Fundamental Mechanisms of SOFC Cathode Reactions

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University of Florida - U.S. Department of Energy
High Temperature Electrochemistry Center Workshop

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***Nguyen Minh**, GE Hybrid Power Generation, "*Industry Perspective and Requirements for SOFC Cathodes"

***Jeff Stevenson**, Pacific Northwest National Laboratory, "*State of the Art SOFC Cathodes"

***Heinz Nabielek**, Forschungszentrum Juelich, "*Effect of Cr Poisoning on SOFC Cathodes"

***Craig Jacobson**, Lawrence Berkeley National Laboratory, "*Infiltration of Catalytic Secondary Phases in LSM/LSF Cathodes **"**

***Meilin Liu**, Georgia Institute of Technology, "*Investigations into Cathode Mechanisms and Novel Materials Development"

***Harry Tuller**, MIT, "*Some Insights Derived from the Study of Lithographically Defined Electrodes"

***Stuart Adler**, University of Washington, "*What we can learn about SOFC Cathode Mechanisms from Macroscopic Measurements"

***Allan Jacobson**, University of Houston, "*Some Insights from Studies of Thin Film Cathode Materials for Solid Oxide Fuel Cells"

***Charles Mims**, University of Toronto, "*Some Insights from Studies of Thin Film Cathode Materials for Solid Oxide Fuel Cells"

***Eric Wachsman**, University of Florida, "*Investigations into Cathode Mechanisms and Novel Materials Development"

***Susan Sinnott**, University of Florida, "Ab-Initio* Study of $La_xSr_{1-x}Co_yFe_{1-y}O_3$ for SOFC Cathodes"

***D. Wayne Goodman**, Texas A&M University, "*Characterization and Properties of Defects on Oxide Surfaces"

***Lane Wilson**, DOE National Energy Technology Lab*

***Michael Krumpelt**, Argonne National Lab*

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Fundamental Mechanisms of SOFC Cathode Reactions

Issues and Questions:

- Performance conditioning
  - -What is time scale and what phenomena is it related to?
- Degradation of cathode performance
  - -Why does Cr degrade while Co, Fe, enhance performance?
  - -Why differences between conventional LSM and advanced LSF cathodes?
  - -Effect of microstructure?
  - -Effect of composition?
  - -Overpotential/temperature induced?
  - -How to separate effects?
- Phase segregation of Sr at cathode/current collector interface
  - -What systems?
  - -What is impact?
  - -Effect on surface rates?
  - -Effect of an electric field on cation distributions?
- Formation of resistive phases (e.g. $SrZrO_3$)
  - -Where do they form?
  - -What are their properties?
- μ_{O2} effect on cathode performance
  - - Non-Nernstian, NEMCA, etc?
  - - Increase in $Vo^{\cdot\cdot}$ @ cathode /electrolyte interface
    - -How much?
    - -Effect on k_o?

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Fundamental Mechanisms of SOFC Cathode Reactions

Suggested Research Approaches/Investigations:

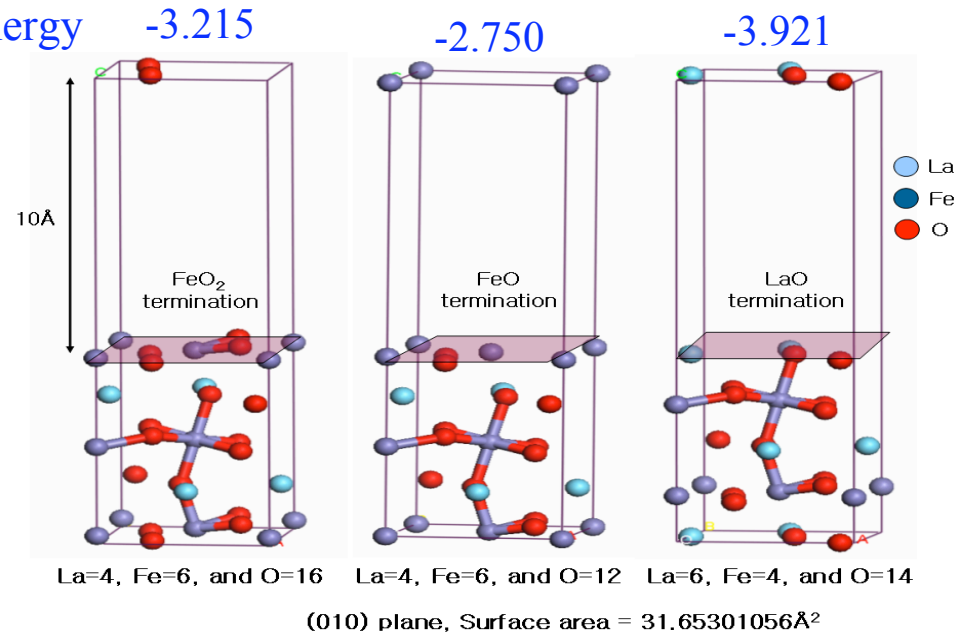
A. Continue to Empirically Develop New Materials and Microstructures

B. Systematically:

- Computational Approach
  - Provide fundamental understanding
  - Calculate surface and bulk energetics
- Surface Science and Spectroscopic Techniques
  - Determine surface sites, vacancies, adsorbed species and effects of surface reconstruction
  - Measure surface and bulk energetics
- Catalysis Techniques
  - Determine O-adsorption/dissociation mechanisms
  - Determine rate constants (k_o)
- Novel Electrochemical Characterization
  - Separate contributions to impedance/polarization
  - Frequency dependence and relation to mechanism
- Quantify Microstructural Effects
  - Fabricate and evaluate model architectures
  - Apply advanced characterization techniques such as FIB/SEM
- Integrate (all of the above) and Deconvolute Mechanisms
  - Develop fundamental models

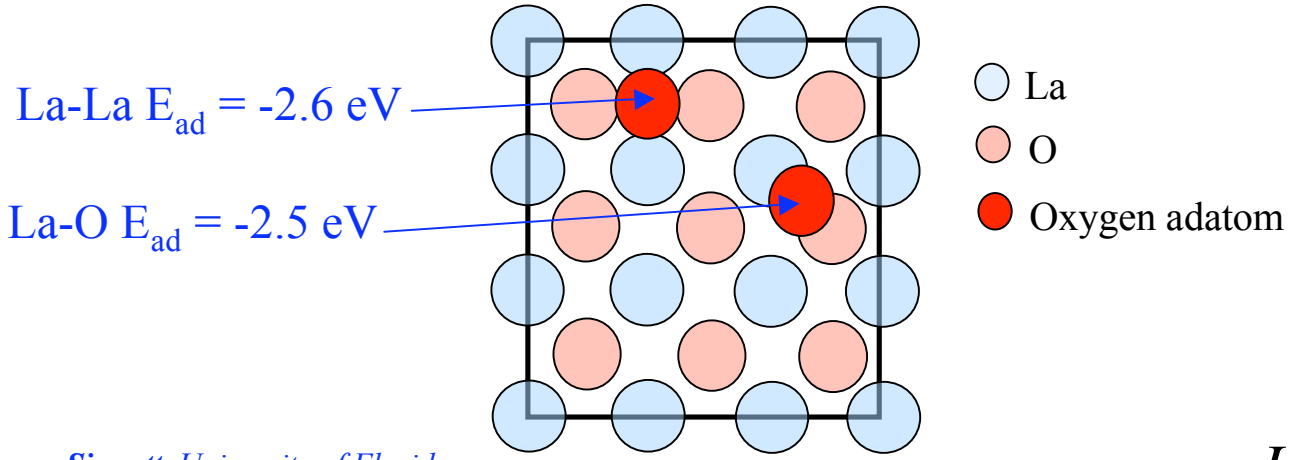
Computational Approach

Surface Free Energy ($eV/Å^2$)



Calculate preferred oxide surface and adsorption site

- LaO termination energetically more favorable



- O_{ads} on La-La site preferred

***Susan Sinnott**, University of Florida*

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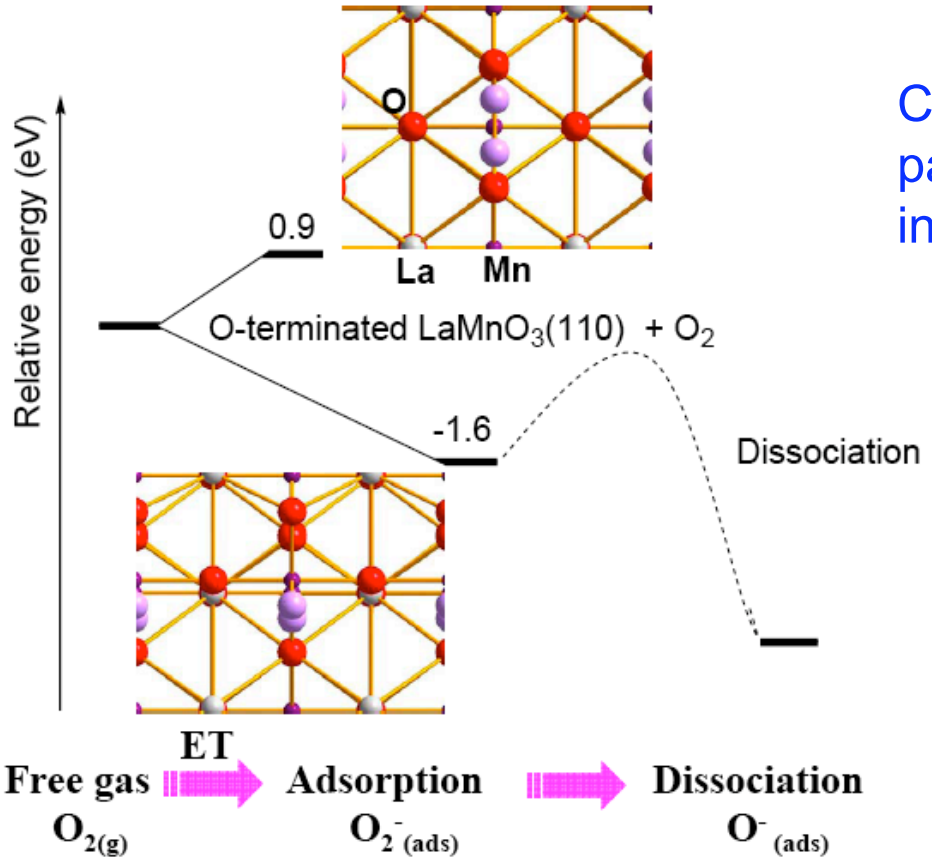
Computational Approach

Elementary steps of oxygen reduction on $LaMnO_3$



Calculate reaction pathway and intermediate steps

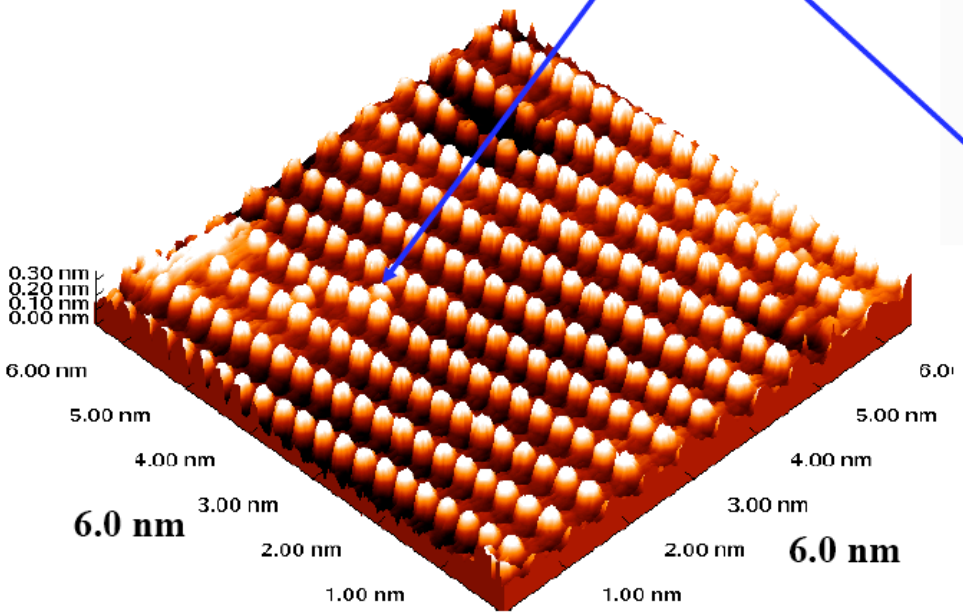
-> k

***Meilin Liu**, Georgia Institute of Technology*

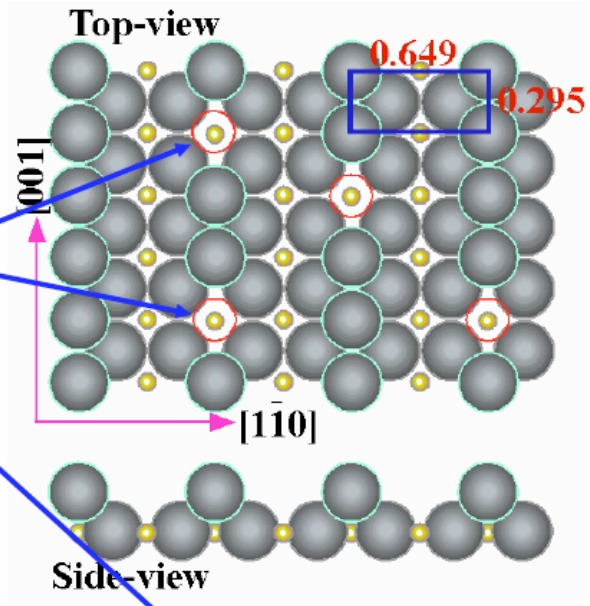
Surface Science and Spectroscopic Techniques

