Deconvolution of SOFC Cathode Polarization Mechanisms

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FLORIDA INSTITUTE for SUSTAINABLE ENERGY

Fundamental Mechanisms of SOFC Cathode Reactions

Systematic Approach to Developing Low Polarization Cathodes:

$R_{Cathode} = R_{Gas\ Difussion} + R_{Surface\ Adsorbtion/Diffusion} + R_{Charge\ Transfer} + R_{Ohmic}$

$R_{Gas\ Difussion}$ and R_{Ohmic} are functions of:

- Microstructure (porosity & phase fraction, tortuosity, connectivity)
- Conductance (solid phase conductivity or gas phase diffusivity)

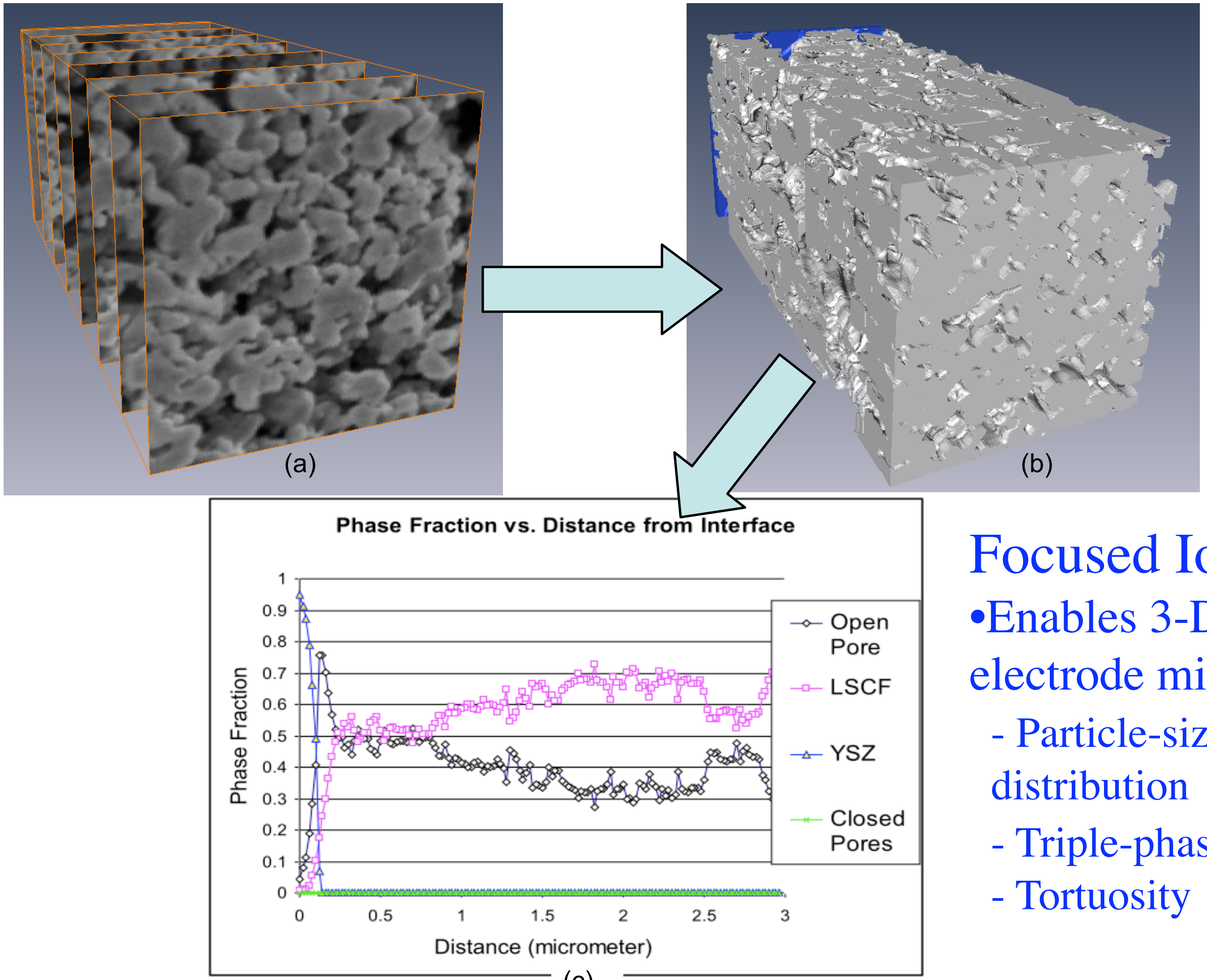
$R_{Surface\ Adsorbtion/Diffusion}$ are functions of:

- Microstructure (surface area/volume)
- Kinetics (surface coverage, surface diffusivity)

$R_{Charge\ Transfer}$ is function of:

- Microstructure (L_{TPB}, surface area/volume)
- Kinetics (Oxygen reduction rate)

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

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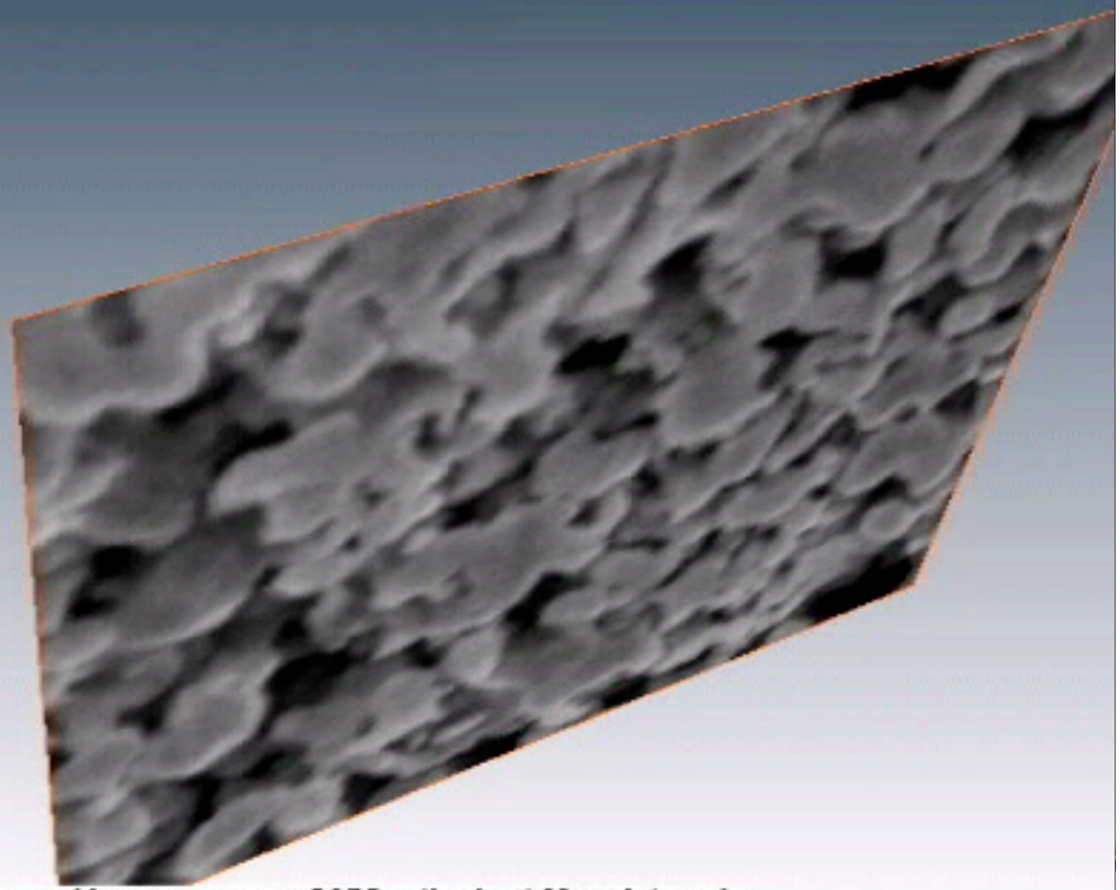
Flight through porous SOFC cathode

