Material Challenges in High Temperature Processes for Hydrogen Production

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GCEP-MIT Fission Energy Workshop
November 29, 2007

Why nuclear hydrogen?

Near-term markets → Mid-term markets → Long-term markets

Fertilizers

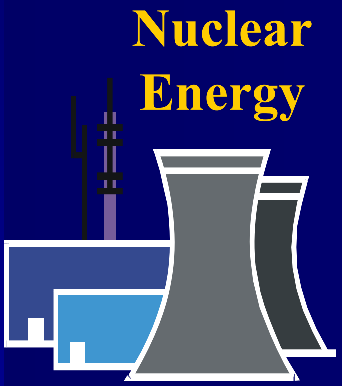
Oil Refining

Coal Liquefaction

Tar Sands

Remote Power

Transportation



Nuclear Energy

- CO$_2$-free
- Efficient and cost-competitive
- Size/location to address the industry needs

Heat and electricity →

Electrolysis and thermo-chemical processes:

$$H_2O_{(g)} \rightarrow \tfrac{1}{2}\,O_{2(g)} + \boxed{H_{2(g)}}$$

Co-electrolysis:

$$H_2O_{(g)} + CO_{2(g)} \rightarrow O_{2(g)} + \boxed{H_{2(g)} + CO_{(g)}}$$

- Hydrogen production using nuclear energy is a clean and promising technology to decrease CO$_2$-emissions. Potential advantages compared to water electrolysis are:
  - high efficiency and reduced electricity requirement,
  - inexpensive materials.

Goal

- Enable durable, efficient, cost-competitive, clean hydrogen production technologies.

Outline

- Nuclear hydrogen production technologies
- High temperature steam electrolysis (HTSE)
- Challenges, and fundamental research in:
    - degradation mechanisms of the present devices
    - interfaces for higher-efficiency in the materials
- Concluding remarks

Nuclear hydrogen production processes

- Research and development in the Nuclear Hydrogen Initiative (NHI) of DOE-NE on a range of hydrogen production technologies that can be supported by nuclear energy.

Temperature range	**Low** (RT)	**Intermediate** (500-700^{o}C)	**High** (>800^{o}C)
Themo-chemical	▨	Cupper-Chlorine	Sulfur-Iodine
Hybrid (Themo-electro-chemical)	▨	Calcium-Bromine	Hybrid-Sulfur
Electro-chemical	Water electrolysis	Steam electrolysis	Steam electrolysis

Sulfur-Iodine (SI) Process

- Purpose: Splitting the H_2O into H_2 and O_2 using catalysis at lower temperatures than pyrolysis.
- SI cycle, with maximum temperature above 850°C, using the thermal energy from the nuclear reactor

High-temperature nuclear reactor

Sulfur-Iodine Thermochemical Water-Splitting Cycle

$2H_2O + I_2 + SO_2 \rightarrow 2HI + H_2SO_4$

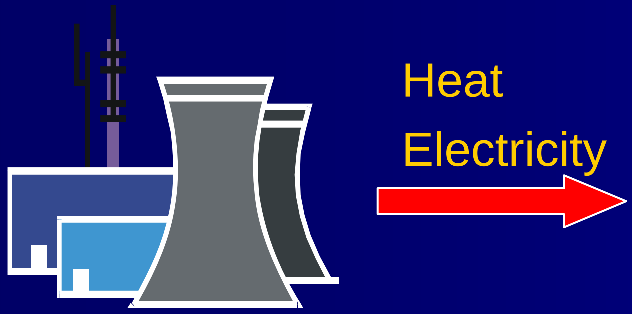
$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2} O_2$

$2HI \rightarrow I_2 + H_2$

Hybrid-Sulfur (Hy-S) Cycle

- Purpose: eliminating some of the corrosive chemical steps from the thermochemical SI cycle
- Hy-S, with maximum temperature above 850°C, using the thermal and the electrical energy from the nuclear plant.

High-temperature nuclear reactor



Heat

Electricity

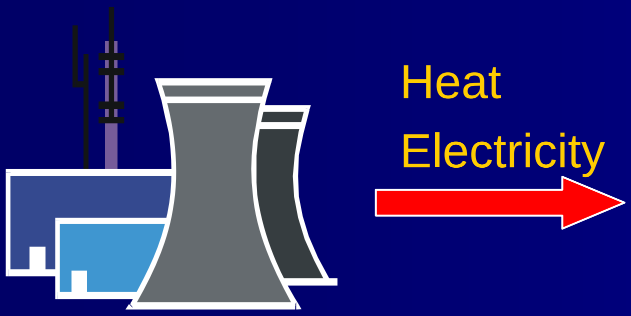
Hybrid-Sulfur Water-Splitting Cycle

$2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$ (El.)

$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2} O_2$

High Temperature Steam Electrolysis (HTSE)

- Purpose: To split steam, $H_2O_{(g)}$, electrochemically while spending >30% less electrical energy than water electrolysis
- HTSE, with maximum temperature at 830°C, using the thermal and the electrical energy from the nuclear plant.



High-temperature nuclear reactor

Heat

Electricity

High Temperature Steam Electrolysis

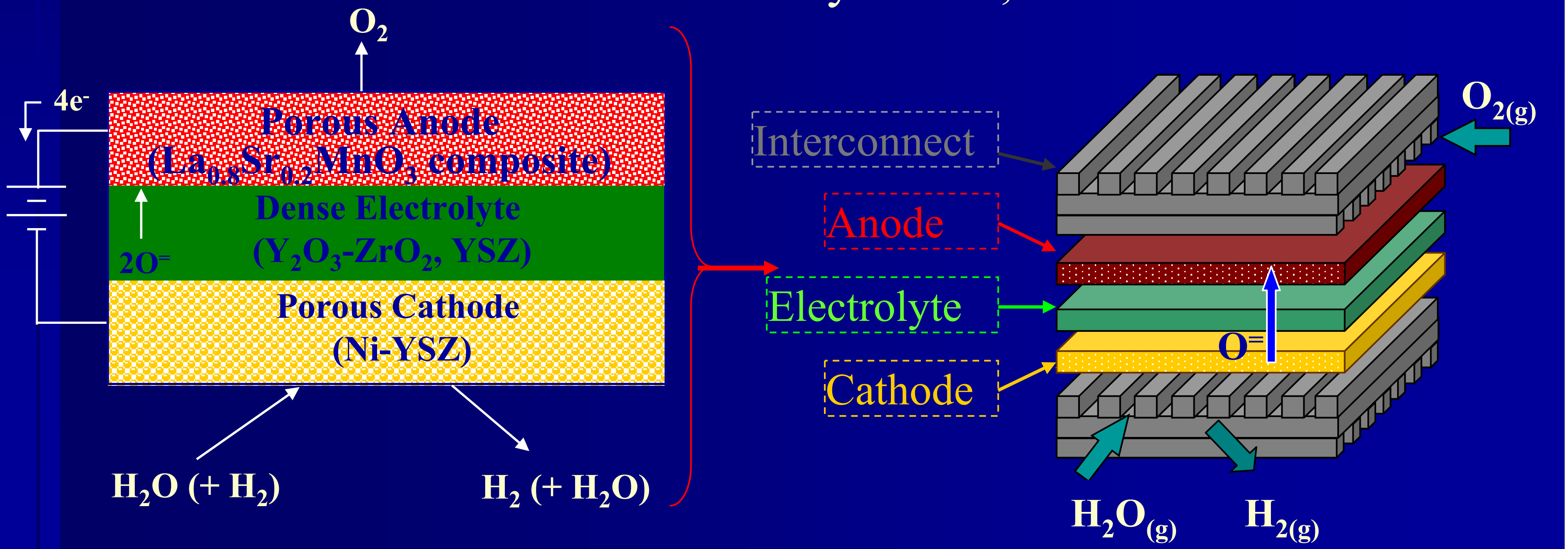
$$H_2O_{(g)} \rightarrow H_{2(g)} + \frac{1}{2}\,O_{2(g)}$$

–Largest amount of hydrogen production rate, and the longest duration of operation demonstrated within the NHI program.

