Biomass Fuel Cell Systems

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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: 50%
- **Budget**
  - Total project funding:
    - DOE Share: $1,665,125
    - CSM Share: $425,018
  - Funding received in FY10: $0
  - Funding for FY11: $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 and architectures for robust operation
  - Integrate barrier-layer technology into tubular SOFC geometry
  - Develop nickel-free, perovskite-based anode supports
- Task 2: Fuel processing of bio-derived fuels
  - Develop fuel-reforming strategies for anaerobic-digester-derived biogas
  - 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
  - System modeling: explore tradeoffs in biogas-processing approaches
    - Use of cyrogenic oxygen on-site at waste-water treatment facilities

Task 1 Approach: Develop materials and architectures to improve SOFC durability under biomass-derived fuels

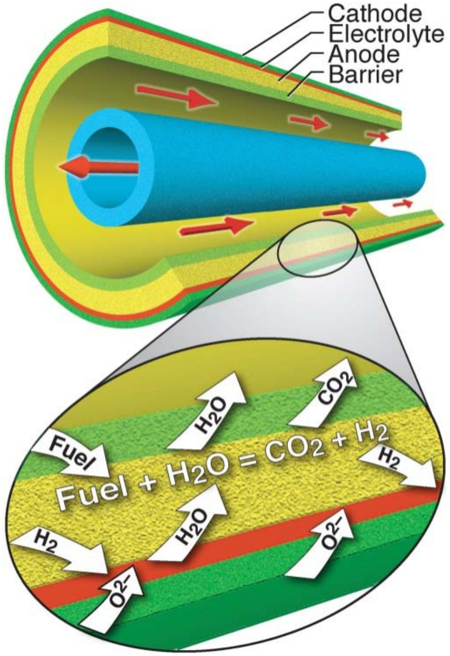
- Apply planar barrier-layer technology to tubular SOFC geometries
  - Inert barrier layer within anode support
    - Reduce gas-transport rates
    - Increase local steam concentration within anode structure
    - Promote internal reforming over deposit formation
  - ~ 1-kW APU target application – tubular geometries for fast start-up
  - Milestone: 50-hrs continuous operation on hydrocarbons (100%)

- Develop perovskite-based, next-generation tubular anode supports
  - Pros: perovskites more tolerant to sulfur, redox, and heavy hydrocarbons
    - Broaden the range of deposit-free SOFC operation
  - Cons: perovskite catalytic activity lower than existing solutions
    - Utilize nickel-based anode function layer to promote internal reforming
  - Milestone: 50-hrs continuous operation on hydrocarbons (60%)

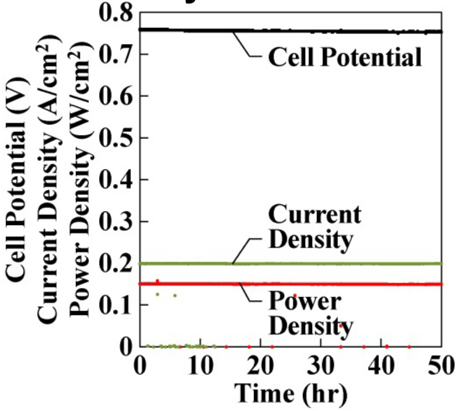
Task 1 Results: Barrier layers synthesized, integrated, and operated with CoorsTek tubular SOFCs

- Tubular perovskite barrier layers synthesized
  - $Sr_{0.8}La_{0.2}TiO_3$ (SLT) materials
  - ~ 40% porosity
  - ~ 15 S / cm conductivity
- Integrated with CoorsTek SOFC
  - Traditional Ni-YSZ anode materials
  - Low-cost “reaction-sintering” fabrication
- > 50 hrs continuous operation demonstrated
  - Biogas fuel: 65% CH_4 / 35% CO_2
  - Current density: 0.20 A / cm^2
  - Minimal degradation; no deposits observed
- Extending effort to perovskite-based SOFCs
  - SLT-based anode support
  - Ni-YSZ anode functional layer
  - Cell development underway

Barrier-layer architecture



Barrier-layer test results



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

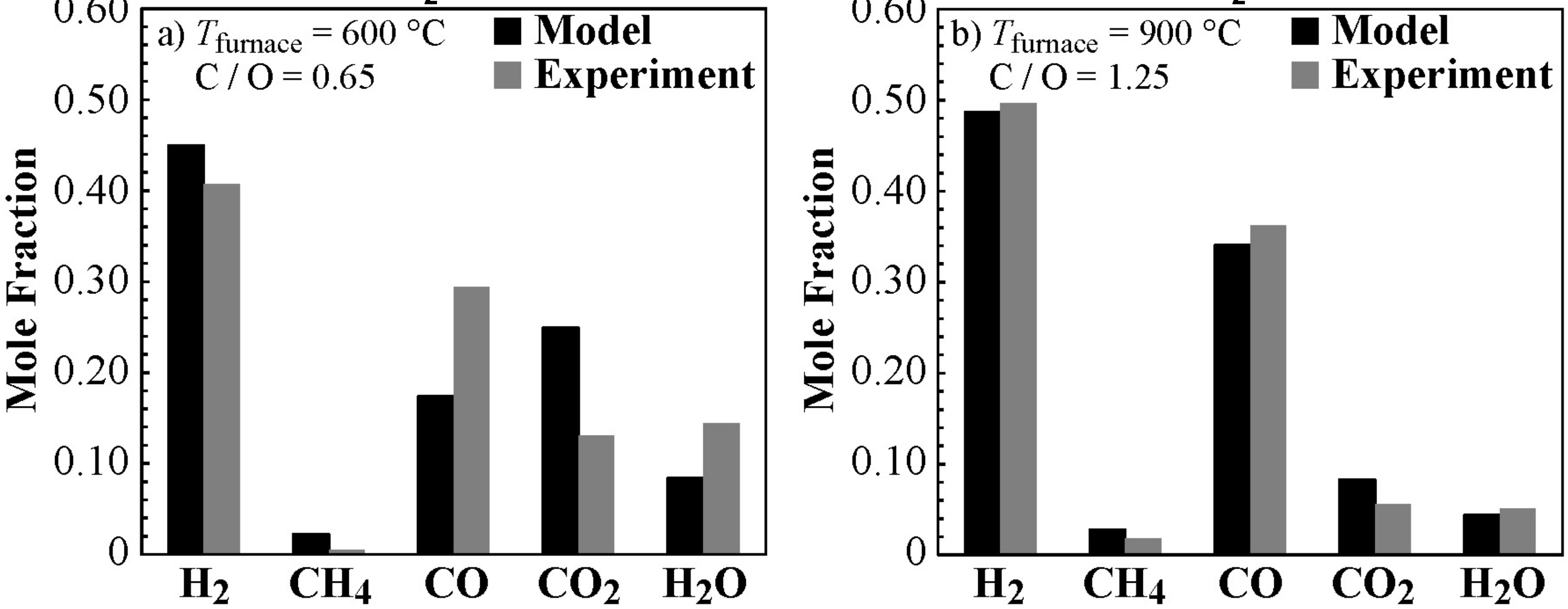
- Biogas fuels: anaerobic digesters at waste-water treatment facilities
  - Low-quality methane stream: 65% CH_4 / 35% CO_2
  - Requires clean-up of sulfur and siloxanes upstream of reformer & stack
    - Commercial clean-up technology exists (e.g. Xebec desiccant system)
  - Target MW-scale power generation
- Explore fuel-reforming options to convert biogas to syngas (H_2 + CO)
  - Catalytic partial oxidation (CPOX - air and / or O_2)
    - Simplest approach, lower capital cost, but lower system efficiency
      - Utilize cryogenic O_2 on-site at waste-water treatment facilities
  - Steam reforming
    - Endothermic, high capital cost, but improved system efficiency
- Milestone: Complete analyses of biogas external-reforming (100%)
- Biomass-derived liquid fuels: butanol (C_4H_9OH)
  - Reduced effort at direction of 2010 DOE AMR reviewers
- Integrate with ceramic microchannel reactor technology
  - Increased effort at direction of 2010 DOE AMR reviewers

