
V.6 Advanced Fuel Cell Development

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Objectives

- Evaluate Department of Energy (DOE)-sponsored solid oxide fuel cell (SOFC) systems to ensure progress in meeting DOE goals.
- Measure response of SOFCs to coal contaminants and develop analysis tools to understand SOFC performance on coal syngas.
- Assess the dynamic performance of SOFC components and systems, and determine control requirements for these advanced systems.
- Develop new coating methods for low-cost fuel cell metallic components.

Accomplishments

- Successfully installed and operated the Solid State Energy Conversion Alliance (SECA) Phase I Prototype units made by FuelCell Energy/Versa Power Systems and Acumentrics to verify performance versus SECA Phase I requirements.
- Measured the effects of arsine and phosphine on SOFC performance, and applied detailed transport models to predict SOFC performance on coal syngas.
- Performed system analysis for coal-based fuel cell and gas turbine hybrid systems. Experimentally characterized hybrid plant response for purpose of control method development, and derived a control method using advanced control theory.
- Experimentally measured the performance of advanced electroplated interconnect coatings.

Introduction

The U.S. DOE is supporting the development of solid oxide fuel cells through the SECA program so that future coal-based power plants will achieve the highest possible fuel efficiency while protecting our environment. It is expected that coal gasification will be employed for these future plants. Therefore, to achieve future coal-based operation will require new understanding of how to integrate the fuel cell with the gasifier technology, and how gasified coal (syngas) will affect the operation of a SOFC. In addition, because of concerns for CO₂ within the environment, these systems must also perform carbon capture and sequestration. The work performed here accomplishes all these by: 1) developing test capability for the evaluation of SOFC systems and components; 2) measuring the effects of coal syngas on cell performance; 3) applying advanced analysis tools for the purpose of understanding solid oxide fuel cell operation on coal syngas; and 4) developing low-cost manufacturing options for metal materials used in SOFCs.

Approach

Systems Test and Evaluation Capability—The U.S. DOE National Energy Technology Laboratory established a fuel cell test facility for evaluating the performance of prototype fuel cell systems developed by government sponsored fuel cell developers. The goal of this work is to provide additional and confirmation testing of the developer units. This testing allows the government to independently evaluate a given unit's performance, and establish whether or not the unit is able to meet expected requirements. The facility is configured to handle fuel cell systems running on natural gas or methane with a nominal power rating of 3 to 10 kW.

Hybrid System Studies—A hybrid experimental simulator is used to investigate the dynamic performance of, and control methods for, fuel cell gas turbine hybrid systems. Here we employ a 'hardware-in-the-loop' approach whereby an experimental gas turbine is coupled to necessary hardware components (i.e., pipe volumes) that simulate the presence of a fuel cell via a real-time dynamic fuel cell model. This experimental capability shows, for example, the extent at which perturbations in the compressor/turbine system can propagate through the piping/hardware and be present in the fuel cell. If pressure waves of significant amplitude reach the fuel cell, risk to failure is possible.

Also important is to develop the time-scales for different process events and control actions. Such information is important to control design/development.

Coal Syngas Operation—Both thermodynamic and experimental work are under way to help us understand the effects of trace syngas species on the operation of solid oxide fuel cells. Because of the numerous trace elements existing in coal, a large number of species could, in principle, be formed during the gasification process. The concern for the fuel cell is that these species can react unfavorably with the fuel cell to cause performance loss or failure. To reduce the scope of the experimental work, thermodynamic models have been applied to help us understand the relative potential of the different species in surviving any of the clean-up stages of the system. A priority in the examination of the likely trace species can then be developed, and experimental focus can be applied to those species with the greatest potential of reaching and reacting with the cell. This year, experimental focus has been given to Cl, As, and P element effects on cell operation, and some of those results are given here.

Coatings for Metallic SOFC Components—Low cost coating methods for applying protective layers on iron alloy steels are needed to provide an effective solution for preventing chromium attack on SOFC cathodes. The approach taken in this portion of our work is to investigate electroplating methods. Such methods have an advantage in regards to their ability to deposit coatings on potentially intricate metallic components (components that have machined or stamped features to allow improved operation of the fuel cell). This year we have studied ‘full cell’ performances using interconnects having three different coatings, two with electroplated cobalt layers, and one with electroplated bi-layers of Co and Mn.

