INL/CON-06-11720
PREPRINT

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2006 Fuel Cell Seminar

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November 2006

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ABSTRACT

A three-dimensional computational fluid dynamics (CFD) model has been created to model high temperature co-electrolysis of steam and carbon dioxide in a planar solid oxide electrolyzer (SOE). A research program is under way at the Idaho National Laboratory (INL) to simultaneously address the research and scale-up issues associated with the implementation of planar solid-oxide electrolysis cell technology for syn-gas production from CO_2 and steam. Various runs have been performed under different run conditions to help assess the performance of the SOE. An experimental study is also being performed at the INL to assess the SOE.

Model results provide detailed profiles of temperature, Nernst potential, operating potential, anode-side gas composition, cathode-side gas composition, current density and syn-gas production over a range of stack operating conditions. Typical results of current density versus cell potential, cell current versus H_2 and CO production, temperature, and voltage potential are all presented within this paper. Plots of mole fraction of CO_2, CO, H_2, H_2O, O_2, are presented.

Currently there is strong interest in the large-scale production of syn-gas from CO_2 and steam to be reformed into a usable transportation fuel. This process takes the carbon-neutral approach where the amount of CO_2 in the atmosphere does not increase. Consequently, there is a high level of interest in production of syn-gas from CO_2 and steam electrolysis. Worldwide, the demand for light hydrocarbon fuels like gasoline and diesel oil is increasing. To satisfy this demand, oil companies have begun to utilize oil deposits of lower hydrogen. In the mean time, with the price of oil currently over $70 / barrel, synthetically-derived hydrocarbon fuels (synfuels) have become economical. Synfuels are typically produced from syngas – hydrogen (H_2) and carbon monoxide (CO) -- using the Fischer-Tropsch process, discovered by Germany before World War II. South Africa has used synfuels to power a significant number of their buses, trucks, and taxicabs. The Idaho National Laboratory (INL), in conjunction with Ceramatec Inc. (Salt Lake City, USA) has been researching for several years the use of solid-oxide fuel cell technology to electrolyze steam for large-scale nuclear-powered hydrogen production. Now, an experimental research project is underway at the INL to investigate the feasibility of producing syngas by simultaneously electrolyzing at high-temperature steam and carbon dioxide (CO_2) using solid oxide fuel cell technology.

High-temperature nuclear reactors have the potential for substantially increasing the efficiency of syn-gas production from CO_2 and water, with no consumption of fossil fuels, and no production of greenhouse gases. Thermal CO_2-splitting and water splitting for syn-gas production can be accomplished via high-temperature electrolysis or thermochemical processes, using high-temperature nuclear process heat. In order to achieve competitive efficiencies, both processes require high-temperature operation (~850°C). High-temperature electrolytic CO_2 and water splitting supported by nuclear process heat and electricity has the potential to produce syn-gas with an overall system efficiency near those of the thermochemical processes. Specifically, a high-temperature advanced nuclear reactor coupled with a high-efficiency high-temperature electrolyzer could achieve a competitive thermal-to-syn-gas conversion efficiency of 45 to 55%.

MODEL DESCRIPTION

This model is based on a planar solid oxide fuel cell from reference [1]. This cell is 8 cm x 8 cm active cell area. All properties and concepts are the same in this model as in Reference [1] with the following exceptions: (1) the activation overpotential is zero, and (2) inlet and outlet regions allow for reaction to complete before entering or exiting the model. The commercial CFD code FLUENT was used to analyze the co-electrolysis of H_2O and CO_2. This is accomplished in FLUENT with the water gas shift (WGS) reaction model. Experimental evidence shows that the reaction kinetics of the steam electrolysis is much faster than that of the pure CO_2 electrolysis. These larger CO_2 molecules diffuse slower and create a concentration overpotential in the cell. For a given voltage, a lot more H_2 will be produced with H2O electrolysis compared to CO produced with pure CO_2 electrolysis. The area specific resistance (ASR) of a cell is closely related to the reaction kinetics. In one experimental test on a button cell, pure H_2O electrolysis had an ASR of 0.59 ohm-cm^2. The inlet gas stream was immediately switched to pure CO_2, after switching the gas stream to CO_2 the ASR rose to 0.90. With the assumption the reaction rate for the water gas shift reaction (WGS) is very fast (instantaneous) compared to pure CO_2 electrolysis, then this model that includes pure H_2O electrolysis with the WGS reaction is a correct assumption. There is an advantage in power consumption to do co-electrolysis compared to pure CO_2 electrolysis because of taking advantage of the WGS reaction. Two other advantages of co-electrolysis are that H_2 is less likely to leak, pure carbon is less likely to be produced. The FLUENT model has electrolysis occurring in the H_2O with the WGS reaction occurring as:

$$CO + H_2O \underset{k_b}{\overset{k_f}{\Longleftrightarrow}} H_2 + CO_2 \tag{1}$$