Task 2 Results: Kinetic models used to guide definition of external-reforming operating windows

- Reacting-flow model with multi-step elementary reaction chemistry
- Exercised across numerous reforming approaches
- Validated with experiments utilizing Rh on porous Al_2O_3 foam
  - High-temperature reforming enables conversion of CO_2 to CO
  - Models generally underpredict CO_2 conversion

Biogas reformate composition

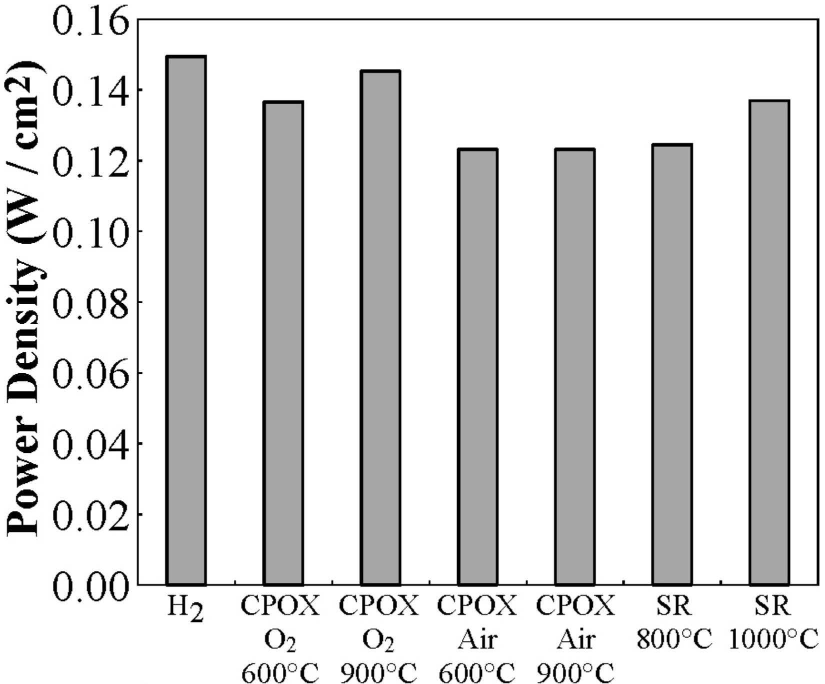
CPOx O_2 at 600 °C **CPOx O_2 at 900 °C**



Task 2 Results: SOFC electrochemical performance under reformed biogas can rival that of humidified H_2

- Reformate fed to CoorsTek SOFC
- Electrochemical performance
  - Current density at 800 °C
  - Cell potential = 0.65 V
  - Fuel utilization = 70 %
- Humidified H_2: *P”* = 0.15 W / cm^2
- CPOX-O_2
  - 900 °C: *P”* = 0.145 W / cm^2
  - 600 °C: *P”* = 0.137 W / cm^2
- Steam reforming
  - 1000 °C: *P”* = 0.137 W / cm^2
  - 600 °C: *P”* = 0.125 W / cm^2

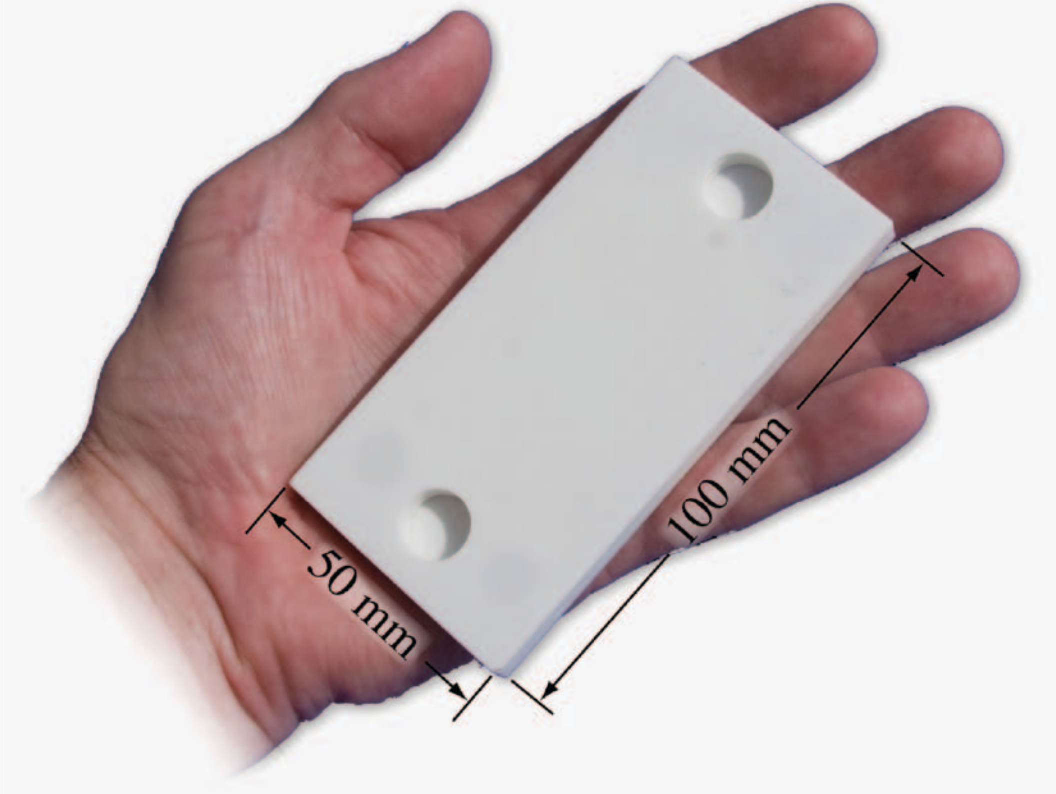
SOFC performance under biogas reformate, baselined to H_2 fuel

