V.0.9 Biomass Fuel Cell Systems*

Neal Sullivan (Primary Contact), Robert Kee, Anthony Dean, Robert Braun, Ryan O'Hayre, Nigel Sammes
Colorado School of Mines
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

Technical Advisor: Walt Podolski
Phone: (630) 252-7558
E-mail: podolski@anl.gov

Contract Number: DE-EE0000260

Project Start Date: October 1, 2009
Project End Date: September 30, 2012

*Congressionally directed project

Objectives

- Develop solid-oxide fuel cell (SOFC) materials for robust operation on renewable/biomass fuel streams.
- Identify optimal fuel-processing strategies for renewable fuels (i.e. biogas and butanol).
- Employ system modeling to optimize SOFC system configurations.
- Extend model-predictive control to integrate system hardware.

Technical Barriers

- Durability: Broaden SOFC operating window under hydrocarbon and bio-derived fuel streams.
- Performance: Increase efficiency through system optimization and balance-of-plant component integration.
- Transient operation: Develop model-predictive control algorithms for use in dynamic control.
- Balance-of-plant costs: Integrate fuel reforming and heat recuperation hardware into a single low-cost ceramic micro-channel reactive heat exchanger.

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, and biomass-derived liquid fuels such as butanol. 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

- Established biogas fuel processing strategies and experimentation.
- Quantified performance of SOFCs under biogas reformate fuel streams, and established performance comparisons under hydrogen fuel streams.
- Demonstrated operation of low-cost ceramic micro-channel fuel reformer/heat exchanger for reformation of butanol fuel stream.
- Developed hybrid computational fluid dynamics (CFD)-chemical kinetics model to examine design tradeoffs in ceramic microchannel fuel reformer/heat exchanger.
- Utilized hybrid models to quantify effects of materials changes on ceramic heat-exchanger effectiveness.
- 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.
- Demonstrated fidelity of lower-order models in mapping reformer response across numerous temperature changes.

✧ ✧ ✧ ✧ ✧

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. These fuel streams include biogas generated by the anaerobic digesters that are widely used in municipal waste-water treatment facilities, and biomass-derived butanol fuel, a gasoline-compatible liquid fuel that boasts an energy density that is 75% that of diesel fuel. In this project, we are developing new SOFC and catalyst materials to improve the robustness of systems operating under these biomass-derived fuel streams. Additionally, modeling and experimentation is being conducted to examine performance tradeoffs across numerous fuel-processing strategies for these fuels. Fuel-reforming processes are being integrated with exhaust-gas recuperation processes through development of a single low-cost ceramic micro-channel reactive heat exchanger, created in collaboration with industrial partner CoorsTek, Inc. Finally, model-predictive control strategies are being developed and applied to improve the dynamic response of the fuel-reformer hardware.

Approach

The Colorado School of Mines 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 examines both the fundamental underpinnings and the key technical problems facing SOFC operation under biomass-derived fuel streams. We develop new SOFC materials for use in biomass-derived fuel streams, addressing the technical challenges and operating windows associated with fuel processing of both gaseous- and liquid-phase fuels. Through development of low-cost ceramic microchannel reactive heat exchangers with industrial partner CoorsTek, Inc., we are creating system-integration strategies to combine balance-of-plant processes into single hardware units, increasing system simplicity and decreasing cost. Model-predictive control strategies are being developed and applied to fuel-reforming hardware in an effort to improve the dynamic response of SOFC systems.

Results

Biomass-Derived Fuel Processing

In this task, we examine fuel-reforming strategies to reform two model fuels into syngas for subsequent electrochemical conversion in SOFCs. These model fuel streams include biogas generated by the anaerobic digesters and biomass-derived butanol fuel. The goal is to develop flexible, efficient fuel-processing strategies for the robust use of biomass-derived fuels in SOFCs. The effort includes computational model development on biomass-derived fuel reforming, and experimental validation and electrochemical-performance measurements of biogas-reformate-fueled SOFCs.