High temperature steam electrolysis (HTSE)

- HTSE uses a solid oxide electrolysis cell (SOEC).
  - Materials are conducting ceramic oxides.
  - Device is based on the solid oxide fuel cells (SOFC).
- Cells are “stacked” together in series for power management.

Solid oxide electrolysis cell, SOEC



O_2

$4e^-$

Porous Anode
($La_{0.8}Sr_{0.2}MnO_3$ composite)

Dense Electrolyte
(Y_2O_3-ZrO_2, YSZ)

$2O^=$

Porous Cathode
(Ni-YSZ)

H_2O (+ H_2)

H_2 (+ H_2O)

Interconnect

Anode

Electrolyte

Cathode

$O^=$

$O_{2(g)}$

$H_2O_{(g)}$

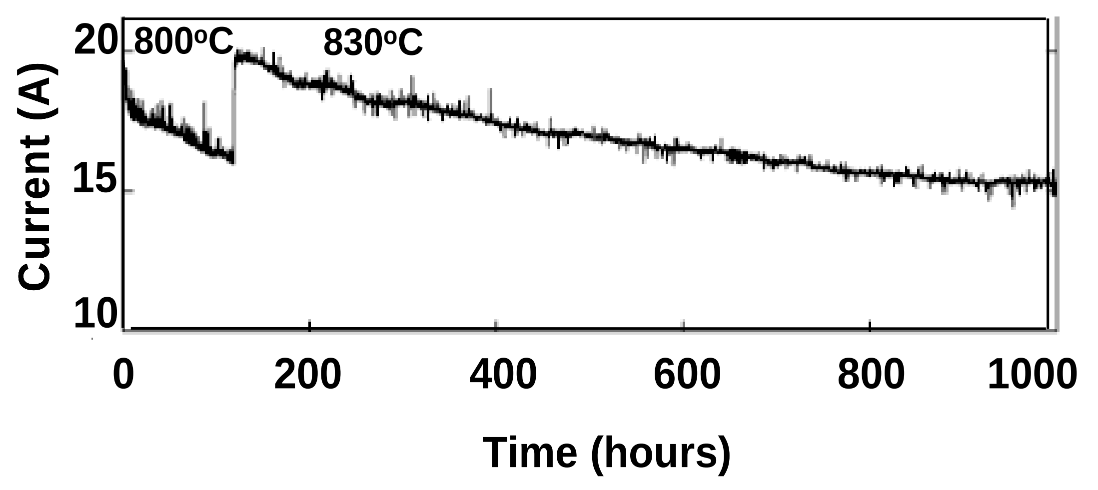
$H_{2(g)}$

Long-term performance of present HTSE

- >1200 NL/hr of H_2 production was demonstrated by Ceramatec & INL with a dual stack module for 2000 hrs.

Dual-stack SOEC module

Courtesy of Ceramatec, Inc.



O'Brien et al, *Nuclear Technology*, 2006

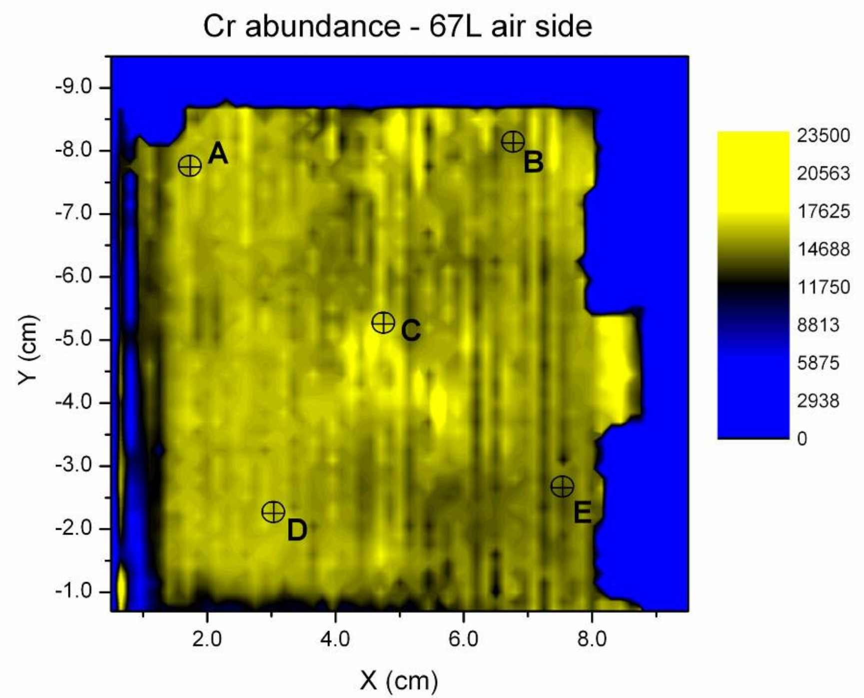
- Degradation of the present SOEC stack performance is the outstanding problem.

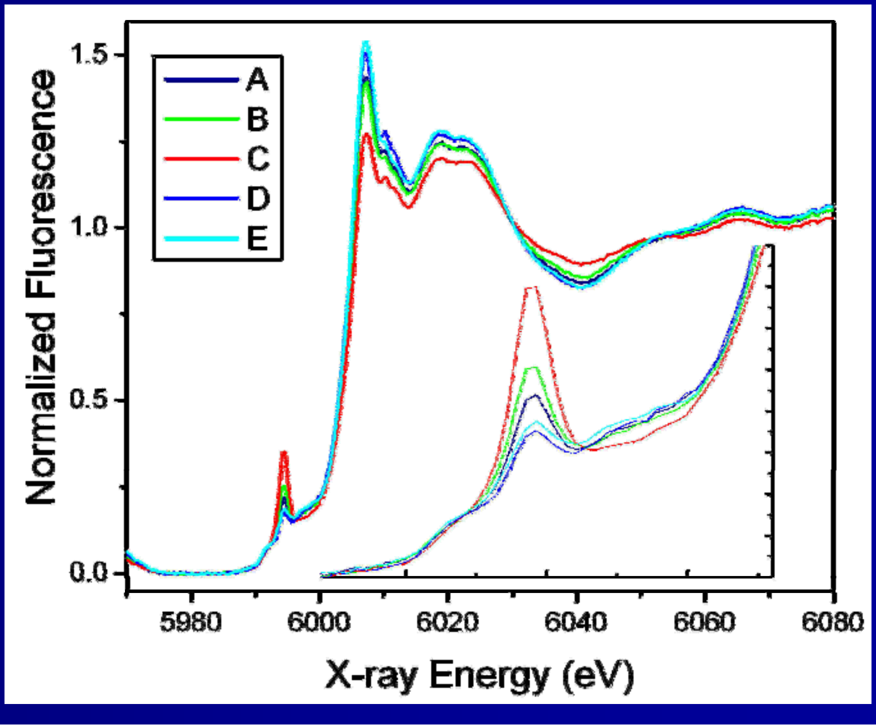
Degradation mechanisms in SOECs

High-level Problem	**Specific Questions on:**
Cr-poisoning, in the oxygen electrode (Cr is coming from the interconnect)	•Distribution and reaction species with Cr •Getter agents for Cr to avoid its entry to the electrode.
Electrode – electrolyte interface delamination, in the oxygen electrode	•Interface mechanical/adhesion stability against high flux of oxygen evolution •Interface chemical stability (interdiffusion) •Secondary blocking phase (zirconate) formation
Decomposition / interdiffusion of cations at the interfaces, of the oxygen electrode	•Between cobaltite-manganite layers •At manganite-zirconia particles •Decreasing electrical conductance of cobaltite due to decomposition
Si-poisoning on the hydrogen/steam electrode (Si is coming from the cell seals)	•Distribution and reaction species with Si •Specific position - on Ni or on Ni-zirconia interfaces. •Electrochemical nature where Si gets deposited.

