Renewable and Logistics Fuels for Fuel Cells at the Colorado School of Mines

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Colorado School of Mines
Golden, Colorado, USA

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Project ID: FC069

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Overview: Improve robustness of hydrocarbon-fueled, solid-oxide fuel cells

- **Timeline**
  - Project start date: 7/1/2008
  - Project end date: 6/30/2010
  - Percent complete: 97%
- **Budget**
  - Total project funding:
    - DOE Share: $1,476,000
    - CSM Share: $362,509
  - Funding received in FY08:
    - $1,476,000
  - Funding for FY09: $0

- **Barriers**
  - Durability: Broaden SOFC operating window under hydrocarbon fuel streams
  - Performance: Increase efficiency through system optimization
  - Transient operation: Develop model-predictive control algorithms
- **Industrial Partners**
  - Protonex Technology Corporation
    - Provide technical data on solid-oxide fuel cell (SOFC) auxiliary power unit
  - Reactions Systems, LLC
    - Develop hydrocarbon-fuel reforming catalyst and catalyst-support materials
  - CoorsTek, Inc.
    - Provide tubular SOFCs for testing
  - Project Lead: Colorado School of Mines

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Objectives / Relevance: Improve performance, durability, and transient response of SOFC systems

- **Task 1: SOFC materials for robust operation on bio-fuels**
  - Sulfur- and redox-tolerant anodes broaden SOFC operating windows
    - Nickel-free, perovskite-based anodes using novel cell architectures
    - Proton-conducting ceramic materials
- **Task 2: Liquid-hydrocarbon / bio-fuel reforming strategies**
  - Examine tradeoffs between reforming approach and cell performance
- **Task 3: Create thermally stable fuel-reforming catalysts and supports**
  - Next-generation catalysts stable under harsh reforming conditions
- **Task 4: Employ system modeling to optimize APU configurations**
  - Optimize thermal management through integrative numerical modeling
- **Task 5: Utilize model-predictive control to integrate system hardware**
  - Improve APU dynamic response, reduce supplementary-storage need

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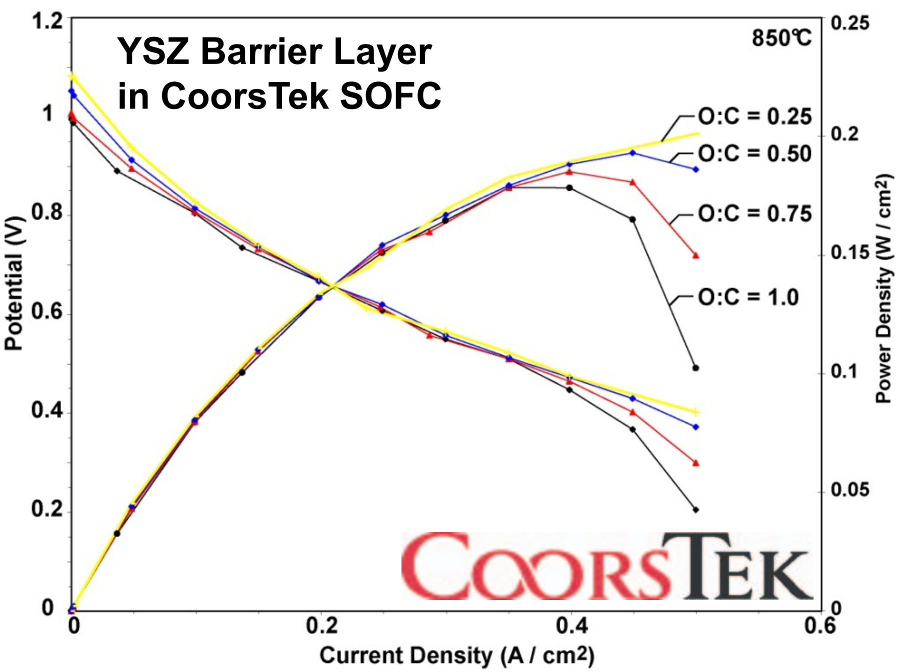
Task 1 Approach: Develop materials to improve SOFC durability under hydrocarbon / alcohol fuels

- **Create advanced SOFC architectures to improve SOFC durability**
  - Anode Barrier and Catalyst Layers improve SOFC robustness under hydrocarbon fuels
  - Milestone: Demonstrate new anode architecture on CH_4 (100%)
  - Milestone: Demonstrate new anode architecture on liquid fuels (90%)
- **Develop nickel-free, perovskite-based, next-generation SOFC anodes**
  - Nickel-free anode more tolerant to sulfur, redox, and heavy hydrocarbons
  - Milestone: Demonstrate next-generation anode operation on CH_4 (70%)
- **Develop proton-conducting SOFC materials**
  - Reduce operating temperature to 400 – 700°C
  - Reduce raw-materials cost through novel ceramic processing
  - Milestone: Fabricate candidate proton-conducting ceramics (100%)
  - Milestone: Evaluate materials stability / durability (85%)

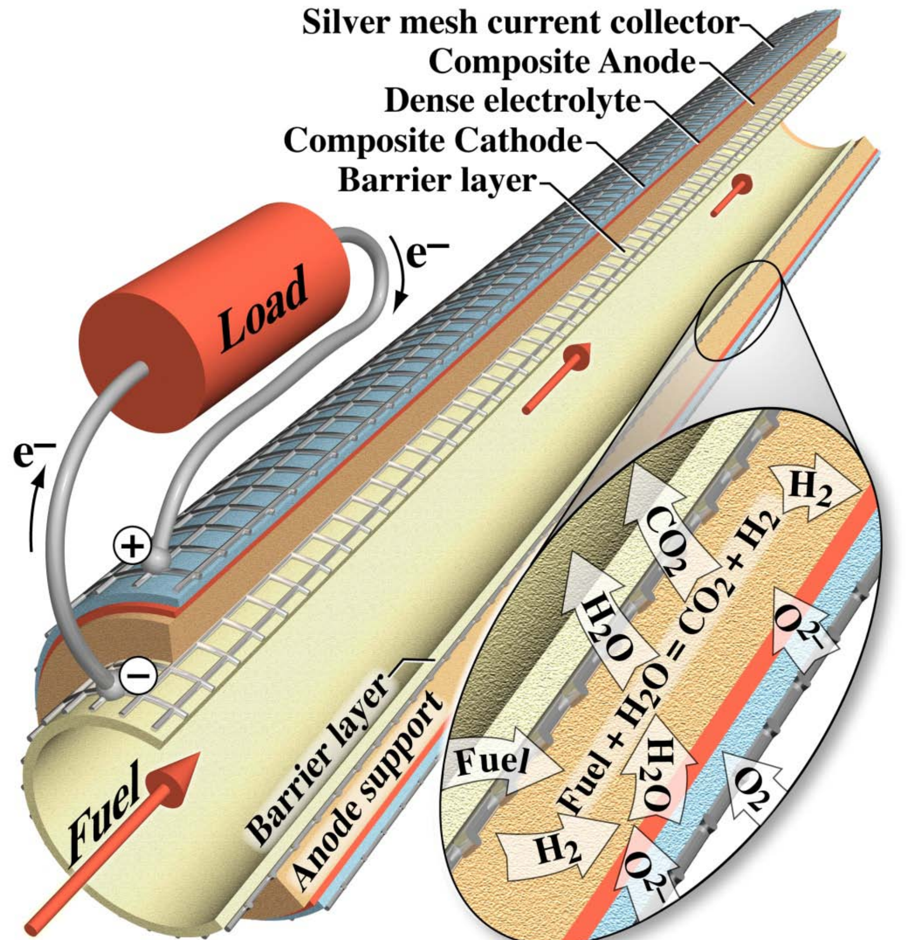
Task 1 Results: Tubular SOFCs with Barrier Layers show expanded operating windows under CH_4 fuel