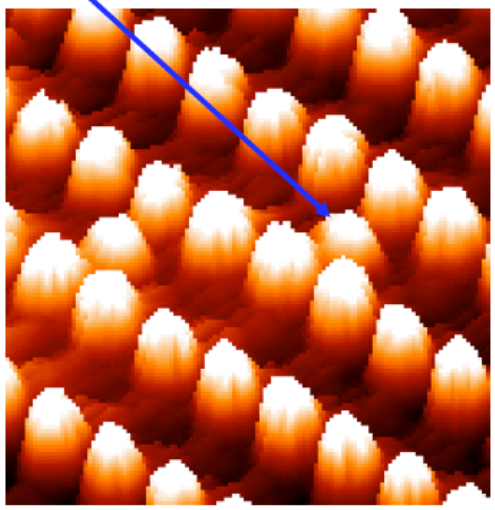
Surface defects on $TiO_2(110)$

Determine presence and location of surface defects



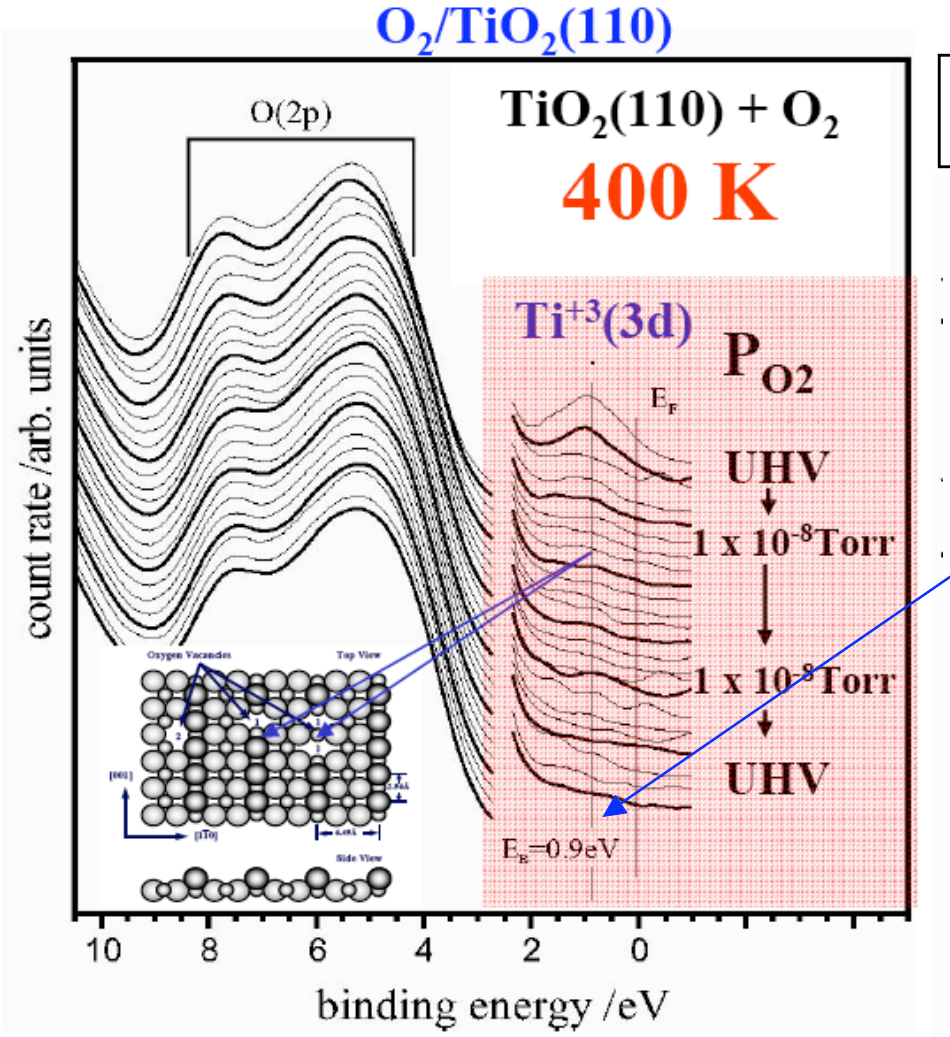
Oxygen vacancies





Atomic Force Microscopy (AFM)

Surface Science and Spectroscopic Techniques



Ultraviolet Photoelectron Spectroscopy (UPS): Defects on $TiO_2(110)$

Measure energy of surface oxygen vacancies

Krischok, Guenster, Goodman, Hoefft, and Kempter, 2005

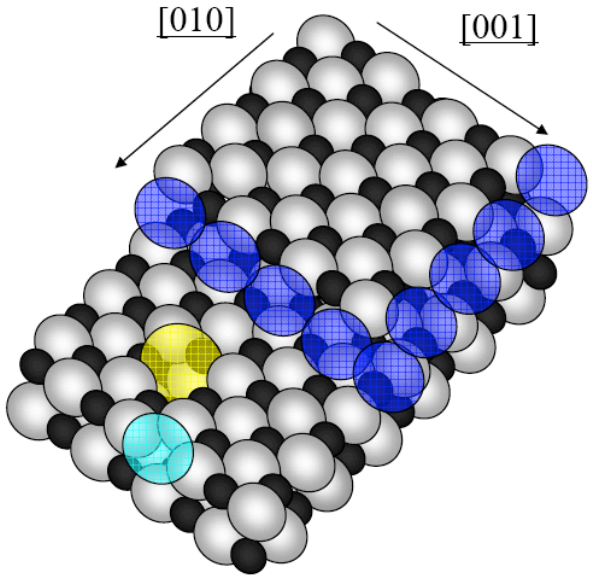
Surface Science and Spectroscopic Techniques

Types of Defects on MgO(100)

Oxygen vacancies (F, F+, F++)

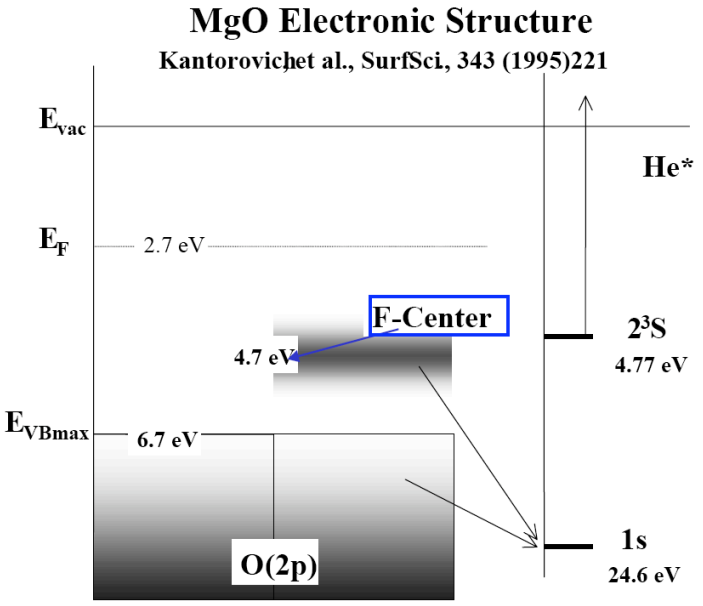
Mg+ vacancies (V, V-, V--)

Extended defects such as steps and corners



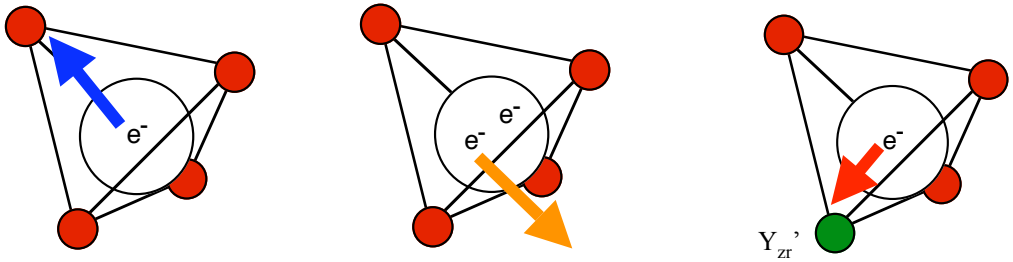
Relate defect energies to electronic band structure

Evaluate steps, etc.

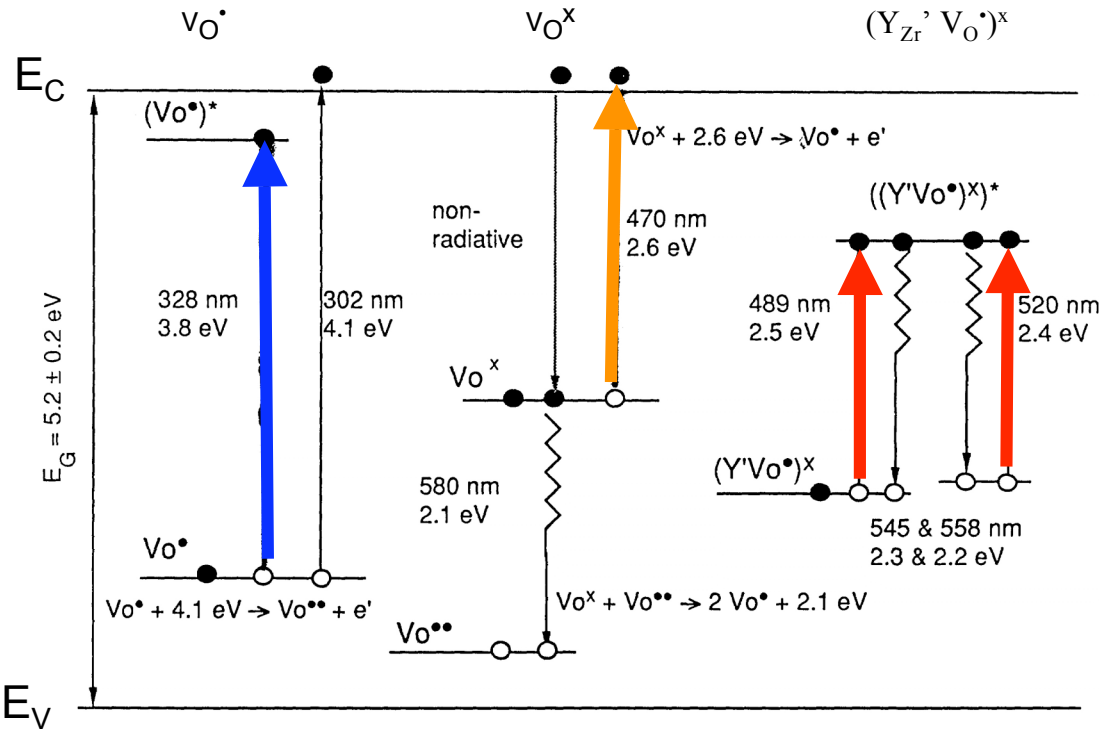


Surface Science and Spectroscopic Techniques

F Centers:



Determine electron occupancy and affect of neighboring cations

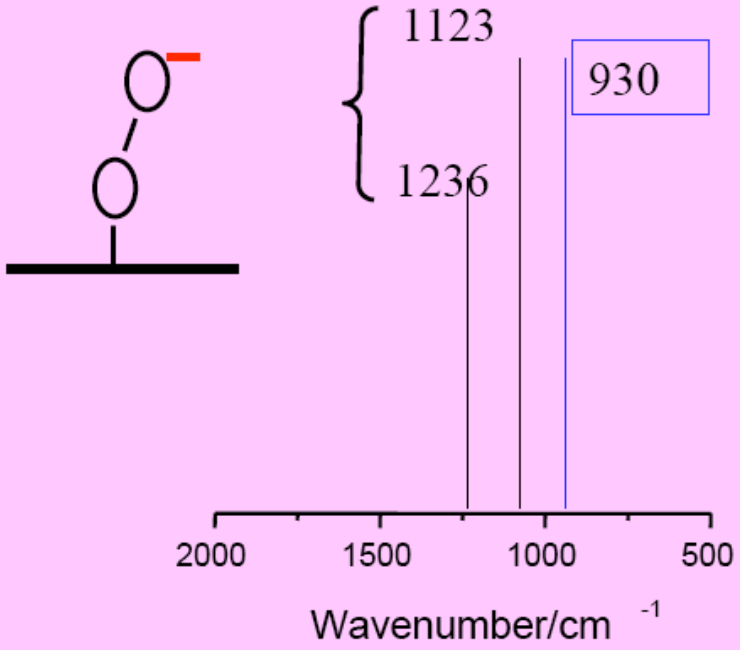


uv/vis Absorption and Fluorescence Spectroscopy

"Spectroscopic Investigation of Oxygen Vacancies in Solid Oxide Electrolytes," E. D. Wachsman, et al., *Applied Physics A* **50**, 545 (1990).
"Luminescence of Anion Vacancies and Dopant-Vacancy Associates in Stabilized Zirconia," E. D. Wachsman, et al., in *Science and Technology of Zirconia* (1993).

