V.14 Direct Utilization of Coal Syngas in High Temperature Fuel Cells

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Objectives

- Characterize the effects of major trace contaminants in coal syngas on solid oxide fuel cell (SOFC) performance.
- Identify the fundamental mechanisms through which these impurities affect performance.
- Develop novel materials to minimize impact of contaminants.
- Propose remedies for adverse effects of contaminants on fuel cell performance.

Accomplishments

- Identified from the available literature the levels of trace elements usually found in coal-syngas that cause performance degradation in solid oxide fuel cells.
- Built two test stands and began initial performance testing and material characterization.
- Purchased material processing equipment and attained capability to make/manufacture fuel cells in our laboratories.
- Initiated modeling activities at the atomistic, molecular, and continuum levels.

Introduction

This project is supported under the Department of Energy (DOE) Experimental Program to Stimulate Competitive Research (EPSCoR), a program designed to enhance the capabilities of EPSCoR states in energy research and economic development through the support of advanced research at academic institutions. Our vision is to establish an internationally recognized, sustainable fuel cell research center for coal-based clean power generation which serves as a technology resource for the emerging fuel cell industry in West Virginia. Under the present project, we will develop a laboratory infrastructure, solidify interactive working relationships, and attain national recognition for the work conducted by the center in the area of coal-based clean power generation via fuel cells. Our project will be conducted in collaboration with the National Energy Technology Laboratory (NETL). Our three-year project started in December 2006.

Approach

The research plan uses a multi-scale, multi-disciplinary approach that is supported by nine faculty members in four departments at West Virginia University (WVU). The work is organized under four integrated projects: (1) anode material development and experimental characterization of fuel cell anodes, (2) sub-micro-scale modeling, (3) multi-scale continuum modeling, and (4) laboratory testing of individual fuel cells and fuel cell systems. At the end of three years, we anticipate four outcomes. First, we will have identified the fundamental processes characterizing the operation of SOFC anodes from the atomic level to the level of the operating fuel cell. Second, strategies will be developed for constructing SOFCs that exhibit stable operation with coal syngas. Third, the research infrastructure (equipment for analysis and for cell fabrication, computers for modeling) and collaborations across disciplines and departments at WVU will be well developed for future research on fuel cells. Fourth, a program of educating and training future energy researchers will be established.

Results

Identification of Contaminants: Data was obtained from the literature on the effects of coal syngas on fuel cell components to identify possible contaminants in coal syngas and their typical concentrations. Coal syngas contains CO, H_2, CO_2, H_2O, CH_4 and N_2 in the majority and trace amounts of many naturally occurring elements [1]. Experimental results (Krishnan [2], [3]) show the effect of HCl, CH_3Cl, Zn, P, As, Cd and Hg found in syngas on SOFC performance. Our literature review [4] provides insight into the effects of coal syngas contaminants on the performance of an SOFC. Based on this knowledge, our initial testing will be performed with syngas containing As and P. Literature was also reviewed on the effects of sulfur. There are two primary sulfur-degradation mechanisms for the anode materials: (1) physical absorption of sulfur that blocks the hydrogen reaction sites and (2) chemical reaction that forms nickel sulfide. The results of our review will appear in *Journal of Power Sources*.

Anode Materials Development and Characterization: This research task seeks to investigate the electro-chemical and structural degradation of SOFC anode materials due to the effect of impurities in coal syngas and to develop new materials that would reduce or eliminate such degradation. We have designed and built a unique button cell testing apparatus (Figure 1a) that is capable of half cell or full cell testing including EIS (electrochemical impedance spectroscopy) and ASR (anelastic strain recovery) measurements. This testing apparatus includes three main components: (a) testing, (b) mass-flow-control (MFC) and (c) furnace assembly. This computer-automated rig can control the temperature and the gas flow through programming. Figure 1b shows EIS curves for a half cell measured by the system at different temperatures.

A second furnace is constructed (Figure 2a) for *in situ* surface deformation monitoring of the anode side of the button cell subjected to attack by impurities in a coal syngas stream. Most likely, the structural degradation will only occur on the surface, which may cause a change in the structural mechanical properties. We shall apply suitable pressure loading to the button cell to "amplify" the state of surface structural degradation coupled with the simultaneous EIS and ASR measurements to correlate the linkage between mechanical and electro-chemical degradation under operating conditions.

A fuel cell manufacturing lab has been set up with a total area of 280 ft^2. The following equipment has been purchased: tape caster with single-blade (TTC-1200, Richard E. Mistler Inc.), jar-mill (755RMV, U.S. Stoneware); spin-coater (KW4A, Chemat Technology Inc.), screen printer (3230B, Aremco), and low-temperature furnace (Carbolite). Figure 2b shows some of the button cells manufactured in our lab. Cells are being tested with different levels of contaminant exposure; results will be available soon.

