Biomass Fuel Cell Systems

Primary Investigator:
Assistant Professor Neal P. Sullivan

Co-Investigators:
Professors Robert Braun, Anthony M. Dean,
Robert J. Kee, Ryan O’Hayre, Nigel Sammes, Tyrone Vincent

Colorado School of Mines
Golden, Colorado, USA

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Overview: Improve robustness of hydrocarbon- and biomass-fueled solid-oxide fuel cells and systems

- **Timeline**
  - Project start date: 10/1/2009
  - Project end date: 9/30/2012
  - Percent complete: 20%

- **Budget**
  - Total project funding:
    - DOE Share: $1,665,125
    - CSM Share: $425,018
  - Funding received in FY09:
    - $1,665,125
  - Funding for FY10: $0

- **Industrial Partners**
  - CoorsTek, Inc. (Golden, CO)
    - Tubular SOFC supplier
    - Integrated ceramic heat-exchanger / fuel-reformer

- **Project Lead:**
  - Colorado School of Mines

- **Barriers:**
  - **Durability**
    - Broaden SOFC operating windows under hydrocarbon / biomass fuels
  - **Performance**
    - Increase efficiency through system optimization / BoP integration
    - Optimize fuel-processing strategies
      - Biogas fuels of anaerobic digesters
      - Bio-derived liquid fuels (butanol)
  - **Transient operation**
    - Develop model-predictive control algorithms
  - **Balance-of-Plant costs**
    - Integrate BoP components
    - Decrease BoP fabrication costs
    - Decrease BoP materials costs
Objectives / Relevance: Improve durability and performance of SOFC systems while lowering costs

- **Task 1: SOFC materials for robust operation on bio-fuels**
  - Sulfur- and redox-tolerant materials to broaden SOFC operating windows
  - Develop Nickel-free, perovskite-based anodes w/ novel cell architectures

- **Task 2: Fuel processing of bio-derived fuels**
  - Utilize methane from anaerobic digesters of waste-water treatment plants
  - Develop fuel-processing for biomass-derived liquid fuels (butanol)
  - Decrease cost of fuel-processing balance-of-plant hardware
    - Integrated ceramic micro-channel heat exchangers / fuel reformer

- **Task 3: Modeling and simulation**
  - Develop chemically reacting flow models of fuel-processing hardware
    - Create design tools for micro-channel heat exchanger (HX) / reformer
    - Utilize model-predictive control to integrate system hardware
    - Improve APU dynamic response, reduce supplementary-storage need
  - Conduct thermal modeling of hot-zone system components
  - Employ system modeling: explore benefits of BoP-component integration
Task 1 Approach: Develop materials to improve SOFC durability under hydrocarbon / alcohol fuels

- Develop nickel-free, perovskite-based, next-generation SOFC anodes
  - Perovskites more tolerant to sulfur, redox, and heavy hydrocarbons
  - Challenges in utilizing perovskites as anode materials in SOFCs
    - Materials stability during SOFC processing and cell operation
    - Electronic conductivity significantly lower than existing solutions
    - Catalytic activity may limit internal reforming of biomass fuels
  - Fabricate novel perovskites with unique material-doping strategies
  - Milestone: Synthesize first next-generation anode material (100%)

- Evaluate perovskite anode performance relative to Ni-YSZ baseline
  - Quantify stability, conductivity, and catalytic activity of new materials
  - Catalytic activity evaluated using unique Separated Anode Experiment
    - Decouples anode internal-reforming processes from electrochemistry
  - Materials conductivity currently under evaluation using 4-pt probe
    - Milestone: Demonstrate electronic conductivity > 10 S / cm (100%)
  - Materials stability measured using thermo-gravimetric analysis
    - Milestone: Demonstrate materials stability using TGA (10%)
Task 1 Results: Perovskite materials synthesized; conductivity baselined against Ni-YSZ materials

- Perovskite anodes synthesized
  - $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$ (SLT)
    - High electronic conductivity
  - $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (LSCM)
    - Internal reforming
  - Multi-phase SLT / LSCM ceramic anode

- DC conductivity baselined against Ni-YSZ
  - Materials-conductivity test stand commissioned
    - Vary temperature, gas composition
  - Ni-YSZ conductivity $> 1000$ S / cm
    - Stable across wide range of steam content
  - SLT conductivity $> 17$ S / cm
    - Decreases as steam content increases
  - LSCM conductivity $< 1$ S / cm
    - Insufficient for SOFC-anode applications
Task 2 Approach: Develop bio-fuel processing strategies for optimal compatibility with SOFC

