Biomass Fuel Cell Systems

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Golden, Colorado, USA

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Colorado Fuel Cell Center

Project ID:
FC076

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

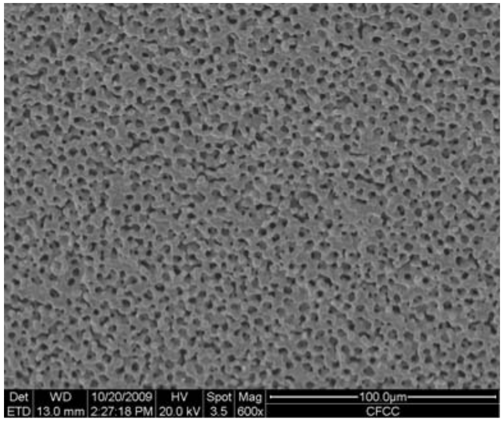
- Develop nickel-free, perovskite-based, next-generation SOFC anodes
  - Perovskites more tolerant to sulfur, redox, and heavy hydrocarbons
  - Challenges in utilizing perovskites as anode materials in SOFCs
    - Materials stability during SOFC processing and cell operation
    - Electronic conductivity 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

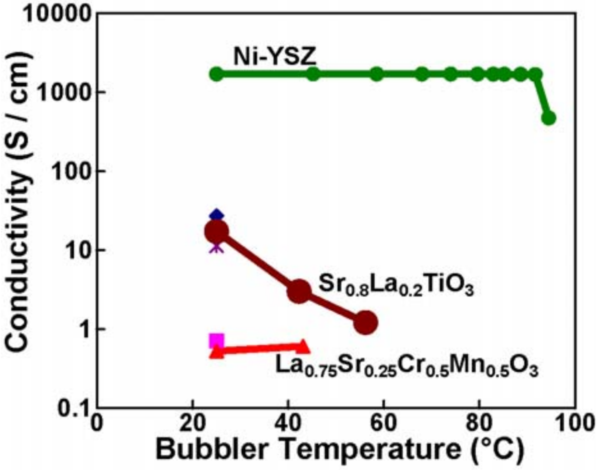
- **Perovskite anodes synthesized**
  - $Sr_{0.8}La_{0.2}TiO_3$ (SLT)
    - High electronic conductivity
  - $(La_{0.75}Sr_{0.25})_{0.95}Mn_{0.5}Cr_{0.5}O_3$ (LSCM)
    - Internal reforming
  - Multi-phase SLT / LSCM ceramic anode

- **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

Micrograph of porous perovskite anode structure



Conductivity under H_2 at 800°C increasing steam addition



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

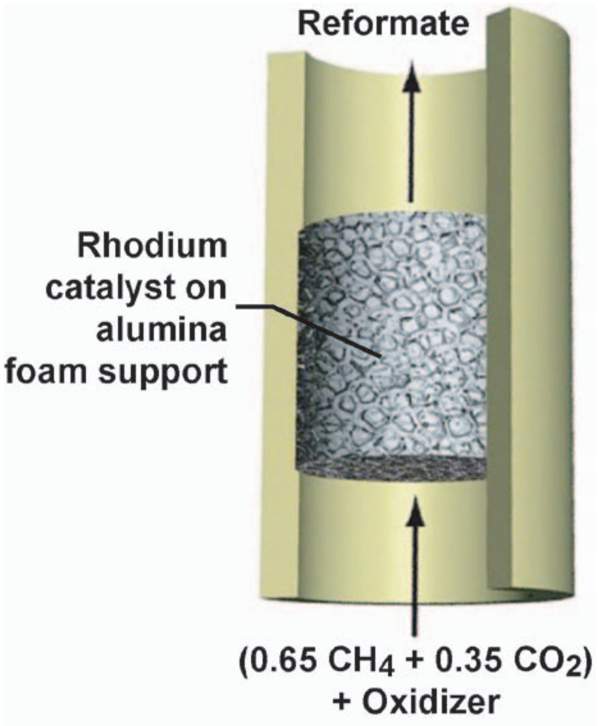
- Biogas fuels: anaerobic digesters at waste-water treatment facilities
  - Low-quality methane stream: 65% CH_4 / 35% CO_2
  - MW-scale power generation
- Explore fuel-reforming options to convert biogas to syngas (H_2 + CO)
  - Catalytic partial oxidation (CPOX - air and / or O_2)
    - Simplest approach, but lowers system efficiency
  - Steam and / or dry reforming (H_2O and / or CO_2)
    - 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 (C_4H_9OH)
  - Butanol energy density 75% of diesel
  - Milestone: Demonstrate integrated liquid-fuel vaporizer / reformer (100%)

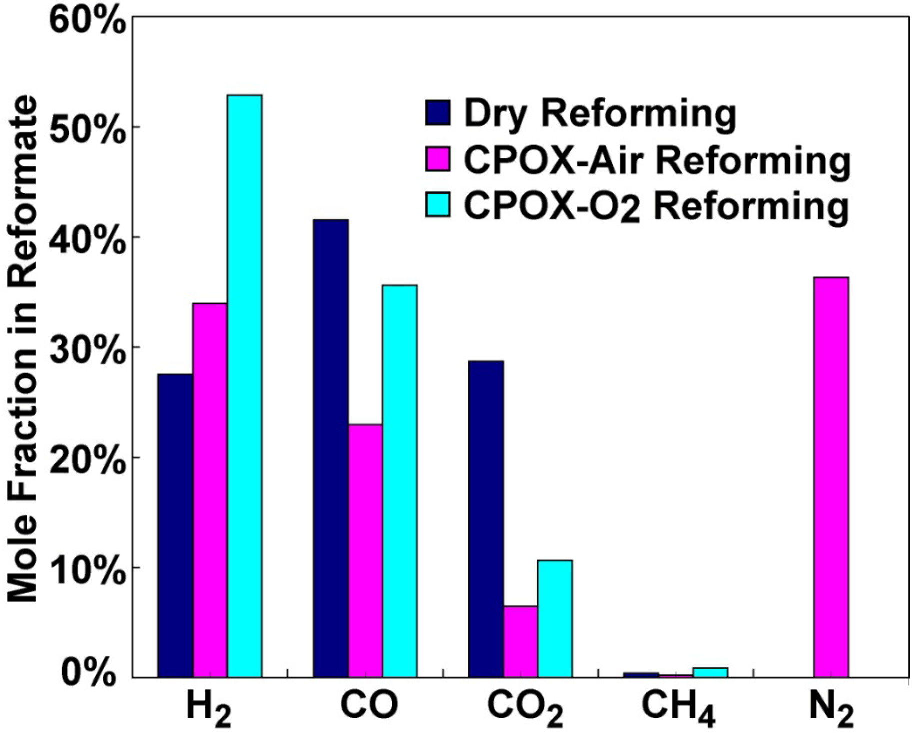
Task 2 Results: Kinetic model for biogas reforming on Rh-based catalyst developed and implemented

