V.O.2 Renewable and Logistics Fuels for Fuel Cells at the Colorado School of Mines*

Neal P. Sullivan (Primary Contact),
Robert J. Kee, Anthony M. Dean, Robert Braun,
Ryan O'Hayre, Tyrone Vincent
Colorado School of Mines (CSM)
1500 Illinois Street
Golden, CO 80401
Phone: (303) 273-3656
E-mail: nsulliva@mines.edu

DOE Technology Development Manager:
Kathi Epping Martin
Phone: (202) 586-7425
E-mail: Kathi.Epping@ee.doe.gov

DOE Project Officer: Reginald Tyler
Phone: (303) 275-4929
E-mail: Reginald.Tyler@go.doe.gov

Contract Number: DE-FG36-08GO8810

Subcontractors:
- Protonex Technology Corporation, Broomfield, CO
- Reaction Systems, LLC, Boulder, CO

Project Start Date: July 1, 2008
Project End Date: June 30, 2010

*Congressionally directed project

Objectives

- Develop solid oxide fuel cell (SOFC) materials for robust operation on renewable and logistics fuels.
- Identify optimal reforming strategies for renewable and logistics fuels.
- Create thermally stable fuel-reforming catalysts and supports.
- Employ system modeling to optimize auxiliary power unit (APU) configurations.
- Utilize model-predictive control to integrate system hardware.

Technical Barriers

- Durability: Broaden SOFC operating windows under logistics fuel streams.
- Performance: Increase efficiency through system optimization.
- Transient operation: Develop model-predictive control algorithms for use in dynamic control.

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

(A) Durability

(C) Performance

(G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

In this project, we conduct a range of studies to improve the durability, efficiency, and transient operation of SOFC auxiliary power units. Insights gained from these studies will be applied toward the design and synthesis of SOFC materials and systems to meet the DOE 2015 Technical Target for durability (35,000 hours), start-up time (15-30 minutes), and cycle capability (250 cycles).

Accomplishments

- Demonstrated expanded trouble-free operating windows of hydrocarbon-fueled tubular SOFCs through addition of barrier-layer architectures.
- Demonstrated stability of next-generation strontium-doped lanthanum titanate ($Sr_{0.8}La_{0.2}TiO_3$ - SLT) SOFC anode materials across all ceramic-processing conditions. These nickel-free perovskite anode materials have far greater resistance to re-oxidation and deposit-formation failure mechanisms than established nickel-yttria-stablized zirconia (YSZ) anode materials.
- Demonstrated solid-state reaction sintering of barium-cerate-zirconate proton-conducting ceramics at $1/10^{th}$ the current fabrication cost. Measurements of ionic conductivity of these materials exceed the highest previously reported levels.
- Established liquid-fuel processing strategies and experimentation.
- Utilized new experimentation to demonstrate catalytic partial oxidation (CPOX) of renewable liquid fuels, including ethanol and butanol.
- Evaluated SOFC performance under CPOX'ed butanol-reformate streams, with comparisons made to performance under hydrogen fuel.
- Developed hybrid computational fluid dynamics (CFD)-electrochemical modeling tools to examine heat transfer within 600-Watt tubular-SOFC stacks.

- Utilized hybrid models to quantify effects of design changes on thermal and chemical non-uniformities within the stack.
- Developed rapid, lower-order dynamic models to map response of slower, high-order physical models for use in dynamic system control.
- Demonstrated fidelity of lower-order models in mapping system response across large changes in system operating conditions.
- Established outreach to national and international scientists in the field of energy through the Distinguished Lecture Series.

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Introduction

The objective of this project is to advance the current state of technology of SOFCs to improve performance when operating on renewable and logistics hydrocarbon fuel streams. While SOFCs can efficiently convert the chemical energy of hydrocarbon fuels into electrical energy, the conversion process can prove problematic if not carefully controlled, due to the risk of carbon-deposit formation, sulfur contamination, and deviations from design set points. In this project, we are developing new SOFC and catalyst materials to improve the robustness of system operation on hydrocarbon fuel streams. Additionally, modeling and experimentation is being conducted to examine and mitigate the formation of carbon deposits during fuel reforming and electrochemical-oxidation processes. Physically based models are being developed to examine SOFC-system operation and performance in auxiliary power unit (APU) applications, including control strategies for improving the dynamic response of such SOFC APU systems. Finally, outreach is being conducted through the Distinguished Lecturer Series, promoting collaboration between fuel cell researchers and scientists.

