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Thermal-fluid and Flow-sheet Modeling of HTE Systems, and In Situ X-ray and Electro-chemical Studies of HTE Electrode Materials

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INL

Overview: Thermal-fluid and Flow-sheet Modeling of HTE Systems

Barriers

- Non-uniform current and temperature profiles leading to faster degradation in electrochemistry and mechanical integrity
- System integration and efficiency

Timeline

- Start – FY'04

Budget (ANL)

- Funding FY'06: 120K
- Funding FY'07: 234K

Partners

- Idaho National Laboratory
- Ceramatec Inc.

Overview: *In Situ X-ray and Electro-chemical Studies of HTE Electrode Materials*

Barriers

- Energy losses at the oxygen electrode and its interfaces, and the lack of knowledge about the underlying causes.

Partners

- University of Nevada – Las Vegas
- Idaho National Laboratory

Timeline

- Start – FY’05

Budget (ANL)

- Funding FY’06: 44K
- Funding FY’07: 76K

Thermal-fluid and Electrochemical Modeling of HTE Cells and Stacks

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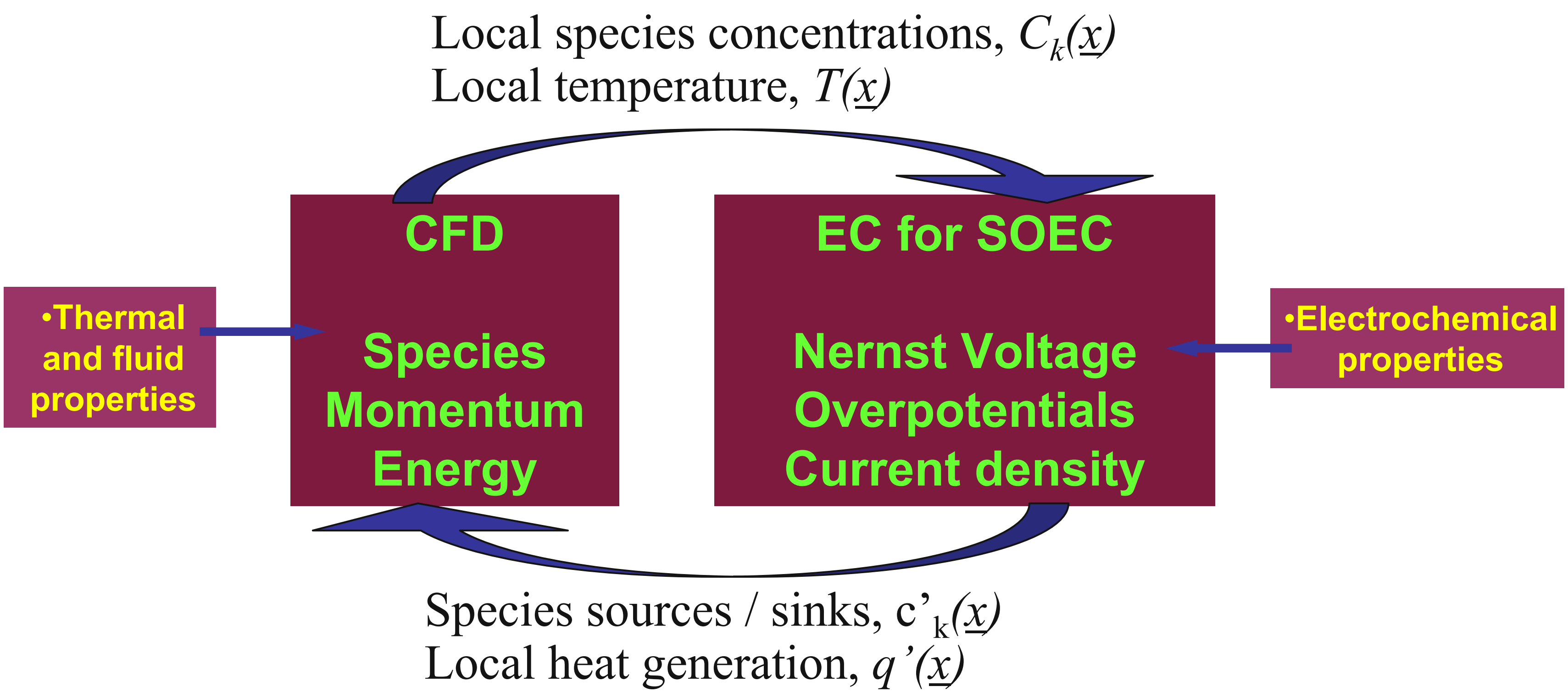
SOEC Thermal-fluid and Electrochemical Analysis

Objective

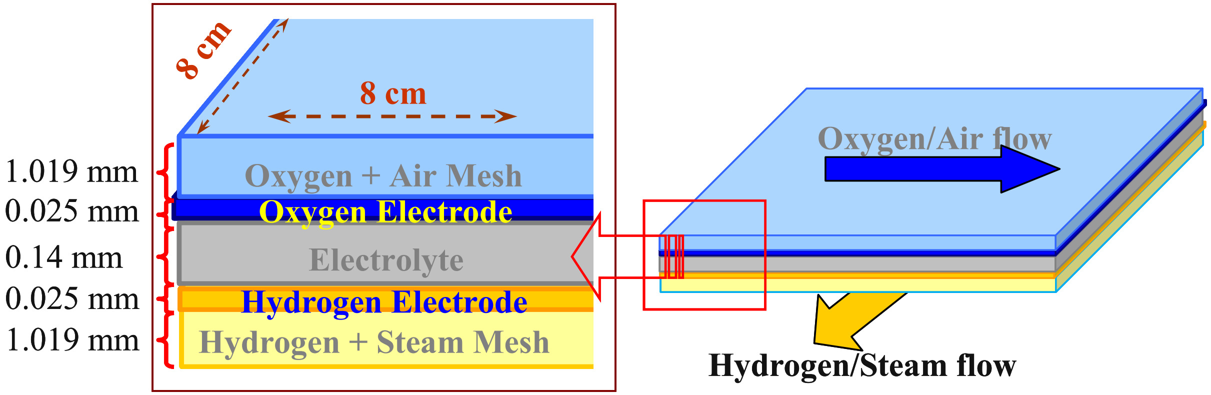
- Identify solid oxide electrolysis cell (SOEC) configurations and operating conditions for favorable electrochemical and thermal performance.

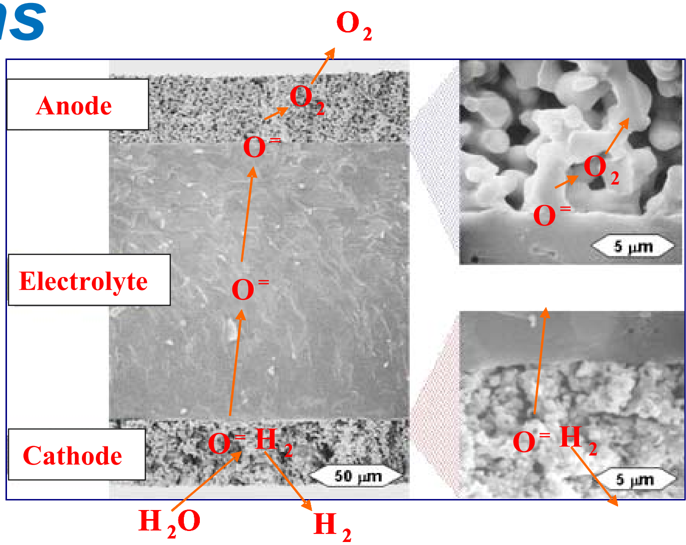
Approach

- Electrochemical (EC) and thermal analysis of the SOECs using a computational fluid dynamics (CFD) technique.



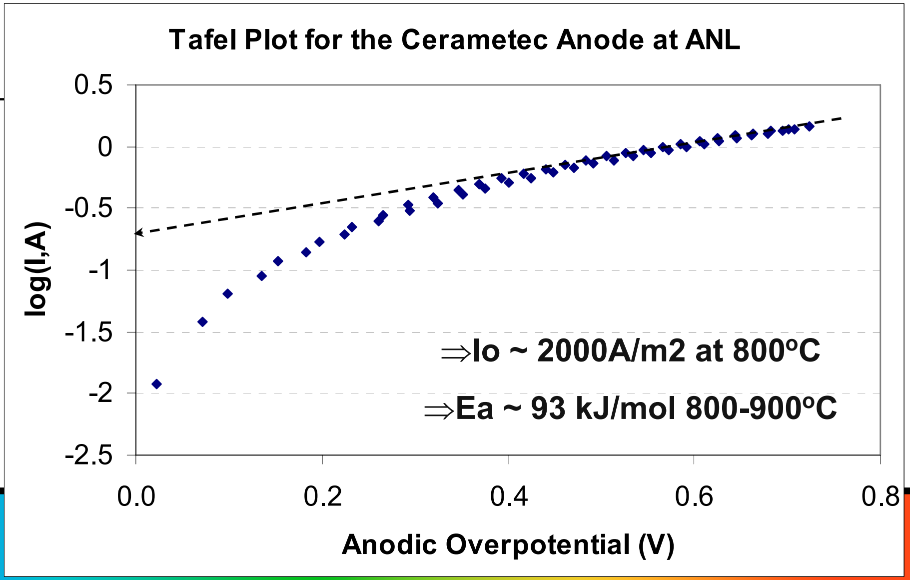
Model Description and Simulations



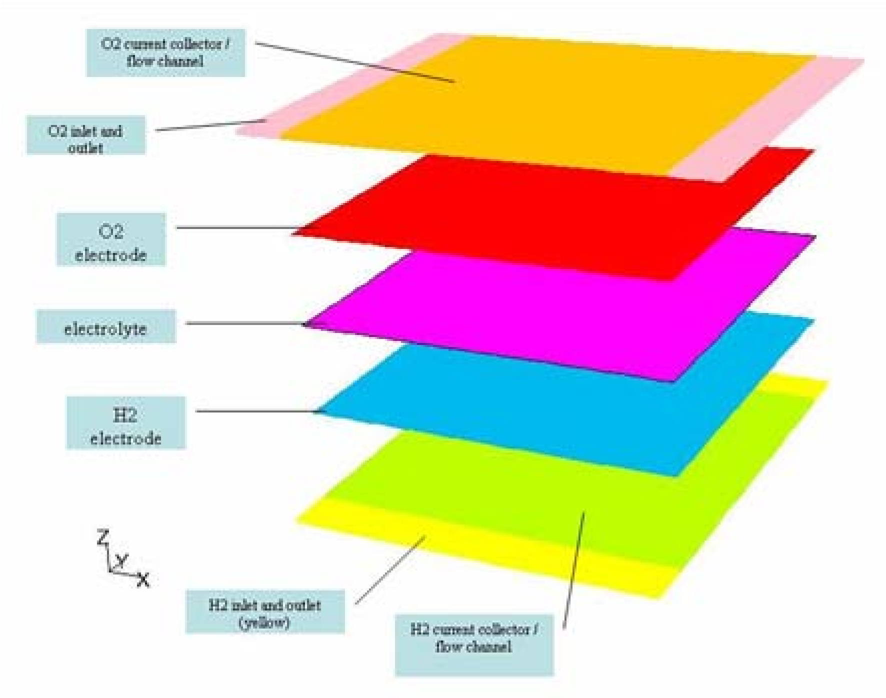


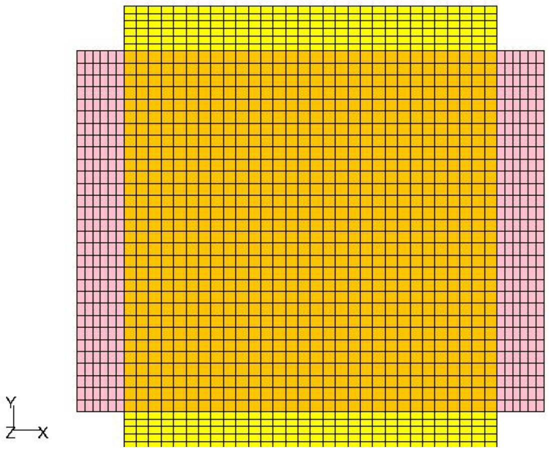
- Operation parameters based on Ceramatec and INL's SOEC system.
- Porous flow meshes and electrodes, and solid electrolyte.
- Major assumption: Reaction activation is controlled by Butler-Volmer kinetics.

