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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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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

Partners

- Idaho National Laboratory
- Ceramatec Inc.

Timeline

- Start – FY'04

Budget (ANL)

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

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



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Thermal-fluid and Electrochemical Modeling of HTE Cells and Stacks

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SOEC Thermal-fluid and Electrochemical Analysis

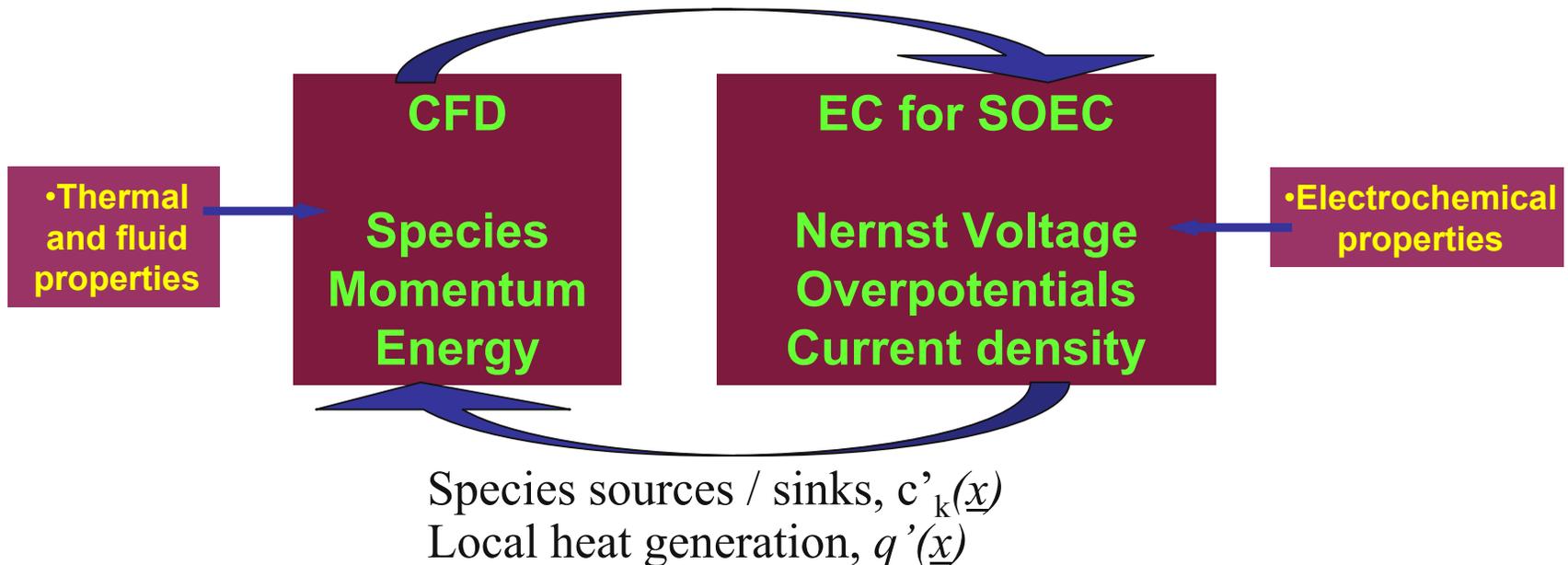
Objective

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

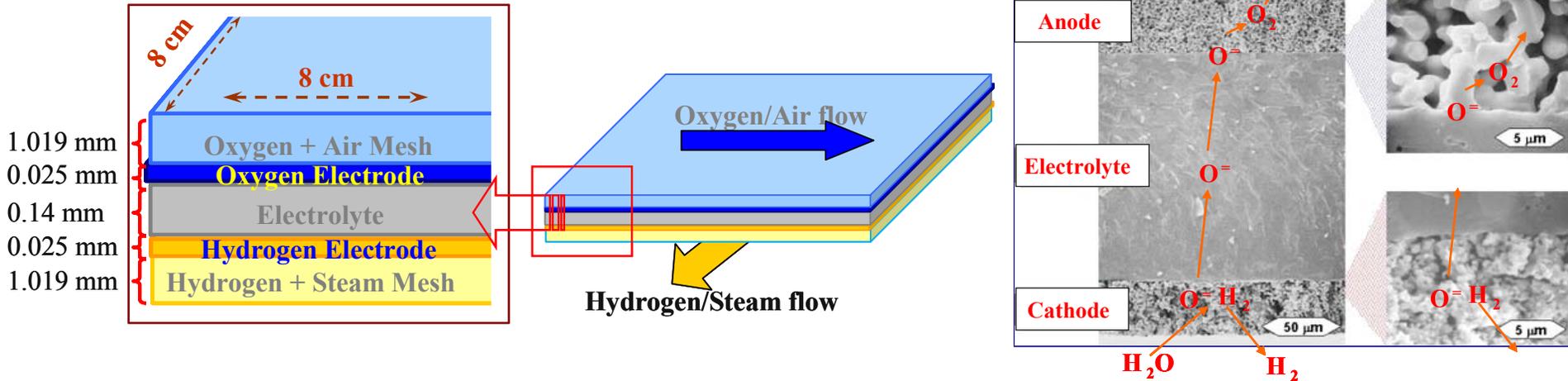
Approach

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

Local species concentrations, $C_k(\underline{x})$
Local temperature, $T(\underline{x})$



Model Description and Simulations

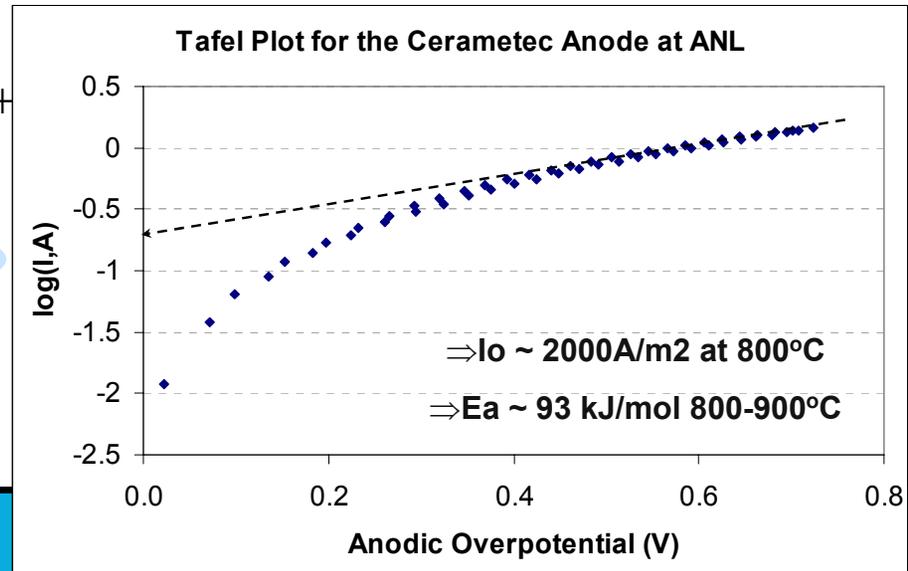


- Operation parameters based on Ceramtec and INL's SOEC system.
- Porous flow meshes and electrodes, and solid electrolyte.
- Major assumption: Reaction activation is controlled by Butler-Volmer kinetics.

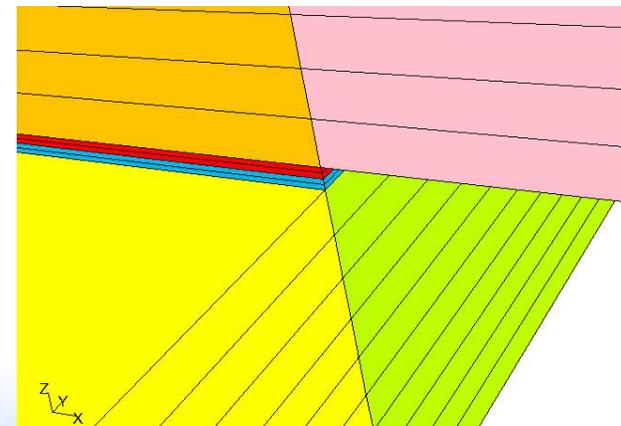
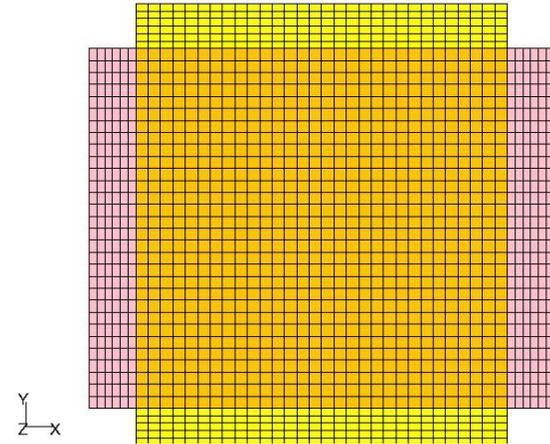
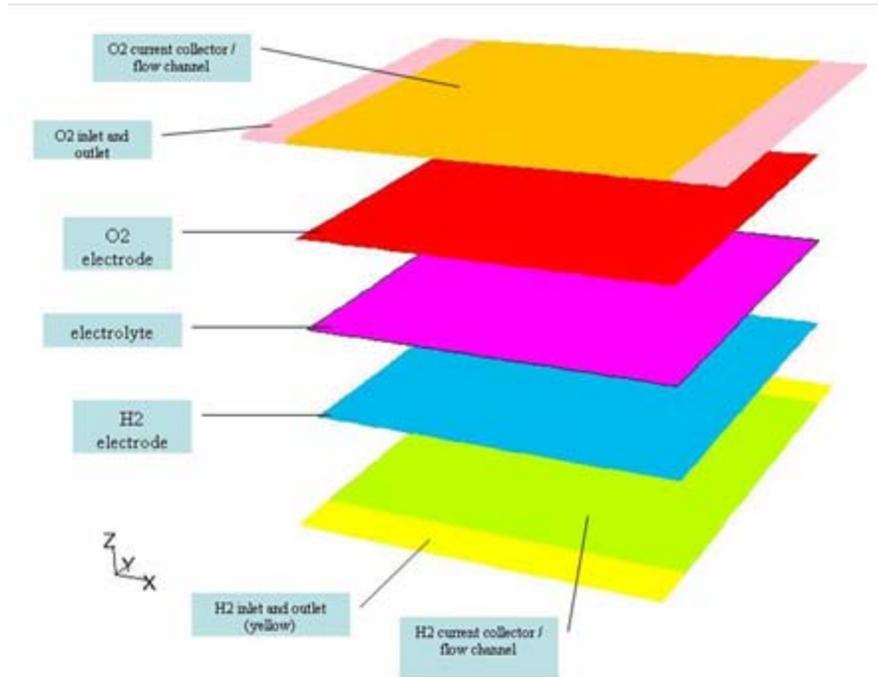
$$V_{appl} - V_{Nernst} = \eta_{\Omega}^{anode} (i) + \eta_{act}^{anode} (i) + \eta_{diff}^{anode} (i) + \eta_{act}^{cathode} (i) + \eta_{diff}^{cathode} (i) + \eta_{\Omega}^{electrolyte} (i)$$