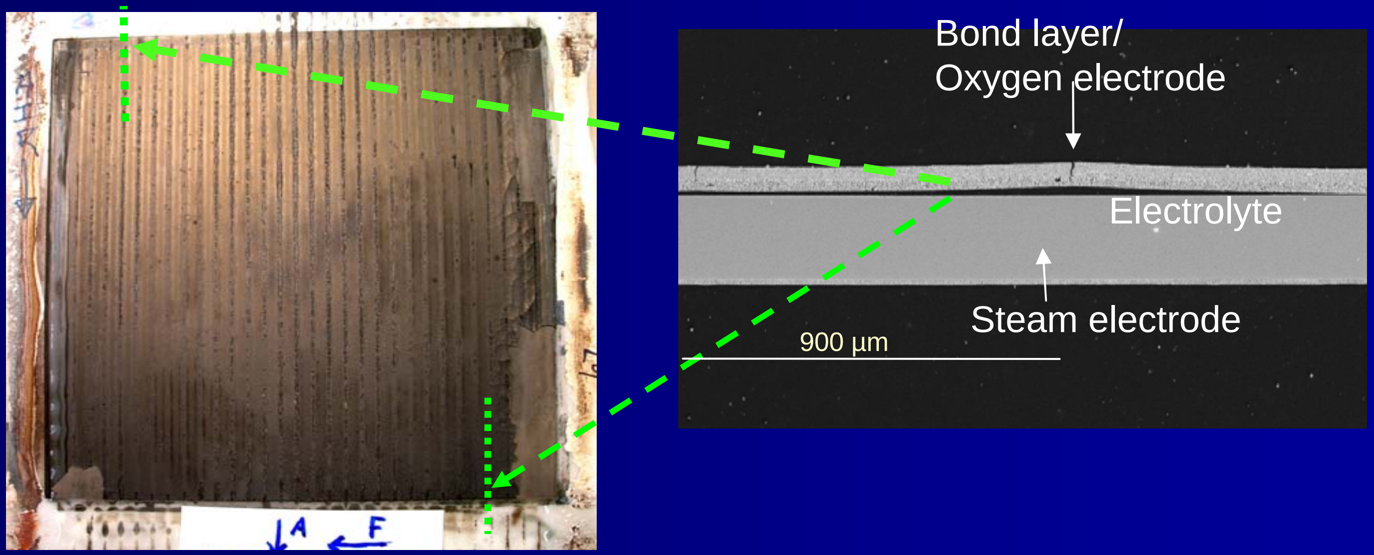
Cr-contamination in oxygen electrode

- Cr fluorescence spectra on the oxygen electrode showed presence of Cr in the bond-layer at ~10v%.
  - A large loss of active surface area
- The pre-edge peak shows evidence of Cr^{6+} near the center of the electrode ➔ Multiple Cr-reaction species
  - Cr transport mechanism – solid state diffusion? Volatilization?





Delamination between electrode and electrolyte


SOEC oxygen-electrode side

SOEC cross-section

- Reasons for deformation at the electrode/electrolyte interface
  - Secondary phase formation with high lattice- and thermal-mismatch
  - Steam-leak leading to reduction and decomposition of the manganite
- Tools to probe the reasons of deformation
  - High-resolution electron microscopy; in diffraction and spectroscopy
  - High-resolution Auger electron spectroscopy

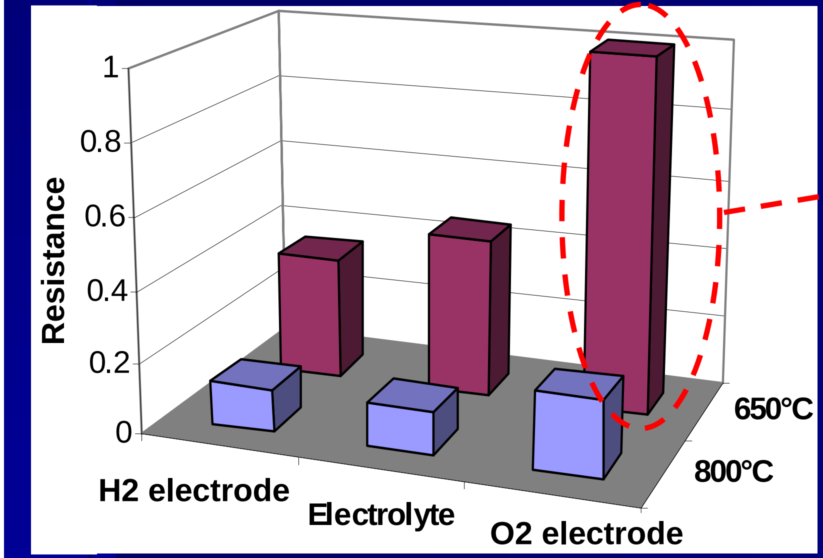
Avoiding degradation in SOECs

- Goal: ensure the chemical stability
  - At the electrode/interconnect interface
    - Protective coating on the interconnect to decrease Cr loss.
  - At the electrode/electrolyte interface
    - Composition gradient, with A-site deficiency, to avoid zirconate formation
    - Thin-film protective interlayer, ceria, to avoid interaction of the electrode material with the zirconia electrolyte.

- Fundamental understanding of the degradation mechanisms in SOECs are leading to ***evolutionary improvements*** in the HTSE performance within the existing framework of materials, device design, and operating temperature (>800°C).

Lower operating temperature for SOEC?

- There is the need to reduce the operating temperature for prolonged life-time, and thus reduced cost.
- Reduced temperature can allow the use of a wider range of nuclear reactors for supporting the SOECs.



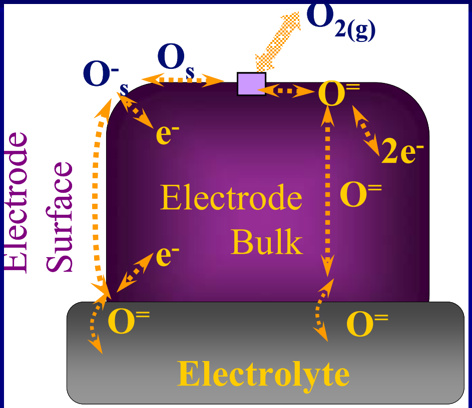
Singhal et al. HT-SOFCs, p281

- At lower temperatures, major source of energy loss is poor performance of the O_2-electrode.
- Goal:
  - ***Revolutionary advances*** in electrode materials (structures and compositions) for higher efficiency in H_2 production at intermediate temperatures (500-700^{o}C).

