gas compositions and distributions, temperature distributions, current, voltage and power distributions, fuel utilization, and electrochemical efficiencies. The combination of new model features coupled with its application to issues of current interest will help further advancements in SOFC research and development.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Energy Research, under DOE contracts DE-AC07-76ID01570 and DE-AC07-94ID13223.

NOMENCLATURE

\begin{align*}
A &= \text{Area, (m}^2) \\
c &= \text{Molar density, (mol/m}^3) \\
cp &= \text{Specific heat at constant pressure, (J/kg-K)} \\
D_i &= \text{Effective diffusivity, (m}^2/s) \\
D_{ij} &= \text{Binary diffusivity, (m}^2/s) \\
E_A &= \text{Activation energy, (J/mol)} \\
F &= \text{Faraday's constant, (9.6485 x 10}^4 \text{ C/mol)} \\
h &= \text{Wall heat transfer coefficient, (W/m}^2\text{-K)} \\
j &= \text{Current density, (A/m}^2) \\
k &= \text{Thermal conductivity, (W/m-K)} \\
n_e &= \text{Number of electrons per atom involved in electrochemical process} \\
N &= \text{Molar flux, (mol/s-m}^2) \\
P_{\text{CH}_4} &= \text{Methane partial pressure, (bars)} \\
q &= \text{Energy equation source term, (W)}
\end{align*}
\( \dot{\text{CH}}_4 \) Methane steam-reforming rate, (mol/m²-s)

\( r_0 \) Frequency factor, (mol/m²-bars-s)

\( r'' \) Volumetric rate constant, (moles reacted/s-moles catalyst)

\( R_g \) Gas constant, (8.3451 J/K-mol)

\( R \) Equivalent thermal resistance, (K/W)

\( T \) Temperature, (K)

\( \bar{T} \) Average temperature, (K)

\( U_G \) Gibbs voltage, (V)

\( x_i \) Species concentration, (mol/m³)

\( \Delta G \) Gibbs free energy, (kJ/mol)

\( \Delta x, \Delta y, \Delta z \) Incremental distance in x-, y-, and z-directions, (m)

Subscripts:

\( a \) Air channel

\( Af \) Anode/fuel channel interface

\( f \) Fuel channel

\( i, j, k, l, m \) Gas species

\( I \) Interconnect

\( la \) Interconnect/air channel interface

\( If \) Interconnect/fuel channel interface

\( (k,l) \) Index of unit cell

\( \sigma^o \) Oxygen ions

\( x \) X-direction

\( y \) Y-direction

REFERENCES

1. E. Achenbach, "Three-Dimensional and Time-Dependent Simulation of a Planar Solid Oxide Fuel Cell Stack," Journal of Power Sources, 49, 333-348, (1994).
2. P. A. Lessing, "Catalytic Bipolar Interconnection Plate for Use in Fuel Cell System, Patent Office Serial No. 08/322660, October 12, 1994.
3. P. C. Kong and P. A. Lessing, "Method and Apparatus to Convert Natural Gas to Methanol and Higher Hydrocarbons," Patent Office Serial No. 08/255603, June 8, 1994.
4. S. W. Angrist, Direct Energy Conversion, Fourth Edition, Allyn and Bacon, 1982.
5. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, John Wiley & Sons, New York, 1960.
6. F. M. White, Heat and Mass Transfer, Addison-Wesley Publishing Co., 1988.
7. R. B. Wright, "Catalytic Conversion of Natural Gas to Useful Chemicals and Fuels: Steam Reforming of Methane," FY 1995 LDRD Proposal, Project No. 8611, July 19, 1994.
8. W. H. Press, et al., Numerical Recipes, The Art of Scientific Computing, Cambridge University Press, Cambridge, 1986.
Table I. SOFC Model Equation Unknowns.

| Region         | Energy     | Mass                      | Electric |
|----------------|------------|---------------------------|----------|
| Fuel channel   | $T_f$      | $N_{CH_4}, N_{H_2O}, N_{H_2}, N_{CO_2}, N_{CO}$ |          |
| Interconnect   | $T_i$      | $N_{CH_4}, N_{H_2O}, N_{H_2}, N_{CO_2}, N_{CO}$ | $J_i$    |
| Anode          | $T_A$      | $N_{CH_4}, N_{H_2O}, N_{H_2}, N_{CO_2}, N_{CO}$ | $J_A$    |
| Electrolyte    | $T_E$      | $N_{O_2}$                 | $J_E$    |
| Cathode        | $T_C$      | $N_{O_2}, N_{N_2}$        | $J_C$    |
| Air channel    | $T_a$      | $N_{O_2}, N_{N_2}$        |          |

No. of unknowns: 6, 20, 4

Figure 1. INEL SOFC stack.

Figure 2. INEL SOFC unit cell model.
Figure 3. SOFC homogeneous equilibrium mixture model results.