The equation is annotated with three categories of losses:

- Ohmic losses**: $\eta_{\Omega}^{anode} (i) + \eta_{\Omega}^{electrolyte} (i)$
- Activation losses**: $\eta_{act}^{anode} (i) + \eta_{act}^{cathode} (i)$
- Diffusion losses**: $\eta_{diff}^{anode} (i) + \eta_{diff}^{cathode} (i)$



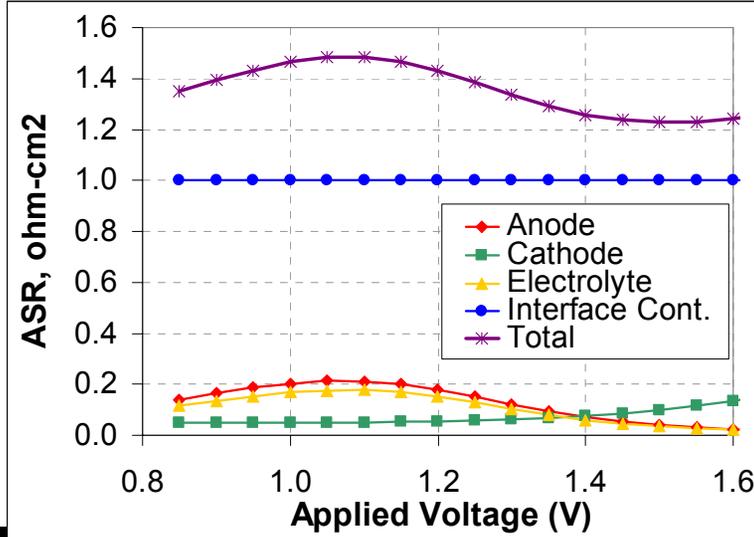
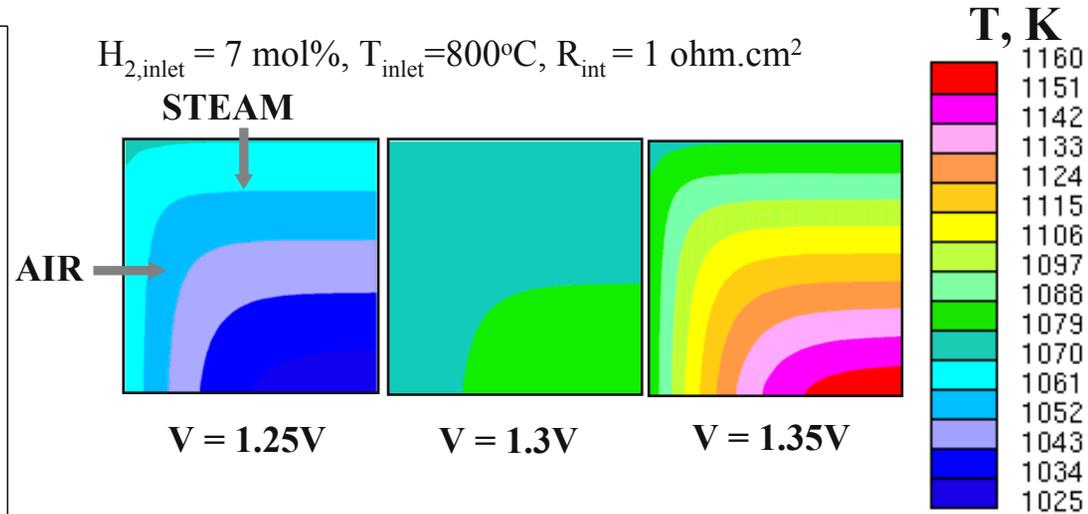
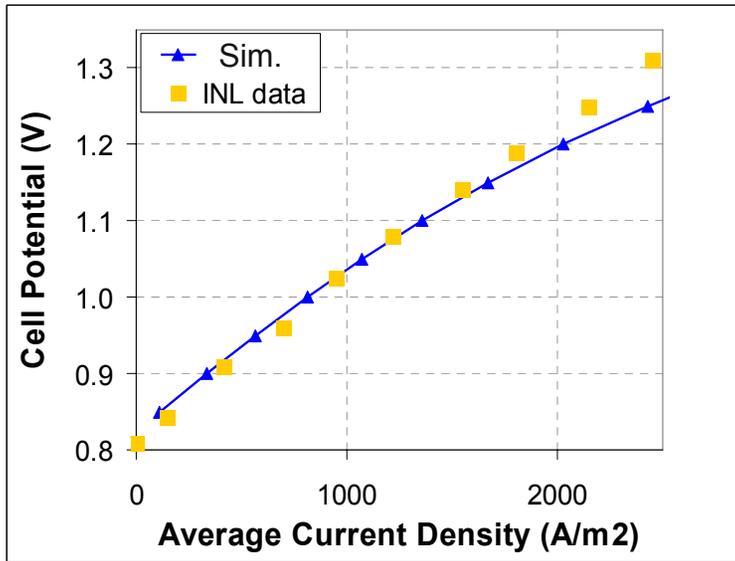
FLUENT Single-Cell SOEC Model



Technical Accomplishments

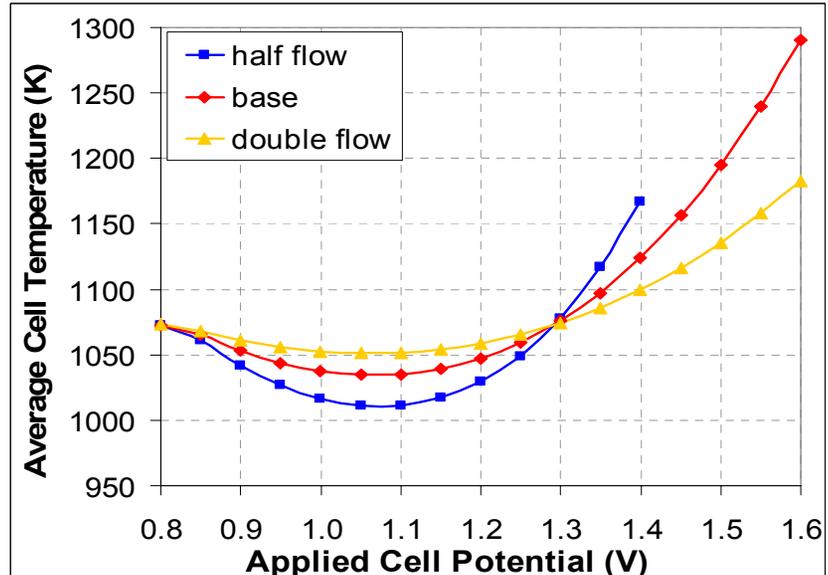
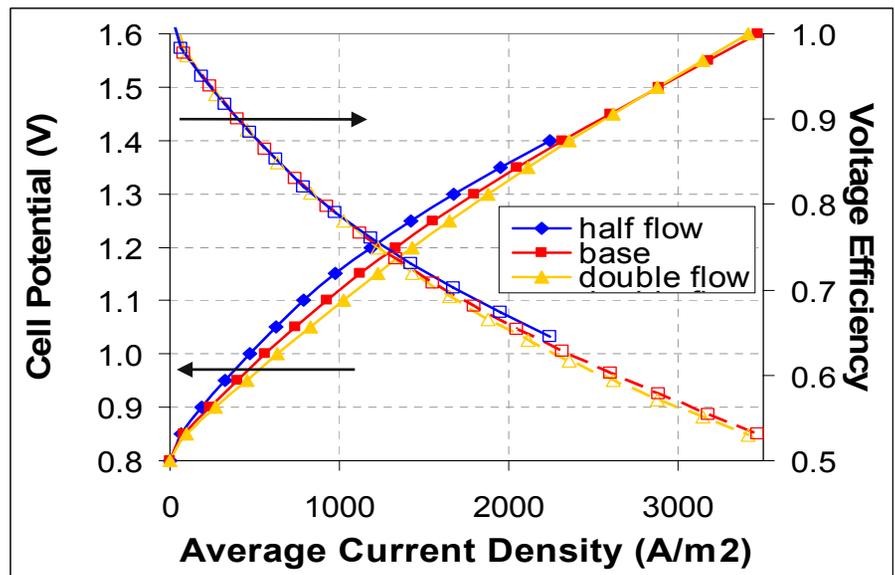
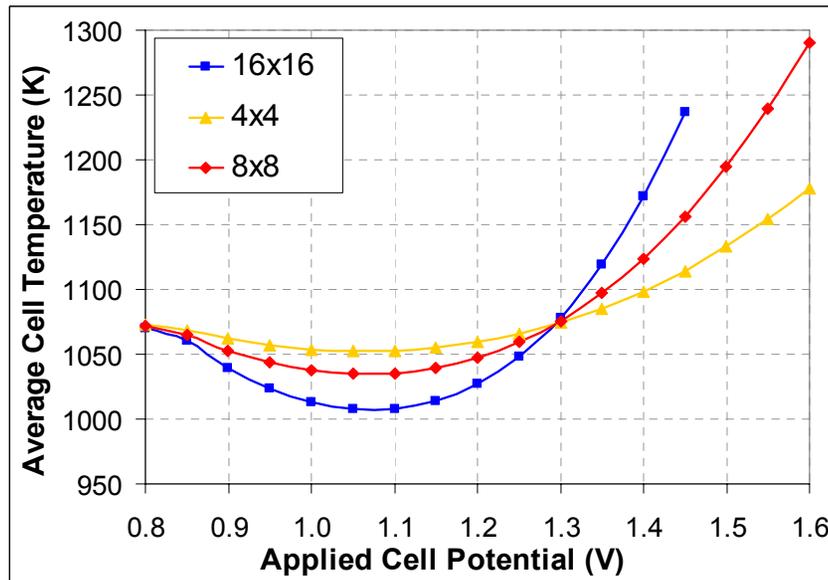
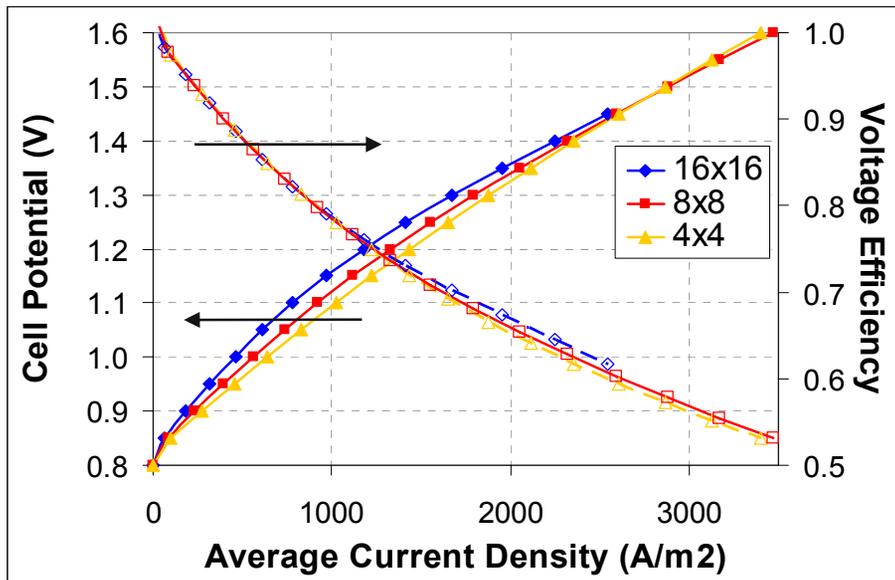
- Identified the contribution of SOEC components to total resistance losses.
- Analyzed the effect of SOEC size and inlet flow rates on the SOEC thermal behavior
- Evaluated various flow inlet configurations
- Identified the effect of oxygen electrode degradation on the thermal and electrochemical behavior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