Surface Science and Spectroscopic Techniques

FTIR Study of Oxygen Adsorption

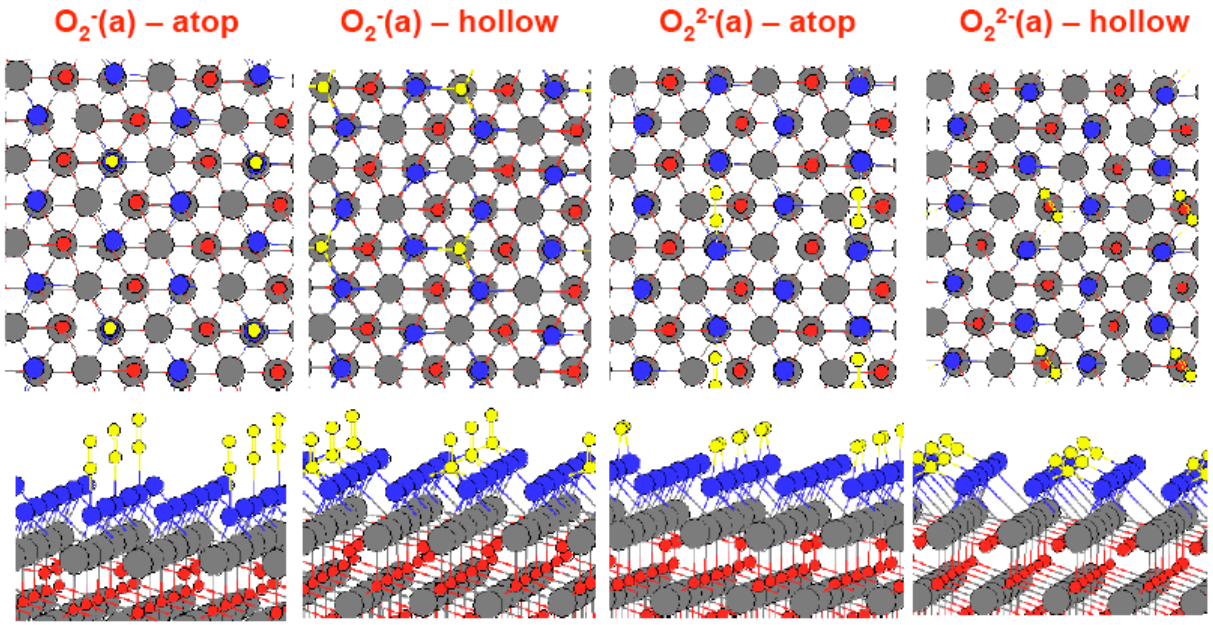


Determine adsorbed species:

- Peroxide O_2^{2-} and Superoxide O_2^- Adsorption occur

H. L. Wan, X. P. Zhou et al., *Catalysis Today* **51** (1999) 161-175

O_2 Adsorption (1)



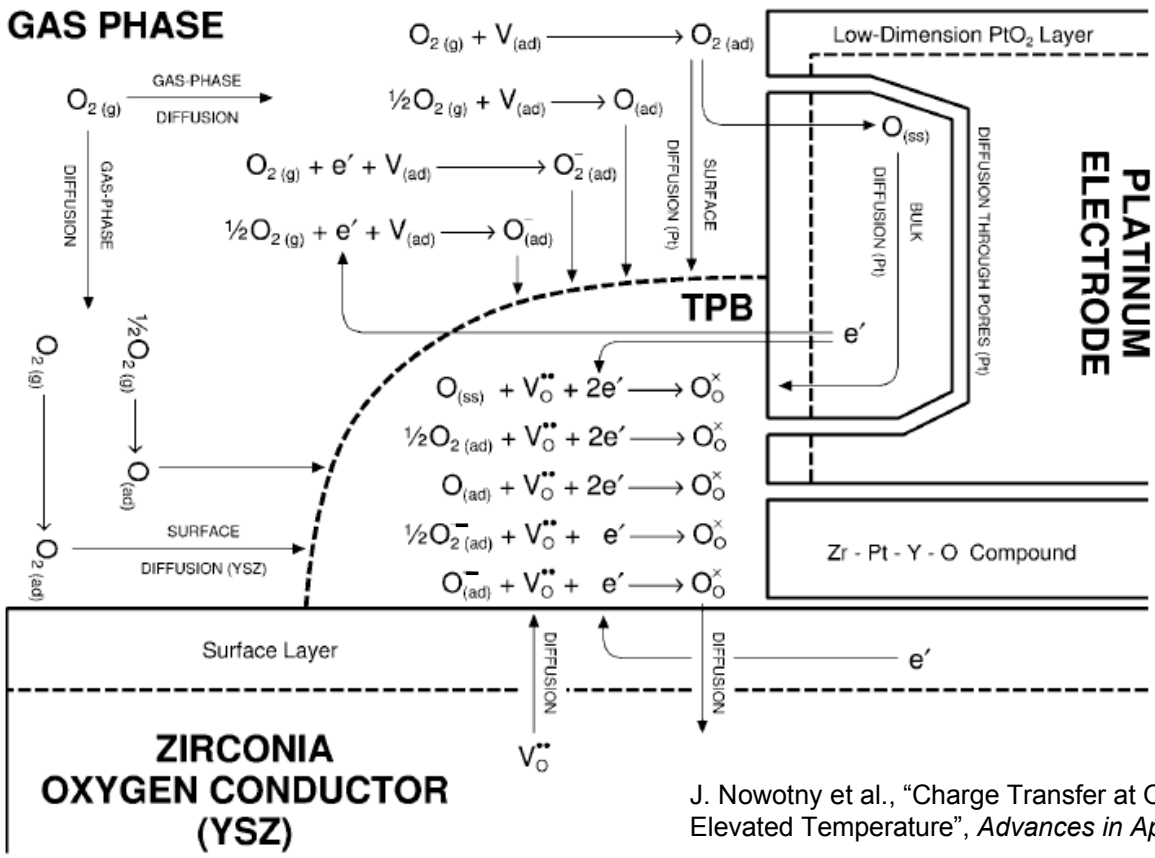
- Peroxide O_2^{2-} adsorption is more stable than superoxide O_2^-
- Hollow side adsorption is more stable than atop adsorption

→ E_{ads} decreasing

*for the most stable O_2^{2-} hollow site adsorption, E_{ads} = 0.87 on Ag(111), E_{ads} = 1.31 on Ag(110)

Catalysis Techniques

What is rate limiting step?

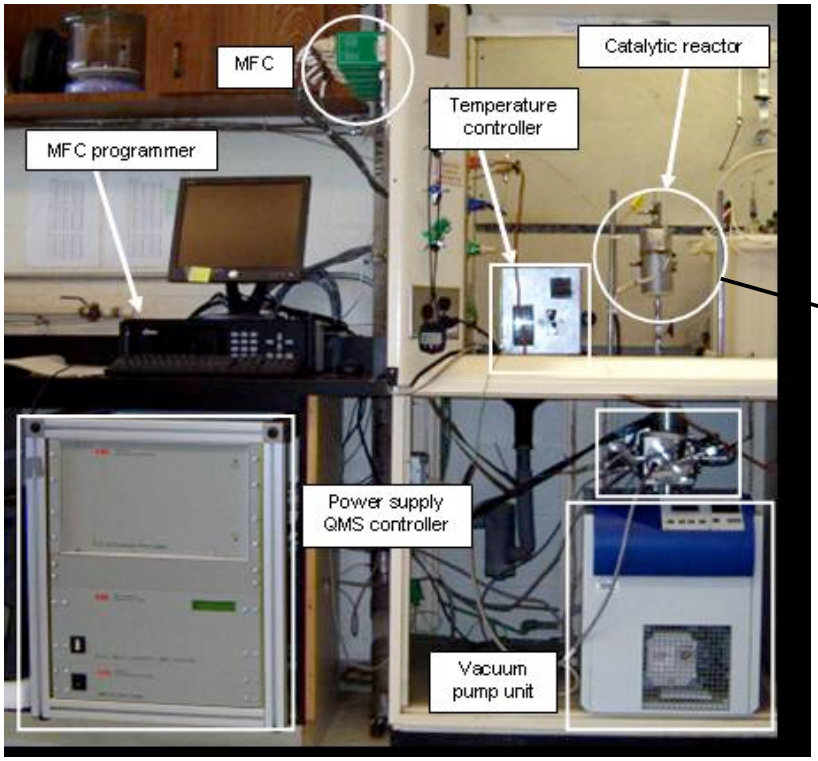


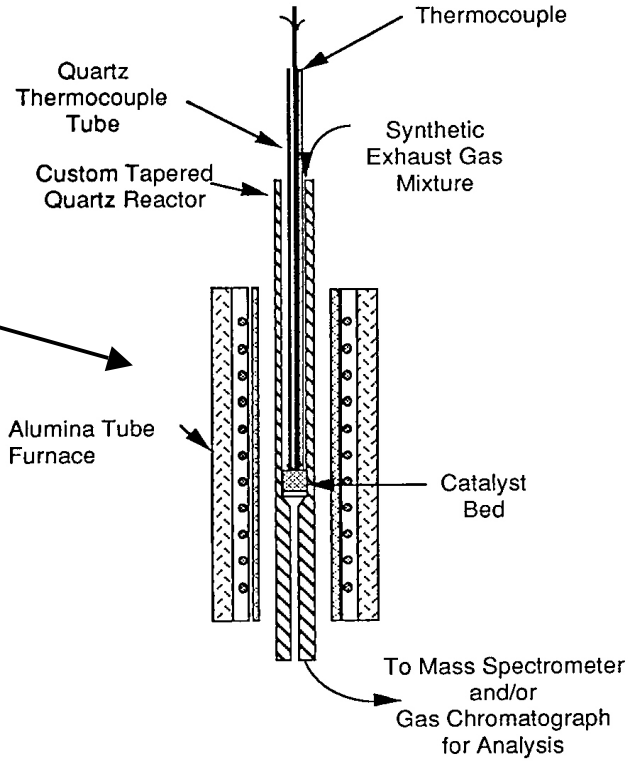
J. Nowotny et al., "Charge Transfer at Oxygen/Zirconia Interface at Elevated Temperature", *Advances in Applied Ceramics* (2005)

Multiple potential mechanisms each having P_{O2} dependence

However, P_{O2} dependence not unique

Catalysis Techniques

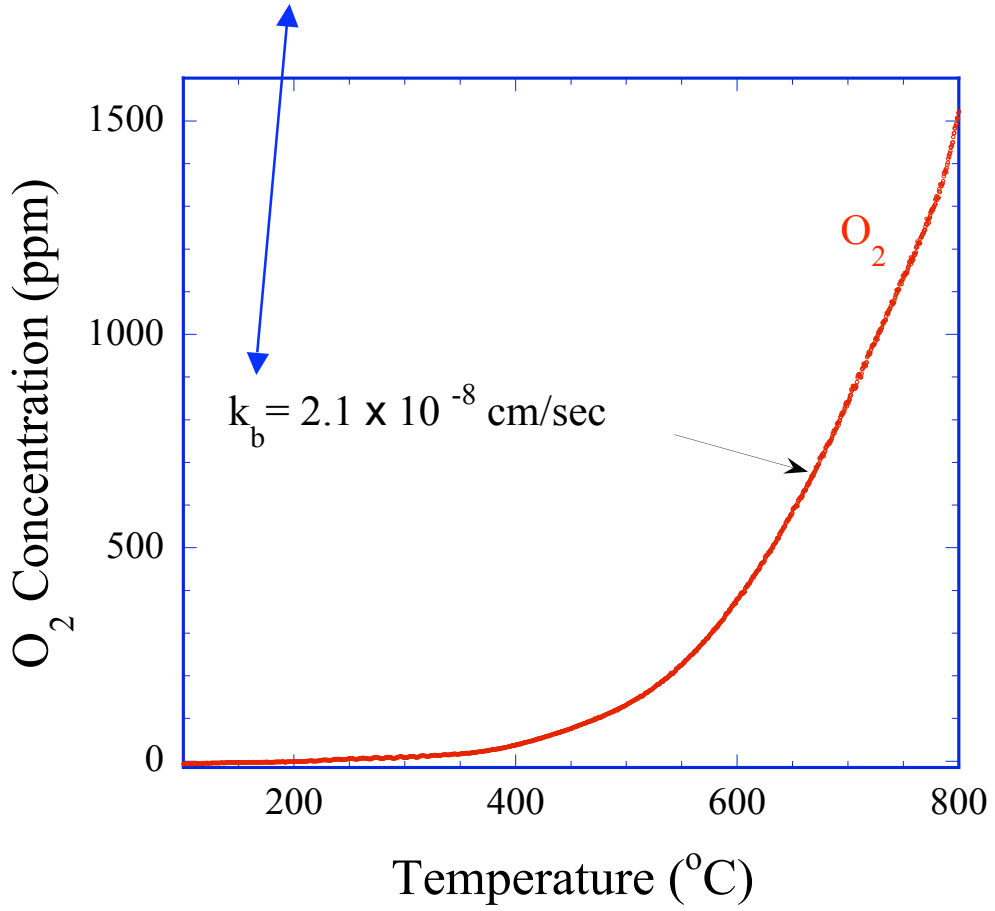




- Temperature programmed desorption (TPD)
  - Ramp temperature in He to determine adsorbed and/or decomposition species
- Temperature programmed oxidation (TPO)
  - Ramp temperature in O_2 gas mixture to determine reaction rates
- Isotope exchange (O^{16} vs. O^{18})
  - Switch gas to separate solid vs gas species contribution to mechanism