UNIVERSITY OF FLORIDA

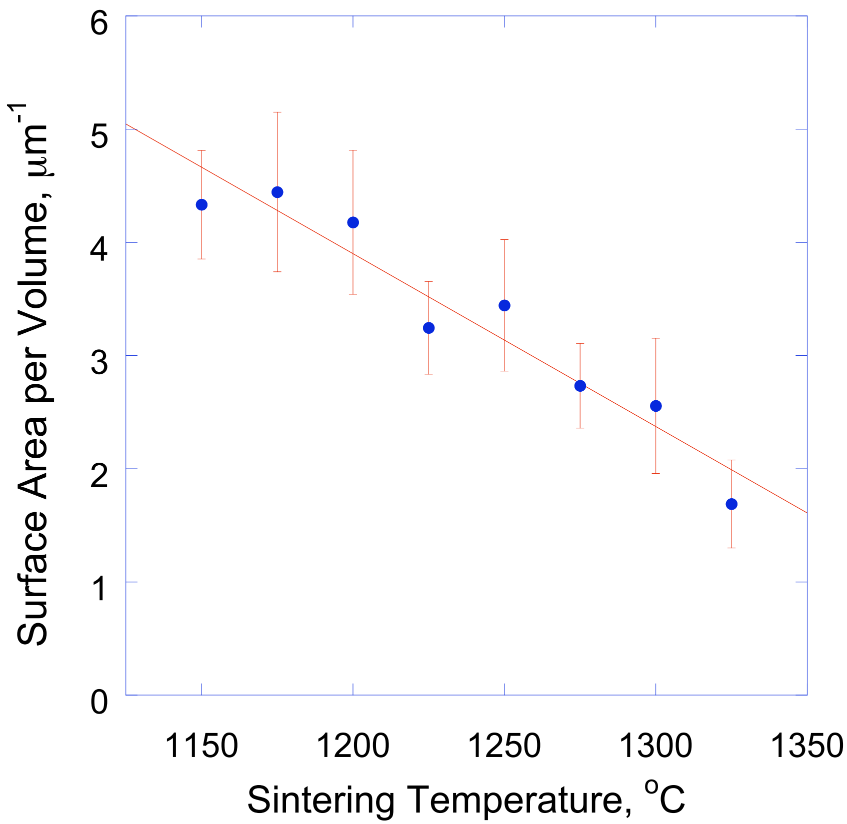
DEPARTMENT OF MATERIALS SCIENCE & ENGINEERING

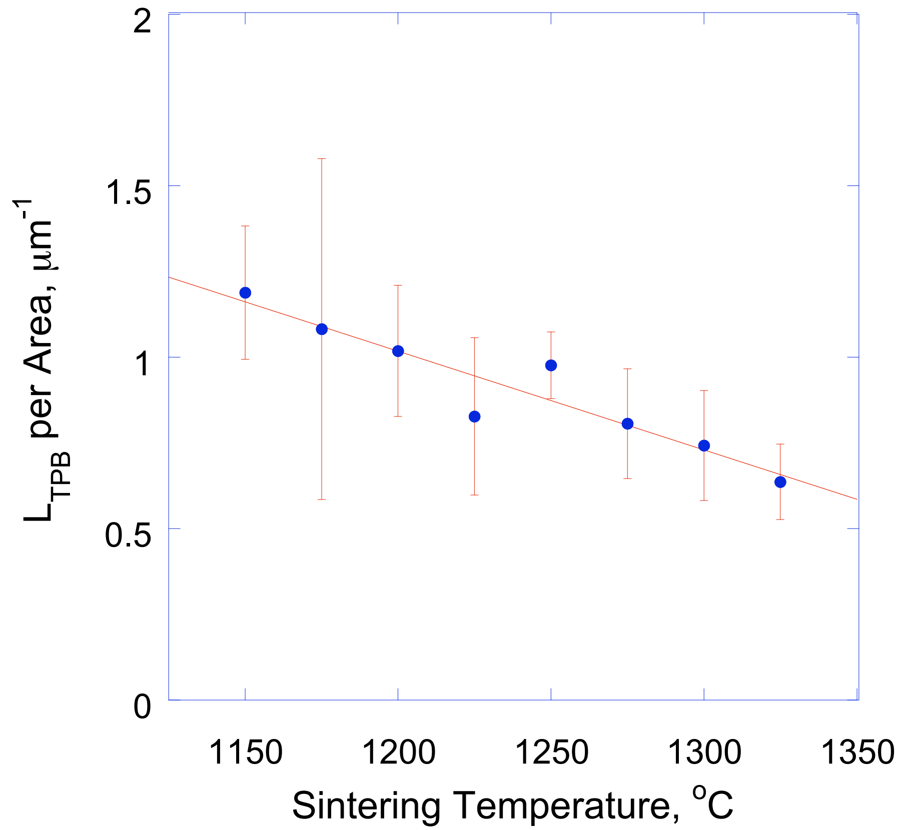
by Dan Gostovic



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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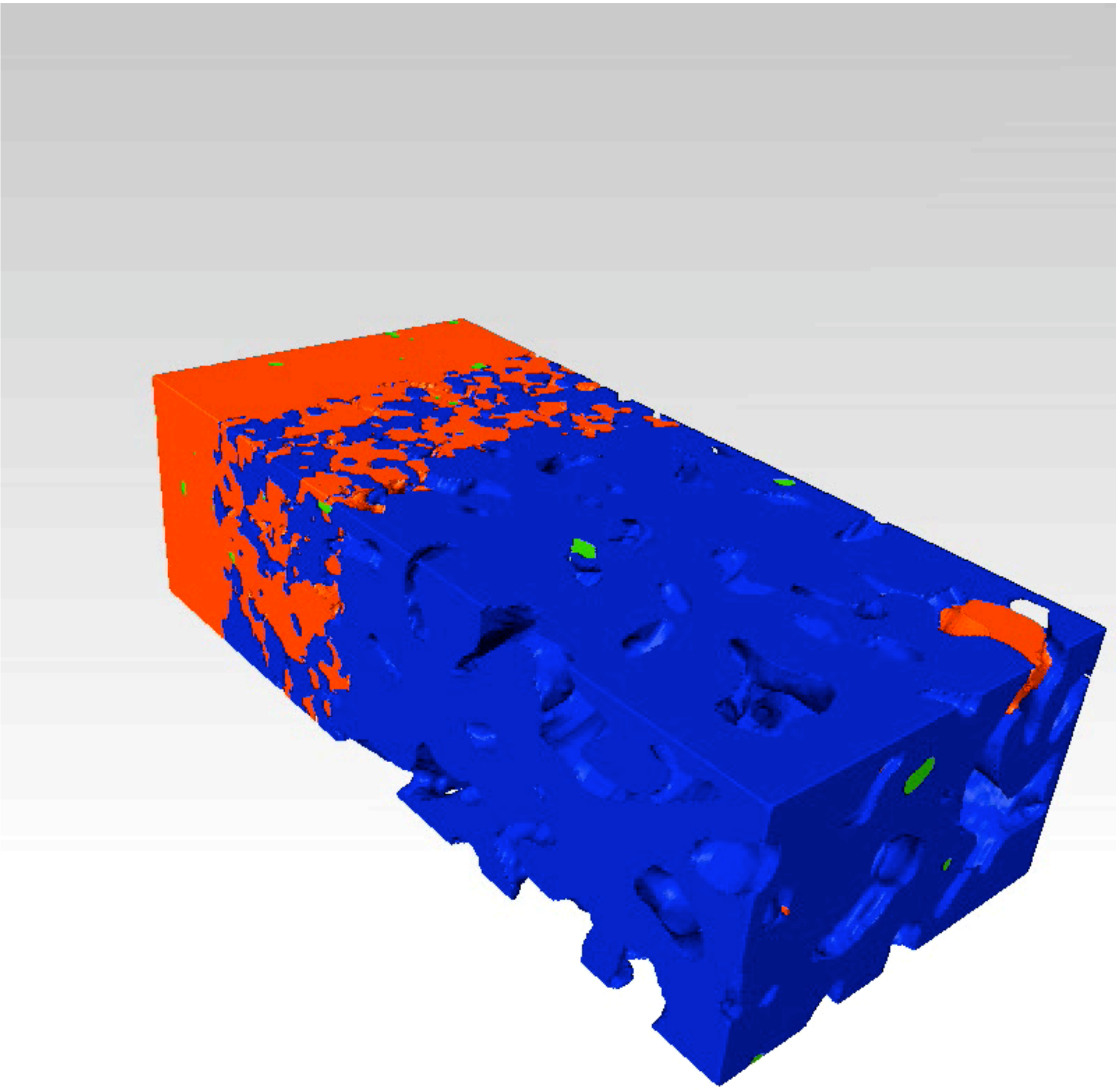
Quantify Microstructural Effects - FIB/SEM



Developed phase contrast for composite cathode structures

Siemens SOFC

Fundamental Mechanisms of SOFC Cathode Reactions

Systematic Approach to Developing Low Polarization Cathodes:

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- Microstructure (porosity & phase fraction, tortuosity, connectivity) ✓ FIB/SEM
- Conductance (solid phase conductivity or gas phase diffusivity) ✓ material property

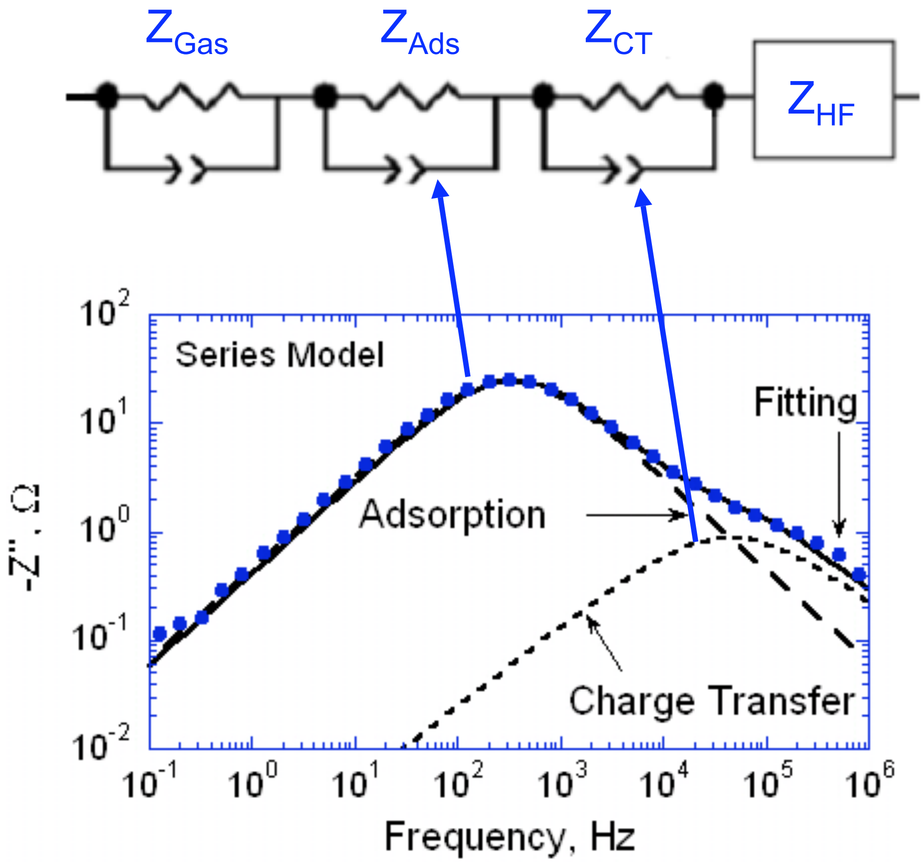
$R_{Surface\ Adsorbtion/Diffusion}$ are functions of:

- Microstructure (surface area/volume) ✓ FIB/SEM
- → Kinetics (surface coverage, surface diffusivity)

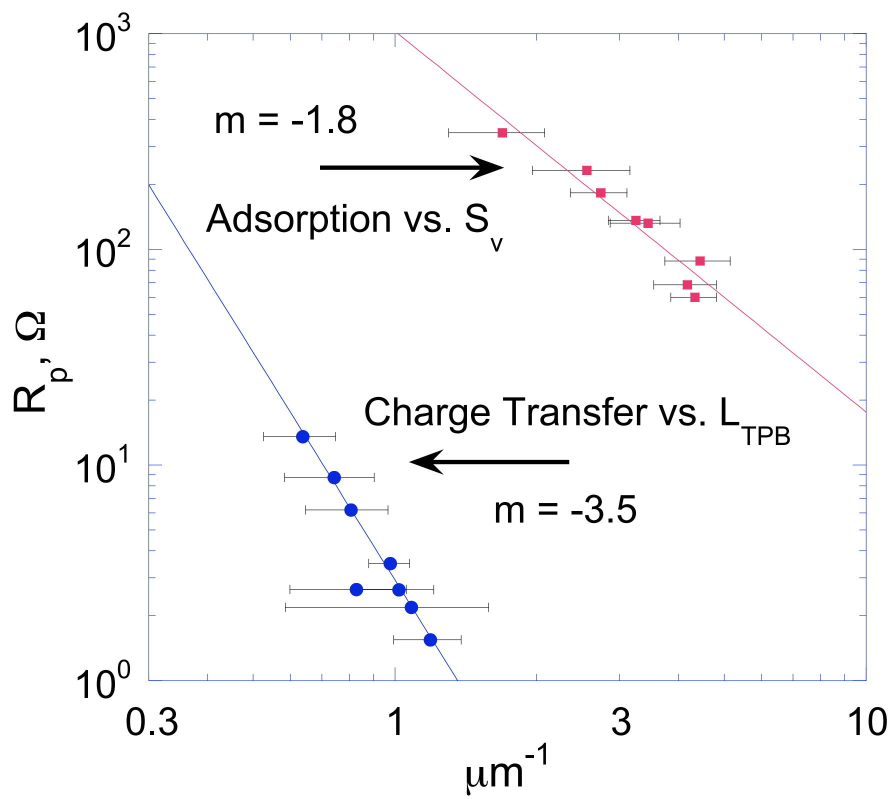
$R_{Charge\ Transfer}$ is function of:

- Microstructure (L_{TPB}, surface area/volume) ✓ FIB/SEM
- → Kinetics (Oxygen reduction rate)

Equivalent Circuit Comparison



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



First direct relationship between SOFC cathode microstructure and impedance

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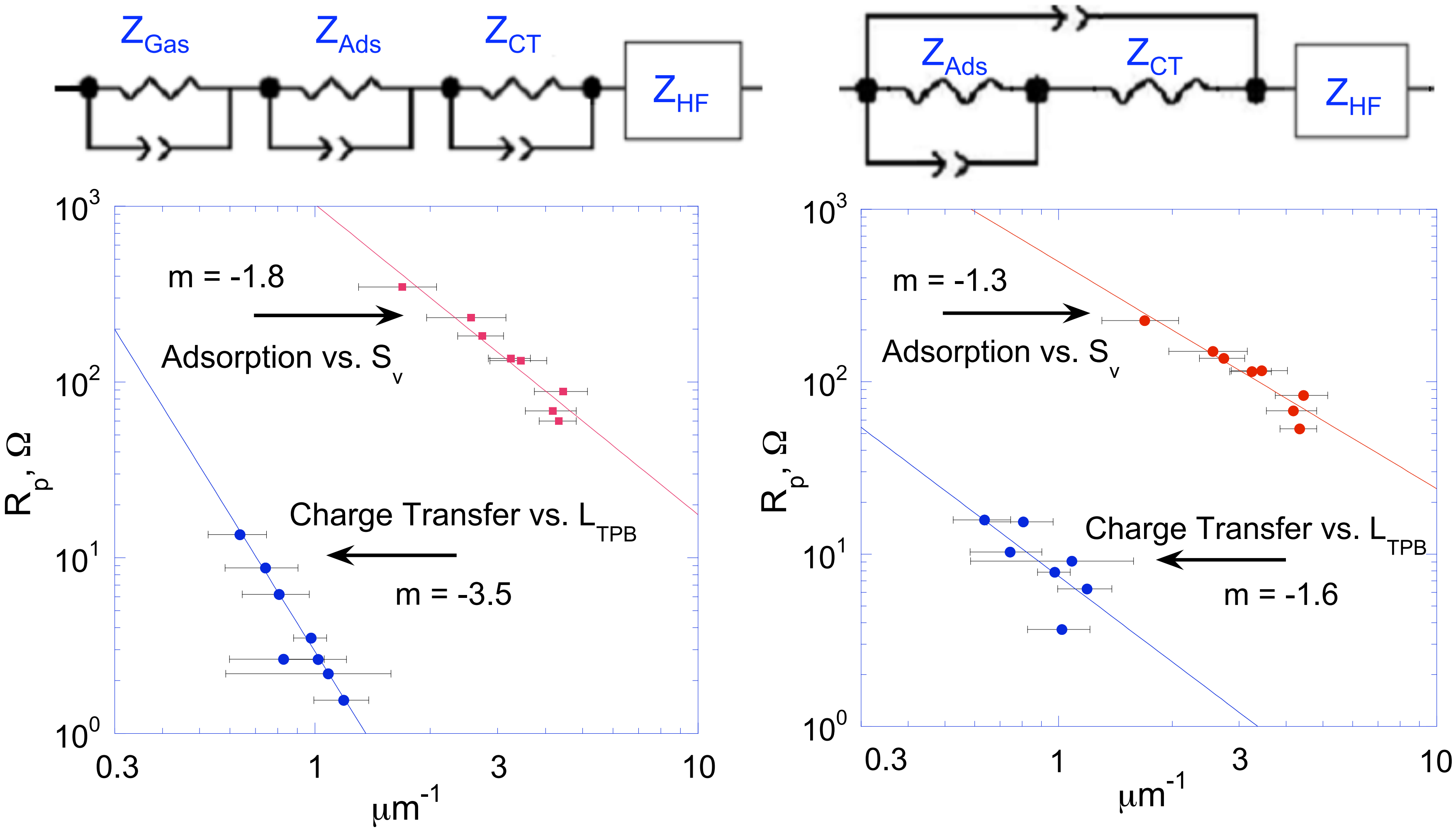
Equivalent Circuit Comparison