Contribution of Cell Components to Resistance

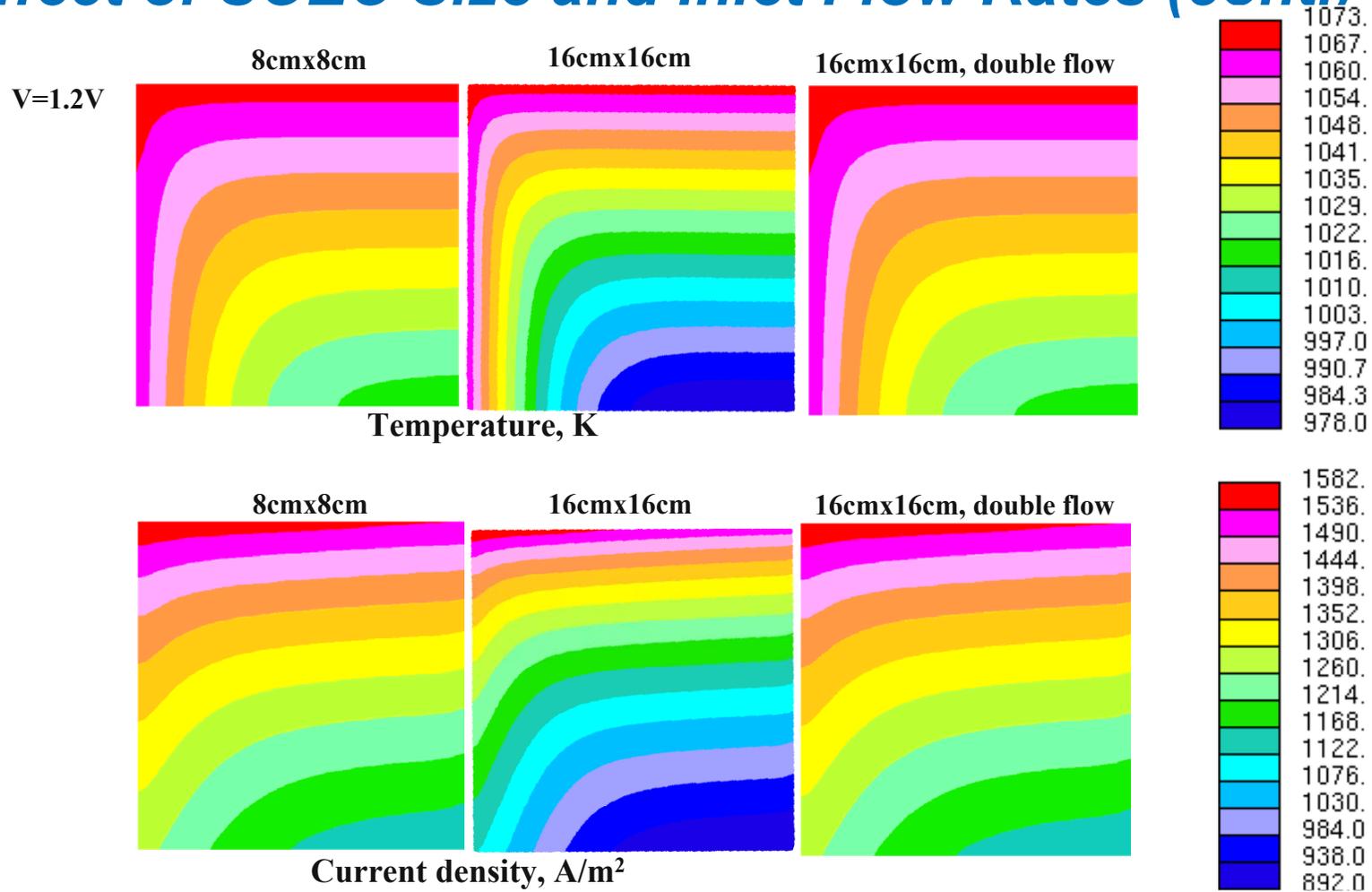


- Interfacial “contact” resistances in SOEC stack is the largest contributor to efficiency loss after the oxygen electrode.

Effect of SOEC Size and Inlet Flow Rates



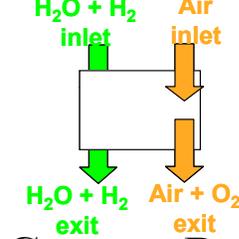
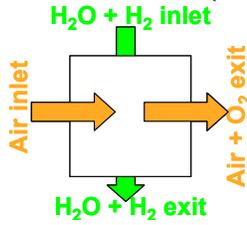
Effect of SOEC Size and Inlet Flow Rates (cont.)



- 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.

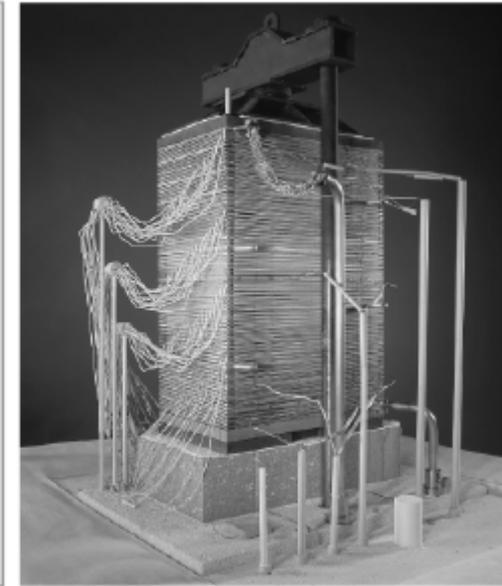
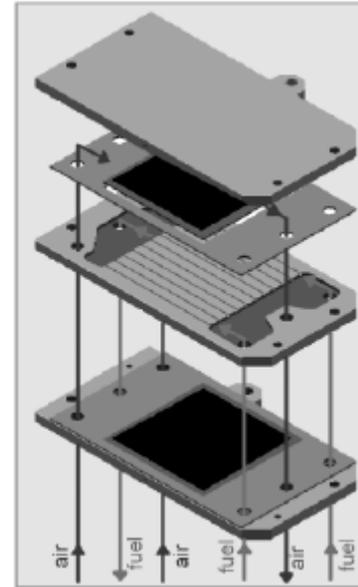
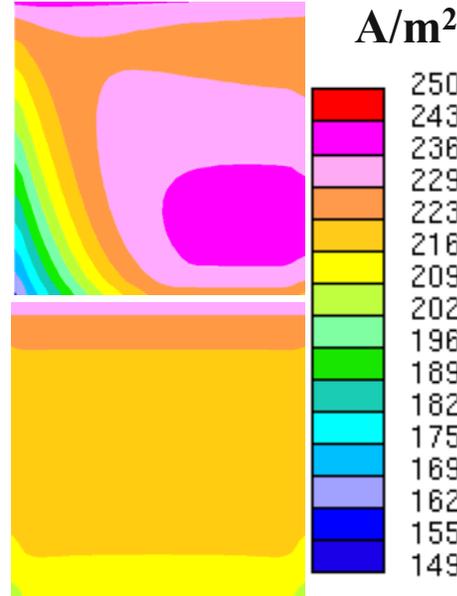
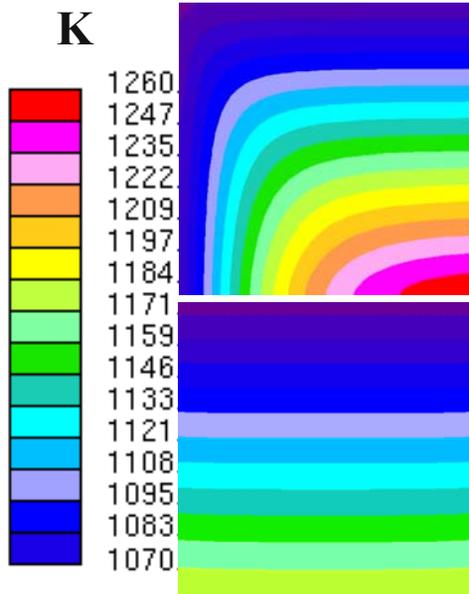
Effect of Flow Inlet Configurations

