V.I.6 Renewable and Logistics Fuels for Fuel Cells at the Colorado School of Mines*

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*Congressionally directed project

Objectives

- Develop solid oxide fuel cell (SOFC) materials for robust operation on diesel fuel.
- Identify optimal hydrocarbon-fuel reforming strategies.
- 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

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

(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 APUs. Insights gained from these studies will be applied toward the design and synthesis of SOFC materials and systems to meet the DOE 2015 technical targets for durability (35,000 hours), start-up time (15-30 minutes), and cycle capability (250 cycles).

Accomplishments

- Successfully fabricated next-generation, high-porosity, nickel-free, perovskite anodes from $(La_{0.75}Sr_{0.25})_{0.95}Mn_{0.5}Cr_{0.5}O_3$ (LSCM) materials, and applied initial deposits of yttria-stabilized zirconia (YSZ) electrolyte. The novel perovskite anode has far greater resistance to reoxidation and deposit-formation failure mechanisms than established nickel-YSZ SOFC anode materials.
- Demonstrated solid-state reaction sintering of barium-zirconate proton-conducting ceramics at $1/10^{th}$ the current fabrication cost.
- Demonstrated improved fuel-reforming strategies through selective oxidation of tar-forming species (such as ethylene).
- Synthesized novel thermally stable catalyst supports, and confirmed improved performance and stability at high-temperature (1,000°C) conditions.
- Designed, fabricated, and commissioned new catalyst test facility to examine catalyst operation on liquid fuel streams.
- Developed system modeling tools to examine 600-Watt SOFC APU generators utilizing low-sulfur diesel fuel.
- Established model-predictive control software, and demonstrated reduced-order models of high-fidelity physically based models for control of 600-W system.

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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 will develop new SOFC and catalyst materials to improve the robustness of system operation on hydrocarbon fuel streams. Additionally, modeling and experimentation will be conducted to examine and mitigate the formation of carbon deposits during fuel-reforming and electrochemical-oxidation processes. Physically-based models will be developed to examine SOFC-system operation and performance in APU applications, including control strategies for improving the dynamic response of such SOFC APU systems. Finally, outreach will be conducted through creation of the Distinguished Lecturer Series to promote nationwide collaboration with fuel cell researchers and scientists.

Approach

The Colorado School of Mines (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 (CFCC), this team proposes to examine both the fundamental underpinnings and the key technical problems facing SOFC operation on renewable and logistics fuels. We will 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 will develop catalyst materials and reforming strategies for optimal processing of liquid hydrocarbons and biomass-derived fuels for use in fuel cells.

We will develop system-integration strategies to create robust SOFC systems that utilize renewable and logistic fuels. Through advanced fuel cell modeling and simulation, we will 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 will 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. Additionally, we investigate alternative fuel cell architectures, seeking to optimize the structure of the cell for maximum efficiency and reliability. Computational modeling is combined with cell fabrication and testing to improve our understanding of the interdependence of cell materials, architecture, and performance.

We are developing a perovskite-based nickel-free anode material for achieving sulfur tolerance and robust, deposit-free operation on renewable and logistics fuels. The primary focus of our next-generation anode material is LSCM. LSCM is a mixed ionic-electronic conductor, and can provide both electronic and ionic conductivity in a single-phase perovskite material, making it ideal for use as an SOFC anode. Being a ceramic material, LSCM also shows greater resistance to carbon-deposit formation and sulfur poisoning in comparison to Ni-YSZ, but its catalytic performance and electronic conductivity is not well understood. In this task, we are examining the performance of LSCM over a wide range of environmental conditions, developing SOFCs that employ LSCM anode material, and evaluating the electrochemical performance of these cells under renewable and logistics fuel streams.

After developing preliminary materials formulations, we have begun coating LSCM anodes with thin (10-μm thick) YSZ electrolytes through a dip-coating process. A scanning electron microscope (SEM) image of a CFCC-fabricated LSCM-anode/YSZ-electrolyte assembly is shown in Figure 1. The micrograph in Figure 1a shows the YSZ surface of the tubular cell; the grain structure is clear, though some pinholes are evident. Improving the integrity of this electrolyte is the focus of our current efforts. The micrograph in Figure 1b shows a cross-section of the cell; the electrolyte has some measure of porosity, but is primarily dense. The LSCM fuel-side electrode shows an open morphology, as desired for facile gas transport. Current efforts are focused on improving the density of the electrolyte by creating a functionally graded electrode structure. We are now adding 10-micron-thick, fine-porosity, low-particle-size functional layers to the fuel-side electrode. These layers decrease the electrode porosity at the interface with the electrolyte, improve our ability to generate a dense electrolyte on a porous electrode, and increase the area of the triple-phase boundaries to increase power density. Such functional layers are common in Ni-YSZ cells, but have not been attempted with LSCM-based cells.

