Deconvolution of SOFC Cathode Polarization

Eric D. Wachsman

UF-DOE High Temperature Electrochemistry Center

Florida Institute for Sustainable Energy

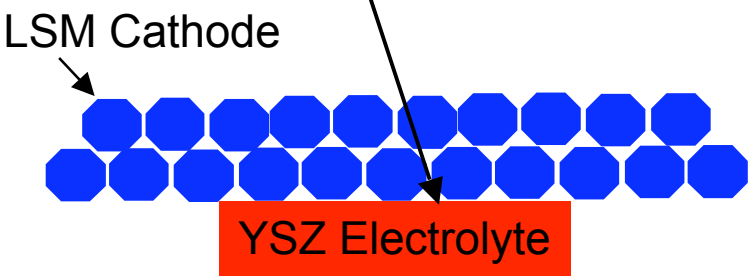
University of Florida

ewach@mse.ufl.edu

Fundamental Mechanisms of SOFC Cathode Reactions

Reaction Limited to TPB

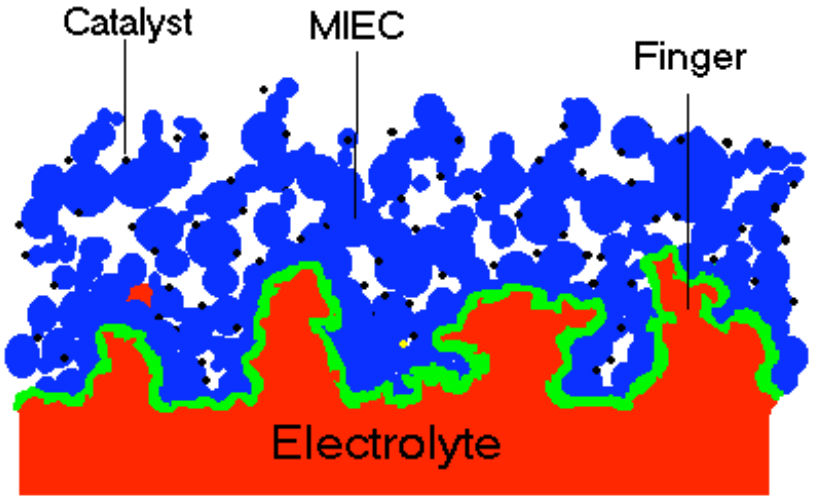
$$O_2 + 2V_O^{\bullet\bullet} \rightarrow 2O_O^{\times} + 4h^{\bullet}$$



1000°C -> 700°C

Multiple Reactions Spread Throughout Microstructure

- Each component having different contribution/mechanism



≤ 700°C

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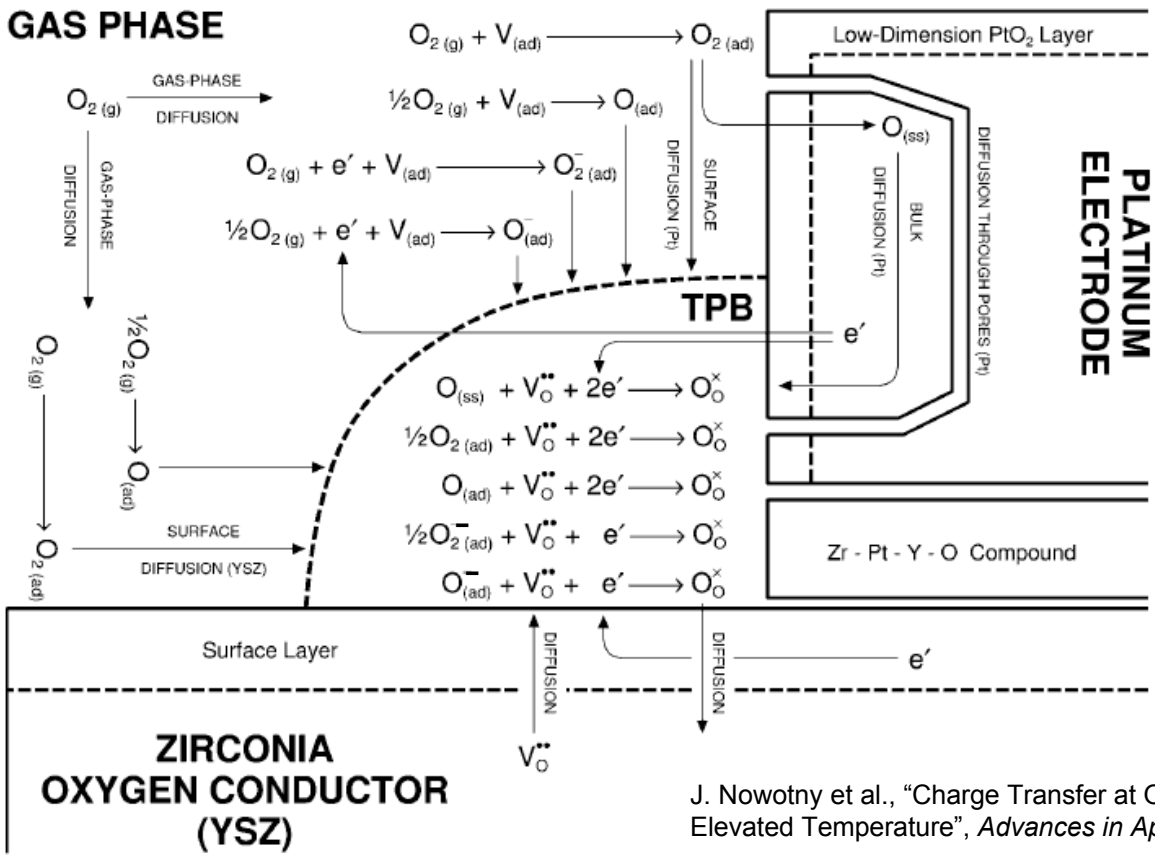
Fundamental Mechanisms of SOFC Cathode Reactions

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

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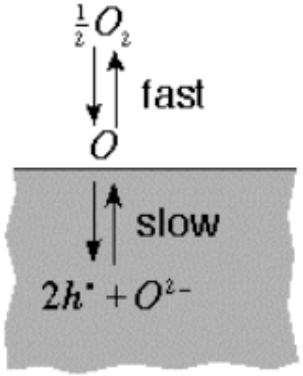
Fundamental Mechanisms of SOFC Cathode Reactions

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

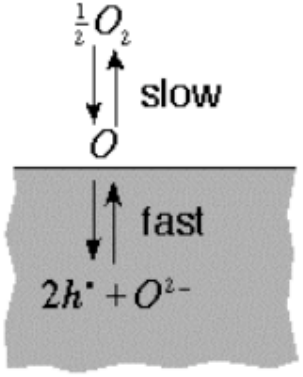
Oxygen exchange limited by vacancy exchange



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

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

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 multiple techniques to determine mechanism

Fundamental Mechanisms of SOFC Cathode Reactions

Systematic Approach to Developing Low Polarization Cathodes:

Computational Approach - *With Prof's Susan Sinnott & Simon Philpott*
- Provide fundamental understanding
- Calculate surface and bulk energetics

Surface Science and Spectroscopic Techniques - *With Prof. Scott Perry*
- Determine surface sites, vacancies, adsorbed species and effects of surface reconstruction
- Measure surface and bulk energetics

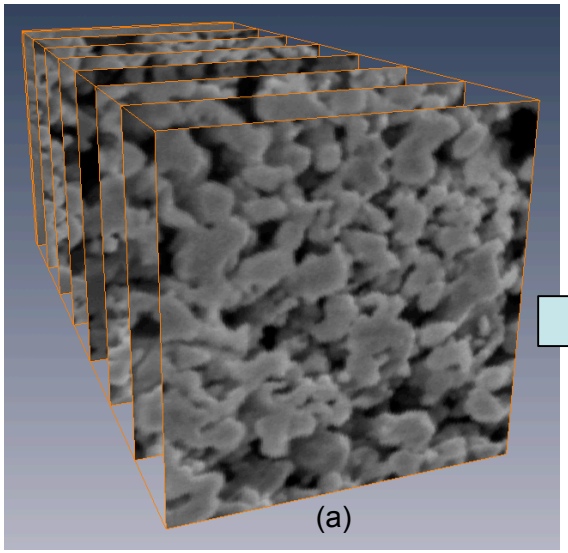
→ Catalysis Techniques
- Determine O-adsorption/dissociation mechanisms
- Determine rate constants (k_o)