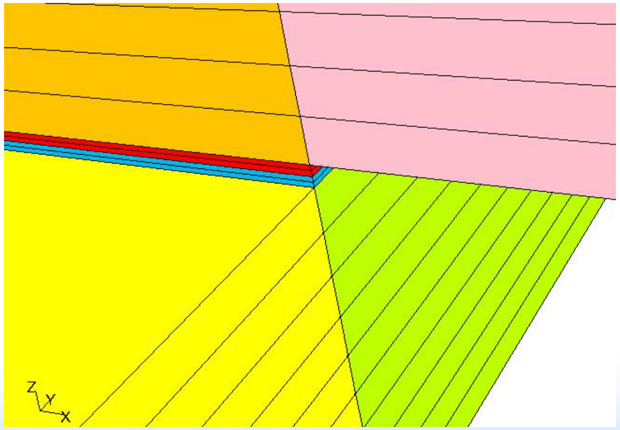
$$V_{appl} - V_{Nernst} = \underbrace{\eta_{\Omega}^{anode}(i) + \eta_{\Omega}^{cathode}(i) + \eta_{\Omega}^{electrolyte}(i)}_{\text{Ohmic losses}} + \underbrace{\eta_{act}^{anode}(i) + \eta_{act}^{cathode}(i)}_{\text{Activation losses}} + \underbrace{\eta_{diff}^{anode}(i) + \eta_{diff}^{cathode}(i)}_{\text{Diffusion losses}}$$



FLUENT Single-Cell SOEC Model







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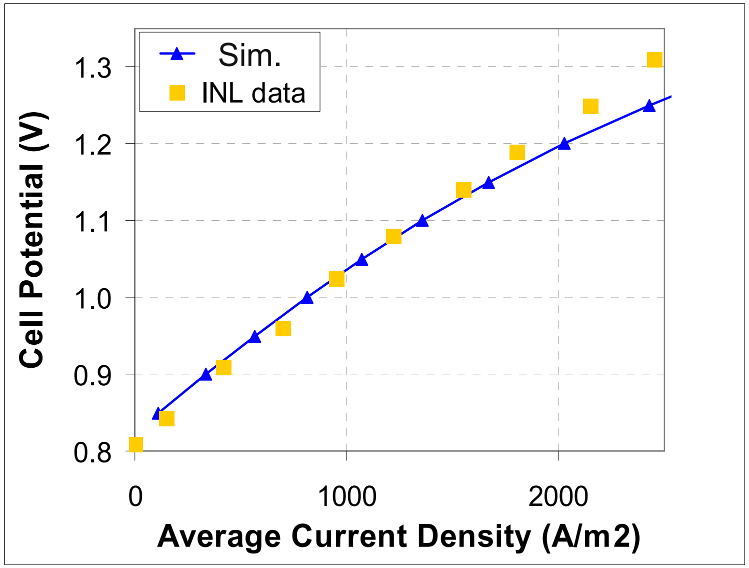
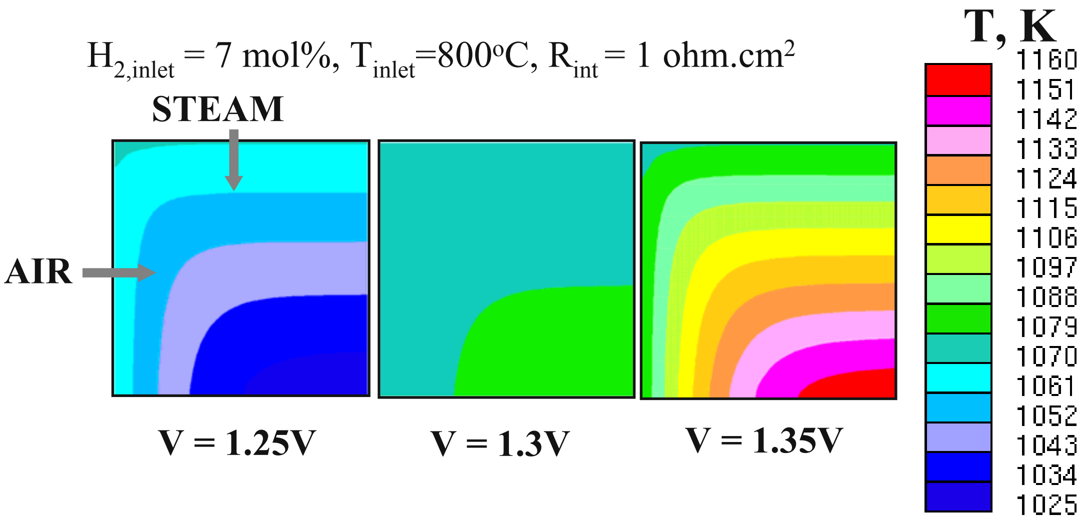
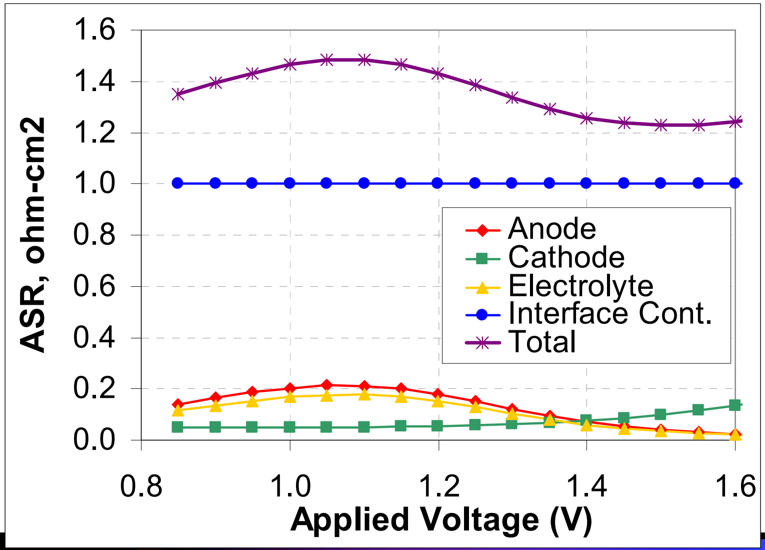
Technical Accomplishments

- Identified the contribution of SOEC components to total resistance losses.
- Analyzed the effect of SOEC size and inlet flow rates on the SOEC thermal behavior
- Evaluated various flow inlet configurations
- Identified the effect of oxygen electrode degradation on the thermal and electrochemical behavior of the planar SOEC.

Contribution of Cell Components to Resistance

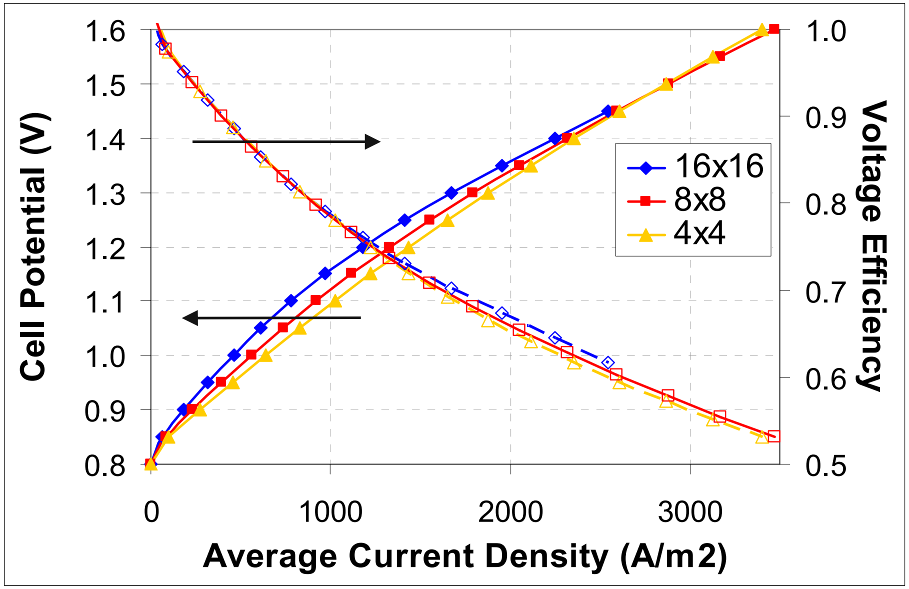


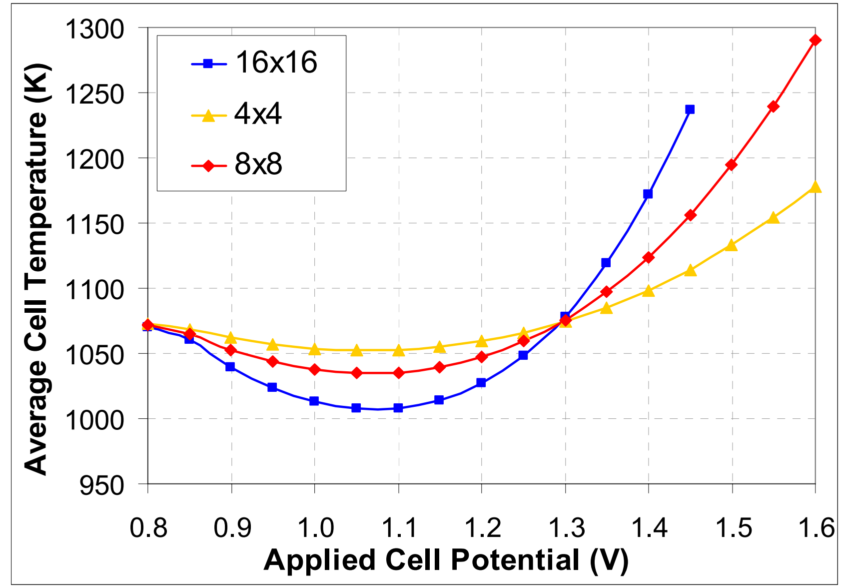


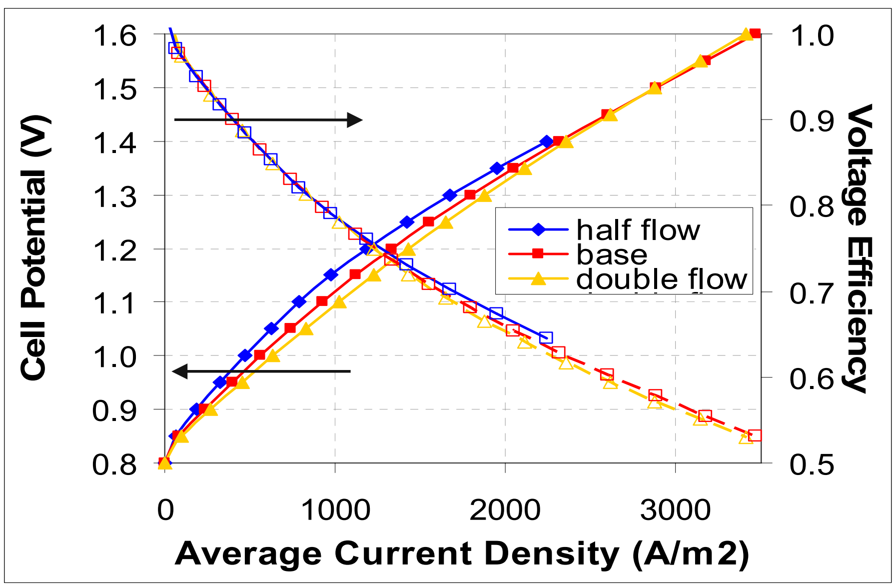


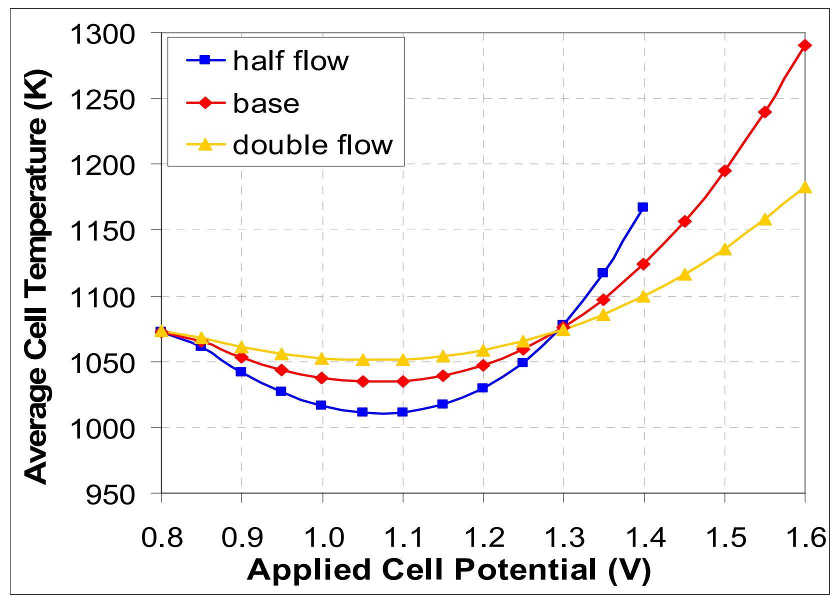
- Interfacial "contact" resistances in SOEC stack is the largest contributor to efficiency loss after the oxygen electrode.

