ABSTRACT

Modeling activities at PNNL support design and development of a modular SOFC systems. The SOFC stack modeling capability at PNNL has developed to a level at which planar stack designs can be compared and optimized for startup performance. Thermal-fluids and stress modeling is being performed to predict the transient temperature distribution and to determine the thermal stresses based on the temperature distribution.

Current efforts also include the development of a model for calculating current density, cell voltage, and heat production in SOFC stacks with hydrogen or other fuels. The model includes the heat generation from both Joule heating and chemical reactions. It also accounts for species production and destruction via mass balance. The model is being linked to the finite element code MARC to allow for the evaluation of temperatures and stresses during steady state operations.

INTRODUCTION

A mathematical simulation of a SOFC is helpful in examining various operating parameters such as temperatures, materials, geometries, dimensions, fuels, reformers, etc, and determining their associated performance characteristics. Such a simulation can be used to determine the effect of varying the design and operating parameters on the power generated, fuel conversion efficiency, maximum cell temperature, stresses caused by temperature gradients, and the effects of different coefficients of thermal expansion (CTE) for the electrolyte, electrodes and interconnect. In addition, such simulations can provide answers to questions such as how much the electrical properties of the cell materials need to be improved, or what the air and fuel flow rates during transient or steady state operations must be to avoid excessive temperature and pressure drop. Thus, mathematical simulation offers the potential to direct the technology development, test the significance of various design features and the effectiveness of developments in materials or fabrication procedures, and select optimum operating conditions. For SOFCs to become a viable commercial product, performance requirements and the associated technical issues of transient thermal stresses and steady-state flow uniformity in the fuel cell stack must be met. These requirements are more stringent for a mobile application, as weight/volume, cost, and integration concerns must be satisfied.
Pacific Northwest National Laboratory (PNNL) is engaged in the design and development of planar SOFC stacks for mobile applications. PNNL is developing computer models for analyzing thermal cycling and steady-state operations.

The feasibility of rapid start-up is being analyzed using thermal-fluids and stress modeling. The startup time is a function of the heating technique, the mass and geometry of the SOFC stack, and the resulting thermal stresses that must be kept below some acceptable value. External heating of cathode air offers the greatest potential for rapid startup. The two inter-related issues of the required air flow at acceptable temperature and pressure drop, and thermal stresses have been simulated using a combination of computer codes. These consisted of two separate, yet coupled, analyses: thermal/flow and stress. PNNL is developing computer models to investigate the rapid start-up of SOFCs using both computational fluid dynamics (CFD) and finite element analysis (FEA). The modeling needs for the fuel cell stack from a thermo-mechanical perspective include two major components: 1) Analyses using a CFD code to predict the transient temperature distribution within each cell contained in the stack, and 2) Stress analyses using FEA based on the temperature distribution to determine the thermal stresses experienced by the stack components.

Current efforts at PNNL also include the development of an electrochemistry model for calculating current density, cell voltage, and heat production in SOFC stacks with hydrogen or other fuels. We have implemented a model for analyzing the steady-state operations of planar SOFCs. This model is currently being linked to the commercial FEA code, MARC.

This paper describes transient thermal-fluids and thermal stress analyses for stack modeling. We also describe an electrochemical model for calculating heat generation and current density within a SOFC stack, and describe an approach for coupling the model with our CFD and FEA codes. Simulation results from these codes, modified with the electrochemical model, will be used for determining thermal profiles and mechanical stresses during steady-state SOFC operation.

**TRANSIENT ANALYSIS**

During fast startup or fast cool down, thermal stresses that develop within the fuel cell stack must be maintained within an acceptable level. The stresses are a consequence of CTE mismatch and temperature gradients. It is necessary then to model the flow of heat and mass transfer through the fuel cell stack to describe the transient temperature distribution. The predicted transient temperature distributions, computed here by CFD models, are used as input to the FEA code to predict the thermal component of the stress. Knowledge gained of the stress in the stack can be used to establish control parameters during transient operations.

**Thermal-Fluids Stack Modeling**

The thermo-fluids modeling of the fuel cell stack is being performed using the commercial CFD code, Star-CD. Sub-models containing the full geometric detail of individual interconnect features, such as a single air flow channel, calculate the pressure drop and heat transfer coefficient for particular channel and interconnect dimensions. These conditions are imposed in the full stack model. The full stack models are then able to solve the bulk flow and heat transfer conditions. With this approach, similar configurations can be tested parametrically using a single full-stack
model. These full stack simulations were an extension of the single channel models, therefore the material properties remain the same. Table I summarizes the material properties used in the stack models.