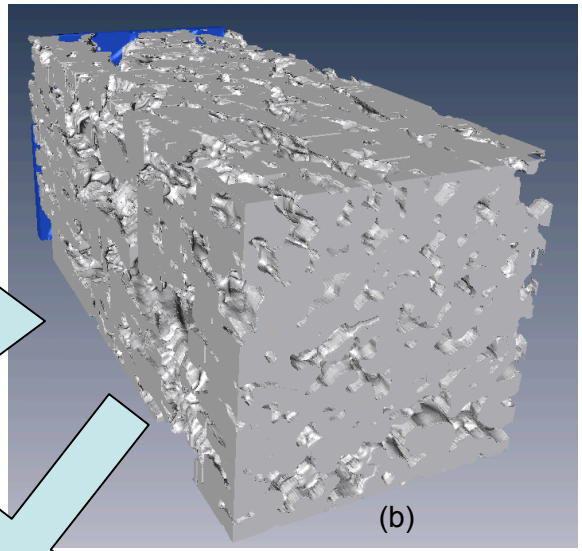
→ Electrochemical Characterization - *With Prof. Mark Orazem*
- Separate contributions to impedance/polarization
- Frequency dependence and relation to mechanism

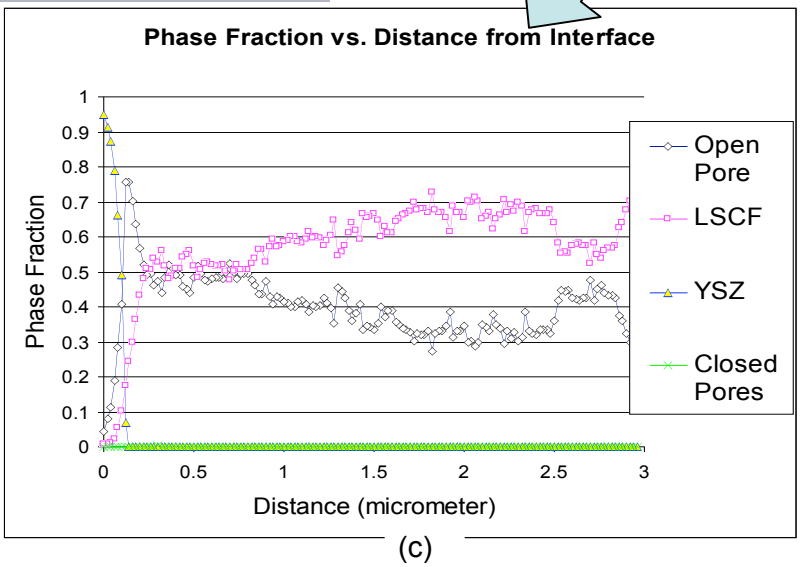
→ Quantify Microstructural Effects - *With Prof. Kevin Jones*
- Fabricate and evaluate model architectures
- Apply advanced characterization techniques such as FIB/SEM

Integrate (all of the above) and Deconvolute Mechanisms
- Develop fundamental models

Quantify Microstructural Effects - FIB/SEM





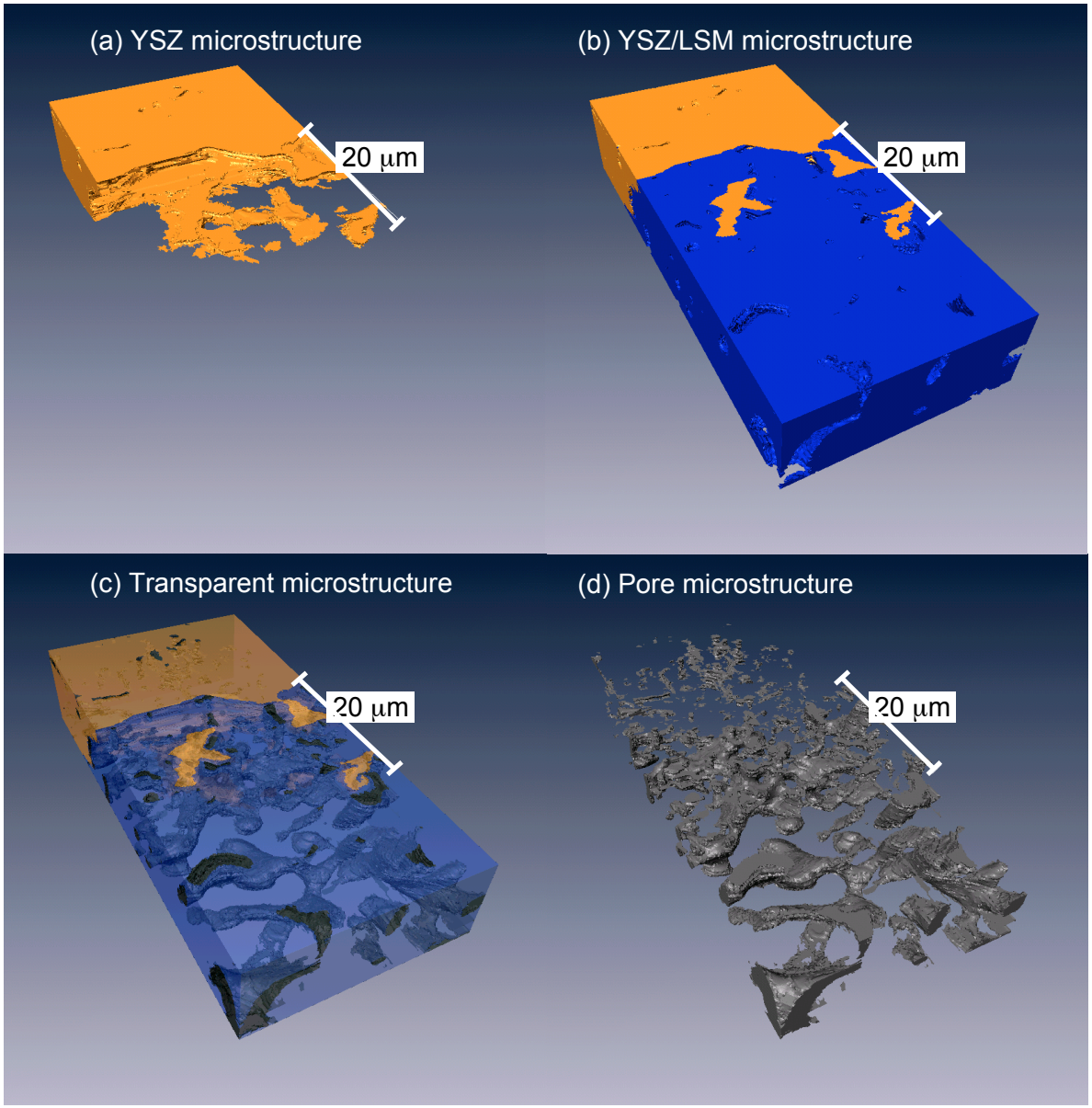


(c)

