VII.18 Modeling and Design for a Direct Carbon Fuel Cell with Entrained Fuel and Oxidizer

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Objectives

- Develop a fuel cell concept in which the anode and cathode are electrically-connected porous beds through which electrolyte flows with fuel and oxidizer entrained.
- Develop preliminary solutions to design problems such as electrode construction, gas-solid-electrolyte separation, and balance-of-plant design.
- Model overall plant mass and energy balances.
- Model processes within the electrodes.
- Develop to a stage where potential can be evaluated and research needs determined.

Approach

- Develop cell design.
- Develop balance-of-plant design.
- Model mass and energy balances for the plant.
- Model mass transfer, charge transfer, and chemical kinetics within the cell.
- Determine performance of cell and plant designs. Compare with alternate systems.
- Determine sensitivity to mass transfer, charge transfer, and chemical kinetic models. Evaluate research needs.

Accomplishments

- Developed cell design that provides circulation and separation of solid fuel, liquid electrolyte, supplied gases, and product gases with short ionic current paths.
- Developed balance-of-plant design that optimizes cell performance for power output and waste heat production.
- Modeled plant mass and energy balances. Determined that anode carbon dioxide/carbon monoxide balance was critical in overall plant performance.
- Reviewed literature to find correlations for mass transfer, reaction rates, and electronic and ionic electrical resistances.
- Modeled performance of cell electrodes with a set of simultaneous differential equations.

Future Directions

- Use electrode models to determine performance of cell designs.
- Use electrode models for first-cut optimization of cell designs.
- Compare performance with alternate systems.
- Determine model sensitivity to mass transfer, charge transfer, and chemical kinetic sub-models.
- Develop designs for experimental electrodes.

Introduction

Modern fuel cell development has concentrated on compact fuel cell designs in which immobile electrolyte is contained between porous membrane electrodes. Fuel and oxidizer are supplied to the electrodes on opposite sides of the electrolyte, and all reactions take place on the electrolyte-wetted surfaces of the electrode membrane. This design is effective for a compact cell using gaseous fuel, but it has serious limitations for utility-scale power generation using coal.

An alternate concept is proposed. In this concept, the anode and cathode are electrically-connected porous beds. Molten salt electrolyte, with carbon fuel and oxidizer entrained, is pumped through the porous beds.

This fuel cell design can use impure solid fuel (coal or coke) and offers economies of scale for utility-size plants.

Approach

The technology is more like a chemical refinery or an electrochemical plant than like a membrane electrode fuel cell. Accordingly, design techniques are those used for chemical reactors and electrochemical plants.

Initial designs for the cells and for the balance-of-plant have been developed. Techniques from the chemical engineering literature are being used to model these designs. The models will be used to predict the performance of the designs and to optimize them. Sensitivity analysis will show which processes have the greatest effects on performance and thus merit further study.

Results

Because molten carbonate fuel cells show promise for direct generation of electricity from coal, cells of this type were the basis for the design. The reactions for a molten carbonate cell using coal are:

At the anode: $C + 2CO_3^{=} \rightarrow 3CO_2 + 4e^-$

$2C + CO_3^{=} \rightarrow 3CO + 2e^-$

At the cathode: $2CO_2 + O_2 + 4e^- \rightarrow 2CO_3^{=}$

Chemical equilibrium and kinetics determine the amounts of CO and CO_2 produced at the anode. If CO is produced, it can be burned in an external burner. Anode exhaust gas is used to supply CO_2 to the cathode.

A major design challenge was to devise a cell that would allow for proper solid-liquid-gas separation and have short ionic conduction distances. After several iterations, the cell shown in Figure 1 was conceived.