Cross Flow (CRF) Parallel Flow (PLF)



$V=1.4V$ Temperature

Current Density



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

Advantages of parallel flow

More uniform utilization of steam

→ *Lower electrochemical degradation*

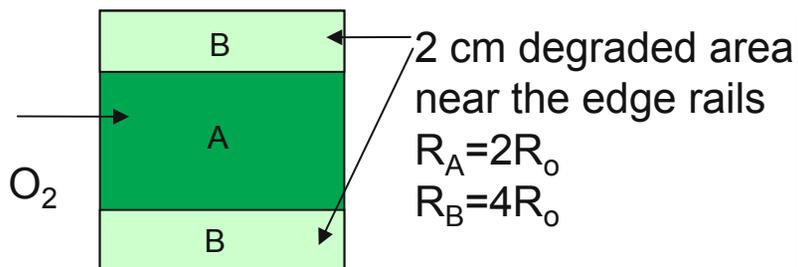
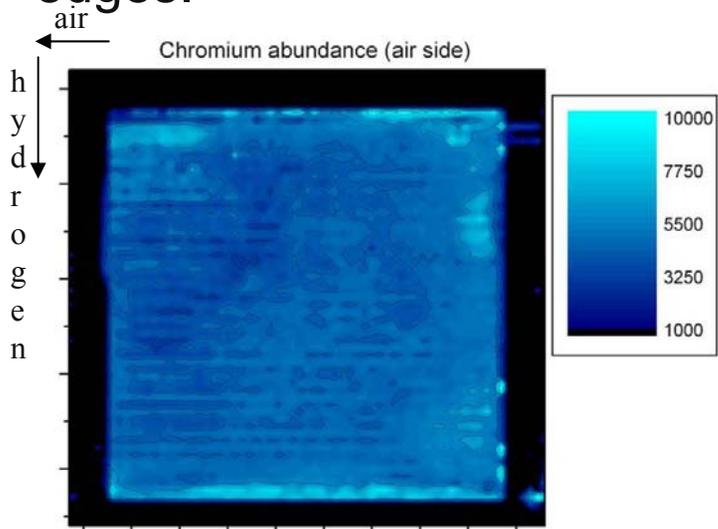
Lower thermal gradients

→ *Better structural integrity*

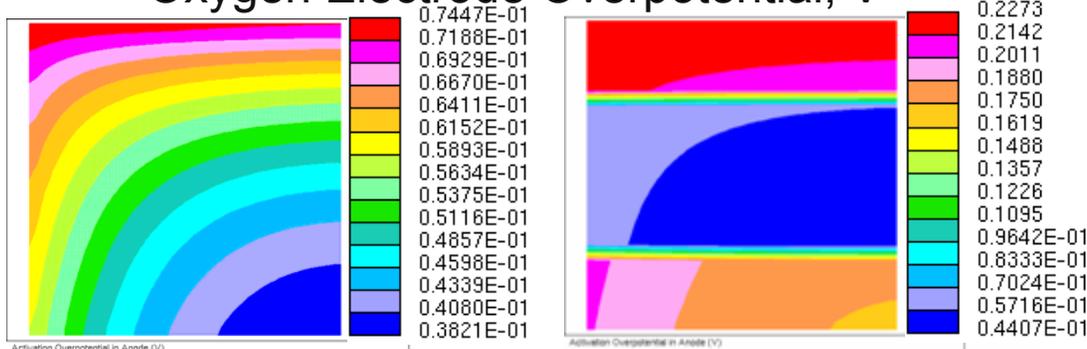
→ Optimization between thermal, electro-chemical and mechanical performance is needed.

Oxygen Electrode Degradation

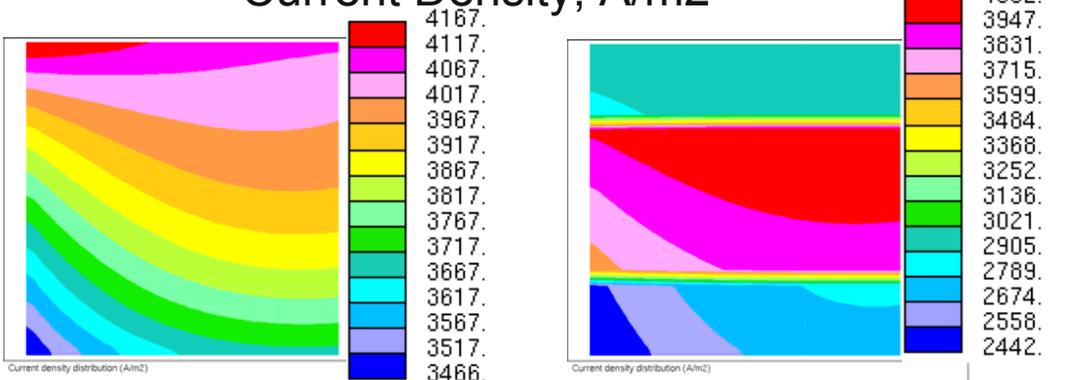
- Cr-deposits, into the electrode and along the edge rails.
- Reaction with seals along edges.



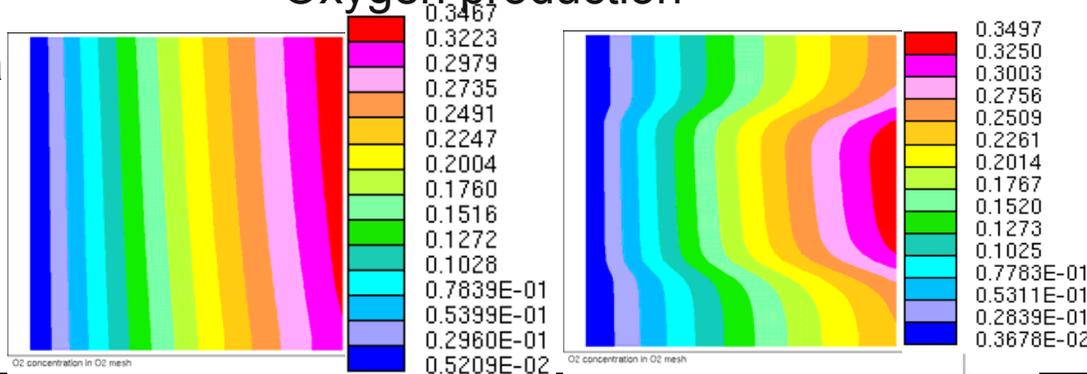
Oxygen Electrode Overpotential, V



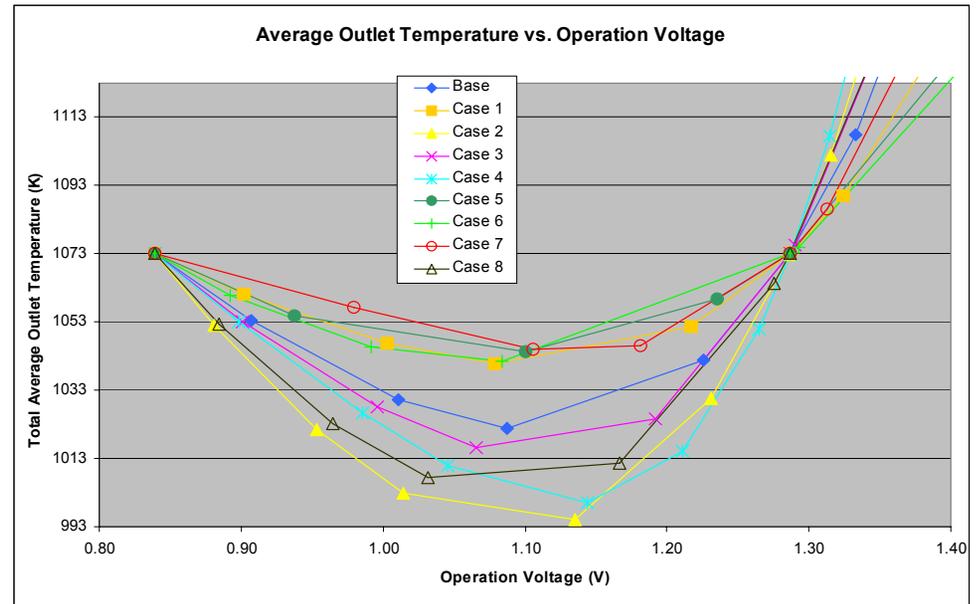
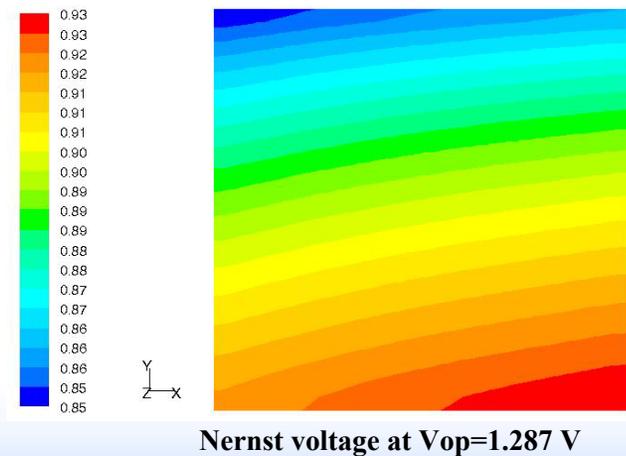
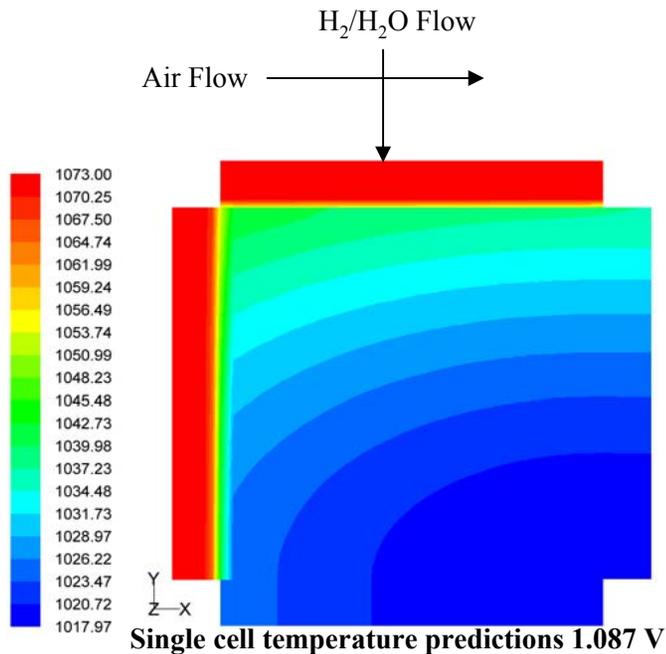
Current Density, A/m²



Oxygen production



FLUENT SOEC Predictions



Average outlet gas temperature versus operating voltage for various cases.