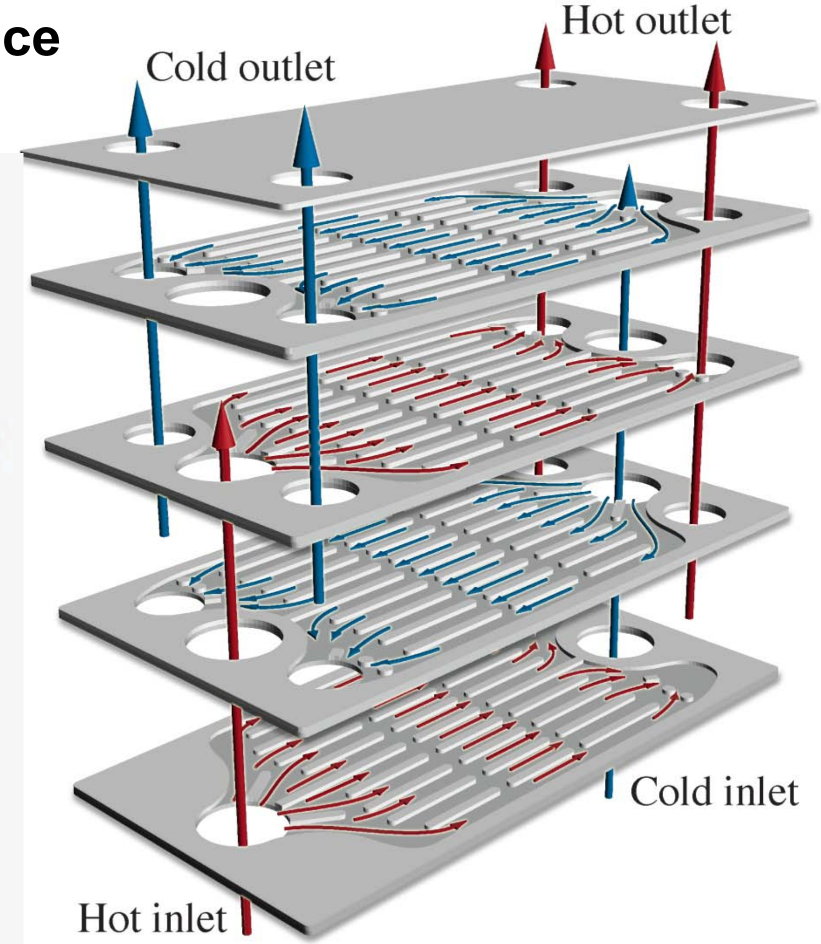


- System performance under study (Task 3)