Ideally, the anaerobic-digester-derived biogas streams could be fed directly to the SOFC anode with no upstream reforming or fuel processing beyond trace-contaminant cleanup. Unfortunately, the composition of biogas (approximately 65% CH_4/35% CO_2) can prove problematic, leading to carbon-deposit within the stack, and rapid performance degradation. To address these concerns, we are developing upstream fuel-reforming processes to efficiently convert the biogas fuel into high-H_2-quality reformate to be subsequently fed into the fuel channels of a SOFC. To examine the tradeoffs in reforming approaches, a fuel-reforming facility has been constructed in the CFCC. The experiment includes extensive reactive-gas manifolding and steam addition to enable creation of a broad range of biogas-reforming streams. These mixtures are then fed to a rhodium-based catalyst coated onto high-performance strontium-hexaaluminate catalyst supports on alumina-foam monoliths. Reformate composition is measured using an Agilent micro-gas chromatograph. The experiment can be integrated with an SOFC electrochemical test stand currently on hand and operational at the CFCC.

In concert with this experiment a chemical-kinetics computational model has been developed to predict reformate composition across the range of reforming approaches. Utilizing the Sandia-developed CANTERA chemically reacting flow software package, this reforming model employs porous-media transport and multi-step elementary heterogeneous chemistry for reformation of methane on a rhodium-based catalyst. The computational and experimental tools developed through this project have been used to explore three types of biogas-reforming approaches: catalytic partial oxidation (CPOX) using air as the oxidizer, CPOX using pure O_2 as the oxidizer, and dry (CO_2) reforming of biogas fuels. It is important to note that waste-water treatment facilities often include cryogenic-oxygen systems for more-efficient oxidation of water-bound wastes. This oxygen could also be directed to the fuel cell system for use in biogas fuel processing, motivating our study biogas-CPOX using pure-O_2 oxidizer streams.

The biogas reformate generated by these three different reforming strategies was fed to a SOFC provided to the CFCC by industrial partner CoorsTek, Inc. Performance results are shown in Figure 1 at an operating temperature of 850°C under flooded-fuel conditions. Cell performance is compared across the different biogas fuel-reforming approaches, and compared to hydrogen-fueled operation. Cell performance under CPOX reforming rivals that of pure hydrogen, while performance under dry-reforming conditions is significantly lower. As these tests were conducted under “flooded-fuel” conditions, fuel dilution and concentration polarization losses were minimized,

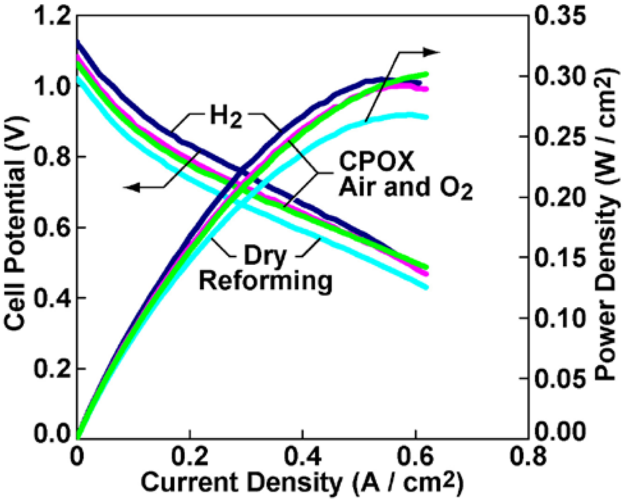
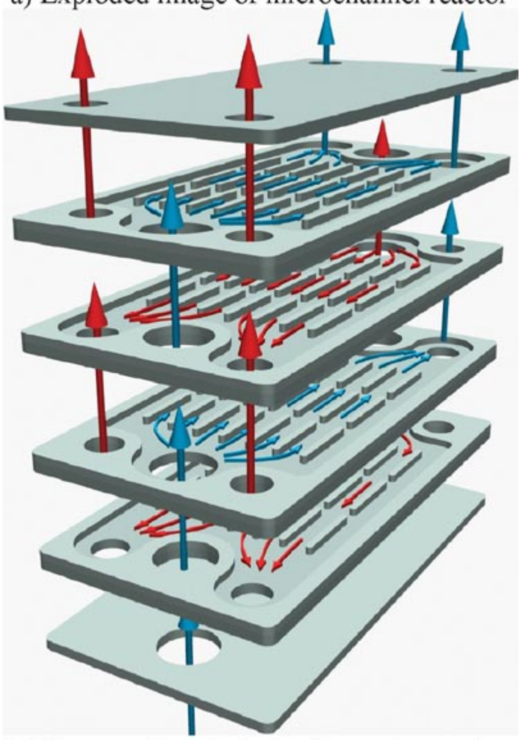