- 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

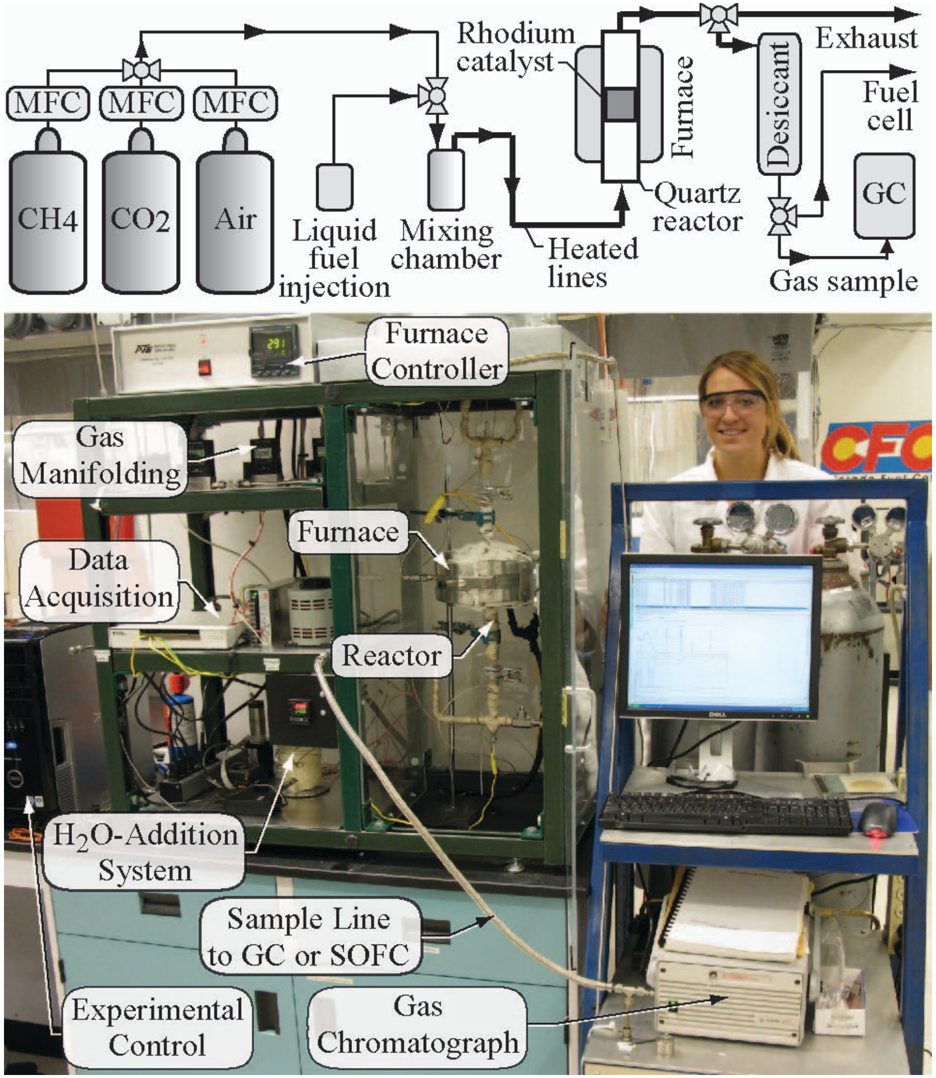


Model-predicted biogas reformate composition for different reforming approaches (900 C)

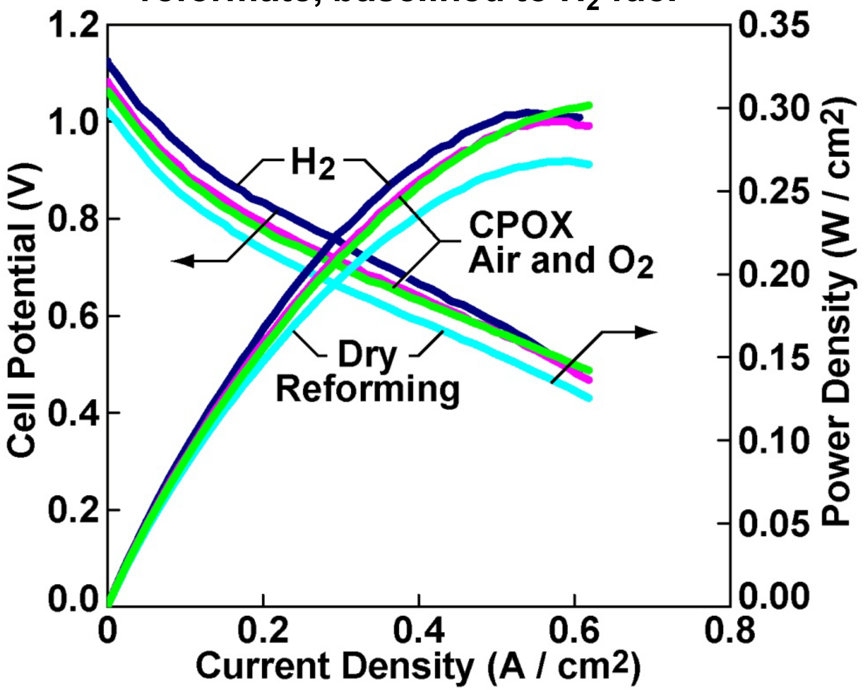


Task 2 Results: Bio-fuel reactor commissioned, integrated with SOFC-performance test stand