Focused Ion Beam

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

Quantify Microstructural Effects - FIB/SEM



Developed phase contrast for composite cathode structures

Siemens SOFC

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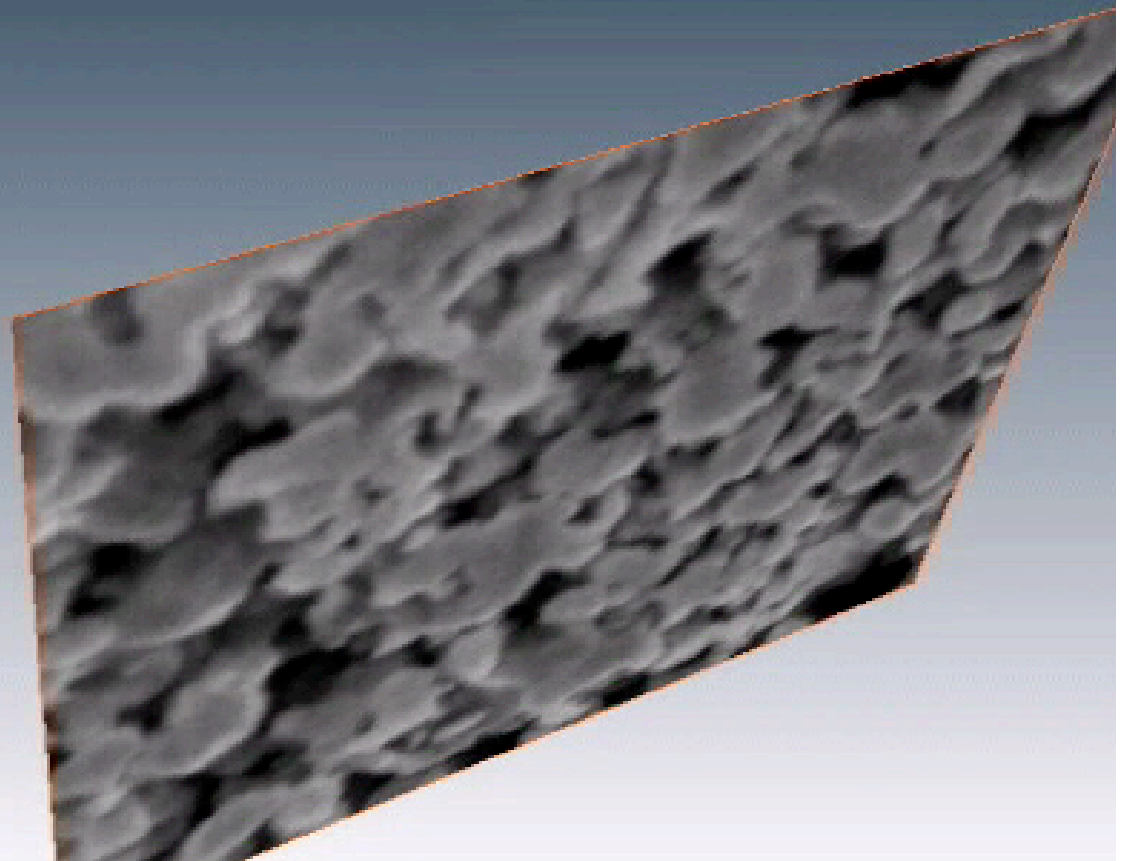
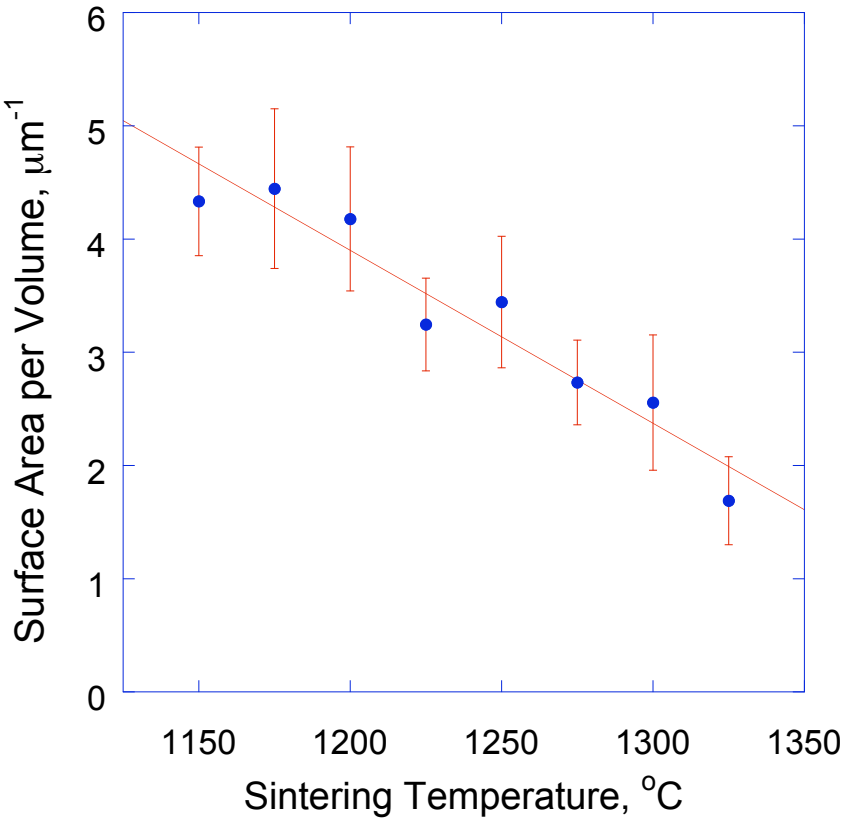
Flight through porous SOFC cathode

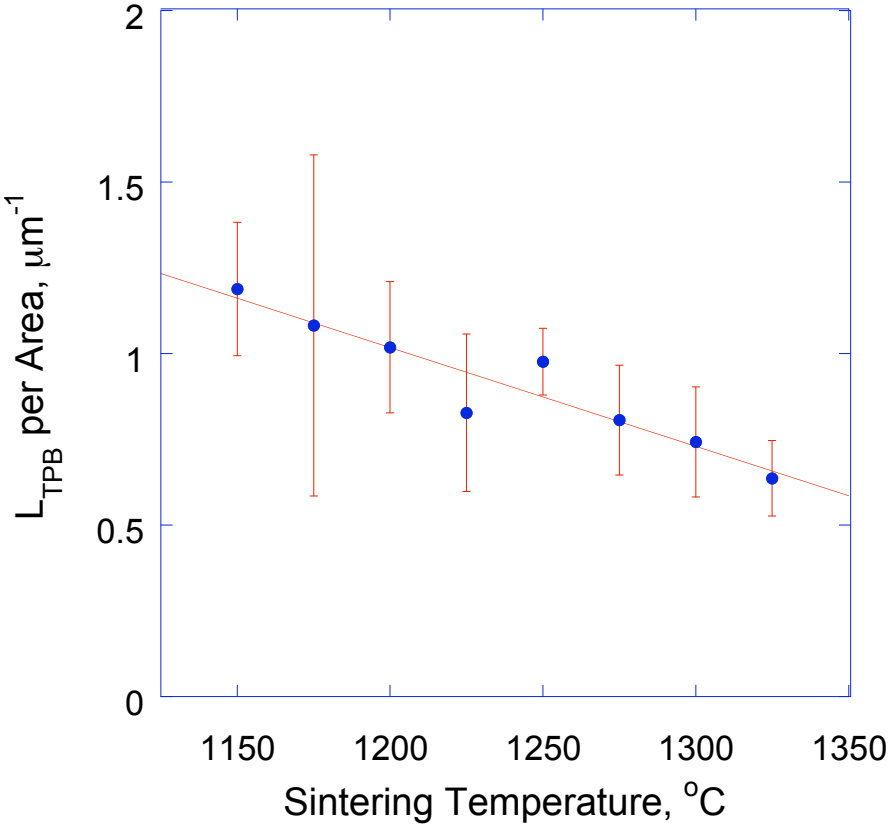
UNIVERSITY OF FLORIDA
DEPARTMENT OF MATERIALS SCIENCE & ENGINEERING
by Dan Gostovic



Dual beam FIB/SEM serially sections, and images porous SOFC cathode at 20nm intervals

Quantify Microstructural Effects - FIB/SEM





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

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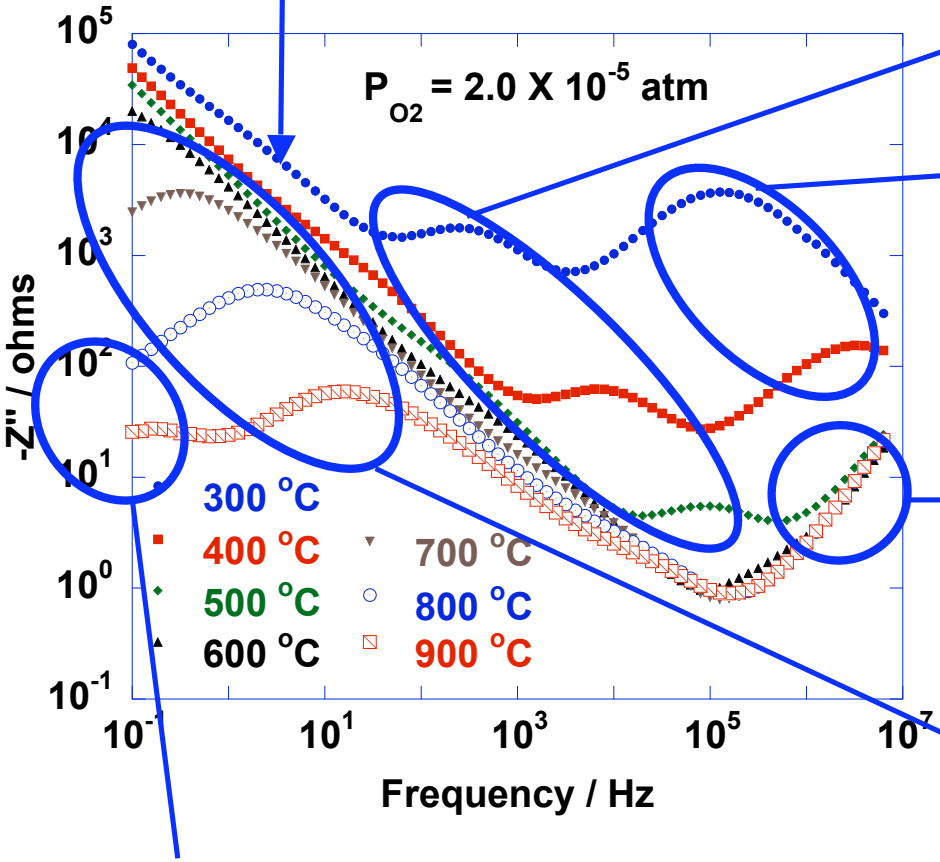
Electrochemical Impedance Spectroscopy of LSM/YSZ