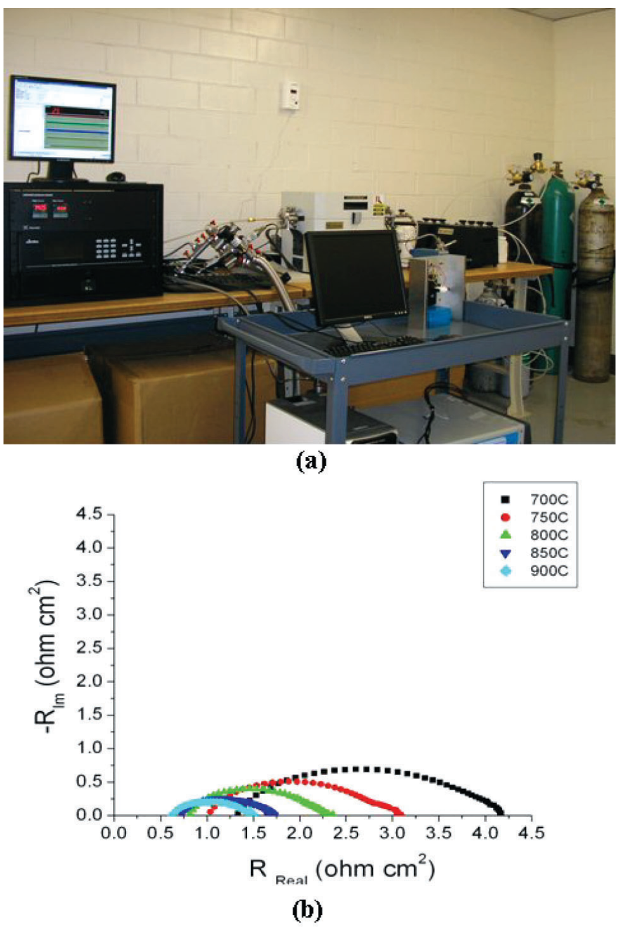

FIGURE 1. EIS Measurement (a) Layout of the Experimental Setup (b) Sample Result

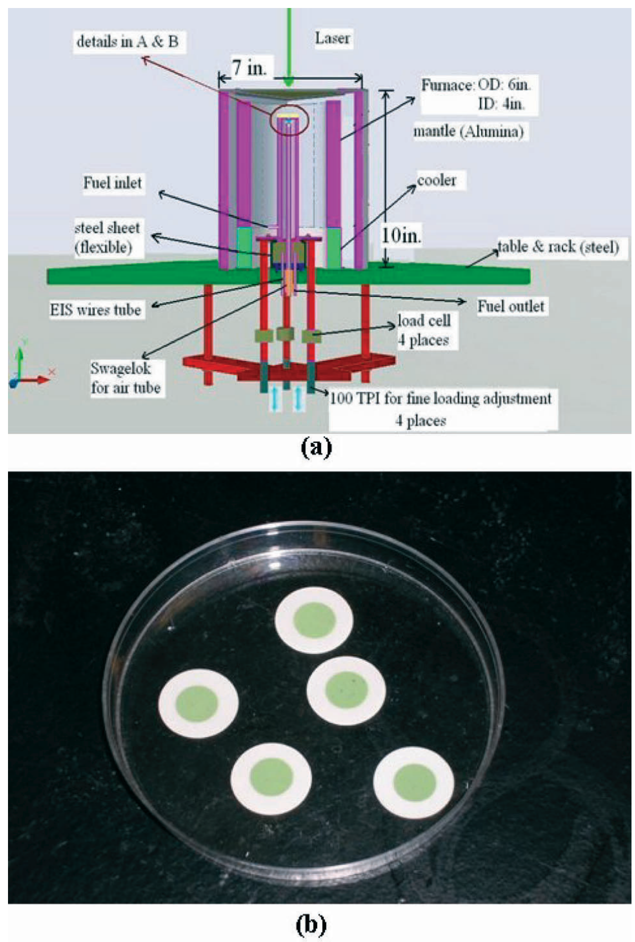

FIGURE 2. Button Cell Testing (a) Schematic of Apparatus Designed for *In Situ* Electrochemical and Structural Measurements (b) Button SOFCs Manufactured at WVU

Sub-Micro-Scale Modeling: Virtual modeling efforts progressed in two fronts: (1) atomistic level and (2) molecular level modeling. Using *ab initio* FP-LMTO techniques based on density functional theory, we calculated the electronic structures for a hydrogen atom adsorbed on the Ni (1,0,0) surface (Figure 3a). Detailed analysis reveals the properties and features of chemical bonding, charge transfer, and Ni surface electronic states. This knowledge helps us to understand the fuel consumption and nickel catalytic mechanisms. It will also serve as a comparison basis to analyze the bonding mechanisms of trace elements on catalysts in our future work. We have also developed an *ab initio* tight-binding parameter base for Ni/S/H, which will be used in tight-binding based molecular dynamics simulations involving larger scale and longer time.