Effect of SOEC Size and Inlet Flow Rates

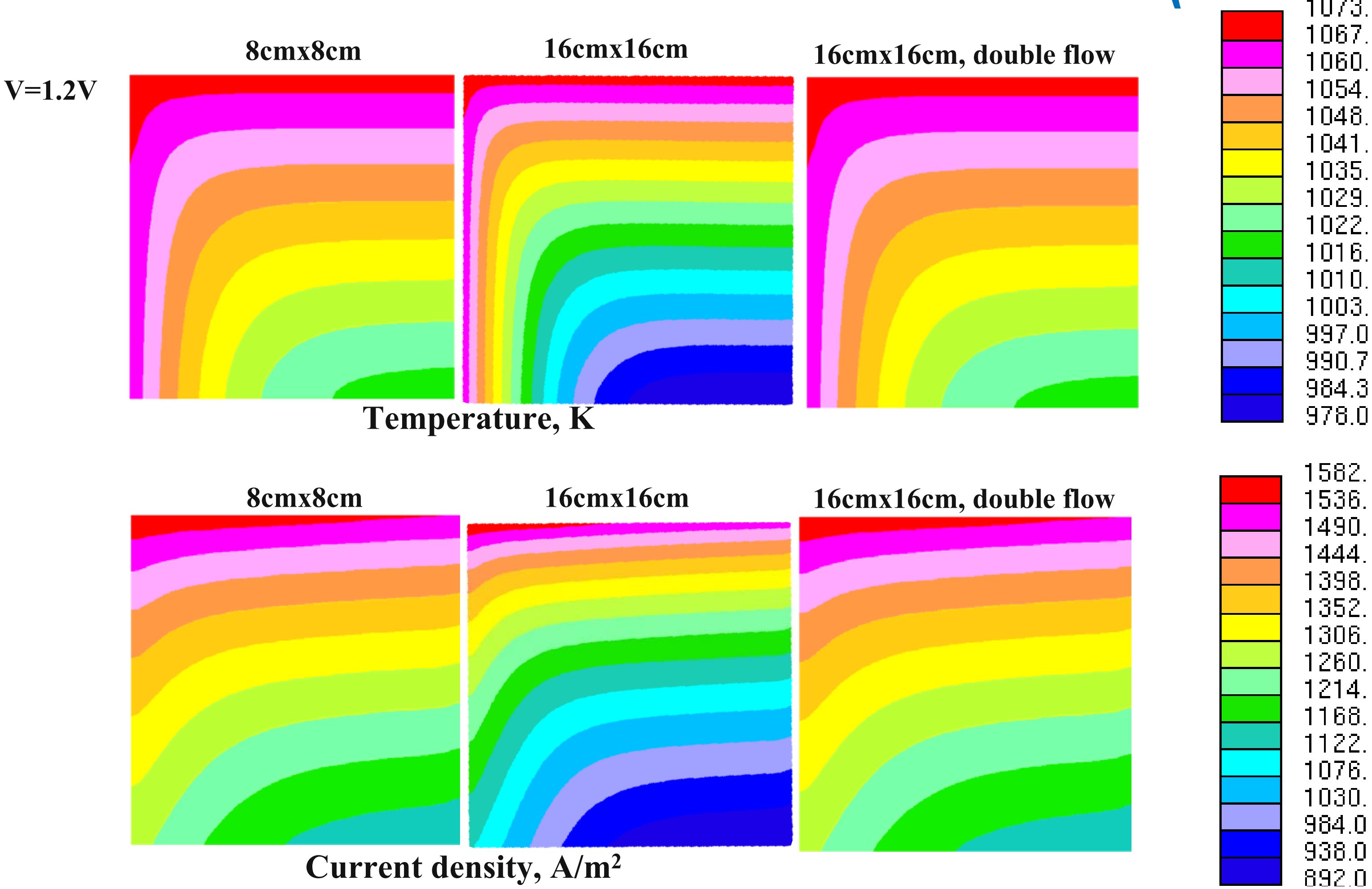






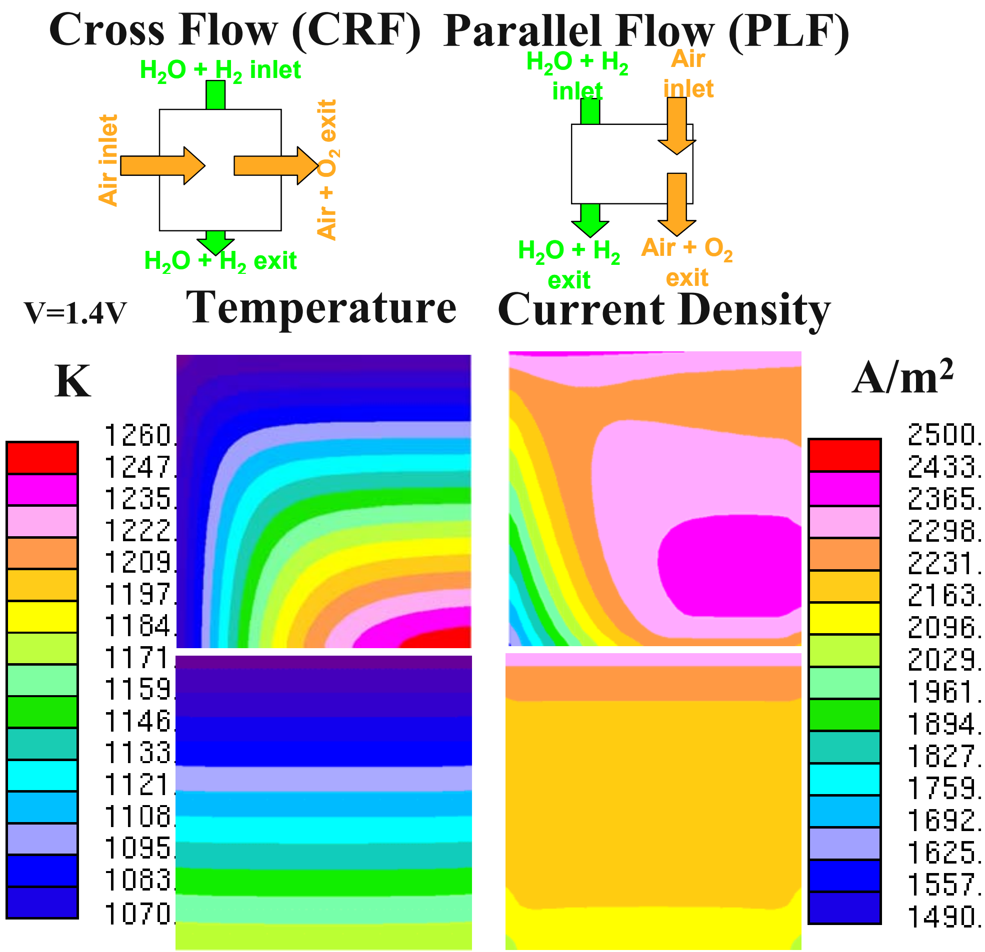


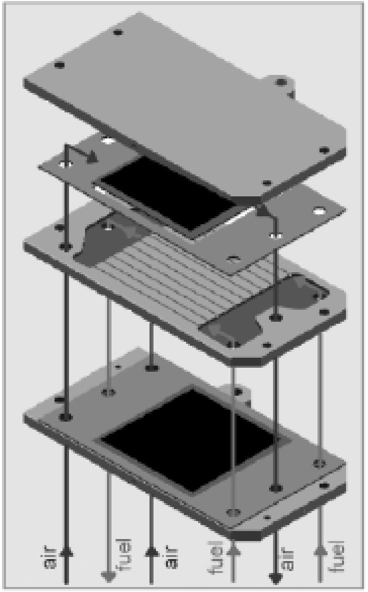
Effect of SOEC Size and Inlet Flow Rates (cont.)

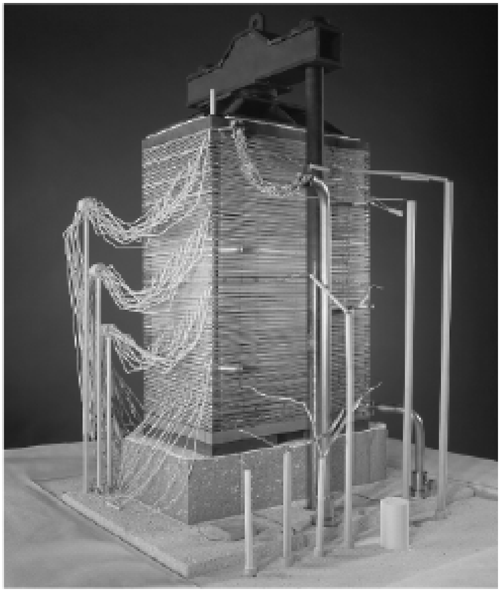


- Larger SOEC cell size can help reduce the capital expenses
- The resulting large thermal and current density gradients can be reduced by an increase in the inlet flow rates.

Effect of Flow Inlet Configurations







Viability → e.g. Forschungszentrum-Julich *counter-flow* design

Advantages of parallel flow

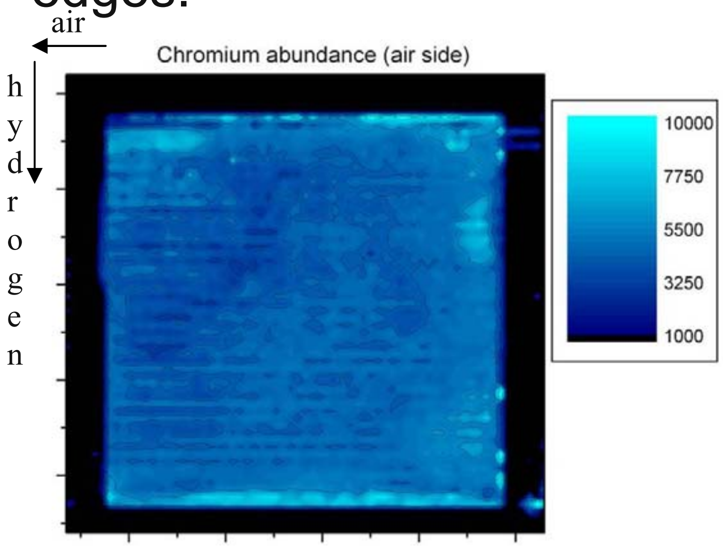
More uniform utilization of steam
→ *Lower electrochemical degradation*

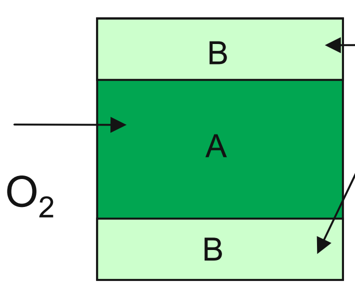
Lower thermal gradients gradients.
→ *Better structural integrity*

➔Optimization between thermal, electro-chemical and mechanical performance is needed.

Oxygen Electrode Degradation

- Cr-deposits, into the electrode and along the edge rails.
- Reaction with seals along edges.