**Table I. Material properties used for SOFC stack startup simulations.**

| Material                                      | Density, kg/m³ | Heat Capacity, J/kg K | Thermal Conductivity, W/m K |
|-----------------------------------------------|----------------|-----------------------|----------------------------|
| Air (at 400°C)                                | 0.524          | 1070                  | 0.0500                     |
| Ceramic Interconnect                          | 6320           | 536                   | 2.36                       |
| Cell Structure (Anode/Electrolyte/Cathode)    | 4200           | 623                   | 13.1                       |
| Ceramic Spacer                                | 6010           | 591                   | 2.2                        |
| Metal Interconnect (430-SS assumed)           | 7700           | 800                   | 25.5                       |

Several start-up simulation cases were run using a single model geometry. This geometry is shown in Figure 1. The upper left portion of Figure 1 shows the full stack geometry. The air (cathode) outflow manifold is sized 1.57 times larger than the inflow manifold to ensure uniformity of flow throughout the stack height. Heating air is introduced at the bottom left hand side of the stack (narrower manifold), travels across the interconnect channels, and exits downward at right (wider manifold). The “zoom” view of the stack at upper-right in Figure 1 shows more detail of the grid. Details of the individual flow channels are simulated using a porous media model in the active area. This 3-dimensional model contains 470,000 computational cells.

![Figure 1. Thermal-fluids stack model geometry.](image)

We have investigated several stack designs and will present results from two cases: 1) Case 1 had metal (430-SS) interconnects of dimension that included the height of the anode and cathode side flow channels. This material extended out at this dimension to include the manifold walls. This first case was massive (stack mass was 12.6 kg). 2) The mass was minimized in Case 2 by removing excess material in the corners and reducing the wall width around the manifolds to 1 mm. The stack mass in Case 2 was reduced to 3.3 kg.

Thermal stack simulation for Case 1 was run to 5 simulation minutes without reaching operating temperature. Thermal gradients were large (350°C or more within each interconnect). Alleviating these thermal gradients while heating from one side
will be difficult. Results from Case 2 showed that while the stack could reach the minimum startup temperature (nominally 500°C) within five minutes, there were still excessive thermal gradients depending on the time during transient. Figure 2 shows the temperature distribution in the uppermost interconnect at 5 minutes as well as the interconnect "footprint" for each case.

![Temperature Distribution](image)

Figure 2. Predicted uppermost interconnect temperatures for Case 1 with large mass (left) and Case 2 with low mass (right) at 5 simulated minutes (temperature contours range from 233 to 1073°C).

We expect, with roughly similar stack dimensions and materials, the actual stack mass to be bounded by Cases 1 and 2. These results show that reducing the stack mass, by itself, will not alleviate the thermal gradient problem.

At PNNL, we investigated several design options for minimizing the temperature and stress gradients. Some of these options include:

- While heating the outer wall of the stack assists in transferring heat to the stack, it does not provide enough heat to reduce thermal gradients within the stack in the 5 minute time frame of rapid startup. Temperature control of the inflow and stack wall temperature allows start-up time to be minimized while avoiding excessive thermal stresses.
- Simulations of shorter, less massive stacks show promise for achieving the goal of a 5 minute start-up with acceptable thermal stresses.
- Beyond the 5 minute start-up from a purely thermal-fluids/thermal stress perspective, the modeling will need to include the electrochemistry during start-up and steady state operation.

**Transient Thermal Stress Modeling**

Figure 3 shows the temperature profile and inverse safety (applied stress/yield stress) factor for the third cell from the bottom of the stack at 300 seconds. This cell was chosen for evaluation because it is the hottest in the entire stack. The highest stress is in the corner radius of the air inlet manifold. However, the inverse safety factor ranges from 2 – 8 over the active area of the cell, indicating that the stresses need to be reduced by nearly an order of magnitude for this cell to survive.
Figure 4 shows the out-of-plane displacement of the cell in this cell at 300 seconds. The peak displacement is 1.6 mm. Curvature in the ceramic plate will give rise to tensile strains which can lead to cracking. Failure criteria for the cell or other ceramic components must be developed in the future as material selections are made and the design is refined.

Results for cells in the middle of the stack and at the top of the stack at 300 seconds were also obtained. As shown in the CFD thermal analysis, the top of the stack takes longer to heat up and the stresses are correspondingly lower at any given time. The lower inverse safety factor is a product of the overall lower cell temperature and decreased thermal gradient.