- **Inert Barrier Layer within SOFC**
  - Increases H_2O content in anode
  - Promotes internal reforming
  - Enable deposit-free operation

Tubular cell performance under CH_4 / air fuel feed



Tubular SOFC equipped with Barrier Layer



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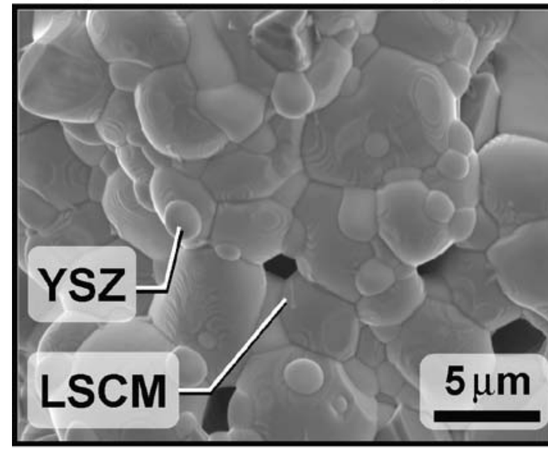
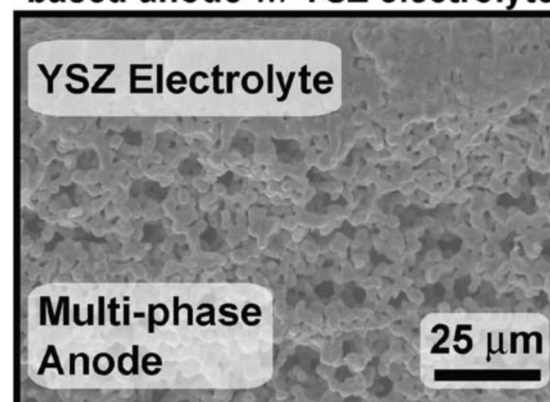
Task 1 Results: Demonstrated materials stability of next-generation SOFC anodes

- **Nickel-free perovskite anode development**
  - Multi-phase ceramic anode
  - $Sr_{0.8}La_{0.2}TiO_3$ (SLT)
    - High electronic conductivity
  - $(La_{0.75}Sr_{0.25})_{0.95}Mn_{0.5}Cr_{0.5}O_3$ (LSCM)
    - Internal reforming
  - Yttria-stabilized zirconia (YSZ)
    - Thermal-expansion matching w/ electrolyte
- **Multi-phase stability established**
  - No Lanthanum-Zirconate phases formed
- **Open pore structure established**
  - Optimal morphology for gas transport

Micrograph of multi-phase perovskite morphology



Micrograph of tubular perovskite based anode w/ YSZ electrolyte



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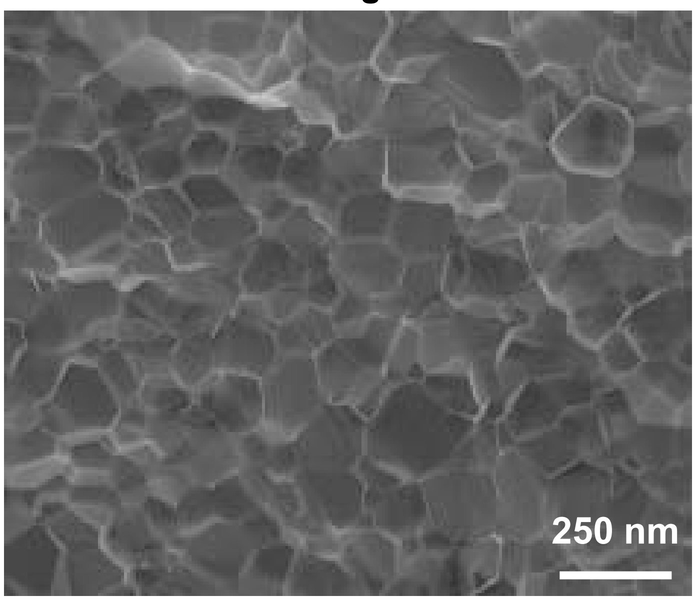
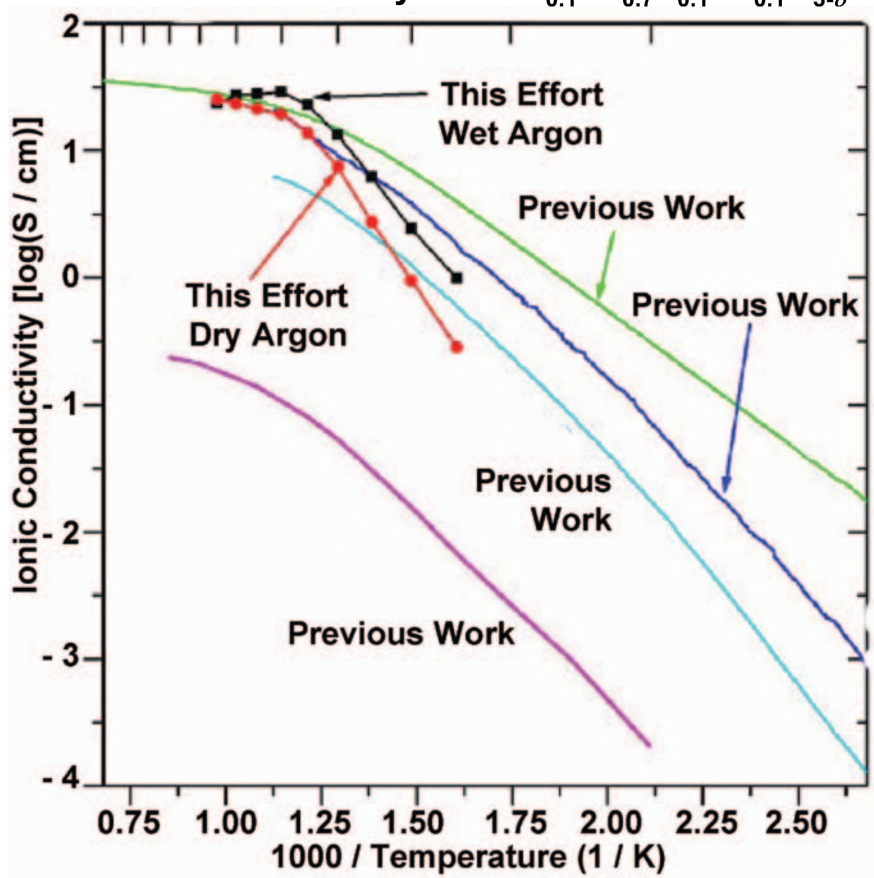
Task 1 Results: Proton-conducting ceramics show near-record conductivities at 1/10th fabrication cost

- **Barium-cerate / zirconate (BCZY) materials**
  - $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$
  - Solid-state reaction sintering
  - Lower processing temperature
  - Lower materials cost

$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ morphology after sintering at 1450°C