Charge transfer at TPB (τ ~0.0001 s)



Ionic conduction through electrolyte grain boundary

Ionic conduction in bulk electrolyte

Artifacts minimized by nulling

O_2 pore diffusion (τ ~ 5.9 s)

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

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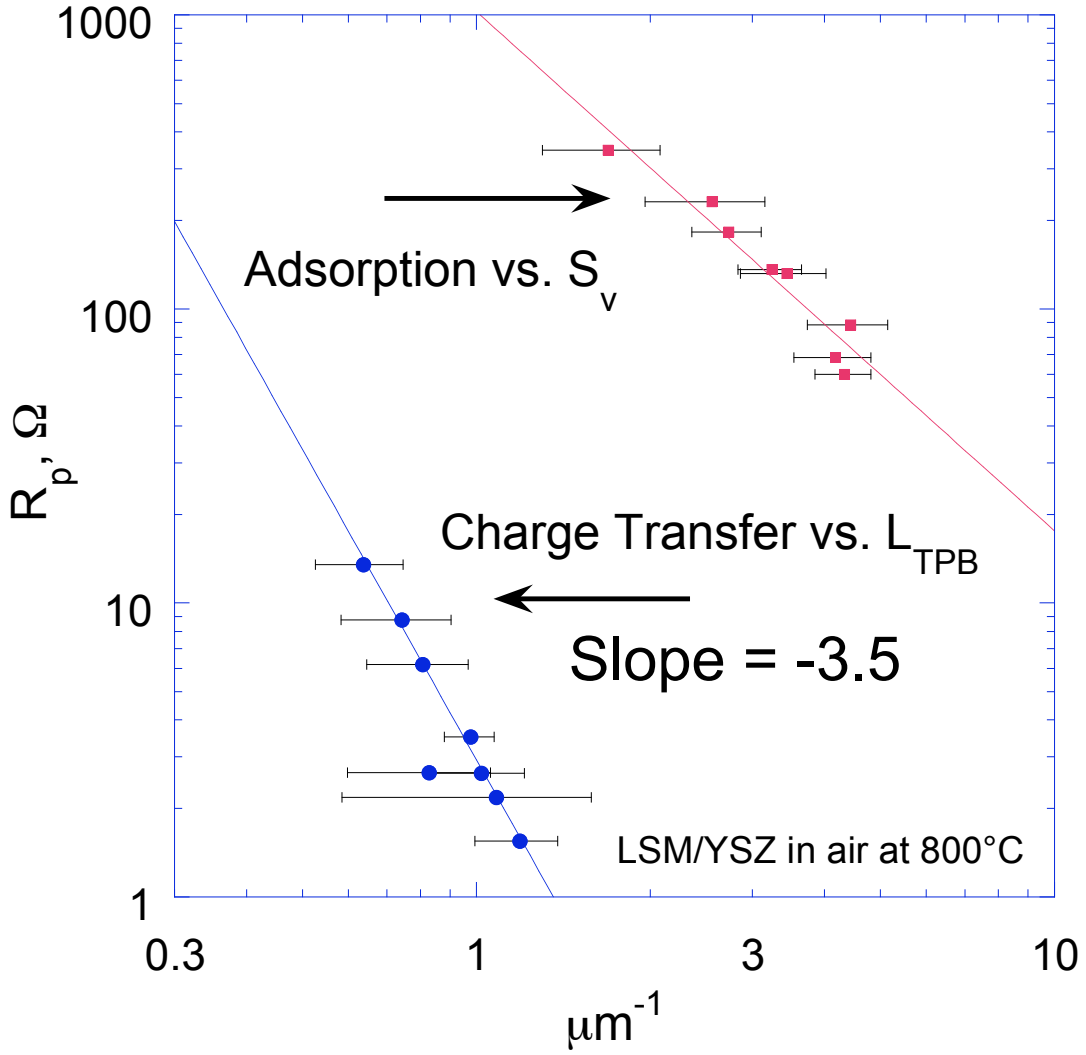
Microstructure - Performance Relationship



For the LSM on YSZ cathode reaction:

$$\tfrac{1}{2}O_{2,ads} + 2e' + V_O^{\bullet\bullet} \rightarrow O_O^{\times}$$

The current is:

$$I_0 = k_f \left[e'\right]^m \left[O_{2,ads}\right]^n \left[V_O^{\bullet\bullet}\right]^p$$

The corresponding charge transfer polarization (R_{ct}) dependence on triple phase boundary length (L_{TPB}) is:

$$R_{ct} \sim k_f^{-1} L_{TPB}^{-3.5}$$

Direct quantified relationship between cathode microstructure and performance

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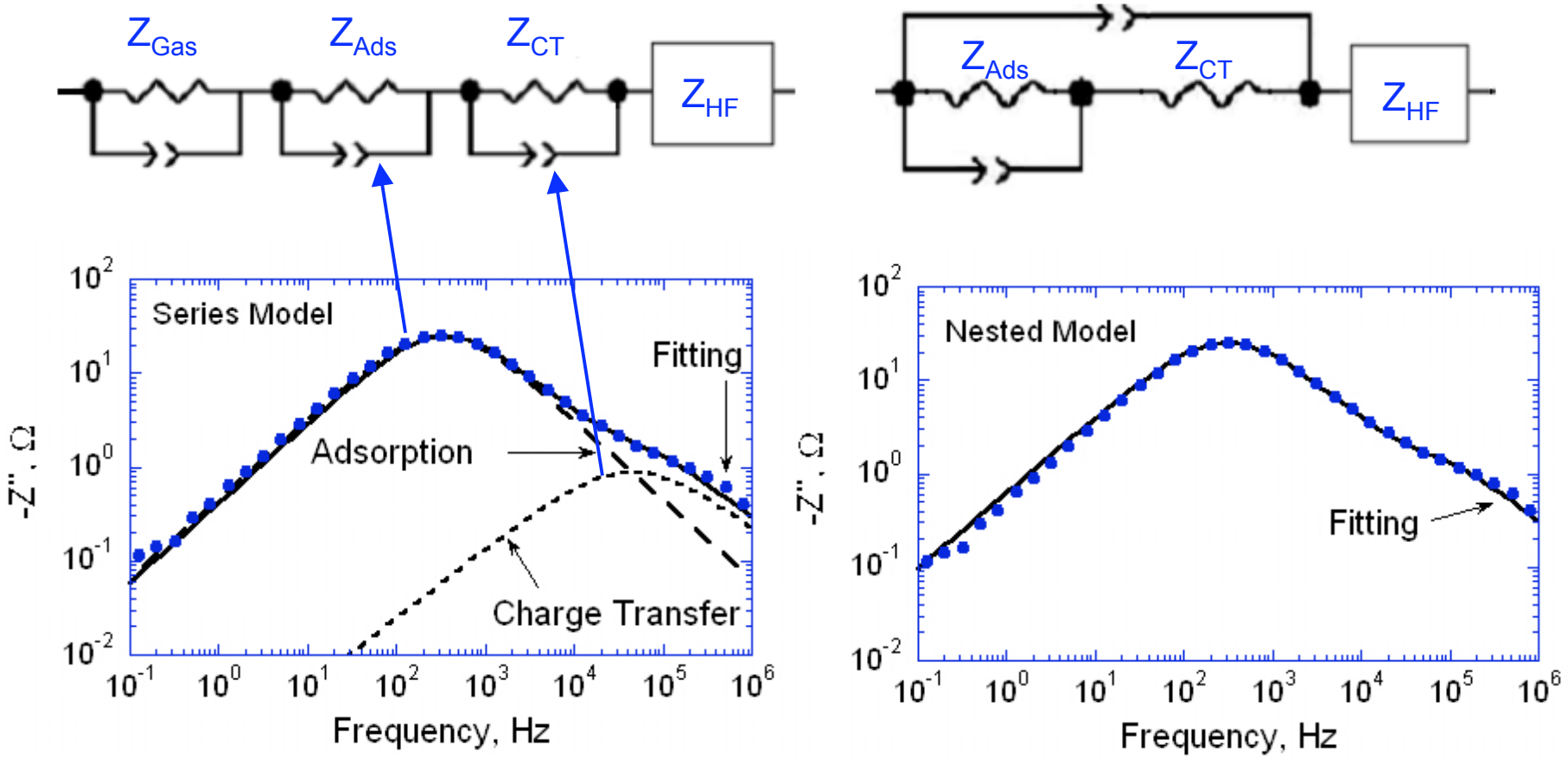
Equivalent Circuit Comparison