FIGURE 1. Electrochemical performance of SOFC under biogas reformate. Chart includes comparison to performance under hydrogen fuel.

possibly masking the effects of the high nitrogen dilution found in CPOX-air conditions. In future studies, we will expand on this biogas fuel-processing work to include steam reforming, and more-widely explore biogas fuel-processing operating windows.

We are also examining the on-board processing of biomass-derived butanol fuel by mating efficient vaporization and mixing with high-performance ceramics-based micro-channel reactive heat-exchanger/fuel-reformer devices. This effort builds on the biogas fuel reforming experiment discussed above, adding a liquid-fuel, gas-oxidizer mixing unit and micro-channel reactive heat exchanger. We are developing the ceramic micro-channel reactive heat-exchanger technology through close collaboration with industrial partner CoorsTek, Inc, with reactor images shown in Figure 2. These micro-channel 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 micro-channel reactors, the hot and cold streams are tightly integrated, so that thermal regulation is maximized. Additionally, this micro-channel heat exchanger is fabricated using low-cost ceramic materials (Al_2O_3) that are joined in a single high-temperature sintering process, greatly reducing the materials and fabrication costs of the device, which greatly decreases SOFC balance-of-plant expenses.

a) Exploded image of microchannel reactor



b) Cross-sectional photo of ceramic reactor

FIGURE 2. Integrated ceramic micro-channel reactive heat exchanger: a) exploded design image; and b) photograph of heat exchanger cross section, highlight micro-channels.

Ceramic heat exchangers are being fabricated at CoorsTek, and provided to the CFCC for application of a catalyst onto the reactive side of the heat exchanger. Building on the biogas-reforming work described above, a rhodium catalyst with a Sr-hexaaluminate support is utilized. The reactive heat exchanger has been used for catalytic partial oxidation of butanol to syngas; reformate compositions are shown in Figure 3 as a function of total fuel flow rate. As flow rate increases, the quality of the reformate composition is found to increase dramatically. This highlights the close coupling of heat transfer and fuel-reforming effectiveness in this type of reactor. While this demonstration is highly encouraging in validating the concept of the integrated ceramic reactive heat exchanger, further work will be conducted during the course of this program to optimize the fuel-processing conditions.

Advanced hybrid computational modeling tools are being developed that mate high-order Fluent-based computational fluid dynamics with high-fidelity Cantera-based chemically reacting flow. The tools are being applied to the integrated reactive heat exchanger discussed above, and used to examine the effects of design choices on heat-exchanger and fuel-reformer effectiveness. A result for the non-reactive case is shown in Figure 4. The flowfield appears to be well

