Mechanistic Enhancement of SOFC Cathode Durability

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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)

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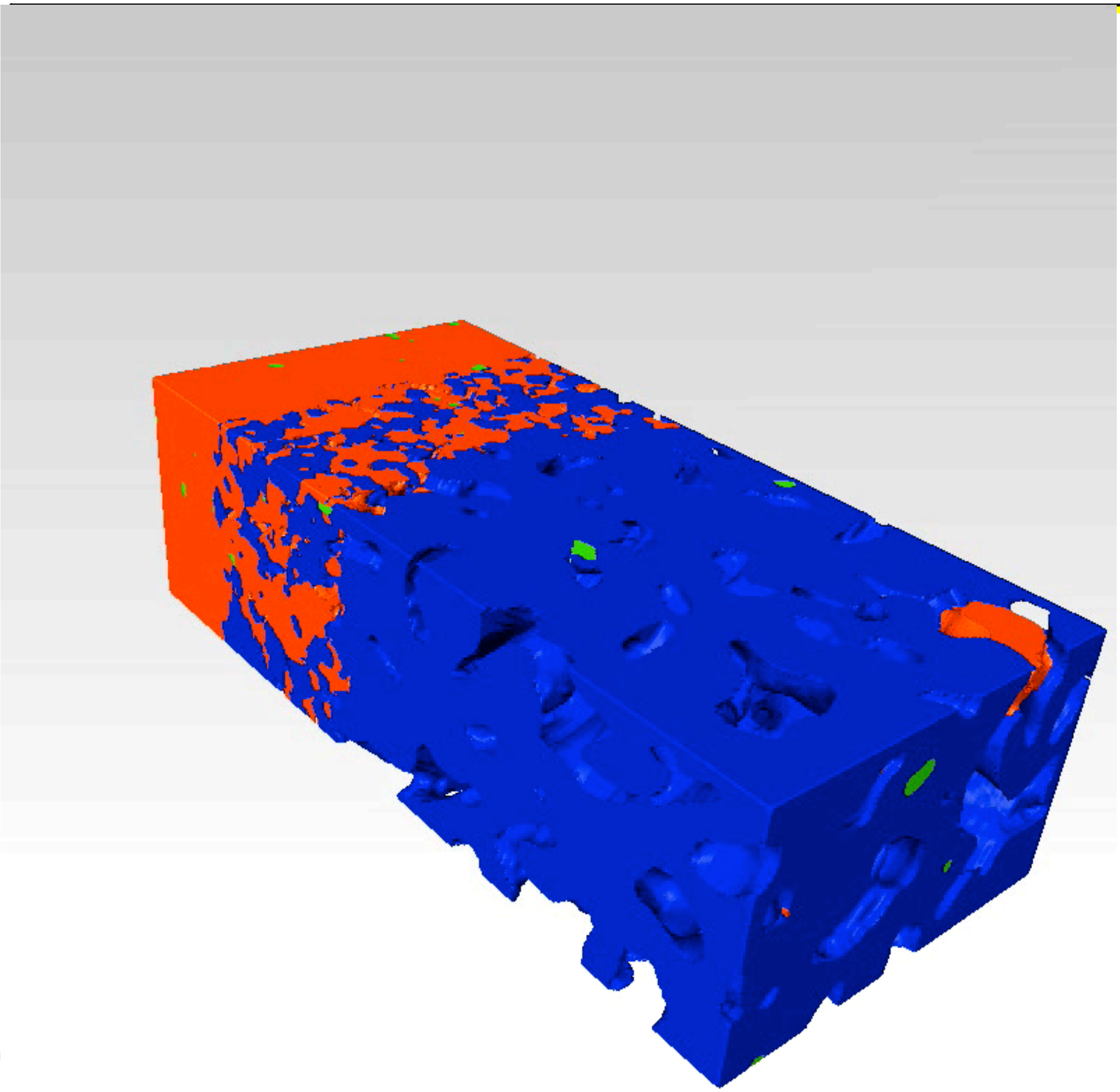
Based on Cathode Workshop January 2006, and presented at SECA Workshop, September 2006

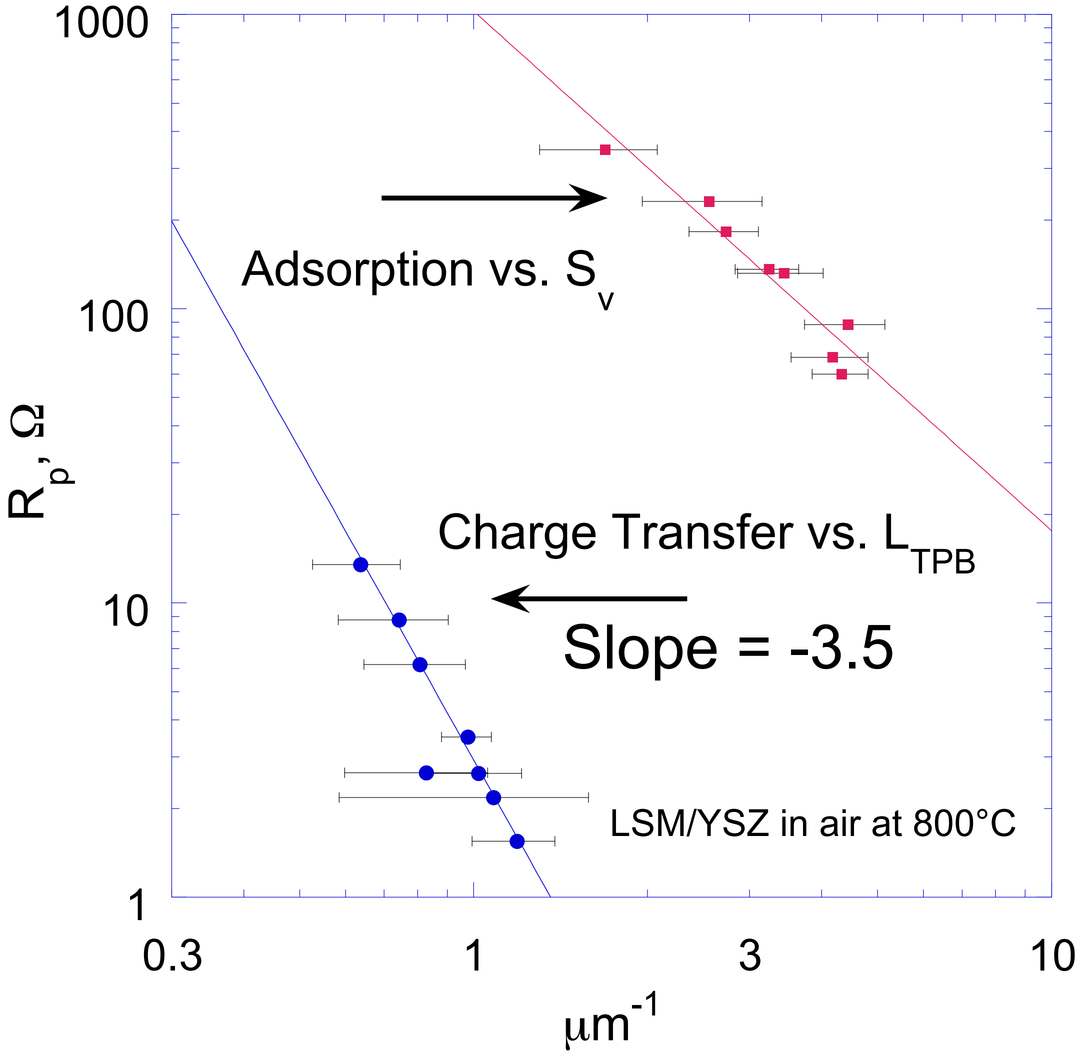
Quantify Microstructural Effects - FIB/SEM



Pioneered use of FIB/SEM to quantify cathode microstructures and developed phase contrast for composite cathodes

Siemens Cathode Sample

Microstructure - Performance Relationship



First direct quantified relationship between cathode microstructure and performance

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:

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

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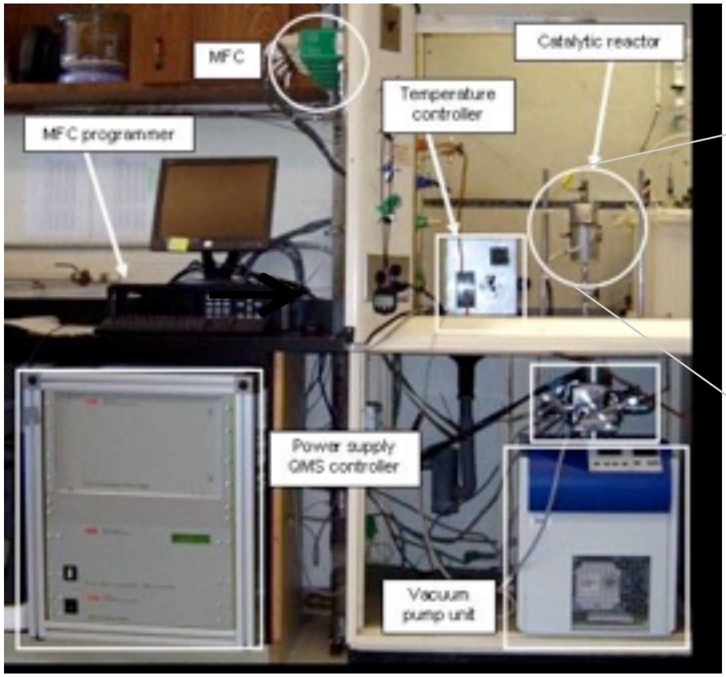
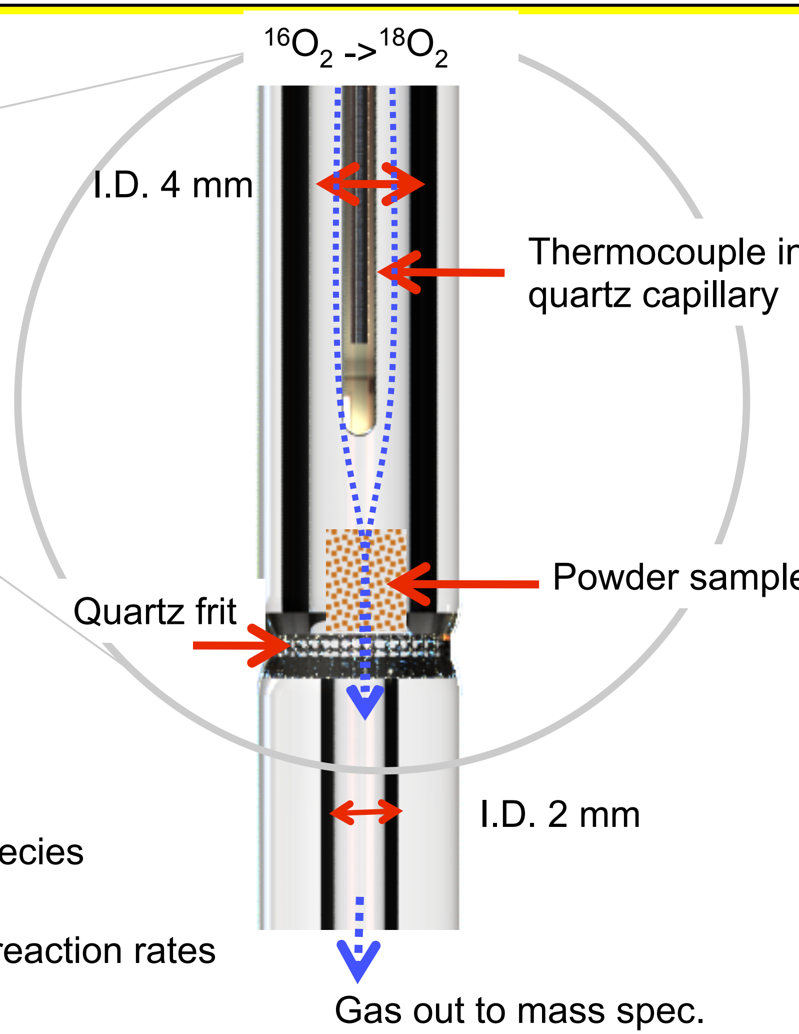
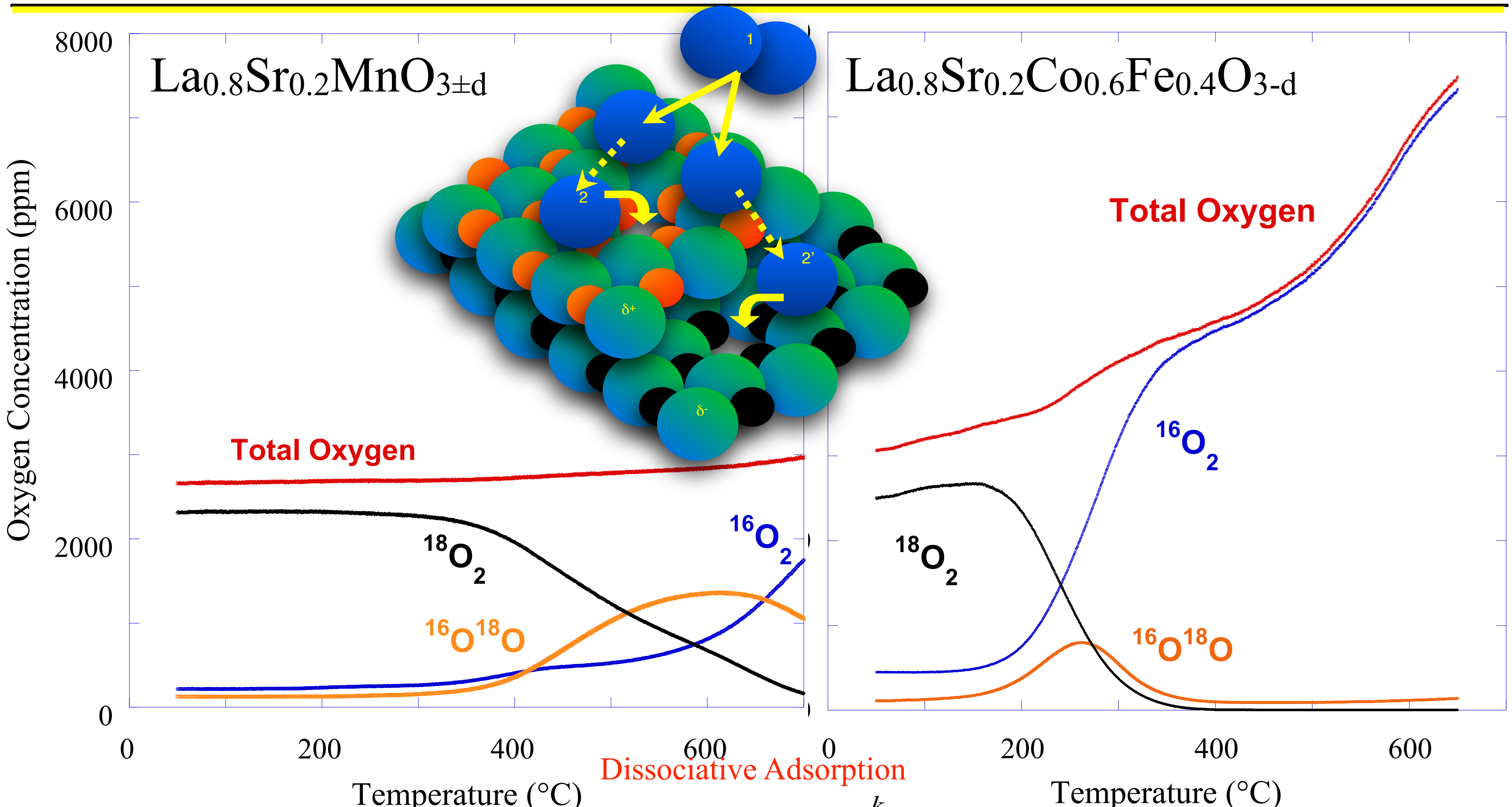
Fundamental Rate Constants - Catalysis





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

Fundamental Cathode Kinetic Mechanisms



Dissociative Adsorption

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

Incorporation

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

Oxygen isotope exchange - TPD in 3000 ppm $^{18}O_2$

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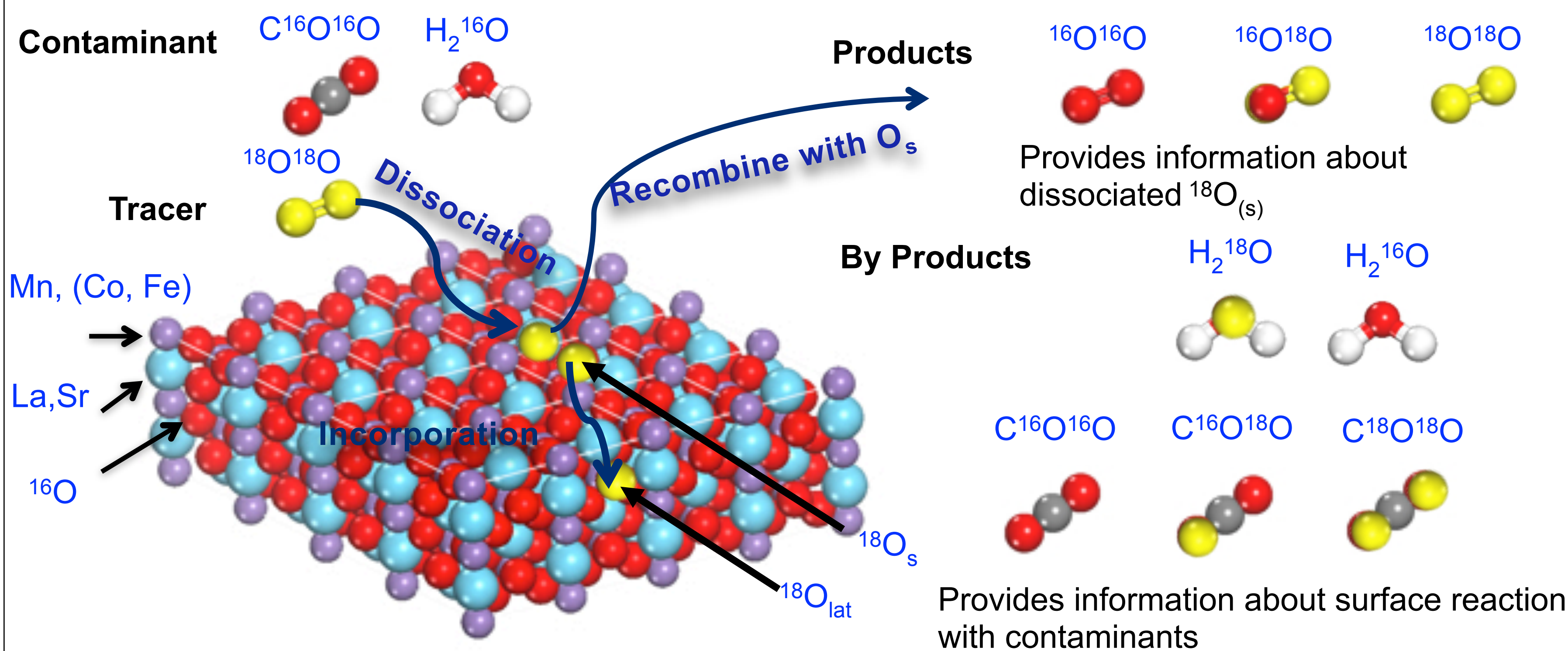
ORR Reaction Mechanisms in Presence of H_2O and CO_2



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

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

Oxygen reduction reaction:

1. **dissociative absorption**
2. **incorporation**

Research Plan

- Determine effects of H_2O, CO_2, and Cr vapor on ORR mechanism
  - Determine surface reaction mechanisms and rates with ^{18}O- exchange in H_2O, CO_2, and Cr vapor
  - Determine operating conditions (Temp. & Conc.) where H_2O, CO_2, and Cr vapor have both major and minor effects on LSM and LSCF cathode performance
- Operate in conditions (Temp. & Conc.) where H_2O, CO_2, and Cr vapor have major effects on LSM and LSCF cathode performance:
  - Quantify microstructural changes with FIB/SEM
  - Relate microstructural and ORR degradation to cell polarization
  - Test using integrated *in situ* electrocatalysis
- Develop predictive mechanistic models for cathode degradation and determine operating conditions for maximum durability