LSM, sintered at 1200 °C, measured at 800 °C in air

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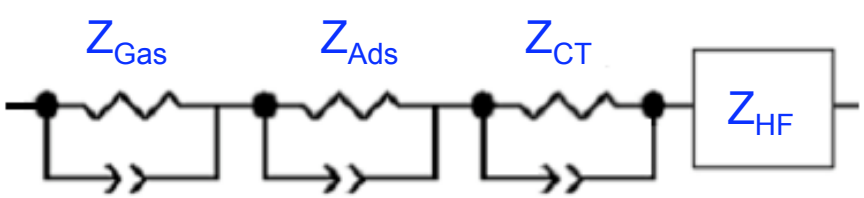
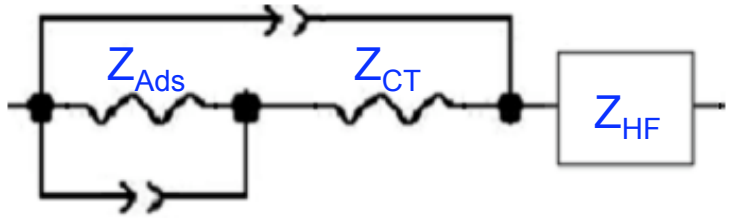
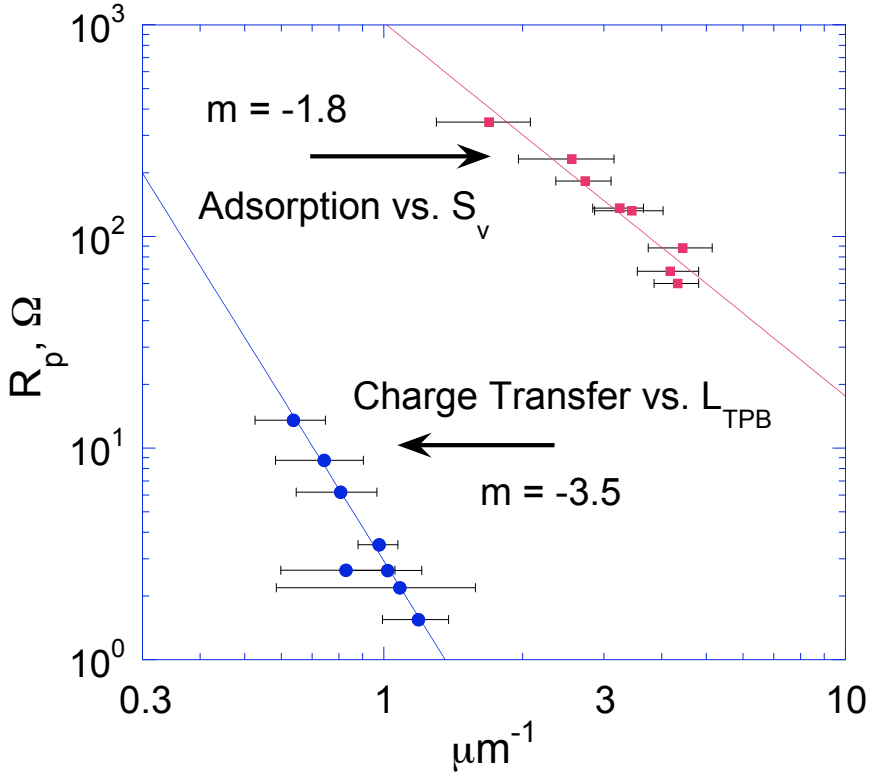
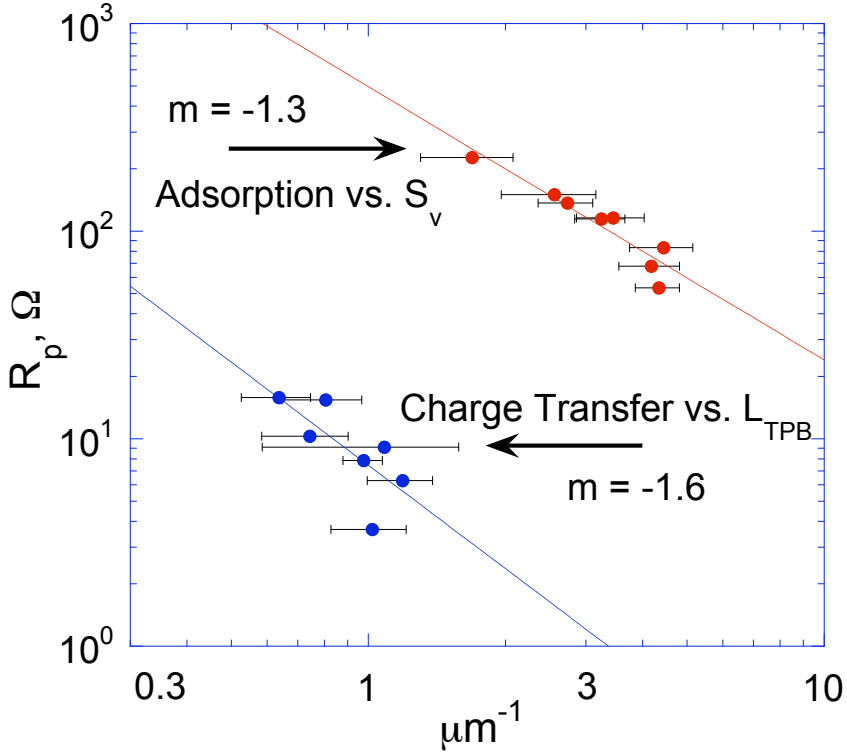
Equivalent Circuit Comparison









Need independent determination of mechanism

LSM, sintered at 1200 °C, measured at 800 °C in air

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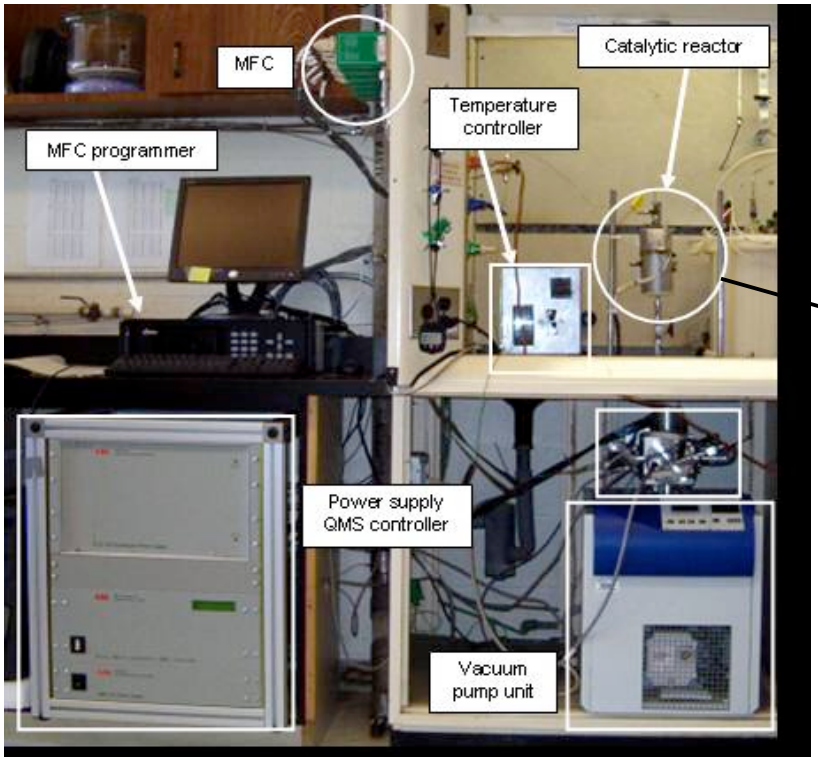
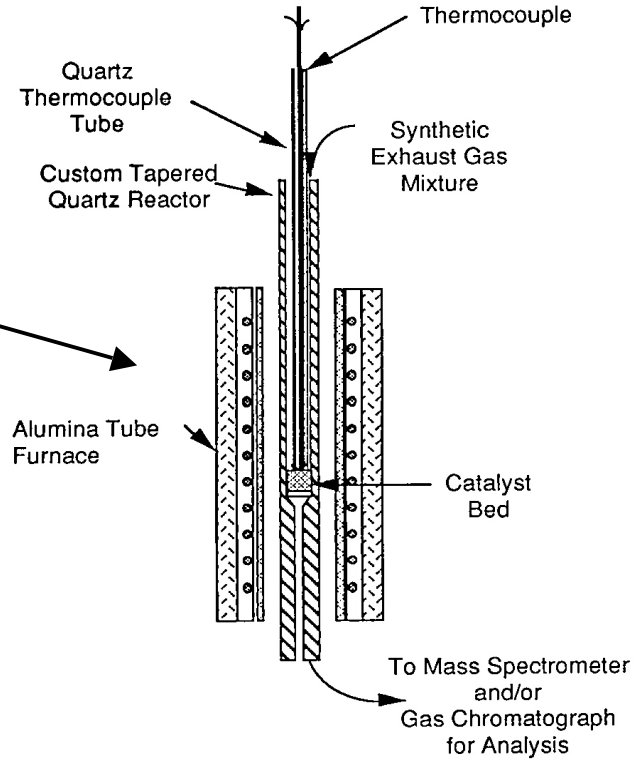
Fundamental Rate Constants - Catalysis