Results

Systems Test and Evaluation Capability—FuelCell Energy/Versa Power Systems (FCE/VPS) provided the first unit tested this past year for independent evaluation. The second unit was provided by Acumentrics Corporation. The FCE/VPS unit was operated on pipeline natural gas, and the Acumentrics unit was operated on bottled methane. In short, both units were able to meet the minimum requirements for the SECA program of >35% efficiency, <2% degradation per 500 hours, and <1% degradation after 10 transients. The testing of both units provided needed information that was able to independently assure SECA program management that progress is being made to achieve program goals.

Dynamic System and Component Studies—Results for work that determined the timescales present in hybrid systems are given here. Frequency modulation

tests were conducted in FY 2007 that yielded dynamic transfer function models that allow for control stability analysis. Figure 1 shows the response of several hybrid system process variables due to modulation of fuel, which is a control variable for the plant. The peak response of the heat exchanger temperature as a function of the modulated frequency of turbine combustor fuel valve is characteristic of the transport delay of the recuperator falling into phase with the previous cycle to yield a resonant feedback within the cycle. This characteristic frequency is consistent with previously observed 90 second step response of the heat exchangers with the energy balance between turbine exhaust heat and compressor air flow back work. The method of modulation and analysis for phase and amplitude of process data has allowed the fully integrated system to be characterized, quantitatively, for time scales that are attributed to the physical parameters of turbine inertia, heat exchanger thermal mass and transfer rates.

Coal Syngas Operation—From thermodynamic analysis using the FACTSAGE commercial software package, it was concluded that Sb, As, Cd, Pb, Hg, P, and Se elements will form the volatile compounds that will potentially interact with the SOFC anode. Specific to a nickel reaction, the elements, Sb, As, and P were found to form secondary phases. To begin to examine these elements, experimental studies of HCl, AsH₃, and PH₃ were performed on single button cells. Our approach is to individually inject such elements (in the forms that they exist under post syngas clean-up conditions) into the fuel gas passing over an SOFC button cell. Because future cleanup systems have not been fully identified, these tests are performed over a range of temperatures and specie concentrations. The results for the effect of arsine for one of the conditions tested are shown in Figure 2. Results show that (for relatively short term studies, ca. 100 hours) arsenic does not affect the performance of the fuel cell for concentrations less than 1 ppm. Longer term studies with 0.1 ppm arsine (ca. 800 hours) did show gradual decay in fuel cell performance, however, by about 10%. In coordination with other research by other organizations we will be able to confirm these results,

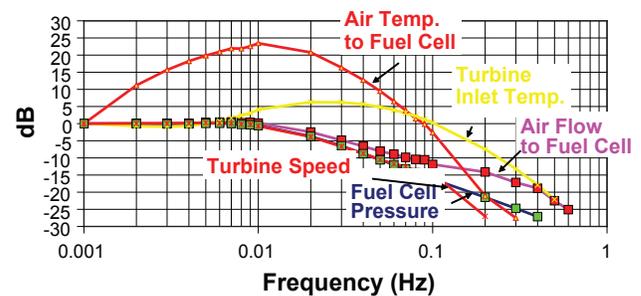


FIGURE 1. Frequency Response of Hybrid System Components Due to Fuel Valve Modulation

and if so confirmed will provide the needed information to researchers developing cleanup technology as to target levels for SOFC applications. Finally, in further support of this investigation into trace specie effects on SOFC operation, the detailed design of a portable test rig capable of testing multiple (~12) cells simultaneously is completed, and hardware is now being constructed. This unit will be taken to gasification facilities to determine more directly the effect of actual syngas on cell performance. The results from that study will be related to those from our individual specie studies to determine the unique behavior that reactant-to-reactant conditions provide.

Coatings for Metallic SOFC Components—The results of short term testing full cells using a coated interconnect of Crofer APU 22 showed that both Co and Co/Mn (as bi-layer) could be effective in preventing chromium from being evolved from the interconnect substrate, and provide stable operation of a SOFC. Results from a case using a 15 μm coating of Co are shown in Figure 3. Only the degradation information shown in the figure is relevant (not the absolute performance) given the fact that a 20 μm electrolyte cell is used for this test. As is evident, there is a conditioning period which is followed by a stable performance of the cell. Post test analysis showed a relatively small

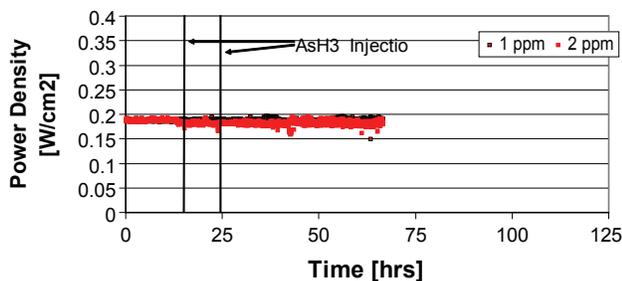


FIGURE 2. SOFC Power Density Operating at 750°C and 0.25 Acm² with AsH₃ Concentrations of 1 and 2 ppm