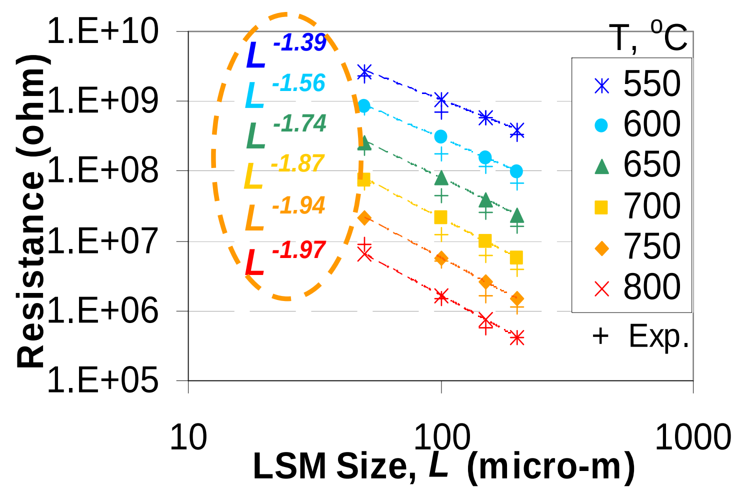
Limiting reactions and pathways in oxygen electrode

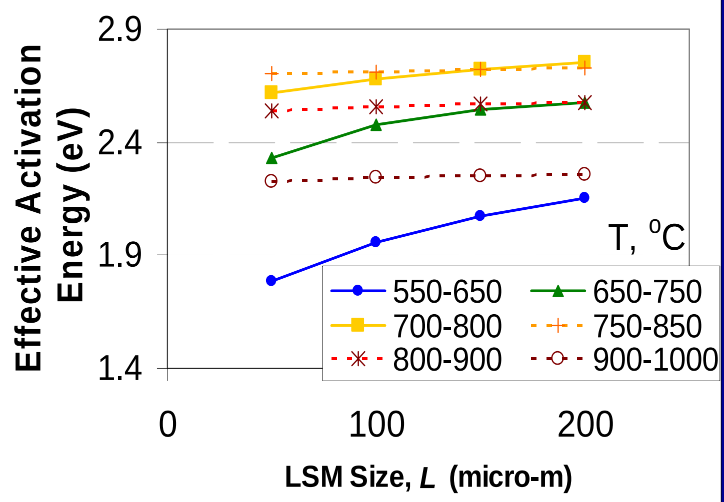
Overall oxygen reaction

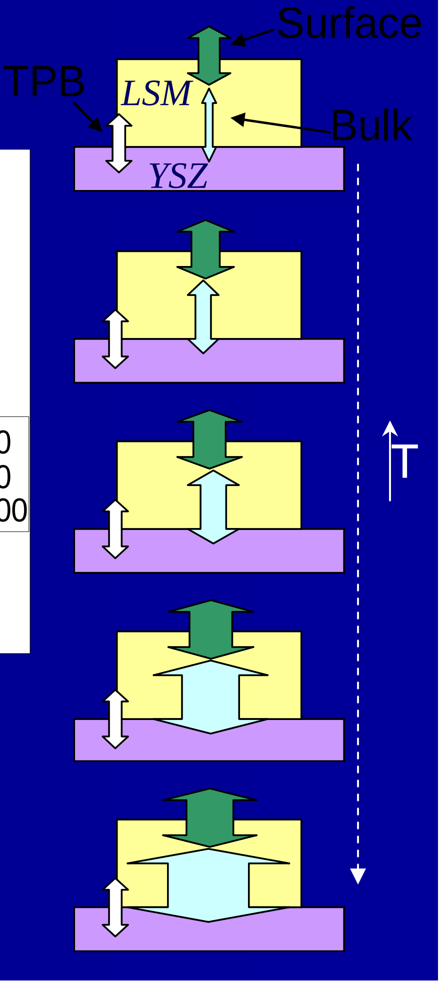
(OR): $O_O \leftrightarrow ½O_2 + 2e^- + Vo^=$



For $La_{0.8}Sr_{0.2}MnO_3$ at a micro-scale



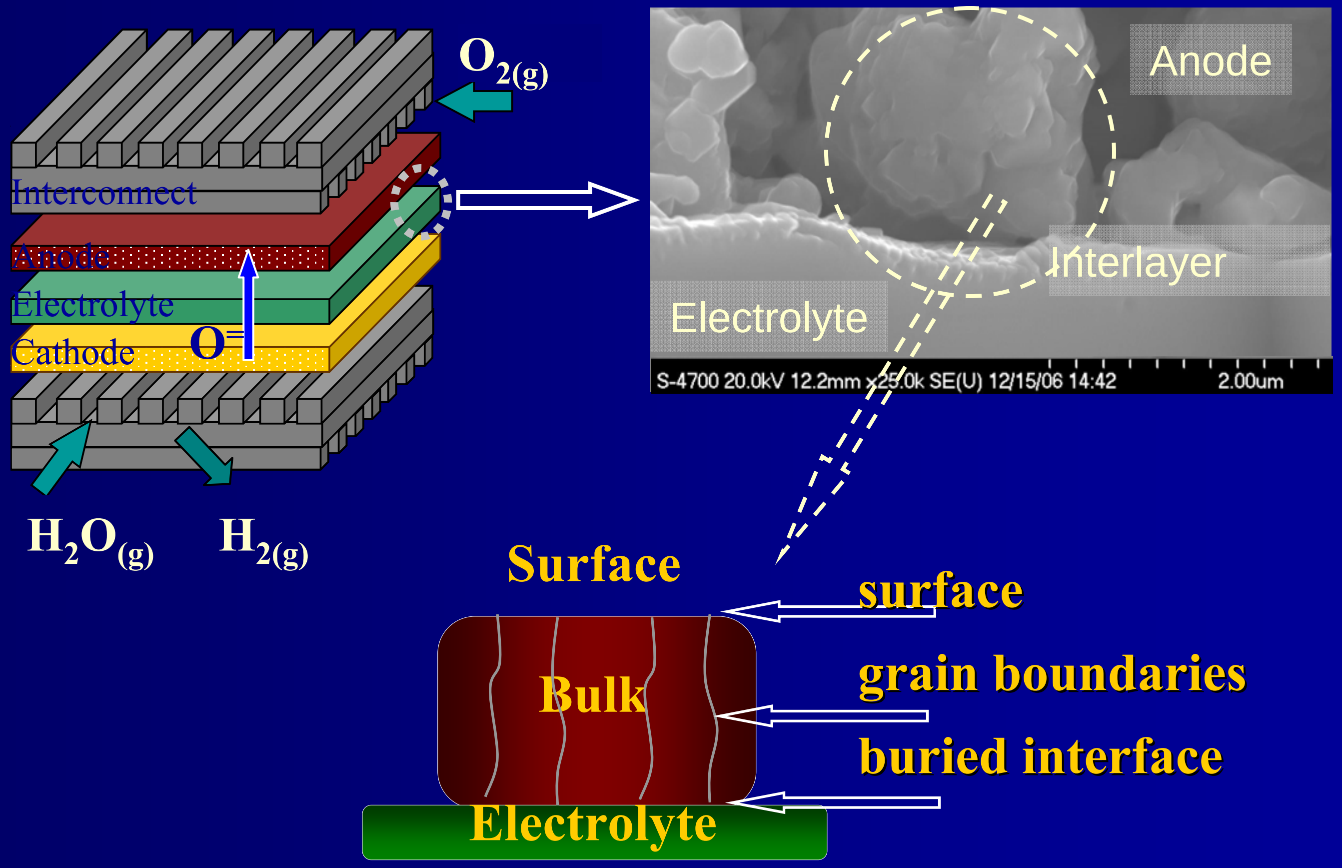




At high temperature: limited by surface charge transfer – external interface

At low temperatures: limited by bulk transport – internal interfaces

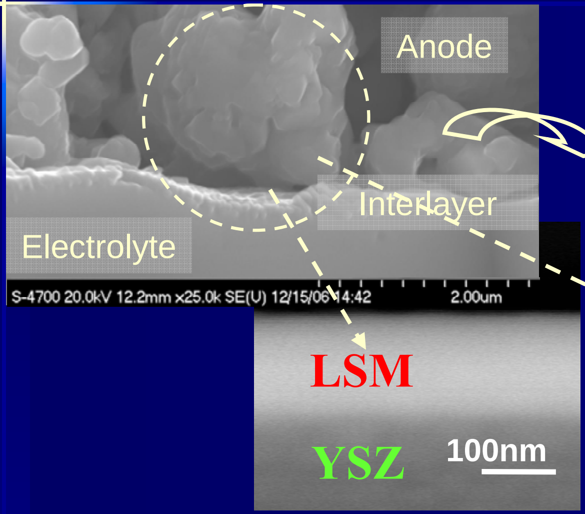
Opportunity for intermediate temperature SOECs