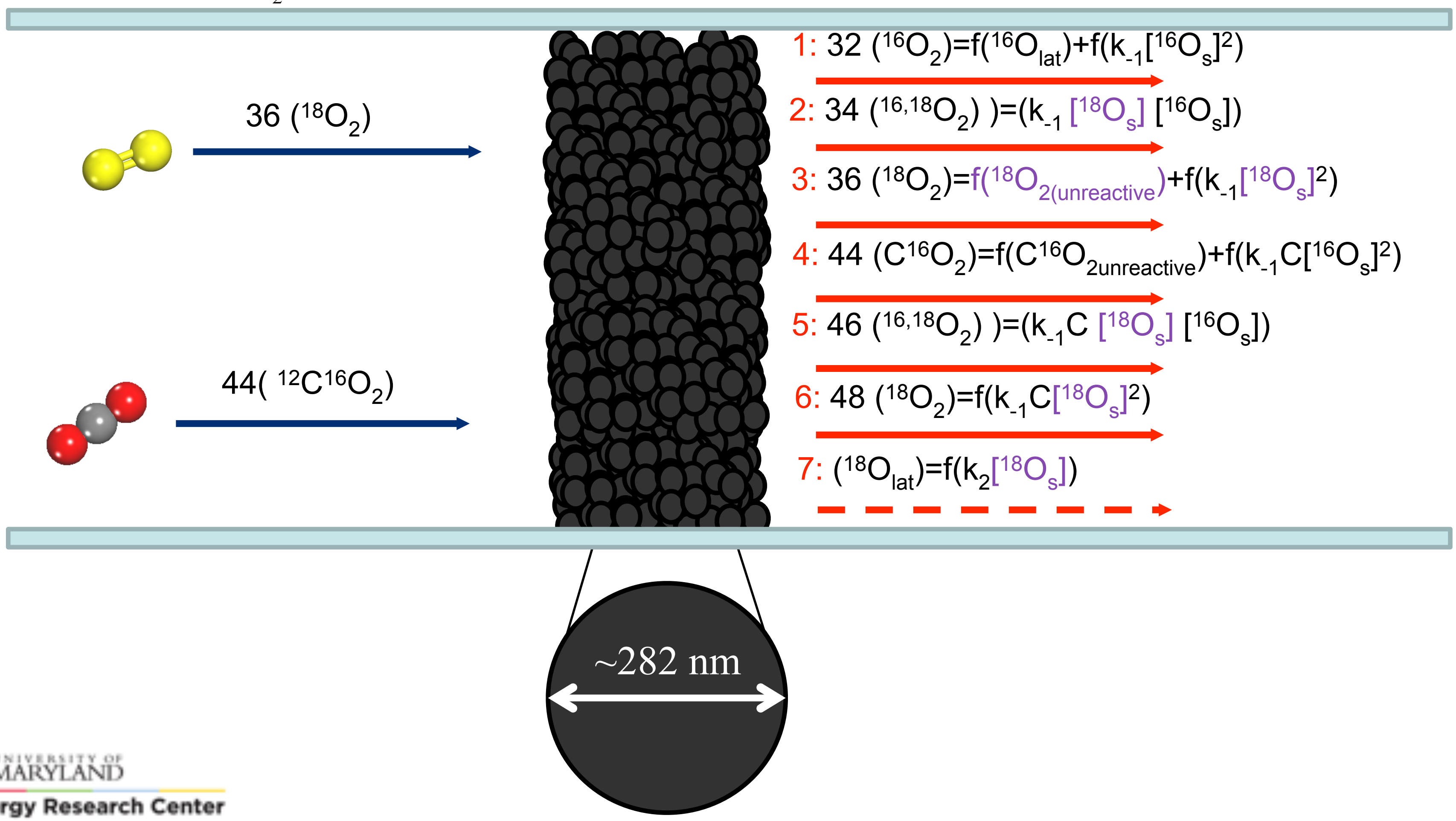
^{18}O-Exchange in CO_2 to Determine Effect on ORR Mechanism

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

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

Oxygen reduction reaction:

1. **dissociative absorption**
2. **2. incorporation**



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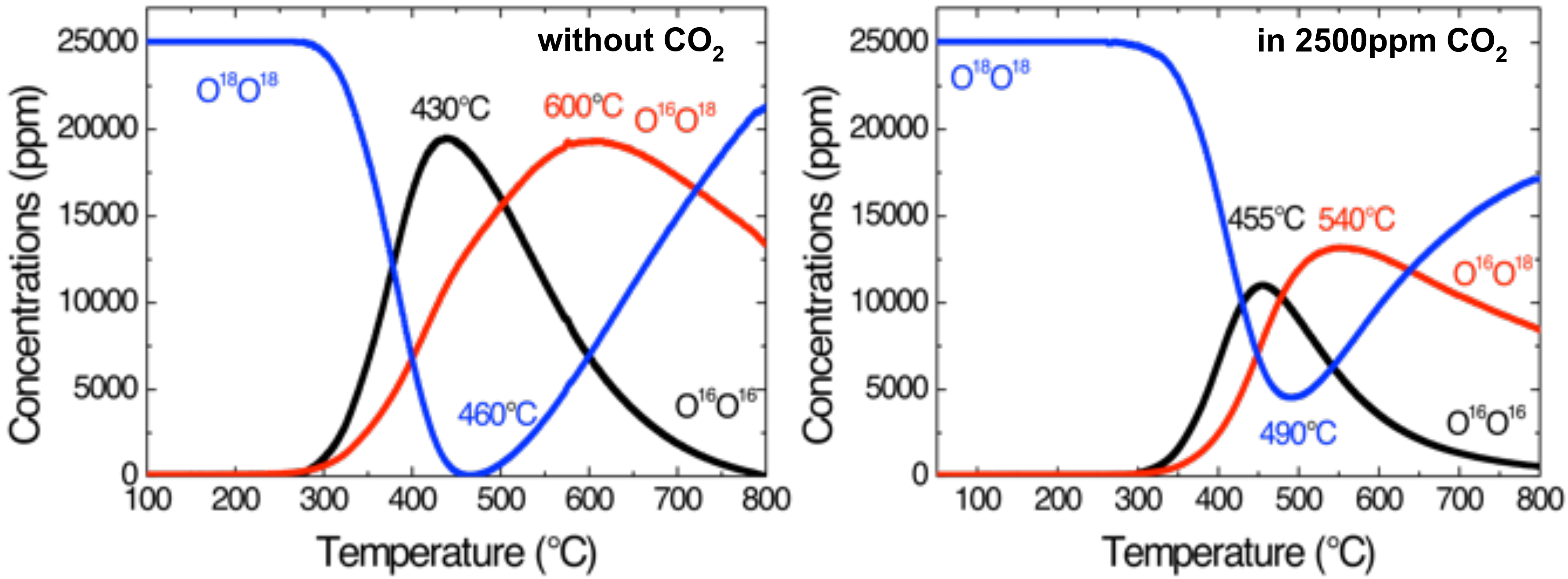
Effect of CO_2 on LSCF Temp. Programed ^{18}O-Exchange

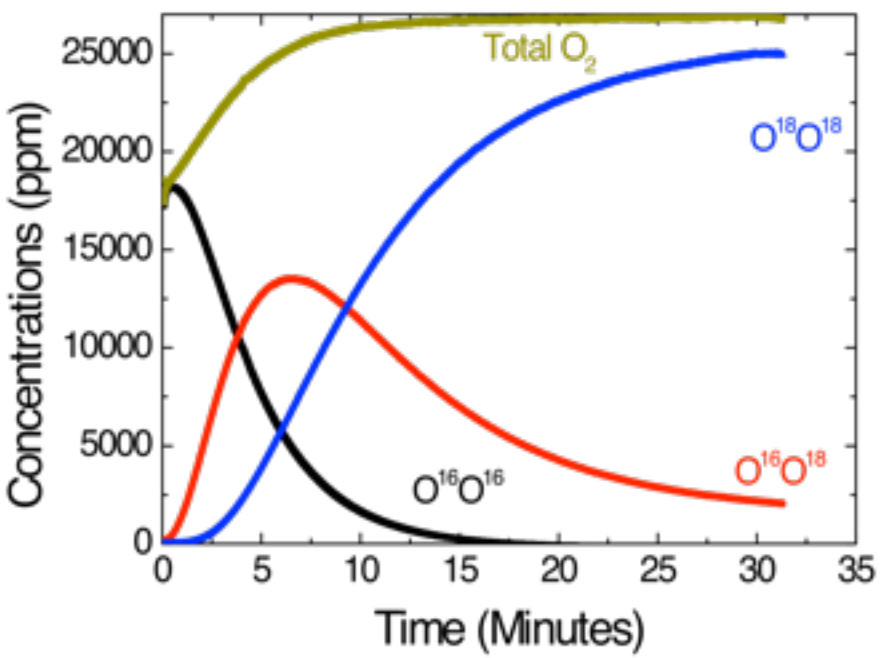


Presence of CO_2:

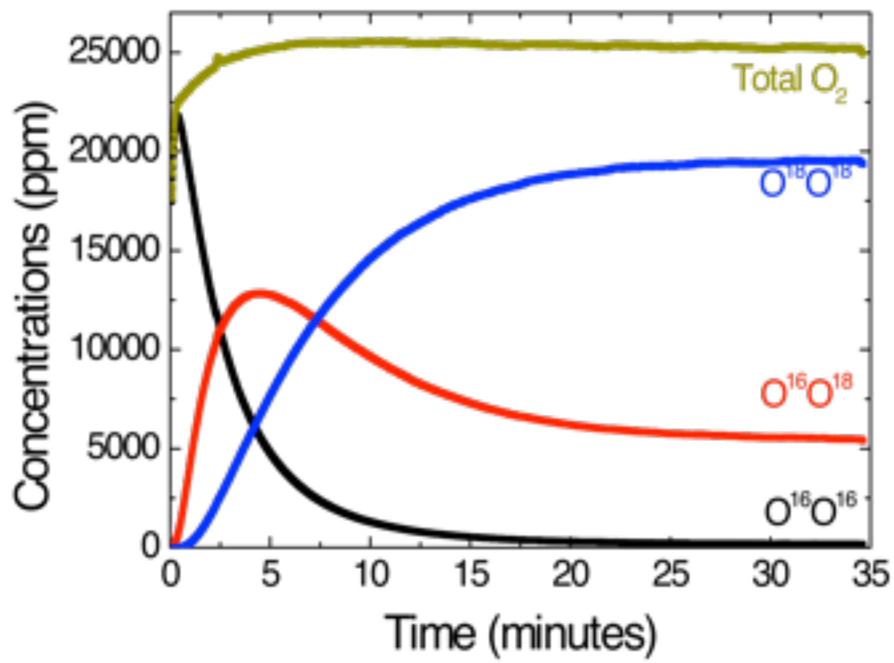
- Shifts O_2 peak temperatures
- Reduces O_2 exchange with LSCF lattice
- Indicating that CO_2 participates in surface exchange