First direct relationship between SOFC cathode microstructure and impedance

Need independent determination of mechanism

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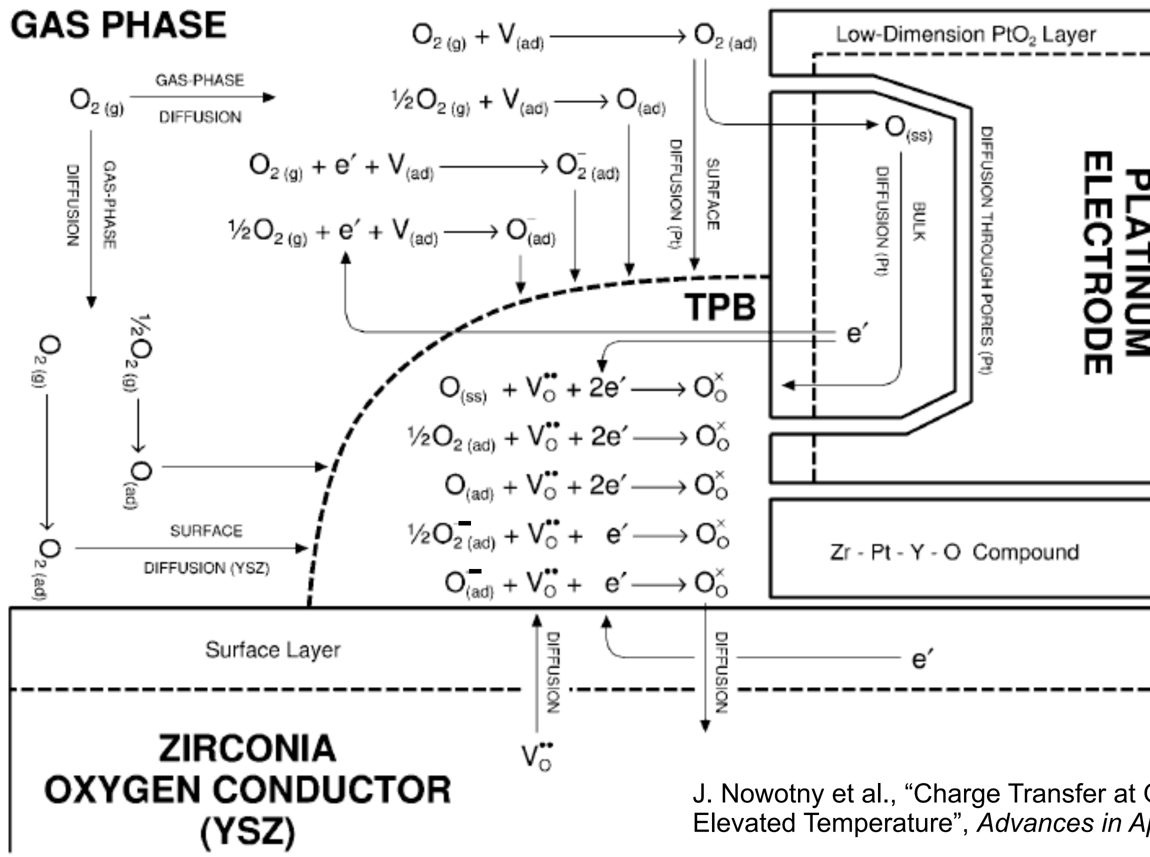
Fundamental Mechanisms of SOFC Cathode Reactions

What is rate limiting step?



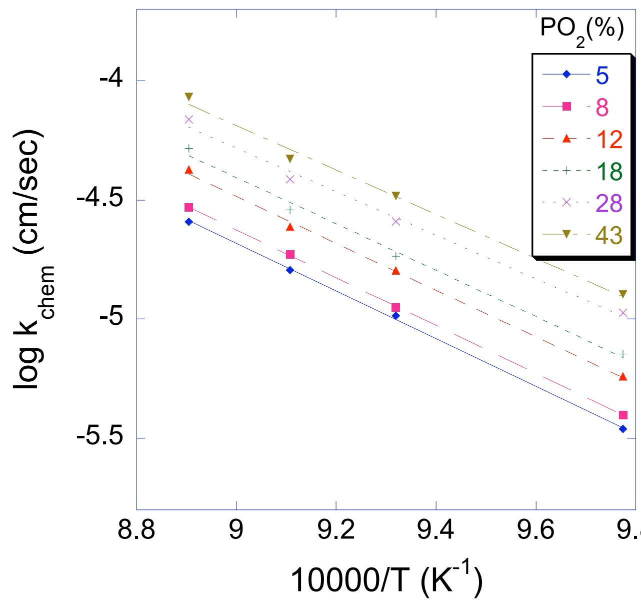
J. Nowotny et al., “Charge Transfer at Oxygen/Zirconia Interface at Elevated Temperature”, *Advances in Applied Ceramics* (2005)

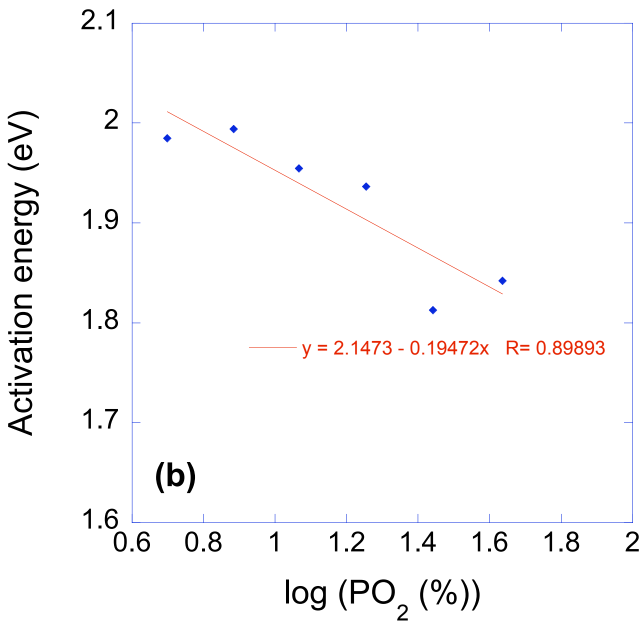
- Multiple potential mechanisms each having P_{O2} dependence
- However, P_{O2} dependence not unique

Fundamental Mechanisms of SOFC Cathode Reactions

Need ***fundamental*** rate constants and rate expressions

Literature full of k_{chem} from Conductivity Relaxation and SIMS Depth Profile





Conductivity relaxation of LSCF at 800°C

k_{chem} and E_A from these experiments are functions of P_{O2}

Fundamental Mechanisms of SOFC Cathode Reactions

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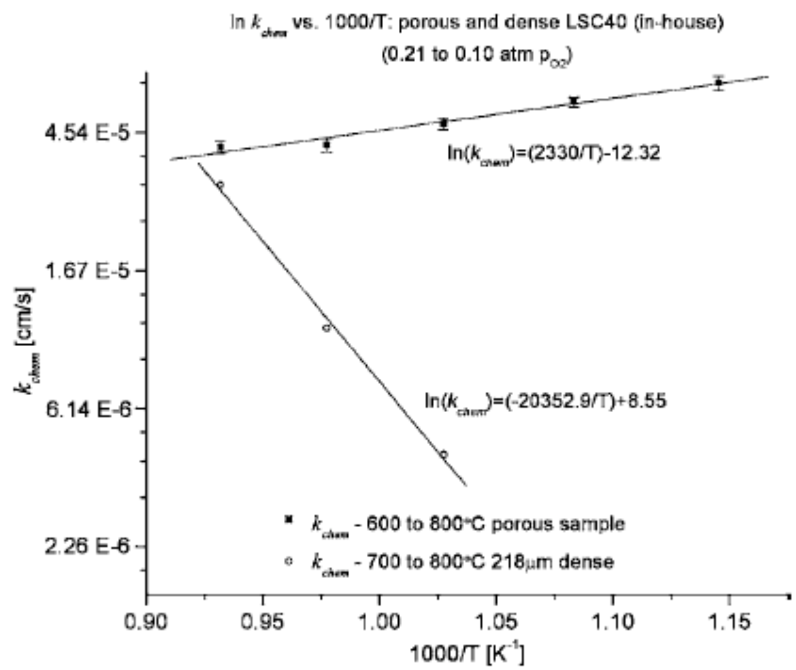
Literature full of k_{chem} from Conductivity Relaxation and SIMS Depth Profile



k_{chem} from porous LSC

k_{chem} from dense LSC

R. Ganeshananthan and A. V. Virkar, J. Electrochem. Soc. 152, A1620 (2005)

k_{chem} and E_A from these experiments are functions of P_{O2}

k_{chem} is also function of sample geometry and thus ***not fundamental***

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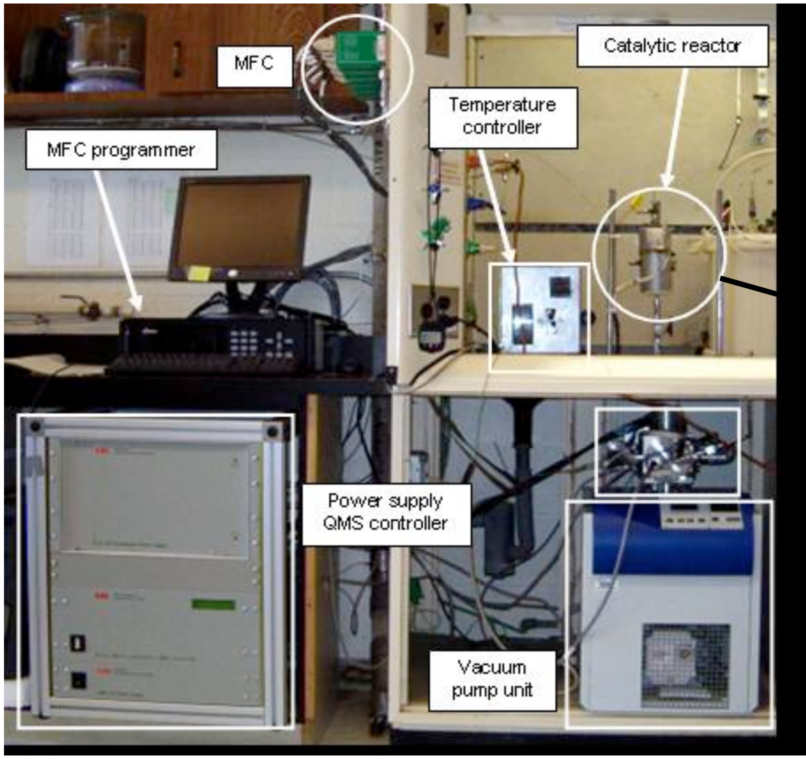
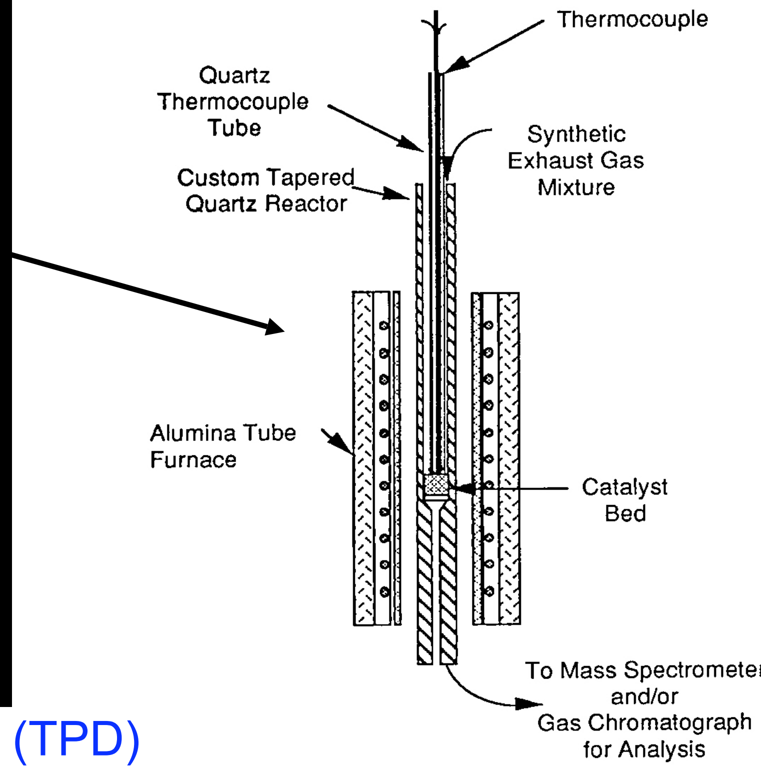
Fundamental Rate Constants - Catalysis





