V.L.6 Biomass Fuel Cell Systems*

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Fiscal Year (FY) 2011 Objectives

- Develop solid oxide fuel cell (SOFC) materials and architectures for robust operation on renewable/biomass fuel streams.
- Identify optimal fuel-processing strategies for renewable fuels, specifically biogas derived from anaerobic digesters commonly utilized for sludge remediation at wastewater treatment facilities.
- Employ system modeling to optimize SOFC system configurations.
- Extend model-predictive control strategies to integrate system hardware for improved load following and dynamic response.

Technical Barriers

- Durability: Broaden SOFC operating windows under hydrocarbon and bio-derived fuel streams.
- Balance-of-plant costs: Integrate fuel reforming and heat recuperation hardware into a single low-cost ceramic micro-channel reactive heat exchanger.
- Performance: Increase efficiency and decrease costs through system optimization and balance-of-plant component development and integration.
- 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 systems. Fuel streams for these systems include anaerobic digester-derived biogas. 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).

FY 2011 Accomplishments

- Demonstrated over 16 days of continuous SOFC power generation on unreformed simulated biogas (65% CH_4 + 35% CO_2).
- Established biogas fuel processing strategies and operating windows for upstream conversion of biogas into syngas.
- Quantified performance of SOFCs under biogas reformate fuel streams, and established performance comparisons under hydrogen fuel streams.
- Developed hybrid computational fluid dynamics (CFD)-chemical kinetics model to examine design tradeoffs in ceramic microchannel fuel reformer/heat exchanger.
- Utilized computation models to examine thermal, chemical, and electrochemical fields within tubular SOFC stack.
- Developed rapid, lower-order dynamic models to map response of slower, high-order physical models for use in dynamic system control of fuel-reformer hardware.

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Introduction

The objective of this project is to advance the current state of technology of SOFC systems to improve performance when operating on biomass-derived fuel streams. The target fuel stream is "biogas" (~65% CH_4/35% CO_2) generated by the anaerobic digesters that are widely used for treatment of sludge in municipal wastewater treatment facilities. In this project, we are developing new SOFC materials and architectures to improve the robustness of systems operating under biogas. Additionally, modeling and experimentation is being conducted to examine performance tradeoffs across numerous fuel-processing strategies for this fuel. Fuel-reforming processes are being integrated with exhaust gas recuperation processes through development of a single low-cost ceramic microchannel reactive heat exchanger, created in collaboration with industrial partner CoorsTek, Inc. System-level models are being used to predict SOFC system efficiencies under biogas fuels utilizing the fuel-reforming microchannel-reactor integration strategies under development. Model-predictive control strategies are being developed and applied to improving the dynamic response of the fuel-reformer hardware.

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, this team examines both the fundamental underpinnings and the key technical problems facing SOFC operation under biomass-derived fuel streams. We develop new SOFC materials and architectures to address the technical challenges and operating windows associated with SOFC operation on biomass-derived fuels. Through development of low-cost ceramic microchannel reactive heat exchangers with industrial partner CoorsTek, Inc., we create system-integration strategies to combine balance-of-plant processes into single hardware units, increasing system simplicity and decreasing cost. A range of computational models are developed to examine the physical processes underway during SOFC and fuel-reformer operation. Model-predictive control strategies are created and applied to fuel-reforming hardware in an effort to improve the dynamic response of SOFC systems.

Results

SOFC Materials and Architectures: Barrier Layers for Improved Robustness

Fuel cell reliability and performance can be greatly improved through development of new materials and architectures that promote robust SOFC operation on renewable and hydrocarbon fuels. In this task, we are currently developing new SOFC anode architectures utilizing anode "barrier layers" that mitigate carbon-deposit formation, seeking to optimize the structure of the cell for maximum efficiency and reliability. A conceptual drawing of a tubular SOFC with an inert barrier layer is shown in Figure 1a. The barrier layer reduces the transport of electrochemically produced steam out of the anode support. This increases the concentration of steam within the support, promoting methane internal-reforming reactions over solid-carbon-forming reactions, preventing carbon deposition and cell deactivation.