Approach

CSM has assembled a strong and diverse team of scientists and researchers with broad skill sets applicable to fuel cell development. Coordinated through the Colorado Fuel Cell Center, this team examines both the fundamental underpinnings and the key technical problems facing SOFC operation on renewable and logistics fuels. We develop new SOFC materials and architectures for use with renewable and logistics (i.e. liquid hydrocarbon) fuel streams, addressing the technical challenges and operating windows associated with carbon-deposit formation and sulfur poisoning. We develop catalyst materials and reforming strategies for optimal processing of liquid hydrocarbons and biomass-derived fuels for use in fuel cells. We develop system-integration strategies to create robust SOFC systems that utilize renewable and logistic fuels. Through advanced fuel cell modeling and simulation, we examine the fundamental underpinnings of the atomic-scale charge-transfer processes occurring during SOFC operation on renewable and logistic fuels, incorporating the effects of load following and system control. Finally, we promote outreach programs through the creation of a Distinguished Lecturer series at the CSM campus to bring fuel cell scientists from across the nation in an exchange of ideas with faculty and students.

Results

Task 1. Ceramic Materials and Architecture

Fuel cell reliability and performance can be greatly improved through development of new materials and architectures that promote robust SOFC operation on renewable and logistics fuels. In this task, we investigate new SOFC anode materials that promote tolerance to sulfur compounds and mitigate carbon-deposit formation. We are developing a perovskite-based nickel-free anode material for achieving sulfur tolerance and robust, deposit-free operation on renewable and logistics fuels. Today's SOFCs are widely designed around a composite nickel/YSZ anode formulation. While this anode material provides high electronic conductivity and good internal fuel-reforming characteristics, the cost of the nickel material can be high. Additionally, nickel suffers from problems during operation, including long-term sintering that decreases cell performance, intolerance to sulfur-containing fuel streams, and susceptibility to oxidation that can lead to cell fracture. Perovskite-based anodes can mitigate a number of these issues, as they have been shown to be more sulfur and redox tolerant than today's nickel anodes, while also achieving high power density in button-cell experiments.

The primary focus of our next-generation perovskite anode material is SLT. Within this project, we have fabricated SLT powders through solid-state powder-processing techniques, and confirmed the stability of the SLT with other SOFC materials (like the YSZ electrolyte material) throughout all high-temperature cell-fabrication processes. We have developed a host of experimental methods to quantify anode performance, including an electronic-conductivity test stand, and a unique separated anode experiment to compare gas transport and internal-reforming chemistry of next-generation anodes to that of traditional Ni-YSZ anodes. We have used this experimentation to confirm that the electronic conductivity of SLT is among the highest of perovskite-based ceramic materials, making it a leading material for replacing the nickel found in today's SOFCs. We are using these results to fabricate complete SLT-based tubular SOFCs, like those shown in the high-resolution micrographs of Figure 1. Note the high porosity of the SLT anode, the finer porosity of the