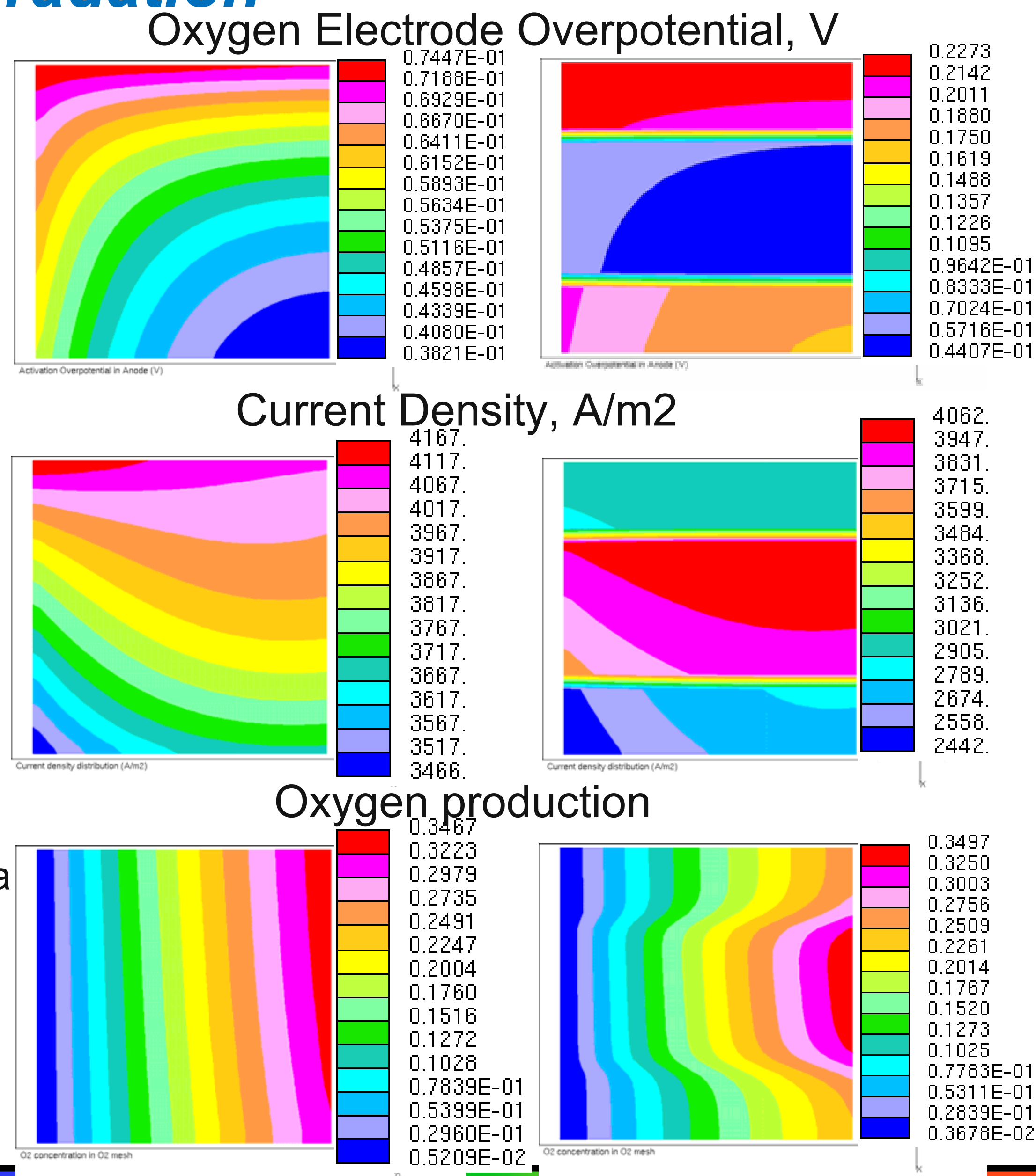




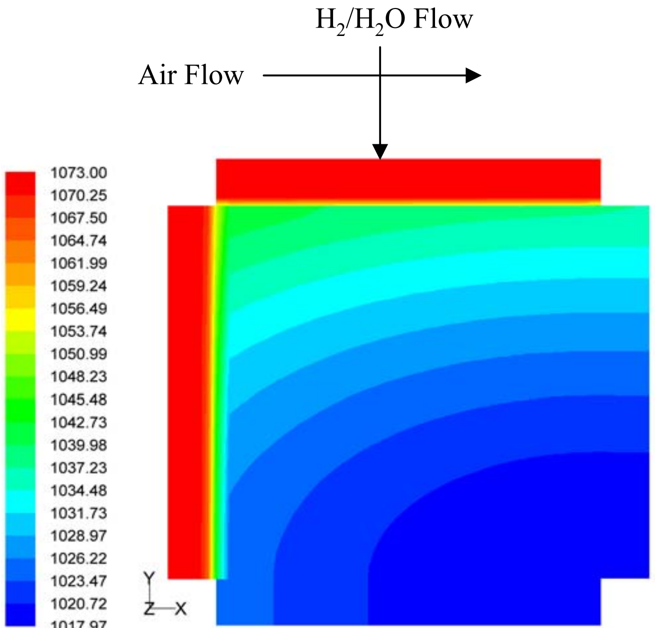
2 cm degraded area near the edge rails

$R_A=2R_o$

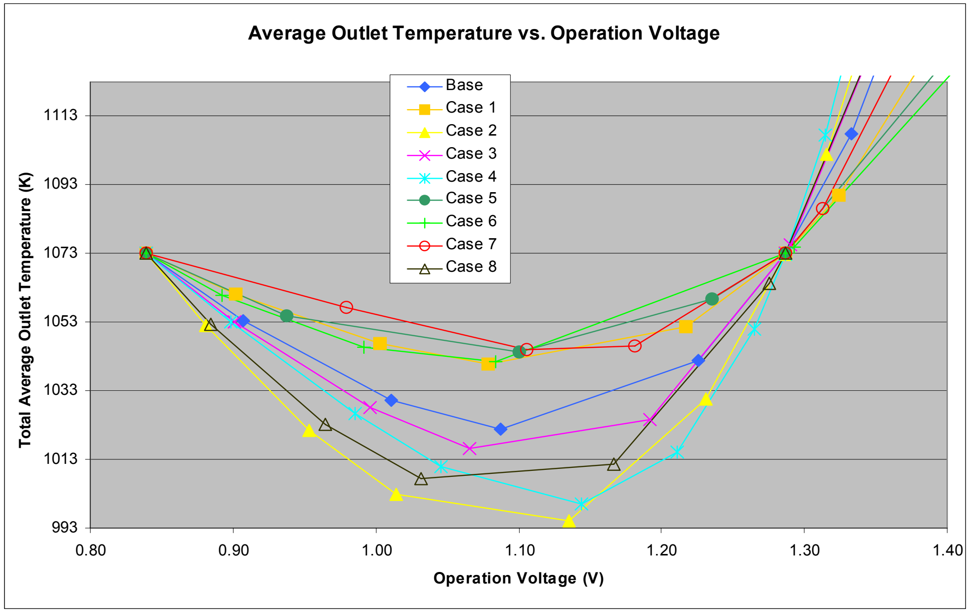
$R_B=4R_o$



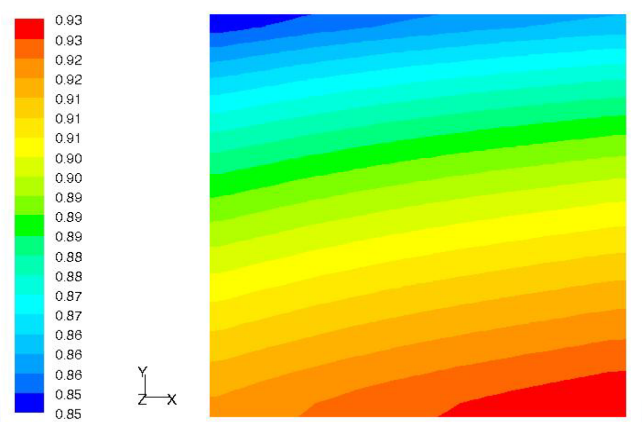
FLUENT SOEC Predictions



Single cell temperature predictions 1.087 V



Average outlet gas temperature versus operating voltage for various cases.



Nernst voltage at Vop=1.287 V

<u>Base Case</u>

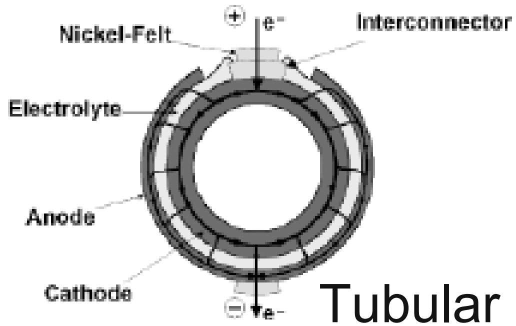
Mass flow rate H_2 side = 8.0e-6 kg/s
Mass flow rate O_2 side = 4.0e-6 kg/s
Mass fractions H_2 side : H_2O = 0.493902, H_2 = 0.006098, N_2 = 0.50
Mass fractions O_2 side : O_2 = 0.2329, N2 = 0.7671
Operating pressure = 101.325 kPa
Inlet temperature H_2 and O_2 side = 1073 K
Case 1: change only mass flow rate on H2 side to 15.0e-6 kg/s
Case 2: change only ref current exchange density on H_2 side to 4000 A/m²
Case 3: change only ref current exchange density on O_2 side to 4000 A/m²
Case 4: change only electrolyte specific resistivity to 0.1 Ω-m
Case 5: change only cont resist electrodes and current collectors to 1.0e-4 Ω-m²
Case 6: change all parameters from cases 1-5
Case 7. change *g* on concentration in activation overpotential from 0.5 to 1.0
Case 8. change *g* on concentration in activation overpotential from 0.5 to 0.1

Conclusions

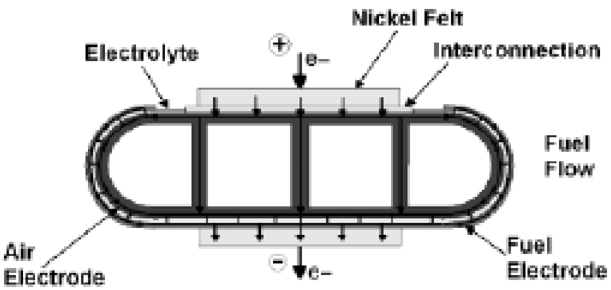
- Thermal, electrochemical and mechanical performance of SOECs can be improved through design.
  - Larger cells with higher inlet steam mass flux can be beneficial for the economics of the SOECs.
  - Contact resistances influence the total cell resistance and cell temperature more significantly than the active components over a large range of operating potentials.
  - Oxygen electrode degradation due to Cr- or glass-interactions near the edges can significantly distort the current density distribution.
  - A parallel-flow geometry for SOEC operation can yield smaller and more favorable temperature gradients and current density gradients and possible to manufacture.

Future Work for SOEC Modeling

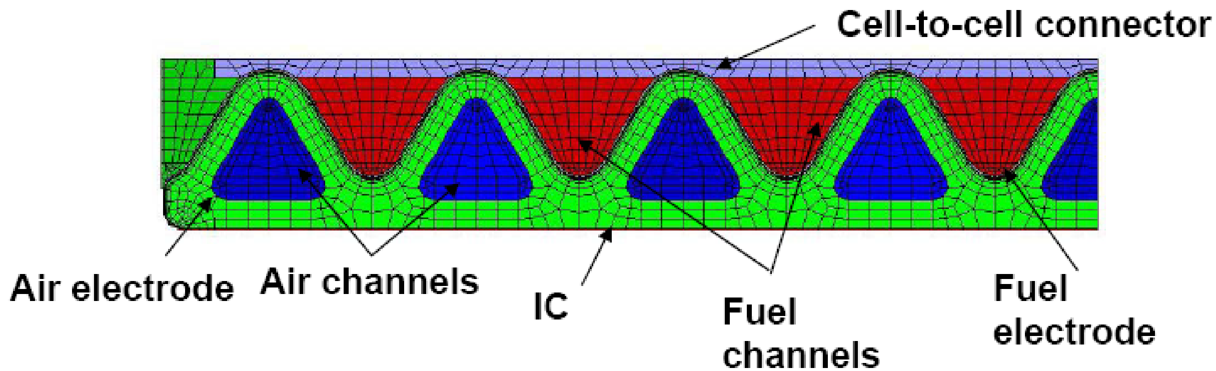
- Continue to identify and analyze SOEC degradation mechanisms and compare with experiments at ANL.
- Update of the model algorithm (ongoing) for flexibility to analyze various cell and stack designs
  - Other new seal-less and high-power-density cell and stacks designs will be evaluated through modeling. Examples:



Tubular



Flattened tubular



Next generation high-power-density Delta 9

All from Siemens designs

Summary

Objective: Identify SOEC configurations for favorable electrochemical and thermal performance.

Approach: Electrochemical (EC) and thermal-fluid analysis of the SOECs using a computational fluid dynamics (CFD) technique.

Technical Accomplishments: Identified the effect of SOEC resistances, SOEC size and inlet flow rates, flow inlet configurations, and oxygen electrode degradation on the thermal and electrochemical behavior of the planar SOEC.