Reforming experiment process flow diagram and photo



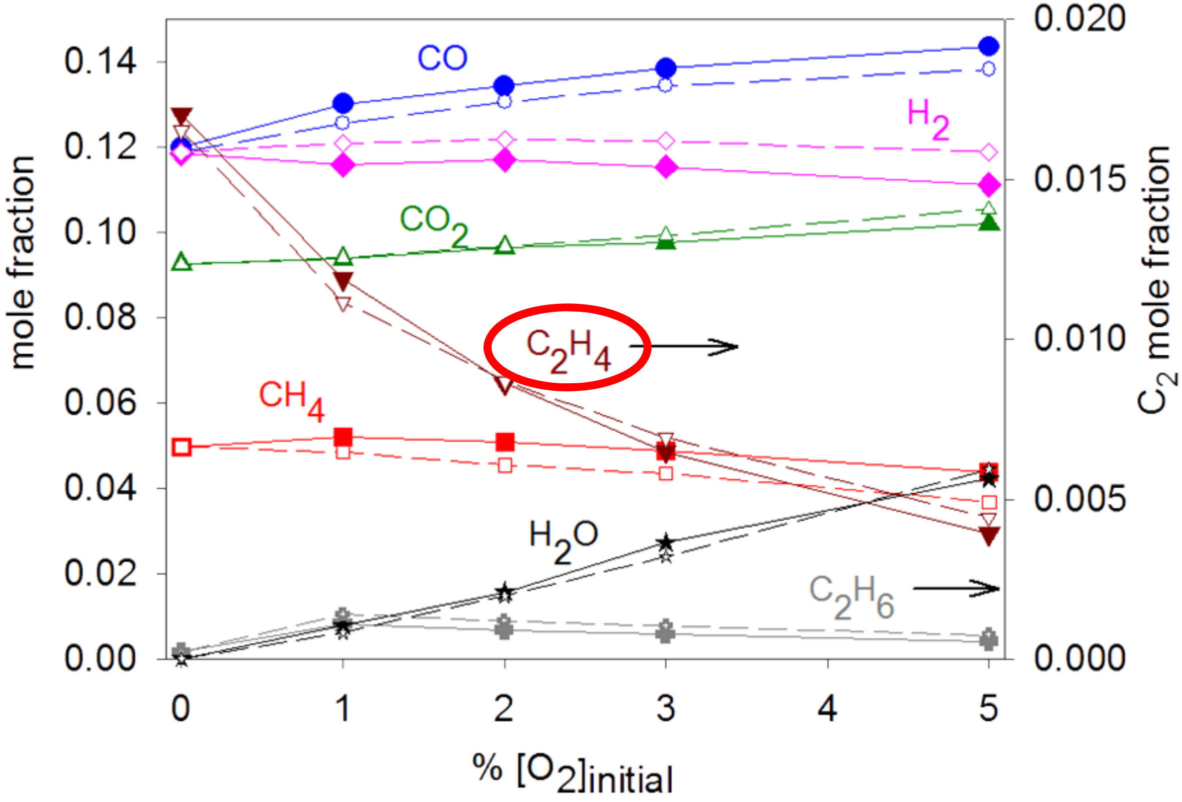
SOFC performance under biogas reformate, baselined to H_2 fuel



- Reforming approach strongly affects cell performance
- Cell performance under CPOX rivals H_2 fuel

Task 2 Results: Carbon-deposit precursors in biogas can be selectively reduced through O_2 addition

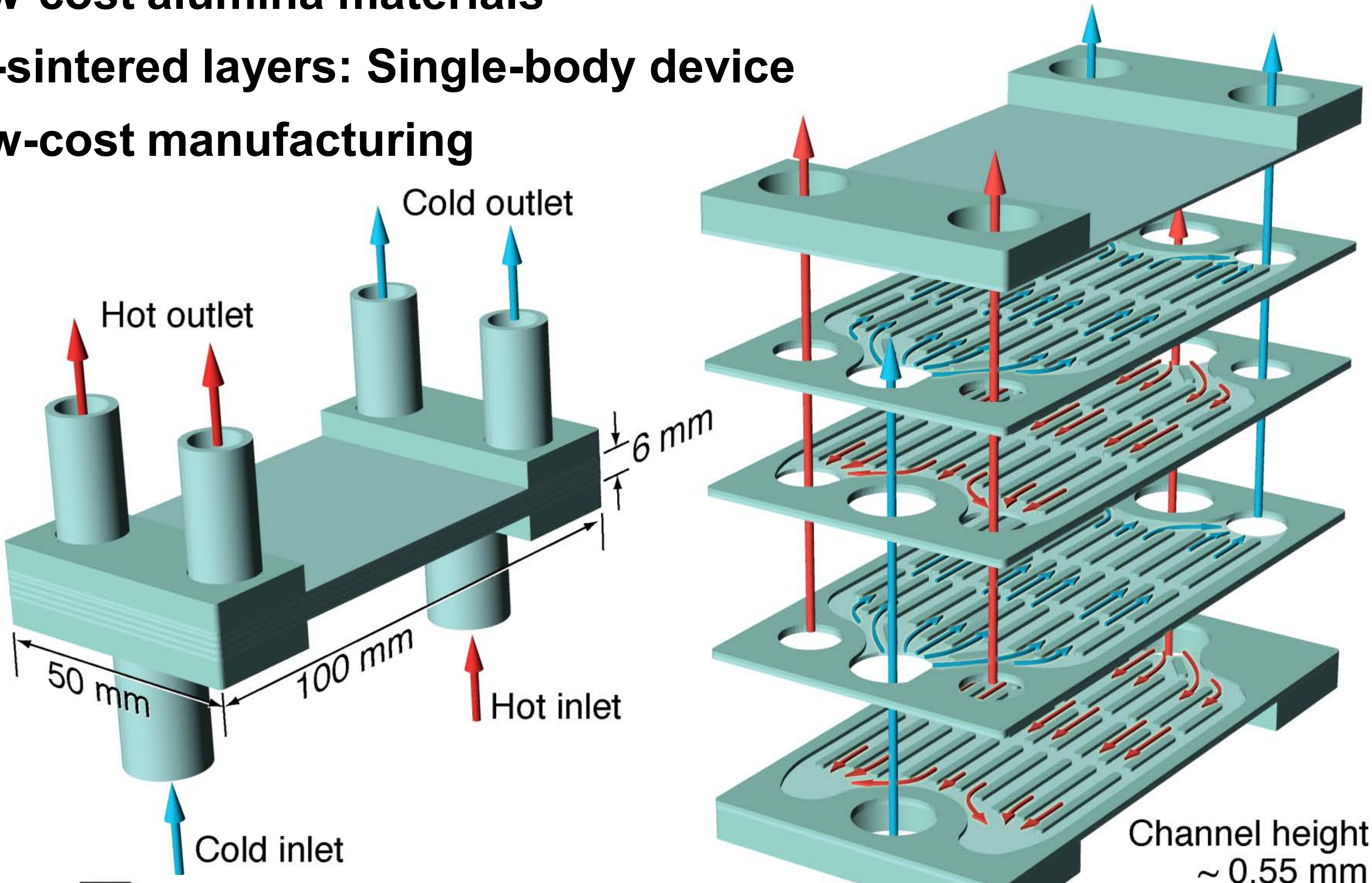
Gas composition changes with O_2 addition (810°C)