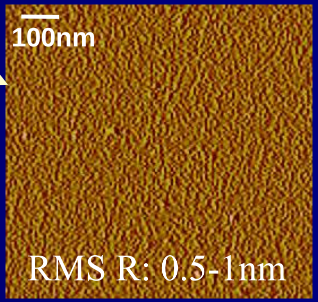


➔ Opportunity for improving the transport properties through the understanding and tailoring of the interfaces:

→ structural and chemical nature

Importance of interface structure

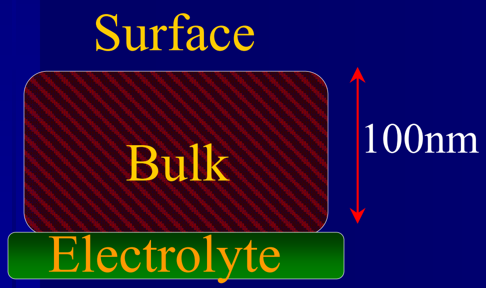




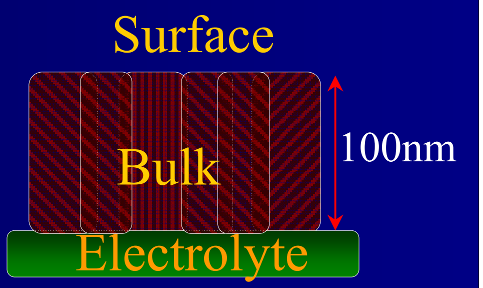
Represent particles as thin-films

- Dense thin-film electrodes
  - Fabricated by pulsed laser deposition.
  - Electrolyte substrate: (100) single-crystal YSZ.

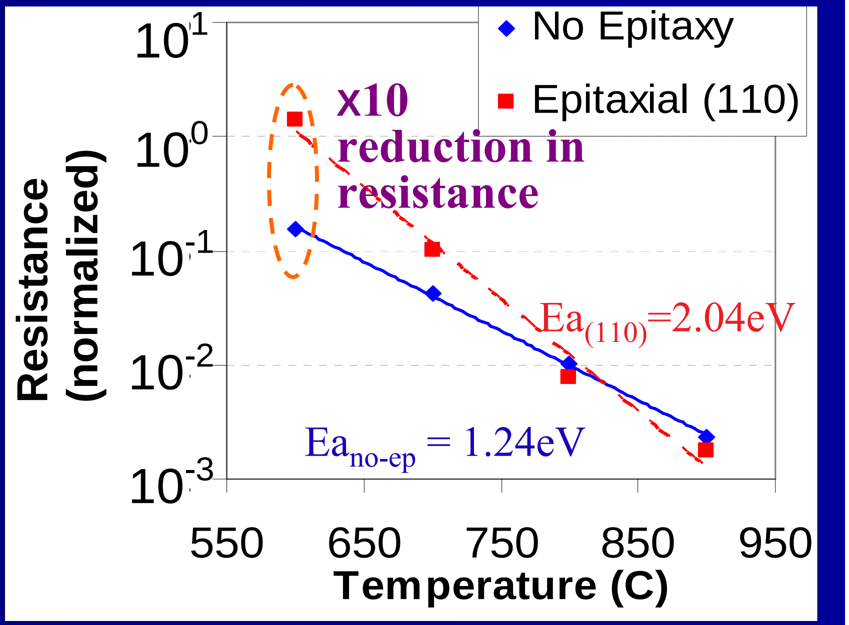
Comparison of epitaxial and non-epitaxial LSM



LSM: Epitaxial (110)



LSM: No epitaxy, textured

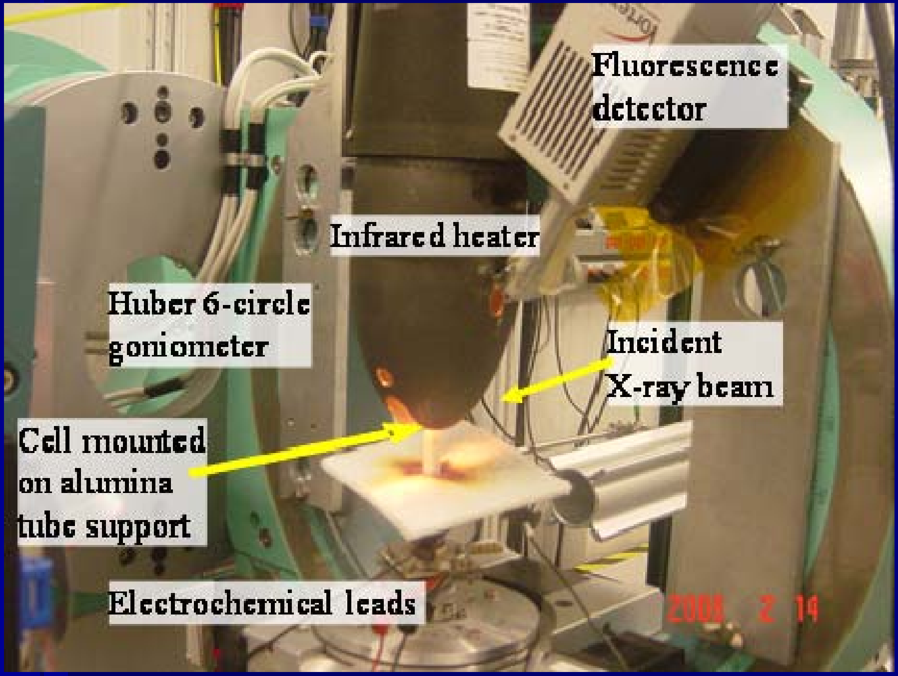


B. Yildiz, and K.C. Chang et al., *Proc. 31st Int. Conf. Advanced Ceramics and Composites*, January 2007

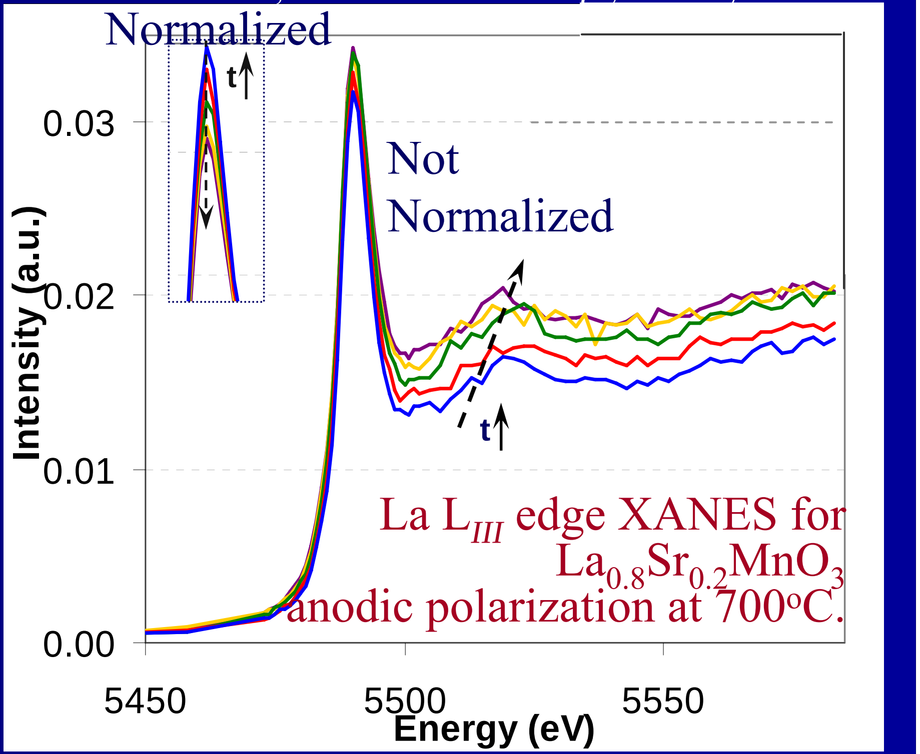
Structure of the surface and the grain boundaries is important.