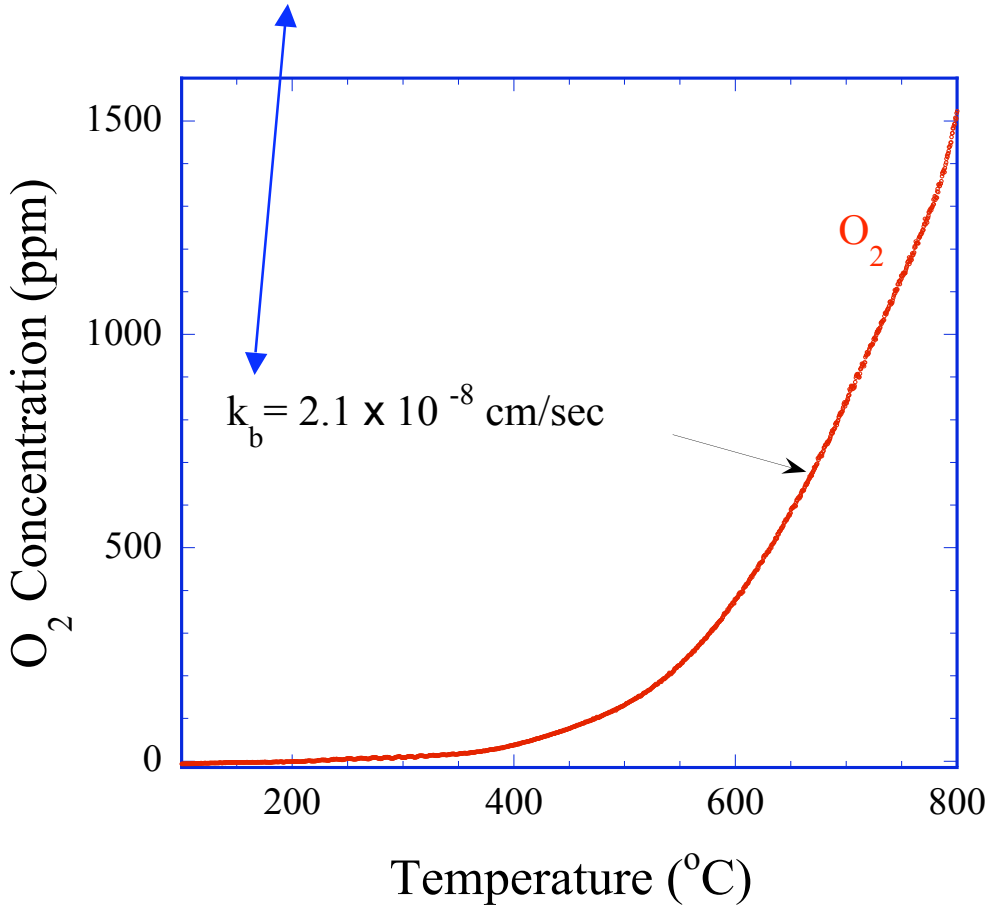




- Temperature programmed desorption (TPD)
  - Ramp temperature in He to determine adsorbed and/or decomposition species
- Temperature programmed oxidation (TPO)
  - Ramp temperature in O_2 gas mixture to determine reaction rates
- Isotope exchange (O^{16} vs. O^{18})
  - Switch gas to separate solid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

Fundamental Rate Constants - Catalysis

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



TPD of LSCF

Bulk-O desorption

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

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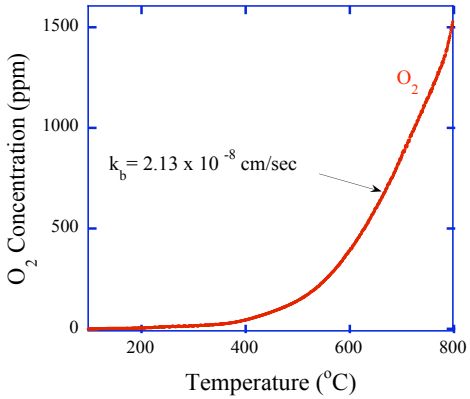
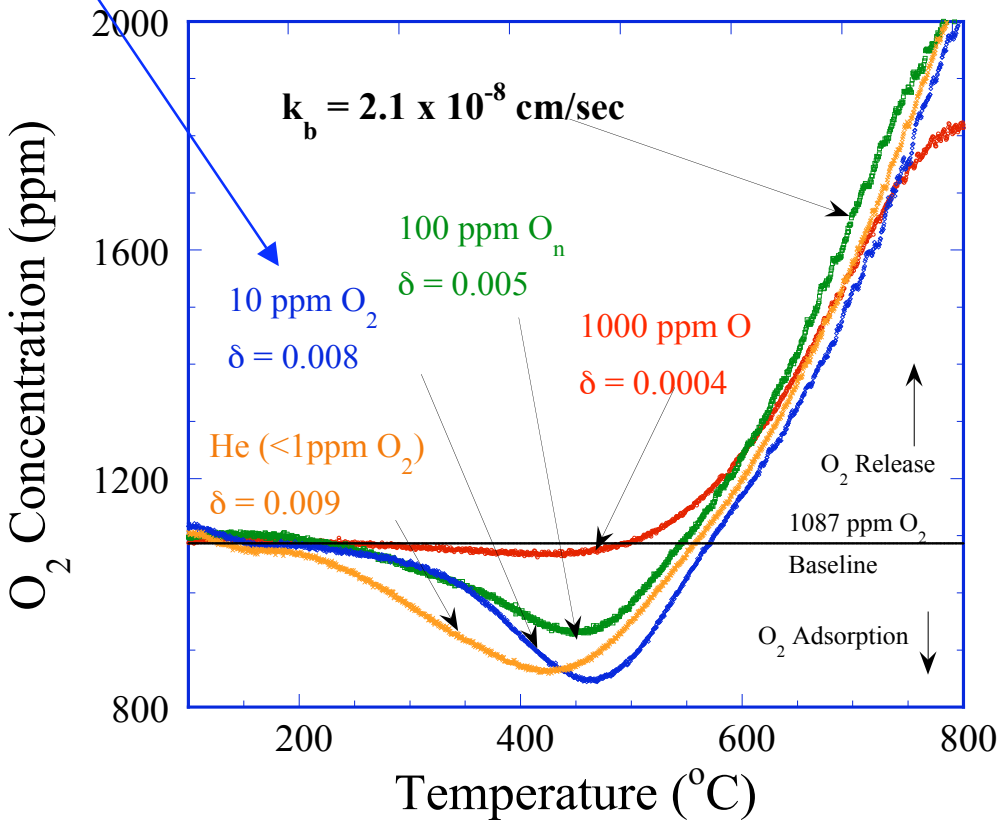
Fundamental Rate Constants - Catalysis