Base Case

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 : $O_2 = 0.2329$, $N_2 = 0.7671$

Operating pressure = 101.325 kPa

Inlet temperature H_2 and O_2 side = 1073 K

Case 1: change only mass flow rate on H_2 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

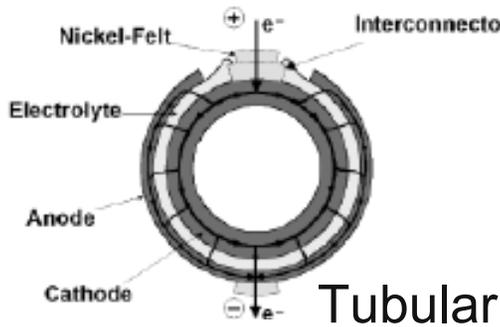
Case 8: change g on concentration in activation overpotential from 0.5 to 0.1

Conclusions

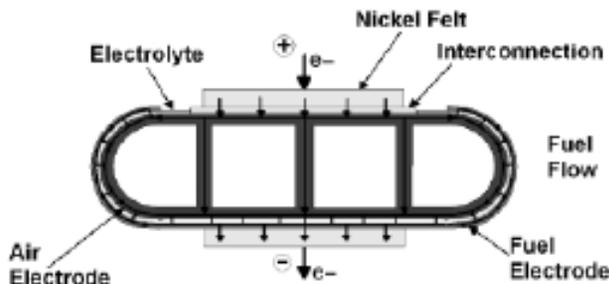
- Thermal, electrochemical and mechanical performance of SOECs can be improved through design.
 - Larger cells with higher inlet steam mass flux can be beneficial for the economics of the SOECs.
 - Contact resistances influence the total cell resistance and cell temperature more significantly than the 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

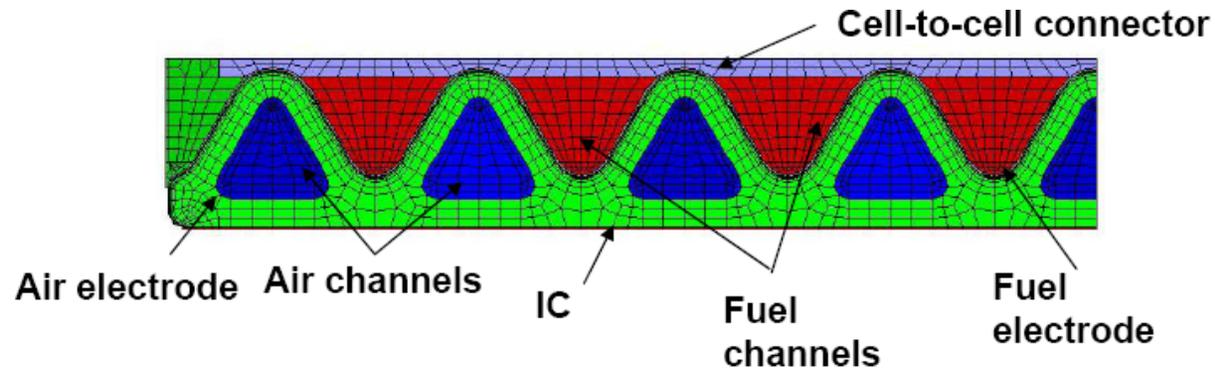
- Continue to identify and analyze SOEC **degradation mechanisms** and compare with experiments at ANL.
- Update of the model algorithm (ongoing) for flexibility to analyze various cell and stack designs
 - Other new **seal-less** and **high-power-density** cell and stacks designs will be evaluated through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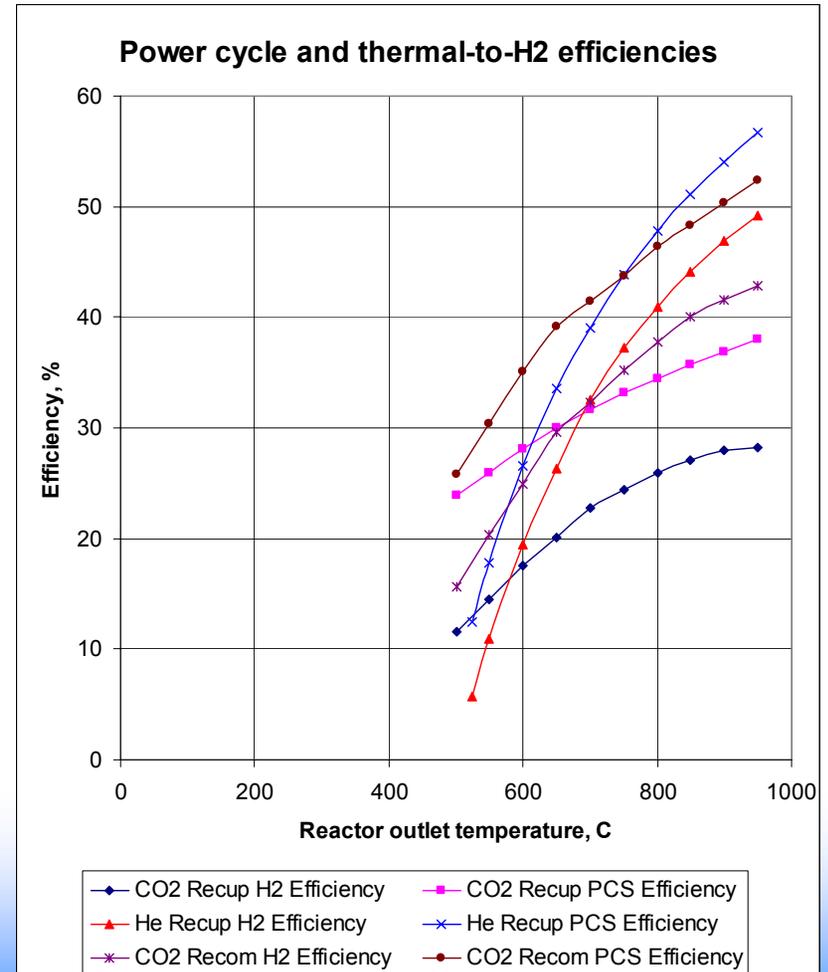
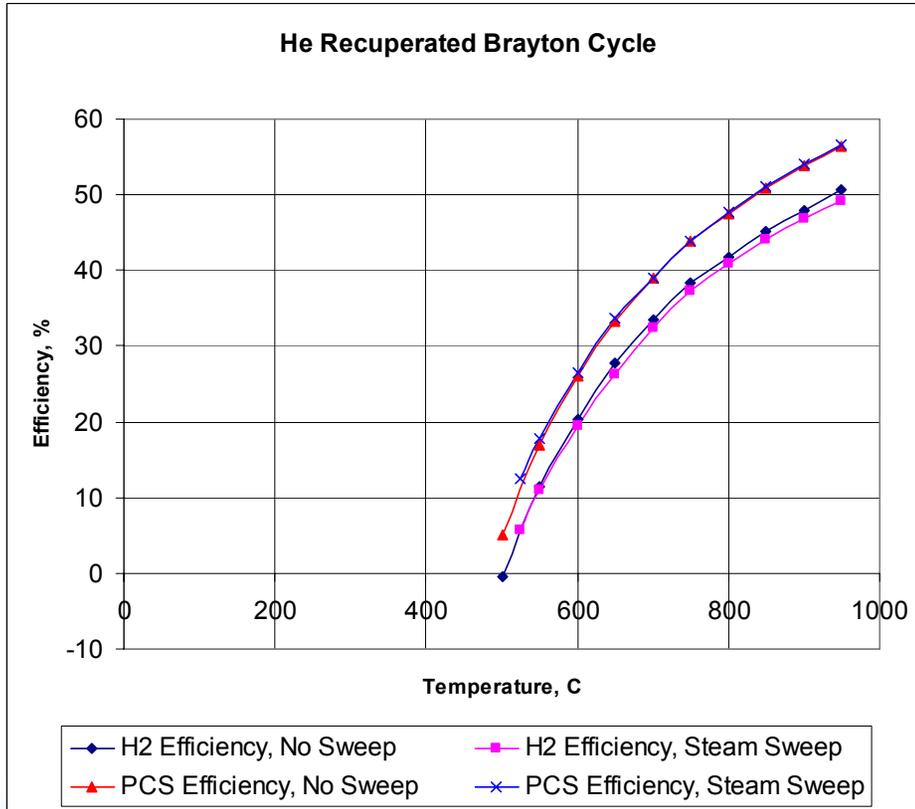
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Power Cycle and Hydrogen Production Efficiencies