- 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

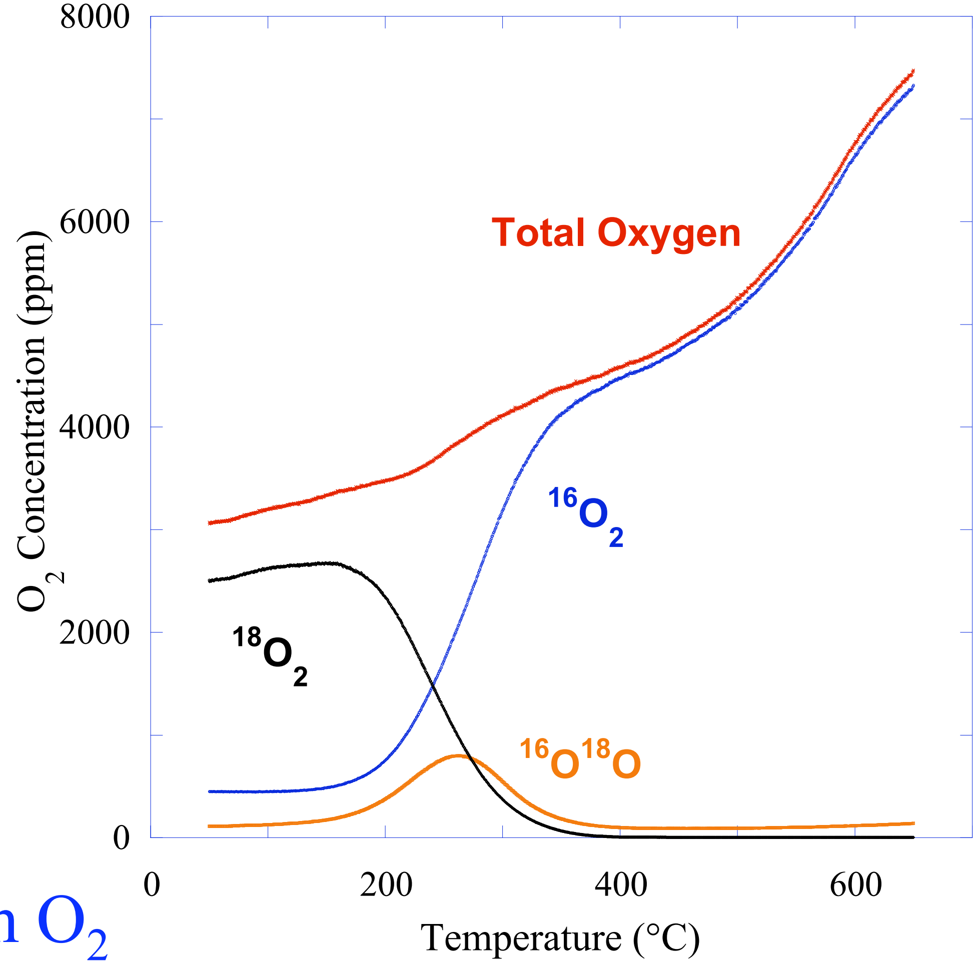
Fundamental Rate Constants - Catalysis

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 - $^{18}O_2$

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

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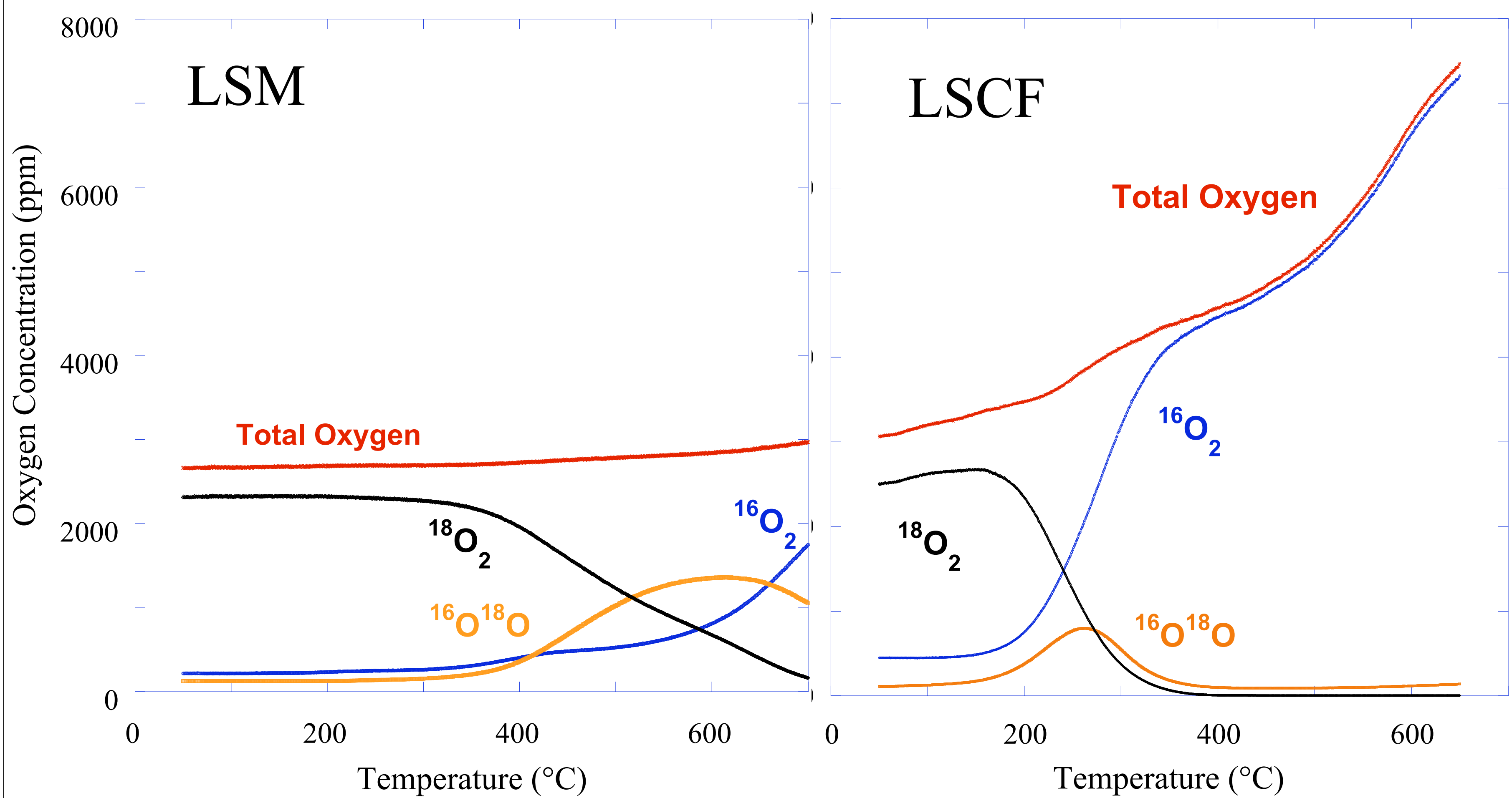
Fundamental Rate Constants - Catalysis



TPD in 3000 ppm $^{18}O_2$

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Fundamental Mechanism - Catalysis

$$\frac{1}{2}O_2 + V_o^{\circ\circ} + 2e' \leftrightarrow O_o^x$$

Step (1) Dissociative Adsorption

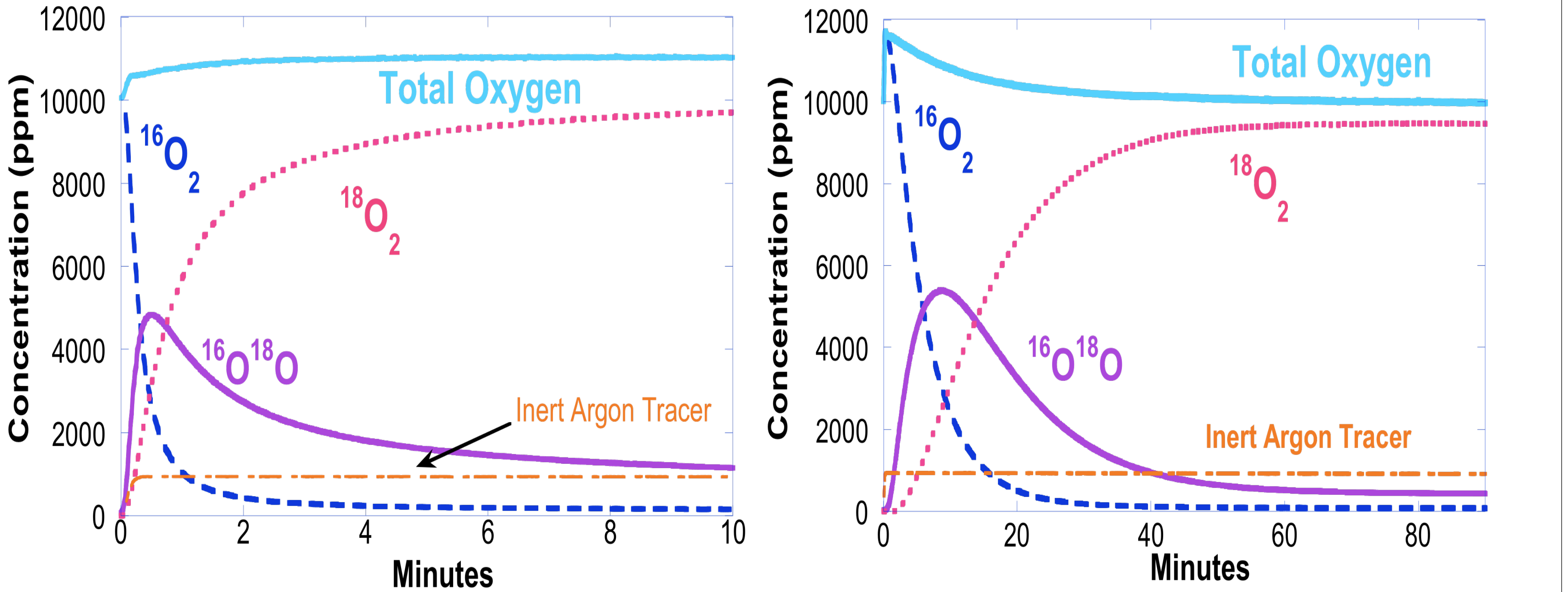
$$O_2(g) + 2S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} 2O_{ads}$$

Step (2) Incorporation

$$O_{ads} + V_o \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} O_o + S$$