Collaborations: Idaho National Laboratory, Ceramatec Inc.

Proposed Future Research: Retrieve input form electrochemical characterizations to improve model results; Analyze seal-less and high-power-density cell configurations.

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Flow-sheet Modeling of HTE Systems

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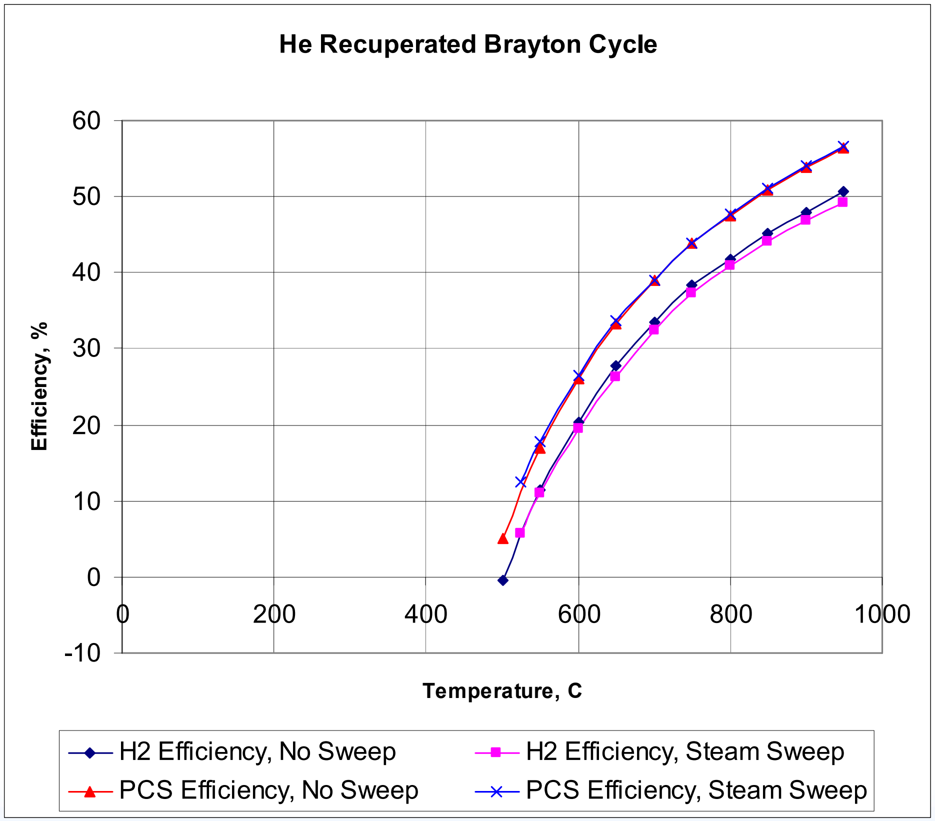
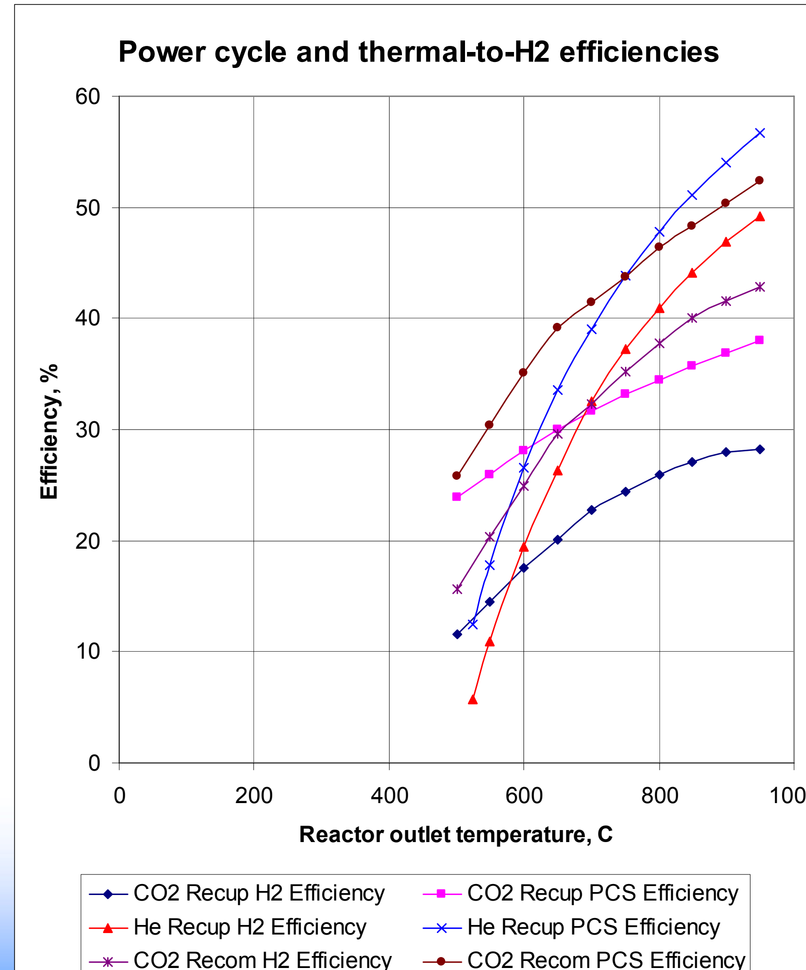
Power Cycle and Hydrogen Production Efficiencies

Objective: Plant flowsheet analysis to thermally optimize the HTE-VHTR plant combination. The highest net efficiency and the lowest net cost requires a detailed understanding of the heat and mass flow processes



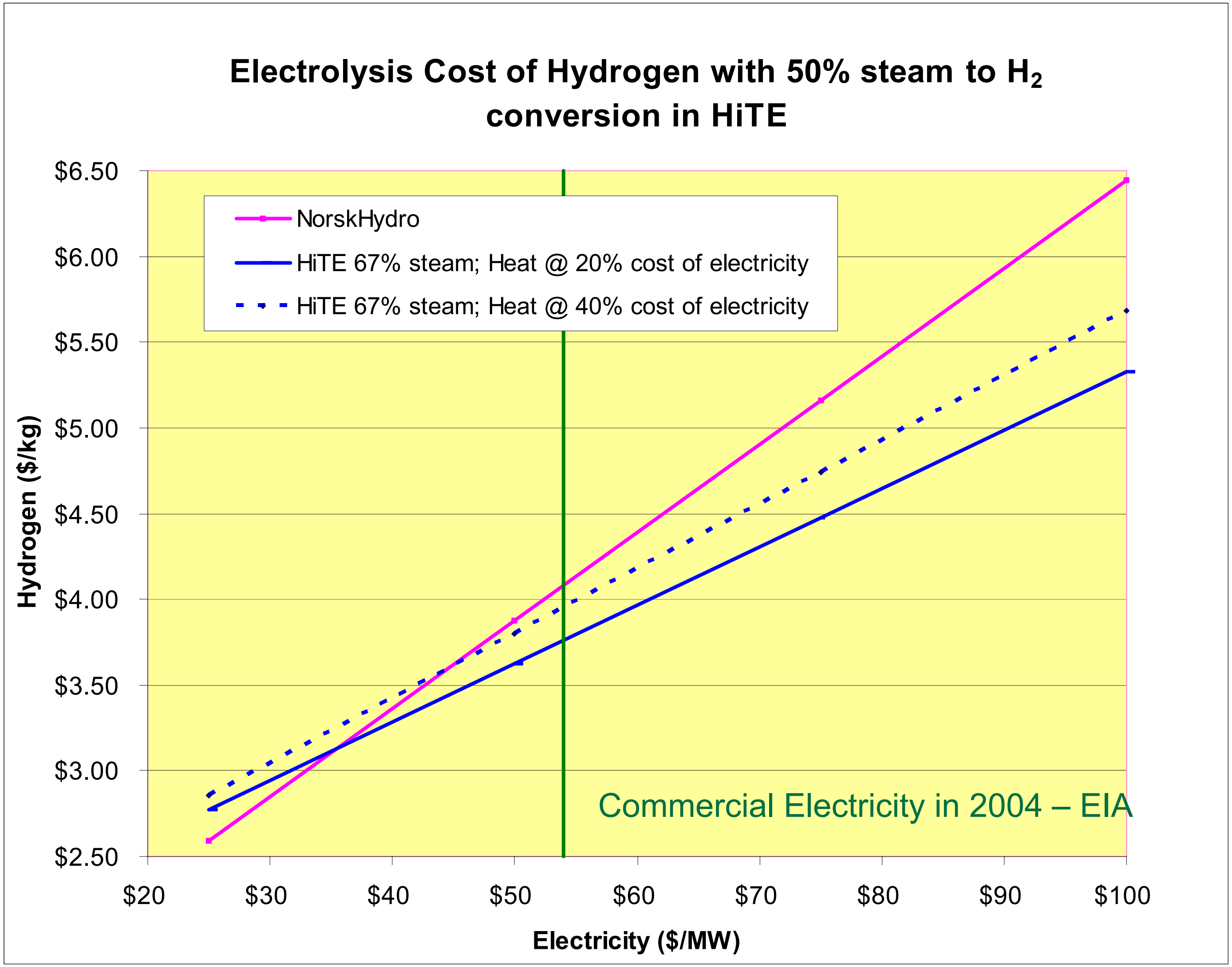


High-Temperature Electrolysis Capital vs. NorskHydro
Higher costs -- Green; Lower costs -- Blue

System		Capital, $K
Direct Costs		
Electrolyzer		
Electrolyzer stack	24.02%	$43,785
Electrolyzer shell & manifold piping	2.55%	$4,656
High-temperature electrolysis equipment	21.52%	$39,228
Electric Power Transformer	3.14%	$5,718
Electric Power Invertor/Conditioning	9.41%	$17,155
Compressor	10.33%	$18,824
Support Facilities		
Pipe, valves, fittings, H_2 & O_2 tanks	7.00%	$12,761
Process insturments and controls	7.00%	$12,761
Electrical equipment and materials - support	5.00%	$9,115
Structural support, insulation, paint	10.00%	$18,230
Direct Costs Sub-total	100.0%	***$182,300***
Indirect Costs		
Erection and installation labor	22.00%	$40,106
General Facilities	7.00%	$12,761
Engineering Fees	10.00%	$18,230
Profit	15.00%	$27,345
Indirect Costs Sub-total		***$280,742***
Direct + Indirect Costs Sub-total		***$463,042***
Interest & Inflation	0.00%	$0
Total Plant Investment-TPI		***$463,042***
Royalties	0.60%	$1,094
Start-up Costs	1.00%	$1,823
Commissioning & spare parts	0.35%	$1,605
TOTAL PROJECT COSTS		***$467,564***

System		Capital, $K
Direct Costs		
Electrolyzer		
Electrolyzer stack	26.80%	$37,788
Electrolyzer shell & manifold piping	2.85%	$4,019
High-temperature electrolysis equipment	0.00%	$0
Electric Power Transformer	7.00%	$9,870
Electric Power Invertor/Conditioning	21.00%	$29,610
Compressor	13.35%	$18,824
Support Facilities		
Pipe, valves, fittings, H_2 & O_2 tanks	7.00%	$9,870
Process insturments and controls	7.00%	$9,870
Electrical equipment and materials - support	5.00%	$7,050
Structural support, insulation, paint	10.00%	$14,100
Direct Costs Sub-total	100.00%	***$141,000***
Indirect Costs		
Erection and installation labor	22.00%	$31,020
General Facilities	7.00%	$9,870
Engineering Fees	10.00%	$14,100
Profit	15.00%	$21,150
Indirect Costs Sub-total		***$217,140***
Direct + Indirect Costs Sub-total		***$358,140***
Interest & Inflation	0.00%	$0
Total Plant Investment-TPI		***$358,140***
Royalties	0.60%	$846
Start-up Costs	1.00%	$1,410
Commissioning & spare parts	0.35%	$1,242
TOTAL PROJECT COSTS		***$361,638***

High-temperature electrolysis looks promising with current INL cell performance at 50% conversion



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In Situ X-ray and Electrochemical Studies of HTE Electrode Materials

Bilge Yildiz, Kee-Chul Chang, Deborah J. Myers, Hoydoo You, and J. David Carter.