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



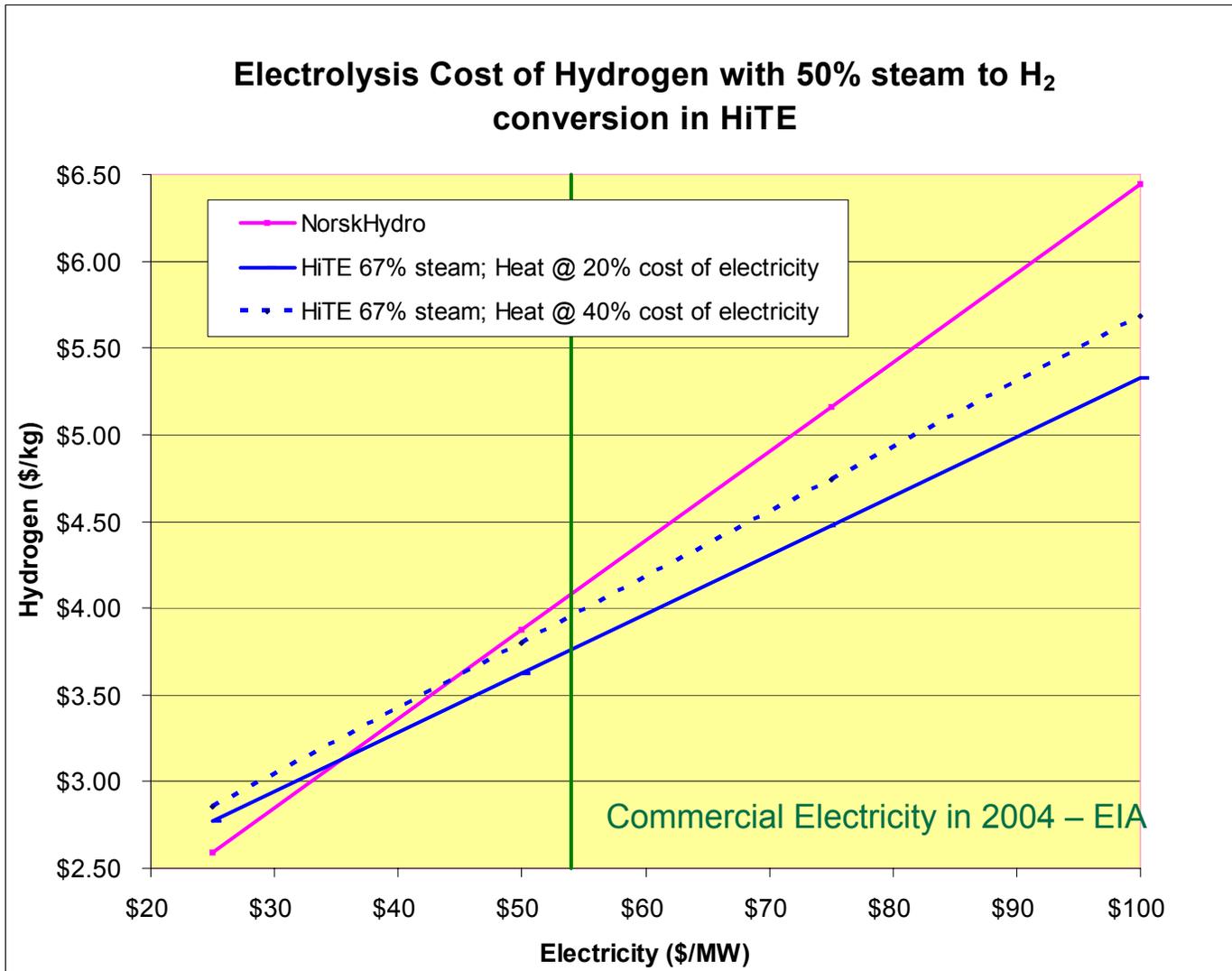
High-Temperature Electrolysis Capital vs. NorskHydro

Higher costs -- Green; Lower costs -- Blue

System	Capital, \$K	
Direct Costs		
<i>Electrolyzer</i>		
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
<i>Compressor</i>	10.33%	\$18,824
<i>Support Facilities</i>		
Pipe, valves, fittings, H ₂ & O ₂ tanks	7.00%	\$12,761
Process instruments and controls	7.00%	\$12,761
Electrical equipment and materials - support	5.00%	\$9,115
Structural support, insulation, paint	10.00%	\$18,230
<i>Direct Costs Sub-total</i>	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
<i>Indirect Costs Sub-total</i>		\$280,742
<i>Direct + Indirect Costs Sub-total</i>		\$463,042
Interest & Inflation	0.00%	\$0
<i>Total Plant Investment-TPI</i>		\$463,042
Royalties	0.60%	\$1,094
Start-up Costs	1.00%	\$1,823
Commissioning & spare parts	0.35%	\$1,605
<i>TOTAL PROJECT COSTS</i>		\$467,564

System	Capital, \$K	
Direct Costs		
<i>Electrolyzer</i>		
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
<i>Compressor</i>	13.35%	\$18,824
<i>Support Facilities</i>		
Pipe, valves, fittings, H ₂ & O ₂ tanks	7.00%	\$9,870
Process instruments and controls	7.00%	\$9,870
Electrical equipment and materials - support	5.00%	\$7,050
Structural support, insulation, paint	10.00%	\$14,100
<i>Direct Costs Sub-total</i>	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
<i>Indirect Costs Sub-total</i>		\$217,140
<i>Direct + Indirect Costs Sub-total</i>		\$358,140
Interest & Inflation	0.00%	\$0
<i>Total Plant Investment-TPI</i>		\$358,140
Royalties	0.60%	\$846
Start-up Costs	1.00%	\$1,410
Commissioning & spare parts	0.35%	\$1,242
<i>TOTAL PROJECT COSTS</i>		\$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

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Objectives

■ Ultimate goal

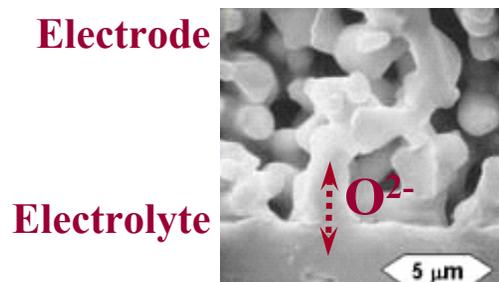
- Provide **efficient and durable materials and systems** for hydrogen production using high temperature steam electrolysis.

■ Near-term goals

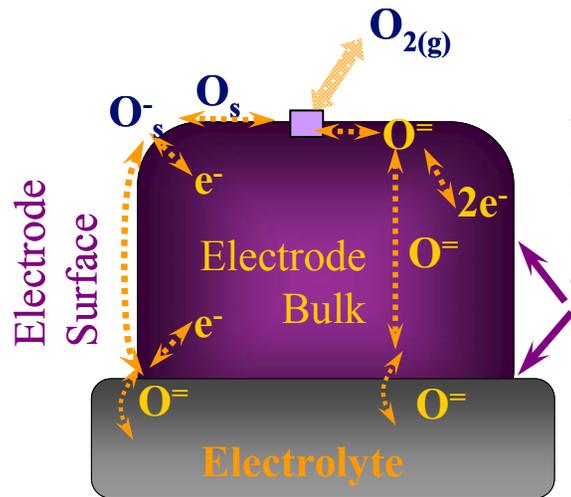
- Obtain **in-depth knowledge on governing mechanisms and properties** of the electrode materials.
 - *Molecular level experimental analysis of electrodes*
- Provide input for electrochemical kinetics modeling

Structure-Property-Performance Relations at Oxygen Electrodes

Oxygen reaction



Which charge-transfer pathway controls the OR mechanism?



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

Charge transport
Catalytic activity



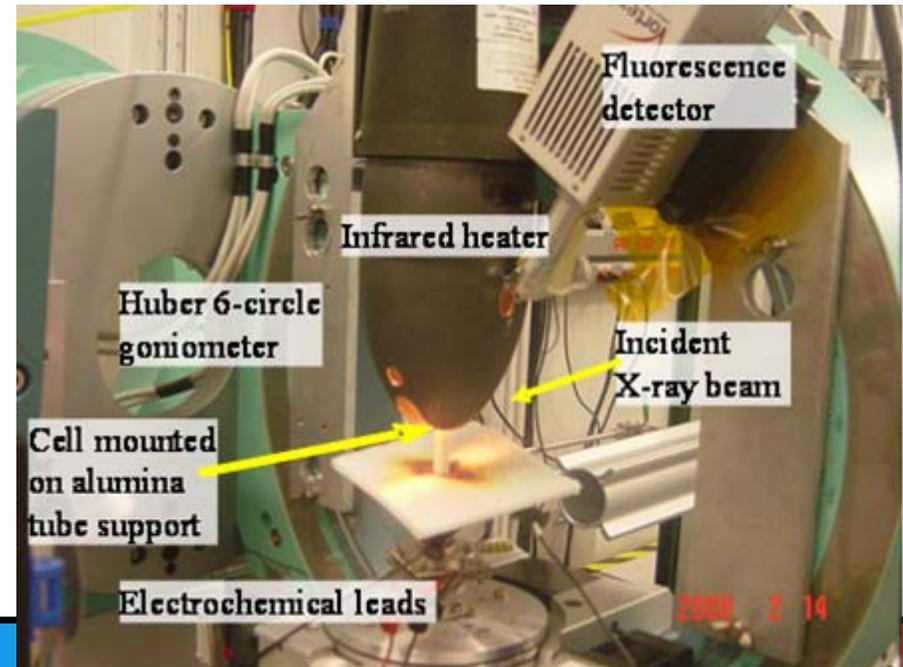
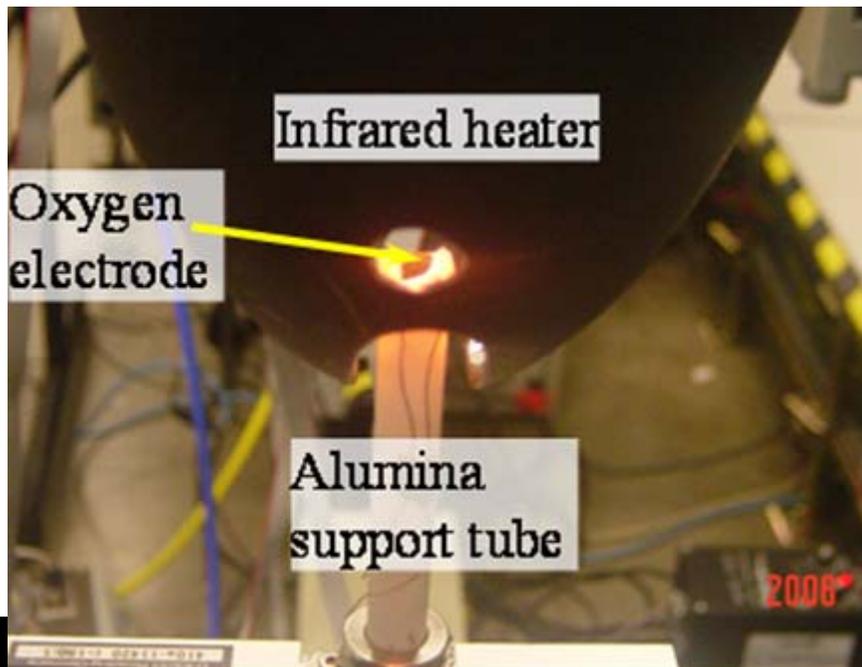
Chemical, physical, and structural properties of the