Where k_f and k_b are the forward and backward reaction rates. The forward and backward reaction rates at three different temperatures for SOFC are given by Lehmert et al. [2] as follows:

Temperature (k)	k_f (kmole m^{-3} Pa^{-2} s^{-1})	k_b (kmole m^{-3} Pa^{-2} s^{-1})
1073	1.5 x 10^{-10}	1.4 x 10^{-10}
1123	3.2 x 10^{-10}	3.5 x 10^{-10}
1163	3.6 x 10^{-10}	4.3 x 10^{-10}

Table 1. Forward and backward reaction rates for water gas shift at equilibrium as a function of temperature given by Lehmert et al. [2].

Where the net reaction rate = $k_f\, P_{CO}\, P_{H2o}$ - $k_b\, P_{CO2}\, P_{H2}$ kmole/m^3-s
Since in FLUENT the net rate of reaction is defined as:
Net reaction rate = $k_{f\_FLUENT}\ [C]_{CO}\, [C]_{H2o}$ - $k_{b\_FLUENT}\ [C]_{CO2}\, [C]_{H2}$ kmole/m^3-s
then $k_{f,\_FLUENT} = k_f\ (R\,T)^2$, *or* $k_{b\_FLUENT} = k_b\ (R\,T)^2$ m^3/kmole-s
The equilibrium constant, Keq=k_f/k_b can now be calculated as a function of temperature by fitting an exponential curve to the kinetic data provided in the Table 1. Where 1.0385x10^8 is the activation energy for the forward reaction.

$$k_f = 1.83x10^{-5}\ e^{\frac{1.0385x10^8}{RT}}$$

$$k_b = 4.25x10^{-4}\ e^{\frac{1.3247x10^8}{RT}}$$

$$K_{equilibrium} = 0.0431\ e^{\frac{2.862x10^7}{RT}}$$

or

$$k_{f\_FLUENT} = 1265\, T^2\, e^{-\frac{1.0385x10^8}{RT}}$$

$$k_{b\_FLUENT} = 29379\, T^2\, e^{-\frac{1.3247x10^8}{RT}}$$

The numerical model geometry represents a single cell, as it would exist in the stack. The numerical domain extends from the bottom of the hydrogen side current collector to the top of the oxygen side current collector as shown in Figure 1. Two views of the numerical grid used in the FLUENT model are shown in Figure 2. Figure 2(a) is a corner view showing 28 elements stacked in the z-direction, representing 5 distinct layers. Figure 2(b) is a top view showing the 42 x 42 element grid pattern used in the model. The center layers visible in Figure 2(a) represent the electrode regions. There are 2 elements for each electrode layer. Note that since the FLUENT SOFC module treats the electrolyte as a 2-D planar element, the electrolyte is not visible in Figure 2(a). A separate small 3D model was created that is 1mm x 5mm x 5cm long. This small model has the CFD model and reaction in it. The model has the temperature set at 1073 K with mass flow in and H_2, H_2O, O_2, CO_2, and CO mass fractions. The WGS reaction takes place and the model comes to equilibrium at the end of 5 cm. These outlet mass fractions for this small model are then input as the inlet boundary mass fractions of the electrolyzer model discussed above. This avoids the WGS reaction occurring in the electrolyzer model. For this model the inlet mole fractions are H_2O=0.838, H_2= 0.045, CO_2=0.068, CO=0.0035. This model has an inlet region of 2 cm and an outlet region of 5 cm so as to allow the reaction to complete before entering or exiting.