Effect of CO_2 on Isothermal Isotope Exchange of LSCF

Oxygen exchange without CO_2 at 800°C

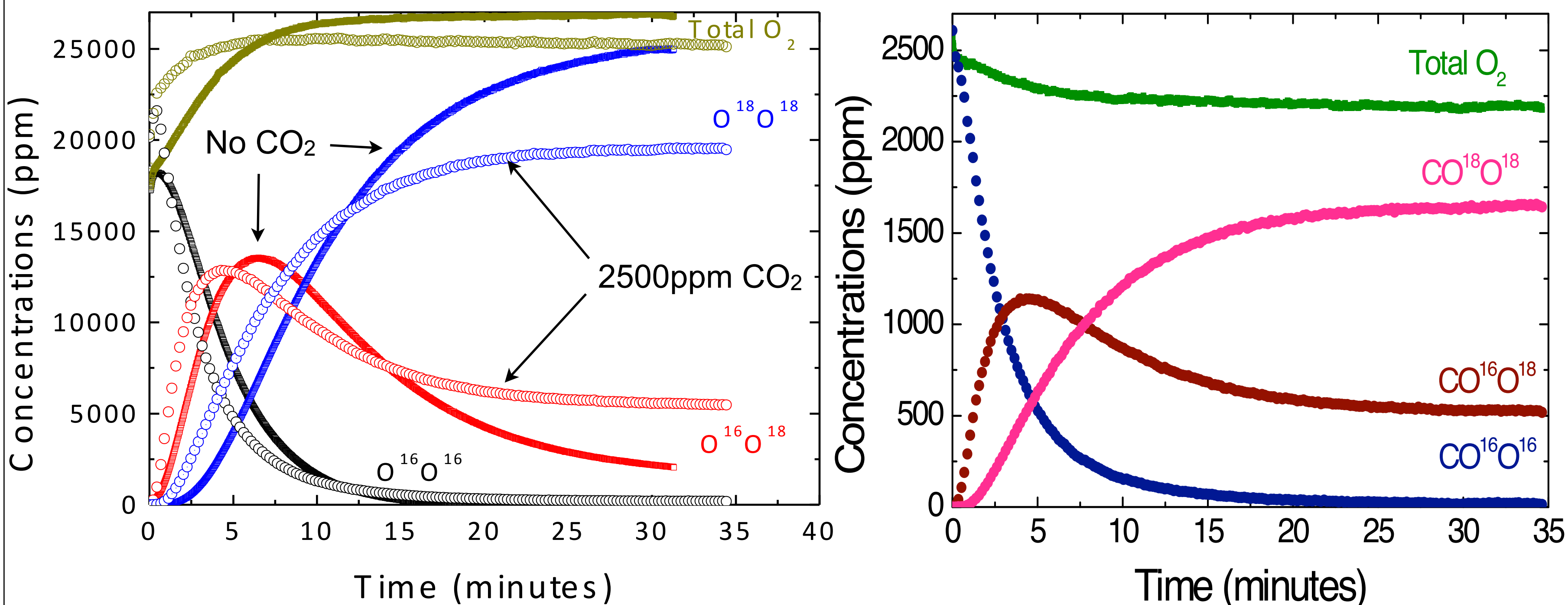


Oxygen exchange in 2,500ppm CO_2 at 800°C



Effect of CO_2 on Isothermal Isotope Exchange of LSCF

O_2 exchange at 800°C



Presence of CO_2:

- Modifies O_2 exchange with LSCF surface
- Surface-O is exchanging with CO_2
- All of the CO_2 dissociates on LSCF surface

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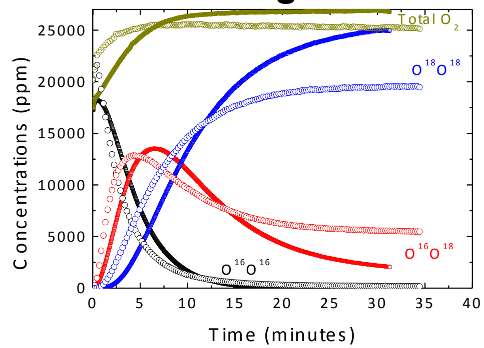
Effect of CO_2 on IIE of LSCF at Multiple Temperatures

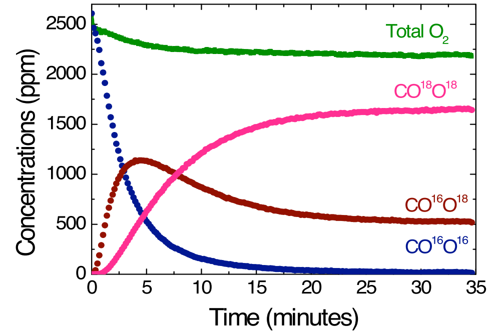
Closed symbol: no CO_2
Open symbol: in 2,500ppm CO_2

- **Decrease in 36 signal indicates CO_2 participation**
- **The O_2 in CO_2 exchange profile (left, open symbol) has a similar shape to the CO_2 exchange profile (right)**
- **CO_2 exchange has lower temperature dependance**

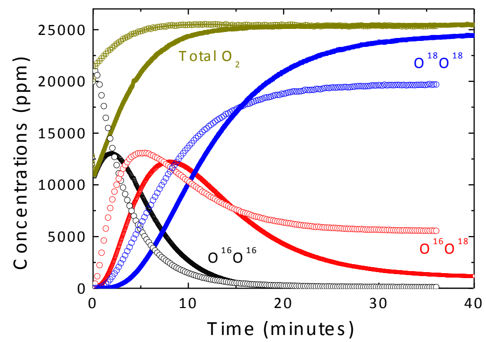
O_2 exchange at 800°C



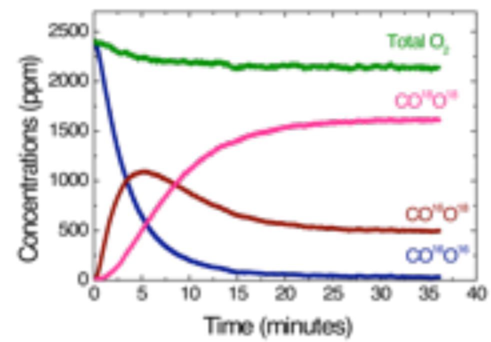
CO_2 exchange at 800°C



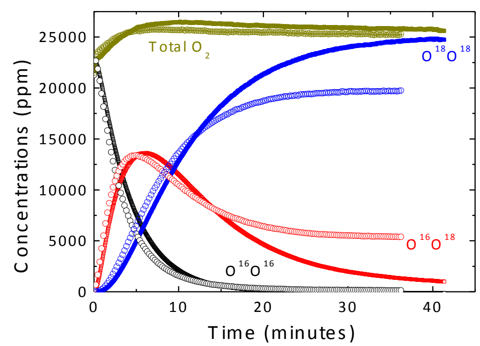
at 700°C



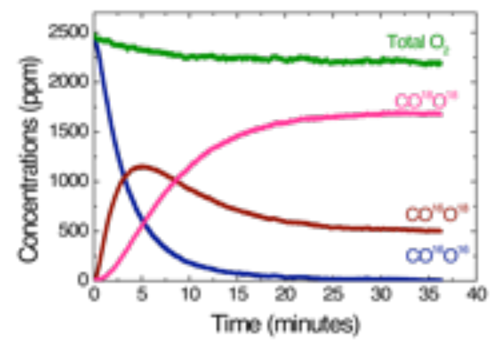
at 700°C



at 600°C



at 600°C



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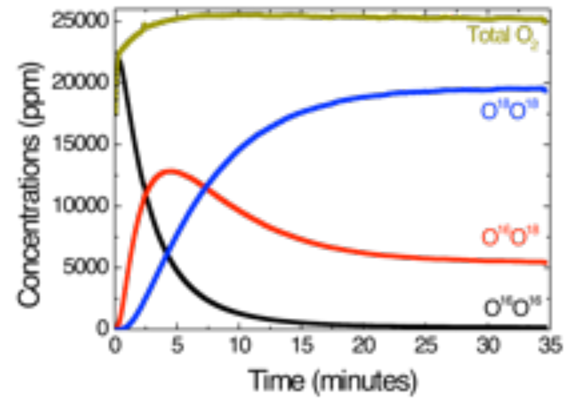
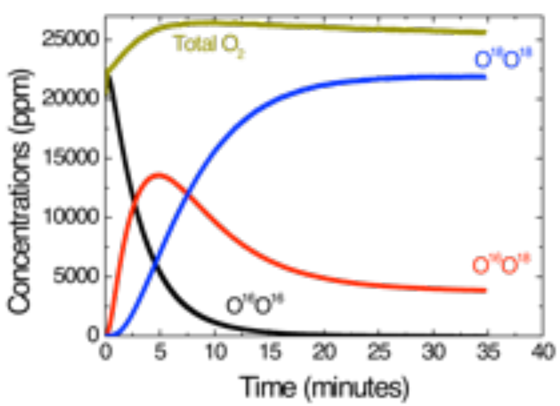
CO_2 Concentration Dependence of IIE of LSCF

- **As CO_2 concentration increases there are changes in O_2 species concentrations (32, 34, 36)**
  - ^{18}O-^{18}O : final concentration decreases
  - ^{16}O-^{18}O : final concentration increases

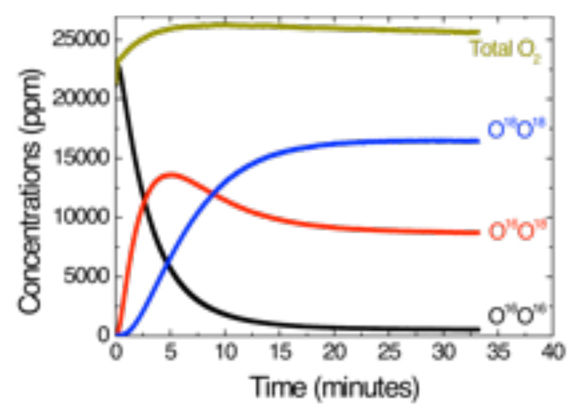
Oxygen exchange in 2500ppm CO_2 at 800°C



Oxygen exchange in 1250ppm CO_2 at 800°C

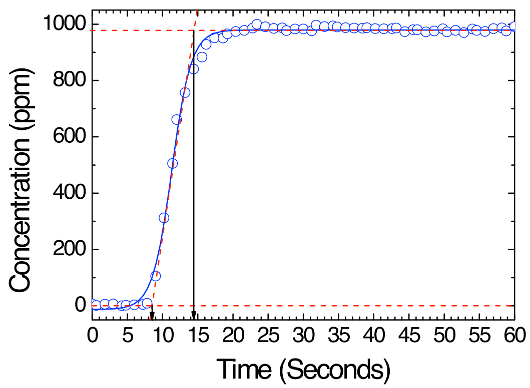


Oxygen exchange in 5000ppm CO_2 at 800°C

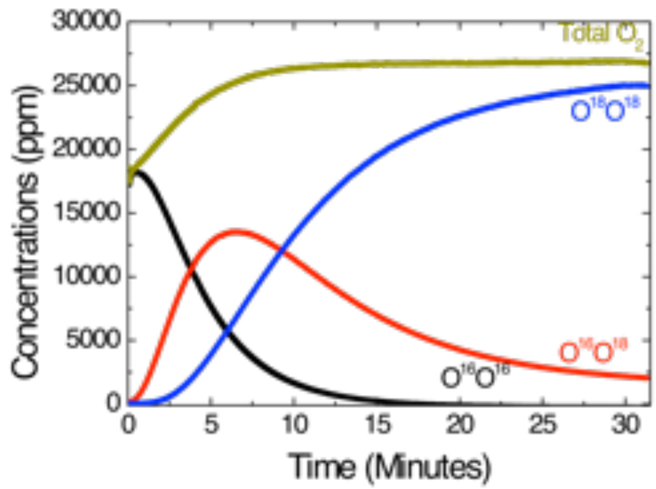


Extracting the Surface Exchange Coefficient from IIE

Switch time (argon tracer)