Argonne National Laboratory

Objectives

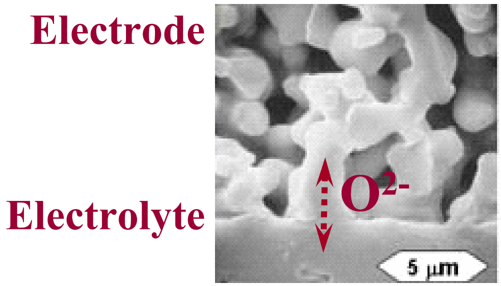
- Ultimate goal
  - Provide efficient and durable materials and systems for hydrogen production using high temperature steam electrolysis.

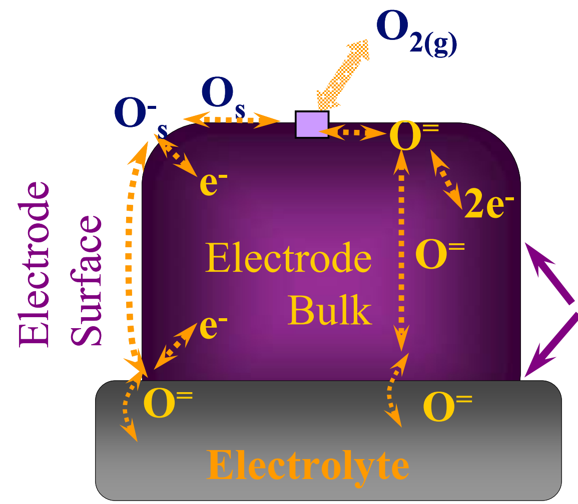
- Near-term goals
  - Obtain in-depth knowledge on governing mechanisms and properties of the electrode materials.
    - *Molecular level experimental analysis of electrodes*
  - Provide input for electrochemical kinetics modeling

Structure-Property-Performance Relations at Oxygen Electrodes

Oxygen reaction (OR): $\frac{1}{2}O_2 + 2e^- + V_O^{\cdot\cdot} \leftrightarrow O_O$

Which charge-transfer pathway controls the OR mechanism?





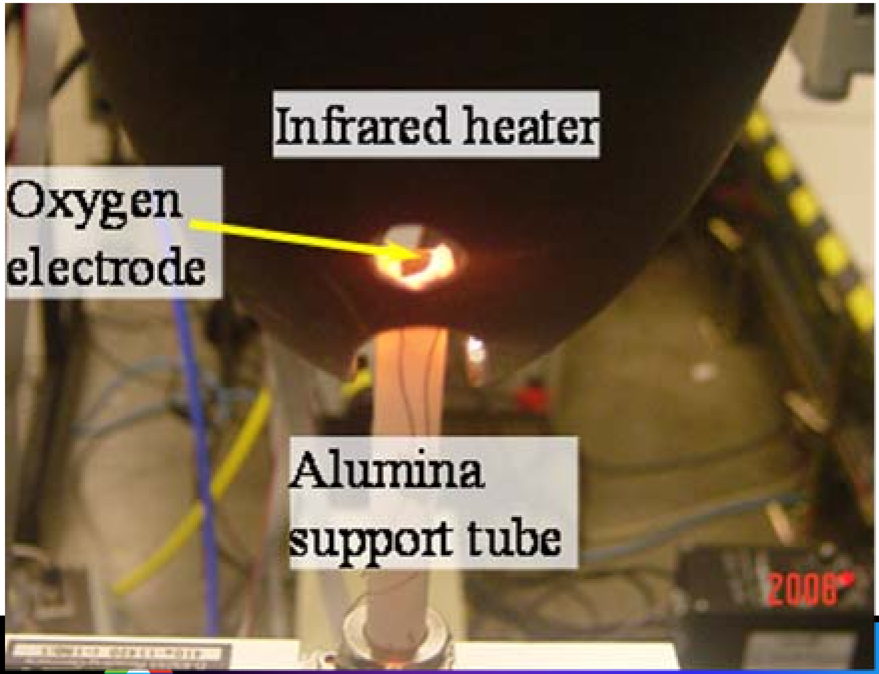
What controls the charge transport and catalytic activity at the interfaces?

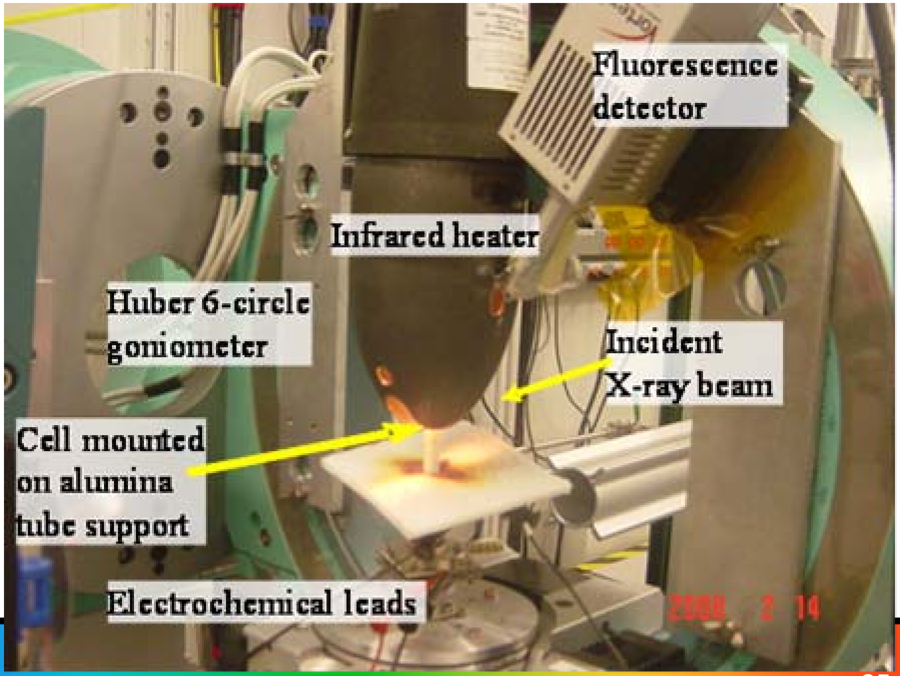
Charge transport Catalytic activity	? ⟷	Chemical, physical, and structural properties of the •Air/Electrode interface •Electrode bulk •Electrode/Electrolyte interface

- ***Fundamental knowledge on OR mechanism is necessary***

Approach: *In situ X-ray and Electrochemical Characterization of the Electrode and its Interfaces*

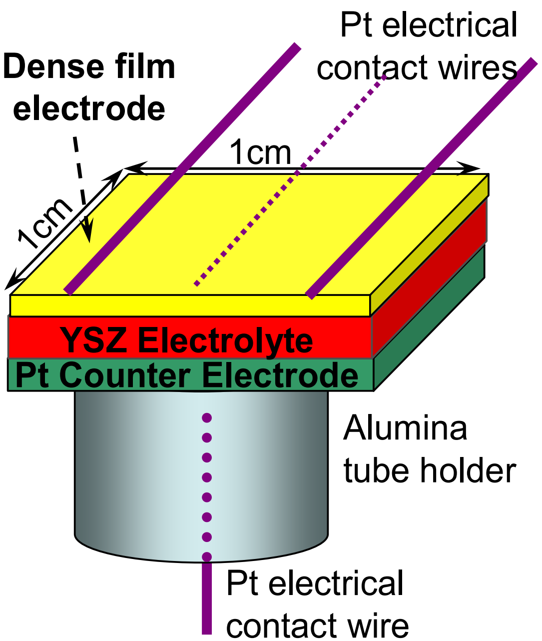
- X-ray characterization of the oxygen electrode and electrolyte materials during oxygen reactions with simultaneous electrochemical characterization
- Small incidence angle
  - *X-ray reflectivity;* morphology
  - *X-ray absorption spectroscopy*; oxidation state, atomic environment
- *In situ* x-ray/electrochemical study of thin-film model electrodes, set-up shown here at Advanced Photon Source, MR-CAT beamline





In Situ *Electrochemical Cell and Model Electrode Materials*

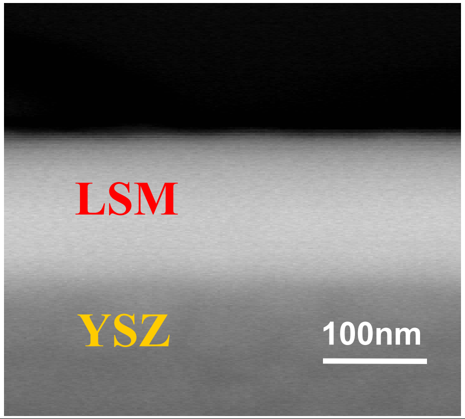
***In situ* electrochemical cell**

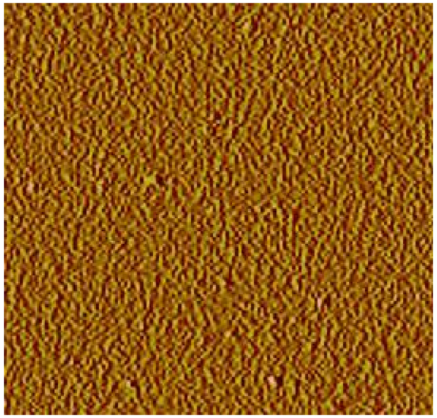


Non-obstructing heater and electrical contacts

Electrically active beam path on the electrode

- Dense thin-film electrodes,
  - t= 20-200nm
  - Allows for x-ray reflectivity at grazing angles for surface sensitivity.
  - Fabricated by pulsed laser deposition.
  - Electrolyte substrate: (100) single-crystal YSZ.
  - Electrodes: $La_{0.8}Sr_{0.2}MnO_3$ (LSM), $La_{0.8}Ca_{0.2}MnO_3$ (LCM), $La_{0.8}Sr_{0.2}CoO_3$ (LSC) deposited at T = 700-780^{o}C, P_{O2}= 25-200mbar.



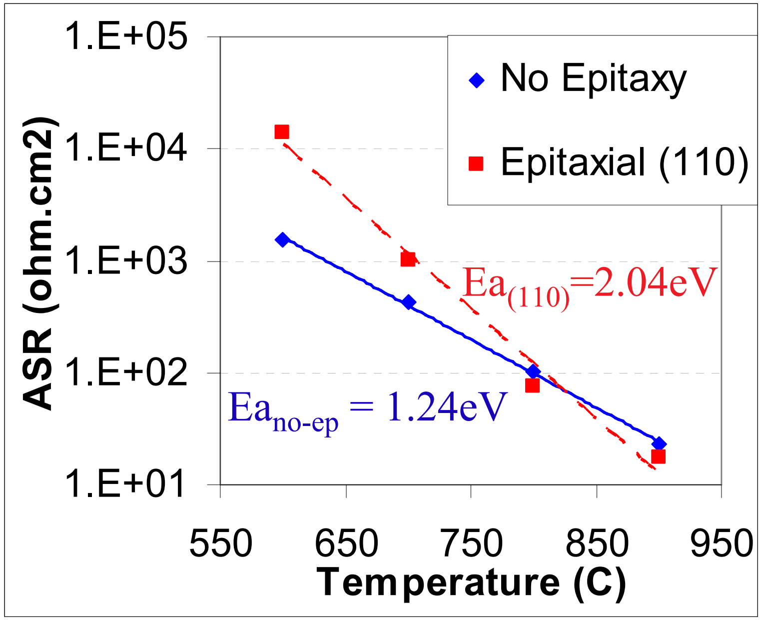


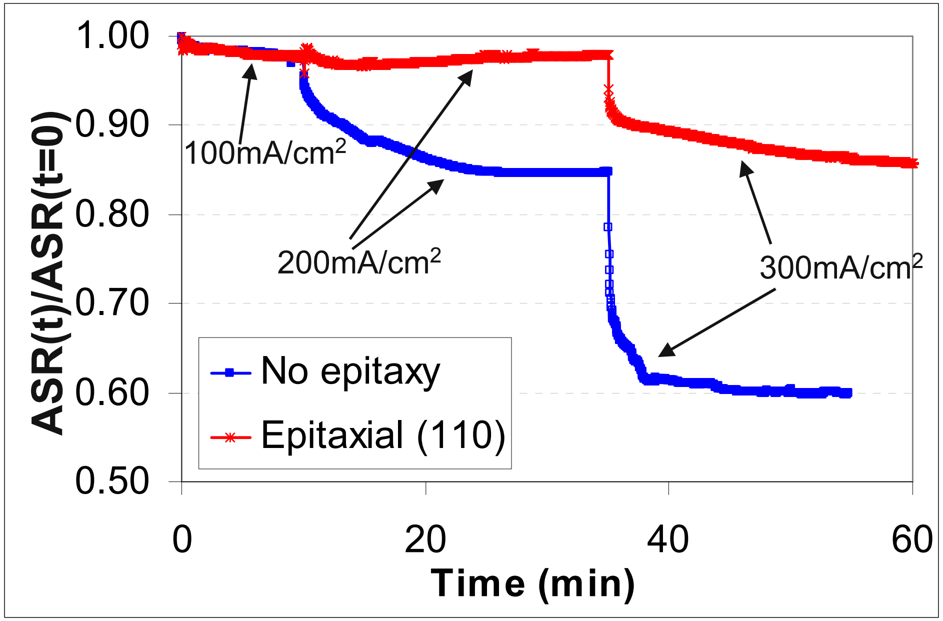
100nm

RMS Roughness: 0.5-1nm

Dense Thin Film Electrodes:
Effect of Crystal Orientation

$La_{0.8}Sr_{0.2}MnO_{3+d}$ (LSM), 100nm-thick, with no epitaxy and with (110) orientation on single crystal YSZ electrolyte.