- Ethylene (C_2H_4) is the common pre-cursor 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

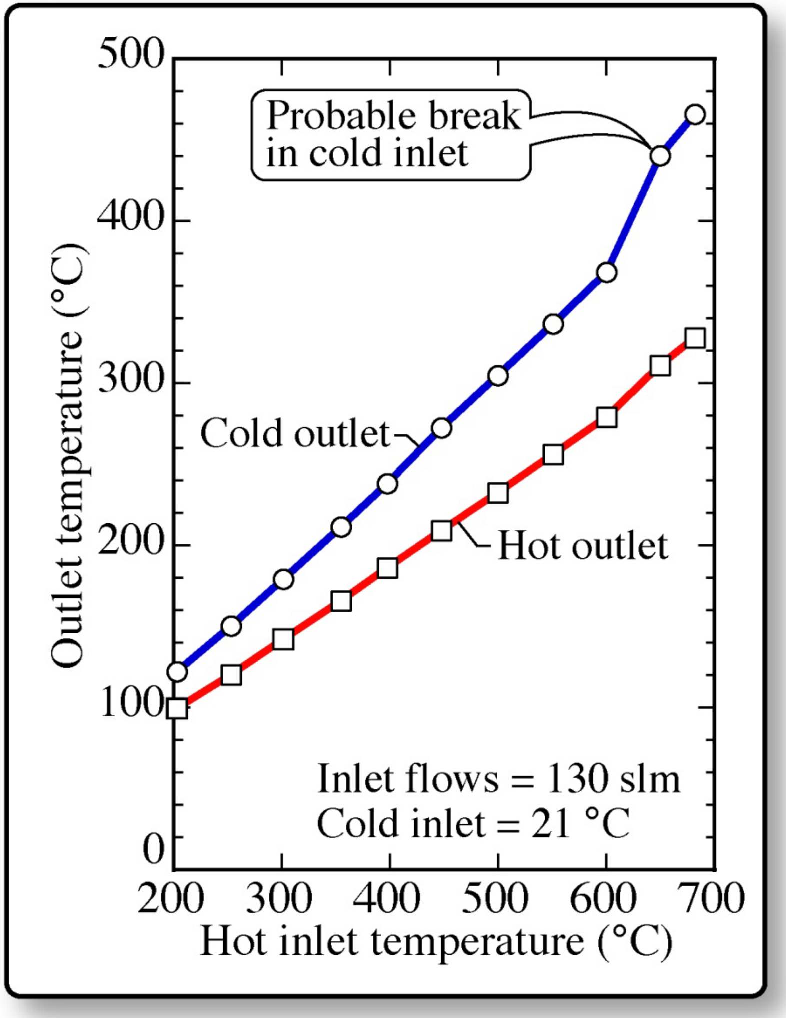
- Low-cost alumina materials
- Co-sintered layers: Single-body device
- Low-cost manufacturing