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

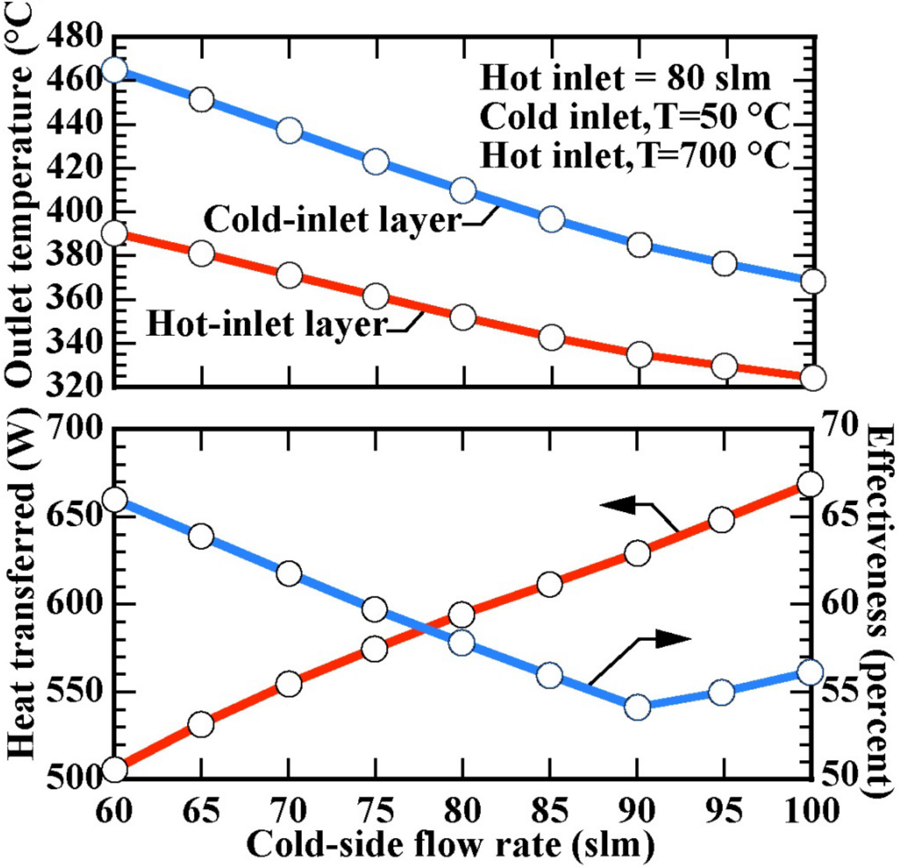




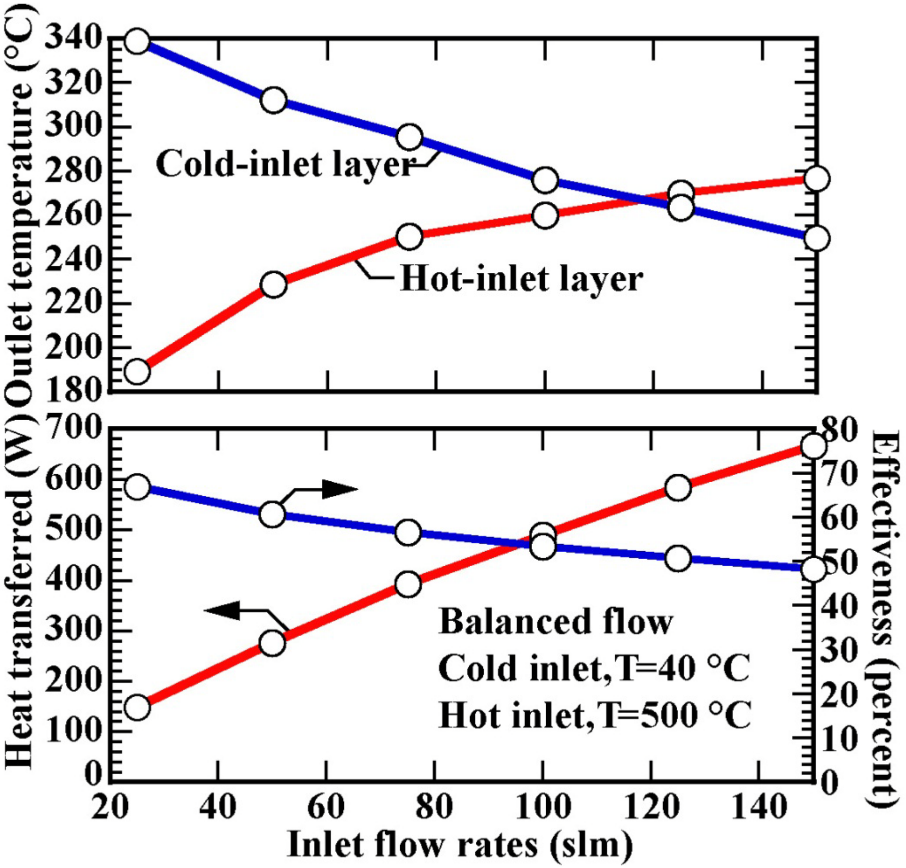
Generation-5 design

Task 2 Result: Performance of ceramic microchannel heat exchanger measured over a broad range

Balanced flow results



Unbalanced flow results



- Effectiveness to nearly 70% demonstrated
- ~ 700 W transferred
- Now moving towards catalyst addition and thermal cycling

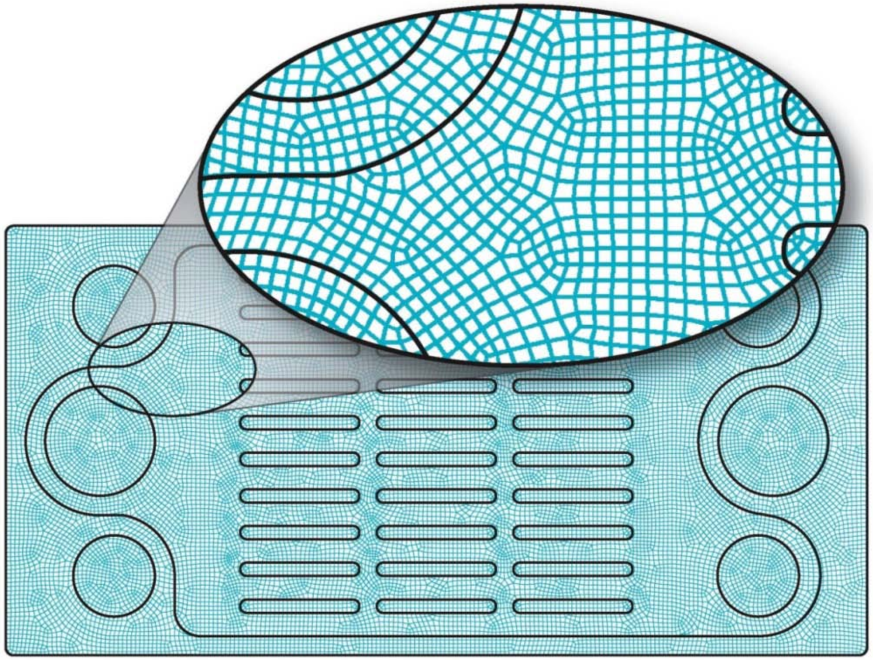
Task 3 Approach: Provide modeling support for Tasks 1 and 2 using CFD and chemically reacting-flow tools

- **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
    - Examine biogas fuel processing options

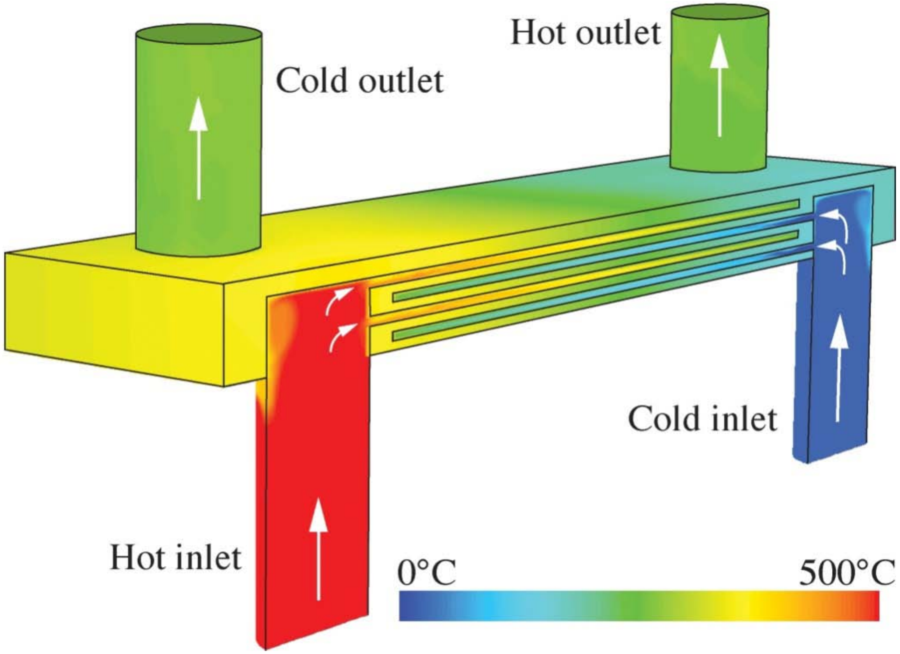
Task 3a Approach: CFD and chemically reacting-flow models integrated to provide HX-design guidance