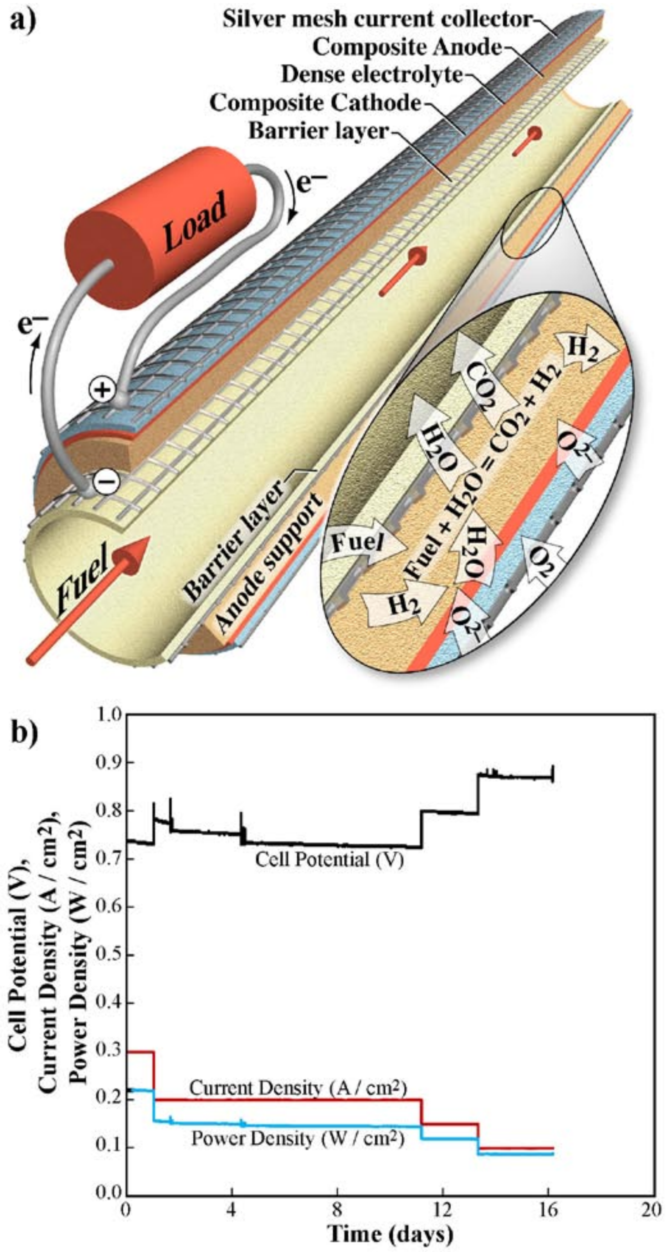

FIGURE 1. a) Illustration of a tubular SOFC employing an anode barrier layer with inset depicting internal-reforming processes; b) extended operation of barrier-layer equipped tubular SOFC under direct biogas fuel. Step changes represent changes in load applied to the cell.

During the previous year, we successfully integrated a barrier layer into a tubular CoorsTek SOFC, and continuously operated this assembly under a simulated humidified biogas fuel stream (63% CH_4 + 34% CO_2 + 3% H_2O). Biogas is a byproduct of anaerobic-digestion processes widely utilized in landfills and wastewater-treatment facilities for sludge remediation. Some cleaning of biogas is generally required to remove siloxanes and sulfur-containing species upstream of biogas-fueled power generators. In this project, biogas is synthesized from near-pure compressed-gas cylinders to simulate the cleaned biogas fuel composition. The barrier-layer equipped SOFC continuously converted the chemical energy in the simulated biogas into electricity for over 16 days with negligible performance degradation as shown in Figure 1b. No biogas fuel reforming upstream of the SOFC was conducted. The barrier layer was fabricated in the Colorado Fuel Cell Center by slip-casting of lanthanum-doped strontium titanate ($Sr_{0.8}La_{0.2}TiO_3$). The CoorsTek SOFC utilizes fairly conventional materials, including a yttria-stabilized zirconia (YSZ) electrolyte, nickel-YSZ anode, and strontium-doped lanthanum manganate cathode. Testing was conducted at 850°C under very low fuel utilization in order to present a "worst-case" scenario for carbon-deposit formation. Steady operation was observed at each current density. This result presents the first long-term operation of a barrier-layer-equipped tubular SOFC under simulated biogas fuel, and the first multi-day performance of an SOFC on unreformed simulated biogas fuel.