Characterization of the electrode surface

- *In situ* x-ray characterization of the oxygen electrode materials
- X-ray absorption spectroscopy: oxidation state, atomic environment
  - Grazing incidence-angle scattering geometry for surface sensitivity
- Set-up, *a first*, shown here at the Advanced Photon Source.

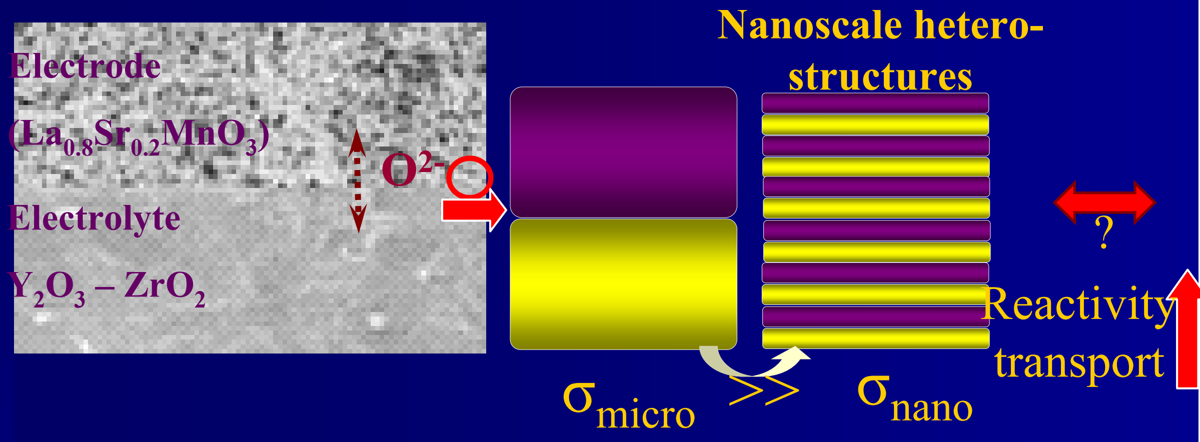


B. Yildiz et al., *Adv. Cer. and Comp.*, January 2007



→The change in the chemical state of the A-site cations is occurring at the surface, associated with the improvement of the electrode.

Interfaces in oxygen electrocatalysis



Electrode

$(La_{0.8}Sr_{0.2}MnO_3)$

O^{2-}

Electrolyte

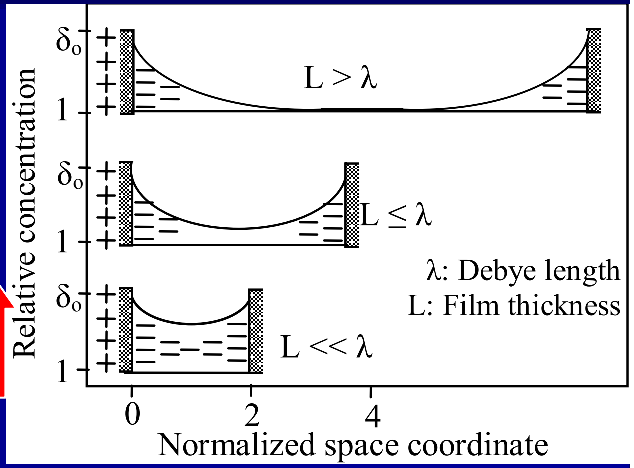
$Y_2O_3 – ZrO_2$

Nanoscale hetero-structures

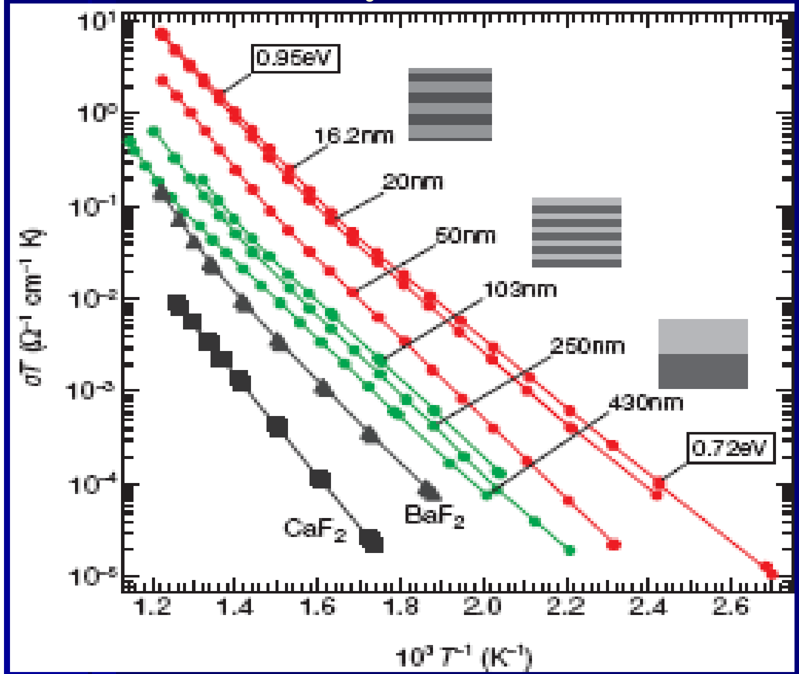
σ_{micro} >> σ_{nano}

?

Reactivity transport



Conductivity Enhancement



Ionic conduction in CaF_2/BaF_2 nanoscale heterostructures, Sata et. al, *Nature*, 408, 2000

- Obtain fundamental level knowledge about the layer/grain size-effect:

Charge transport
Catalytic activity

↔

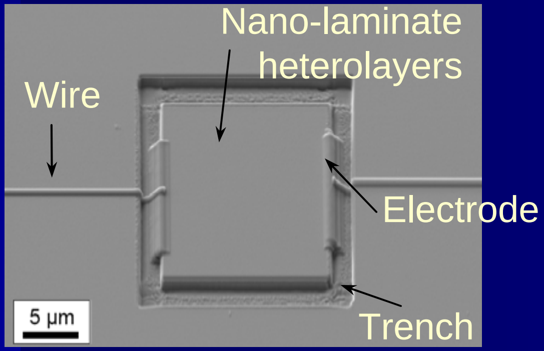
Chemical, physical, and structural properties of the electrode interfaces

- Defect chemistry
- Strain state

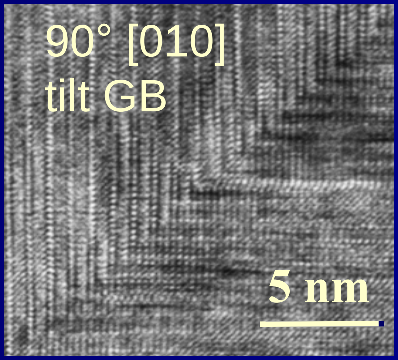
Characterization of interface transport properties

- Site-specific high-resolution microscopy and spectroscopy is needed to characterize:
  - Important relationship between the defect chemistry and strain and the conductivity and catalytic activity at the interface and near-interface regions (while under polarization):