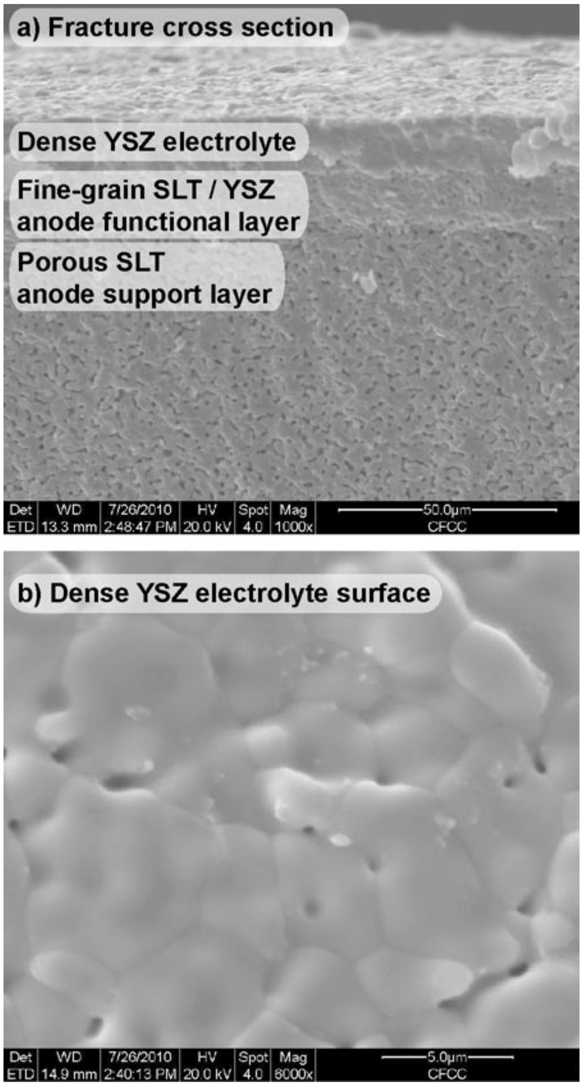

FIGURE 1. Scanning electron micrographs of SLT-based, tubular SOFC developed through this project: a) fracture cross-section of porous anode support, fine-grain anode-functional layer, and dense electrolyte assembly, and b) YSZ-electrolyte surface.

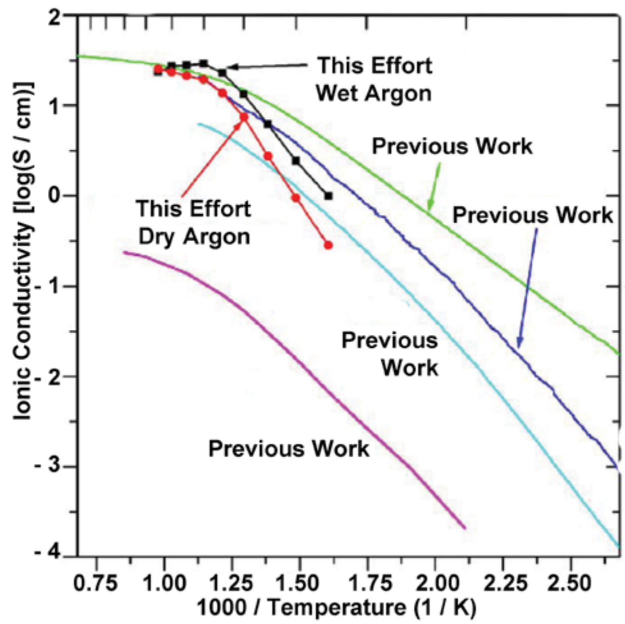

FIGURE 2. Ionic conductivity of proton conductors developed in this work, along with comparisons to previously published conductivities for alternate materials.

SLT/YSZ anode functional layer, and the thin and dense YSZ electrolyte layer captured in these images.

We have also extended our development of a novel, inexpensive solid-state reactive-sintering (SSRS) technique from fabrication of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ to creation of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCY), two proton-conducting ceramics. As shown in Figure 2, we have demonstrated that the ionic conductivity of our SSRS-fabricated BZCY material is higher than any previously reported proton-conducting ceramic, while be fabricated at one tenth the cost of traditional fabrication methods.

Task 2. Fuel Processing

Robust operation of fuel cells on renewable and logistic fuel streams hinges on the emergence of fuel-reforming technology that is compatible with SOFC requirements. In this task, we develop reforming strategies for optimal processing of liquid hydrocarbons and biomass-derived liquid fuels for use in SOFCs. Within this task, CSM researchers work with subcontractor Reaction Systems, LLC to synthesize thermally stable catalysts and catalyst supports, and then measure their activity and stability for reforming of both renewable and logistics fuels. Novel catalyst supports have been fabricated, and the improvements in thermal stability demonstrated. Construction of a catalyst testing rig has been completed, and used to explore operating windows for catalytic partial oxidation of butanol, a high-energy-density biomass-derived liquid fuel. After establishing operating windows, the CPOX'ed butanol reformate has been fed to a conventional tubular SOFC fabricated by industrial partner CoorsTek, Inc, with cell-performance comparisons made to that under hydrogen fuel streams. As shown in Figure 3, cell performance under CPOX'ed butanol reformate fuel reached 60% of the pure-hydrogen performance level.