- 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
- Tight collaboration with developers at ANSYS / FLUENT

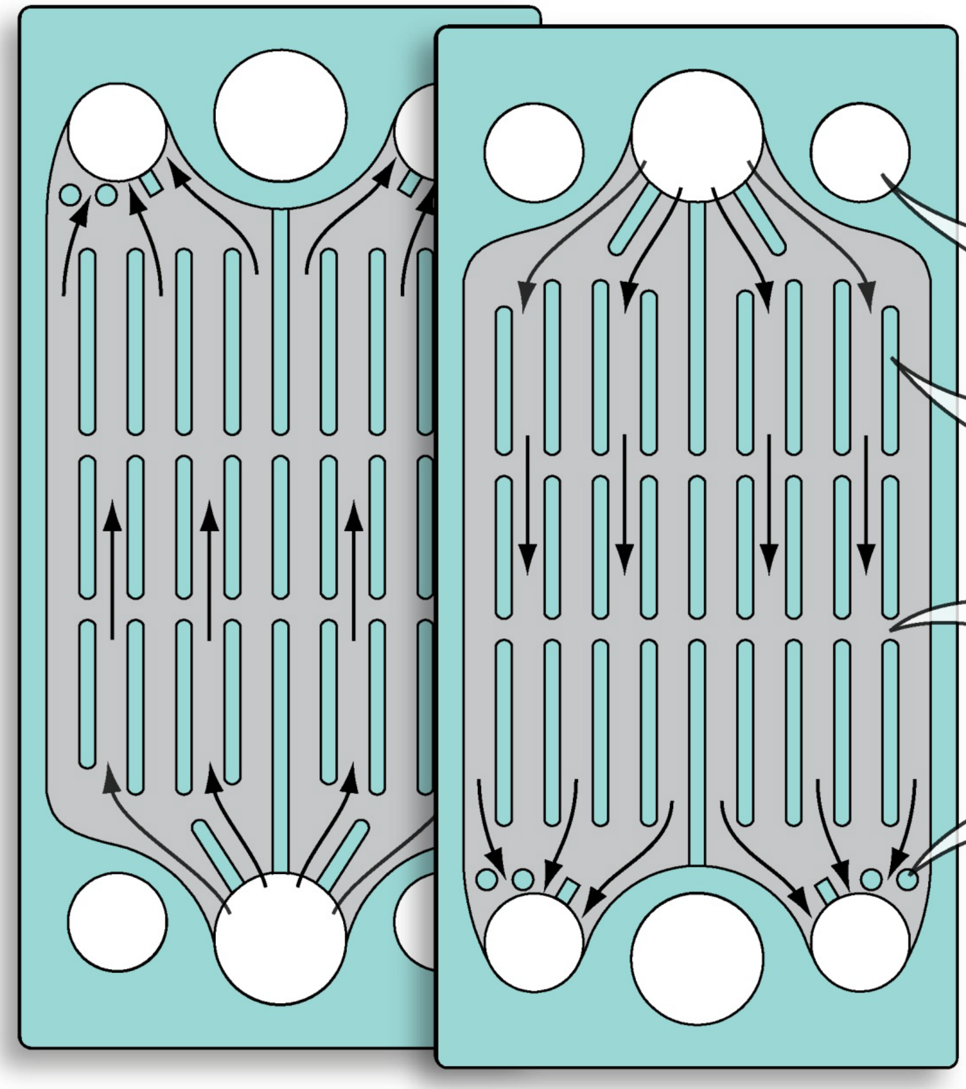
Numerical mesh used in FLUENT simulations



Characteristic ANSYS/FLUENT solution Thermal-field, non-reacting flow



Task 3a Result: Three new generations of heat-exchanger design optimize fabrication with operation



Layer symmetry
- Alternate layers flip 180°
- Same geometry for all layers

Large manifold diameters
- Enable multiple layers

Free standing ribs
- Promote flow uniformity

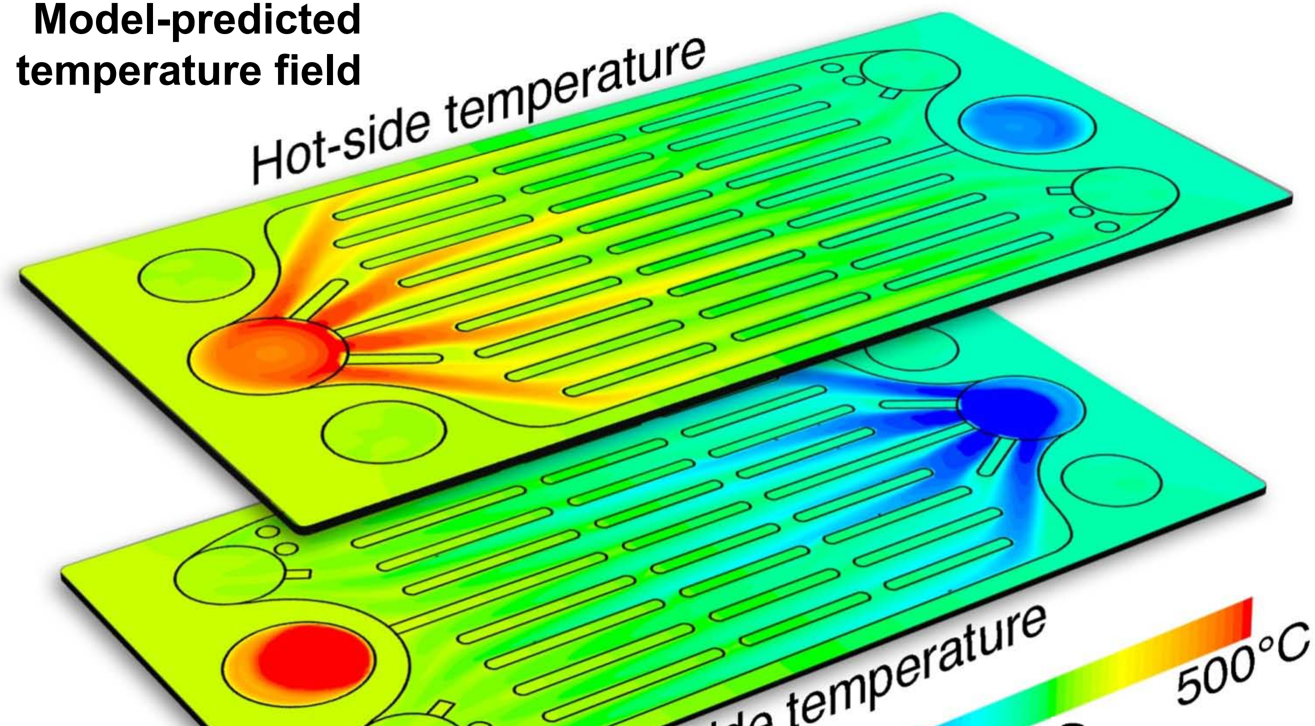
Gaps between ribs
- Reduce axial conduction
- Enhance flow uniformity