Biomass-Derived Fuel Processing

In this task, we examine fuel-reforming strategies to convert biogas into syngas for subsequent electrochemical conversion in SOFCs. Upstream reforming of biogas prior to introduction into the SOFC stack presents a nearer-term solution to SOFC operation on biogas in comparison to barrier-layer architectures. The goal is to develop flexible, efficient fuel-processing strategies for the robust use of biogas fuels in SOFCs. The effort includes computational model development of biogas fuel reforming, experimental validation, and electrochemical performance measurements of biogas-reformate-fueled SOFCs. As part of this task, we examine the relationship between SOFC performance and biogas fuel-reforming approach, contrasting results of steam reforming with catalytic partial oxidation (CPOX) using air, and CPOX using oxygen. While CPOX with oxygen may at first seem impractical, many wastewater treatment facilities utilize cryogenically stored pure oxygen to decrease energy usage during waste-aeration processes. Such an oxygen source could potentially be utilized by a co-located SOFC electric generator.

During the previous year, a series of numerical and physical experiments were conducted to quantify biogas-reformate composition across a number of reforming approaches and operating conditions. Both modeling and experimentation focused on use of a rhodium-based catalyst on a porous alumina foam support. The operating conditions probed included reforming temperature, steam-to-carbon ratio, oxygen-to-carbon ratio, and space velocity. Computational modeling was first conducted to identify optimal biogas-reforming conditions over a wide operational space. These numerical results were then analyzed, and then experimentally validated for select conditions with high methane-conversion levels.

The high CO_2 content of biogas can result in surprising reformate compositions. Through dry-reforming reactions ($CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$), the biogas-borne CO_2 is reduced to CO. Higher reforming temperatures are required to drive this endothermic reaction. Within the SOFC anode, carbon monoxide is further internally reformed through the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). Thus the CO generated from CO_2 during dry reforming directly leads to additional H_2 formation within the cell. This additional H_2 is in-turn electrochemically oxidized, resulting in additional electricity generation. Because of internal reforming, it is important to consider the CO content of the reformate as a fuel in the SOFC. Generating reforming conditions that maximize conversion of biogas-borne CO_2 to CO is critical to realizing peak efficiency. Increased dry reforming decreases the parasitic thermal requirements for addition of steam or air oxidizers to reform the biogas into syngas.

Our experimental and modeling efforts found that while steam reforming generates the highest H_2 mole fraction in the reformate (~54%), the combined H_2 + CO mole fraction reaches only 78%. In contrast, biogas reforming via CPOX with O_2 results in a combined H_2 + CO mole fraction of nearly 86%, and 10% higher utilization of the biogas chemical potential. This potential benefit comes with the added simplicity of the CPOX system design, as catalytic partial oxidation is a far more elegant reforming approach in comparison to that of steam reforming. Such results may prove valuable to engineers and scientists that design biogas-fueled SOFC systems.

After establishing the desired reforming conditions and reformate compositions for each of the three different approaches, SOFC electrochemical performance under the different reformate compositions was measured. Using the experimental results from the simulated-biogas reforming experiments, biogas reformate was synthesized and supplied to a tubular SOFC operating at 800°C in the Colorado Fuel Cell Center. An important aspect to the performance testing was ensuring that each test resulted in the same utilization of the supplied fuel (70%), and that each cell was operated at the same electric potential (0.65 V). Performance on reformate was compared to that under hydrogen fuel, with results shown in Figure 2.

Not surprisingly, the highest performance was observed under hydrogen-fuel conditions. Power density under reformate generated via CPOX using O_2 is 0.145 W/cm^2, only 3% lower than that of the pure-hydrogen condition (~0.15 W / cm^2). In contrast, cell performance under reformate generated by steam reforming and CPOX with air is approximately ~0.124 W/cm^2, nearly 20% lower than the hydrogen condition. These electrochemical-performance differences can have significant impacts on the size, footprint, and cost of biogas-fueled SOFC systems.