Fundamental Rate Constants - Catalysis

LSM | LSCF



Isothermal (650°C) switch in 10000 ppm $^{18}O_2$

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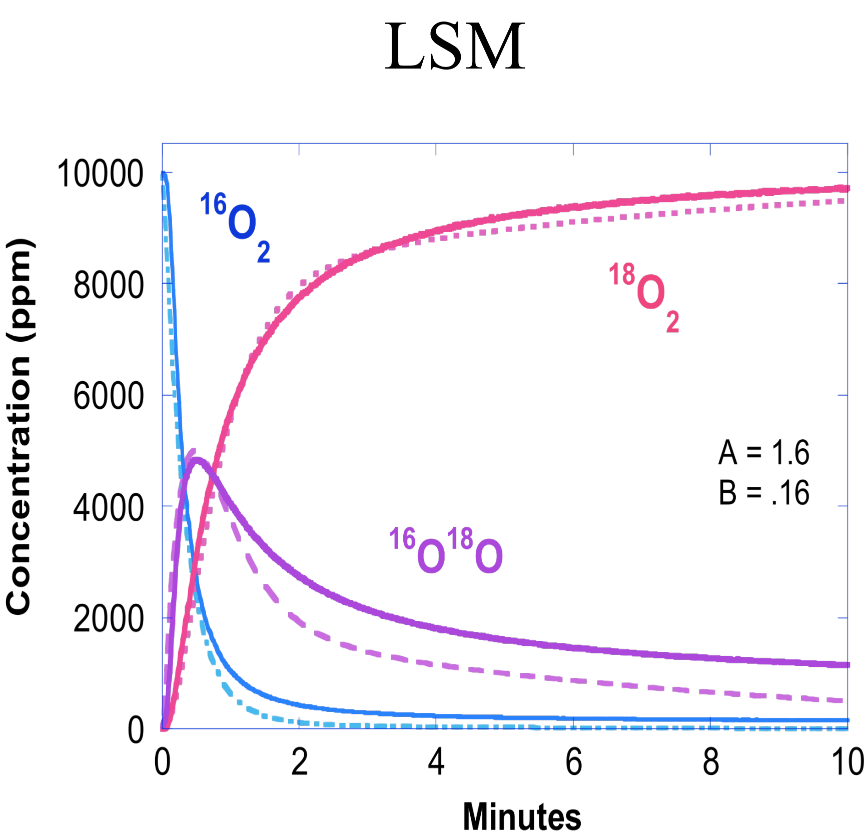
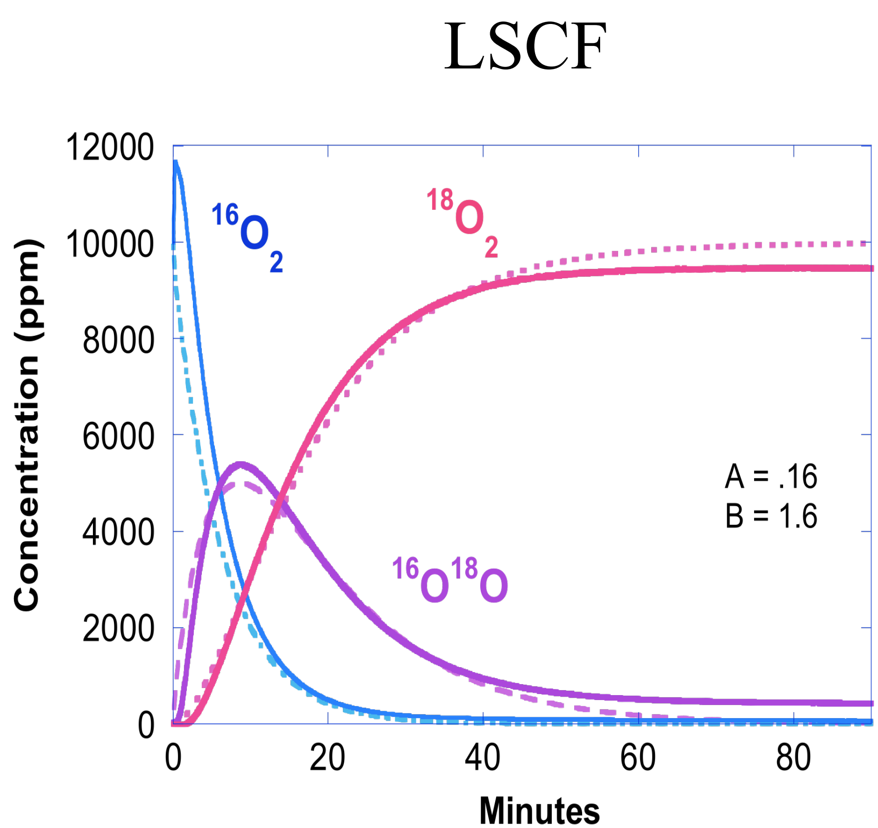
Fundamental Rate Constants - Catalysis





Isothermal (650°C) switch in 10000 ppm $^{18}O_2$

Dashed curves generated using Polymath 5

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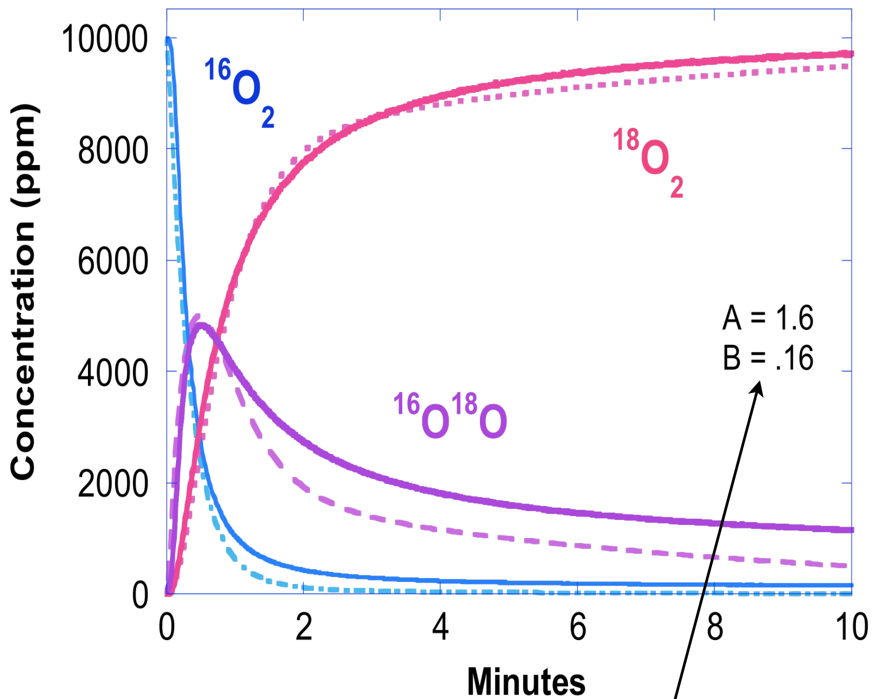
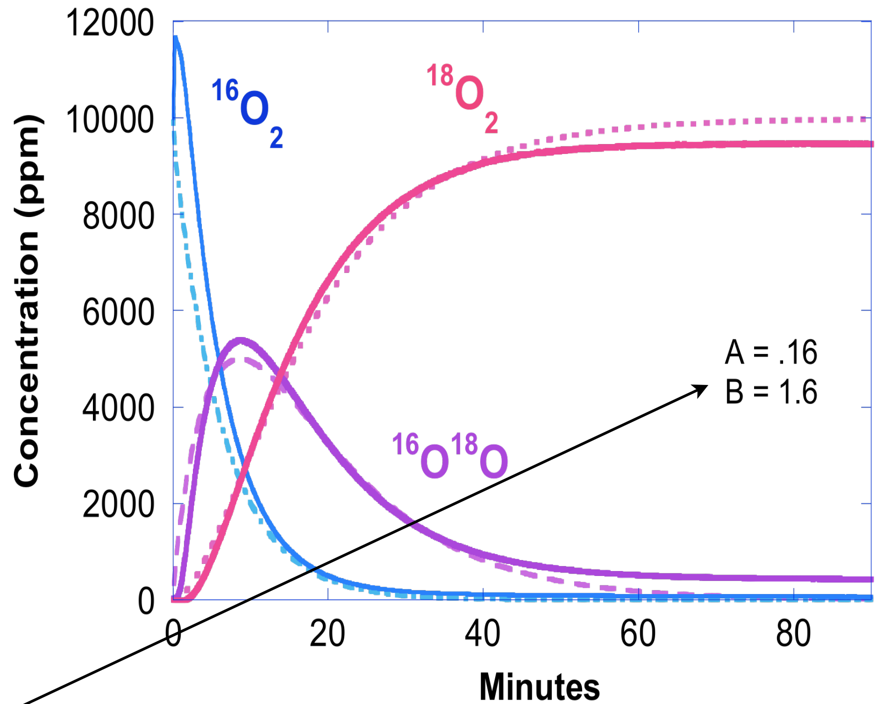
Fundamental Rate Constants - Catalysis

LSM



LSCF



$$A = \frac{k_1[S]^2\, pO_2}{[O_a]} = \frac{Rate_{Step1}^{forward}}{[O_a]}$$

$$B = k_2[V_o] = \frac{Rate_{Step2}^{forward}}{[O_a]}$$

Step 1 is faster for LSM

Step 2 is faster for LSCF

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Fundamental Mechanism - Catalysis

Quasi-Equilibrium Dissociative Adsorption

$$K_1 = \frac{[^{18}O_{ads}]^2}{P_{^{18}O_2}[S]^2}$$

$$\frac{d[^{18}O_o]}{dt} = k_2[V_o][^{18}O_{ads}] - k_{-2}[^{18}O_o][S]$$

$$\frac{d[^{18}O_o]}{dt} \overset{t\approx 0}{=} k_2[V_o][S]\sqrt{K_1 P_{^{18}O_2}}$$

Quasi-Equilibrium Incorporation Step

$$K_2 = \frac{[S][^{18}O_o]}{[^{18}O_{ads}][V_o]}$$

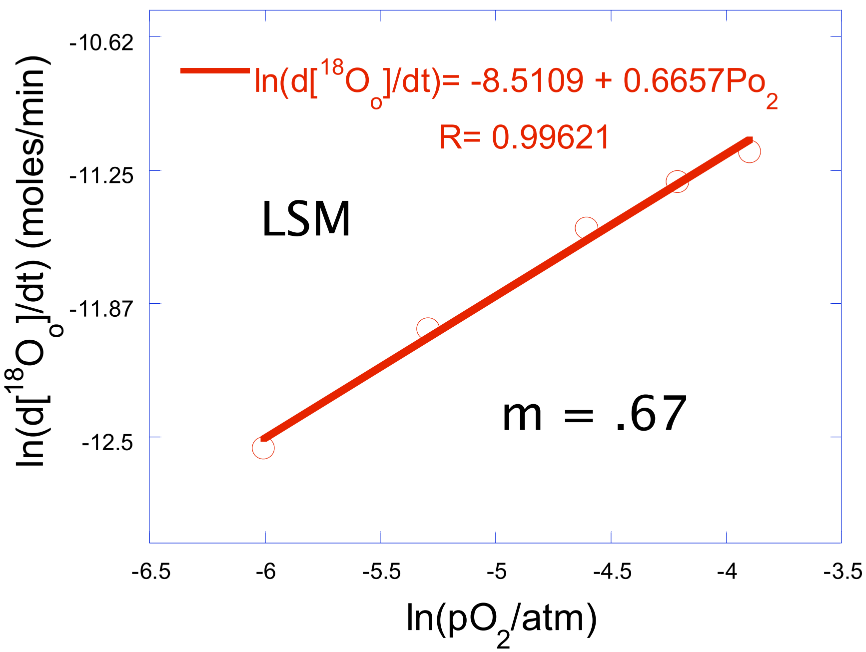
$$\frac{d[^{18}O_o]}{dt} = \frac{K_2[V_o]}{[S]}\frac{d[^{18}O_{ads}]}{dt}$$

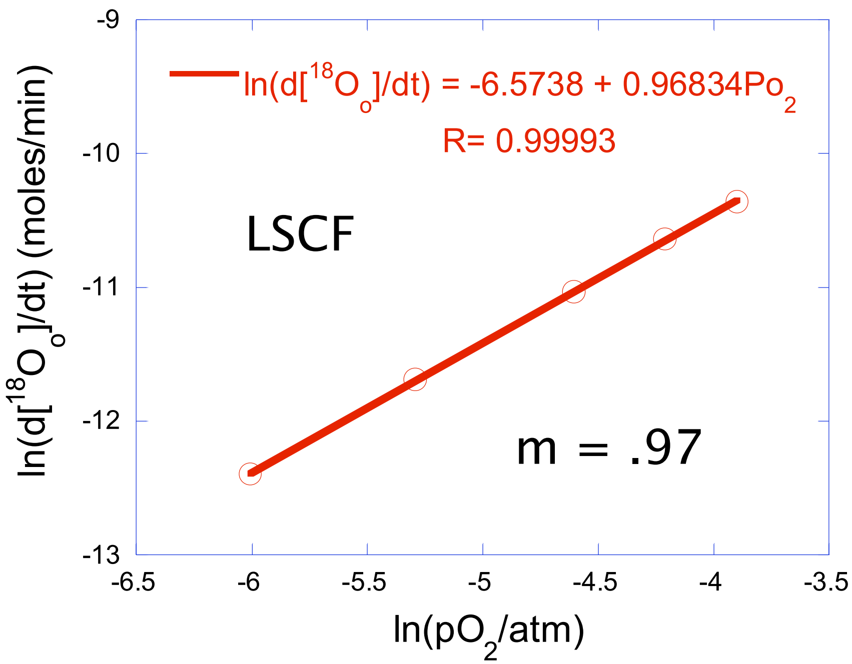
$$\frac{d[^{18}O_o]}{dt} \overset{t\approx 0}{=} 2K_2 k_1[V_o][S]P_{^{18}O_2}$$