We have also developed a novel, inexpensive solid-state reactive-sintering (SSRS) technique for formation of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20), a proton-conducting ceramic. The SSRS technique enables fabrication of near net-shape ceramic parts with density as high as 97% and
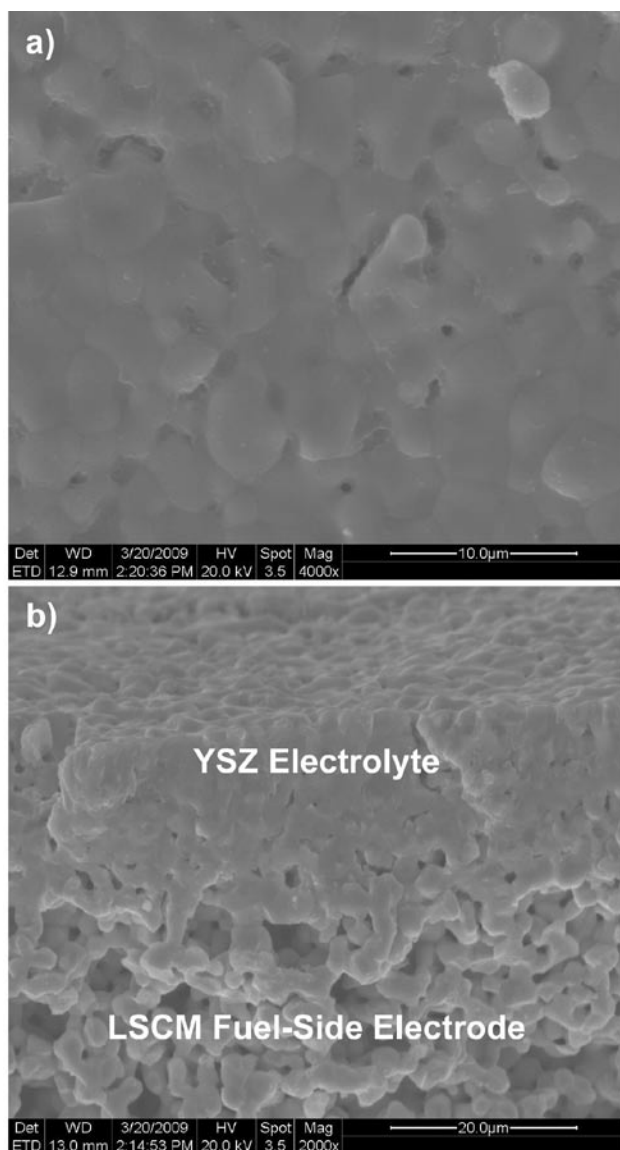
FIGURE 1. SEM of LSCM-based, tubular SOFC, a) YSZ-electrolyte surface; and b) fracture cross-section of LSCM anode-YSZ electrolyte assembly.

grain size as large as 5 μm while sintered at a relatively low temperature of 1,350°C. Now we are seeking to understand the fundamental formation and densification mechanisms for this process.

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 as well as biomass-derived fuels for use in SOFCs. This task examines both external fuel reformers as well as on-anode reforming. The impact of gas-phase partial
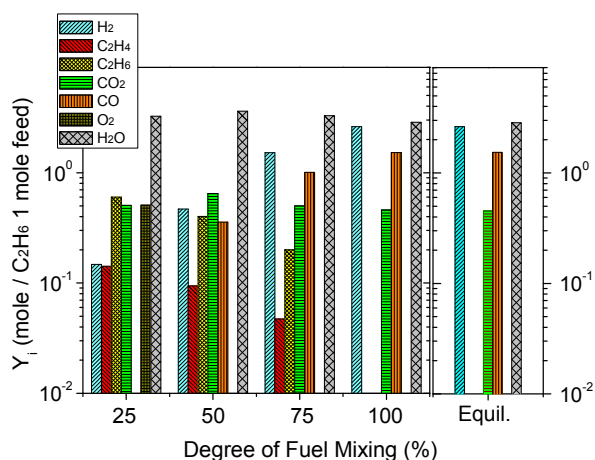

FIGURE 2. Product Distributions as a Function of the DFM

oxidation reactions is explored as an alternative to tar and sulfur-mitigation strategies. This project involves three components: (1) identification of fuel surrogates, (2) characterization of relevant gas-phase kinetics, and (3) characterization of catalytic kinetics.