IIE of LSCF 800°C

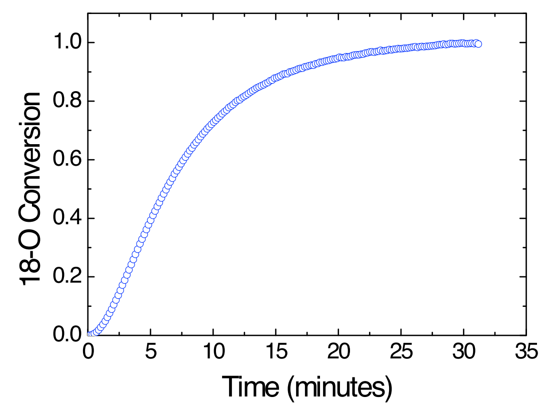


- Use equation below to extract the fraction of ^{18}O that exchanges with lattice ^{16}O
- Can be fit with Crank's solution for sphere

$$\frac{M(t)}{M_\infty} = 1 - \left[\sum_{n=1}^{\infty} \frac{6L^2 \exp\left(-\frac{\beta_n^2 D(t - t_0)}{a^2} \right)}{\beta_n^2 \left(\beta_n^2 + L^2 - L \right)} \right]$$

$$M(t)=2*\text{Total Oxygen} - \{2*(^{36}O_2) + {}^{34}O_2\}$$

^{18}O exchange with ^{16}O lattice



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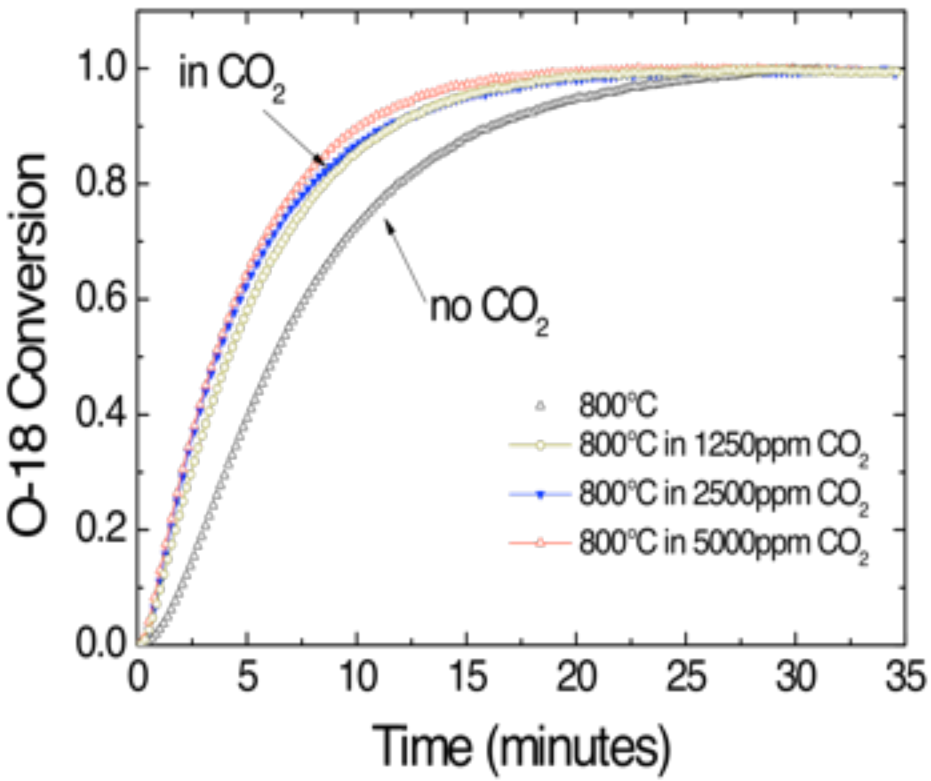
Effect of LSCF Surface Exchange on CO_2 Concentration



k dependence on temperature and CO_2

Temp (°C)	CO_2 Concentration (ppm)	k (cm/s)
600	0	9.96E-09
600	2500	1.38E-08
700	0	1.06E-09
700	2500	1.40E-08
800	0	1.48E-08
800	1250	1.50E-08
800	2500	1.54E-08
800	5000	1.64E-08

Fraction of $^{18}O_2$ exchanged with LSCF surface ^{16}O as function of $C^{16}O_2$ concentration

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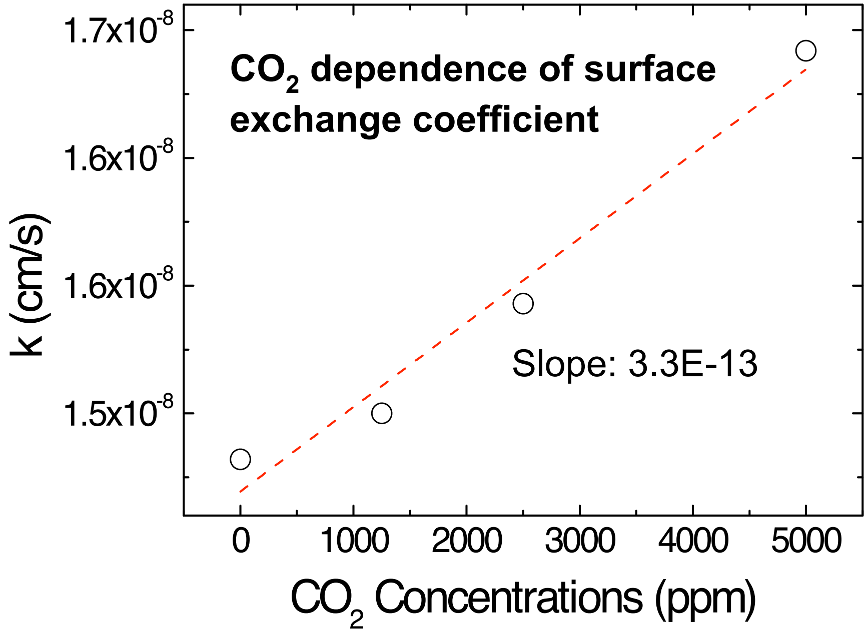
Effect of LSCF Surface Exchange on CO_2 Concentration



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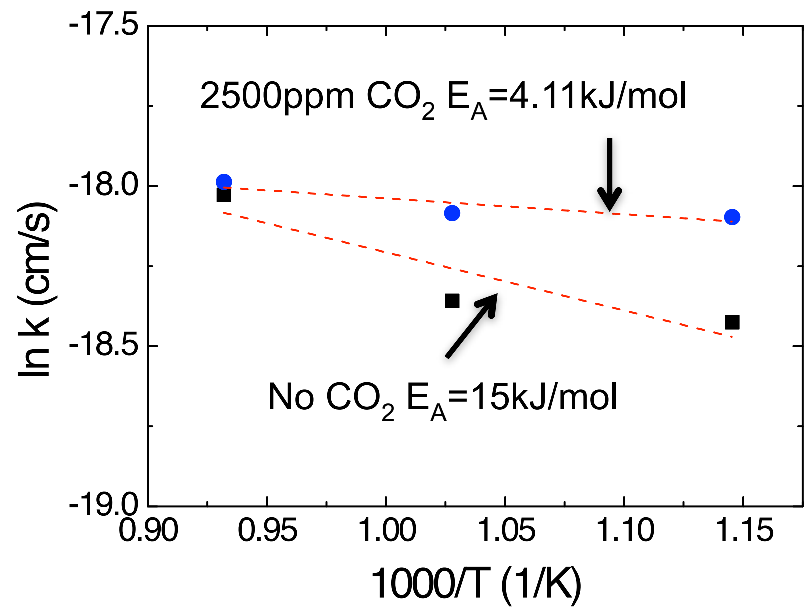

- **Oxygen exchange coefficient increases with CO_2 concentration**
- **Activation energy decreases with increasing CO_2 concentration**

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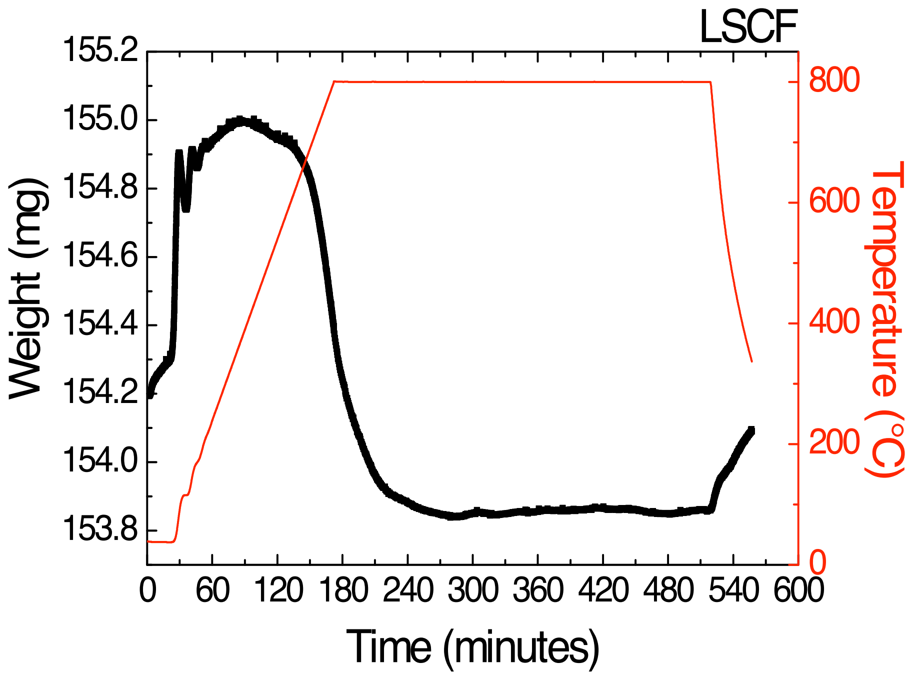
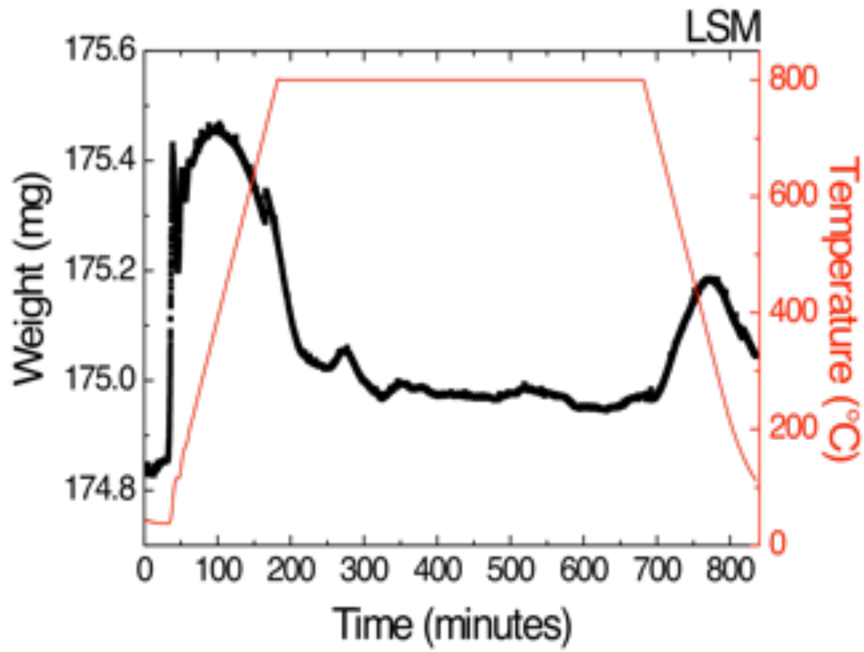
TGA of LSCF and LSM in 30% CO_2