Fundamental Mechanism - Catalysis

pO_2 Dependence 600°C

$$\ln\left(\frac{d[^{18}O_o]}{dt}\right) = \ln(k_{obs}) + m\ln(P_{^{18}O_2})$$

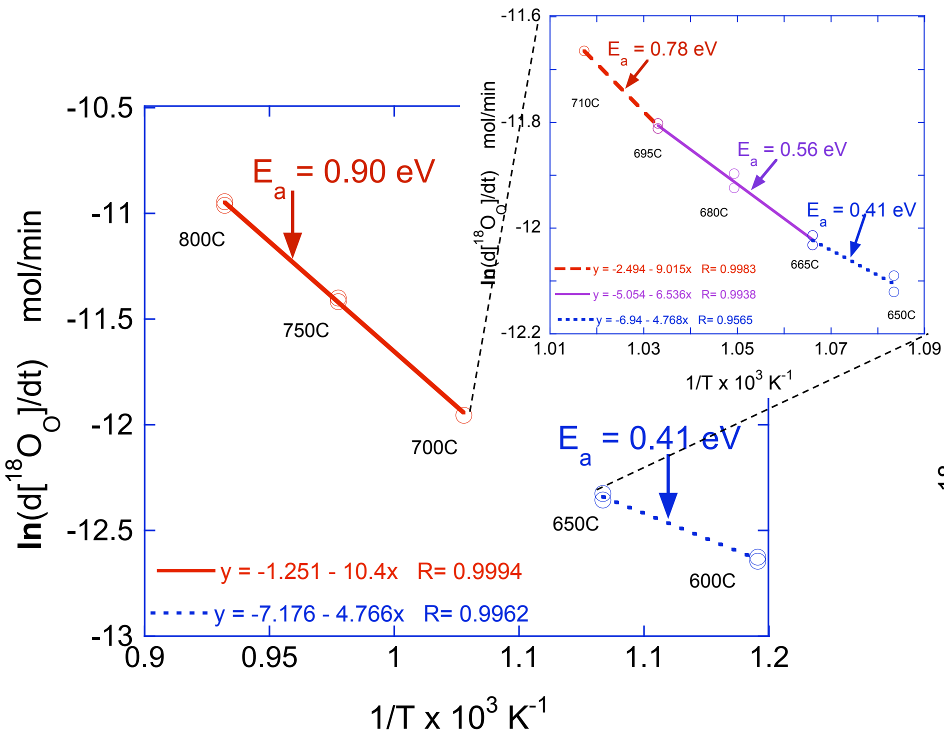




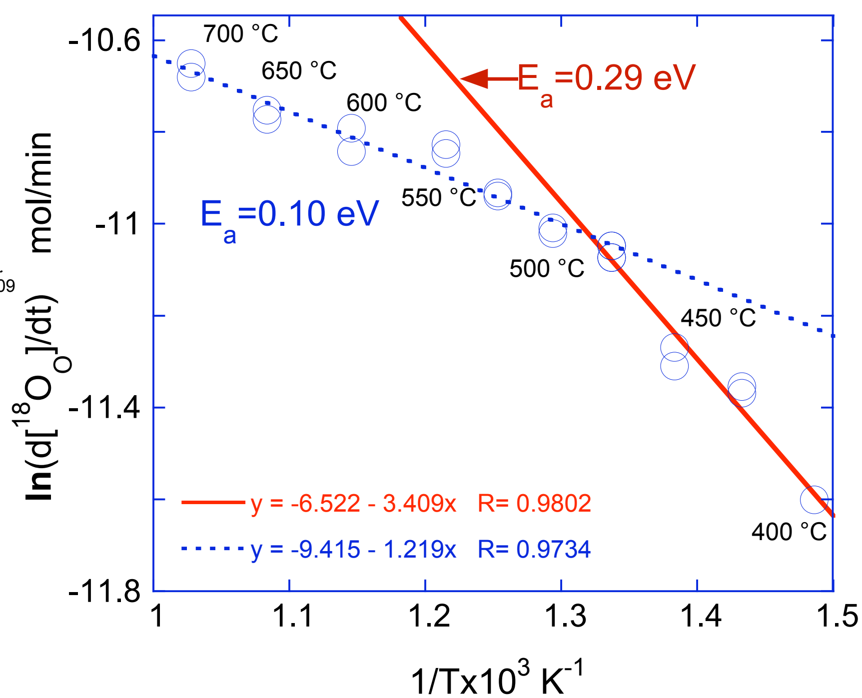
- LSCF limited by dissociative adsorption
- LSM mixed but limited primarily by oxygen incorporation step

Fundamental Mechanism - Catalysis

LSM



LSCF



Ahrrenius plots of exchange rates for LSM and LSCF.

"Investigating Oxygen Surface Exchange Kinetics of $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ Using an Isotopic Tracer," C. C. Kan, H. H. Kan, F. M. Van Assche, E. N. Armstrong and E. D. Wachsman, *J. Electrochem. Soc.*, **155**, B985-B993 (2008).

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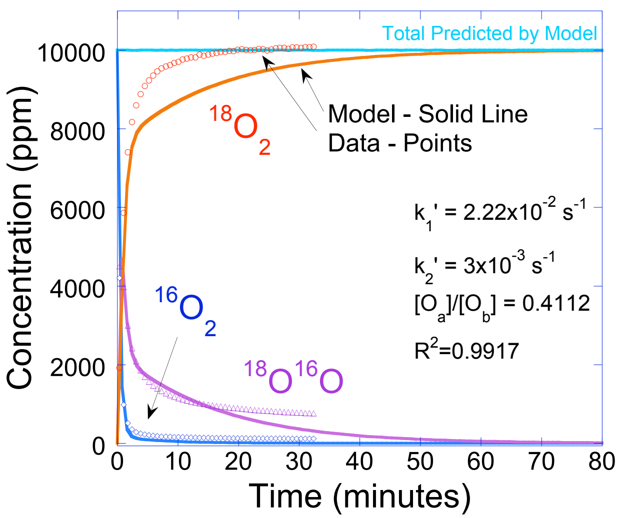
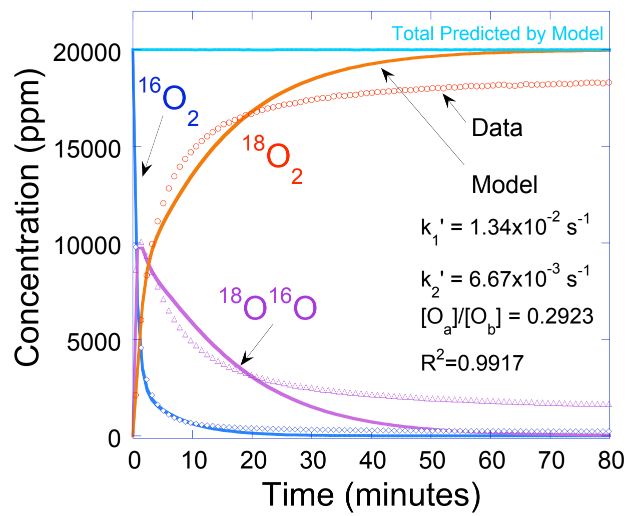
Fundamental Mechanism - Catalysis

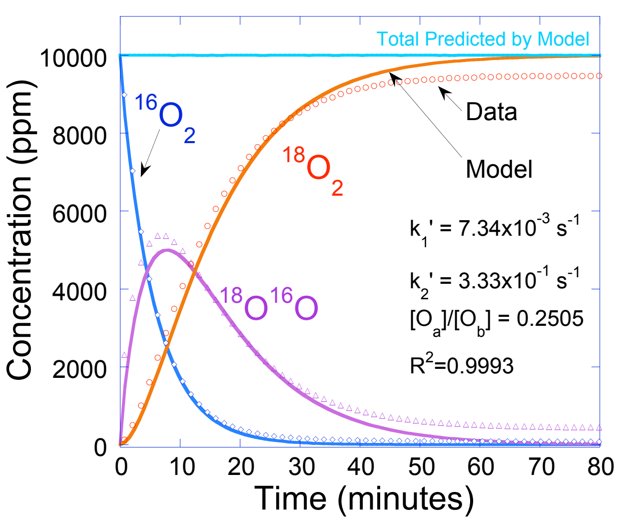
LSM Isosotpe Exchange
pO_2 = 0.01 atm T = 923 K



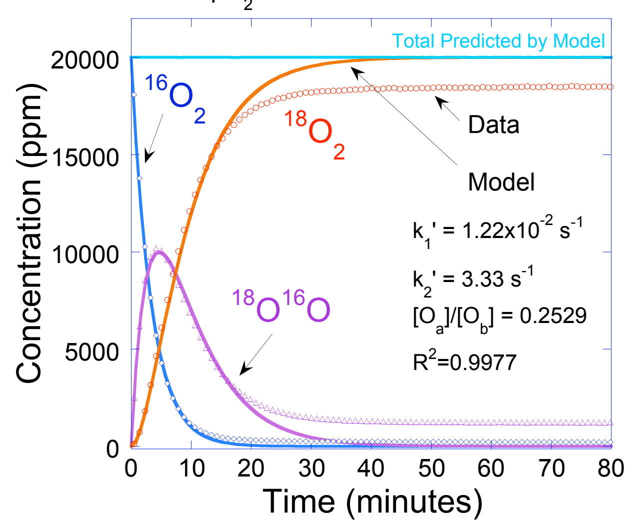
LSM Isosotpe Exchange
pO_2 = 0.02 atm T = 1073 K



LSCF Isosotpe Exchange
pO_2 = 0.01 atm T = 923 K



LSCF Isosotpe Exchange
pO_2 = 0.02 atm T = 1073 K



$$O_2(g) + 2S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} 2O_{ads}$$

$$O_{ads} + V_o \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} O_o + S$$

MATLAB iterative solution

$$k_1' = \frac{k_1 pO_2 [s]^2}{[O_{adsorbed}]}$$

$$k_2' = k_2[V_o]$$

$$[O_a]/[O_b] = \frac{[O_{adsorbed}]}{[O_{bulk}]}$$

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Fundamental Mechanism - Catalysis

TABLE 1. Rate constants and activation energies from mechanistic and apparent kinetic expermients

	LSM	LSCF
Mechanistic Kinetics		
k_1' (s^{-1}) @ 650 °C	2.22×10^{-2}	7.3×10^{-3}
@ 800 °C	1.34×10^{-2}	1.2×10^{-2}
k_2' (s^{-1}) @ 650 °C	3.0×10^{-3}	0.33
@ 800 °C	6.7×10^{-3}	3.3
$[O_{ads}]/[O_{bulk}]$ @ 650 °C	0.41	0.25
@ 800 °C	0.29	0.25
Activation energy for step 1 (Eq. 1), E_{a1} (eV)		0.29
Activation energy for step 2 (Eq. 2), E_{a2} (eV)		1.3
Apparent Kinetics		
Isotope Exchange – Overall Reaction, Apparent E_a (eV)	(< 650 °C) 0.41 (> 700 °C) 0.90	(< 500 °C) 0.29 (> 500 °C) 0.10
Conductivity Relaxation – k_{chem} (cm/s) — unaged		4×10^{-4}
@ 800 °C — aged (for 400 h)		8×10^{-5}
(400 h aged samples) Apparent E_a (eV)		1.9

$$O_2(g) + 2S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} 2O_{ads}$$

$$O_{ads} + V_o \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} O_o + S$$

$$k_1' = \frac{k_1 pO_2[s]^2}{[O_{adsorbed}]} \qquad k_2' = k_2[V_o] \qquad [O_a]/[O_b] = \frac{[O_{adsorbed}]}{[O_{bulk}]}$$