- **Biogas fuels:** anaerobic digesters at waste-water treatment facilities
  - Low-quality methane stream: 65% CH₄ / 35% CO₂
  - MW-scale power generation

- **Explore fuel-reforming options to convert biogas to syngas (H₂ + CO)**
  - Catalytic partial oxidation (CPOX - air and / or O₂)
    - Simplest approach, but lowers system efficiency
  - Steam and / or dry reforming (H₂O and / or CO₂)
    - Endothermic, but improves system efficiency and cell performance

- **Milestone:** Demonstrate biogas-reforming reactor (100%)
- **Milestone:** Identify optimal reforming conditions (25%)
- **Milestone:** Demonstrate SOFC operation on biogas reformate (75%)

- **Biomass-derived liquid fuels:** butanol (C₄H₉OH)
  - Butanol energy density 75% of diesel
  - **Milestone:** Demonstrate integrated liquid-fuel vaporizer / reformer (100%)
Task 2 Results: Kinetic model for biogas reforming on Rh-based catalyst developed and implemented

- Reacting-flow model with multi-step elementary reaction chemistry
- Exercised across numerous reforming approaches
- Excellent conversion of CH$_4$ and CO$_2$ to syngas at 900 °C
  - Highest hydrogen content realized with CPOX using pure O$_2$

Illustration of reforming approach

Model-predicted biogas reformate composition for different reforming approaches (900 °C)
Task 2 Results: Bio-fuel reactor commissioned, integrated with SOFC-performance test stand

- Reforming approach strongly affects cell performance
- Cell performance under CPOX rivals H₂ fuel
Task 2 Results: Carbon-deposit precursors in biogas can be selectively reduced through O$_2$ addition

- Ethylene (C$_2$H$_4$) is the common precursor to deposits
- O$_2$ additional leads to significant reduction in ethylene
- H$_2$ and CH$_4$ concentrations are relatively unchanged
- CO preferentially formed over CO$_2$
Task 2 Approach: Develop low-cost ceramic micro-channel reactive heat exchangers for fuel reforming

- Low-cost alumina materials
- Co-sintered layers: Single-body device
- Low-cost manufacturing

Generation-3 design

Channel height
~ 0.55 mm

Hot outlet
Cold outlet
Hot inlet
Cold inlet

50 mm

100 mm

6 mm
Task 2 Result: Experimental results demonstrate ceramic micro-channel HX at 700°C hot-inlet temp

Inlet and outlet gas temperatures

Total heat transferred

Inlet flows = 130 slm
Cold inlet = 21 °C

Probable break in cold inlet

Probable break in cold inlet

Hot flow
Cold flow
Task 3 Approach: Provide modeling support for Tasks 1 and 2 using CFD and chemically reacting flow tools

- **Task 3a: Design tools for ceramic micro-channel reactive heat exch**
  - **ANSYS-FLUENT** Computational Fluid Dynamics software
    - Flow through complex heat-exchanger channel geometries
  - **CANTERA** chemically reacting flow software
    - Open-source code under development at Sandia National Labs
    - Elementary chemical kinetics for fuel-reforming simulations
  - Two models integrated through FLUENT “User-Defined Functions” feature
    - Enables high-fidelity chemically reacting flow with high-fidelity CFD

- **Task 3b: Model-predictive control for dynamic-load following**
  - Map high-fidelity CANTERA model results to rapid low-order linear models
  - Apply to fuel-reformer hardware for dynamic control of pump and blower

- **Task 3c: System-level modeling tools to advance thermal integration**
  - Map ANSYS-FLUENT results to lower-order hot-zone thermal models
  - Utilize system tools to estimate benefits of thermal-integration strategies
    - Integrated reactive heat exchangers
Task 3a Approach: CFD and chemically reacting flow models integrated to provide HX-design guidance

- ANSYS-FLUENT software utilized for computational fluid dynamics
- CANTERA software developed for chemically reacting flow simulation
- Two models integrated in FLUENT “User-Defined Functions” feature

Numerical mesh used in FLUENT simulations
Task 3a Result: Models indicate that baseline design shows axially uniform flow and temperature fields.

- Efforts leveraged by current NETL program at Colorado School of Mines.