Manifold-area supports
- Promote lamination bonding

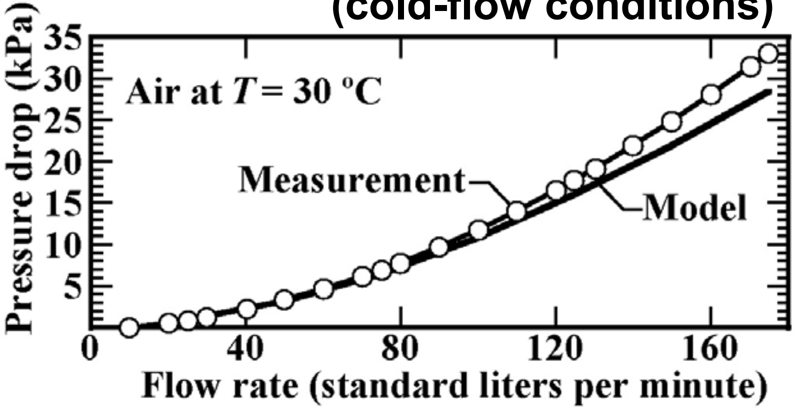
PLIS fabrication
- Each layer is one piece
- Enables free-standing features

Task 3a Result: Model results show even distribution of temperature / flow; match pressure-drop measurements

Model-predicted temperature field

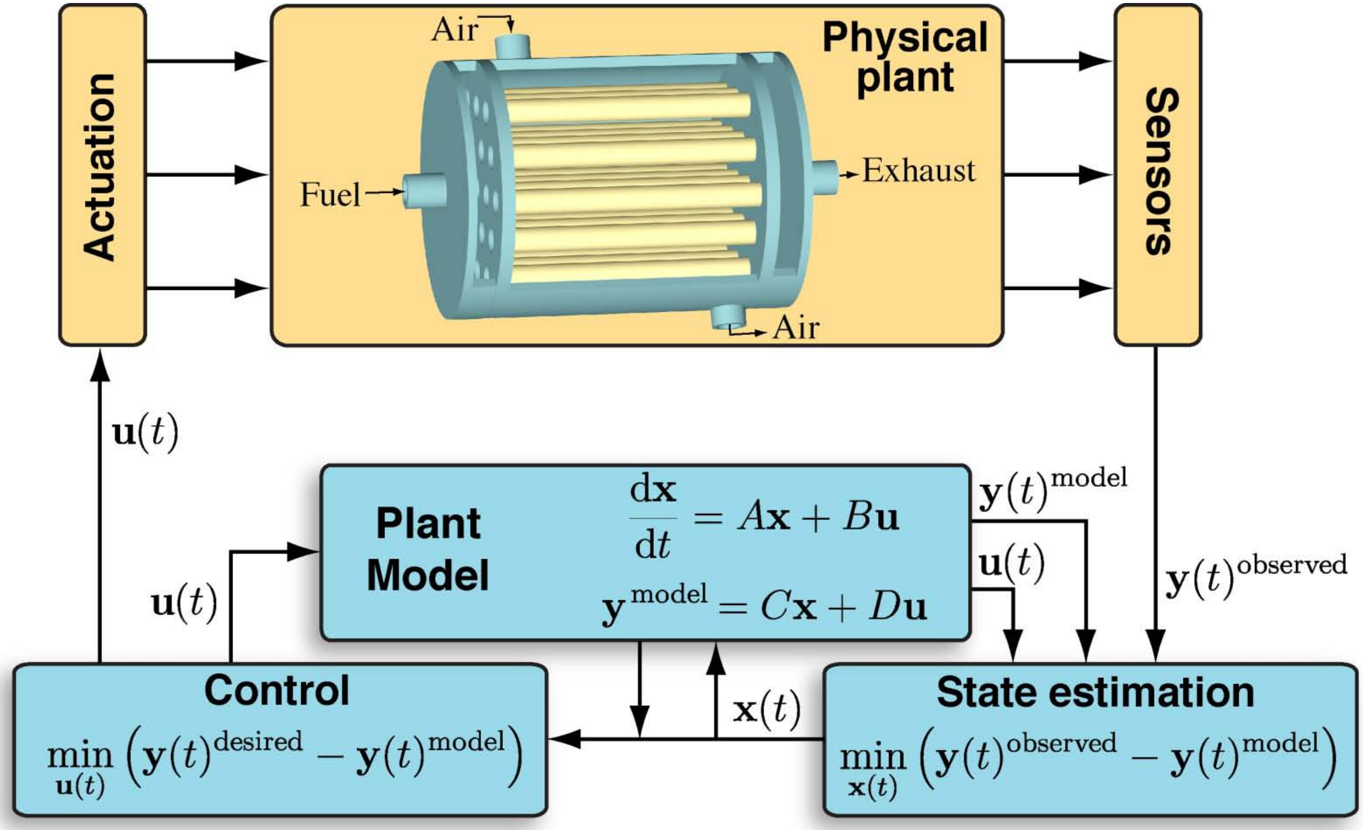


Pressure drop (cold-flow conditions)