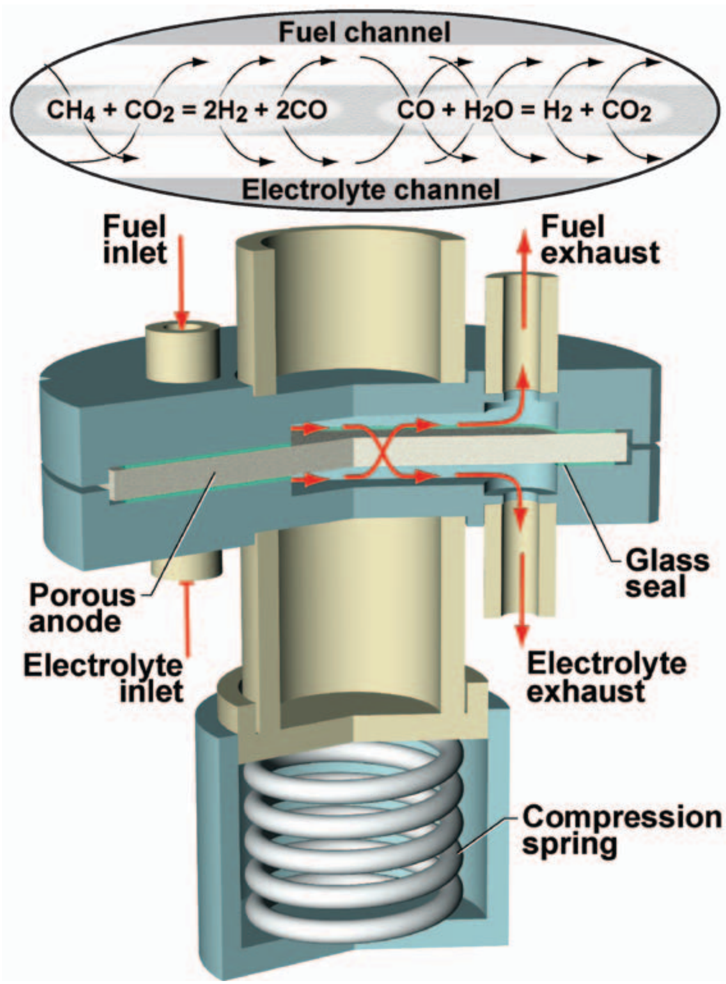


Ionic Conductivity of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$

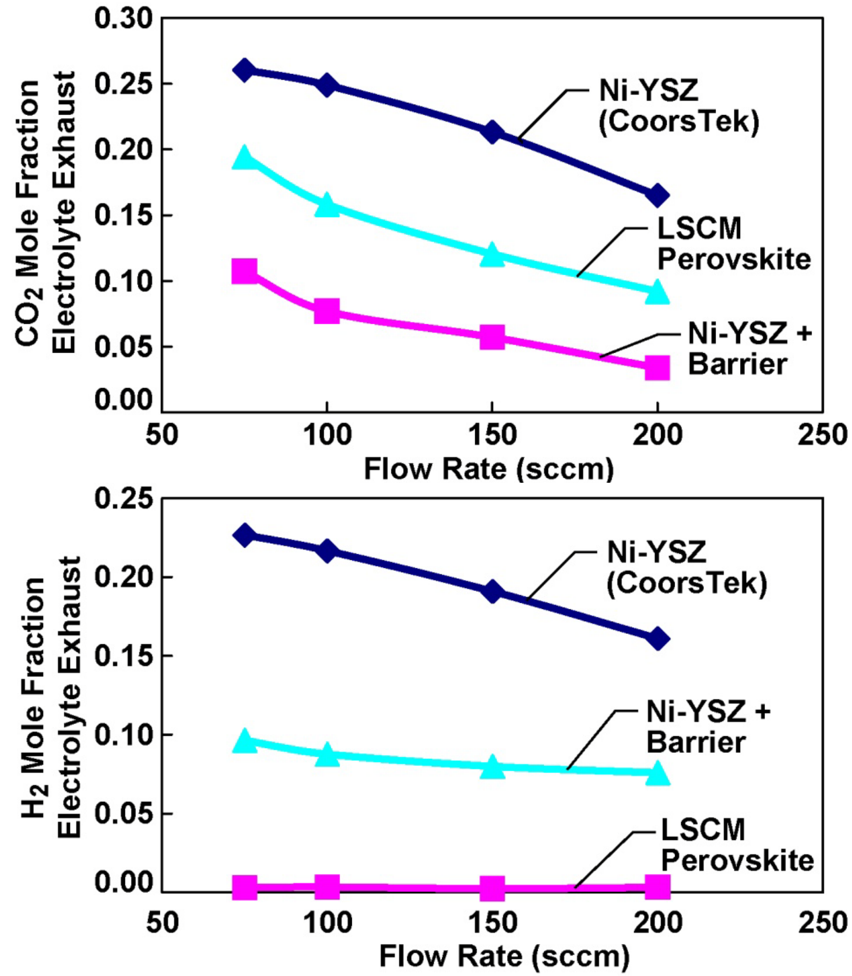


Task 1 Results: Characterized gas transport and internal-reforming chemistry of anode structures

Separated Anode Experiment



Gas transport (top) and reforming chemistry (bottom)



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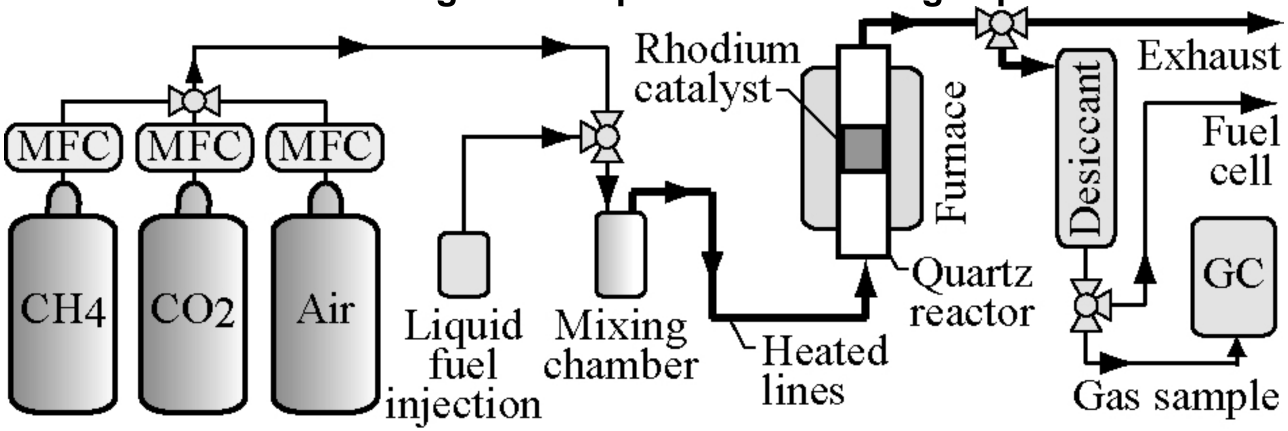
Task 2 Approach: Develop liquid-fuel processing strategies for optimal compatibility with SOFC