We have identified ethylene to be the gas-phase species that plays the most-critical role in the formation of deposits, and have explored potential routes for formation of ethylene during hydrocarbon reforming. For example, in the case of diesel autothermal reforming (ATR), one expects that the fuel might pyrolyze if it is not mixed with the steam/air oxidant stream. This has been confirmed in our ATR experiments. We have explored the impact of fuel mixing on the formation of deposit precursors. To simulate imperfect mixing or the degree of fuel mixing (DFM), we assumed a very simple model in which two separate reactors are used. One contains some fraction of the fuel with no steam or air (a pyrolysis reactor), while the remaining fuel fraction is perfectly mixed in the second reactor with all the steam and air (an oxidation reactor).

Figure 2 illustrates our results regarding how DFM affects the product distribution, assuming exothermic autothermal reforming conditions ($T_i = 800°C$, $H_2O/C = 1.25$, $O/C = 1.4$, $\tau \sim 1$ s). Note in Figure 2 that ethylene (a deposit precursor) is formed in all cases of imperfect mixing. If only a part of the fuel mixed with the oxidant (e.g., DFM = 50%), this approach predicts formation of ethylene from the pyrolysis reactor and excess CO_2 production. The higher CO_2 level is directly traceable to the higher temperature predicted in the oxidation reactor. For the DFM = 50% case, the temperature of the oxidation part (~2,400 K) is high enough to thermally damage the catalysts. Thus imperfect mixing is expected to result in an increased potential for both deposit formation and thermal damage to a catalyst. Furthermore, it is very interesting to note that the 100% mixing case has same product distribution to

equilibrium state, meaning that gas-phase reactions alone are sufficient to drive the system to equilibrium (no olefins or methane formed). We expect even more severe impact in diesel reforming since the large alkanes in diesel fuel are much more reactive than ethane. Therefore, enhanced mixing is essential to inhibit the formation of deposit precursors.

Also within this task, subcontractor Reaction Systems, LLC synthesizes thermally stable catalysts and catalyst supports and then measures 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. Additionally, construction of a catalyst testing rig has been completed.

Reaction Systems characterized the thermal stability of the supports by measuring their surface areas after preparation and again after aging of the materials for eight hours at 1,000°C. This temperature reflects the upper end of those needed to obtain high concentrations of CO and H_2 during the catalytic partial oxidation reaction. We used the single-point Brunauer-Emmett-Teller method to measure surface area in all cases. The support surface areas before and after aging are listed in Table 1. Overall, the results indicate that aging at 1,000°C did not produce substantial reduction in these catalyst supports. Although the aging step needs to be increased in length, these results are encouraging because the sintering process, which causes surface area reduction, is most rapid in the initial stages of exposure to high temperature. Thus, we would expect even lower percent losses in surface area in subsequent periods of exposure.

TABLE 1. Support Surface Areas before and after Aging

Catalyst	Surface Area (m²/g)		
	As Prepared	Post Aging	% Decrease
$LaAl_{11}O_{18}$	56.3	56.7	< 0.1
$SrAl_{11}O_{18}$	82.1	77.6	5.5
La-Al Mixed Metal Oxide (Fine Filter Paper Template)	20.7	19.2	7.2
La-Al Mixed Metal Oxide (Coarse Filter Paper Template)	13.5	14.1	<0.1

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. Due to the importance of weight and volume constraints in mobile applications, opportunities for process intensification through the quantitative evaluation of novel reactive heat exchanger hardware within the system will be examined. Modeling and analysis efforts shall be applied to the ongoing APU development efforts of Protonex Technology Corporation with the specific aims of improving both system performance prediction under sensor uncertainty and heat-loss estimation methods.

A preliminary energy and exergy analysis on a 600-W Protonex SOFC system was completed in order to understand the energy flows and to pinpoint thermodynamic inefficiencies in the design. The utility of this type of analysis is both in locating and quantifying the magnitude of the irreversible losses and identifying opportunities to improve the system efficiency. Figure 3 depicts the finalized energy and exergy flow diagram for the baseline Protonex APU system. The system components are not adiabatic devices, and this is reflected in the flow diagram which depicts both component thermal energy and exergy flows that are rejected from the component to the hot-zone surroundings.