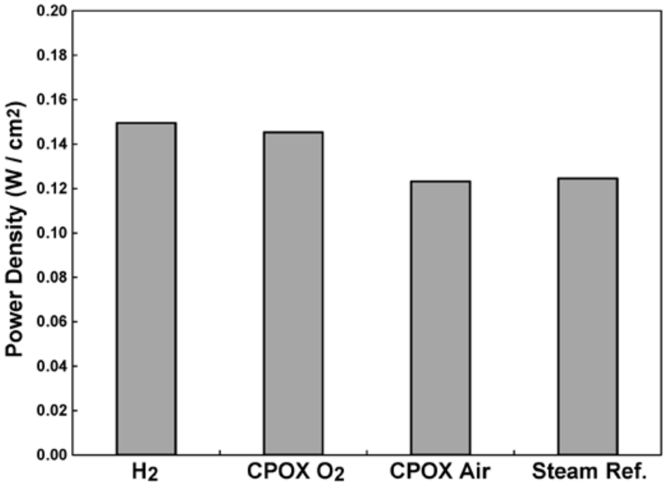

FIGURE 2. SOFC electrochemical performance at 0.65 V and 70% utilization under hydrogen and biogas-reformate fuel streams.

Ceramic Microchannel Reactors

Building on the biogas-reforming results, we are now configuring our ceramic microchannel reactor technology for biogas reforming. An illustration of this reactor is shown in Figure 3a and 3b. The reactor is fabricated by industrial partner CoorsTek, Inc. using low-cost ceramic materials (Al_2O_3) that are joined in a single high-temperature sintering process. This greatly reduces the materials and fabrication costs of the heat-exchanger device, with significant potential for decreasing SOFC balance-of-plant expenses. These microchannel reactors offer great advantages over conventional shell-and-tube reactors through improved heat transfer and thermal regulation of reforming processes. Exothermic reforming processes can cause hot spots in conventional reactors that reduce the efficiency and effectiveness of the reforming process. Similarly, supplying heat for endothermic-reforming processes can pose significant parasitic losses in SOFC systems. In microchannel reactors, the hot and cold streams are tightly integrated, so that thermal regulation, reforming activity, and reformate selectivity are maximized.

We are developing deposition processes of catalyst materials within the microchannel reactor. Sealing and manifolding of the microchannel reactors is also an area of development, with manifolding design and testing ongoing. An important aspect to our microchannel-reactor effort is the development and application of high-fidelity computational models to guide reactor design and operation. ANSYS-FLUENT CFD models are being modified to incorporate elementary chemical kinetic mechanisms for high-fidelity modeling of fuel reforming within the microchannel reactor. Such incorporation of elementary chemistry into CFD models is quite challenging; CSM is working directly with ANSYS-FLUENT developers on this effort.

Characteristic methane-steam-reforming results from the hybrid CFD-kinetics model are shown in Figure 3c and 3d.