- Air/Electrode interface
- Electrode bulk
- Electrode/Electrolyte interface

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

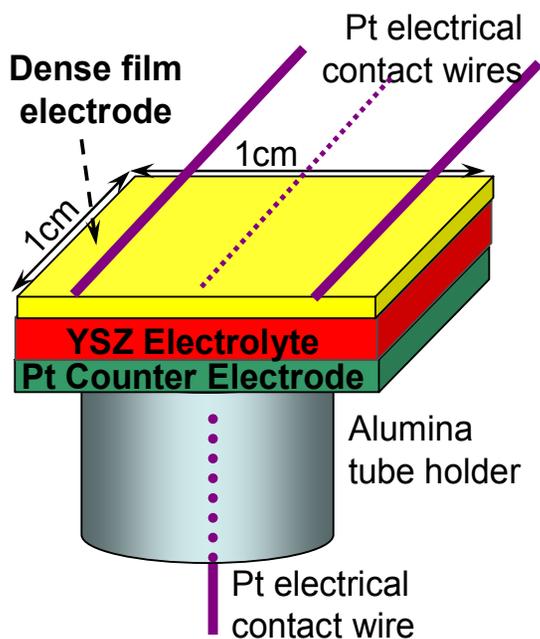
Approach: *In situ* X-ray and Electrochemical Characterization of the Electrode and its Interfaces

- 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

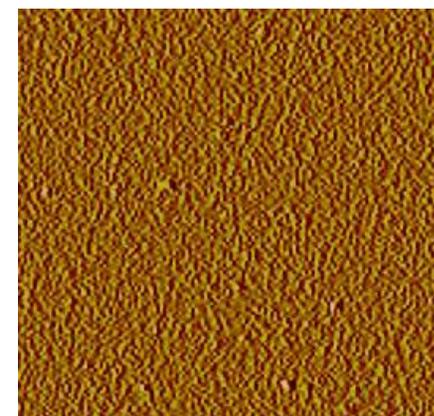
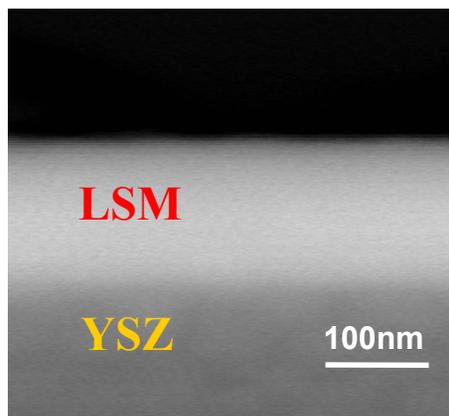


Non-obstructing heater and electrical contacts

Electrically active beam path on the electrode

■ Dense thin-film electrodes,

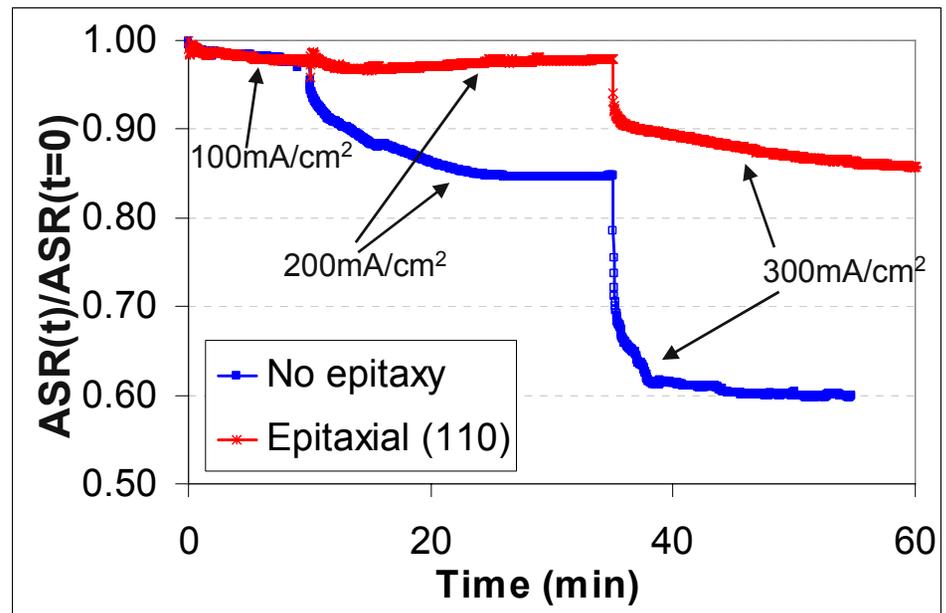
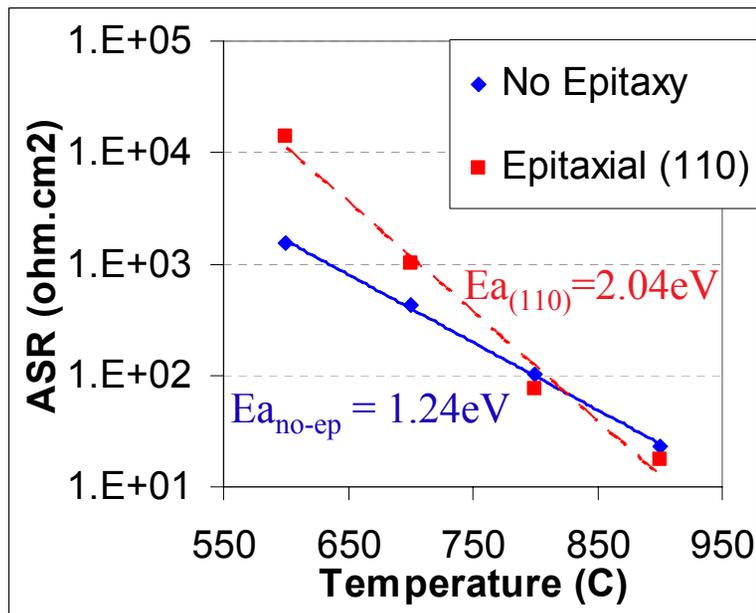
- $t = 20\text{-}200\text{nm}$
- Allows for **x-ray reflectivity at grazing angles** for surface sensitivity.
- Fabricated by pulsed laser deposition.
- Electrolyte substrate: (100) single-crystal YSZ.
- Electrodes: $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM), $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ (LCM), $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSC) deposited at $T = 700\text{-}780^\circ\text{C}$, $P_{\text{O}_2} = 25\text{-}200\text{mbar}$.



100nm
RMS Roughness: 0.5-1nm

Dense Thin Film Electrodes: Effect of Crystal Orientation

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+d}$ (LSM), 100nm-thick, with no epitaxy and with (110) orientation on single crystal YSZ electrolyte.



Near OCP; $T > 700^\circ\text{C}$, $\text{ASR}_{\text{no-ep}} > \text{ASR}_{(110)}$
 $T < 700^\circ\text{C}$, $\text{ASR}_{\text{no-ep}} < \text{ASR}_{(110)}$

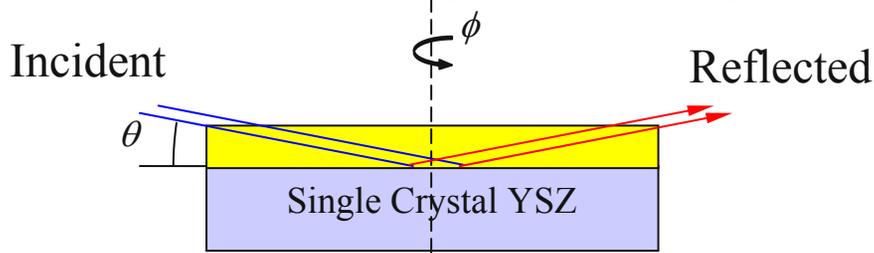
Under DC polarization at 700°C
 $\text{LSM-Activation}_{\text{non-ep}} > \text{LSM-Activation}_{(110)}$

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

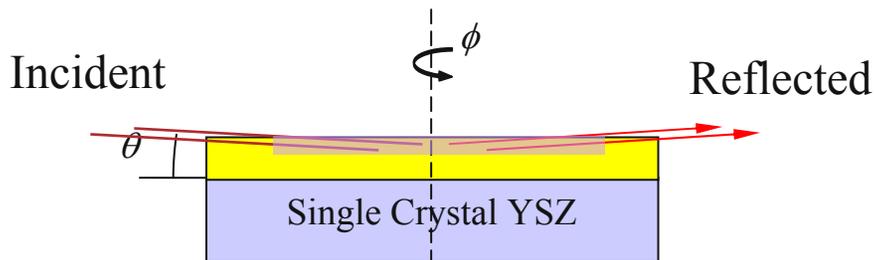
X-ray Reflectivity and X-ray Absorption Spectroscopy

What information do we get from XRR and XAS?