Catalysis Techniques

$$i_o = k_f P_{O2}^{1/2} [V_O^{\bullet\bullet}] - k_b [O_O^X] [h^\bullet]^2$$



TPD of LSCF

Bulk-O desorption

$LaSrCoFeO_3 \rightarrow LaSrCoFeO_{3-\delta} + \delta/2O_2$

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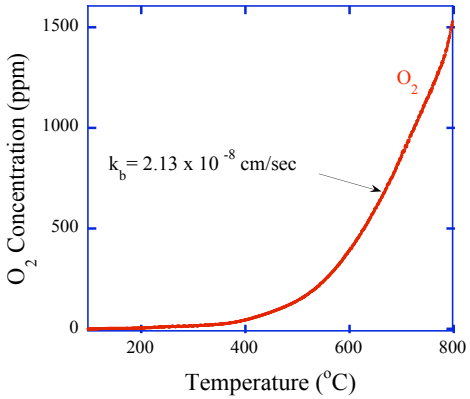
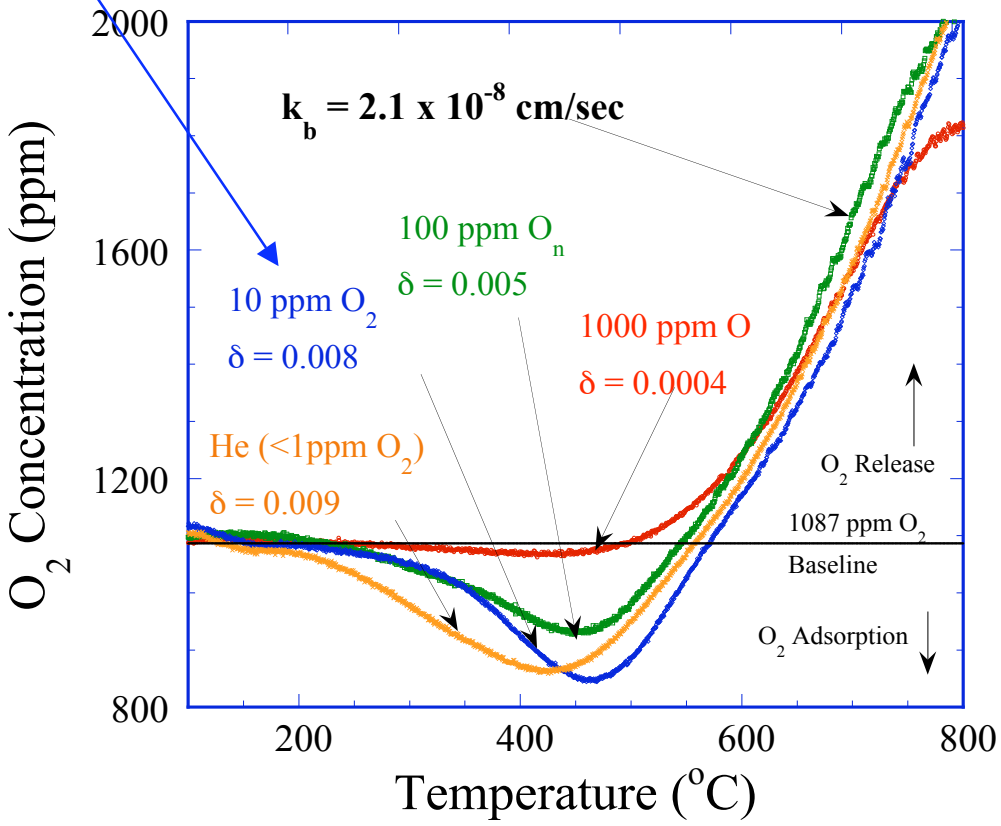
Catalysis Techniques



$k_{chem} = k_f [V_O^{\bullet\bullet}]$



TPO of LSCF

O-Absorption to fill $V_O^{\bullet\bullet}$
depending on P_{O2} history

$LaSrCoFeO_{3-\delta} + \delta/2O_2 \rightarrow LaSrCoFeO_3$

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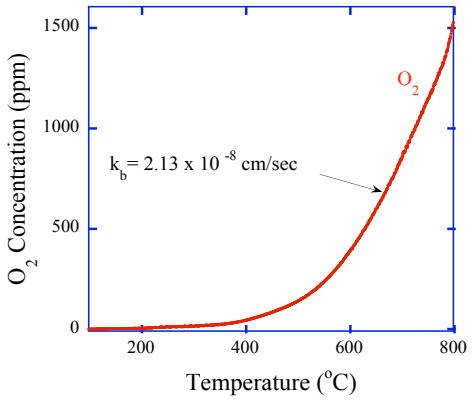
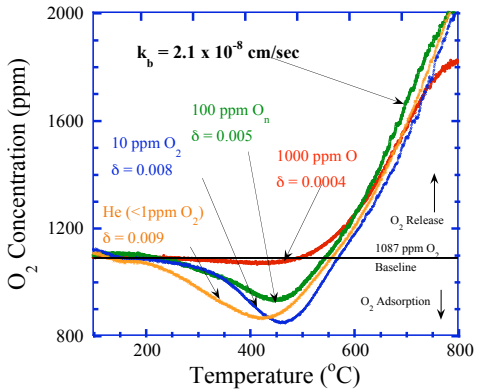
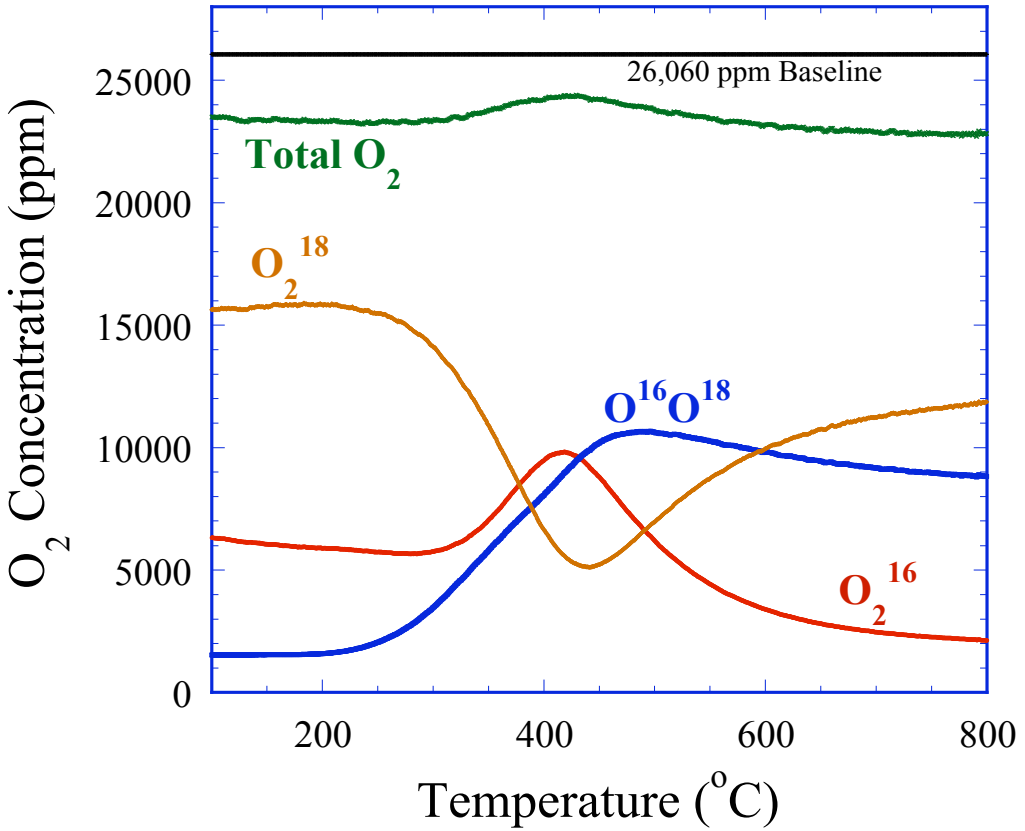
Catalysis Techniques







LSCF Isotope exchange elucidates complex mechanism

O_2^{18} = gas phase oxygen, O_2^{16} = lattice oxygen

$O^{16}O^{18}$ = scrambled product due to surface reaction

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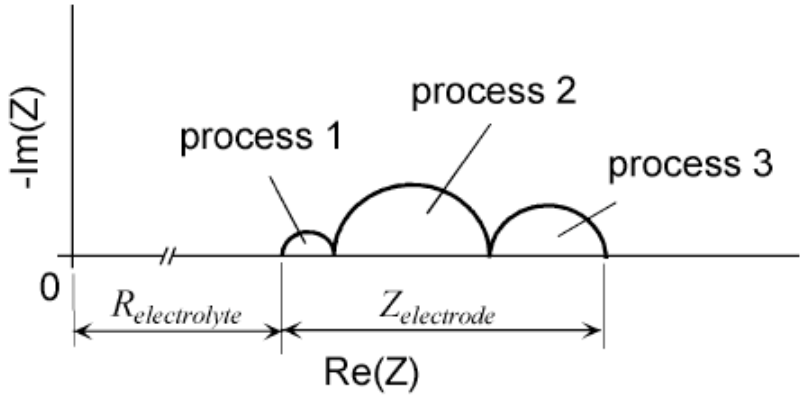
Novel Electrochemical Characterization

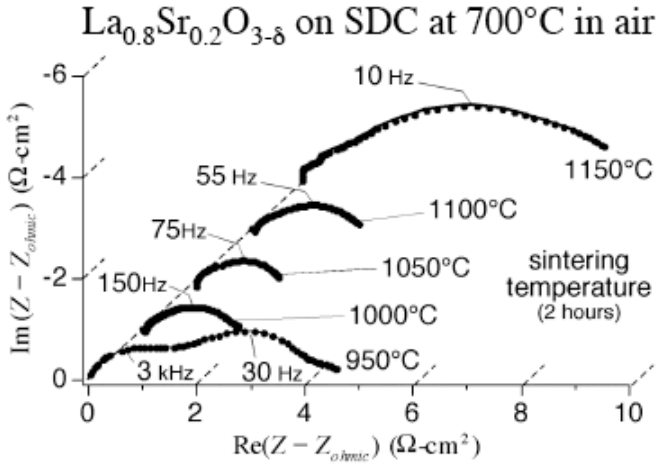
EIS as a Diagnostic Tool for Probing Electrode Mechanism

The idea:



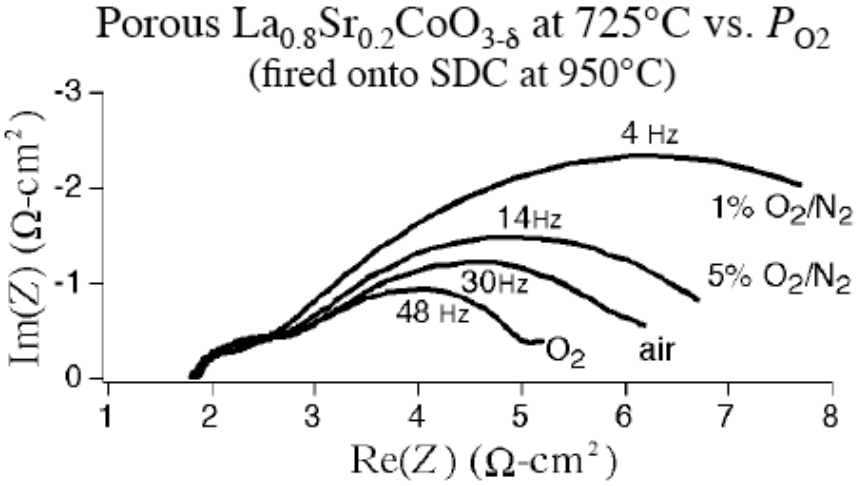
Electrochemical Impedance Spectroscopy has been a primary tool for understanding electrode phenomena

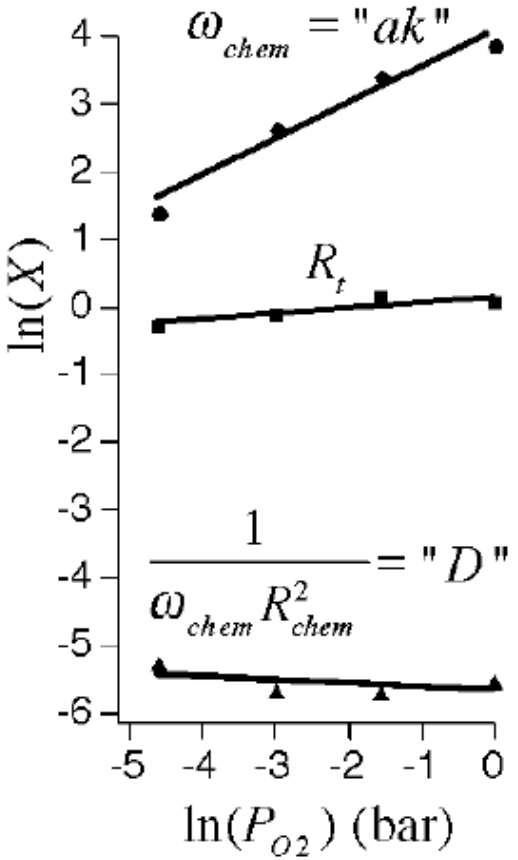
The reality…



Novel Electrochemical Characterization

Dependence on Operating P_{O2}





If: $ak \sim \omega_{chem} \sim P_{O_2}^{0.53\pm0.08}$

Then: $r_{(O_2\ exchange)} \sim P_{O_2}^{0.53\pm0.08}$

Oxygen exchange rate $\sim P_{O2}^{1/2}$

***Stuart Adler**, University of Washington*

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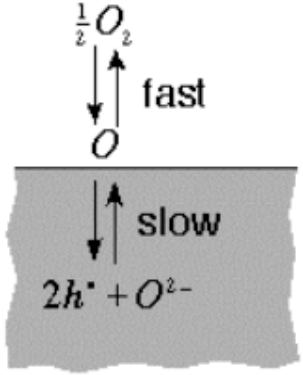
Novel Electrochemical Characterization

Many mechanisms are consistent with $k \sim P_{O2}^{1/2}$

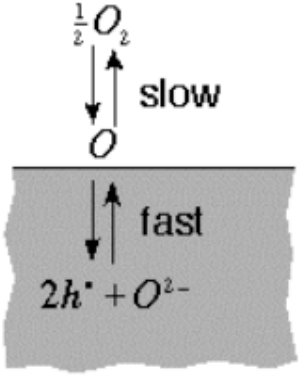
Oxygen exchange limited by vacancy exchange



$$r_{ads} = k_1\left(\left(f_{O_2}^{surf}\right)^{\frac{1}{2}} - \left(f_{O_2}^{solid}\right)^{\frac{1}{2}}\right)$$

$$r_{exch} = k_1\left(P_{O_2}\right)^{\frac{1}{2}}$$

Oxygen exchange limited by dissociative adsorption



$$r_{ads} = k_1\left(\frac{\left(P_{O_2}^{gas}\right)}{\left(f_{O_2}^{surf}\right)^{\frac{1}{2}}} - \left(f_{O_2}^{surf}\right)^{\frac{1}{2}}\right)$$

$$r_{exch} = k_1\left(P_{O_2}\right)^{\frac{1}{2}}$$

Same!