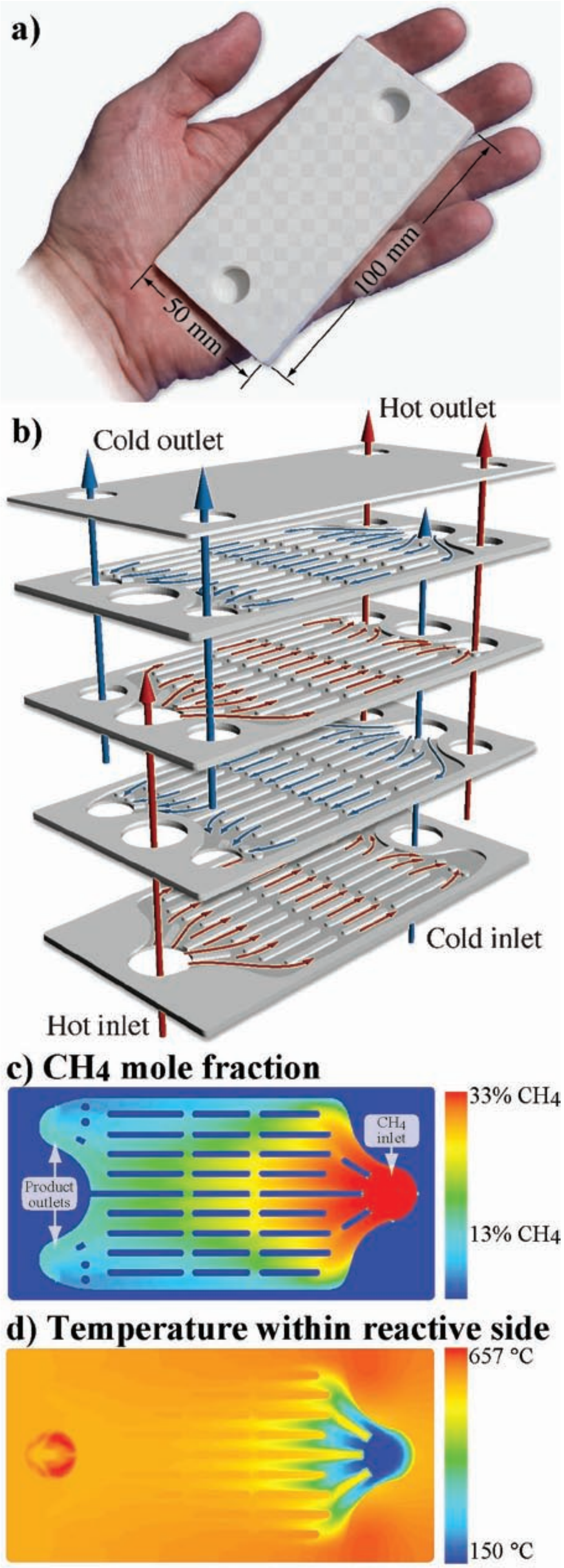

FIGURE 3. a) Image and b) exploded illustration of ceramic microchannel reactor; c) results from hybrid CFD-chemical kinetics model predicting methane mole fraction and d) temperature fields over the catalytically active layer of the microchannel reactor.

The catalytically active layers are fed with a methane–steam mixture at a ratio of 1 CH_4 : 2 H_2O flowing from the inlets at the right to the outlets at the left at a flow rate of 4 SLPM and temperature of 150°C. The model catalyst is rhodium, which has exceptional methane-steam-reforming activity and resistance to carbon-deposit formation. The heterogeneous reforming chemistry takes place on the walls of the catalytically active layers within the microchannel reactor. The non-reactive backing channels are fed with air flowing at 60 SLPM and an inlet temperature of 800°C. The hybrid model solves the complete three-dimensional flow field, and the conjugate heat transfer between the two inlet gas streams and the solid ceramic reactor body. These operating conditions result in 51% conversion of methane. The methane-steam inlet gas is heated from 150°C to reforming temperature within the first bank of microchannels, with reactions taking place primarily in the first and second banks of channels. Flow uniformity is reasonable, though some improvements seem possible. Peak temperatures within the reactive side reach approximately 600°C, a bit lower than desired for optimal steam reforming. This temperature could be increased through higher flow rates of the air supplied to the non-reactive backing channels, or higher inlet temperatures of either the air or the reactive methane-steam mixture.

This result demonstrates the application of a powerful research and development tool in which three-dimensional computational fluid dynamics and heat transfer are coupled to high-fidelity elementary chemical kinetics. Over the remainder of the project, we will utilize this tool to define operating windows for biogas reforming that result in high methane conversion and high selectivity to hydrogen and carbon monoxide.

System-Level Modeling

The complex component geometries of the SOFC hot zone and the chemical and electrochemical reactions within are coupled with heat transfer and three-dimensional fluid flow to simulate hot zone thermal energy management of representative SOFC geometries. A central feature of this task is to accurately capture the three-dimensional transport phenomena within the hot zone and derive representative reduced-order models. In this task, these reduced-order models are directed towards use in system process design and parameter specification. The domain of the CFD model includes the entire cathode and stack endplates along with the majority of the recuperator, fuel/air preheat flow, and system insulation. The hot zone is modeled after the 600-W tubular SOFC stack developed by industrial partner Protonex Technology Corporation.