Near OCP; T>700°C, $ASR_{no\text{-}ep} > ASR_{(110)}$

T<700°C, $ASR_{no\text{-}ep} < ASR_{(110)}$

Under DC polarization at 700°C

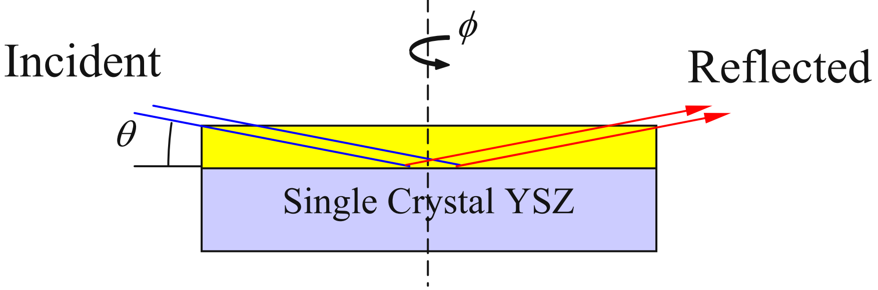
$\text{LSM-Activation}_{non\text{-}ep} > \text{LSM-Activation}_{(110)}$

Which crystal orientation and termination layers at the electrode are more active for oxygen reactions at the surface and in the bulk?

X-ray Reflectivity and X-ray Absorption Spectroscopy

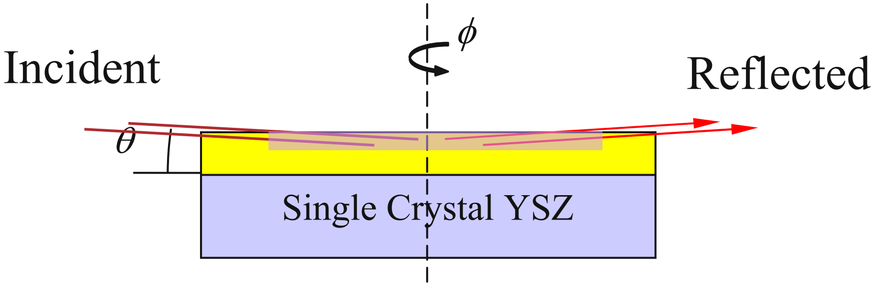
What information do we get from XRR and XAS?

Specular x-ray reflectivity



Small incident angle, $\theta > \theta_{critical}$

→ Measurement sensitive to the bulk of the electrode film.

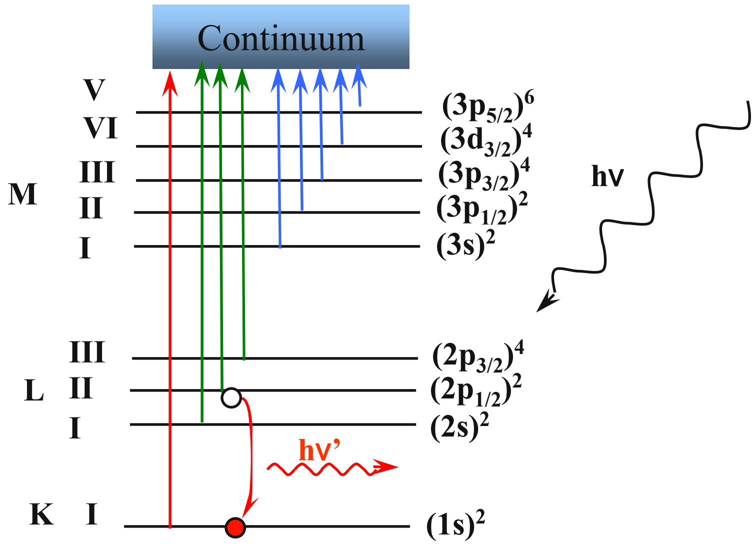


Grazing incidence angle, $\theta < \theta_{critical}$

→ Evanescent wave with finite penetration depth into the sample

→ enhanced signal from the surface, of ~1nm-depth into material.

X-ray absorption Spectroscopy

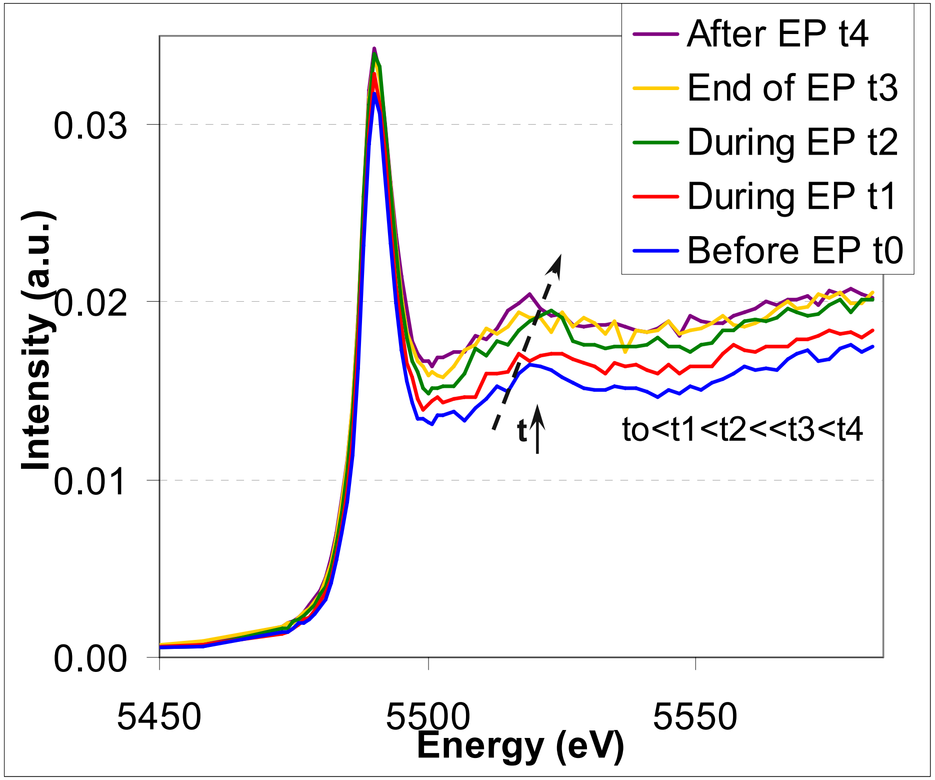


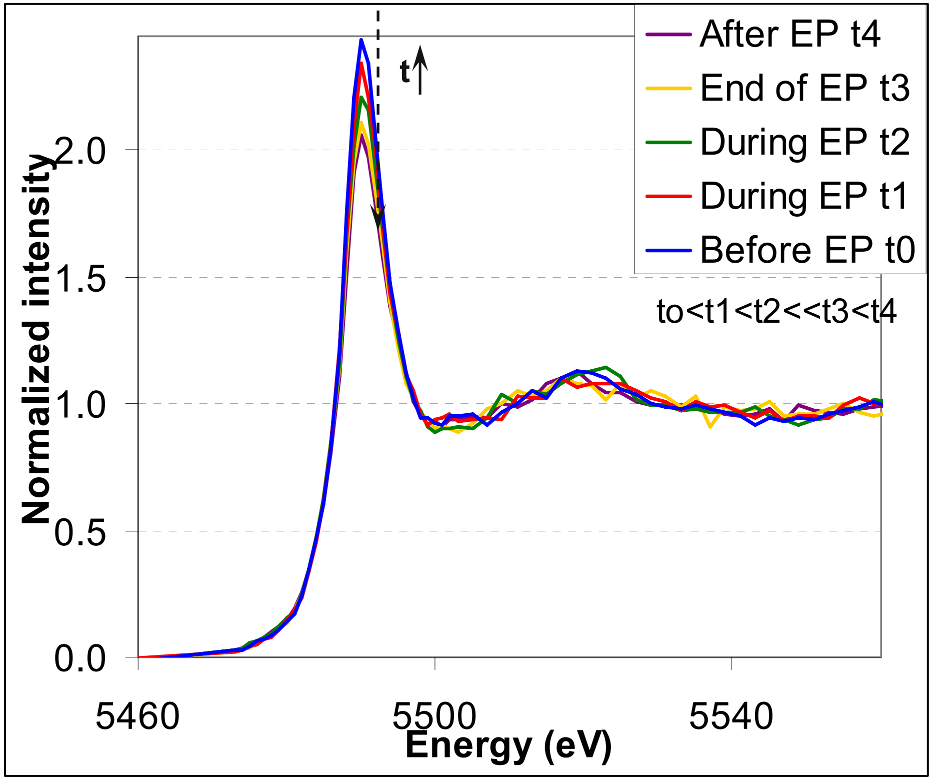
Decay of the excited states through fluorescence gives rise to the x-ray absorption spectroscopy

La Chemical State Change at Dense Thin-Film LSM Electrodes during Polarization?

La L_{III} edge XANES with anodic polarization at 700°C.

At the surface of the dense thin-film LSM



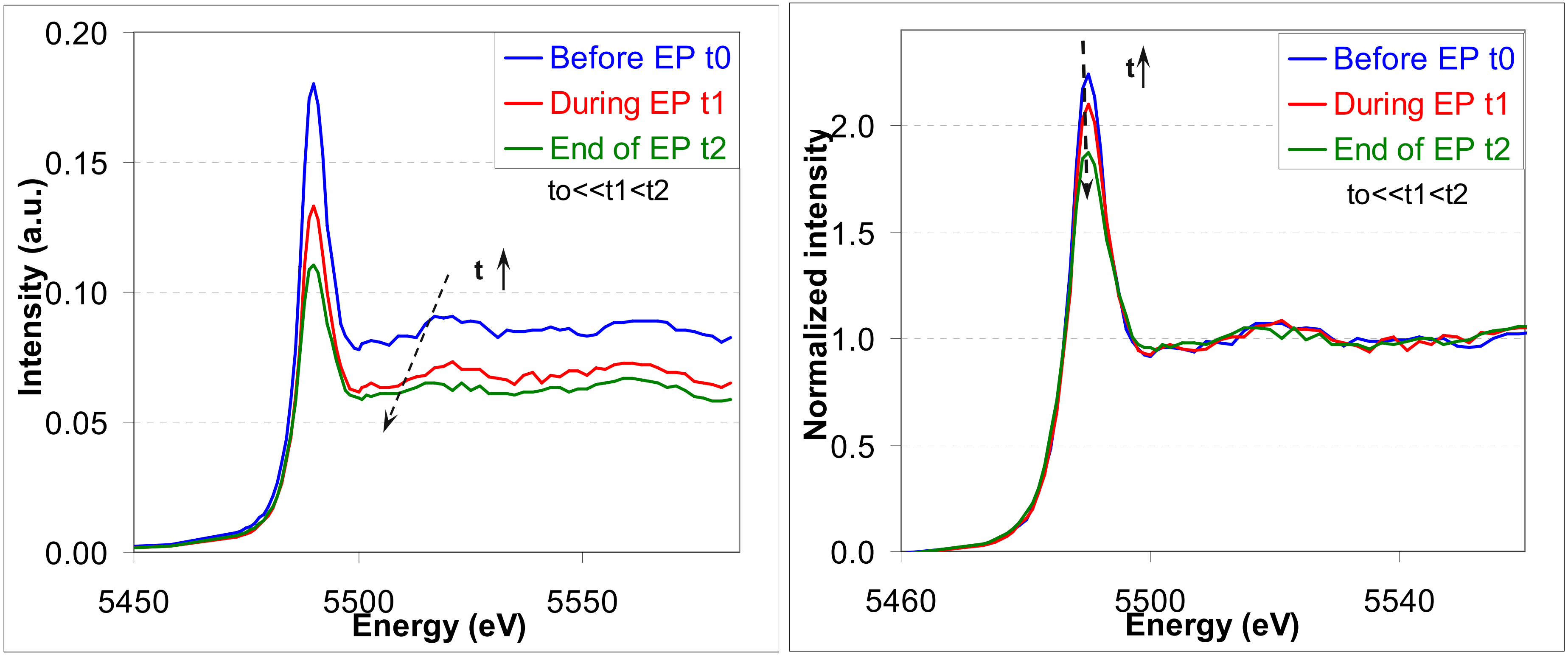


→ The change in the chemical state of the La is occurring at the top air-electrode film interface, only during the improvement of the electrode.