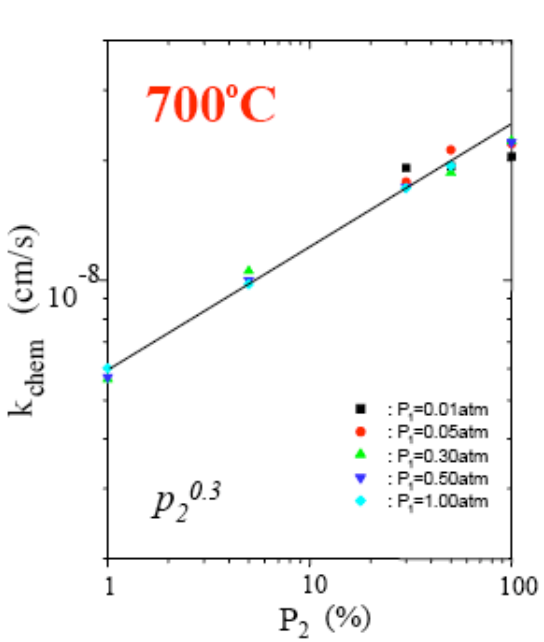
Need to combine with other techniques to determine mechanism

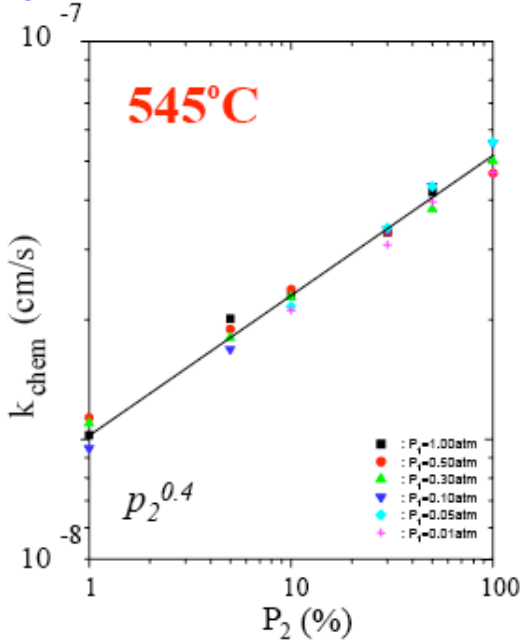
Novel Electrochemical Characterization

Electrical Conductivity Relaxation Data

$$i_o = k_f [V_O^{\bullet\bullet}] P_{O2}^{1/2} - k_b [O_O^X] [h^\bullet]^2$$

$$k_{chem} = k_f [V_O^{\bullet\bullet}]$$





as synthesized

annealed at 900 °C

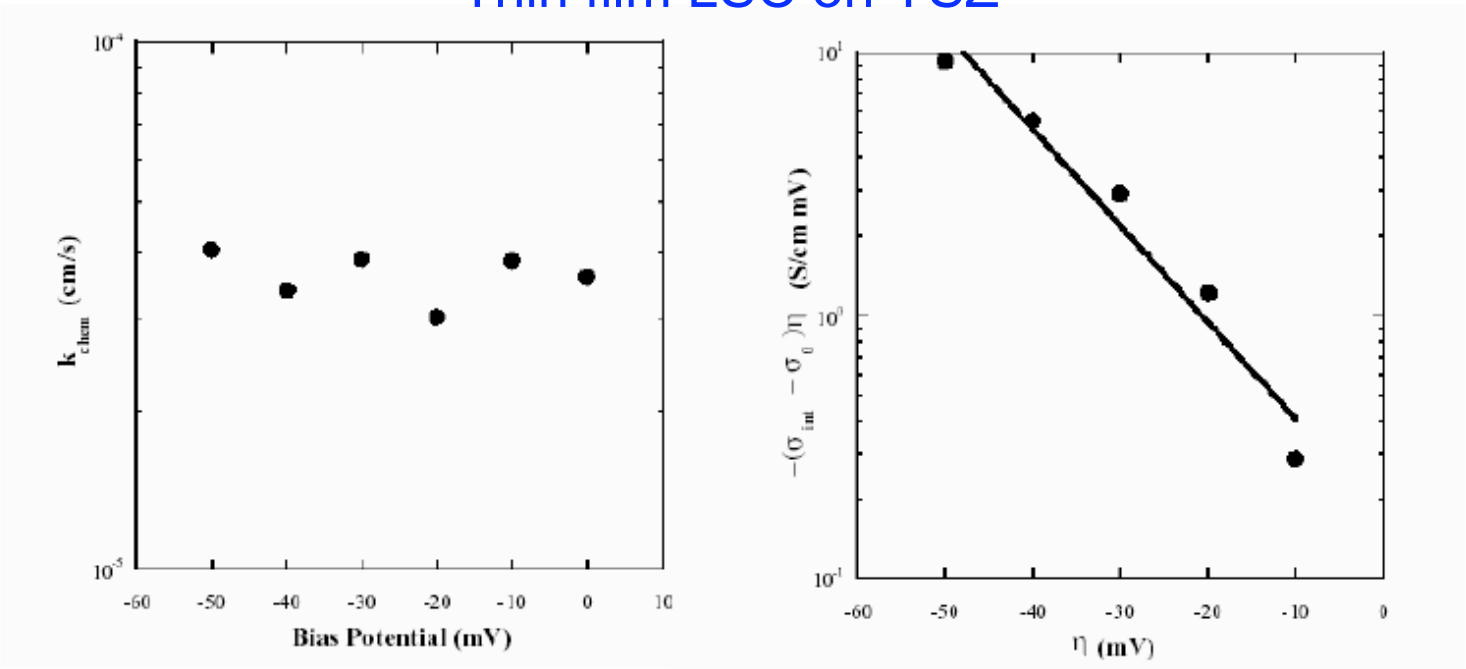
k_{chem} = f(P_{O2}^n) - *Need to combine electrochemical and catalysis techniques*

= f(surface structure) - *Need surface crystallographic information*

***Allan Jacobson**, University of Houston*

Effects of bias potential

Thin film LSC on YSZ

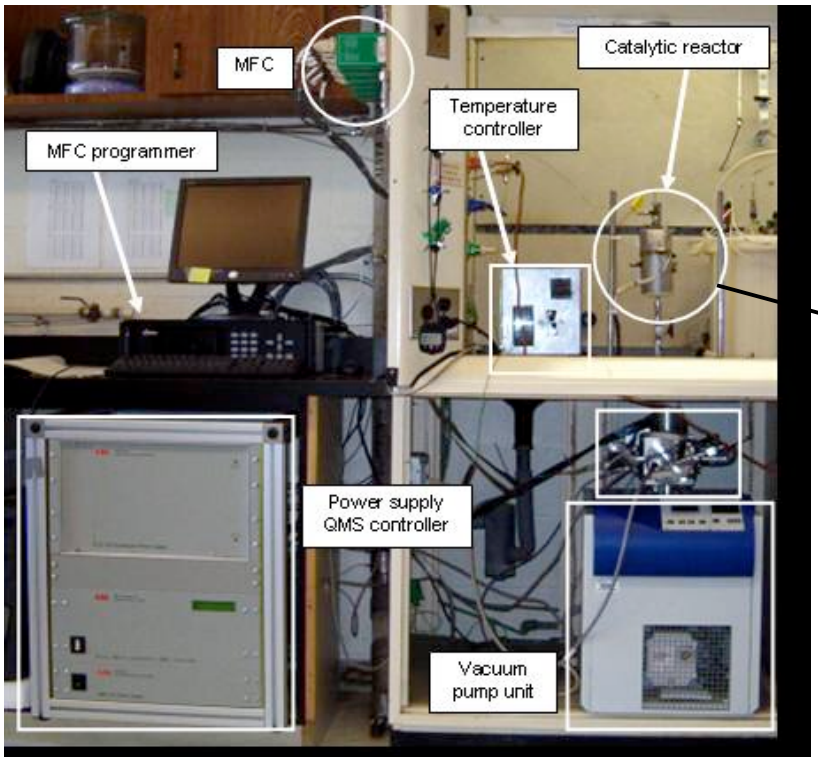


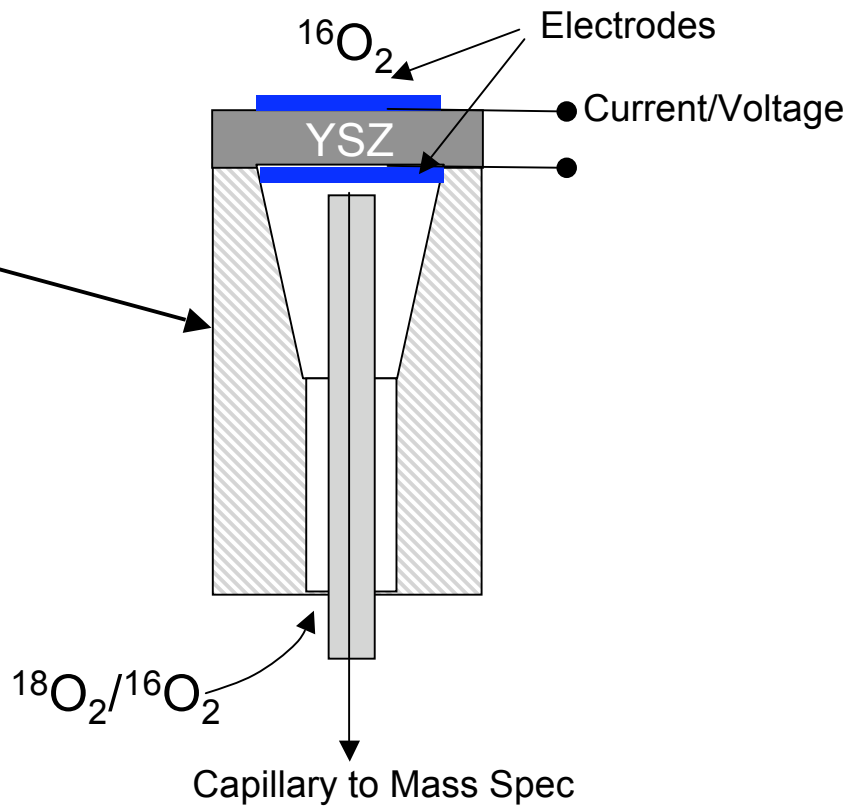
surface reaction rate independent of bias

interfacial resistance decreases with increasing bias potential

Potential influences defect distribution at interfaces

Novel Electrochemical Characterization





Combine electrochemical and catalysis techniques:

$k_{chem} = k_f [V_O^{\bullet\bullet}] \sim f(P_{O2}^n)$

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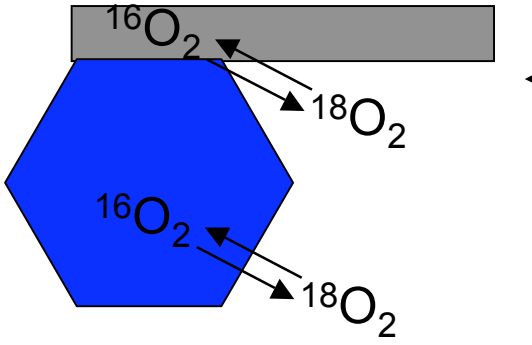
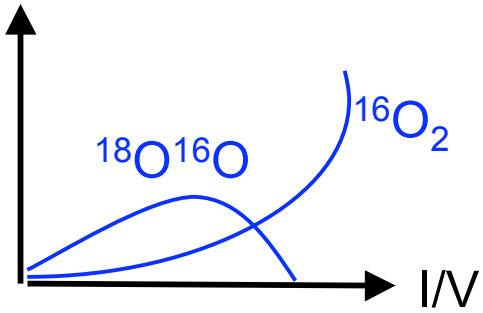
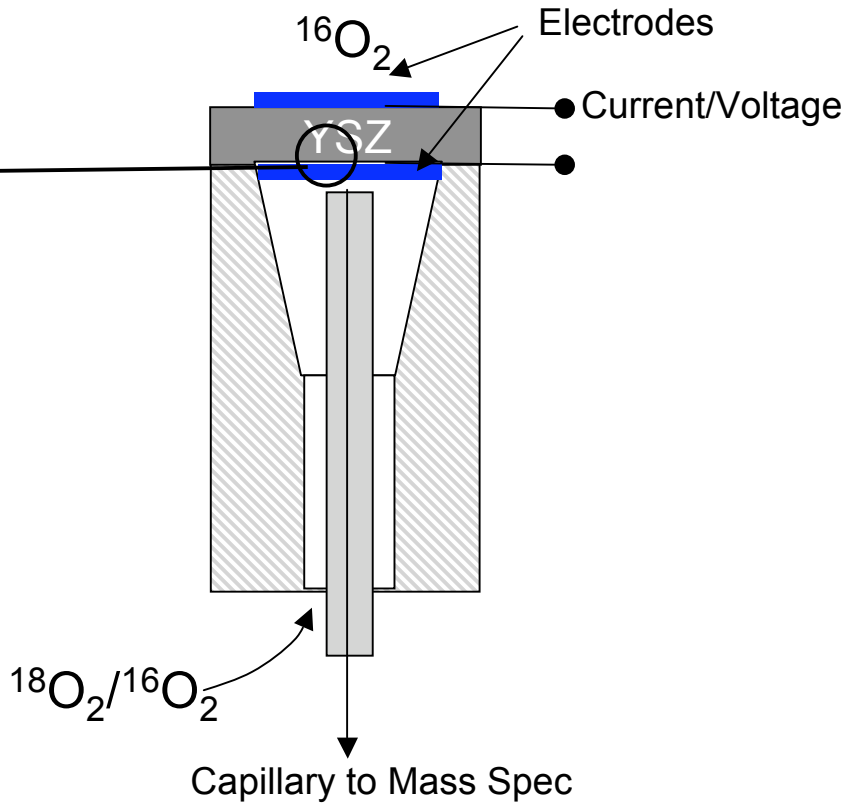
Novel Electrochemical Characterization

$$O_O^{\times} \leftrightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2$$

$$K_R = \vec{k_o}/\overleftarrow{k_o}$$







Include:

- Electrode structure
- Current-voltage behavior: $i_o \sim k_o$, $k = f(V)$

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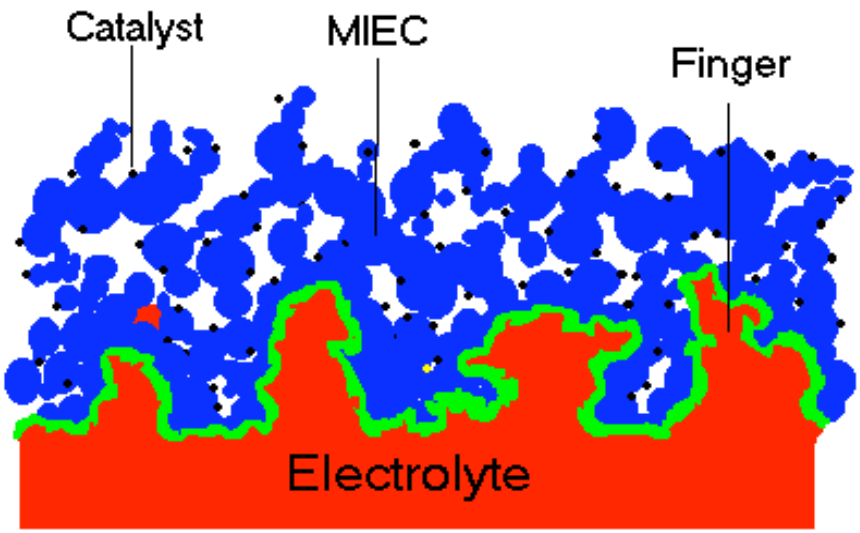
Quantify Microstructural Effects

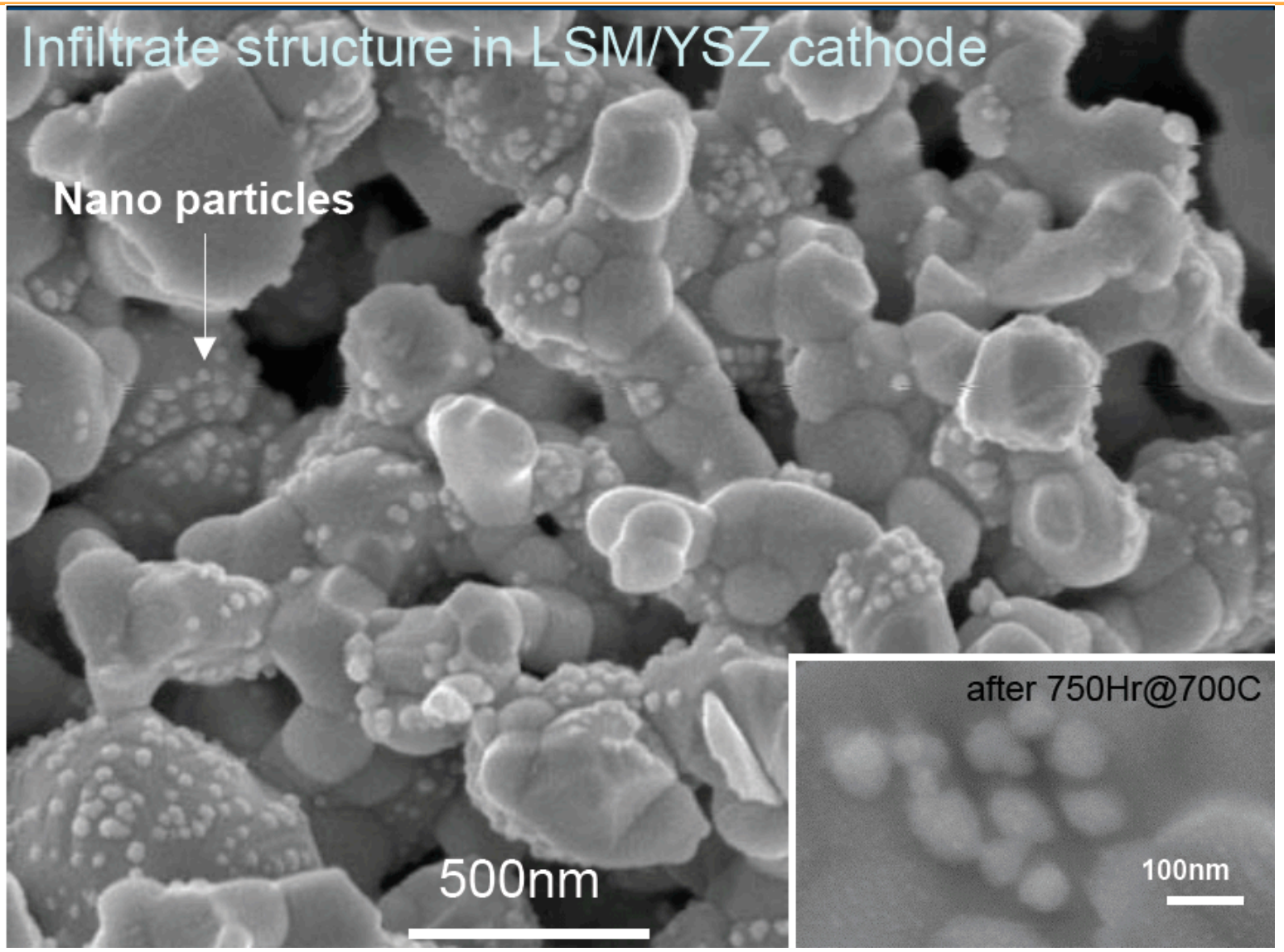
$$O_O^{\times} \leftrightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2$$



Optimize Microstructure for:

- Activation Polarization
  - Electrocatalytic Activity
    - Increase specific catalytic activity
    - Increase TPB
    - Dispersed catalyst
- Ohmic Polarization
  - Electronic vs. Ionic Transport
    - Electronic conduction path
    - Ionic conduction path
- Concentration Polarization
  - Gas transport
    - Graded porosity
    - Gas vs. solid state transport

Quantify Microstructural Effects

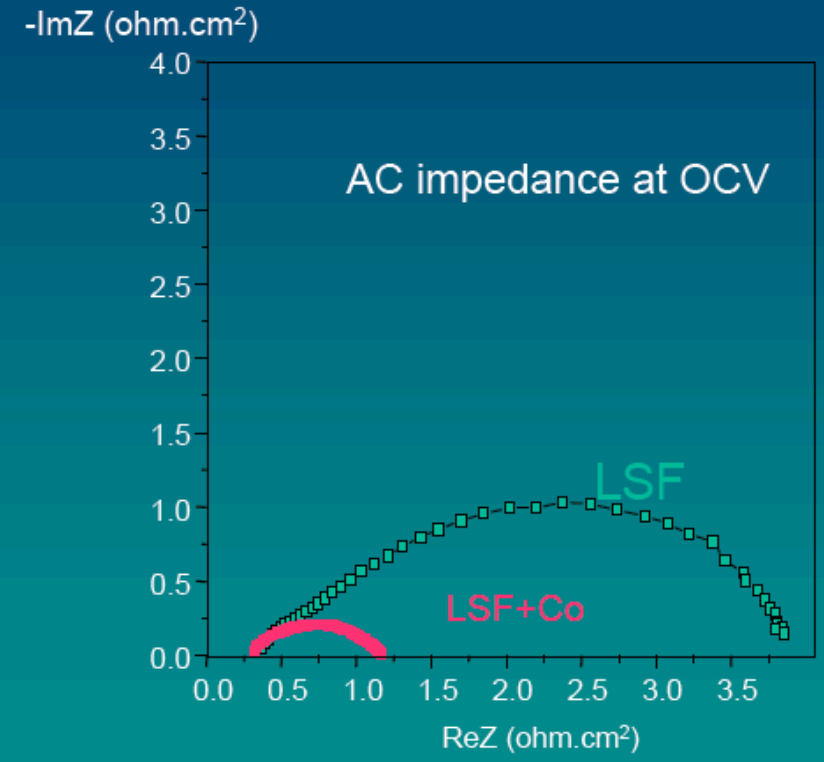


***Craig Jacobson**, Lawrence Berkeley National Laboratory*

Quantify Microstructural Effects

Dual Infiltration: 1-step LSF($La_{.8}Sr_{.2}FeO_{3-\delta}$) followed by Co nitrate infiltration

cathode initial impedance @ 650°C.



***Craig Jacobson**, Lawrence Berkeley National Laboratory*

Quantify Microstructural Effects

Model materials to study individual steps

Single phase material

Surface and bulk

Two phase (films on single xtals)

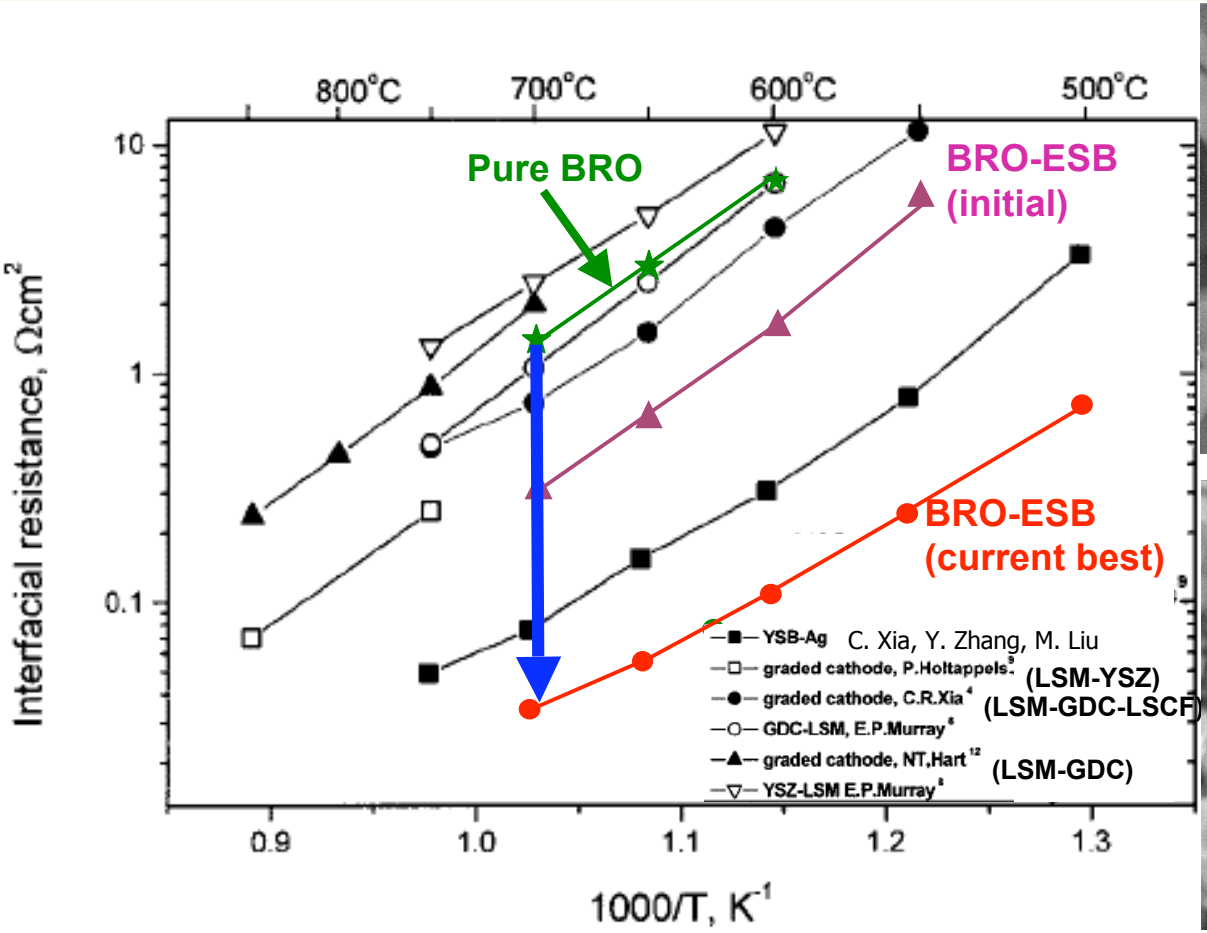
Surface, interface and bulk(s)