A characteristic result is shown in Figure 4. It is increasingly clear that the outer tubes located near the periphery act as radiation shields, keeping inner-radii tube groups warmer. Local species concentration fields identify of critical O_2-depletion zones. These results and modeling tools can be utilized by stack developers to improve stack design, performance, and efficiency.

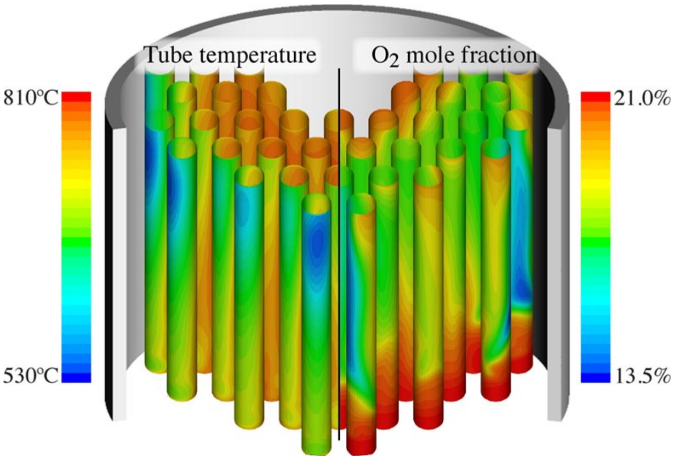

FIGURE 4. Model Predictions of Thermal and Oxygen-Concentration Fields across 600-W Tubular Stack

Model-Predictive Control

Dynamic control efforts have focused on the effects of balance-of-plant components on performance and control. The balance-of-plant components of the stack include the fuel reformer, air and fuel blowers, heat exchanger, and tail-gas-combustion burner. A complete SOFC system is highly connected via the temperatures and mass compositions that flow through each of these components. As such, model-based dynamic control must incorporate the dynamics of all balance-of-plant components within safe operating limits. For example, the reformer outlet gas composition must be controlled in order to prevent carbon deposition within the stack. At the same time, carbon deposition is dependent upon the stack operating temperature and power level, which drives the operation of the reformer. Additionally, limits on reformer catalyst temperature need to be maintained while ensuring the mass flow and fuel composition provided to the stack are sufficient for the desired current output. The stack air temperature must also be high enough to prevent stack excessive stack cooling. It is for these reasons, that a system-wide control-oriented dynamic model is needed.

Current work has provided a system-wide model consisting of the fuel reformer, tubular SOFC stack, and heat exchanger. Improvements over existing system-wide models include the use of component models that allow for composition estimation throughout the system. Although increasing the required model complexity, composition is highly coupled with both performance of the system and robustness to real-world inputs. A characteristic result of this model is shown in Figure 5, which shows that even small changes on the inlet fuel composition to the fuel reformer has impacts on the stack performance.