A model of the reduced mass geometry analyzed as Case 2 in the CFD thermal analyses was constructed in ANSYS. Results for cells at the bottom of the stack at 300 seconds are shown in Figure 5. The figure is plotted with exaggerated distortions. The peak inverse safety factor occurs at the intersection of the manifold with the plate and is due in large part to the bending induced in the manifold.

As noted in the CFD thermal analysis section, the reduced mass design heats up faster, so that for any given cell at a given time, the temperature is higher and the thermal gradients are decreased. For example, comparison of the results demonstrates that in the upper cell at 300 seconds, the temperatures are higher, the thermal gradients less, and both the peak and average inverse safety factors are decreased for the reduced mass design.
However, as also pointed out earlier, this suggests that the thermal gradients have simply been shifted to an earlier point in time. The thermal gradient is significantly larger at 300 seconds than that at 100 seconds. However, the magnitude of the inverse safety factors in both cases is similar. This is primarily the consequence of the cell at 100 seconds being at an overall lower temperature, which increases the stainless steel yield strength and lowers the inverse safety factor. An additional factor is the CTE mismatch between the stainless steel and the ceramic cell structure. Several additional analyses (not reported here) were conducted to investigate this effect.

Figure 5. Temperature and inverse safety factor for reduced mass lower cell (IC) at 300 seconds

ELECTROCHEMISTRY MODELING

Practical SOFC performance is usually described in terms of cell voltage and current density. The cell dc voltage and current depend on conditions that include fuel flow, oxidant flow, pressure, temperature, and the demands of the load circuit. These parameters affect the electrochemical processes that ultimately determine the generated power and cell voltage. By taking into account (a) ohmic losses, (b) concentration polarization based on the assumption of binary diffusion of gaseous species through porous electrodes, and (c) Tafel-type activation polarization in composite electrodes, it is shown that the V vs. i traces can be adequately described by [1]:

\[
V(i) = E_{\text{open}} - iR_i - b \sinh(i/2i_0) + \frac{RT}{4F} \ln(1-\frac{i}{i_{02}}) + \frac{RT}{2F} \ln(1+\frac{i}{i_{12}}) - \frac{RT}{2F} \ln(\frac{i}{i_{0H2O}}) \tag{1}
\]

where \(i_0\) is the effective exchange current density. For \(i>>i_0\), Equation [1] reduces to the form proposed in (1), while eliminating its Tafel logarithmic singularity. In Equation [1], \(E_{\text{open}}\) is the open circuit voltage, usually referred to as Nernst potential. \(R_i\) is the area specific resistance of the cell, \(b\) is the Tafel parameter. \(i_{02}\) and \(i_{12}\) are respectively the cathode- and anode-limiting current density, \(p_{0H2}\) and \(p_{0H2O}\) are respectively the partial pressure of hydrogen and water vapor in the fuel channel, \(R\) is the gas constant, \(F\) is the Faraday constant, and \(T\) is the temperature.

Equation [1] is used as the basic electrochemistry model in our overall SOFC modeling approach. Equation [1] is used mainly because (a) its parameters have clear physical origins and the microscopic description allows correlation of the parameters
with cell components and operating conditions, and (b) the experimental temperature dependence of the parameters are available. Here we report the detailed analysis of Equation [1] and implementation results in order to provide insight into the optimization of overall system operation.

According to thermodynamics, the Nernst potential, or the reversible electromotive force, $E_{\text{open}}$ is simply $-\Delta G/2F$, where $\Delta G$ is the free energy change of the reaction $H_2+(1/2)O_2 \rightarrow H_2O$. Using state equations of ideal gas to describe that of the species at SOFC operating temperatures, we have

$$E_{\text{open}} = \left(\frac{-\Delta G_{\text{po}}}{2F}\right) + \frac{RT_1}{2F}\ln P_1 + \frac{RT_2}{4F}\ln P_2 - \frac{RT_3}{2F}\ln P_3$$

where $\Delta G_{\text{po}}$ is the free energy change when all of the species are at $P_0=1$ atm. Subscript 1, 2, and 3 refer to $H_2$, $O_2$, and $H_2O$, respectively. Writing specific heat capacity as

$$C_p = a + bT + cT^2$$

which is found to be able to fit the experimental data of many gases to within 0.5% over $T$ from 0°C to 1250°C, we have

$$G(T, P_0) = G(T_0, P_0) + a(T - T_0) + (b/2)(T^2 - T_0^2) + (c/3)(T^3 - T_0^3) - [TS(T, P_0) - T_0S(T_0, P_0)]$$

$\Delta G_{\text{po}}$ can be computed at $T$ with the above expressions and parameters $a$, $b$, $c$, and experimental data for the entropy $S(T_0, P_0)$ and $\Delta H(T_0, P_0)$ or $\Delta G(T_0, P_0)$.