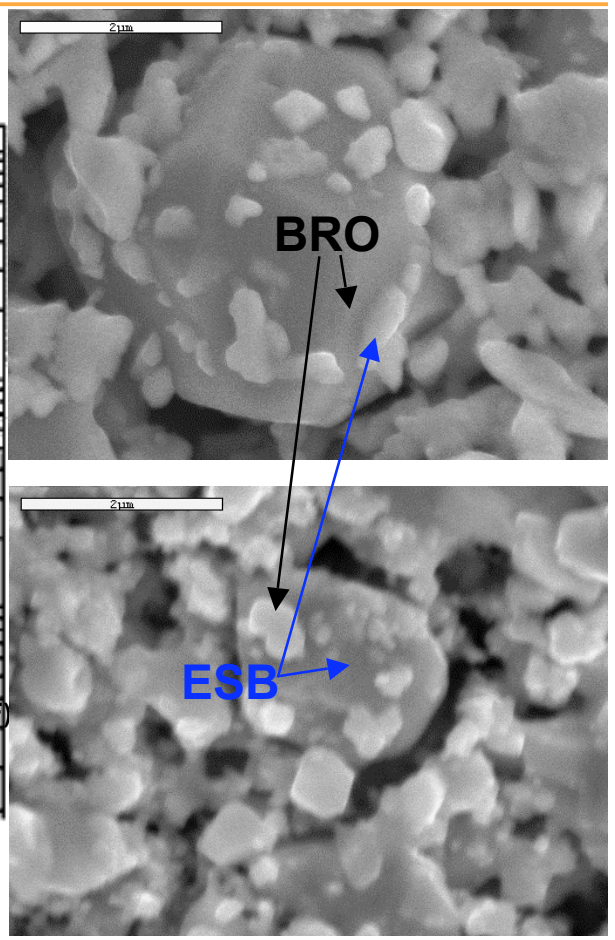
Patterned materials
(masked films, printed patterns)

Surfaces, interface, bulk(s) and TPB
Combinatorial investigations

Electronic Conductors (reaction at TPB): Pt and LSM
Mixed Conductors (reaction spread over electrode): LSF, LSCF, etc.

Quantify Microstructural Effects





$Bi_2Ru_2O_7$/ESB 2-Phase Cathode

Adding ionic phase and optimizing microstructure reduced 700°C ASR from 1 Ωcm^2 to 0.03 Ωcm^2

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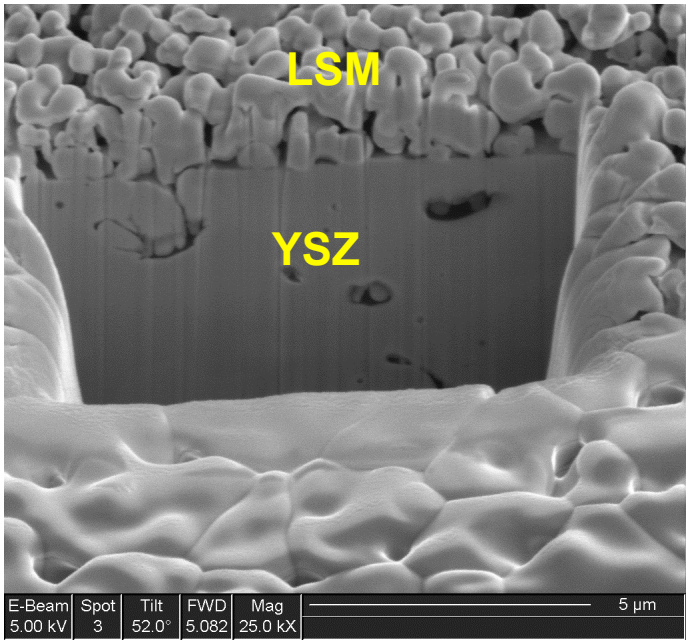
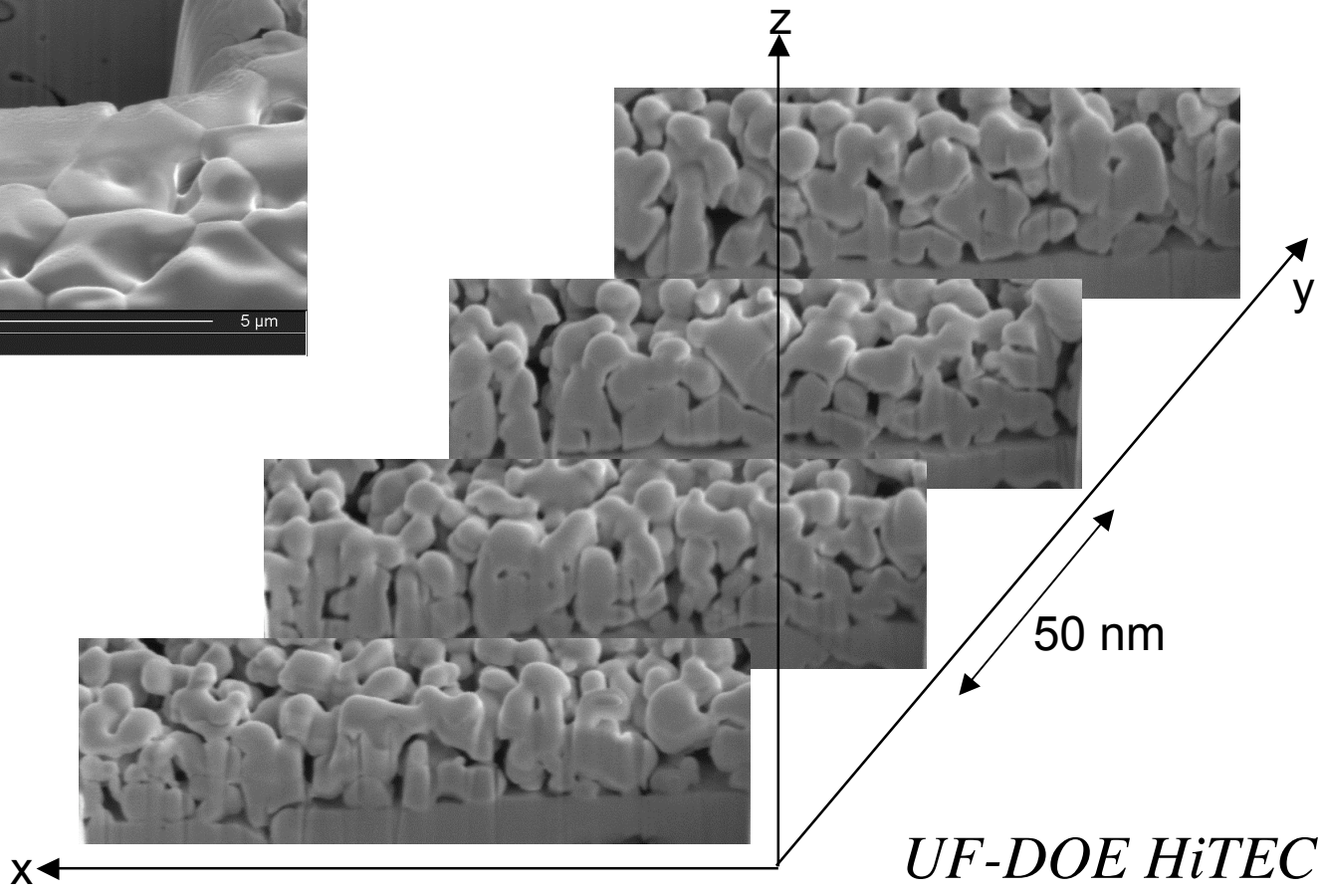
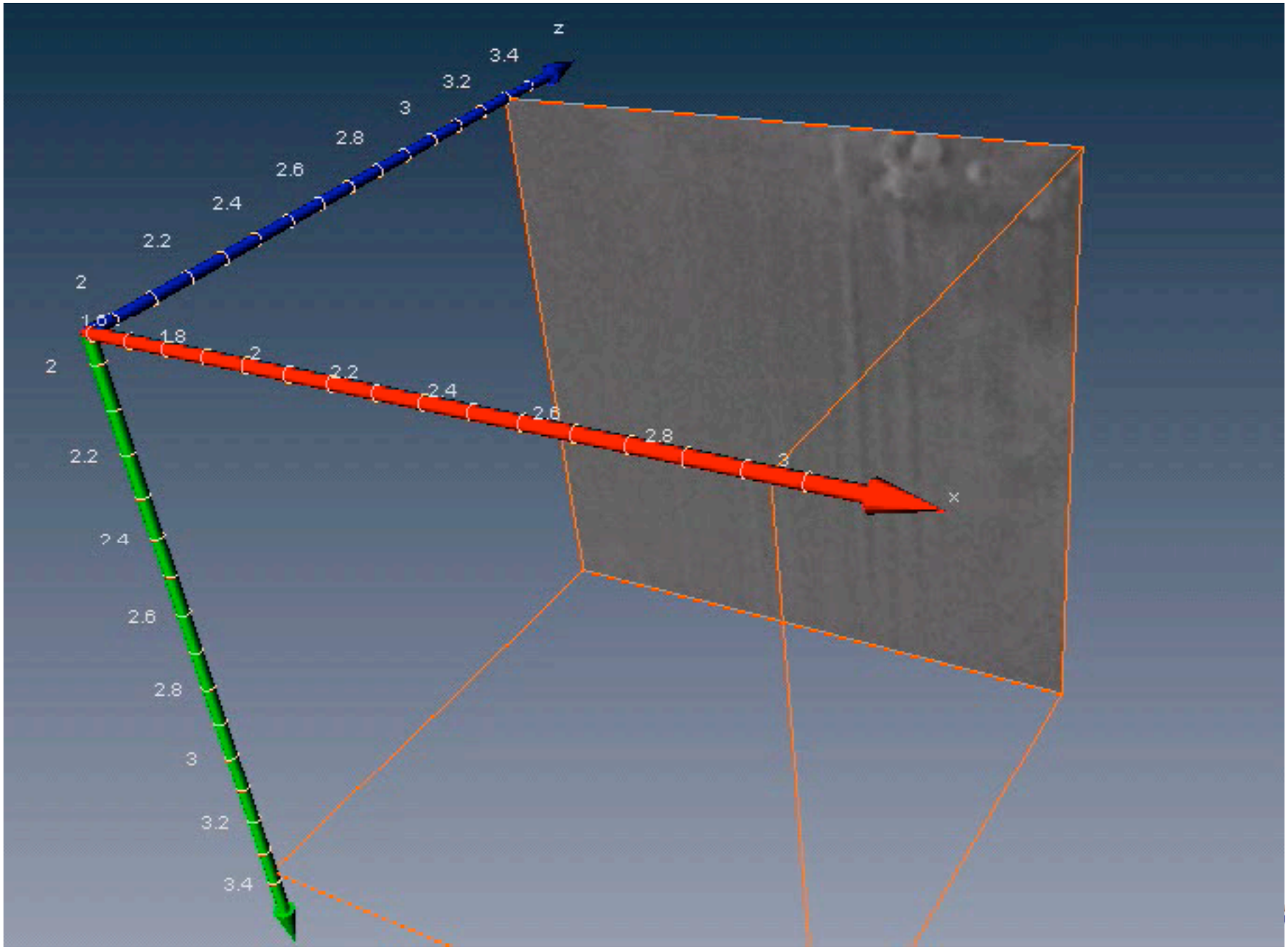
Quantify Microstructural Effects