Molecular dynamics modeling will provide enough statistical data to retrieve macroscopic properties of the substance, such as effective diffusion coefficient, thermal expansion coefficients and heat capacities, as well as molecular kinetic parameters of importance for determining reaction rates. So far, a literature review has been performed and the necessary hardware and software for this task have been procured and tested. The work on the first C++ prototype of the sequential simulation code has been initiated. The implementation of the essential classes is underway, which include: (a) Atom: to represent indivisible atomic species, e. g., H, O, C, S, Ni. (b) Molecule: to represent chemical compounds, such as H_2, O_2, H_2O, H_2S, CO_2. Figure 3b shows a computer simulation of crystal bonding structure which can be used to analyze the effect of lattice defects and lattice deformations caused by doping elements.

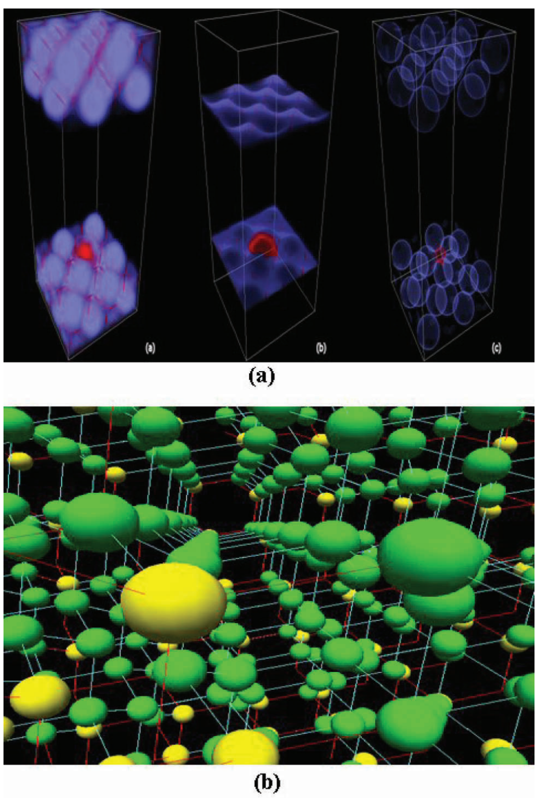

FIGURE 3. Sub micro-scale modeling - 3-D visualizations of results obtained using FP-LMTO techniques: Section (a) - (a) the total charge density distribution, (b) the surface states, and (c) Ni-H chemical bond. A 2x2x2 (32 atom) Ni supercell is used. Section (b) Computer simulation of crystal bonding structure which can be used to analyze the effect of lattice defects and lattice deformations caused by doping elements.

Multi-Scale Continuum Modeling: Preliminary results were obtained from modeling of a small button cell, similar to those to be tested in our laboratory, using an in house code DREAM SOFC. Figure 4a shows the calculated temperature distribution on the top (anode) and bottom (cathode) surfaces of the button cell with prescribed H_2 and O_2 concentrations on the anode and cathode sides, respectively.

Two models for multi-component molecular diffusion transport inside a typical anode were tested. These models are the Stefan Maxwell Model including the Knudsen diffusion and Fick's law using an effective multi component diffusion coefficient. Based on our results using both models, the simpler Fick's model performed sufficiently well that it can be used for future calculations. Transient mass transport calculations for a typical coal syngas operated anode revealed that chemical kinetics play a critical role in cell performance. This model will be expanded to include the trace species with detailed reaction mechanisms. Laboratory conditions will be simulated as closely as possible to provide feedback to the experimental work.

Cell and System Laboratory Testing: A survey of chemical literature was done for relevant information on measurements of electron transfer kinetics. A complete impedance spectroscopy set up (Solartron Model 1287 potentiostat, Model 1252 frequency response analyzer, ZPlot and ZView software for electrochemical impedance spectroscopy and CorrWare and CorrView software for other electrochemical measurements) was installed in our lab and concerned personnel developed expertise with the hardware and software using model electrochemical cells. This system is capable of performing the three electrochemical methods: (1) electrochemical impedance spectroscopy, (2) cyclic voltammetry, and (3) current-interrupt measurements. An SOFC test stand (Figure 4b) is also made