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





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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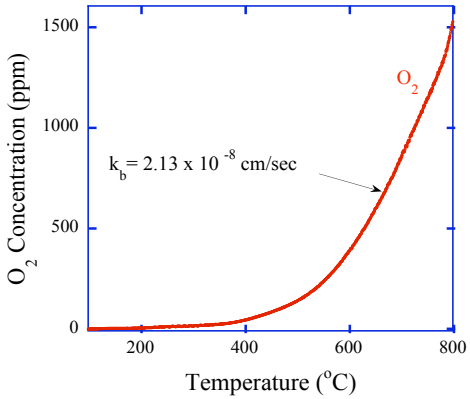
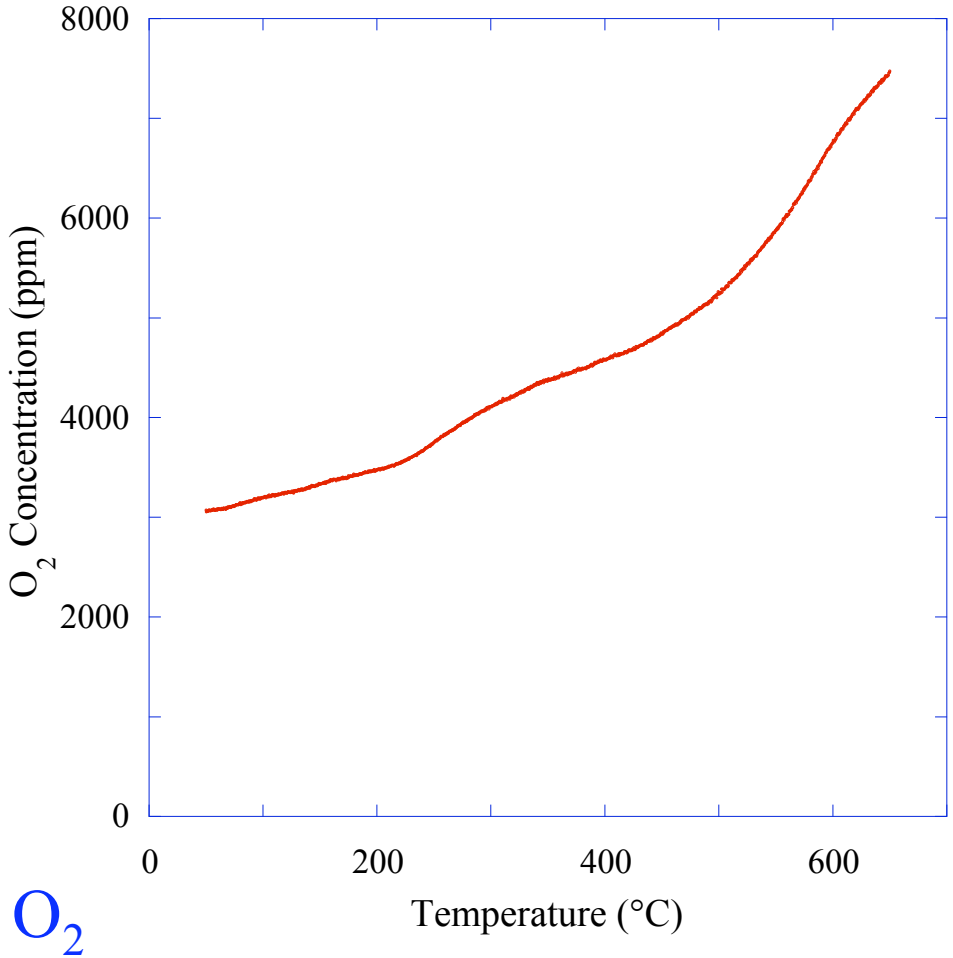
Fundamental Rate Constants - Catalysis





TPD of LSCF in 3000 ppm O_2

Bulk-O desorption

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

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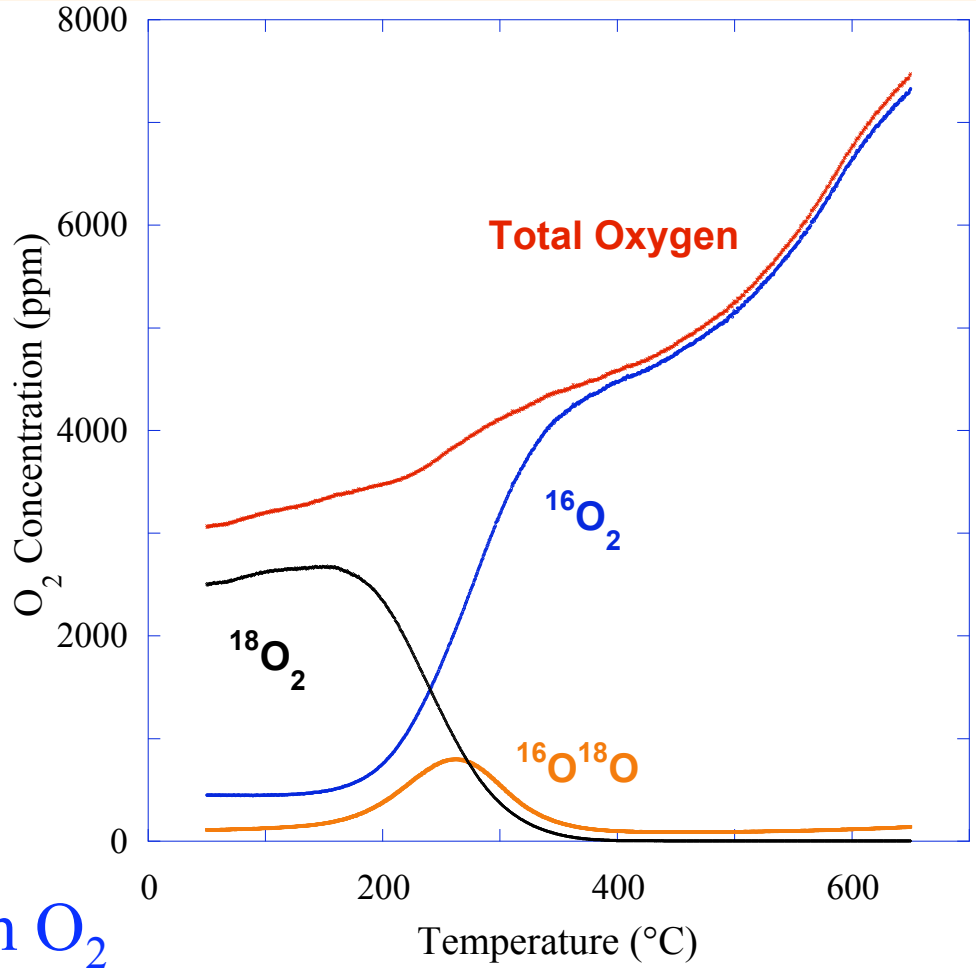
Fundamental Rate Constants - Catalysis

Indicates complex mechanism

$^{18}O_2$ = gas phase oxygen

$^{16}O_2$ = lattice oxygen

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



TPD of LSCF in 3000 ppm O_2

Isotopically Labeled - $^{18}O_2$

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

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Fundamental Rate Constants - Catalysis