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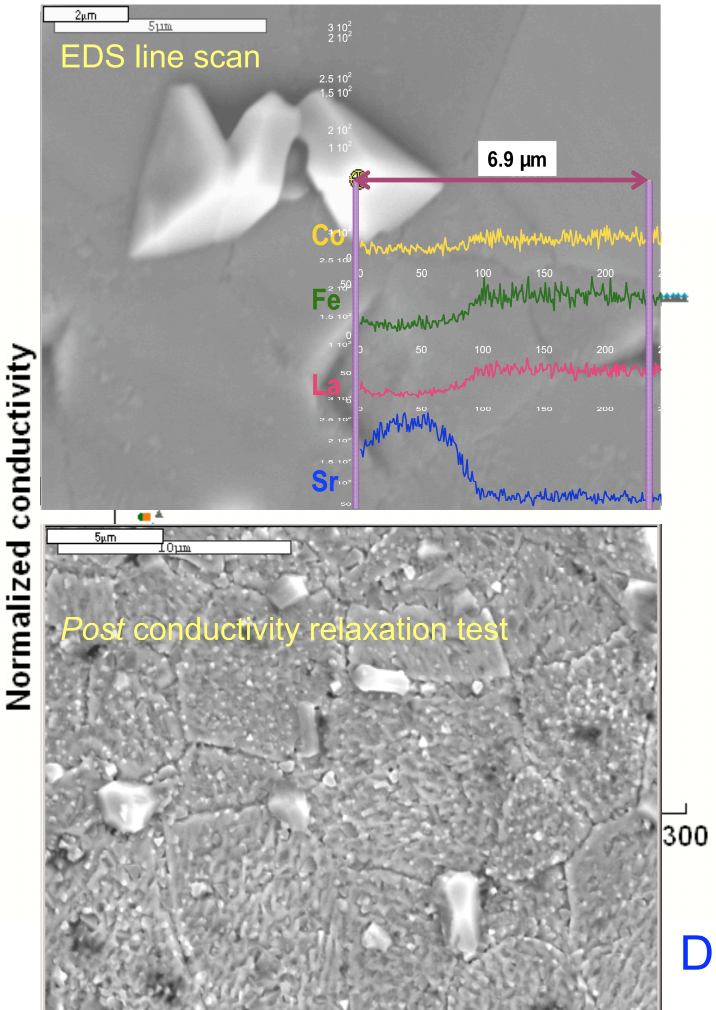
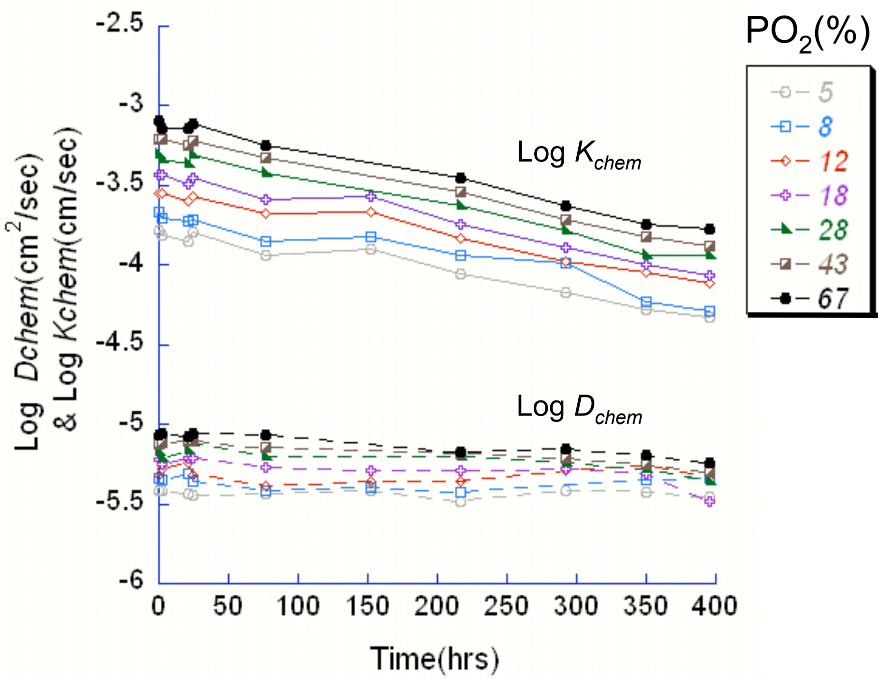
Aging Effect on D_{chem} & k_{chem}



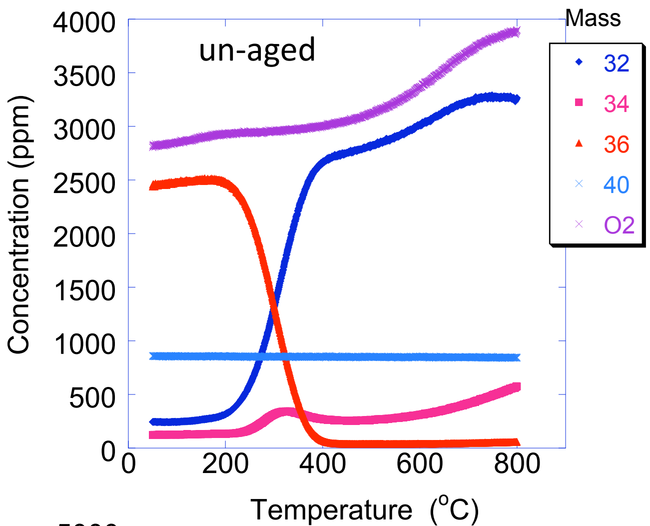
Conductivity Relaxation of LSCF

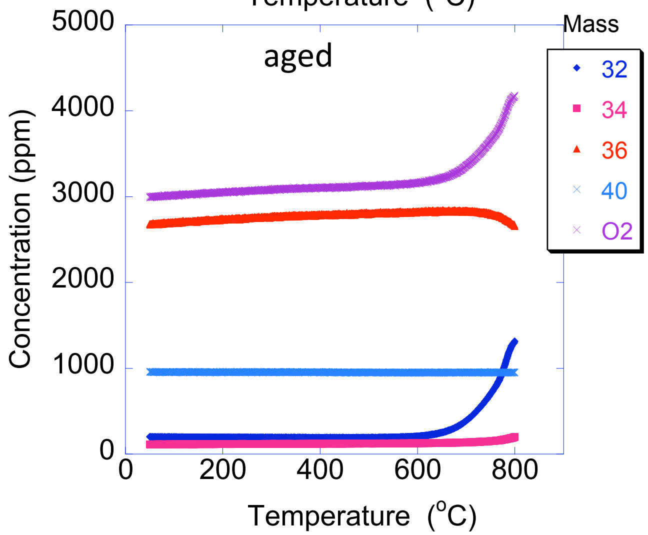


Degradation due to reduction in surface exchange caused by Sr segregation

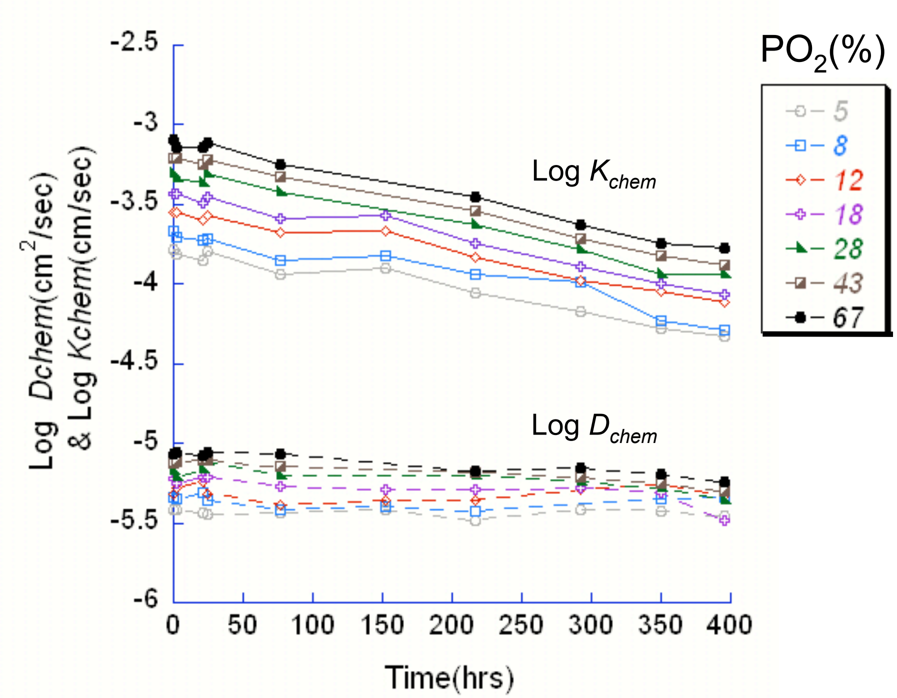
Aging Effect on D_{chem} & k_{chem}

TPX of LSCF



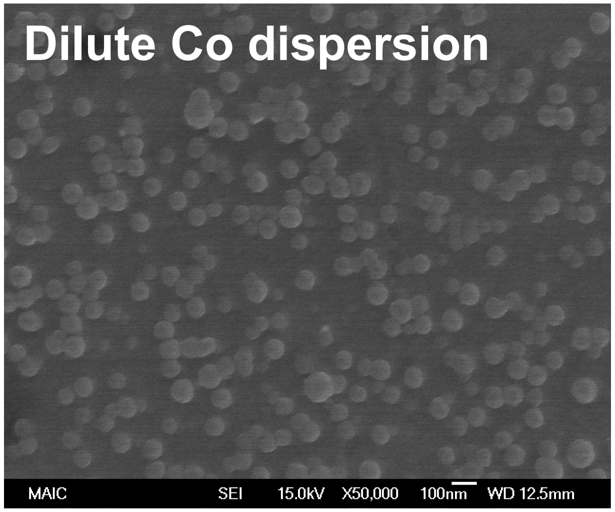


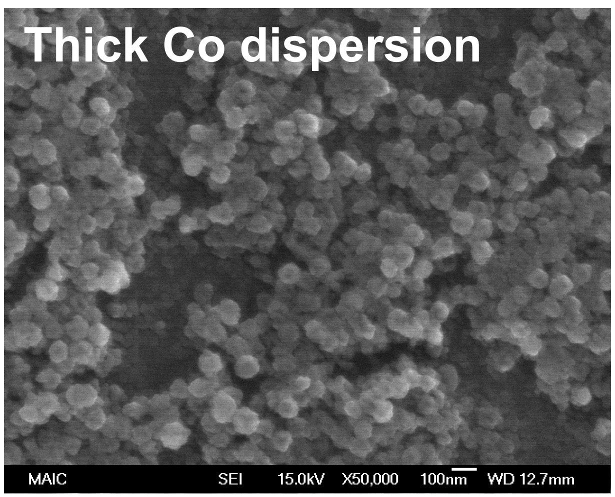
Conductivity Relaxation of LSCF



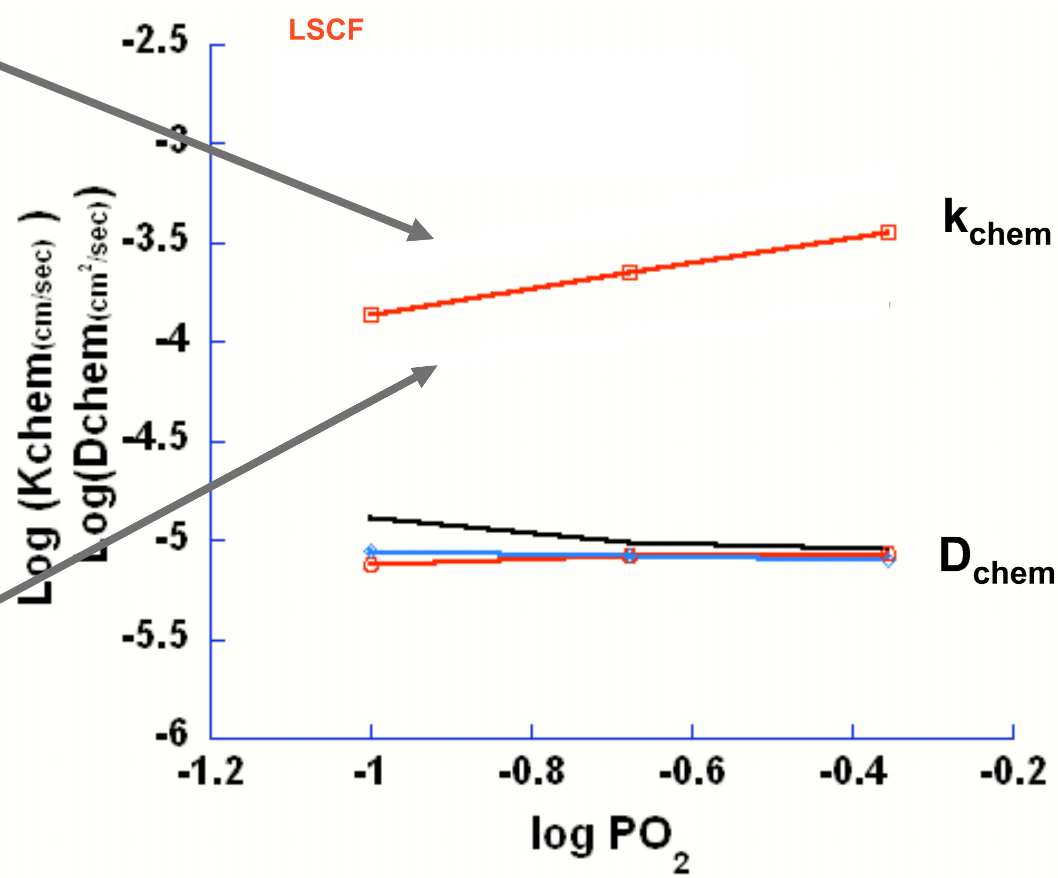
Heterogenous catalysis confirms degradation due to reduction in surface exchange and provides approach to understand mechanism