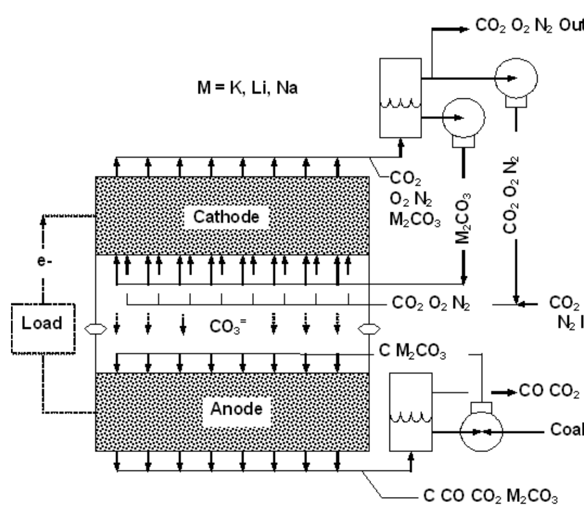

Figure 1. Coal-Fueled Molten Carbonate Fuel Cell with Porous Bed Electrodes

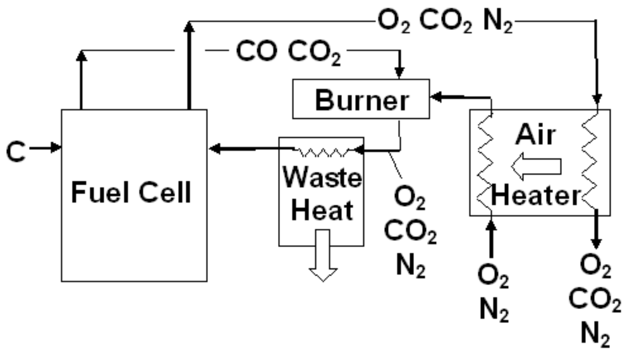

Figure 2. Balance-of-Plant Components for Coal-Fueled Molten Carbonate Fuel Cell

Molten carbonate salt, with carbon particles entrained, is pumped downward through the anode bed. It reacts with $CO_3^=$ ions diffusing from the cathode to form CO and CO_2, sending electrons to the load. Downward velocity of the salt ensures that both carbon particles and gas bubbles are entrained downwards. Salt, evolved gases, and excess carbon exit the bottom of the anode and gases are separated from the liquid/solid slurry. The slurry is enriched with more carbon and recirculated through the anode, while the gases supply CO_2 to the cathode.

Molten carbonate salt is pumped upward through the cathode bed, with O_2, N_2, and CO_2 entrained. O_2 and CO_2 molecules receive electrons from the load and react to form $CO_3^=$ ions, which diffuse to the anode. Excess gases exit the top of the anode and are separated from the liquid. The liquid and part of the gas stream are enriched with O_2 and CO_2 and recirculated, while the remainder of the gas stream is exhausted.

It was also necessary to develop a design for the "balance-of-plant" components necessary for fuel cell operation. The balance-of-plant design is shown in Figure 2. CO and CO_2 generated in the anode are supplied to a burner, where they are combusted with excess air. The resulting O_2-N_2-CO_2 mixture is supplied to the cathode. The air supplied to the burner is preheated by the N_2, CO_2, and excess O_2 leaving the cathode, and waste heat is recovered from the gases leaving the burner.

Based on this plant concept and assuming uniform temperatures within the fuel cell itself, mass

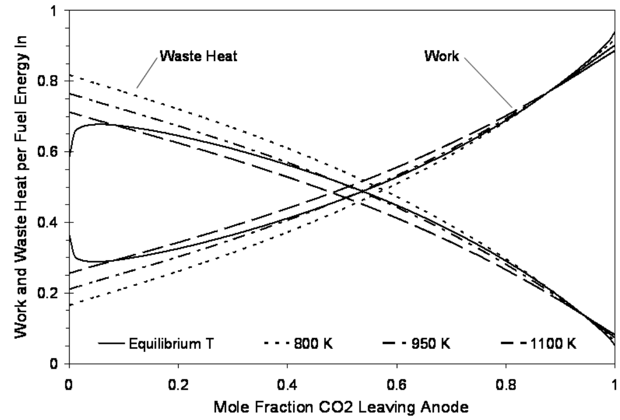

Figure 3. Work and Waste Heat Output vs. CO_2 Fraction Leaving Anode – Various Cell Temperatures

and energy balances were used to determine overall plant performance as a function of cell temperature, cell internal efficiency, excess air, air heater temperature difference, and CO-CO_2 ratio leaving the anode. This last was important because research has shown that the fraction of CO_2 produced in a carbon-fueled molten carbonate cell is much higher than predicted by chemical equilibrium.