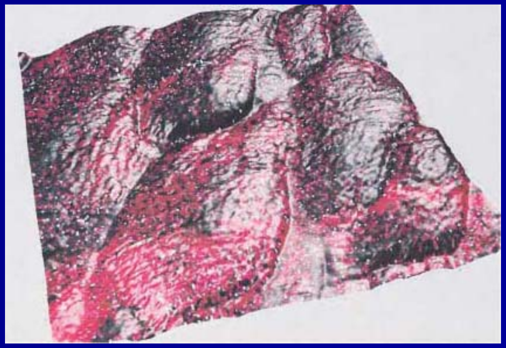
Synthesis and nano-fabrication



Structure and defect chemistry



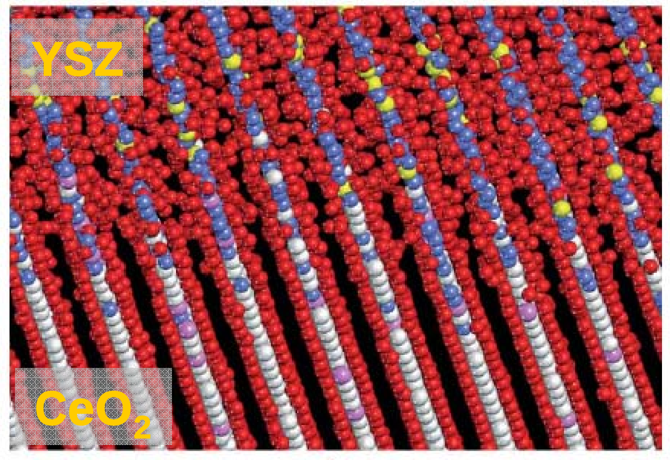
Transport and electronic structure *in situ*



Becker et al., *PRL*, **89**, 2002

Modeling and simulations of transport properties

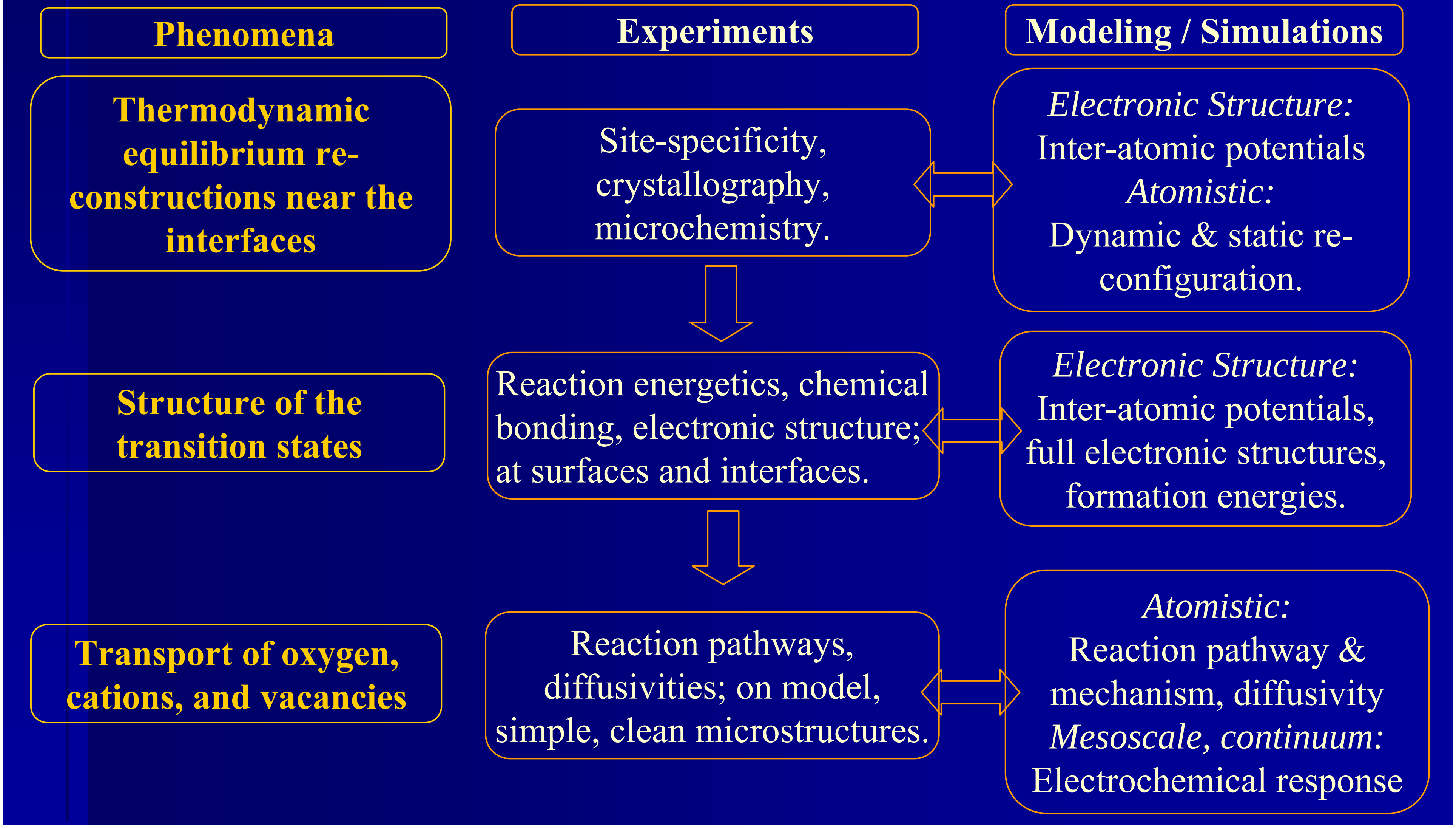
- Predictive modeling capability is needed for identifying the promising interface structures in a more efficient way.
    - Close coupling with the experiments using model material systems.
- Goal: Elucidating and predicting the transport properties
    - First principles calculations:
        - formation energies for charged defects in a given interface configuration
        - Strain state of the interface
    - Atomistic simulations
        - Charge transfer and transport properties at the interface



Model representation of the YSZ-CeO_2 near-interface region. Sayle et al., *J. Matls. Chem.*, **16** (11) 2006.

Multidisciplinary approach for studying the conducting interfaces

- With capabilities that we have and are developing at MIT, and with external collaborations:



Phenomena

Experiments

Modeling / Simulations

Thermodynamic equilibrium re-constructions near the interfaces

Site-specificity, crystallography, microchemistry.

Electronic Structure: Inter-atomic potentials *Atomistic:* Dynamic & static re-configuration.

Structure of the transition states

Reaction energetics, chemical bonding, electronic structure; at surfaces and interfaces.

Electronic Structure: Inter-atomic potentials, full electronic structures, formation energies.

Transport of oxygen, cations, and vacancies

Reaction pathways, diffusivities; on model, simple, clean microstructures.

Atomistic: Reaction pathway & mechanism, diffusivity *Mesoscale, continuum:* Electrochemical response

Concluding remarks

- Nuclear energy can provide clean non-electric energy carriers.
- Hydrogen production processes at high temperature and corrosive environment have severe materials constraints.
- Degradation of materials for steam electrolysis must be mitigated.
- "Activity" and "degradation" are competing phenomena in determining the operating temperature of the SOECs.
- A fundamental understanding is needed for the important role of interfaces on the activity of the conducting materials for steam electrolysis electrodes, using advanced scientific characterization tools.
- A predictive capability is needed using advanced multiscale modeling and simulations.

