

II.K.1 Adapting Planar Solid Oxide Fuel Cells for Distributed Power Generation*

David J. Bayless (Primary Contact), Jason Trembly, Andres Marquez
Ohio University
248 Stocker Center
Department of Mechanical Engineering
Athens, OH 45701
Phone: (740) 331 4536; Fax: (740) 593 0476
E-mail: bayless@ohio.edu

DOE Technology Development Manager:
Roxanne Garland
Phone: (202) 586-7260; Fax: (202) 586-9811
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

Technical Advisor: Jamie Holladay
Phone: (202) 586-8804; Fax: (202) 586-9811
E-mail: Jamie.Holladay@pnl.gov

Subcontractors:

- SOFCo-EFS, Alliance, OH
- Case Western Reserve University, Cleveland, OH

Project Start Date: August 13, 2003
Project End Date: October 1, 2008

*Congressionally directed project

Technical Targets

This project is conducting fundamental studies of syngas tolerant SOFCs. Insights gained from these studies will be applied toward the design and synthesis of fuel cell stacks that meet the following targets:

- H₂S level: 200 ppm
- CO tolerance: <5% increase in area specific resistance (ASR)
- Durability: <5% degradation in power density for typical syngas

Accomplishments

- Showed thermodynamically that the effect of trace species contained in syngas could significantly affect fuel cell operation.
- Thermodynamic screening was used as a first level means to predict the partitioning between the gas and condensed phase and form of trace species contained in syngas since experimental testing of each trace specie was not feasible.
- Quantified the degradation caused by identified species (H₂S, HCl, Arsine) on fuel cell performance through experimentation and post-testing material analysis.



Objectives

- Integration of existing solid oxide fuel cells (SOFCs) and syngas technologies.
- Identify contaminants in syngas that affect SOFC stack operation.
- Study the technologies allowing separation of contaminants from the fuel stream.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

Introduction

Commercialization of fuel cells capable of using abundant domestic supplies of fuel is not only critical to development of power-related industries in Ohio, it also has much broader economic and infrastructure security implications. At present, fuel cell development is focused on using natural gas, ignoring a plentiful, inexpensive, and domestically available fuel source – syngas derived from solid fuels such as coal and biomass. Because we are focusing our research efforts on the planar solid oxide fuel cell platform, which can use CO as a fuel, it may also be possible to separate the CO from the H₂ produced during gasification of the solid fuel. The CO or CO enriched stream could be used to fuel the planar solid oxide fuel cells for stationary power generation, while a pure H₂ stream could be used to supply transportation fuel cell needs.

The proposed project intends to study the integration of existing SOFC and solid fuel-derived syngas technologies. Integration of the technologies will include (a) modeling of a SOFC with syngas to predict

the effects of the composition and elevated temperature of syngas on the chemical reactions and energy conversion of the fuel cell, (b) performance testing of the cells using synthetic syngas, a fixed mixture of gases that simulate syngas, with and without contaminants, including sulfur, mercury, and particulates, and (c) development of hot-gas electrostatic separation and precipitation to purify the syngas stream. Pilot-scale demonstration, with minimum test durations of 500 hours, will be performed with single cells and small SOFC stacks (two to five cells each).

Approach

The approach taken in this work was to do theoretical modeling, mostly thermodynamic, to identify the effects of various syngas constituents on fuel cells, then to perform empirical tests to quantify the performance of the cells. Experimental conditions were typically set as galvanostatic operation (0.21 ± 0.01 amps/cm²) at 850°C utilizing simulated O₂ blown syngas, measuring planar SOFC (PSOFC) ASR by completing voltage-current (V-I) scans; ASR histories plotted and studied, voltage (power) performance over time monitored and studied. Material analyses on the anodes (before and post tests) were done using scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) to determine if any structural or composition changes had taken place.

Work in separation technologies was focused on experimental validation of theoretical modeling of novel electrostatically enhanced cyclonic separation.

Results

The results of the work are far too extensive to adequately summarize here. The reader is highly encouraged to refer to the quarterly technical reports. However, a brief synopsis is provided.