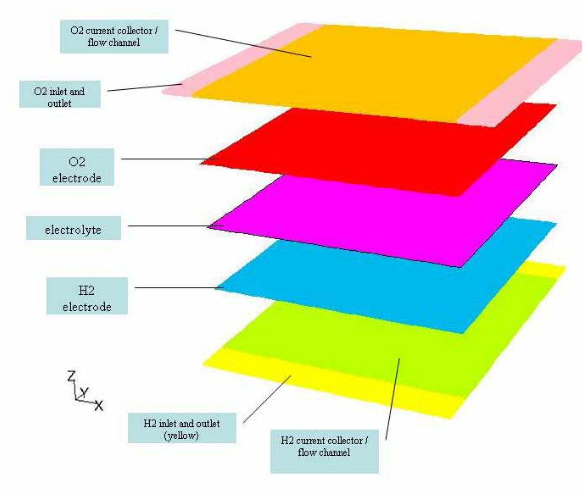
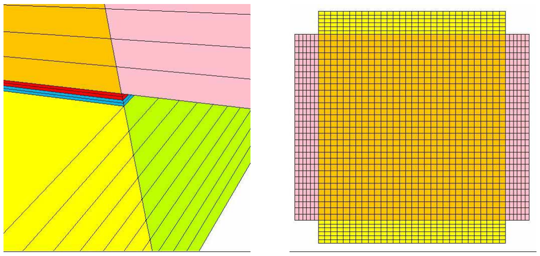


Figure 1. FLUENT single cell SOEC model.



(a) (b)

Figure 2. Details of 3D numerical mesh; (a) close-up of corner showing vertical element stacking, (b) top view showing grid.

RESULTS

The results are shown in Figures 3 through 7. Figure 3 shows the operation voltage versus current density for a sweep of various currents. The activation overpotential is set to zero for this model. Figure 4 shows the outlet mole fractions as a function of current density. Figure 5 shows the outlet mole fraction of the various components as a function of current density. The H_2, H_2O, CO_2, and CO are linear with current as they should be. The O2 varies as x/(1+x). Figure 6 shows the Arrhenius rate of reaction as a function of axial position along the H_2 current collector (flow channel). Notice that the flow is in equilibrium for the entrance distance, followed by the reaction taking place where the electrolysis occurs, followed by the exit region where the flow is in equilibrium again. Figure 7 shows the axial profiles of the mole fraction of the various components on the fuel side. This is for an operation voltage of 1.30 volts. This happens to be the thermal neutral voltage for this flow rate and mass fraction inlet constituency. All temperatures in the model are at 1073 K.

REFERENCES

[1] G. L. Hawkes et. al., "CFD Model of a Planar Solid Oxide Electrolysis Cell for Hydrogen Production from Nuclear Energy", Paper LOG # 326, The 11th International Topical Meeting on Nuclear Reactor Thermal-Hydraulics (NURETH-11), Popes Palace Conference Center, Avignon, France, October 2-6, 2005. (REFEREED)

[2] Lehnert, W., Meusinger, J., Thom, F., "Modeling of gas transport phenomena in SOFC anodes", Journal of Power Sources, 87, 57-63, 2000.

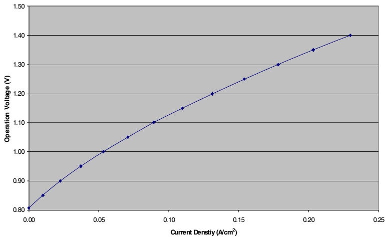


Figure 3. Operation voltage versus current density.

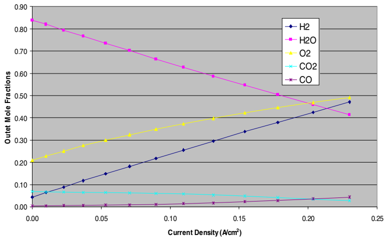


Figure 4. Outlet mole fractions versus current density.

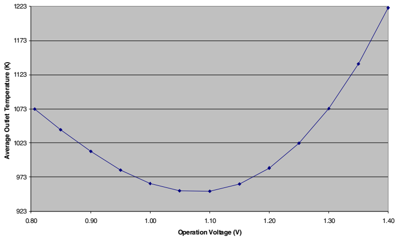


Figure 5. Mean outlet gas temperature versus operation voltage.

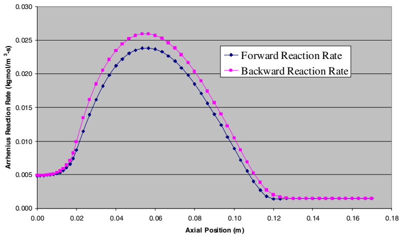


Figure 6. Reaction rate versus axial position

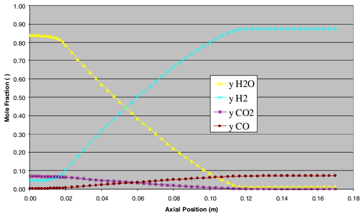


Figure 7. Mole fraction versus axial position.