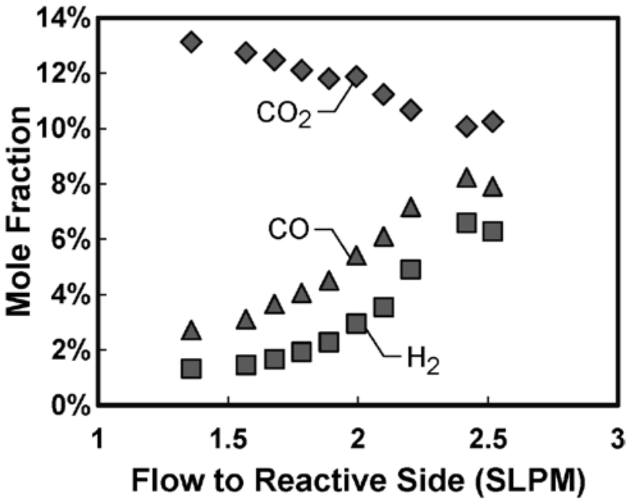


FIGURE 3. Butanol reformate composition as a function of total fuel flow rate supplied to the reactive heat exchanger.

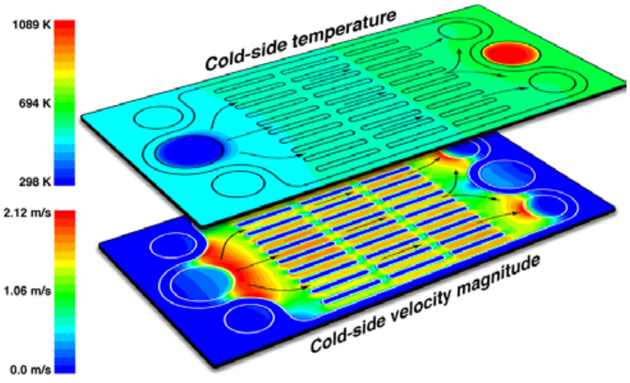


FIGURE 4. Hybrid CFD/chemical kinetics model results of flow and temperature in micro-channel heat exchanger.

balanced, with near-uniform flow conditions across the micro-channels that constitute the heat exchanger. Additionally, the gradual changes found in the temperature field create confidence that thermal stress is well balanced in the device, a significant concern when utilizing ceramic components. Further modeling work will include the chemically reacting flow simulations to provide guidance for optimizing fuel-reforming operating windows in the reactive heat exchanger.

Model-Predictive Control

Model-predictive control provides a means to incorporate fundamental physical and chemical understanding into real-time, multiple-input/multiple-output, process-control strategies. The reduced-order models are derived from large high-fidelity physical models, while system identification is accomplished by driving the physical models with actuation inputs consisting of pseudo-random binary series and observing the responses. The process depends upon having time-accurate physical models. The effort here is two-fold. First is to develop and validate the physical models for SOFC systems operating on reformed biomass-derived fuels. Unlike many fuel cell models based upon steady-state assumptions, the models here must be written to represent time-accurate transient solutions. Moreover, they must be written to accept pseudo-random binary series inputs and return high-accuracy transient response signals used for the system identification.

In this task, we are applying model-predictive control strategies to operation of fuel reformers like the micro-channel devices described previously. Initial efforts are directed toward the simpler ceramic-foam reformer utilized in the biogas experiments. We are now examining the thermal capacitance of the biogas reactor to establish dynamic response to process variations. We have successfully mapped the thermal response of the reactor under non-reactive conditions, and compared this response to dynamic-model predictions; excellent agreement was obtained. In future efforts, we will expand this work to reactive conditions; as model fidelity improves, we will expand this work to examine and control the response of the micro-channel reactive heat exchanger devices.

Future Directions

Biomass-Derived Fuel Processing

- Explore steam-reforming and anode-recycle processing of biogas fuels.
- Extend partial-oxidation experiments on butanol fuel in integrated ceramic micro-channel reactive heat exchanger.
- Develop process windows for deposit-free SOFC operation under butanol reformate.
- Extend hybrid CFD/chemical-kinetics modeling to examine effects of fuel-processing strategies on heat-exchanger effectiveness and fuel-reformate composition and quality.

System Control

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