Stack Testing with and Without H₂S in Syngas

The performance of two-cell planar solid oxide fuel cell stacks using coal syngas, with and without hydrogen sulfide (H₂S), was studied. All cells were tested at 850°C with a constant current load of 15.2 A (current density of 0.22 A/cm² per cell) and 30% fuel utilization. The H₂S injection immediately and significantly affected the power degradation of the stack system regardless of the carrier fuel as seen in Figure 1. Results for the test with only H₂ and N₂ in the presence of H₂S (119-120 ppm) indicated that the power decay and ASR degradation values were lower than those for the tests where simulated syngas containing CO and increased water content was used. The results indicate that contact points in the stack contributed to the power degradation

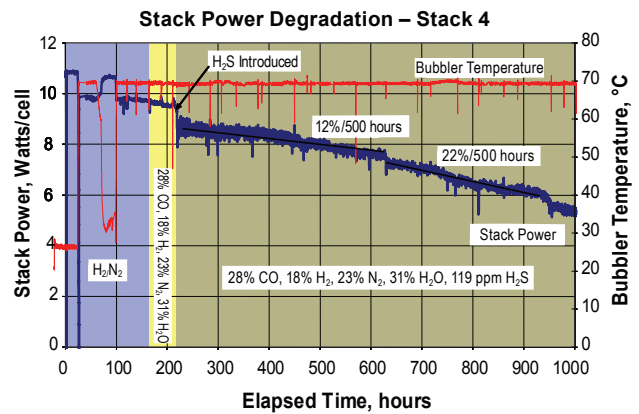


FIGURE 1. Power and bubbler temperature history for the test of Stack 4, run with syngas and H₂S. CO was introduced after 165 hours; H₂S was added after 219 hours.

of the system. Other factors, including contamination from the upstream fuel gas tubing, may have contributed to the higher degradation under simulated syngas conditions. In general the data confirm previous results for single cell testing, and showed that for these specific short stacks (two cells) both fast and slow response to H₂S injection eventually stabilized.

Contaminant Identification

Thermodynamic simulations may be used to predict the partitioning behavior of trace elements in coal syngas between the gas and solid phases. The thermodynamic evaluations suggest that most of the trace species in syngas will not reach the SOFC anode. The elements Be, Cr, K, Na, V, and Z were all found to form condensed phase species under warm gas cleanup system conditions, where it will be collected at high levels in the cleanup systems. The thermodynamic evaluations also showed that Sb, As, Cd, Hg, Pb, P, and Se vapor phase forms were found in the coal syngas at warm gas cleanup conditions. Vapor forms of the trace species will allow the species to travel to the SOFC module and potentially interact with the SOFC anode.

Interactions between the vapor phase forms of the elements were investigated with typical SOFC anode materials Ni and yttria-stabilized zirconia (YSZ). These evaluations revealed that no interactions between the vapor species forms with the oxide components ZrO₂(s) and Y₂O₃(s) would take place. No interactions between the Se vapor species and Ni were found. However, Sb, As, and P vapor phase species were shown to have the potential to interact with Ni in the SOFC anode even with such low trace species concentrations found in syngas. The oxidation of the fuel species was shown to have a large effect on the amount of secondary Ni phases formed in the anode of the SOFC since the increases oxygen partial pressure in the system

inhibits the formation of $\text{PH}_3(\text{g})$. The oxidation of the trace metal vapor species Cd, Hg, and Pb were also investigated and shown not to be feasible.

Testing the Effects of HCl on SOFC Anodes

The performance of SOFCs using simulated syngas, with and without hydrogen chloride (HCl), was studied. Electrolyte-supported SOFCs were tested potentiostatically at 0.7 V at 800 and 900°C with simulated coal syngas containing 0, 20, and 160 ppm HCl. The results from the tests without HCl show good performance with little degradation over 100 h of operation. Both 20 and 160 ppm HCl were shown to cause performance losses in the SOFCs after injection into the system, as shown in Figure 2. Although the tests showed that HCl does cause degradation to SOFC performance, the cell performance was recoverable upon the removal of HCl from the fuel. Also, recent results from anticipated warm/hot-gas-cleanup technologies suggest that HCl will be removed to levels that will not cause any significant performance losses in SOFCs.

Testing the Effects of Arsine on SOFC Anodes

The performance of SOFCs using simulated coal-derived syngas, with and without arsine (AsH_3), was studied. Anode-supported SOFCs were tested galvanostatically at 0.25 A/cm^2 and 0.50 A/cm^2 at 750°C and 800°C with simulated coal syngas containing 0, 1, and 2 ppm HCl. The results from the tests without AsH_3 show good performance with little degradation over 100 and 800 h of operation, as seen in Figure 3. Trials completed for 100 h with concentrations of 1 and 2 ppm AsH_3 showed little degradation and no formation of secondary nickel arsenide phases. A test operated for 800 h was completed with 0.1 ppm AsH_3 did indicate that it is possible to form a secondary nickel arsenide phase in the SOFC anode. Overall the results indicate that AsH_3 is not nearly as detrimental to SOFC operation as other previously tested trace coal syngas species such as HCl or H_2S .