Task 3. System Optimization and Control

The system modeling and optimization effort centers on creating optimal SOFC-based APU system architectures, and is inclusive of an examination of dynamic component interactions during various operating modes. Modeling and analysis efforts are applied to the ongoing APU development efforts of Protonex Technology Corporation with the specific aims

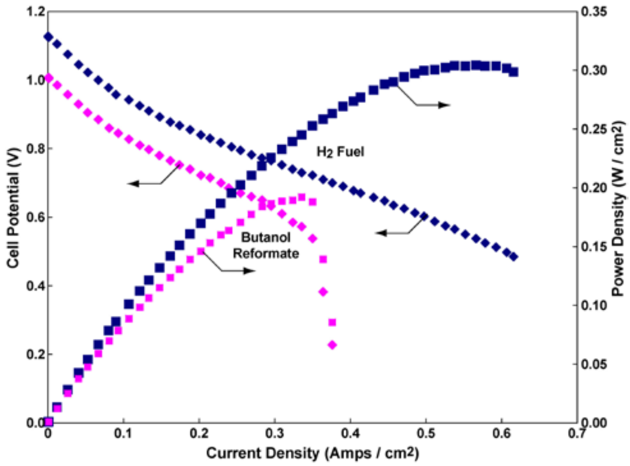

FIGURE 3. Electrochemical performance of CoorsTek SOFC under hydrogen and CPOX'ed-butanol reformate fuel streams. Performance under reformate reaches 60% of peak power density of hydrogen-fueled conditions.

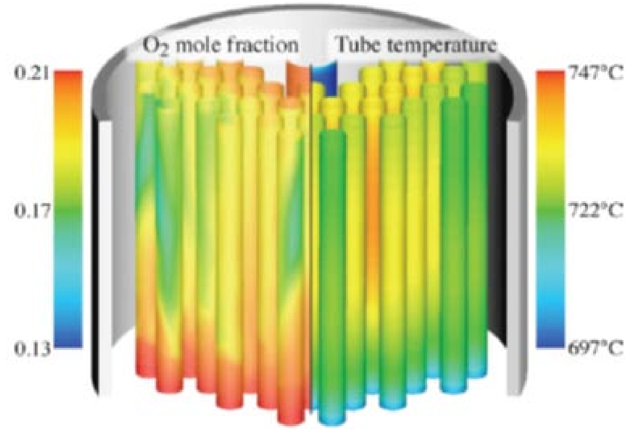

FIGURE 4. Model-predicted oxygen mole fraction (left) and temperature distributions (right) within the Protonex 600-W tubular SOFC stack. While the O_2 mole fraction is fairly uniform, significant temperature differences are predicted within the stack bundle.

of improving both system performance prediction under sensor uncertainty and heat-loss estimation methods.

Utilizing the commercially available Fluent CFD software, a hybrid CFD/electrochemistry model of the 600 W tubular Protonex stack has been established and utilized to examine heat transfer and oxygen usage within the stack tube bundle. Results are shown in Figure 4; imbalances in O_2 mole fraction are fairly modest. However, temperature variations from cell to cell can reach nearly 50°C, presenting significant degradation issues to tubular-stack developers. Alternative designs may enable a more-uniform temperature distribution within the stack.

The goal of the Fuel Cell System Control task is the design of a control system to regulate the operation of a complete SOFC system. The control system design is based on a dynamic model that can predict system behavior given perturbations in actuator settings, such as air and fuel flows and power loads. Ideally, these models are based on physical first principles; however, physically based models are often very complex, and take considerable computational resources to compute. When utilized for real-time control, computational complexity can become a limiting factor in the usefulness of the model, and it becomes necessary to capture the dominant behavior in a lower order models that can be run quickly. Our approach is to start with physically based models, and apply system-identification techniques to develop the required reduced-order models.

This project has focused on control of the fuel cell stack in isolation. We have implemented this reduced order model in MATLAB/Simulink, along with the state estimation and model-predictive control components. The state-estimation component uses the reduced-order model of the plant and measurements of the inputs and outputs to find the current internal state that best matches the observed behavior. Then, the model-predictive-control component calculates the future actuator commands that are needed to drive the system from the current state to the desired future behavior. This future behavior is specified in terms of either desired signal trajectories (e.g. current set-point) or desired signal bounds (e.g. minimum voltage or fuel utilization). We have utilized this model to demonstrate robust dynamic control of SOFC stack performance with a broad load variation. This control was established within the constraints of cell voltage and fuel utilization, validating the performance of the reduced-order models for capturing the response of the higher-order physical models.