Overall, 3.0 kW of energy (2.98 kW exergy) associated with the liquid hydrocarbon fuel flows into the system. Exergetic analysis in reforming of the fuel indicates that the process occurs at an exergetic efficiency of approximately 80%. Some 490 W of exergy are destroyed within the catalytic partial oxidation (CPOx) unit itself and an additional 120 W are lost via heat transfer to the hot zone surroundings. By comparison, the SOFC tube bundle operates at an exergetic efficiency of 84.3%, slightly higher than the CPOx unit, and most of the irreversibility occurs within the unit.

The tail-gas burner and the recuperative heat exchanger operate with exergetic efficiencies of 71.8% and 44.6%, respectively. Heat loss from the hot-zone surface to the surroundings is over 700 W, and the hot system exhaust carries away an additional 1.66 kW of thermal energy (0.65 kW exergy). Overall, the system exergetic efficiency is 20.1%, and opportunities for improvement appear to reside with improving the thermal management within the hot zone of the system and reducing the hot exhaust gas temperature. Improvements via process intensification might include integration of a tail-gas burner and recuperator to reduce these inefficiencies. Such system modifications will be investigated as the project moves forward.

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,
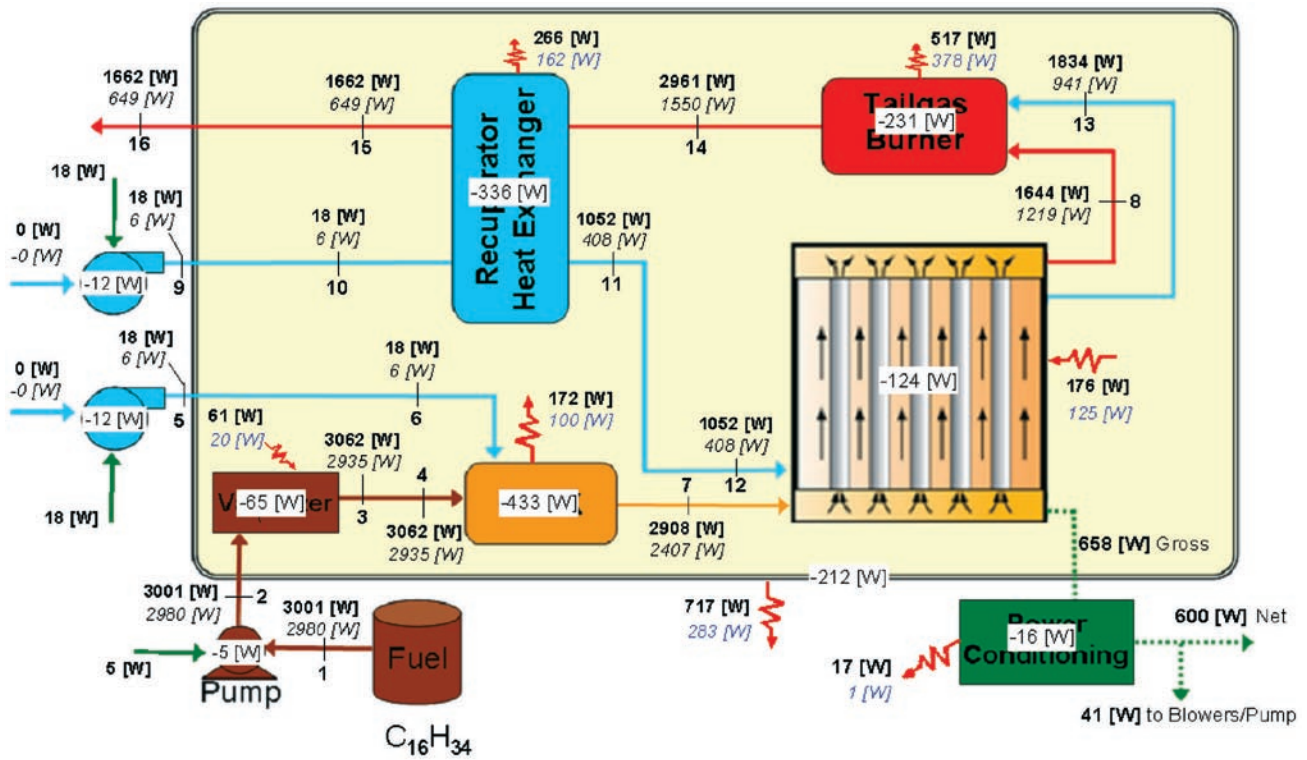
FIGURE 3. Energy/Exergy Flow Diagram of 600-W Protonex APU System

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 model 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.