Conclusions and Future Directions

- Trace species can have a significant impact on fuel cell performance.
- Longer term testing is critical, as shown with the Arsine results. Small levels of contamination can be significant to performance over long periods ($>1,000$ h) while short-term testing may not be able to identify these problems.
- H_2S tolerance is key to long-term operation, as any biomass syngas system will be supplemented with coal in the gasifier.
- CO and H_2O have noticeable interactions in the presence of H_2S on SOFC anodes.

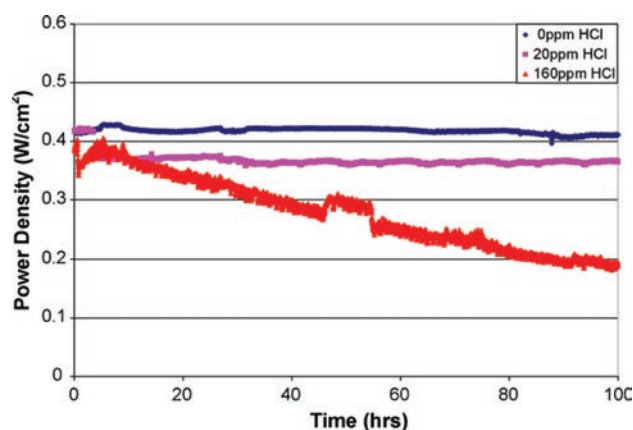


FIGURE 2. SOFC Power Density Curves at 900°C and 0.7 V Over Time with HCl Concentration of 0 ppm, 20 ppm, and 160 ppm

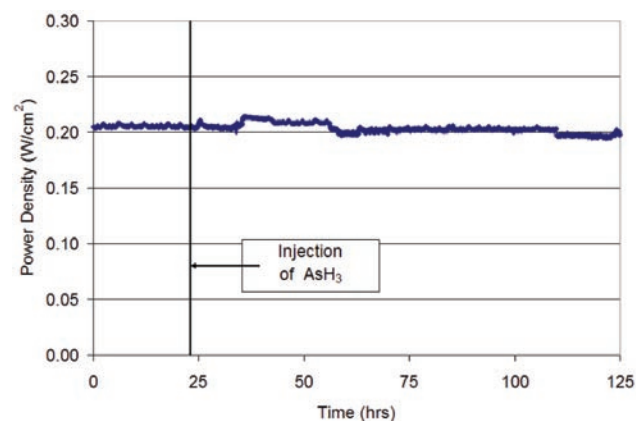


FIGURE 3. SOFC Power Density Operating at 800°C and 0.25 A/cm^2 with 2.0 ± 0.1 ppm AsH_3

FY 2007 Publications/Presentations

1. Trembly, J.P., Gemmen, R.S., Bayless, D.J., "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," *Journal of Power Sources*, (169):2, pp. 347-354, 2007.
2. Shi, L., Bayless, D., Kremer, G., and Stuart, B., "Numerical Investigations of the Flow Pattern in an Electrically Enhanced Cyclone," accepted for publication in *Journal of the Air and Waste Management Association*, (57), pp. 489-496, 2007.
3. Shi, L. and Bayless, D., "Comparison of Boundary Conditions for Predicting the Collection Efficiency of Cyclones," *Powder Technology*, (173) pp. 29-37, 2007.
4. Trembly, J.P., Gemmen, R.S., Bayless, D.J., "The Effect of IGFC Warm Gas Cleanup System Conditions on the Gas-Solid Partitioning and Form of Trace Species in Syngas and Their Interactions with SOFC Anodes," *Journal of Power Sources*, (163):2, pp. 986-996, 2007.

5. Marquez, A., Ohrn, T., Trembly, J., Ingram, D., and Bayless, D., “Effects of Coal Syngas and H₂S on the Performance of Solid Oxide Fuel Cells: Part 2: Stack Tests,” *Journal of Power Sources*, (164):2, pp. 659-667, 2007.