Task 4. Outreach

In this task, CSM hosts a seminar series that brings prominent fuel cell researchers to the CSM campus for interaction with our students and our faculty. This exchange of ideas will promote national collaboration, further the development of fuel cells, and grow the CSM program. During the previous year, Prof. Robert Dibble of the University of California, Berkeley provided CSM Engineering Division students with a seminar entitled Recent "Developments in the Combustion Analysis Laboratory at the University of California at Berkeley". Additionally, Dr. Marco Hartmann of the Karlsruhe Institute of Technology provided a talk entitled "Generation of Hydrogen and Synthesis Gas from Higher Hydrocarbon Fuels by Catalytic Partial Oxidation." This talk was given as part of CSM's Chemical Engineering Department Seminar Series.

Future Directions

Task 1. Ceramic Materials and Architecture

- Measure electrical conductivity and catalytic activity of novel anode compositions over a range of anode conditions.
- Establish fabrication protocols for perovskite-based tubular SOFCs.
- Evaluate the long-term stability of protonic conductors using thermogravimetric analysis, differential thermal analysis, and dilatometry.

Task 2. Fuel Processing

- Extend partial-oxidation experiments on butanol fuel.
- Develop process windows for deposit-free SOFC operation under butanol reformate.

Task 3. System Optimization and Control

- Extend tube-stack models to examine relationships between stack design and performance.
- Implement explicit form for model predictive control.

FY 2010 Publications/Presentations

1. Jianhua Tong, Daniel Clark, Ryan O'Hayre, "Solid-State Reactive Sintering Mechanisms for Improving Total Conductivity of Proton Conducting Ceramic, Yttrium-Doped Barium Zirconate", *Electronic Materials and Applications 2010.*

2. Stephanie M. Villano, Jessica Hoffmann, Hans-Heinrich Carstensen, and Anthony M. Dean, "Selective oxidation of ethylene in a model "dirty" synthesis gas stream: an experimental and kinetic modeling study," Spring 2010 ACS National Meeting.

3. J. Tong, D. Clark, R. O'Hayre, "A solid-state reactive sintering method to improve the manufacturability and conductivity of yttrium-doped barium zirconate", *Journal of Materials Chemistry*.

4. A.E. Richards, N.P. Sullivan, R.J. Kee, H. Zhu, and C. Moyer, "Internal Reforming Chemistry in Novel SOFC Anode Materials and Structures," *2009 Fuel Cell Seminar and Exposition*, Palm Springs, CA, USA, November 16–19, 2009.

5. D.D. Storjohann, N.P. Sullivan, A. Colclasure, R.J. Kee, and H. Zhu, "Barrier Layer Structures in Tubular Solid-Oxide Fuel Cells," *2009 Fuel Cell Seminar and Exposition*, Palm Springs, CA, USA, November 16–19, 2009.

6. A. Subramaniyan, J. Tong, N. Sammes, R. O'Hayre, Sintering Studies on 20mol% Yttrium doped barium cerate, *Journal of American Ceramic Society*, **submitted**.

7. J. Tong, D. Clark, R. O'Hayre, Cost-effective solid-state reactive sintering method for proton conducting ceramics, *Solid State Proton Conductor 15(**SSPC 15**)*, August 15–20, **2010**, Santa Barbara, CA, USA.

8. A. Subramaniyan, J. Tong, N.M. Sammes, R. O'Hayre, *Solid State Proton Conductor 15(**SSPC 15**)*, August 15–20, **2010**, Santa Barbara, CA, USA.

9. S. Babiniec, N.P. Sullivan, A. Richards, N. Faino, "Multi-Phase Tubular Perovskite-Based Anodes for Use in Hydrocarbon-Fueled Solid-Oxide Fuel Cells," *2010 European Fuel Cell Forum*, Lucerne, Switzerland, June 28 – July 2, 2010.

10. N.E. McGuire, N.P. Sullivan, H. Zhu, and R.J. Kee, "Catalytic Reforming on Hexaaluminate-Based Catalyst Supports," *2010 European Fuel Cell Forum*, Lucerne, Switzerland, June 28 – July 2, 2010.

11. A. Richards, N.P. Sullivan, R.J. Kee, and H. Zhu, "Internal Reforming Chemistry in Novel SOFC Anodes and Architectures," *2010 European Fuel Cell Forum*, Lucerne, Switzerland, June 28 – July 2, 2010.