- CO_2 adsorption peaks at 400ºC
- Gains 0.5% weight during heating
- Weight loss at 800ºC due to decrease in oxygen stoichiometry

- CO_2 adsorption peaks at 350ºC
- Gains 0.4% weight during heating
- Maintains 0.1% weight gain at 800ºC possibly due to carbonate formation

➡Starting LSM $^{18}O_2$ in CO_2 experiments

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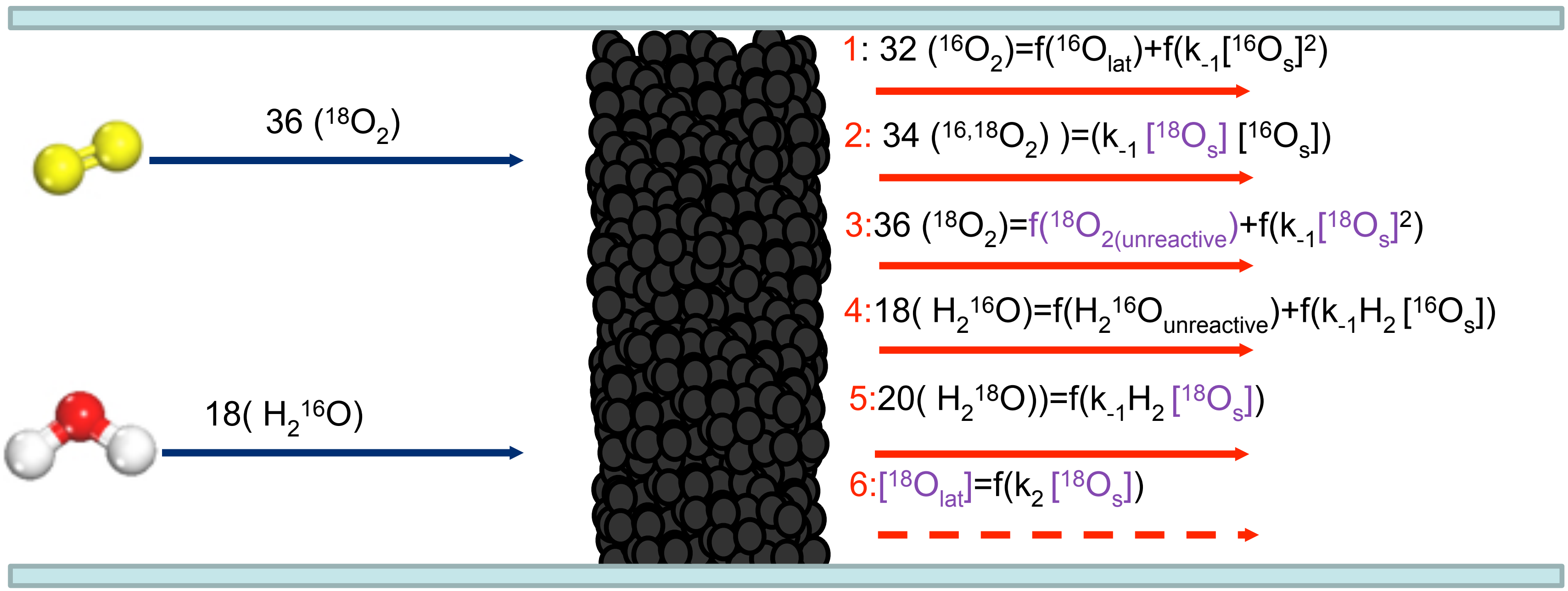
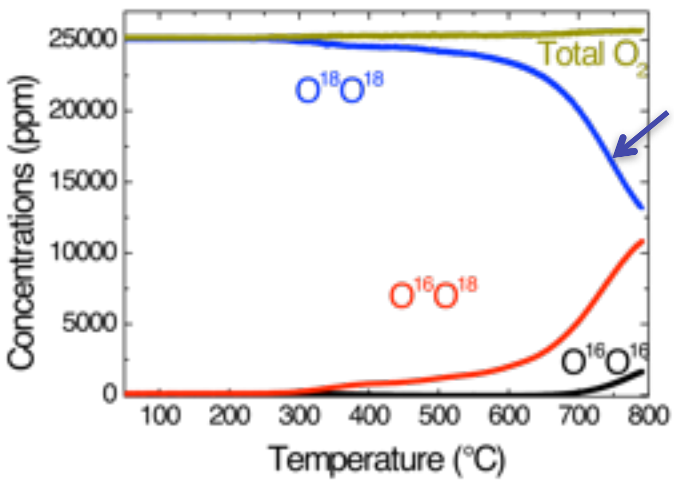
^{18}O-Exchange in H_2O to Determine Effect on ORR Mechanism

0.5 SCCM 100% $^{18}O_2$ balanced in 19.5 SCCM He + 0.3% H_2O

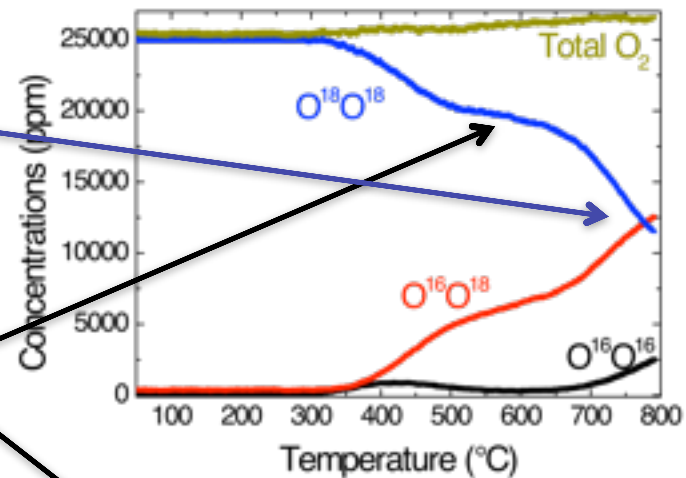


Effect of H_2O on LSM Temp. Programed ^{18}O-Exchange

TPX of LSM without H_2O



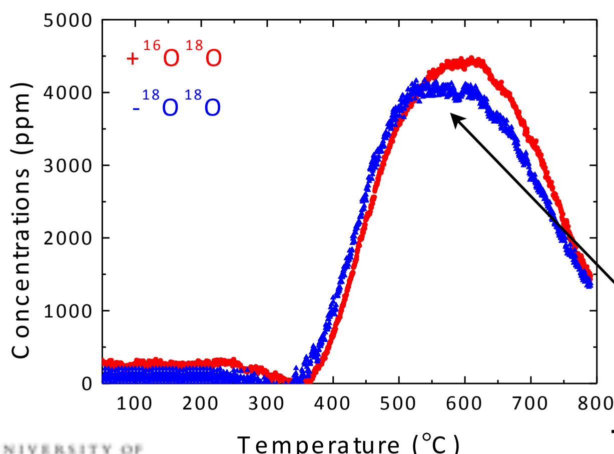
TPX of LSM in ~0.3% H_2O



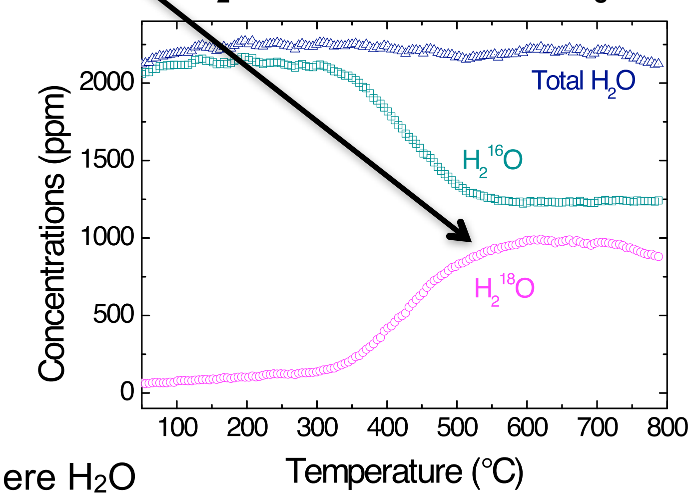
At higher temperature exchange with LSM surface-O dominates