Eventually, this project will encompass the entire fuel cell system, but current work has focused on control of the fuel cell stack in isolation. The control strategy for the fuel cell stack is illustrated in Figure 4. 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
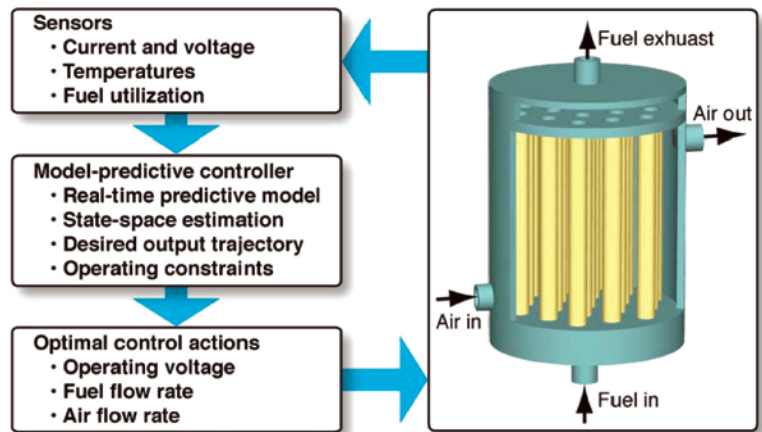

FIGURE 4. Control Strategy for the Fuel Cell Stack

of either desired signal trajectories (e.g. current set-point) or desired signal bounds (e.g. minimum voltage or fuel utilization). The current implementation of the model-predictive control is a strategy based on online optimization, but we will be working in the future to develop a pre-computed implementation based on recent work in multi-parametric optimization.

An example of feedback control is shown in Figure 5. In this figure, the controller adjusts the cell voltage and fuel flow rate to meet a desired current output trajectory while at the same time meeting
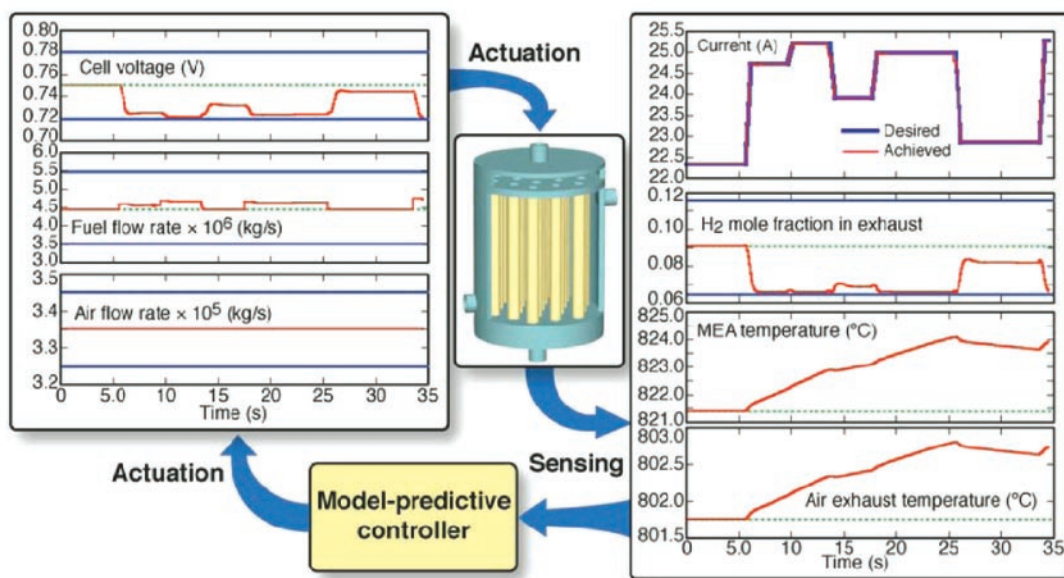
FIGURE 5. Example of current control while meeting constraints inputs and outputs. Blue lines represent constraints.

constraints on the inputs and outputs, which are shown as horizontal blue lines. In particular, note that the current trajectory is achieved while meeting the lower constraint on hydrogen mole fraction in the exhaust.