- Biomass-derived liquid fuels: ethanol (C_2H_6O) and butanol (C_4H_9OH)
  - Butanol energy density 75% of diesel
- High-pressure spray vaporizes liquid fuels
- Co-flow air stream mixes fuel vapors with oxidizer
- Catalytic partial oxidation fuel reforming converts fuels to syngas
  - Milestone: Syngas production from biomass-derived liquid-fuel (100%)
  - Milestone: Demonstrate steady operation with liquid-fuel reformate (80%)

Process flow diagram of liquid-fuel reforming experiment



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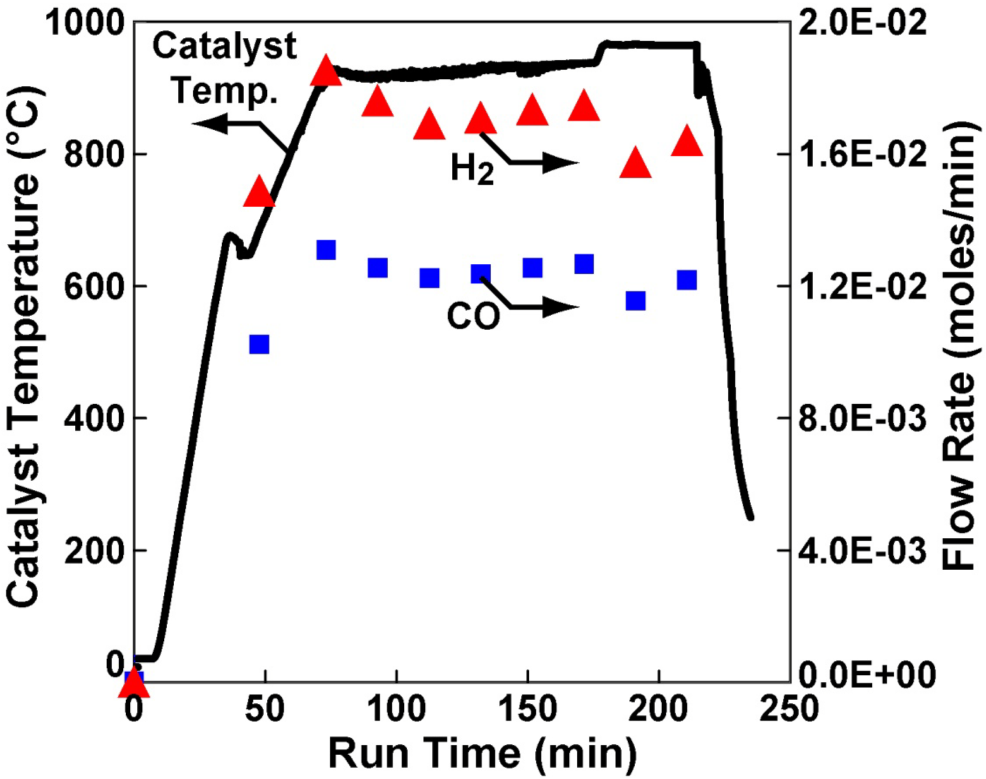
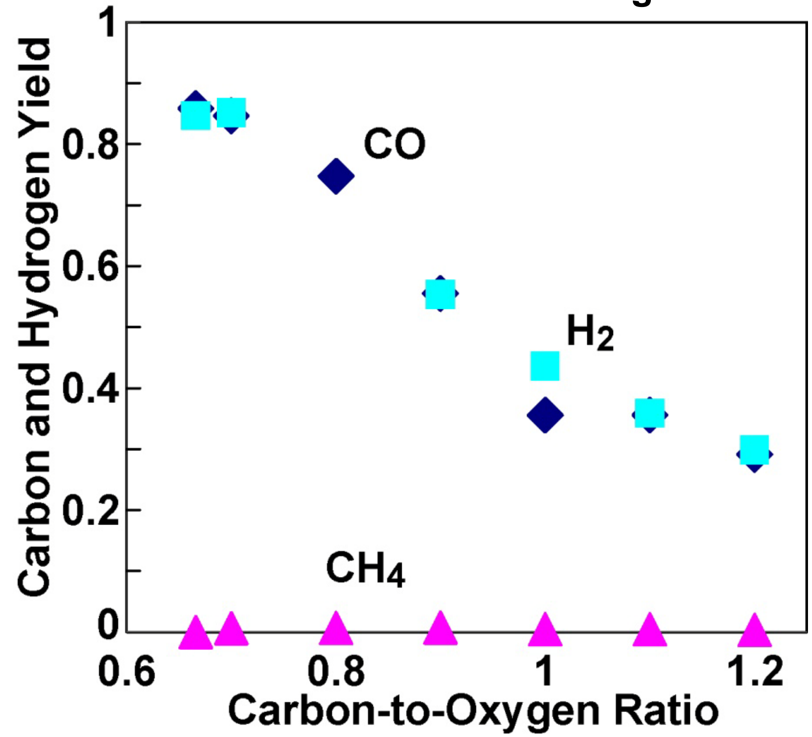
Task 2 Results: Established biomass-derived liquid-fuel processing for SOFC operation

- Demonstrated ethanol and butanol CPOX reforming
  - Rhodium catalyst on hexaaluminate catalyst support

Ethanol CPOX reformate over time



Butanol reformate composition under CPOX reforming



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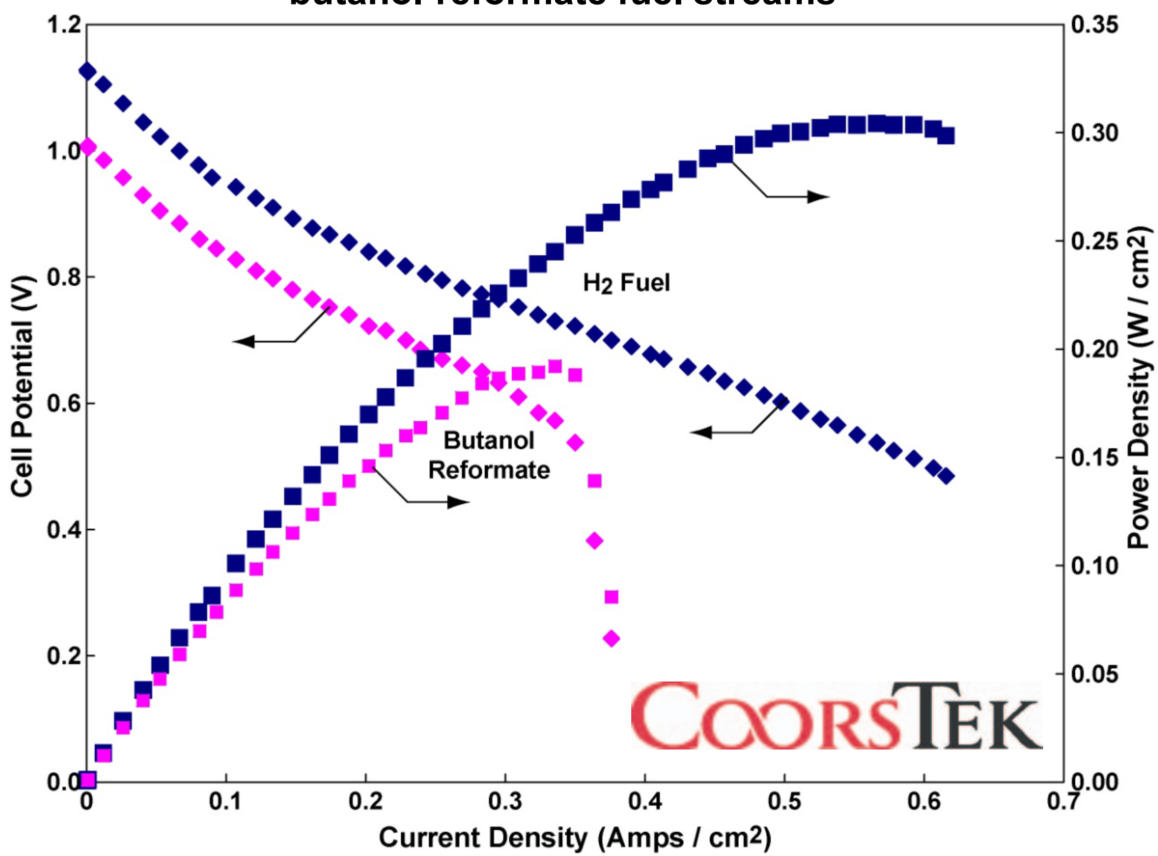
Task 2 Results: Demonstrated tubular SOFC operation under CPOX'ed butanol reformate