At lower temperature surface-H_2O exchange dominates

Difference of TPX with and without H_2O



H_2O exchange with $^{18}O_s$



Temperature region where H_2O exchange dominates ORR

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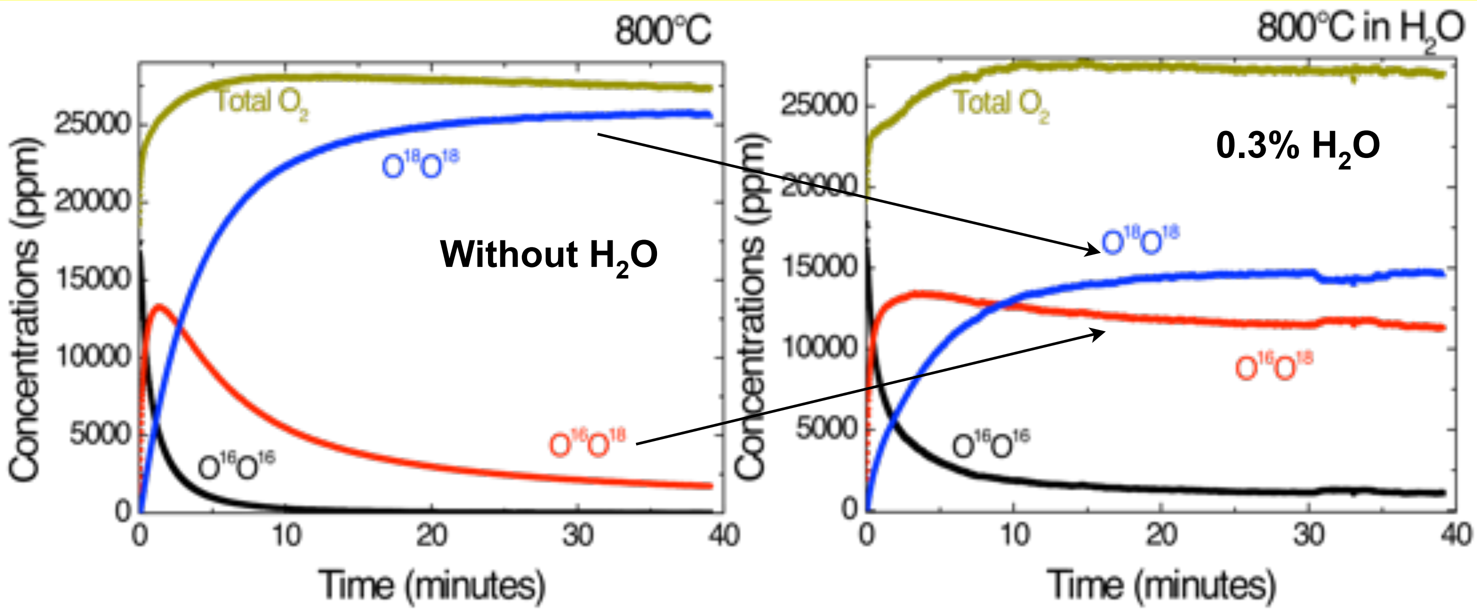
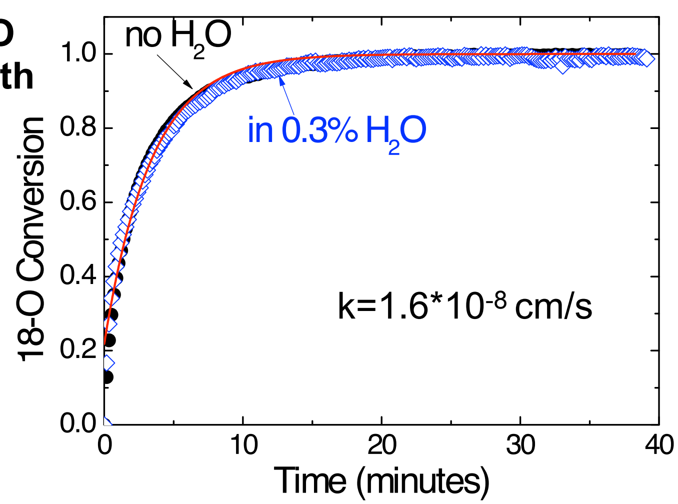
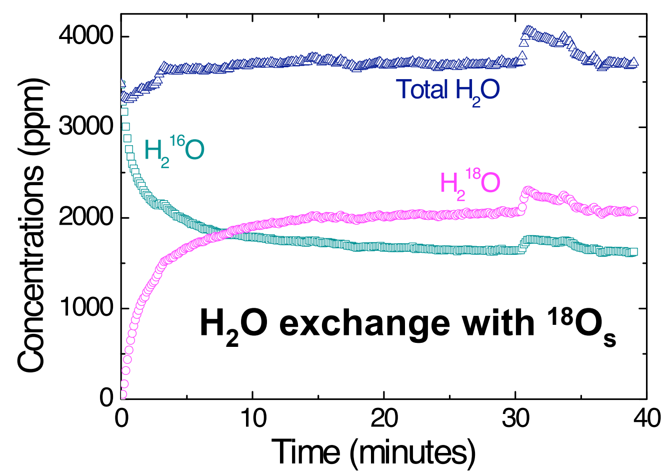
Effect of H_2O on Isothermal Isotope Exchange of LSM



Fraction of ^{18}O exchanged with ^{16}O lattice





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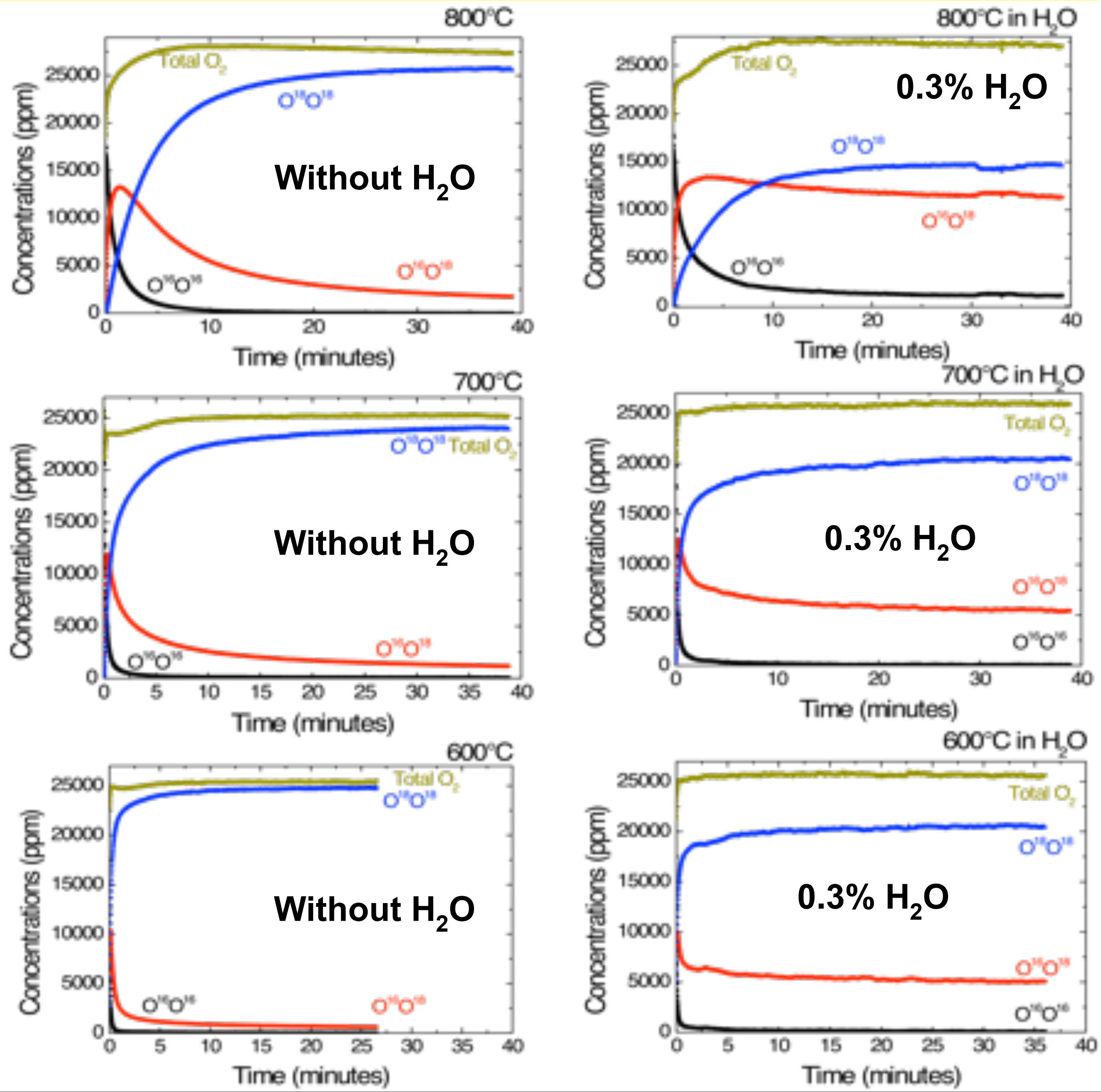
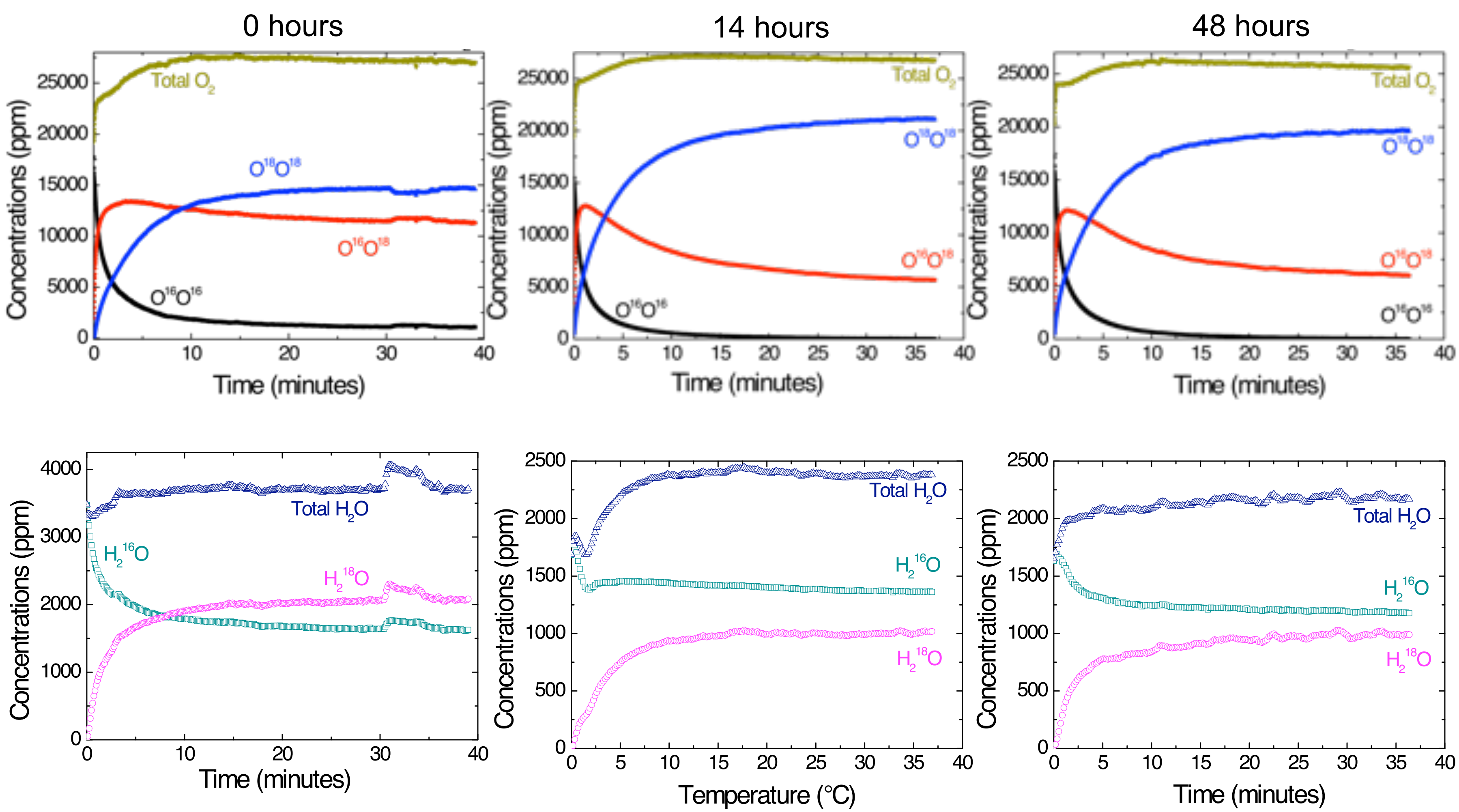
LSM surface comes to $^{18}O/^{16}O$ equilibria with H_2O

Effect of H_2O on Isothermal Isotope Exchange of LSM

- LSM is limited to surface or near surface exchange
- Much smaller exchange at lower temperature
- ^{16}O in $^{16}O^{18}O$ from H_2O or LSM surface oxygen