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, many speakers have participated in the program. Dr. Ellen B. Stechel of Sandia National Laboratories provided CSM students and faculty with a talk entitled "Sunshine to Petrol," reviewing Sandia's program on conversion of solar power to liquid-hydrocarbon fuels. Additionally, scientists Annamalai Karthikeyan (Harvard University) and Jianhua Tong (California Institute of Technology) visited the Colorado School of Mines and provided overviews of their research in well-attended seminars. One visit led to an offer of employment for Dr. Tong, who is now a research professor in the Metallurgical and Materials Engineering Department at CSM, and works actively on materials development for this DOE project.

Future Directions

Task 1: Ceramic Materials and Architecture

- Measure electrical conductivity and catalytic activity of novel anode compositions over a range of anode conditions.

- Measure the ionic conductivity of protonic conductors.
- Evaluate the long-term stability of protonic conductors using thermal gravimetric analysis, differential thermal analysis, and dilatometry.

Task 2: Fuel Processing

- Extend gas-phase mechanism to characterize selective partial oxidation of tars.
- Extend partial-oxidation experiments to toluene.
- Develop process windows for deposit-free SOFC operation.
- Measure catalyst activity and stability for logistics-fuel reforming.
- Conduct extended-aging tests with catalysts and support materials.

Task 3: System Optimization and Control

- Create optimal system configurations for liquid-fueled SOFCs.
- Including anode recycle with ATR.
- Evaluate performance/cost advantage of process-intensification efforts.
- Extend reduced-order model to complete SOFC system, including CPOx.
- Experimentally validate models: CPOx-control experimentation under development at CSM; collaborate with industrial partner and subcontractor (Protonex) for experimental data.

- Implement explicit form for Model Predictive Control.
- Drastically reduce requirements for computational control.

FY 2009 Publications/Presentations

1. J. Tong, D. Clark, M. Hoban, R. O'Hayre, "Cost-effective solid reaction method for proton conducting yttrium-doped barium zirconate ceramics," 17th International Conference on Solid State Ionics, Toronto, Canada, June 28, 2009.

2. M. Sanders, S. Elangovan, G. Coors, R. O'Hayre, "Results of steam flux measurements in BZY20," 17th International Conference on Solid State Ionics, Toronto, Canada, June 28, 2009.

3. M. Sanders, S. Elangovan, G. Coors, R. O'Hayre, "Using dilatometry to measure the hydration thermodynamics of perovskite-based steam-permeable ceramics", 8th International Pacific Rim Conference on Ceramics and Glass, Vancouver, B.C., June 1–5, 2009.

4. M. Sanders, G. Coors, R. O'Hayre, "Modeling of material parameters for increased steam permeation in gadolinium-doped barium cerate ceramic membranes," 6th Annual ASME Fuel Cell Science and Technology Conference, Denver, Colorado, June 17th, 2008.

5. I. Kang, A.S. Al Shoaibi, H.-H. Carstensen, and A.M. Dean, "Ethylene pyrolysis and the subsequent molecular weight growth reactions," American Chemical Society National Meeting, March 22–26, 2009.

6. L. Huynh, A.S. Al Shoaibi, H.-H. Carstensen, and A.M. Dean, "Low-temperature partial oxidation of ethane and propane," American Chemical Society National Meeting, March 22–26, 2009.

7. D. Storjohann, J. Daggett, N.P. Sullivan, R.J. Kee, H. Zhu, S. Menzer, D. Beeaff, "Fabrication and evaluation of SOFC anodes employing reaction-sintered yttria-stabilized zirconia," Journal of Power Sources, accepted for publication, 2009.

8. J. Daggett, N. Sullivan, R. J. Kee, H. Zhu, A. Dean, "Ethanol transport and chemistry in solid-oxide fuel cells," 6th Annual Fuel Cell Science, Engineering & Technology Conference, Denver, CO, June 16–18, 2008.

9. D. Storjohann, S. Menzer, D. Beaff, J. Daggett, R. Kee, N. Sullivan, "Comparative study of reaction-sintered anode-supported tubular solid oxide fuel cells," 6th Annual Fuel Cell Science, Engineering & Technology Conference, Denver, CO, June 16–18, 2008.