- Catalytic partial oxidation of butanol
  - Nitrogen dilution
  - Lower OCV
  - Concentration polarization
- 35% decrease in cell power density
- Longer-term operation to be established

Tubular SOFC performance under hydrogen and butanol-reformate fuel streams



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Task 3 Approach: Synthesize thermally stable fuel-reforming catalysts to improve APU durability

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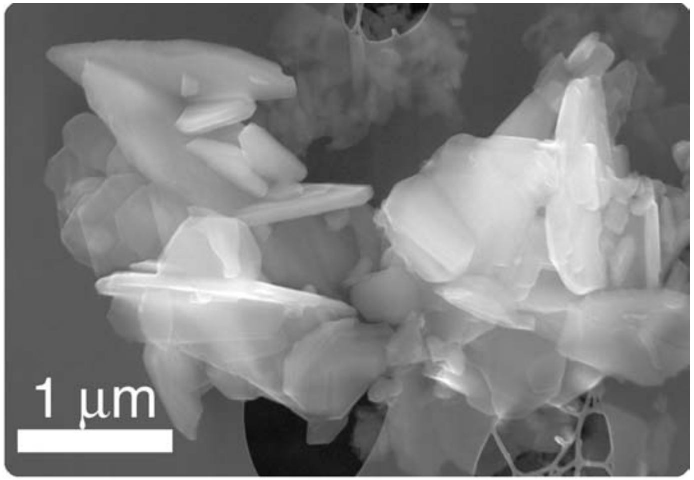
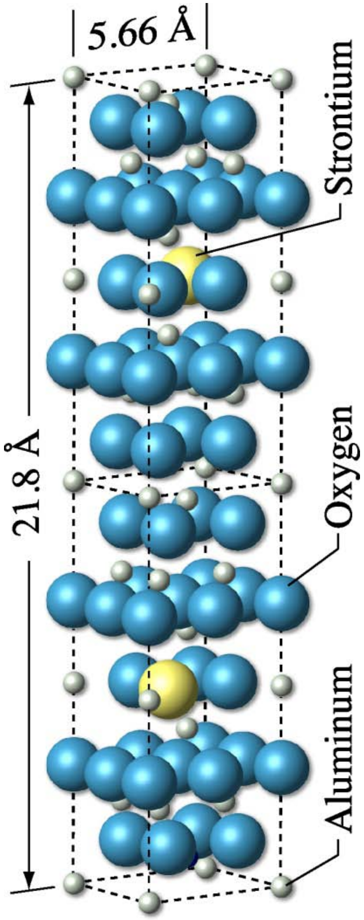
- Prepare stable hexaaluminate catalyst supports
  - Strontium disturbs Al_2O_3 crystal structure
  - Limits sintering in [1 0 0] axis
  - Enables high-temperature stability
  - Milestone: Prepare catalyst supports (100%)
- Evaluate catalysts for biomass fuel processing
  - Milestone: Demonstrate with biomass fuels (100%)
    - Tie to Task 2
      - Ethanol
      - Butanol



Micrograph of hexaaluminate

Sr-hexaaluminate atomic structure



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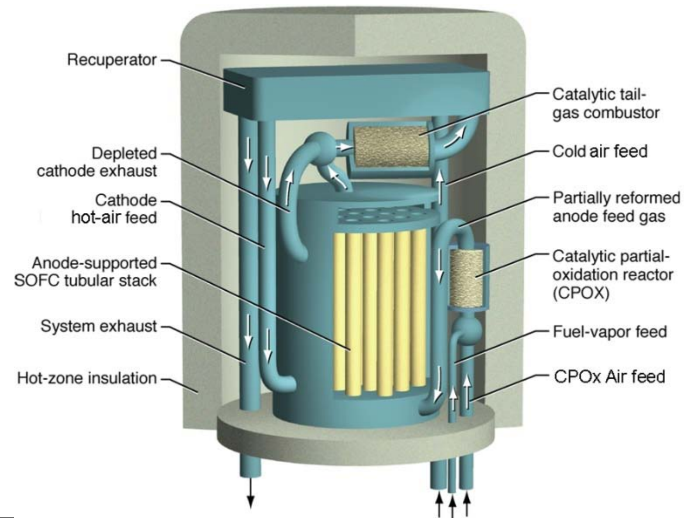
Task 4 Approach: Create optimal SOFC system designs through process and thermal modeling

- Develop physics-based component models
  - Detailed thermal management models
  - High-order electrochemistry models
  - Computational fluid dynamics

SOFC Hot Module



- Apply to systems design and simulation
  - Reduced-order models for steady-state process design and simulation
  - 1st-generation Protonex 4x600-W tubular SOFC system
  - Milestone: 90% complete

- Generate optimal system configuration(s) and operating parameters
  - Improved heat-transfer estimates within temperature control
  - Predict system performance under sensor uncertainty
  - Milestone: 75% complete