La Chemical State Change at Dense Thin-Film LSM Electrodes during Polarization?

La L_{III} edge XANES with Cathodic polarization at 700°C.

At the surface of the dense thin-film LSM



→The change in the chemical state of the La is occurring at the top air-electrode film interface, only during the improvement of the electrode.

➔A more favorable composition or electronic state than the initial conditions of the doped lanthanum manganite electrode surface.

Future Work

- Identify the chemical state of other A-site cations, Sr, on the surface of the electrodes as a function of temperature and electrical current (on going).
- Continue to identify and analyze the special and favorable crystallographic orientations of SOEC oxygen electrode materials.

Summary

Objective: Understand and improve the relations between the electrode interface properties and the oxygen reaction kinetics in SOECs.

Approach: First ever *In situ x-ray and* electrochemical studies of model SOEC electrode materials.

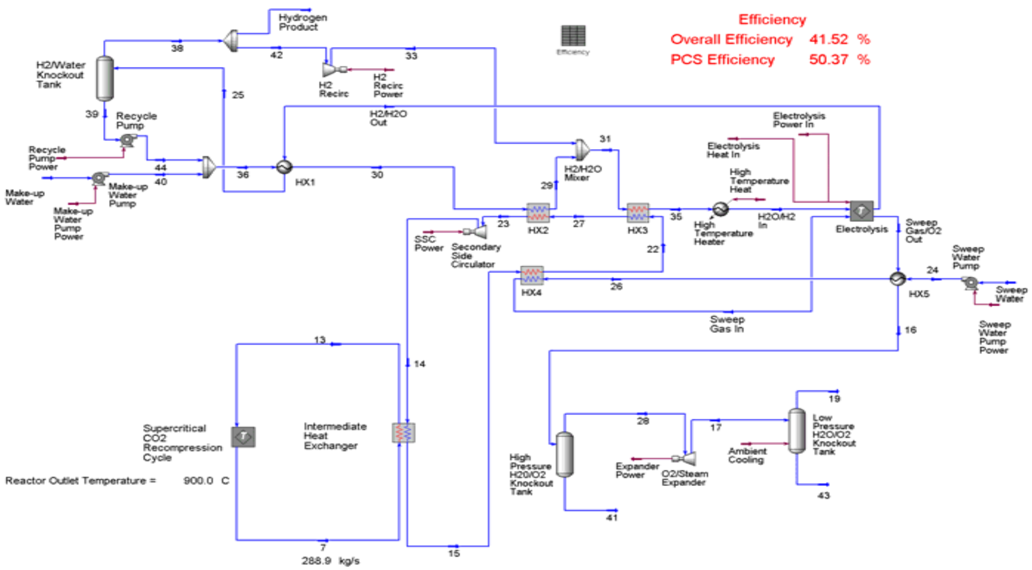
Technical accomplishments: Found that particular crystal orientations and A-site (La) chemical state changes, during anodic and cathodic polarization, at the surface of the doped lanthanum manganite can make the electrodes electrocatalytically more active.

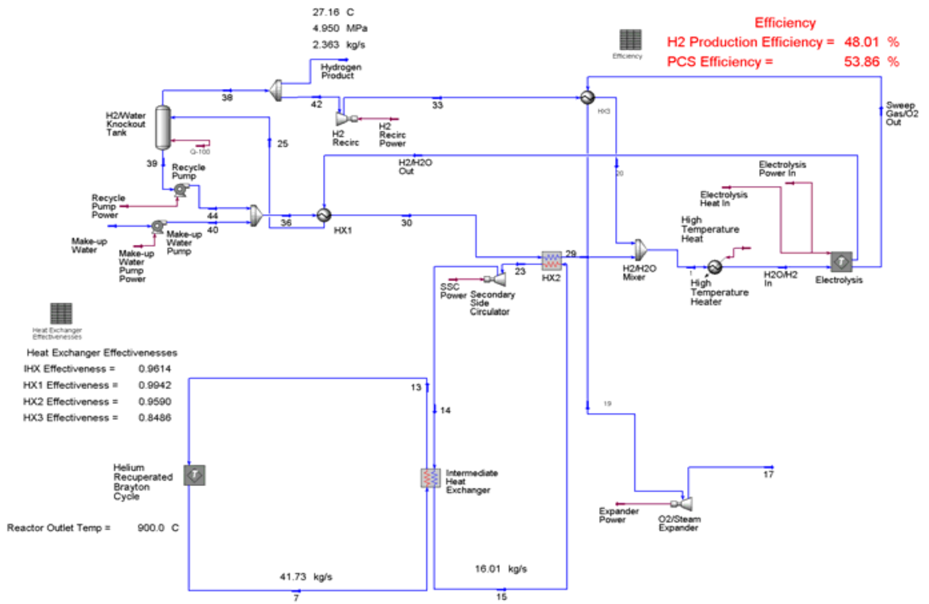
- *Surface enhancement may yield significant improvement even for the doped lanthanum manganite electrodes, thought to be bulk diffusion limited.*

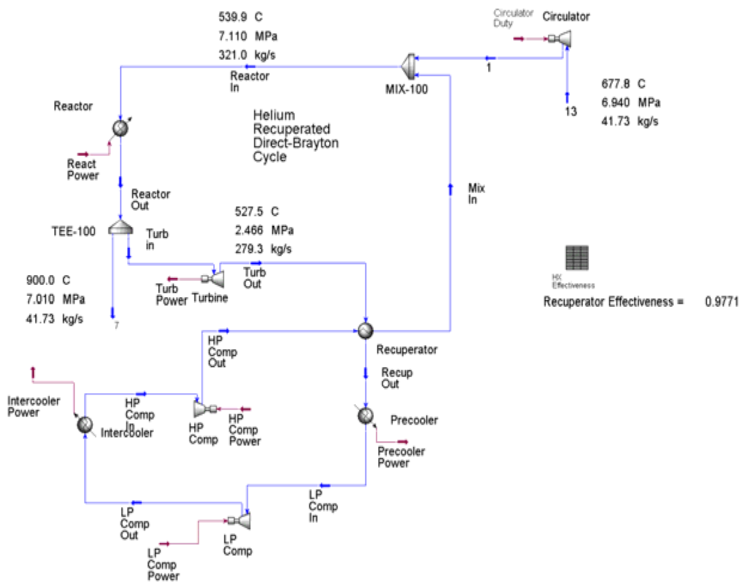
Proposed Future Research: Study the chemical and structural property evolution and electrochemical activation in various crystallographic structured of perovskite-based oxygen electrodes.

Back-up Slides

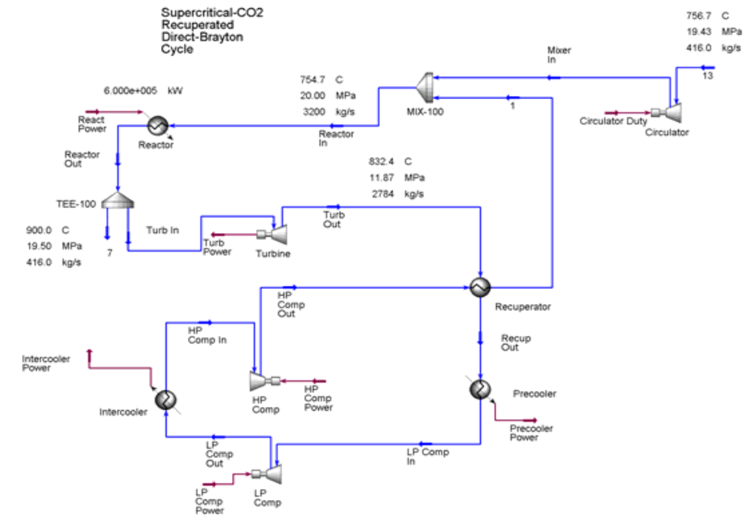
Nuclear-driven HTE Process Models with Steam Sweep and No Sweep



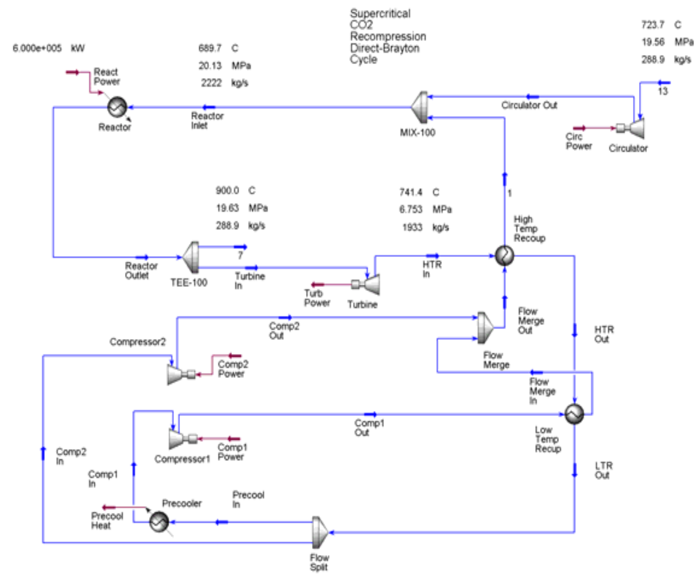




Helium Recuperated Direct-Brayton Cycle
539.9 C
7.110 MPa
321.0 kg/s
Circulator Duty
Circulator
Reactor In
MIX-100
1
13
677.8 C
6.940 MPa
41.73 kg/s
Reactor
React Power
Reactor Out
Mix In
TEE-100
Turb in
527.5 C
2.466 MPa
279.3 kg/s
Turb Out
Turb Power
Turbine
900.0 C
7.010 MPa
41.73 kg/s
7
HX Effectiveness
Recuperator Effectiveness = 0.9771
HP Comp Out
Recuperator
Recup Out
Intercooler Power
HP Comp In
Intercooler
HP Comp
HP Comp Power
Precooler
Precooler Power
LP Comp In
LP Comp Out
LP Comp
LP Comp Power



Supercritical-CO2 Recuperated Direct-Brayton Cycle
756.7 C
19.43 MPa
416.0 kg/s
Mixer In
13
754.7 C
20.00 MPa
3200 kg/s
6.000e+005 kW
React Power
Reactor
Reactor In
MIX-100
1
Circulator Duty
Circulator
Reactor Out
832.4 C
11.87 MPa
2784 kg/s
TEE-100
900.0 C
19.50 MPa
416.0 kg/s
7
Turb In
Turb Power
Turbine
Turb Out
HP Comp Out
Recuperator
HP Comp In
Recup Out
Intercooler Power
Intercooler
HP Comp
HP Comp Power
Precooler
Precooler Power
LP Comp Out
LP Comp In
LP Comp Power
LP Comp



Supercritical CO2 Recompression Direct-Brayton Cycle
6.000e+005 kW
689.7 C
20.13 MPa
2222 kg/s
723.7 C
19.56 MPa
288.9 kg/s
React Power
Reactor
Reactor Inlet
MIX-100
Circulator Out
13
Circ Power
Circulator
900.0 C
19.63 MPa
288.9 kg/s
741.4 C
6.753 MPa
1933 kg/s
1
High Temp Recoup
Reactor Outlet
TEE-100
7
Turbine In
HTR In
Turb Power
Turbine
Comp2 Out
Flow Merge Out
HTR Out
Compressor2
Comp2 Power
Flow Merge
Flow Merge In
Comp1 Out
Low Temp Recup
Comp2 In
Compressor1
Comp1 Power
Comp1 In
LTR Out
Precooler
Precool In
Precool Heat
Flow Split