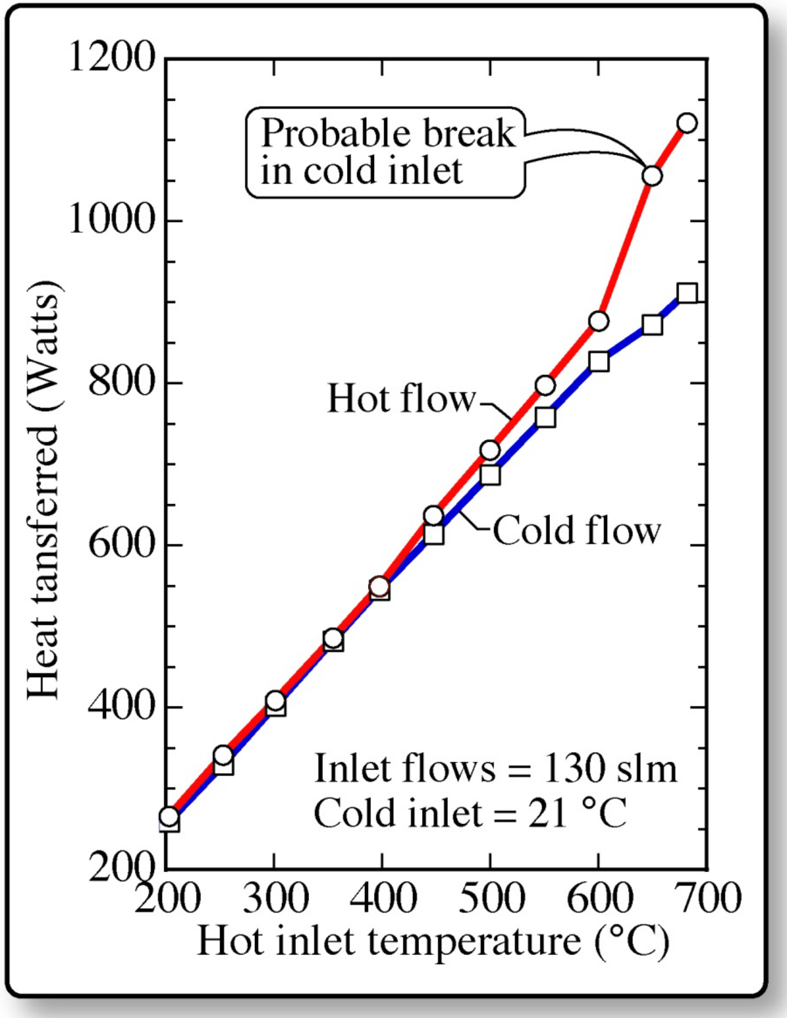
Generation-3 design

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

Inlet and outlet gas temperatures



Total heat transferred



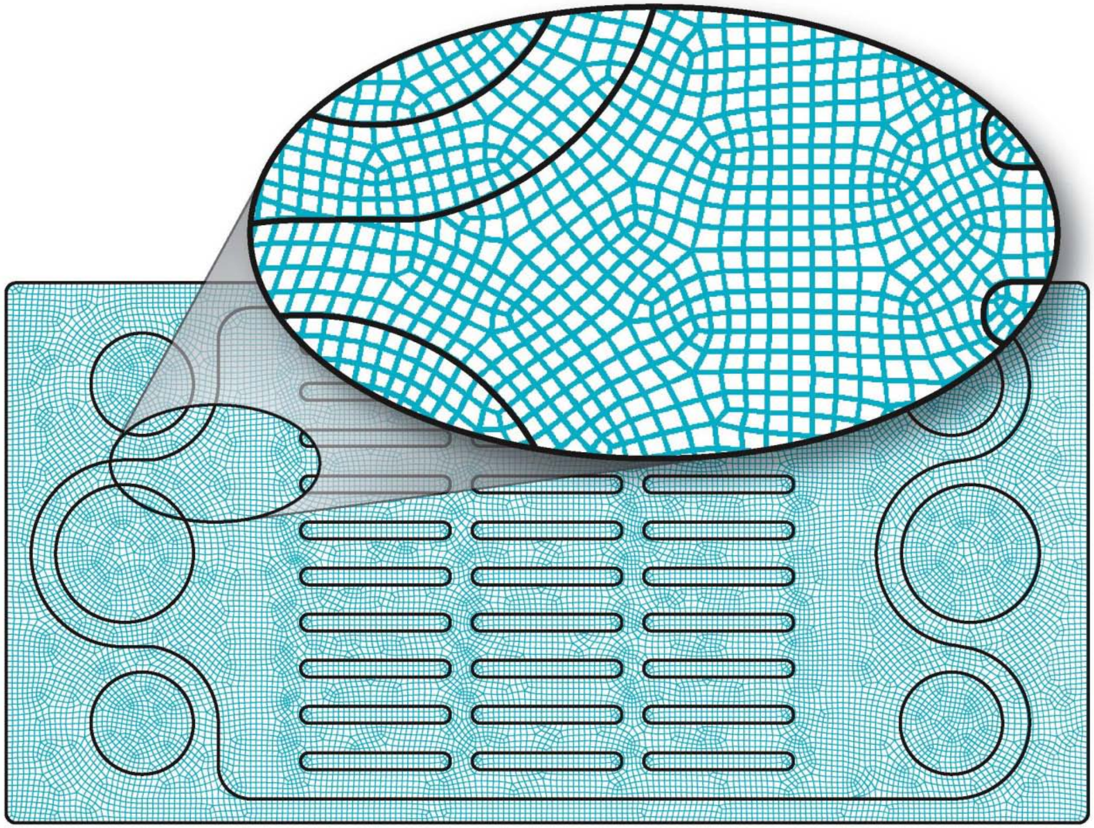
Task 3 Approach: Provide modeling support for Tasks 1 and 2 using CFD and chemically reacting flow tools

- 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

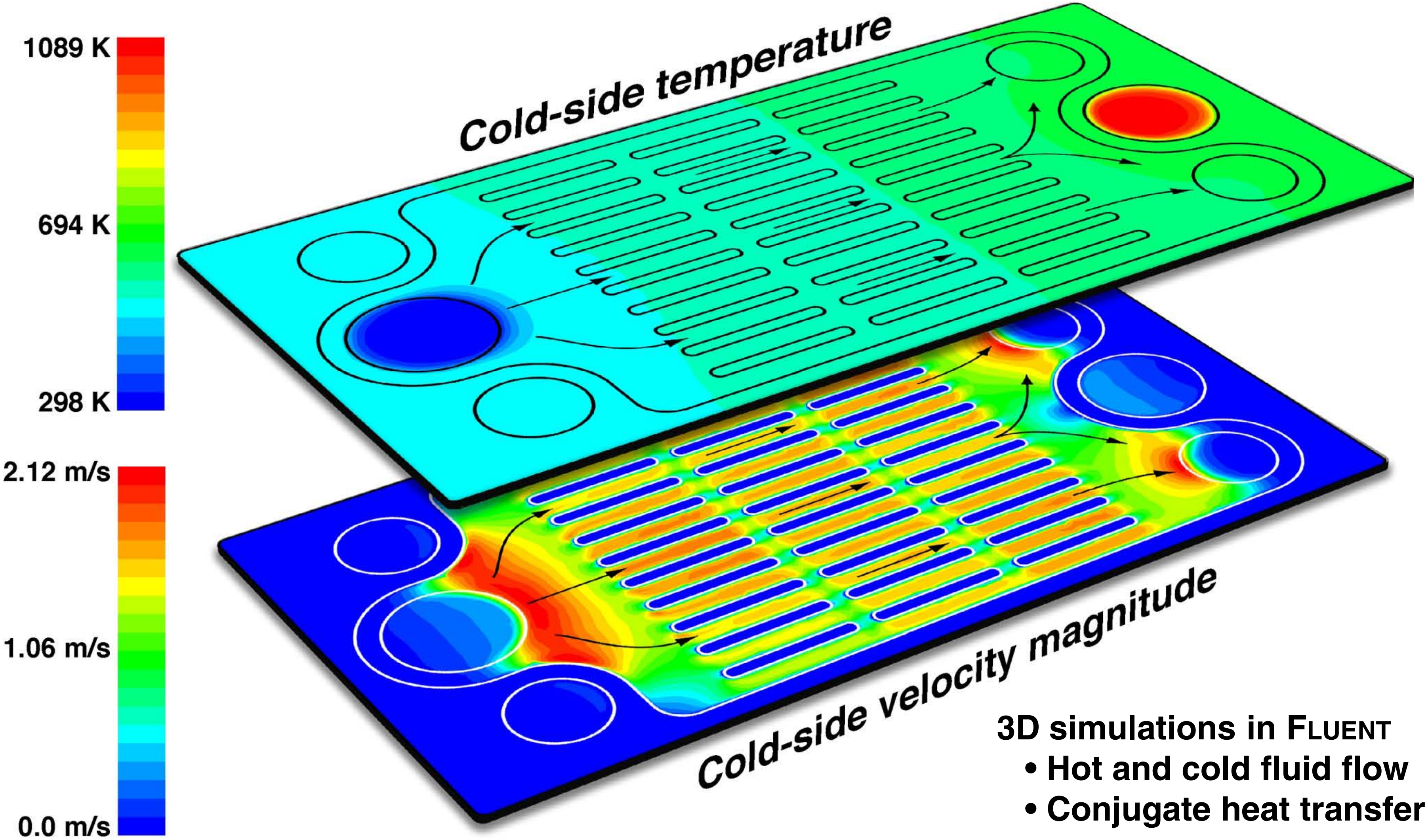
Task 3a Approach: CFD and chemically reacting flow models integrated to provide HX-design guidance