The modeling showed that the CO-CO_2 ratio leaving the anode was dominant in determining plant efficiency. The effect of excess air was negligible, and the effect of heat exchanger temperature difference was small. Cell temperature and cell internal efficiency were significant, but less important than CO-CO_2 ratio.

Figure 3 shows work per fuel energy in (efficiency) and waste heat per fuel energy in, plotted against the volume fraction CO_2 leaving the anode. Cell temperature is a parameter, with curves shown for fixed values and also for cell temperature corresponding to the CO_2 fraction for chemical equilibrium. Cell internal efficiency is 100%, air heater minimum temperature difference is zero, and there is no excess air. Plant performance is a strong function of CO_2 fraction and a weaker function of cell temperature.

Figure 4 also shows work per fuel energy in and waste heat per fuel energy in plotted against the volume fraction CO_2, but with cell internal efficiency as a parameter. Cell temperature is 950 K, air heater minimum temperature difference is zero, and there is

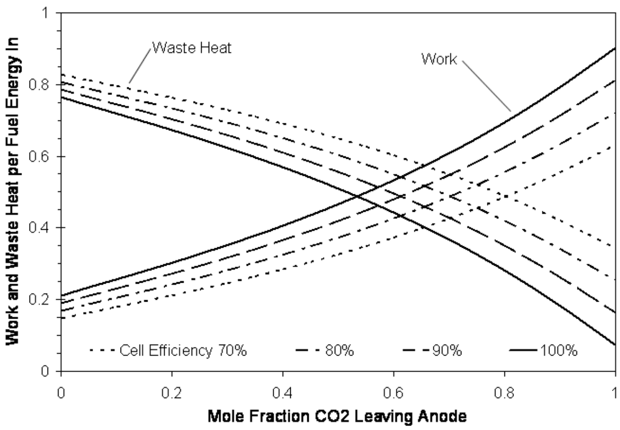

Figure 4. Work and Waste Heat Output vs. CO_2 Fraction Leaving Anode – Various Cell Internal Efficiencies

no excess air. Cell internal efficiency variation has a greater effect on performance than cell temperature, but its effect is less important than that of CO_2 fraction.

A model for the internal processes within the fuel cell is now close to completion. This model calculates the rates of mass transfer between gas and liquid, mass transfer between liquid and solid, ion diffusion through the electrolyte, and chemical reactions at the surfaces to determine a cell design for given voltage and current requirements. Results from this model are expected in the near future.

Conclusions

The most important conclusions from the work to date are:

- The fuel cell design shown in Figure 1 allows effective handling of solid, liquid, and gas phases within the cell while maintaining a short ionic conduction path.
- The balance-of-plant design shown in Figure 2 effectively maintains the cell at proper operating temperature, controlling cell temperature by controlling the temperature of the gaseous feed stream.
- The most important factor for good performance of the carbon-fueled molten carbonate fuel cell is high production of carbon dioxide (as opposed to carbon monoxide) in the anode.

FY 2004 Publications/Presentations

1. "Energy Balance for a Direct Carbon Molten Carbonate Fuel Cell," R. Agarwal and A. Kornhauser, ASME Heat Transfer / Fluids Engineering Summer Conference, July 11-15 2004, Charlotte NC, Paper HT-FED2004-56887.

2. "Modeling and Design for a Direct Carbon Fuel Cell with Entrained Fuel and Oxidizer," A. Kornhauser and R. Agarwal, DOE University Coal Research Contractors Review Meeting, June 9-10 2004, Pittsburgh PA.