Acknowledgements

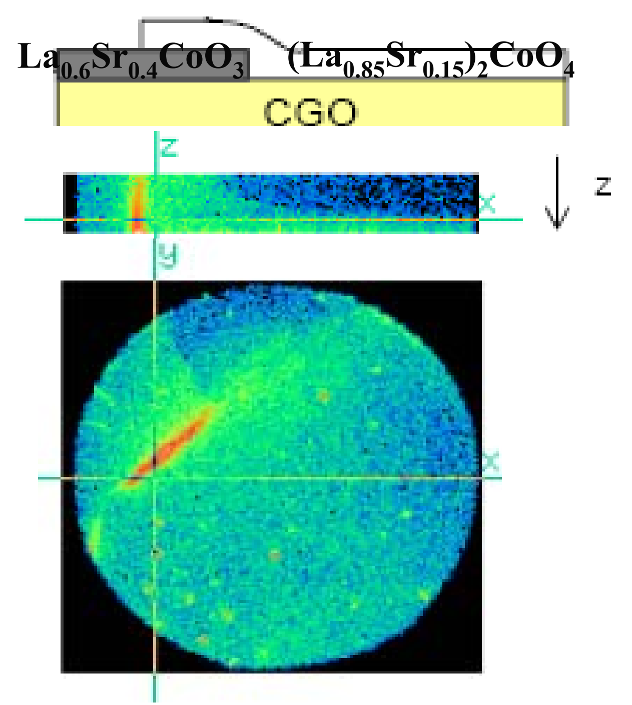
- Drs. David Carter, Deborah Myers and Jennifer Mawdsley, ANL, for SOEC materials and degradation.
- Drs. Kee-Chul Chang and Hoydoo You, ANL, for *in situ* x-ray characterization of surfaces.
- Dr. Burc Misirlioglu, MIT, for transport at interfaces.

Backup slides

Internal / buried interface transport properties

- Important relationship between: the phases and defect chemistry and the conductivity and catalytic activity at the interface and near-interface regions (while under polarization):
  - Site-specific high-resolution microscopy and spectroscopy is needed.

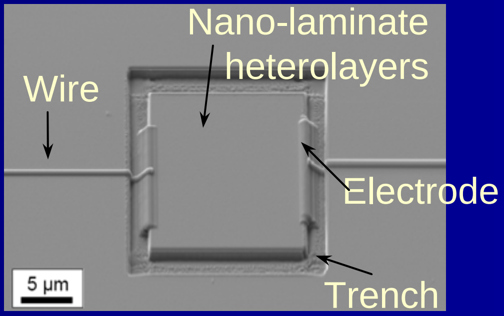
Oxygen Incorporation Enhancement



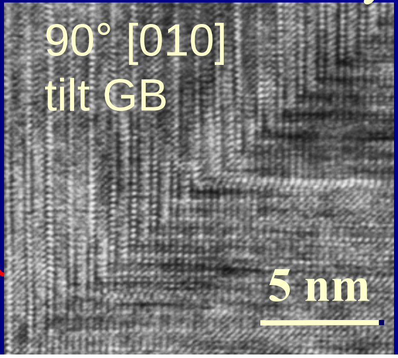
Oxygen exchange profile using SIMS

Sase et al. *Proc. 7th Eur. SOFC Forum*, 2006

Synthesis and nano-fabrication



Structure and defect chemistry

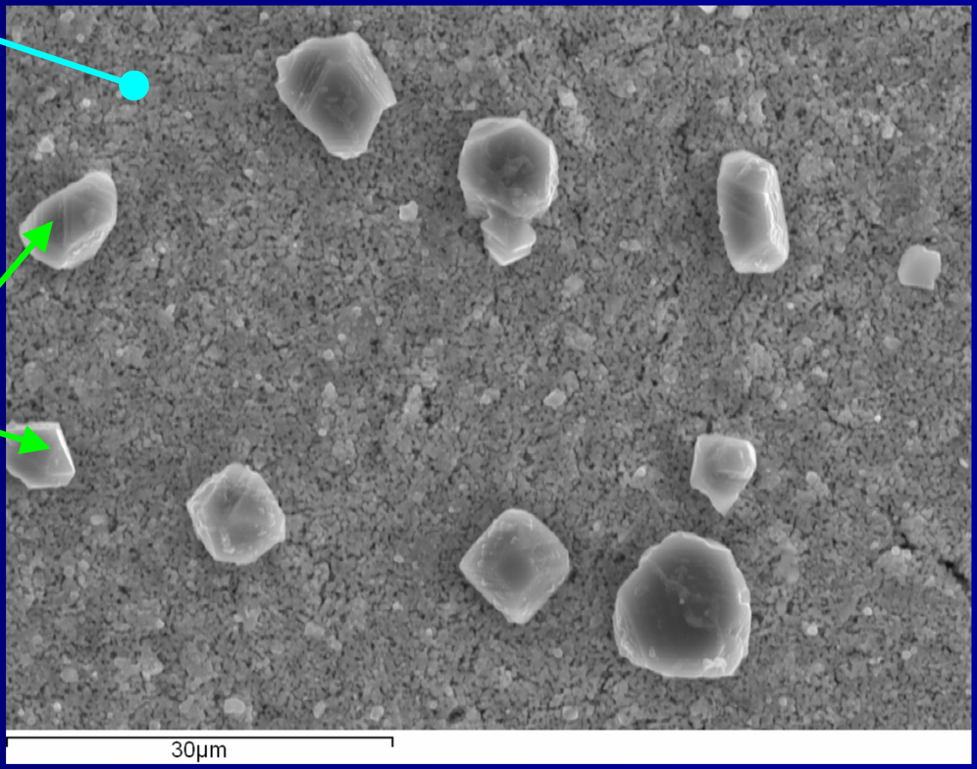


Transport and electronic structure

VT - STS / STM

Cr-Co-O particles found on the surface of the oxygen electrode bond coat

- Plan view of bond coat of a cell from the 2000 h stack
- X-ray diffraction revealed a spinel phase (AB_2O_4)
    - Cr:Co ~ 9:7 by EDS
- Cr-containing spinel also found using SEM and Raman spectroscopy in the 1000 h stack
    - Particles ~ 1 µm
    - Cr:Co ~ 2:3



Comparison of Four Nuclear Hydrogen Technologies

Hydrogen Production Process	Nuclear Reactor Type	Product Flexibility Hydrogen/Electricity?
High-pressure, low-temperature water electrolysis (HPE)	Advanced Light Water Reactor (ALWR)	Yes
High-temperature steam electrolysis (HTE)	High-Temperature Gas-Cooled Reactor (HTGR)	Yes
High-temperature sulfur-iodine cycle with extractive HI (SI)	High-Temperature Gas-Cooled Reactor (HTGR)	Pure hydrogen
Hybrid sulfur thermo-electro chemical (HyS)	High-Temperature Gas-Cooled Reactor(HTGR)	Fixed hydrogen and electricity production

Cost and performance assumptions based on information from Technology Insights (06, 07).

Plant	Levelized Cost [$/kg]
HPE-ALWR	2.98
HTE-HTGR	2.93
SI-HTGR	3.26
HyS-HTGR	2.97

Plant Evaluations: Summary of Results

- Price assumptions
  - Average prices: Electricity 50 \$/MWh, Hydrogen 3 \$/kg
  - Price volatility: 0.12 (per year), GBM process
  - Hydrogen/electricity correlation: 0.5

Technology	Product Flexibility	Expected Profit [M \$]	Std.Dev. Profit [M \$]	Expected IRR [%]	Expected H_2 production	
					Prod. [%]	Time [%]
HPE-ALWR	No	17	1084	9.99	100.0	100.0
	Yes	283	1078	**10.85**	69.2	65.7
HTE-HTGR	No	83	1183	9.80	100.0	100.0
	Yes	**295**	1170	10.52	82.4	80.5
SI-HTGR	No	-348	1249	8.89	100.0	100.0
HyS-HTGR	No	19	841	9.72	100.0	100.0

- With current cost and performance estimates, the flexible electrochemical technologies (HPE-HTGR and HPE-ALWR) are the most profitable
  - Hydrogen remains the main product for these plants, but they switch to electricity production a substantial amount of time