Surface Modification - Effect of Co dispersion on D_{chem} & k_{chem}

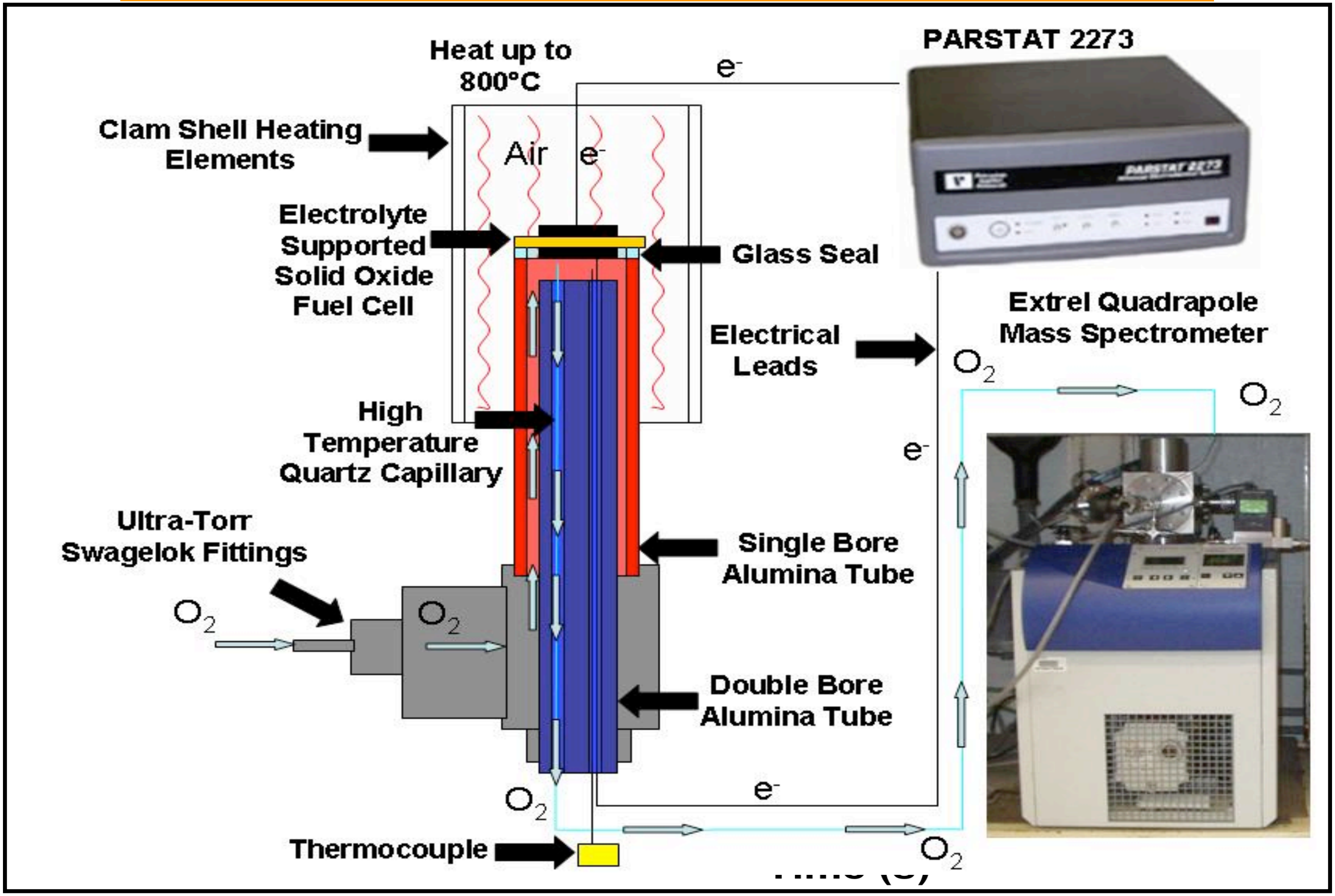




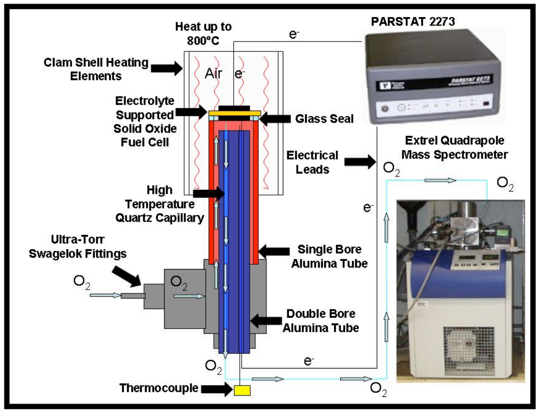
Conductivity Relaxation of LSCF



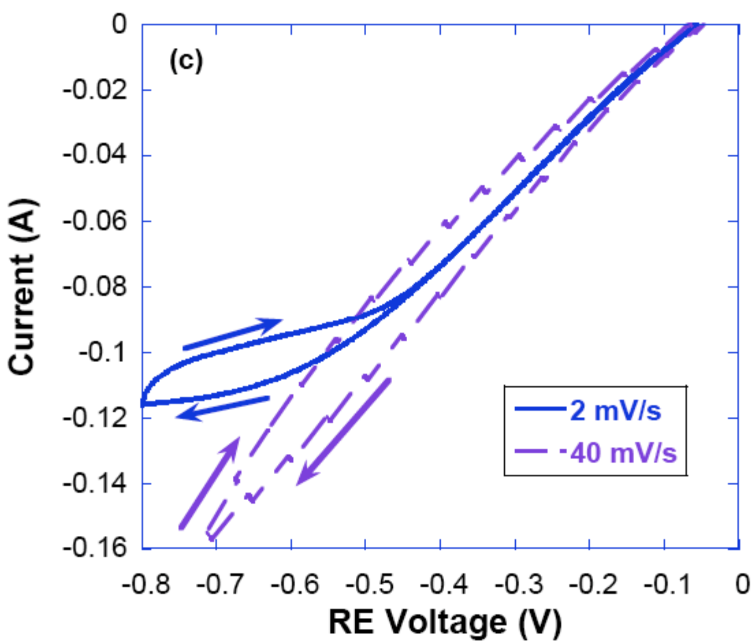
In Situ Integrated Electrocatalysis



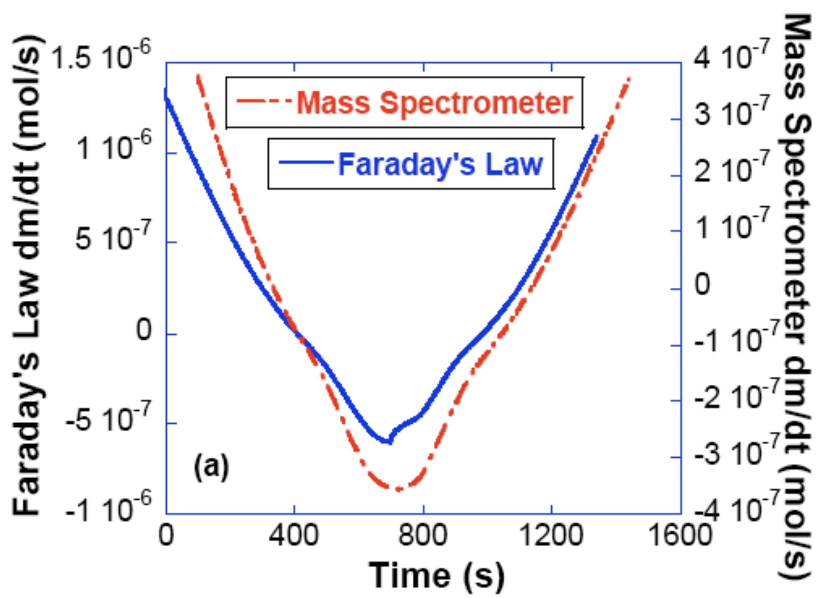
In Situ Integrated Electrocatalysis



- **LSCF on GDC symmetric cell tested at 700°C using Cyclic Voltamograms with simultaneous gas phase analysis**



Cyclic voltamograms for LSCF from 0 to -800 mV at two different scan rates in 1% O_2.



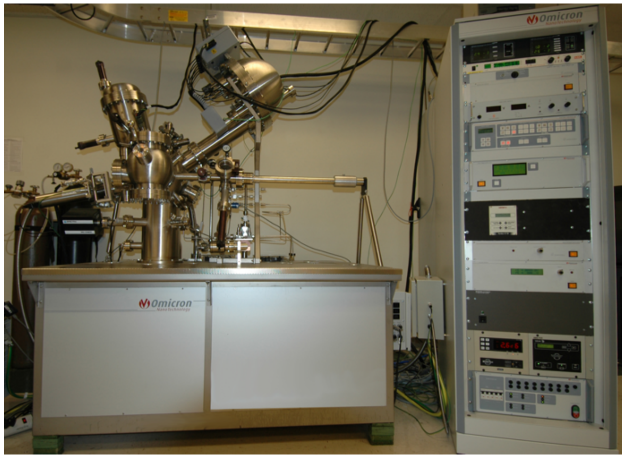
Change in oxygen concentration through LSCF over time from Faraday's law and from mass spectra at a scan rate of 2 mV/s in 1% O_2

Summary

- Cathode polarization critically depends on microstructure:
  - Solid state (ionic/electronic conductivity) transport - *Ohmic*
  - Gas transport - *Concentration*
  - TPB/Surface area - *Activation*
- We have developed direct *quantitative* relationship between cathode microstructure and polarization
- ^{18}O- exchange demonstrates LSCF is more active than LSM
- Determined reaction order/mechanisms from P_{O_2} dependence:
  - LSM is limited by oxygen incorporation step
  - LSCF is limited by dissociative adsorption step
- Determined fundamental rate constants for LSCF and LSM
- LSCF degradation due to reduction in oxygen surface exchange
- Developing *in situ* integrated electroanalytical-catalysis technique
- Integrating reaction kinetics and microstructure will allow rational cathode design

Future Work?

- Obtain k values from additional materials (Co/Fe/Sr/La dispersed on surface) and conditions (temperature, pO_2), and determine the effect of surface segregation on catalytic activity by isotope exchange.
- Evaluate methods to determine oxygen surface coverage and expand rate data to higher 21% pO_2 (Langmuir Isotherm).
- Determine effect of Co/Fe dispersions on surface reaction kinetics by comparing electrical conductivity relaxation with isotope exchange results.
- Elucidate the mechanistic steps for oxygen reduction by *in situ* tests in the integrated electrochemical-catalysis system using isotopically labeled oxygen ($^{18}O_2$) in conjunction with (i) EIS, (ii) isothermal-switching experiments with applied current/potential, and (iii) potential programmed reactions.



- Combine Kelvin Probe and XPS to measure *Work Function* and oxidation state as a function of composition, pO_2 and temperature to determine electric effects on charge transfer reaction.
- Integrate kinetic results into impedance/ microstructure results to deconvolute contributions to cathode polarization.

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