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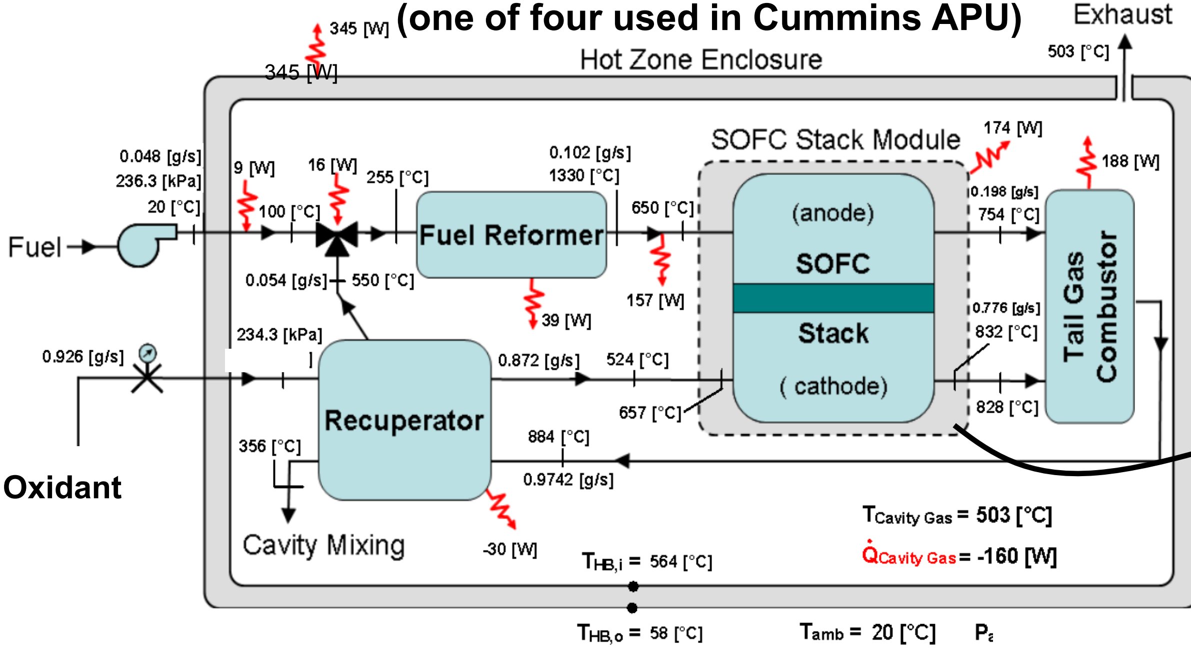
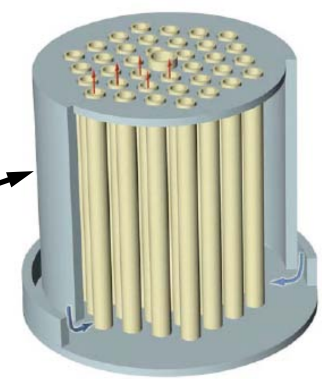
Task 4 Approach: Systems-level design explored from multiple viewpoints and modeling tools

- High-order CFD-electrochemical models
- Reduced-order thermal models coupled with 0-D process design
- Exergy-analysis models

Protonex 600-W system process diagram (one of four used in Cummins APU)



SOFC shell-and-tube stack geometry



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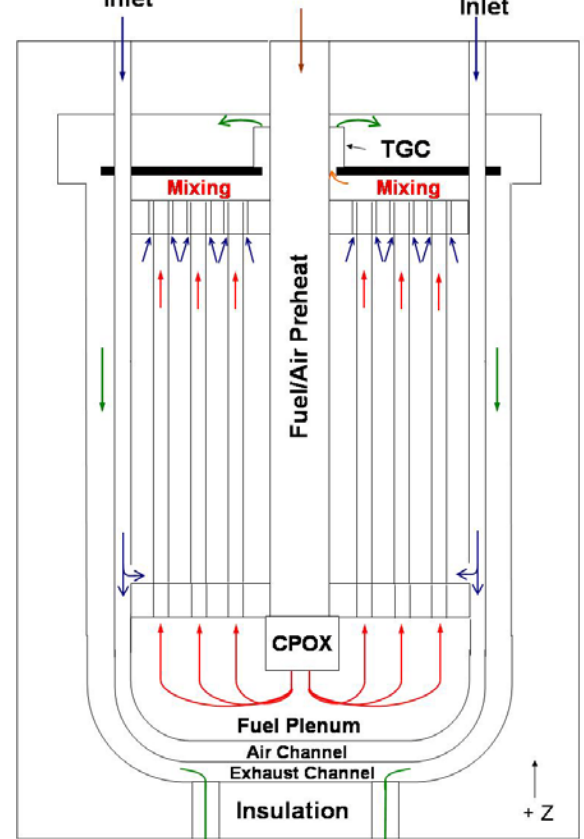
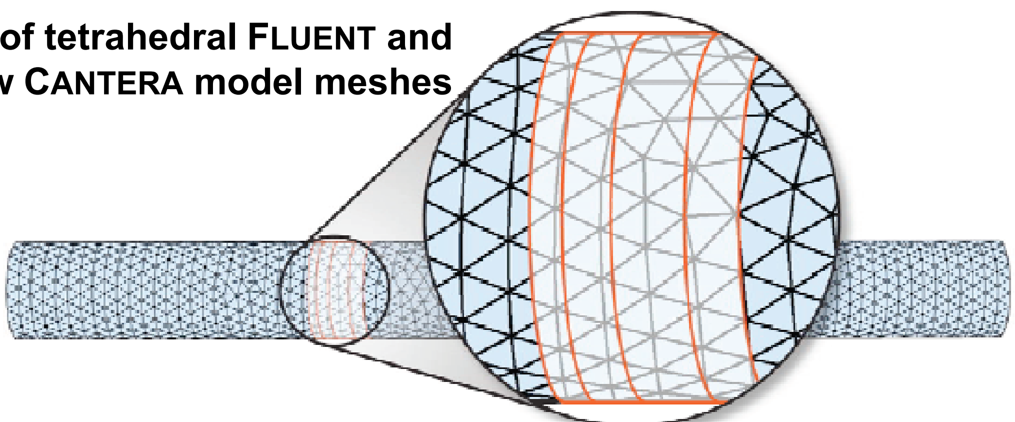
Task 4 Approach: Hybrid CFD-electrochemical model bridges chemical and geometrical complexities

- Separate complex chemistry and flow
  - Chemically reacting anode flow: CANTERA
  - Cathode air flow: CFD in FLUENT
  - Iterate models to find coupled solution
- Enables high-fidelity system simulation
- Extension to thermally integrated system
  - Tail-gas combustor (TGC), CPOX processes

Integrated Shell-and-Tube System



Coupling of tetrahedral FLUENT and plug-flow CANTERA model meshes



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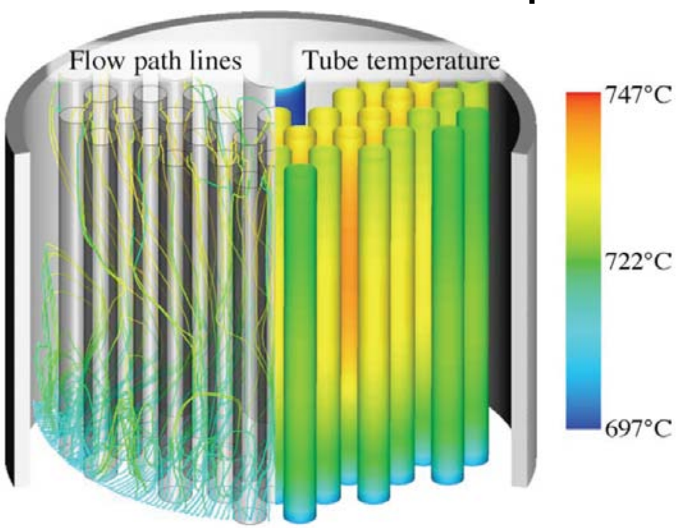
Task 4 Results: Coupled model predicts detailed performance information, internal stack conditions