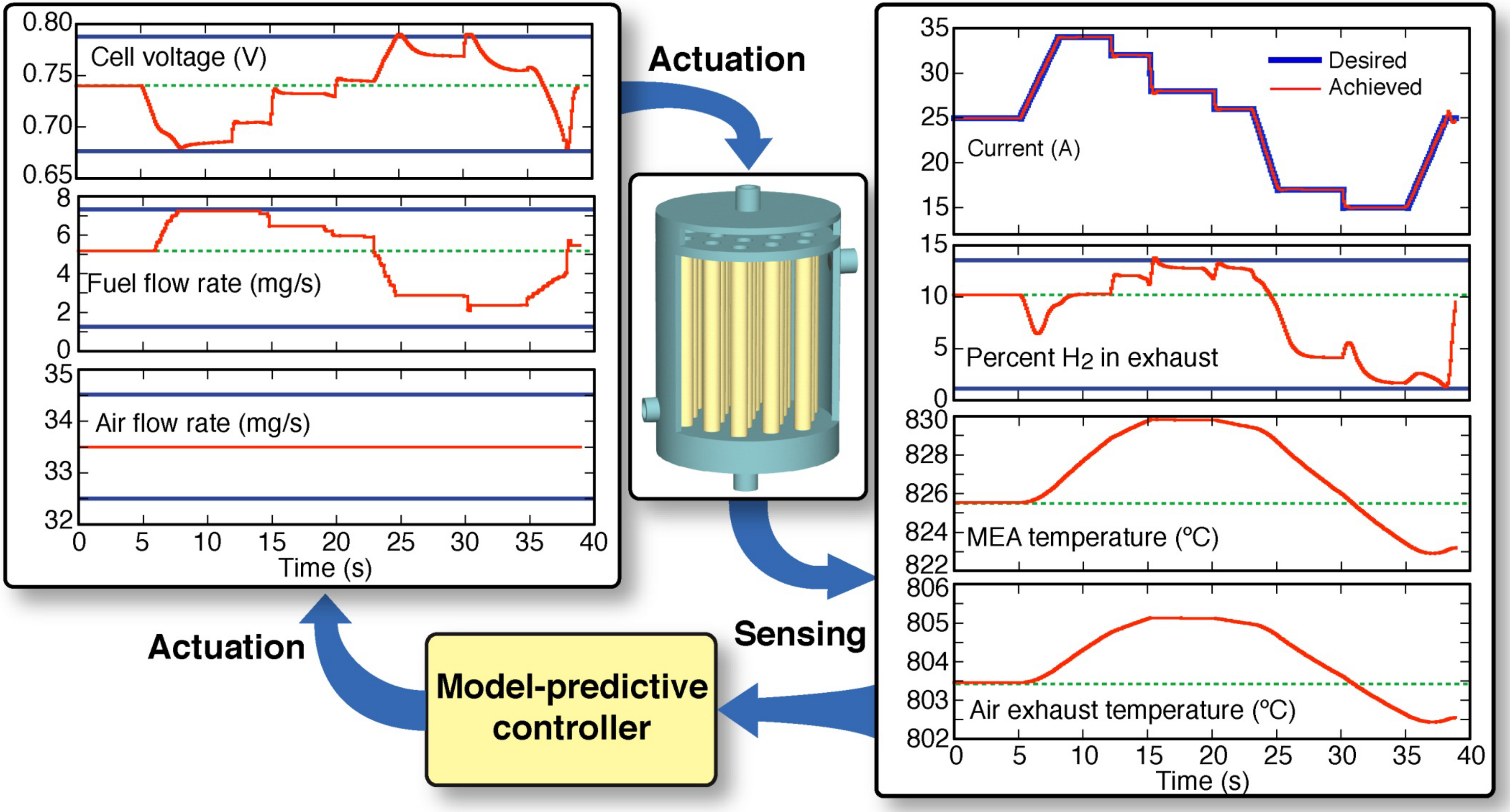
Task 3b Approach: Extend high-fidelity chemically reacting flow models to model-predictive control

- Map high-fidelity CANTERA model results to rapid linear models
- The model-predictive controller (MPC) enables real-time optimization
  - Controller satisfies constraints on actuation and observables
  - Multiple-input--multiple output (MIMO) enables sensor fusion



Task 3b Result: controller makes a complex set of decisions to meet load demand, satisfy constraints