- 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



3D simulations in FLUENT

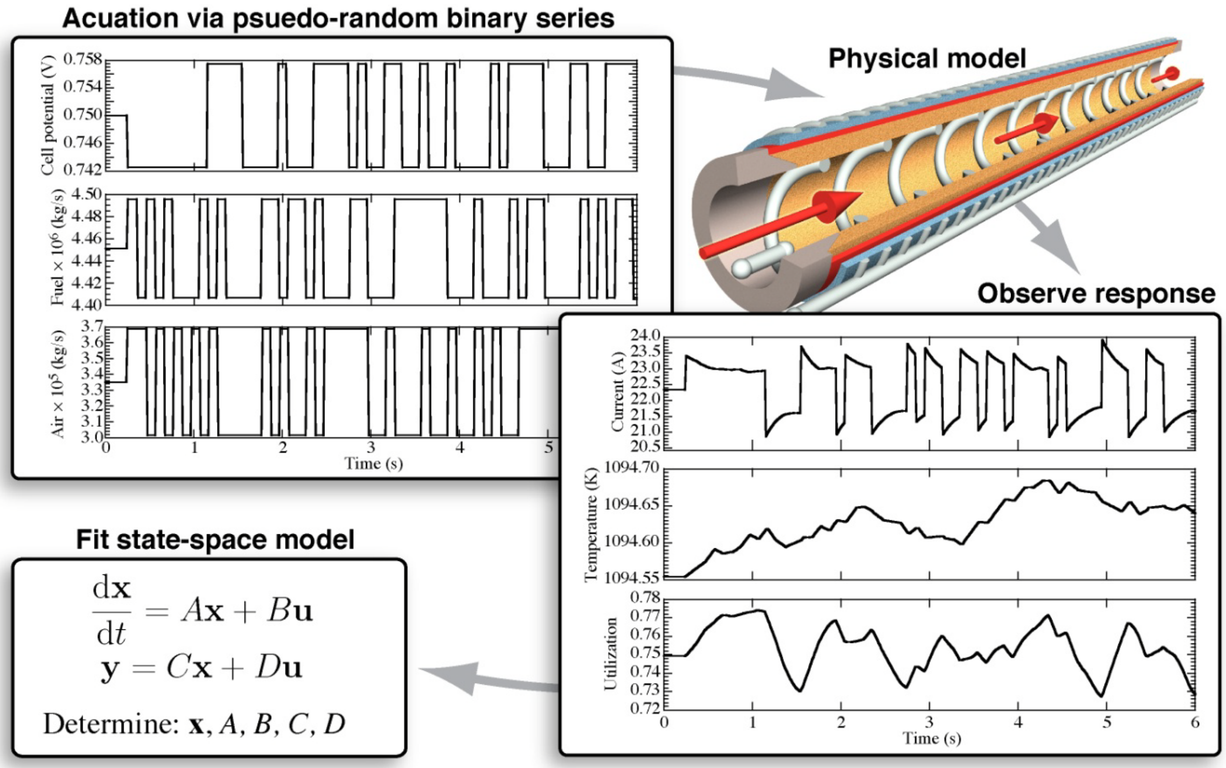
- Hot and cold fluid flow
- Conjugate heat transfer