3D simulations in FLUENT:
- Hot and cold fluid flow
- Conjugate heat transfer
Task 3b Approach: Extend high-fidelity chemically reacting flow models to model-predictive control

- Map high-fidelity CANTERA model results to rapid linear models
- Apply to dynamic control of fuel-reformer hardware
- Validate models with experimental apparatus
  - Milestone: Establish experimental fuel-reformer test bed (30% - Task 2)

Mapping of high-fidelity physical models to rapid low-order linear models

\[
\frac{dx}{dt} = Ax + Bu \\
y = Cx + Du
\]

Determine: \( x, A, B, C, D \)
Task 3b Result: Dynamic model of reformer developed; tuned to thermal response of experiment

Model-validation: reformer dynamic response (non-reactive conditions)
Task 3c Approach: Apply hot-zone modeling tools for creation of lower-order thermal networks

- **FLUENT high-fidelity CFD**
  - Hot-zone thermal interactions

- **Map to thermal networks**
  - Rapid modeling tools

Physical representation of SOFC-system concept

Thermal model resistive network
Task 3c Result: Radiative model of tubular SOFC hot zone shows impacts of cell pitch on temperature

Tubular stack geometry

Model predictions of tube temperature variations

- Tube temperature (°C)
- Tube number
- Cell pitch (mm)
- Heat transfer coefficient (W/m²K)
- Wall temperature (°C)

- $p = 14$ mm
- $h = 20$ W/m²K
- $T_w = 600$ °C

- $p = 17.5$ mm

- $p = 21$ mm

- $h = 0$ W/m²K
- $h = 3$ W/m²K
- $h = 10$ W/m²K

- $h = 20$ W/m²K
- $h = 35$ W/m²K

- Tube number
- Tube temperature (°C)

- Diagram showing tube temperature variations for different cell pitches and heat transfer coefficients.
Industrial collaborations: CoorsTek Inc., Golden, CO

- Largest ceramics company in the United States
- Supplier of SOFCs and materials for use across multiple tasks
  - Task 1: Provider of baseline Ni-YSZ materials
    - CSM compares Ni-YSZ to next-generation perovskite anodes
  - Task 2: Supplier of tubular SOFCs
    - CSM adds cathode layer to CoorsTek anode-electrolyte assemblies
    - CSM evaluates cell performance under bio-fuels reformate streams
  - Task 2: Fabricate ceramic micro-channel heat exchangers
    - CSM adds catalyst to reactive side of micro-channel heat exchanger
    - CSM develops test protocol, evaluates performance of reactive HX
    - CSM develops computational modeling to provide design guidance
Future work

- **Task 1: Next-generation SOFC materials and architectures**
  - Use Ni-free perovskite anode materials in fabrication of complete cells
  - Use proton-conducting materials in fabrication of complete cells

- **Task 2: Reforming of biomass-derived fuels**
  - Widen biogas operating windows: steam reforming, anode recycle
  - Establish fuel-processing of biomass-derived liquid fuel (butanol)
  - Validate processing strategies on operational SOFCs

- **Task 3: Modeling and simulation**
  - **Task 3a: Ceramic micro-channel reactive heat exchanger**
    - Add chemically reacting flow to established FLUENT CFD model
    - Exercise model; explore integrated reformer-HX operating windows
  - **Task 3b: Model-predictive control of fuel-reforming BoP hardware**
    - Expand mapping of high-fidelity models to rapid linear models
    - Develop control algorithms; validate on experimental facility
  - **Task 3c: Thermal modeling of SOFC stack and system**
    - Predict impacts of integrated reformer / HX on system efficiency
Summary: CSM program is focused on improving system robustness, decreasing BoP costs

- **Relevance**
  - Improve durability: advanced materials, improved control strategies
  - Decrease costs: Develop low-cost integrated reactive heat exchangers

- **Approach**
  - Create next-generation SOFC materials
  - Optimize fuel-reforming strategies for biomass-derived fuel sources

- **Results**
  - Demonstrated processing of next-generation SOFC-anode materials
  - Demonstrated modeling and experimentation for trouble-free SOFC operation on biogas reformate
  - Demonstrated operation of low-cost ceramic micro-channel heat exch.

- **Future work**
  - Establish SOFC operation using nickel-free perovskite anode materials
  - Define trouble-free cell operation on biomass-derived liquid fuel (butanol)
  - Extend heat-exchanger models to include chemically reacting flow
  - Explore effect of integrated reactive heat exchanger on system efficiency