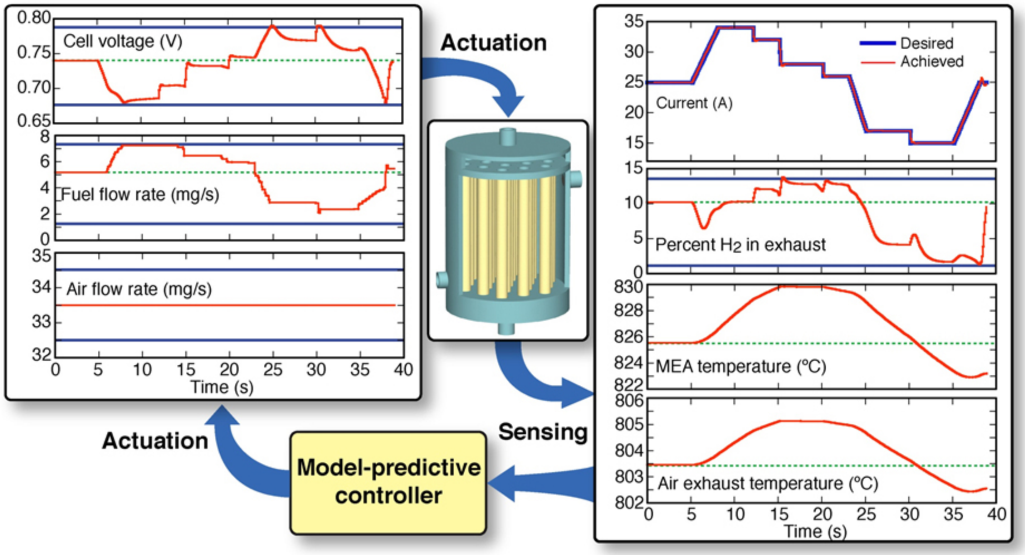

FIGURE 5. Dynamic Response Predictions from Model-Predictive Control Algorithms

Future Directions

Biomass-Derived Fuel Processing

- Explore operating windows for reforming of biogas within ceramic microchannel reactor.
- Extend hybrid CFD/chemical-kinetics modeling to examine effects of fuel-processing strategies on heat-exchanger effectiveness and fuel-reformate composition and quality.

System Modeling

- Quantify efficiency of SOFC operation on biogas under the different reforming conditions that may be utilized.
- Examine benefits of integrated unit processes enabled by utilization of the ceramic microchannel reactor.

System Control

- Implement explicit form for Model Predictive Control for use in biogas-reforming system.
- Extend model-predictive control strategy to reactive heat exchanger.

FY 2011 Publications/Presentations

1. R.J. Kee, B.B. Almand, J.M. Blasi, B.L. Rosen, M. Hartmann, N.P. Sullivan, H. Zhu, A.R. Manerbino, S. Menzer, W.G. Coors, J.L. Martin, "The design, fabrication, and evaluation of a ceramic counter-flow microchannel heat exchanger," *Applied Thermal Engineering* (in press, 2011).

2. A.E. Richards, N.P. Sullivan, R.J. Kee, and H. Zhu, "Internal reforming chemistry in novel SOFC anodes and architectures," *European Fuel Cell Forum*, Lucerne, Switzerland, June 28 – July 2, 2010.

3. S. Babiniec, N.P. Sullivan, A.E. Richards, and N. Faino, "Multi-phase tubular perovskite-based anodes for use in hydrocarbon-fueled solid-oxide fuel cells," *European Fuel Cell Forum*, Lucerne, Switzerland, June 28 – July 2, 2010.

4. D. Storjohann, and N.P. Sullivan, "Barrier-layer structures to mitigate carbon formation in tubular bio-fueled solid oxide fuel cells," *European Fuel Cell Forum*, Lucerne, Switzerland, June 28 – July 2, 2010.

5. A. Colclasure, B. Sanandaji, T. Vincent, R.J. Kee, "Modeling and control of tubular solid-oxide fuel cell systems. I: Physical models and linear model reduction" *Journal of Power Sources* 196:196-207 (2011).

6. B. Sanandaji, A. Colclasure, T. Vincent, R.J. Kee, "Modeling and control of tubular solid-oxide fuel cell systems: II. Nonlinear model reduction and model predictive control" *Journal of Power Sources*, 196:208-217 (2011).

7. K.J. Kattke and R.J. Braun, "Implementing thermal management modeling into SOFC system-level design," *ASME Journal of Fuel Cell Science, Engineering and Technology* (in press 2010).

8. K.J. Kattke, R.J. Braun, A. Coclasure, and G. Goldin, "High-fidelity stack and system modeling for tubular SOFC system design and thermal management," submitted to *Journal of Power Sources* (2010).

9. K.J. Kattke and R.J. Braun, "Implementing thermal management modeling into SOFC system-level design," Proceedings of the ASME 2010 Eighth International Fuel Cell Science, Engineering and Technology Conference, New York, NY, June 2010.

10. A.A. Shoaibi, A.M. Dean, "Kinetic analysis of C4 alkane and alkene pyrolysis: Implications for SOFC operation" *Journal of Fuel Cell Science and Technology* 7 (2010).