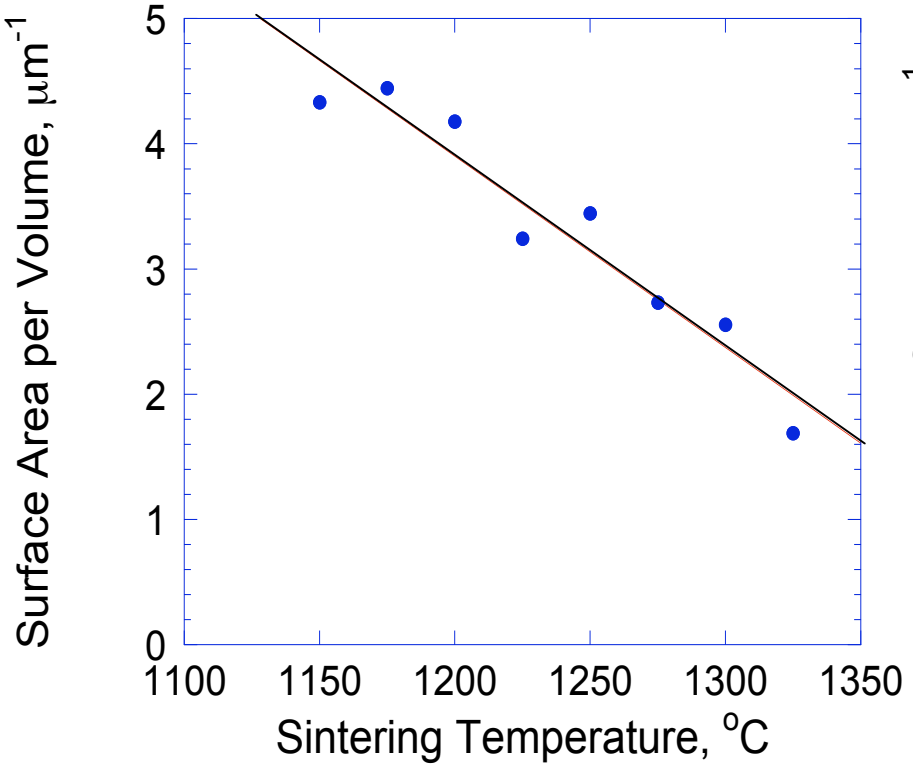
Focused Ion Beam

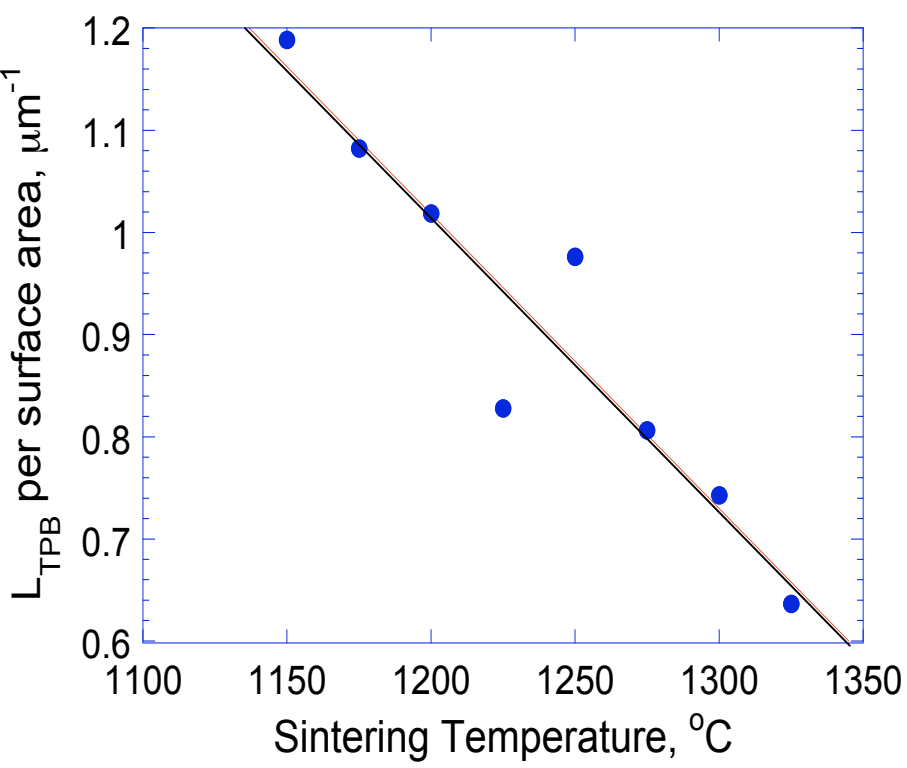
- Enables 3-D analysis of electrode microstructure
  - Particle-size, pore-size, & distribution
  - Triple-phase boundary density
  - Tortuosity




z
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
2
2.2
2.4
2.6
2.8
3
x
2
2.2
2.4
2.6
2.8
3
3.2
3.4

Quantify Microstructural Effects





LSM cathode microstructural features ***directly*** related to sintering:

- Pore surface area decreases linearly with increasing sintering temperature
- TPB length decreases linearly with increasing sintering temperature

Integrate and Deconvolute Mechanisms

MIEC Cathode Models

Adler and Steele: J. Electrochem. Soc., 143, 3554 (1996); SSI, 135, 445 (2000)

$$ASR\ (\Omega - cm^2) = \left(\frac{RT}{2F^2}\right)\sqrt{\frac{\tau}{(1-P)aC_oC_vD_vk}}$$

τ = tortuosity; P = fractional porosity; a = surface area/volume; C_o = concentration of oxygen sites; C_v = concentration of oxygen vacancies; D_v = oxygen vacancy diffusion coefficient; k = surface exchange coefficient

Liu: J. Electrochem. Soc., 145, 142 (1998)

$$G(L) = \frac{1}{\sqrt{\rho_i\rho_r / a}}\arctan\left(\frac{L\sqrt{\rho_i}}{\sqrt{\rho_r / a}}\right)$$

L = electrode thickness, ρ_i = ionic resistivity of cathode material, ρ_r = resistivity to the surface exchange reaction at the cathode/gas interface, a = surface area of cathode per unit volume. The arctan term reflects the fact that the rate of increase of G decreases rapidly with L.

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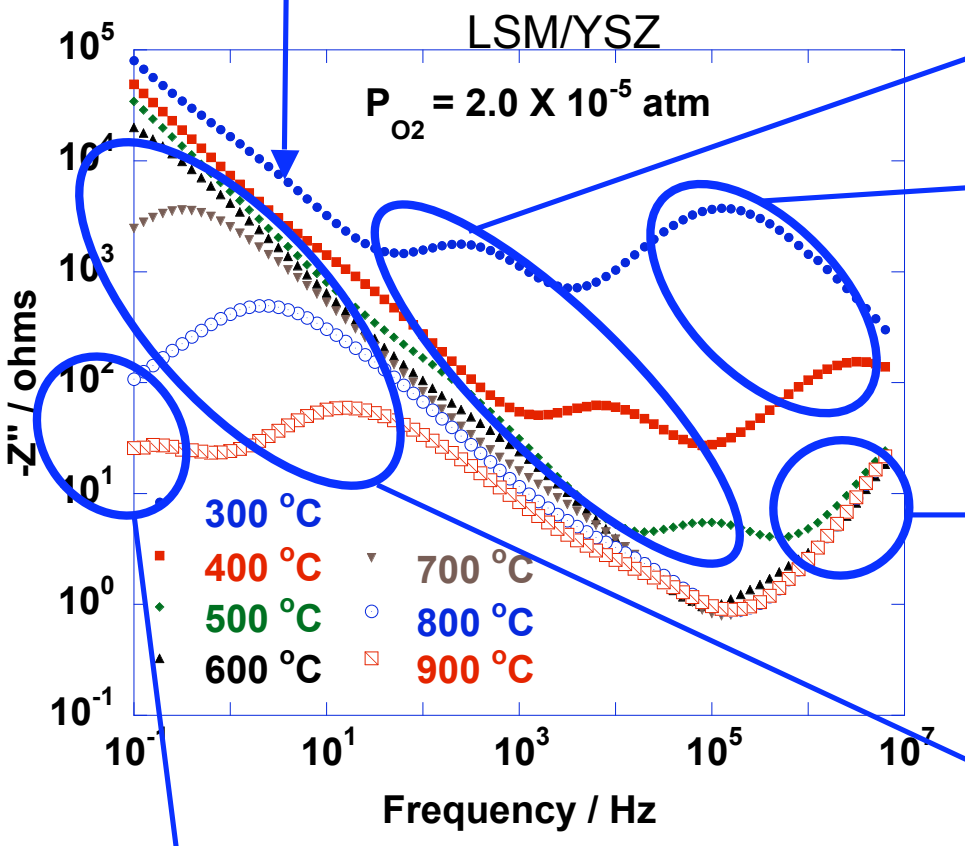
Integrate and Deconvolute Mechanisms

Charge transfer at TPB (τ ~0.0001 s)



Ionic conduction through electrolyte grain boundary

Ionic conduction in bulk electrolyte

Artifacts minimized by nulling

Dissociation and surface diffusion of O-species on LSM to TPB (τ ~ 0.18 s)

O_2 diffusion through porous cathode (τ ~ 5.9 s)

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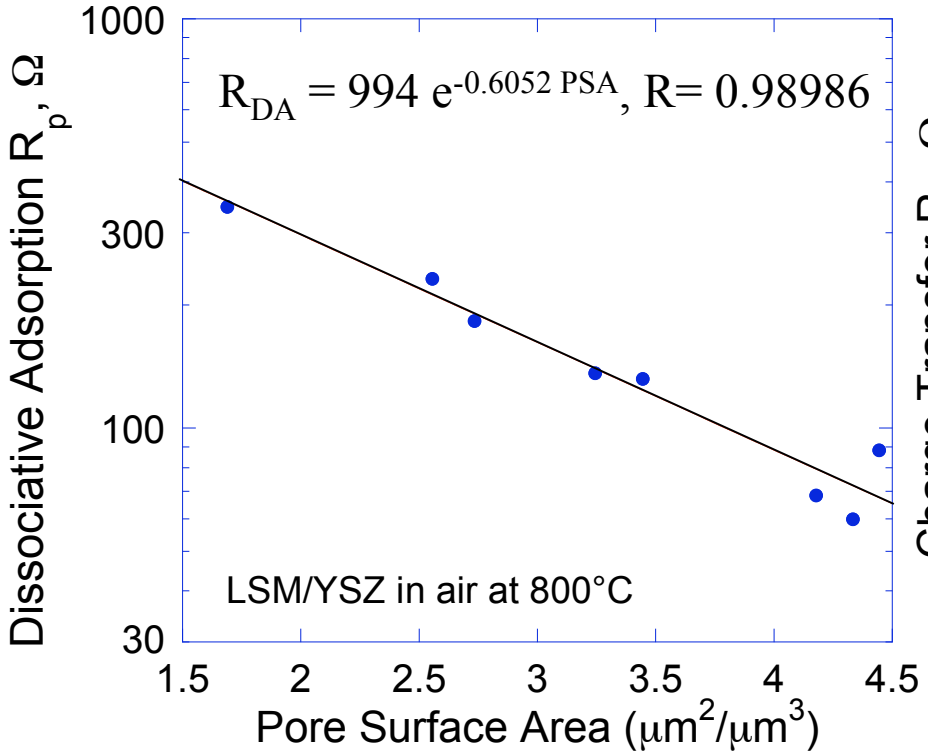
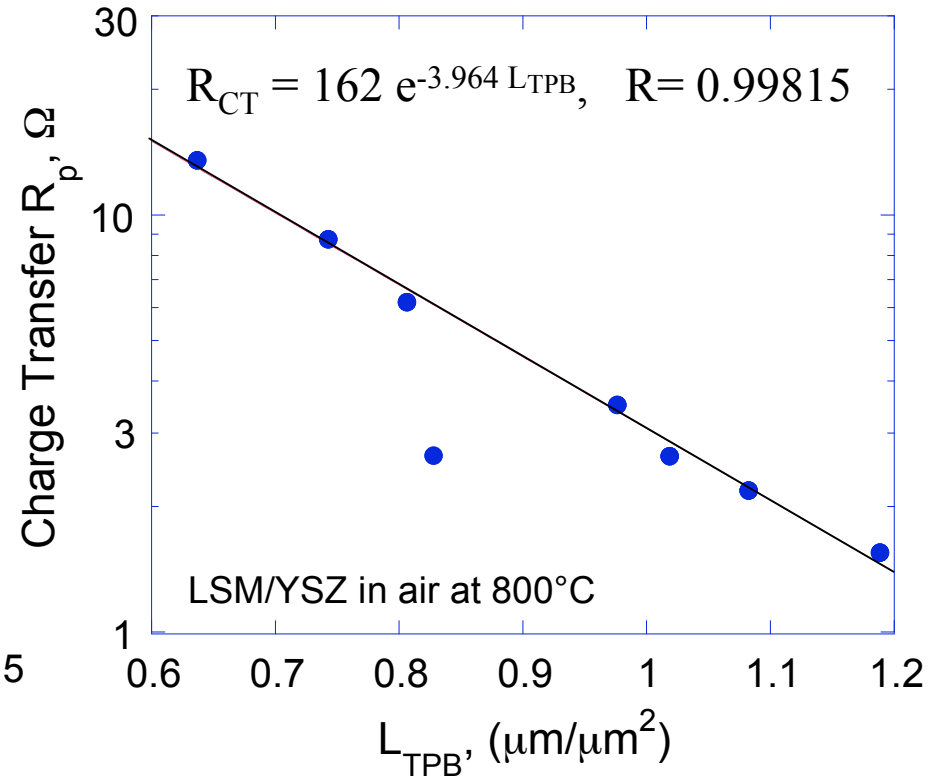
Integrate and Deconvolute Mechanisms





LSM cathode impedance components ***directly*** related to microstructure:

- Dissociative-Adsorption impedance decreases exponentially with increasing pore surface area
- Charge Transfer impedance decreases exponentially with increasing TPB length

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Fundamental Mechanisms of SOFC Cathode Reactions

Suggested Research Approaches/Investigations:

- Computational Approach
  - Provide fundamental understanding
  - Calculate surface and bulk energetics
- Surface Science and Spectroscopic Techniques
  - Determine surface sites, vacancies, adsorbed species and effects of surface reconstruction
  - Measure surface and bulk energetics
- Catalysis Techniques
  - Determine O-adsorption/dissociation mechanisms
  - Determine rate constants (k_o)
- Novel Electrochemical Characterization
  - Separate contributions to impedance/polarization
  - Frequency dependence and relation to mechanism
- Quantify Microstructural Effects
  - Fabricate and evaluate model architectures
  - Apply advanced characterization techniques such as FIB/SEM
- Integrate (all of the above) and Deconvolute Mechanisms
  - Develop fundamental models
- ***Rationally*** Design New Materials ***and*** Advanced Microstructures
  - Predict performance and validate models

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Dr. Fereshteh Ebrahimi - Mechanical Properties
Dr. Juan Nino - Novel Oxide Materials Development
Dr. Wolfgang Sigmund - Novel Synthesis & Microstructures

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