Using the data in (3), Table II shows that $E_{\text{open}}$ is weakly temperature dependent. $E_{\text{open}}$ changes less than 1% when operation temperature changes by 50K. The change of $E_{\text{open}}$ vs. $T$ is approximately linear. Due to endothermal and exothermal reactions in the cathode and anode respectively, the air and fuel can have a substantial temperature difference. The variation of $E_{\text{open}}$ vs. such temperature difference is also found to be small. For fuel and air temperature difference of 20°C across a cell structure, computations using the average $T$ may cause about 1% error. Though the error is insignificant compared to other approximations, it is still recommended to compute the temperature dependence.

Table II: Nernst potential vs. temperature for $P(H_2)=0.97$atm, $P(O_2)=0.21$atm & $P(H_2O)=0.03$atm.

| $T$ (C) | 500  | 600  | 700  | 800  | 900  | 1000 | 1100 |
|--------|------|------|------|------|------|------|------|
| $E_{\text{open}}$ (V) | 1.1565 | 1.1423 | 1.1283 | 1.1139 | 1.0998 | 1.0859 | 1.0722 |

Table III shows the open cell voltage vs. the fuel composition change. Clearly, the open voltage has strong dependence on the fuel composition. The Nernst potential drops by about 20% from 1.11V ($P(H_2)=0.97$atm) at the fuel inlet to 0.89V at gas outlet for an 80% fuel utilization. High fuel utilization is necessary for high cell efficiency, however, operation at very high utilization suffers from the decreased Nernst potential. In such cases, the cell operating voltage may be limited by the Nernst potential of the depleted fuel as both electrodes are typically good conductors and therefore each electrode surface is at a constant voltage. Since cell efficiency is determined by fuel utilization and the ratio of operating voltage to the open voltage, higher fuel utilization does not always mean higher efficiency, though this is usually true. There exists an optimal fuel utilization for the best cell efficiency. One
possibility to further improve cell efficiency is to operate the cell with fuel recycling. Another possibility is by multistage oxidation of fuel.

Table III: Nernst potential vs. fuel composition at T=800°C, P(O2)=0.21atm and P(H2O)=1-P(H2)atm

| P(H2)  | 0.9  | 0.7  | 0.5  | 0.3  | 0.2  | 0.1  | 0.05  |
|--------|------|------|------|------|------|------|-------|
| Eopen  | 1.0548 | 0.9924 | 0.9532 | 0.9141 | 0.8891 | 0.8516 | 0.8171 |

The other quantities in Equation [1] are calculated in a more empirical way. The area specific resistance of the cell is the sum of the cathode, Rp, electrolyte, Re, anode, Rn, and bipolar, Rb, electrical resistances and each increases proportionally with the thickness of respective cell component. Rp, Rn, and Rb are assumed to be ohmic and increase linearly with temperature. For typical cell structures and materials currently in use, these electrical resistances are much smaller than that of the electrolyte, but they are included for the code to be general. The ionic resistance of electrolyte is assumed to be le c_e T exp(Q_e/T). The best fit to data in (1) gives Q=61kJ/mol and c_e=6.83x10^5 ohm cm K^-1 and le is the thickness of the electrolyte. These parameters have effectively taken the contribution from charge transfer resistance. The dependences of electrode-limiting current density, i02 and i12, on the electrode thickness and gas composition as proposed in (1) are assumed to be valid. Based on the given experimental data, interpolation/extrapolation is used to obtain i02 and i12 as well as b and i0 at different temperatures.

Figure 6 shows representative plots of the cell voltage (a) and power density (b) vs. current density for a cell with 10, 50, and 750µm thickness of electrolyte, cathode and anode layers, respectively, at seven temperatures: 600, 650, 700, 750, 800, 850, and 900°C. It can be seen that voltage- and power-current curves for different temperatures are very different from each other. The maximum output powers differ by a factor of 5 for 600°C and 900°C. However, the cell operating voltages corresponding to the maximum output powers are almost identical, increasing from 0.47V for 600°C to 0.49V for 900°C.