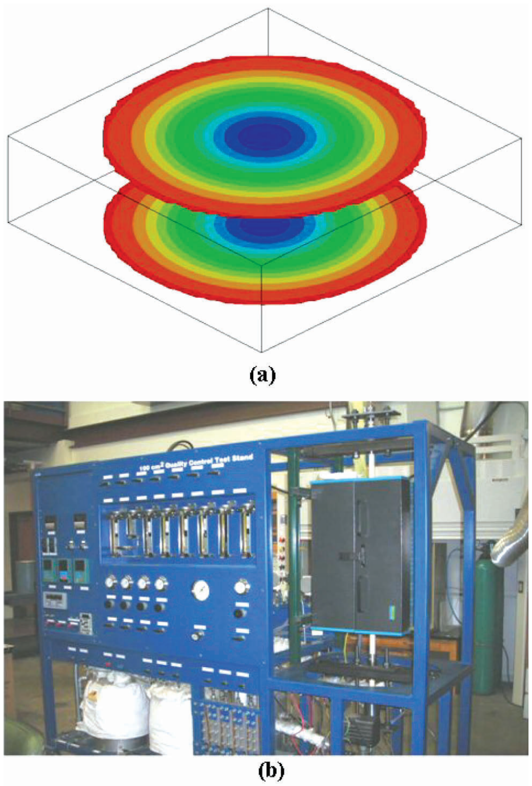

FIGURE 4. (a) Temperature distribution on top and bottom surfaces of a button cell calculated using DREAM SOFC. Red color indicates hotter region and blue indicates colder region. (b) SOFC test stand.

operational. Cell testing with standard yttria-stabilized zirconia (YSZ) material is currently underway.

Conclusions and Future Directions

- The operation of the cell test stand will be verified using the commercially available fuel cells using pure hydrogen fuel as a baseline. A variety of operating conditions will be tried so that the experimental capabilities of the test stand can be established before testing the fuel cell performance in the presence of contaminants.
- Electrochemical characterization (impedance spectroscopy, cyclic voltammetry, current-interrupt measurements) of the commercial fuel cells will be undertaken soon. In particular, scanning electron microscopy and X-ray diffraction will be utilized to establish baseline characterization techniques and to gain familiarity with the testing procedures.
- Cell manufacturing capability will be perfected and new types of materials will be tried.
- Atomistic and molecular dynamics modeling will first focus on sulfur mechanisms to validate our approach against literature, and then mechanisms for contaminants such As and P will be investigated.
- Continuum modeling will proceed towards full simulation of conditions being tested in the laboratory.

FY 2007 Publications/Presentations

1. M. Gong, X. Liu, J. Trembly, C. Johnson: Sulfur-Tolerant Anode Materials for Solid Oxide Fuel Cell Application, Accepted J. of Power Sources (2007).

2. X. Liu, C. Johnson, C. Li, J. Xu, C. Cross: Developing TiAlN Coatings for Intermediate Temperature SOFC Interconnects Applications, submitted, Int. J. of Hydrogen Energy (2007).

3. R. Dastane, C. Johnson, X. Liu: Degradation of SOFC Metallic Interconnect in Coal Syngas, abstract submitted to Materials Science & Technology 2007 conference.

4. J. Wu, Y. Jiang, C. Johnson, M. Gong, X. Liu: Pulse Plating of Manganese-Cobalt Alloys for SOFC Interconnect Application, abstract submitted to Materials Science & Technology 2007 conference.

5. S. R. Pakalapati, F. Elizalde-Blancas, I. Celik (2007): Numerical Simulation of SOFC Stacks: Comparison between a Reduced Order Pseudo Three-dimensional Model and a Multidimensional Model, abstract submitted to the Fifth Int. Fuel Cell Sci., Eng. and Tech. Conference, June 18-20, NY.

6. N. Cayan, M. Zhi, S. R. Pakalapati, I. Celik, N. Wu: Coal Syngas Contaminants and Their Effect on Operation of SOFC: a Literature Review, in preparation.

References

1. Trembly, J.P., Gemmen, R.S. and Bayless, D.J. (2007), "The effect of IGFC warm gas cleanup system conditions on the gas-solid partitioning and form of trace species in coal syngas and their interactions with SOFC anodes", vol. 163, pp. 986-996.

2. Krishnan, G. (2006), 7th Annual SECA Review Meeting September 12–14, Philadelphia, PA.

3. Dr. Gopala N. Krishnan (2007), Private communication, Seminar presentation at National Research Center for Coal and Energy (NRCCE) at WVU, March 21.

4. N. Cayan, M. Zhi, S. R. Pakalapati, I. Celik, N. Wu: Coal Syngas Contaminants and Their Effect on Operation of SOFC: a Literature Review, in preparation.