Dynamic response to varying load



Actuation

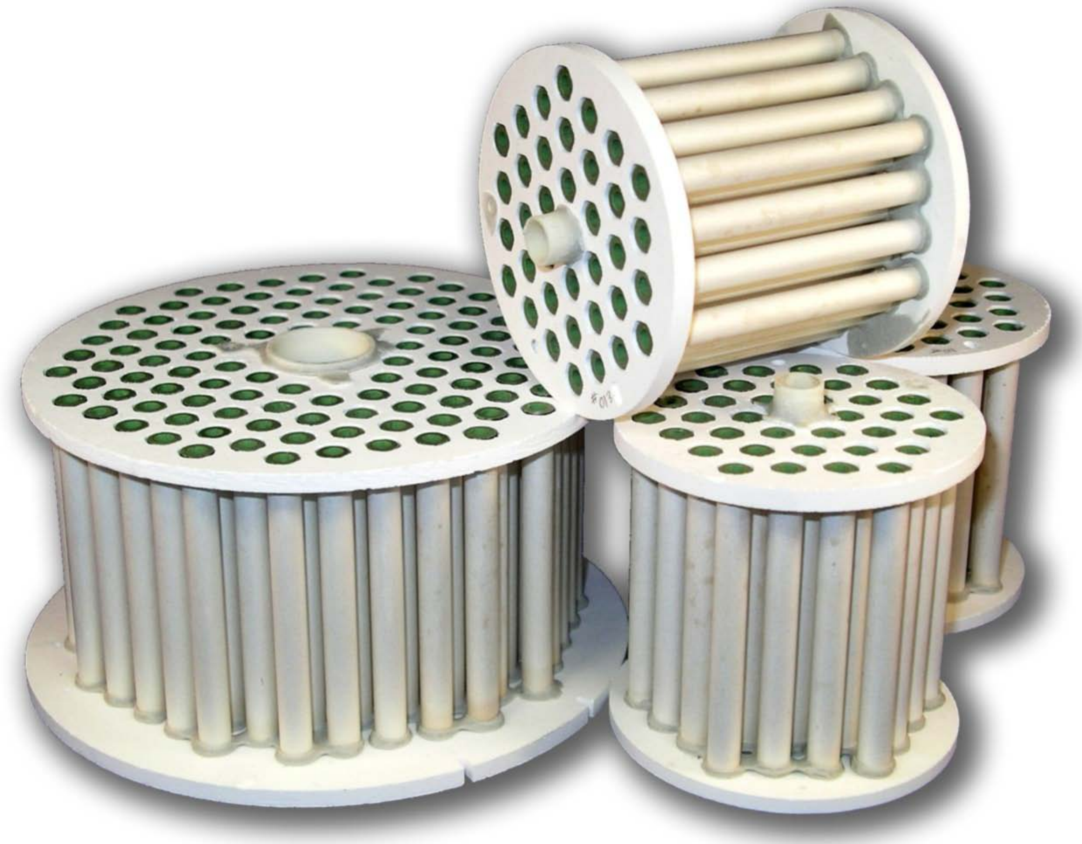
Sensing

Actuation

Model-predictive controller

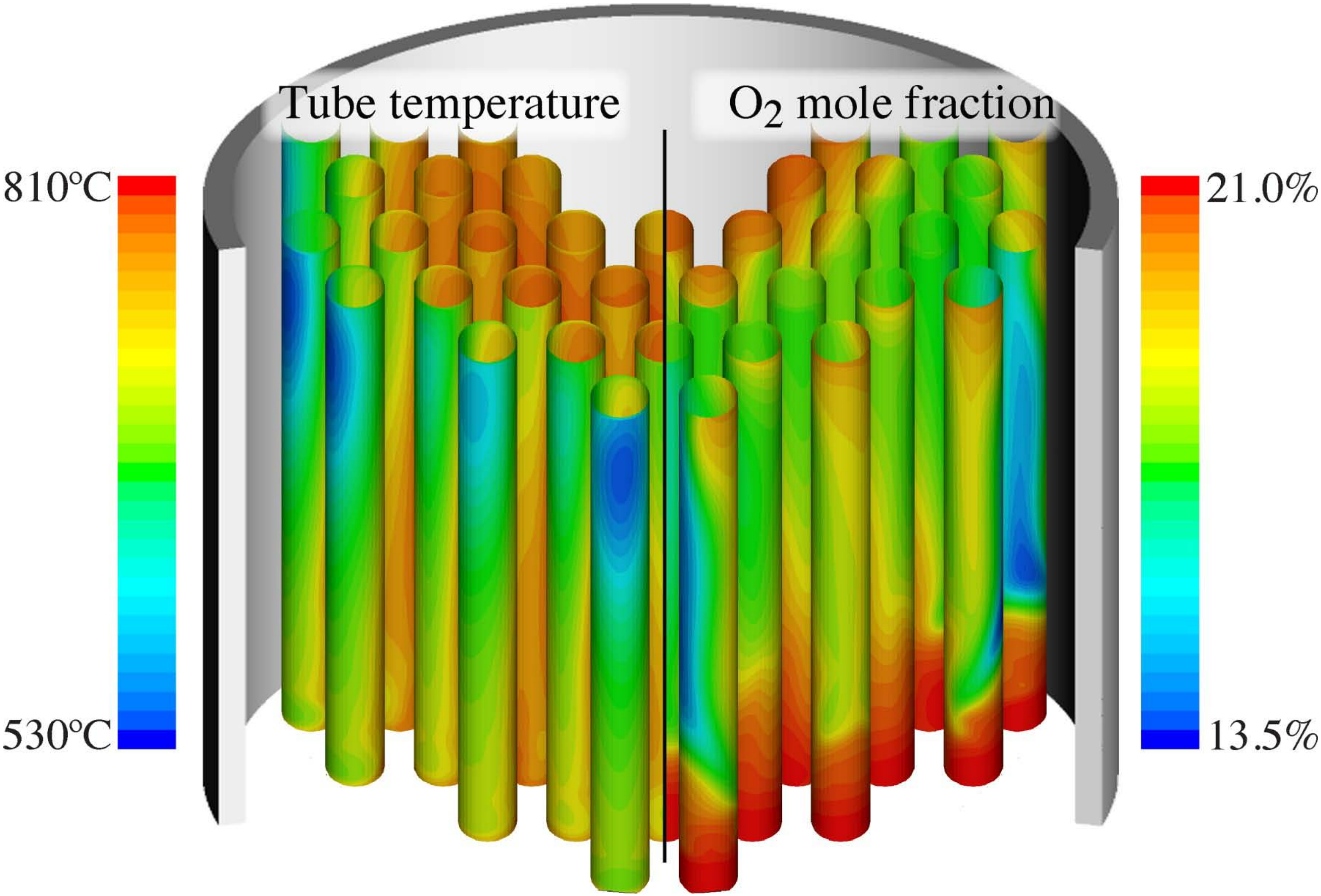
Task 3c Approach: Integrate chemically reacting flow models with FLUENT CFD models

Protonex tubular stacks



- Focus on Protonex stacks
  - Tubular geometry
  - 600-W rated power
  - CPOX reformer
  - Shell-and-tube design
- Cell performance
  - CANTERA chemically reacting flow models
  - Porous media transport
  - Plug-flow within tubes
- Stack fluid dynamics
  - 3-D FLUENT CFD models
  - Coupled to CANTERA
    - User-defined functions

Task 3c Result: Wide variability in temperature and cell-performance within stack



Efficient coupling between external cathode air and chemistry within cells

Industrial collaborations: CoorsTek Inc., Golden, CO

- Largest ceramics company in the United States
  - Recently acquired Ceramatec and St. Gobain
- Supplier of SOFCs and materials for use across multiple tasks
  - Task 1: Provider of baseline Ni-YSZ materials
    - CSM develops barrier layers to extend range of SOFC operation
    - CSM compares Ni-YSZ to next-generation perovskite anodes
  - Task 2: Supplier of tubular SOFCs
    - CSM evaluates cell performance under bio-fuel reformate streams
  - Task 2: Fabricate ceramic micro-channel heat exchangers
    - CSM adds catalyst to reactive side of microchannel 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
  - Better define operating windows for barrier-layer-equipped tubular SOFCs
  - Extend barrier layer concept to integrated anode support with Ni-YSZ anode functional layer
- Task 2: Reforming of biomass-derived fuels
  - Establish deposition process for ceria-based catalyst support in ceramic microchannel reactors
  - Improve sealing approaches; validate through thermal cycling
- 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
    - Develop control algorithms; validate using experimental facility
  - Task 3c: System-level modeling
    - Explore effects of biogas fuel-processing strategies on performance

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 and architectures
  - Utilize microchannel-reactor technology for tight thermal integration
- Results
  - Demonstrated extended operation of first tubular barrier-layer SOFC
  - Explored unconventional biogas fuel-reforming strategies
  - Measured performance of ceramic microchannel heat exchangers
  - Utilized modeling tools for design of stacks, controllers, and BoP
- Future work
  - Establish SOFC operation using perovskite anode-support materials
  - Extend microchannel-reactor technology to biogas fuel reforming
  - Explore effects of biogas-reforming approaches on system efficiency