The heat generated in the cell structure due to the current passage is \( i [E_{\text{open}} - V(\theta)] \), the power consumed by the ohmic, activation and concentration polarizations. Heat generated by each R_i component is released to each respective cell component. Heat from i02-term is released in cathode, and heats generated by i12 and i12C terms are released in the anode. Heat from the b-term, which describes cathode activation polarization, is released in cathode, mainly in the reaction zone (about 10µm thick) at the cathode/electrolyte interface. Figure 7 shows the current heat generation in the cell.
structure for cell operating with $P(H_2)=0.97\text{atm}$, $P(O_2)=0.21\text{atm}$, $P(H_2O)=0.03\text{atm}$. As can be seen, the electrical heat is large and increases rapidly with increasing current density. The heat may raise the cell temperature and induce temperature gradient field and thermal stress. Severe non-uniform temperature distributions will result in cracking due to thermal stresses. Therefore, thermal stress analysis, by finite element method in our case, is necessary to properly assess cell operation and optimization.

![Figure 7. Heat generated by current passage. $P(H_2)=0.97\text{atm}$, $P(O_2)=0.21\text{atm}$, $P(H_2O)=0.03\text{atm}$.](image)

The heat generation severely limits the cell performance. At maximum output power operations, only 40% ($T=600^\circ\text{C}$) to 45% ($T=900^\circ\text{C}$) of the free energy changes are converted to the output power. If one requires the electrical efficiency to be more than 75%, the output powers are only about half of that of maximum power outputs.

The software for the above model is arranged as a user-defined function (UDF) written in Fortran. The details of the UDF will be described elsewhere and can be summarized as the following. The UDF calculates current density, cell voltage and distributed heat production as a function of 3D grid in a SOFC stack, taking as inputs local values of the gas partial pressures and temperatures. Grids across PEN structure, $z$, are associated pair-wise. One can use any number of $z$ grid points for each individual cell component. For a set $x$, $y$ in a cell plate, current is constant over the $z$-grid. Equation [1] is used to compute cell voltage if current density is given, or to find the current density consistent with a given cell voltage. All cells in the stack have the same grid, but corresponding grid points in different cells can have different current densities. If the total current through the stack is being specified, the potential across each cell is adjusted so that the integral of current densities is equal to the specified total current for each cell. If the total voltage is to be specified, all the cell voltages are adjusted so their sum is the specified value while the total current is the same for each cell. The self-consistency is achieved by bisection search for every cell in the stack and every $(x,y)$ node in a cell plate. CPU cost of the calculations increases linearly with the number of cells in the stack and the grid points in the $x$-$y$ plan, and sub-linearly to the number of $z$ grid points in a cell. The model was recently enhanced to include the following:

- Model treating the effects of ribs. The dimensions of the gas channels and ribs should be taken into consideration. This will also allow us to find reasonable effective local species concentrations for any $x$, $y$ grid.
• Heat model for the chemical reactions at the electrodes and transport.
• Mass balance correlating the species production/destruction (chemical reactions) and current distribution.
• Self-consistent method for current distribution and species concentration, thermal equilibrium for heat production and transmission (conduction/convection/radiation).

Due to space limitations, we will not discuss these enhancements in this paper.

COUPLING ELECTROCHEMISTRY AND CFD/FEA MODELS

PNNL currently is linking the enhanced electrochemistry computer code described in Section 3 and both the commercial computer codes: Star-CD and MARC. The electrochemistry code is being treated as a user defined subroutine in each of the commercial codes. This new computer model will be used for design optimization in terms of cost, start-up time and steady state power delivery/fuel utilization.

CONCLUSIONS

We presented an overview of the modeling efforts at PNNL, which are focused on modeling transient and steady state operations, and design trade-off studies for planar SOFC stacks.

ACKNOWLEDGEMENTS

Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. The work summarized in this paper was funded as part of the Solid State Energy Conversion Alliance (SECA) Core Technology Program by the U.S. Department of Energy’s National Energy Technology Laboratory (NETL), and as part of the internal Laboratory Directed Research and Development (LDRD)

REFERENCES

1. J. W. Kim, Anil Virkar, K.Z. Fung, K. Mehta, S. Singhal, J. Electrochem. Soc., 146, 69 (1999).
2. CRC Handbook of Solid State Electrochemistry, CRC Press, p. 291, (1997).
3. W. J. Moore, Physical Chemistry, 3rd edition, p. 62, Prentice-Hall, Englewood Cliffs, New Jersey (1962).