Efforts leveraged by current NETL program at Colorado School of Mines

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



Acuation via psuedo-random binary series

Physical model

Observe response

Fit state-space model

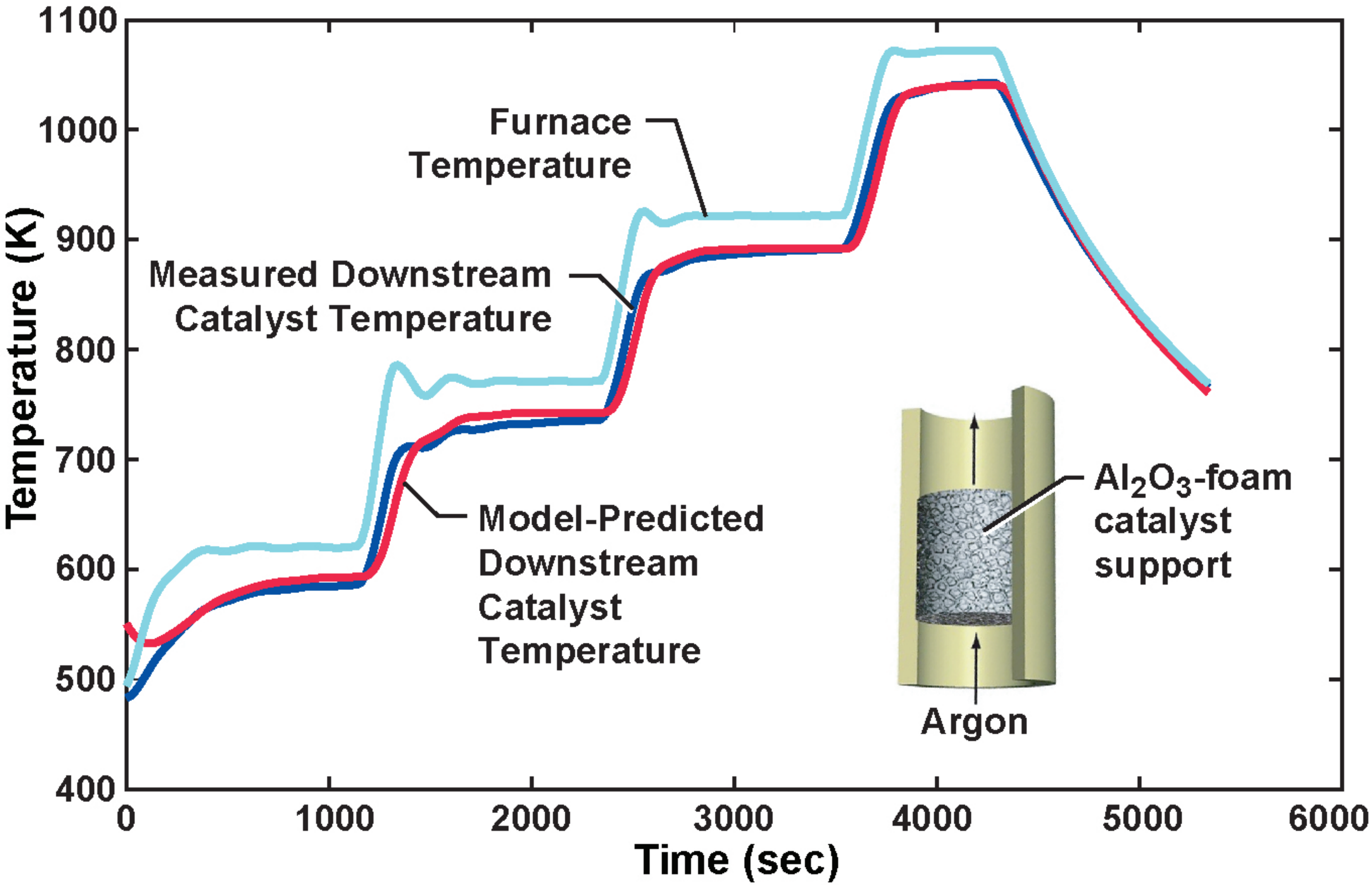
$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = A\mathbf{x} + B\mathbf{u}$$

$$\mathbf{y} = C\mathbf{x} + D\mathbf{u}$$

Determine: $\mathbf{x}$, A, B, C, D

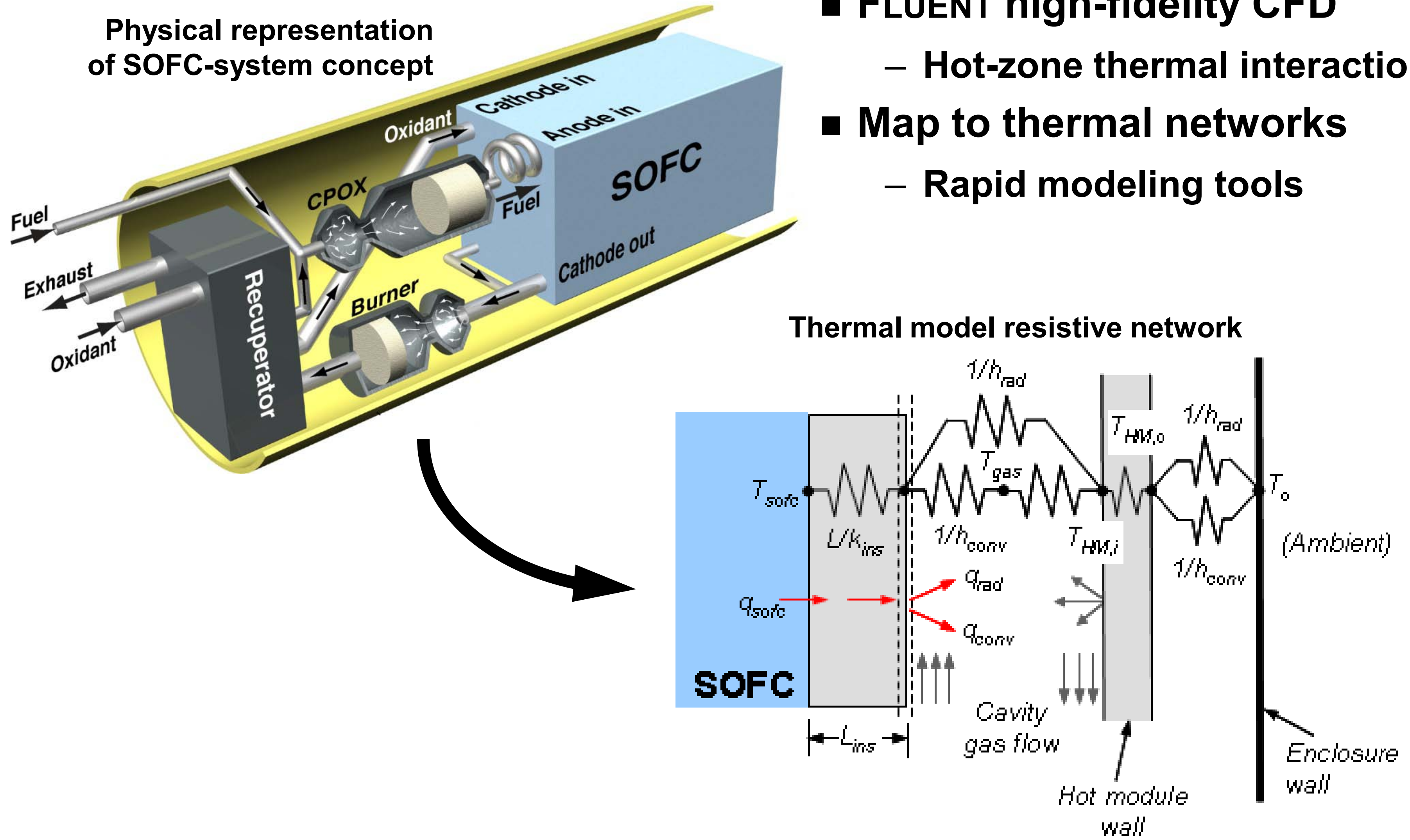
Task 3b Result: Dynamic model of reformer developed; tuned to thermal response of experiment