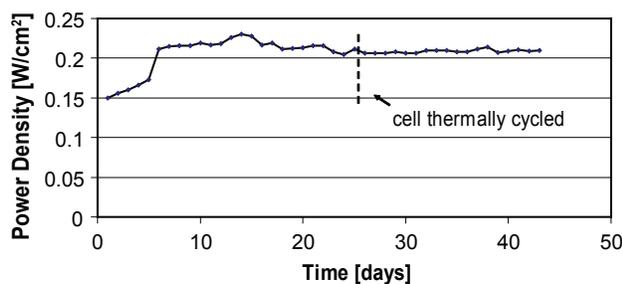


FIGURE 3. SOFC Cell Power Density as a Function of Time Using Anode Supported Cell with a 20 μm Thick Electrolyte and Co₃O₄ Coating on Crofer APU 22 Substrate

concentration of Cr in the outer coating layer, and no Cr was seen in the cross-sections of the cathode. X-ray diffraction (XRD) data showed that the Co formed a protective Co₃O₄ spinel as expected, and also showed the CoCr₂O₄ spinel phase. While longer tests need to be completed, these results favorably suggest that electroplated coatings will operate effectively in SOFC applications.

Conclusions and Future Directions

The DOE Fuel Cell Test Facility has completed evaluation of the SECA Phase I prototype units, and the important finding is that developers are presently meeting program requirements. Beginning in FY 2007, the major level of our work is focused on investigating coal-based fuel cell systems, and in particular the effects of trace species on fuel cell operation. Testing to date shows that certain trace species (e.g., HCl) behave very closely to what has been seen for H₂S, and similar clean-up requirements are expected. As shown in this report, AsH₃, on the other hand, is likely to require lower concentration requirements based on the presently available data. Tests for the effects of Sb-, Cd-, Hg-, and Pb-based compounds on fuel cell performance remains to be completed. While these basic technical studies will be the main focus of our work, we also anticipate the need to improve our understanding of these future coal-based systems via steady and dynamic modeling investigations in order to be assured that proposed hybrid systems will operate safely at peak efficiency. Finally, progress has been shown in achieving low-cost interconnect coatings suitable for SOFC conditions, and future work will now examine the effects of coal syngas contaminants on these materials.

FY 2007 Publications/Presentations

1. Christopher Johnson, Xingbo Liu, Caleb Cross. Proceedings of Material Science & Technology 2006 Conference and Exhibition, Materials and Systems: Volume I, October 15-19, 2006, Cinergy Center, Cincinnati, OH.
2. Christopher D. Johnson, Junwei Wu, Xingbo Liu, Randall S. Gemmen, "Solid oxide fuel cell performance using metallic interconnects coated by electroplating methods," ASME Fuel Cell Science, Engineering and Technology Conference, June 18-20, 2007, New York, NY.
3. J.P. Trembly, R.S. Gemmen, D.J. Bayless, "The effect of coal syngas containing HCl on the performance of solid oxide fuel cells: Investigations into the effect of operational temperature and HCl concentration," J. Power Sources 169, 2007, pp. 347-354.
4. J.P. Trembly, R.S. Gemmen, D.J. Bayless, "The effect of trace As, Cl, P, and Se coal cyngas species on the performance of a planar solid oxide fuel cell," ASME Fuel Cell Science, Engineering and Technology Conference, June 18-20, 2007, New York, NY.

5. J.P. Trembly, R.S. Gemmen, D.J. Bayless, "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 SFOC anodes," *J. Power Sources* 163, 2007, pp. 986-996.
6. J.P. Trembly, R.S. Gemmen, D.J. Bayless, "The effect of coal syngas containing AsH_3 on the performance of SOFCs: Investigation into the effect of operational temperature, current density and AsH_3 concentration," accepted for publication in *J. Power Sources*, 2007.
7. D. Tucker, J. VanOsdol, E. Liese, L. Lawson, S. Zitney, R. Gemmen, J.C. Ford, C. Haynes, "Evaluation of methods for thermal management in a coal-based SOFC turbine hybrid through numerical simulation," *Proceedings of the 7th International Colloquium on Environmentally Preferred Advanced Power Generation*, September 5-8, Irvine, CA.