- At low temp $^{18}O_2$ is incorporated into lattice

  $^{18}O_2 + 2V_O^{\bullet\bullet} = 2{}^{18}O_O^x$

- At intermediate temp $^{18}O_2$ dissociates on surface

  $^{18}O_2 = 2{}^{18}O_{ads}$

  and is then either incorporated into lattice

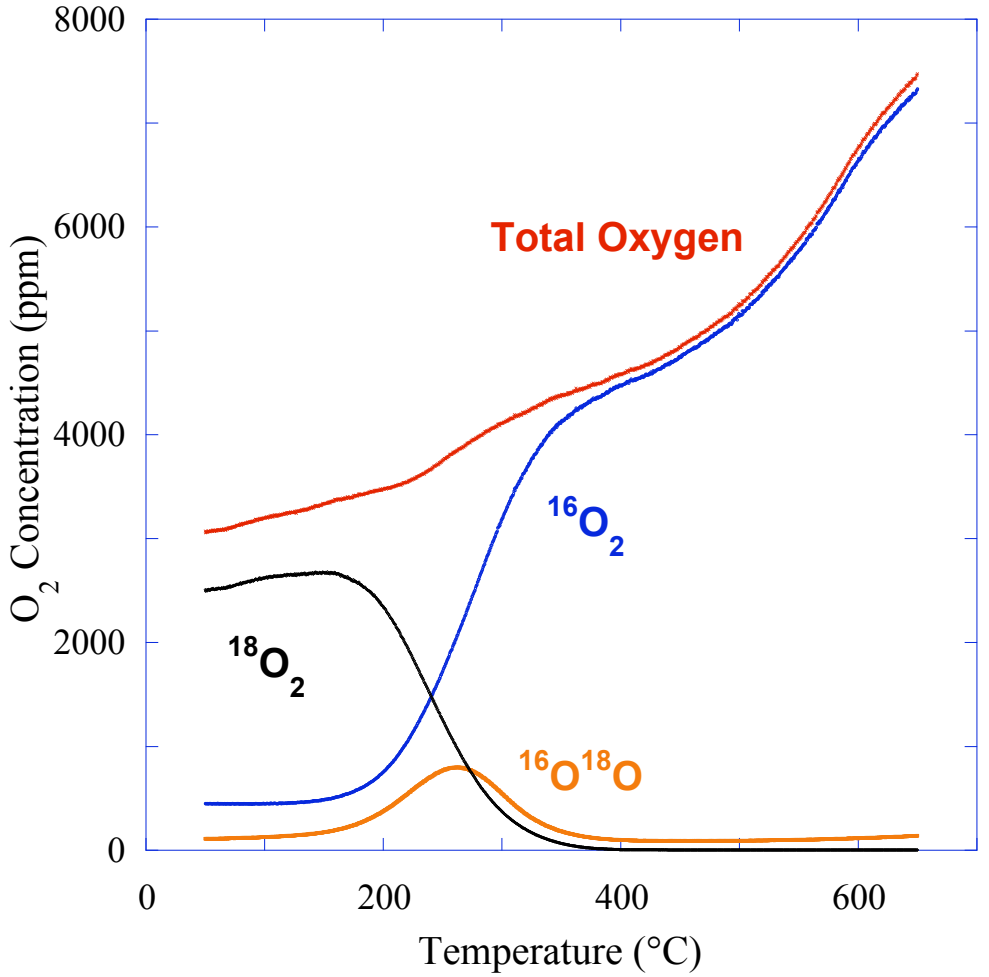
  $^{18}O_{ads} + V_O^{\bullet\bullet} = {}^{18}O_O^x$

  or reacts with bulk/surface $^{16}O_O^x$ and desorbs

  $^{18}O_{ads} + {}^{16}O_O^x = {}^{18}O^{16}O$

- At high temp $^{18}O_2$ incorporates completely into lattice but at a rate less than $^{16}O_2$ evolution from the lattice

  $k_f P_{^{18}O_2}{}^n [V_O^{\bullet\bullet}] < k_b [{}^{16}O_O^X]$



TPD of LSCF in 3000 ppm $^{18}O_2$

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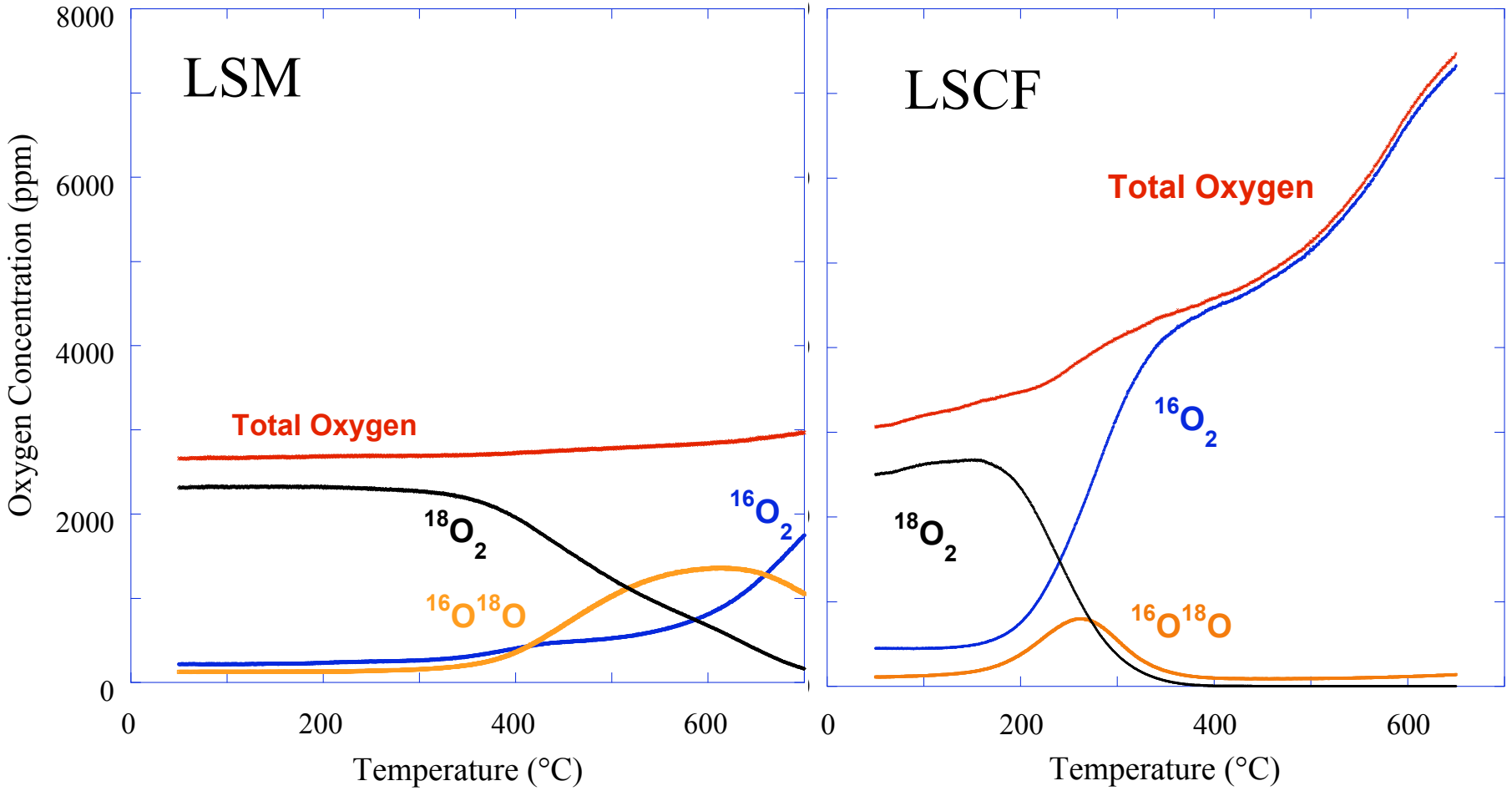
Fundamental Rate Constants - Catalysis



TPD in 3000 ppm $^{18}O_2$

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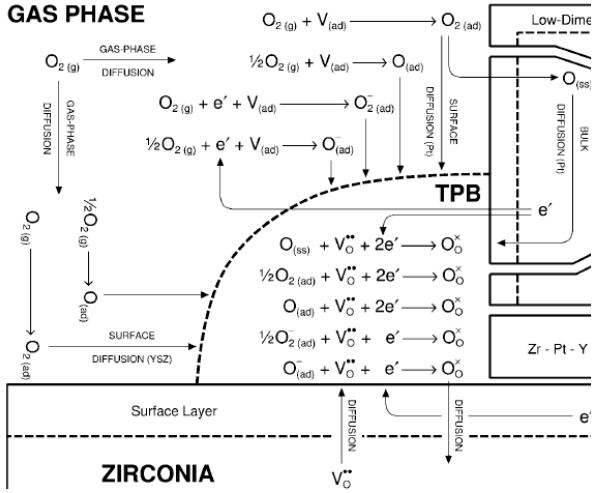
Future Work

- Isothermal O^{18} isotope exchange of LSM and LSCF
  - Determine reaction order/mechanisms from P_{O_2} and O^{18}/O^{16} dependence
    - ➢ $r \sim k P_{O_2}^{n}$
  - Determine rate constant activation energies from temperature dependence



- Integrate isotope results into impedance/microstructure results to deconvolute contributions to cathode polarization

- Compare/contrast LSM vs. LSCF results and gain fundamental insight into cathode materials/microstructure development

ACKNOWLEDGEMENT

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TPD & Isotope Exchange:

Cynthia Kan, Martin VanAssche and Eric Armstrong