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

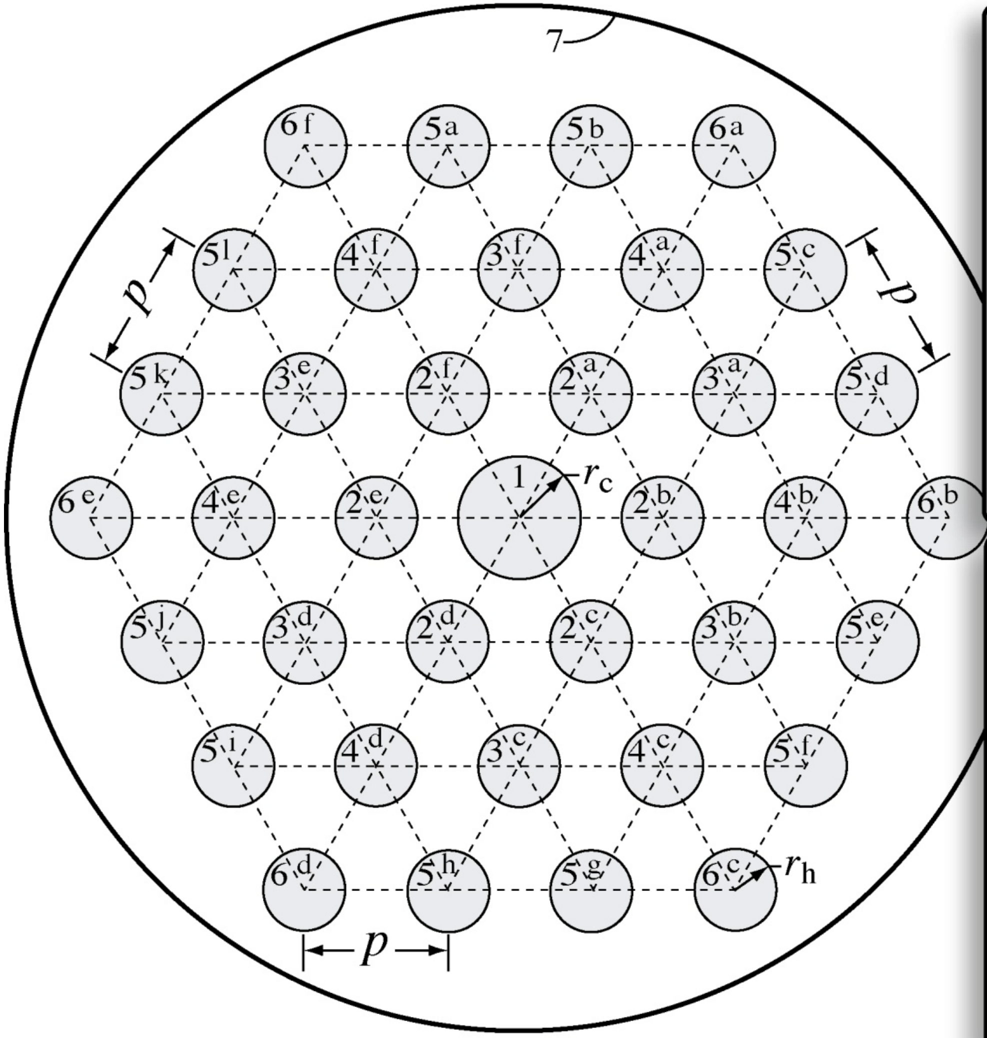


Physical representation of SOFC-system concept

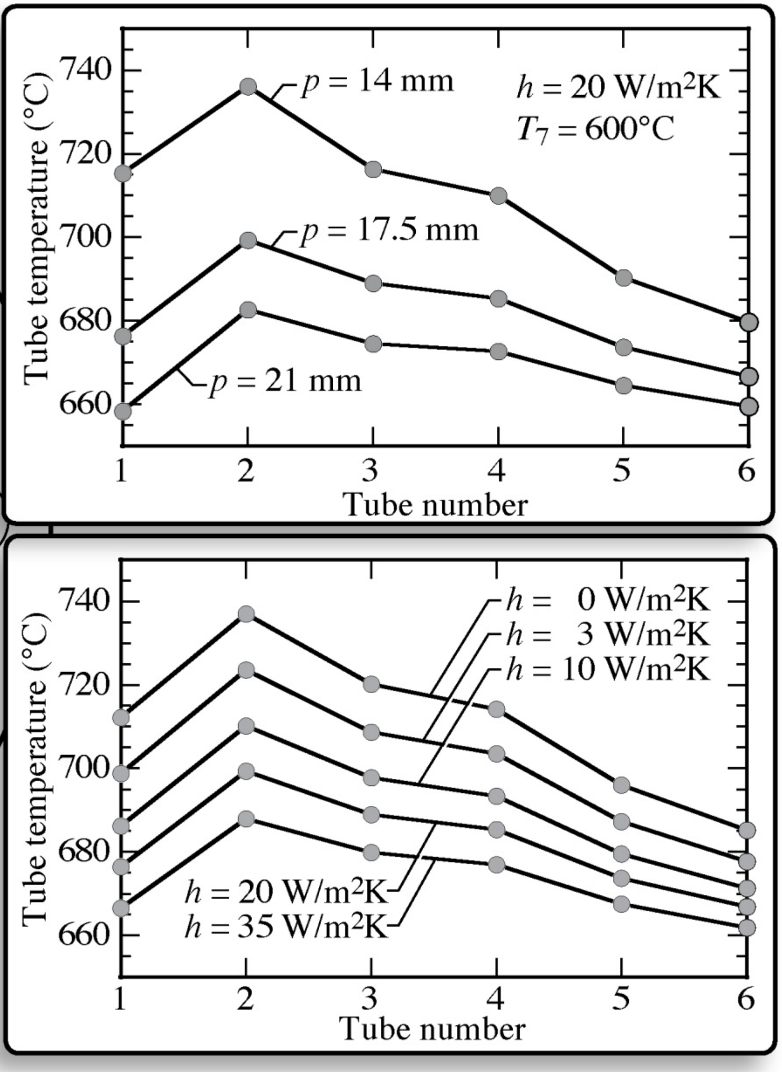
Thermal model resistive network

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



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

CoorsTek

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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: 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