Specular x-ray reflectivity

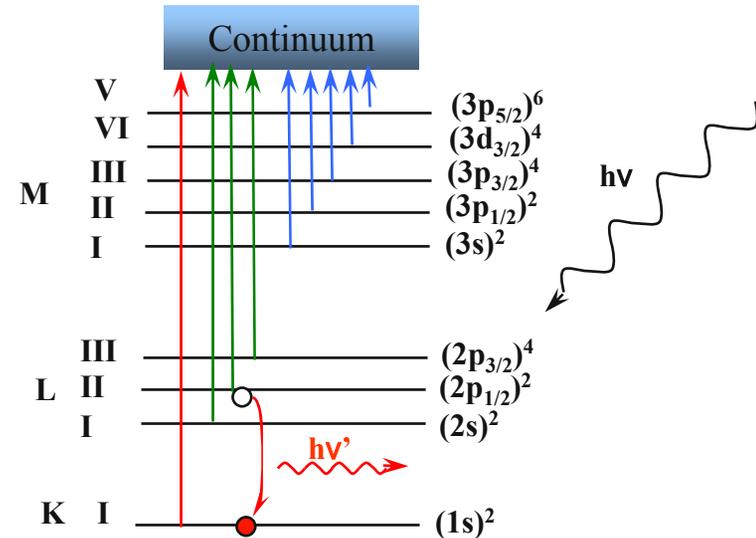


Small incident angle, $\theta > \theta_{critical}$
→ Measurement sensitive to the **bulk** of the electrode film.



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

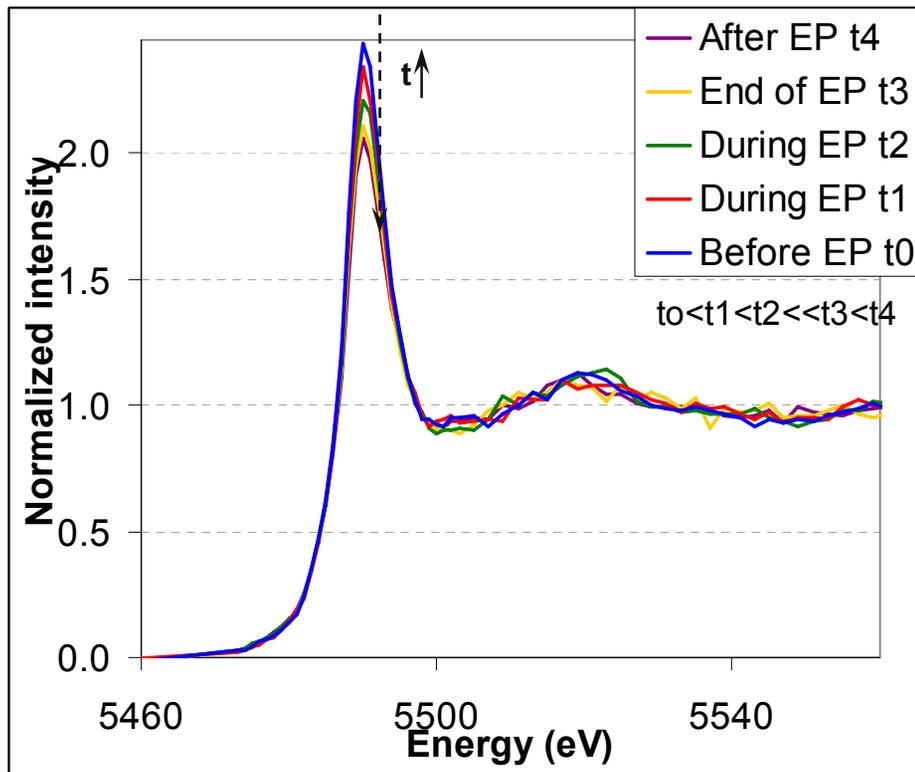
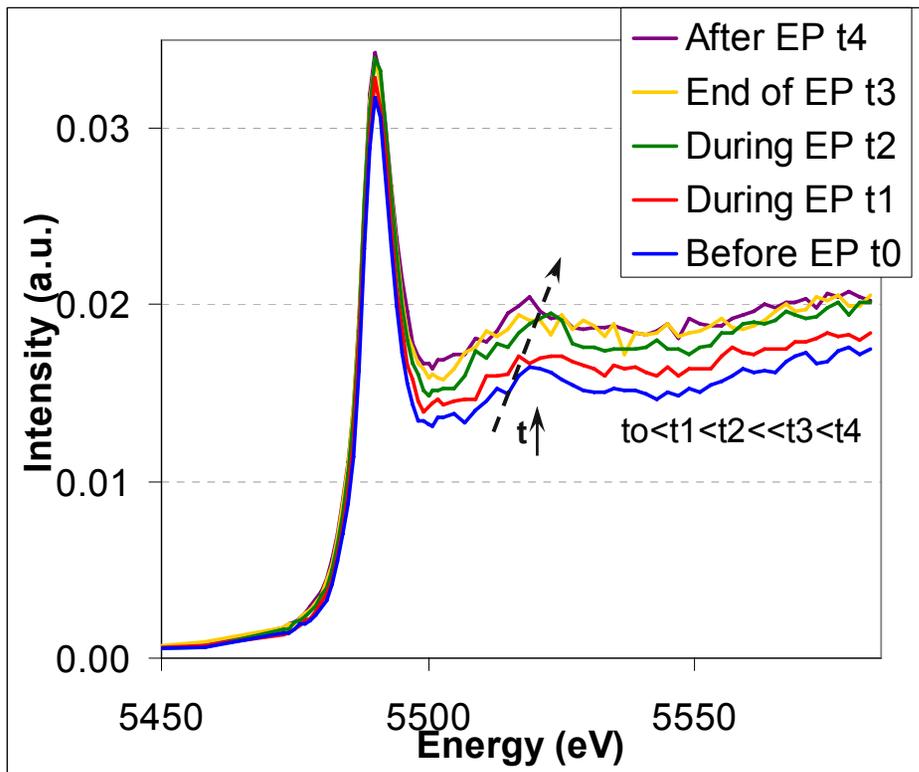


Decay of the excited states through fluorescence gives rise to the x-ray absorption spectroscopy

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

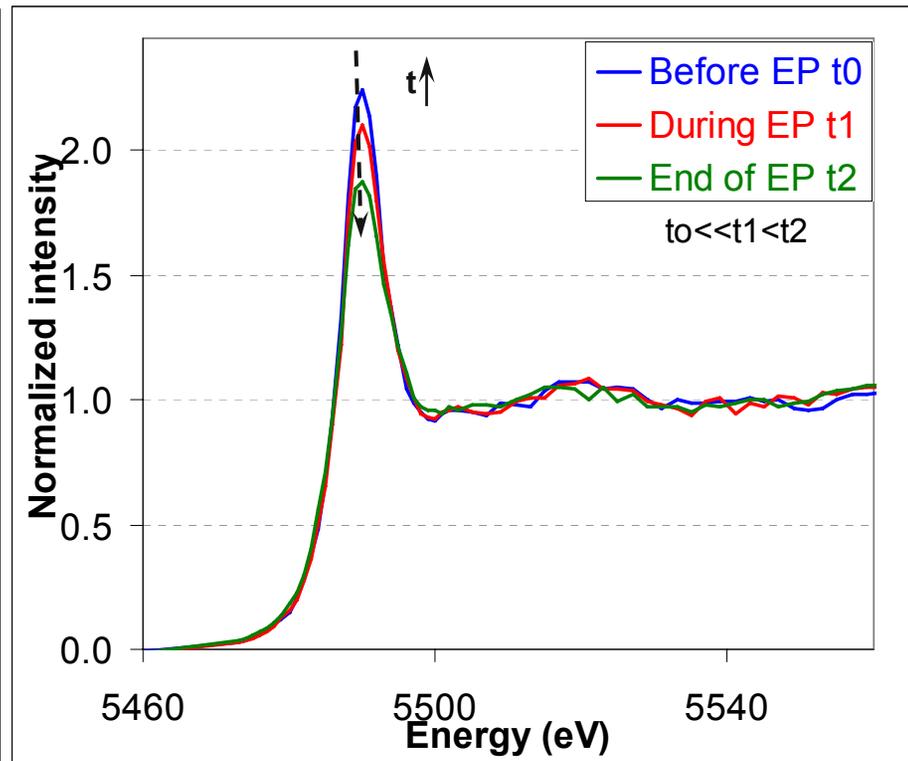
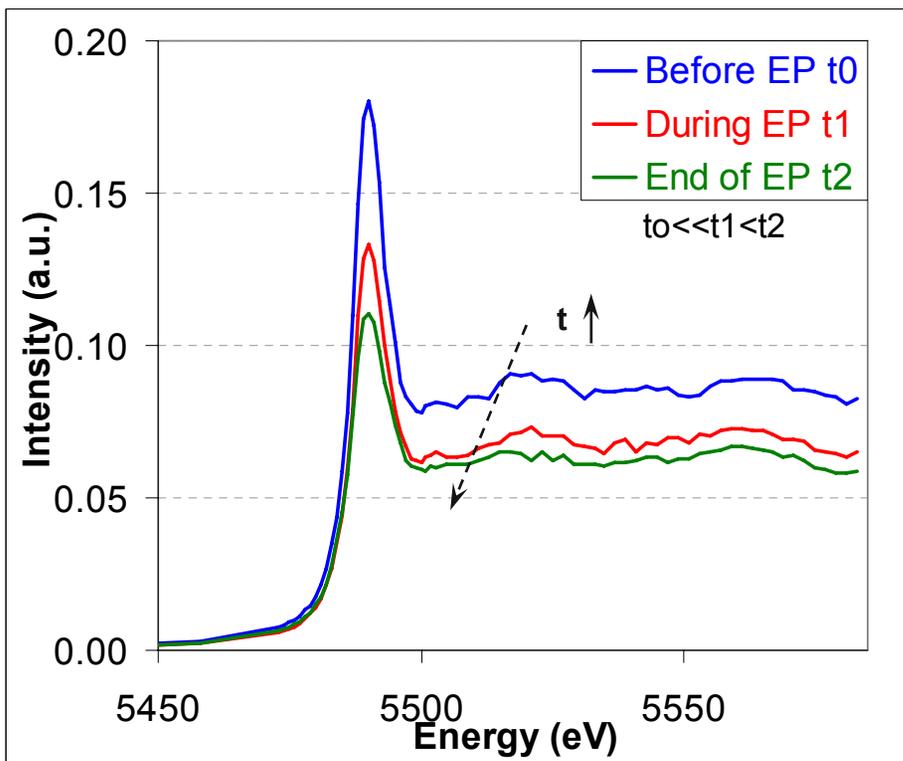


→ The change in the chemical state of the La is occurring **at** the top air-electrode film interface, only during the improvement of the electrode.

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