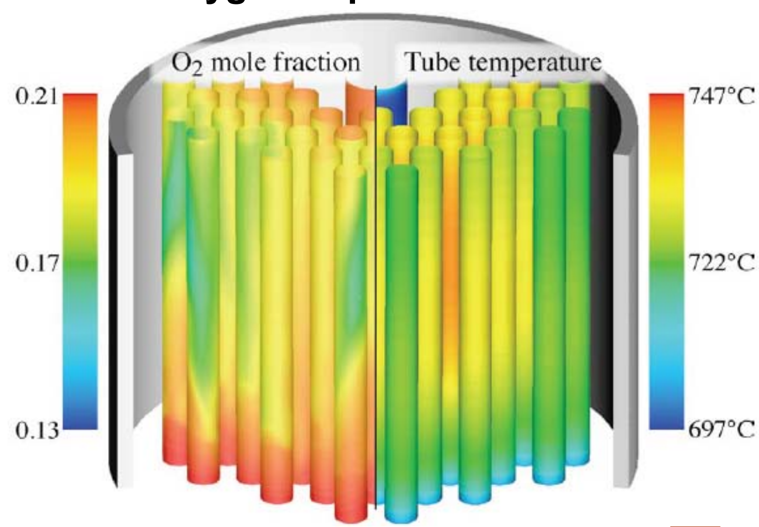
- **Radiation heat transfer**
  - >75% of total heat transfer in tube bundle
  - Outer tubes act as radiation shields
  - Inner tubes up to 50°C warmer
- **Resolve local O_2 concentration**
  - Enables identification of oxygen-depletion zones

SOFC stack geometry

Cathode flow lines and tube temperature



Oxygen-depletion zones



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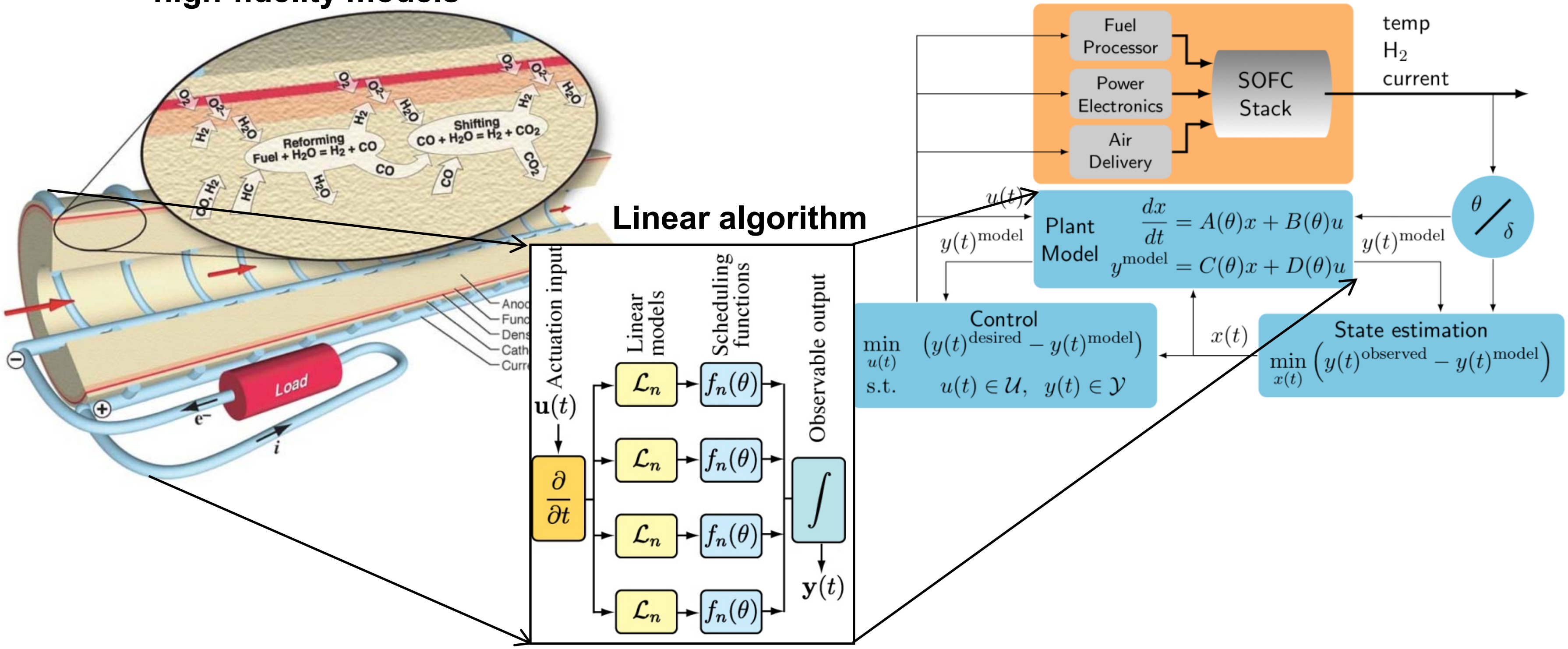
Task 5 Approach: Improve APU dynamic response through model-based predictive control

Physical processes captured in high-fidelity models

Low-order linear model representation



- **Fast low-order models built from detailed physical models**
  - **Dimensionality reduction while matching dominant dynamic behavior**

Task 5 Approach: Physics-based models are reduced for use in rapid model-predictive control

- Reduce slow, high-order physics-based models
  - Employ sampling approach to high-order model reduction

- Create fast, low-order models for use in model-predictive control
  - Linear, parameter-varying model structure
    - Stable over wide APU-system operating range
  - Milestone: Model reduction of SOFC stack (100% complete)
  - Milestone: Model reduction of complete SOFC system (80% complete)

- Develop real-time control schemes to improve system response
  - Milestone: Model-predictive control of SOFC stack (100% complete)
  - Milestone: Model-predictive control of SOFC system (80% complete)
  - Milestone: Real-time model-predictive implementation (100% complete)

Task 5 Results: Demonstration of fuel-cell stack control with broad load variation

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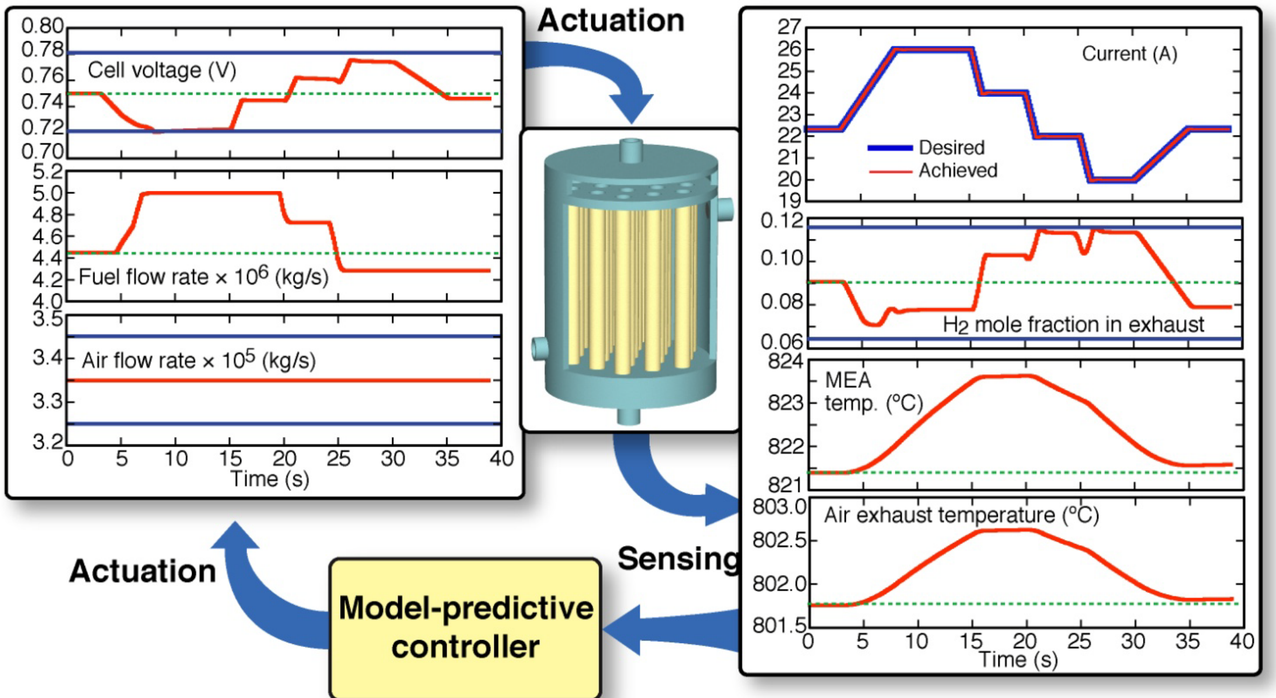

- Control demonstrated using high-order physical model
  - Desired current trajectory (blue) achieved while meeting constraints on cell voltage, fuel flow rate, and hydrogen utilization
  - Validates reduced-order models

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Task 5 Results: Reduced-order models match single-tube response over wide operating range

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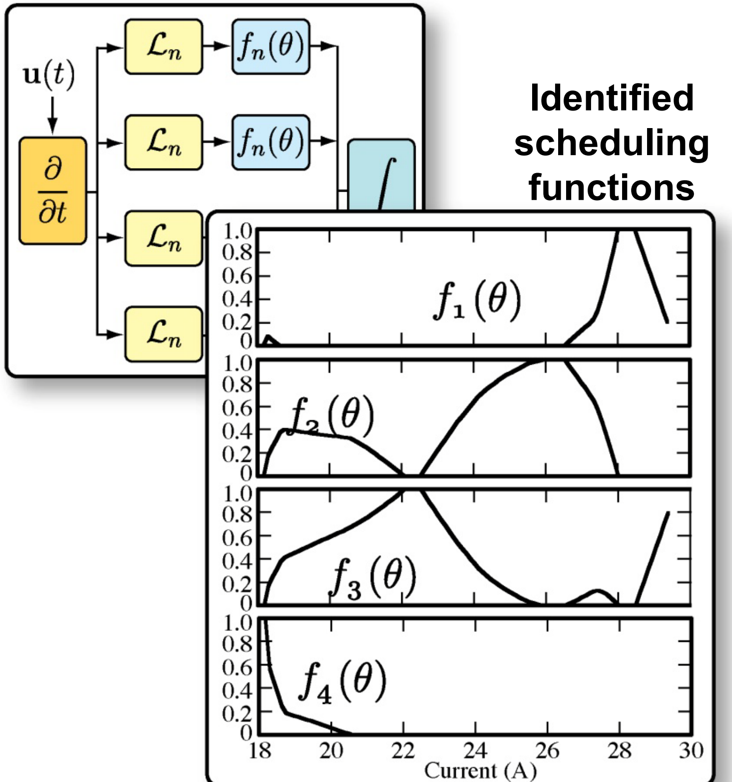
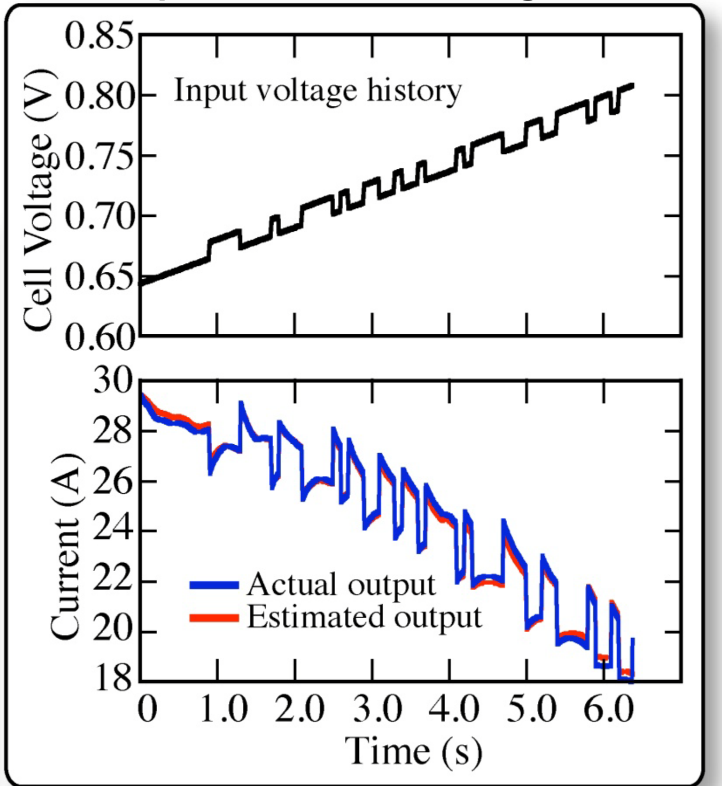
- Scheduling functions select appropriate model for operating condition

Linear parameter-varying model

Identified scheduling functions



Comparison between high-order and low-order model for large-scale perturbation in voltage



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Industrial collaborations: Protonex Technology Corporation, Reaction Systems LLC, CoorsTek Inc.

- Protonex: subcontractor to CSM; provide technical data and support
  - Hot-zone developer for EERE long-haul truck APU project
    - Subcontractor to Cummins Power (Program DE-FC26-01NT41244)
  - CSM system- / control-model results incorporated into Protonex designs
    - Task 4 and Task 5
  - Collaboration with CSM on next-generation SOFC materials (Task 1)
    - Leveraged by Sandia LDRD on high-temperature electrolysis
- Reaction Systems: subcontractor to CSM for catalyst development
  - Novel catalysts developed by Reaction Systems (Tasks 2 and 3)
  - Catalyst fundamental chemistry examined at CSM
    - Leveraged by Phase II SBIR program
    - Funded by Air Force Research Lab (Contract #FA8650-07-C-2722)
- CoorsTek, Inc.: Tubular SOFC supplier (Tasks 1 and 2)

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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: Biomass-derived liquid-biofuel reforming
  - Quantify stability of catalyst and SOFC for CPOX-reforming of butanol
  - Extend testing to longer durations (1000 hours)
- Task 3: Fuel-reforming catalyst development
  - Conduct extended aging tests with catalysts and support materials
- Task 4: System-level modeling
  - Update tubular SOFC geometry to 3rd-generation Protonex design
  - Perform parameter-sensitivity study on mobile SOFC system concepts
- Task 5: System-control effort
  - Extend model-reduction and control strategy to Balance-of-Plant

Summary: CSM program improves robustness of liquid-hydrocarbon / biomass-fueled SOFC APUs

- **Relevance:**
  - Improve reliability: materials, architectures and system-level models
  - Expand operating windows: liquid-fuel reforming, system-control strategy
- **Approach:**
  - Create next-generation SOFC materials and reforming catalysts
  - Develop fuel-reforming, system-modeling, and system-control tools
  - Collaborate / validate new materials and designs with industrial partners
- **Results:**
  - Demonstrated improved SOFC operation on ethanol and butanol fuels
  - System/control models developed and tuned to Protonex/Cummins APU
- **Future work:**
  - Long-term testing of SOFCs and catalysts under CPOX'ed butanol
  - Sensitivity analyses of system-level modeling tools

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