Effect of H_2O on IIE of LSM Powder Aged in 3% H_2O



Aging in 3% H_2O decreases ^{18}O-exchange

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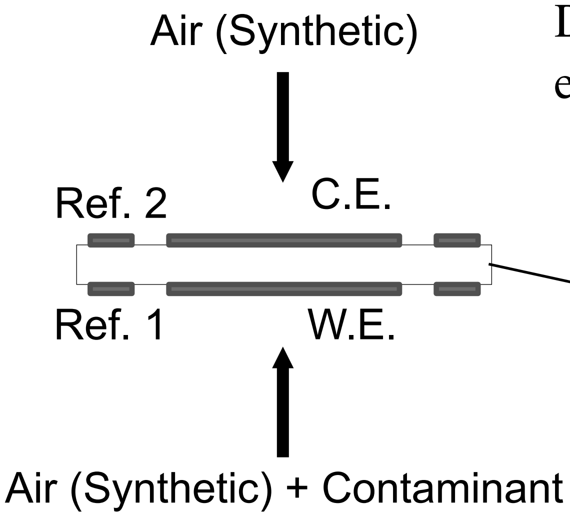
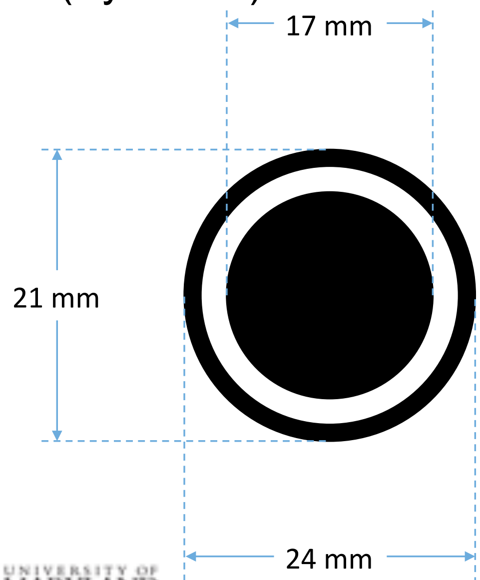
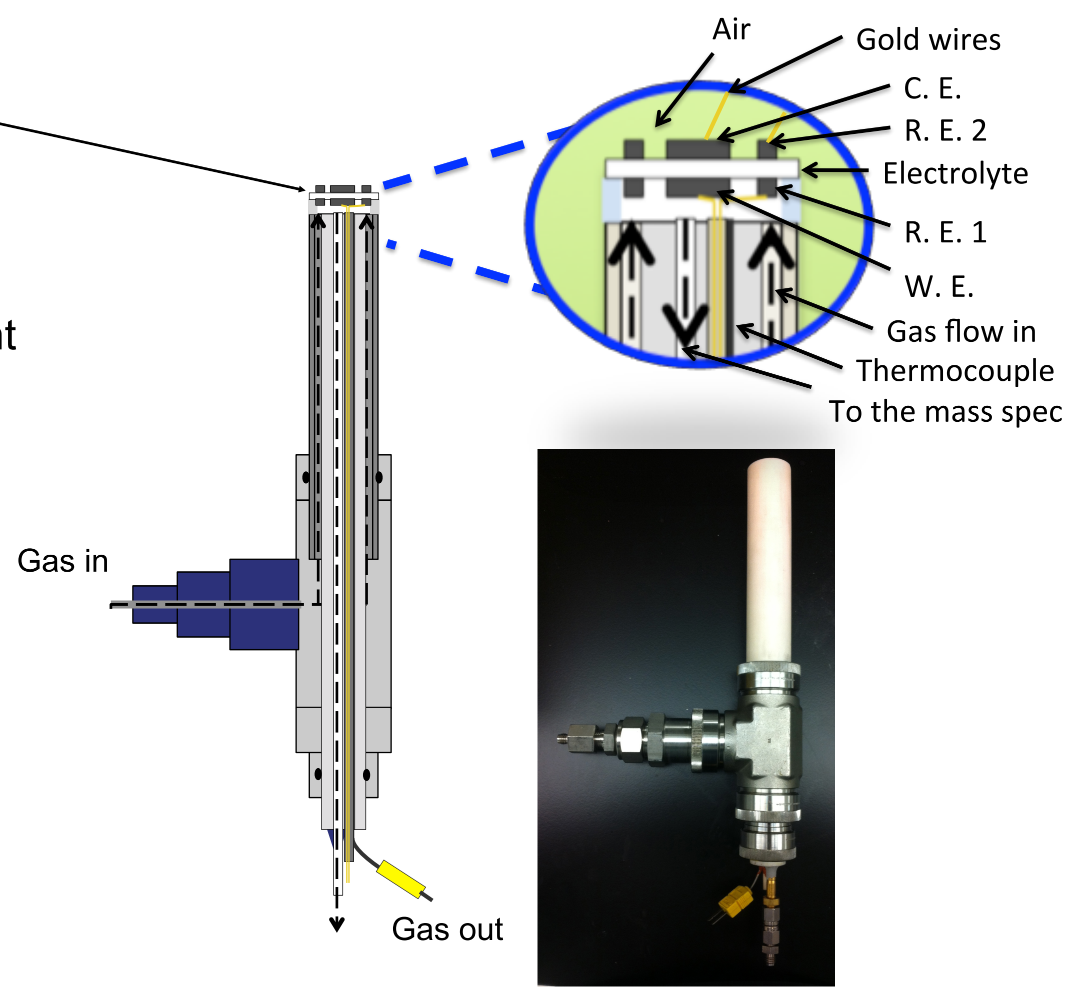
Comparison with Symmetric Cell Testing

Direct comparison of cathodes with and without exposure to contamination with same thermal history

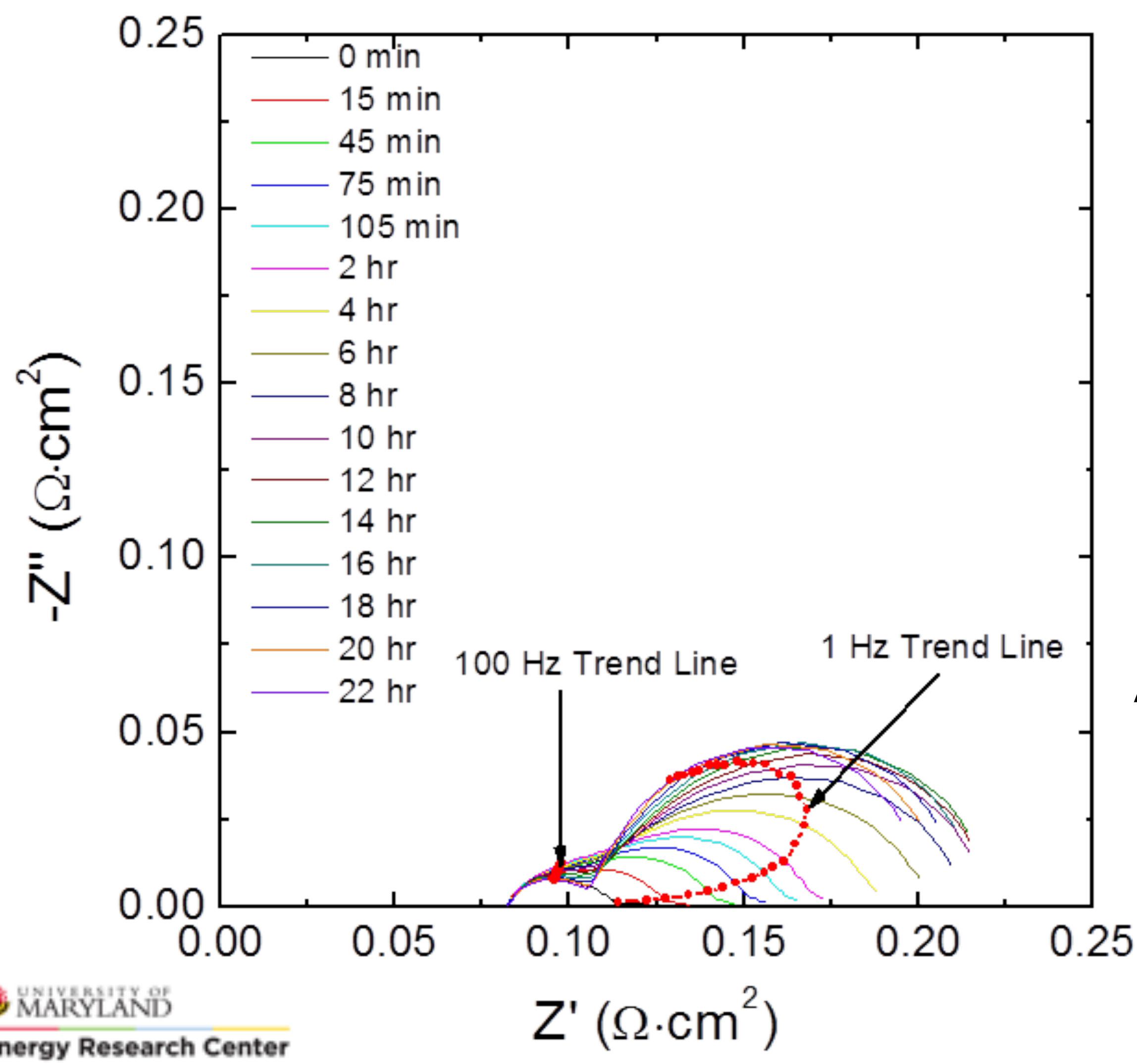


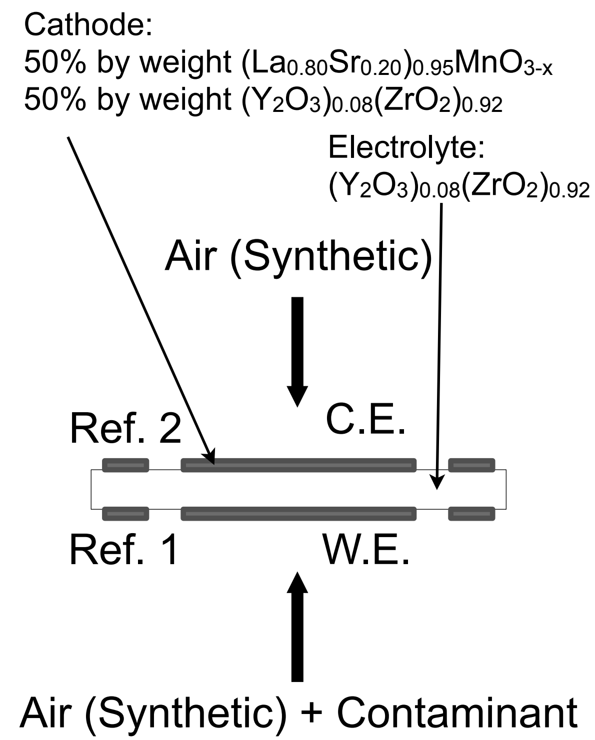




Effect of H_2O on LSM/YSZ Cathode Impedance (EIS)

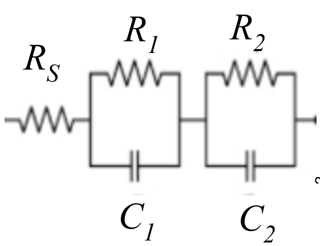
LSM/YSZ Composite in Air + 3% H_2O at 800°C, no bias

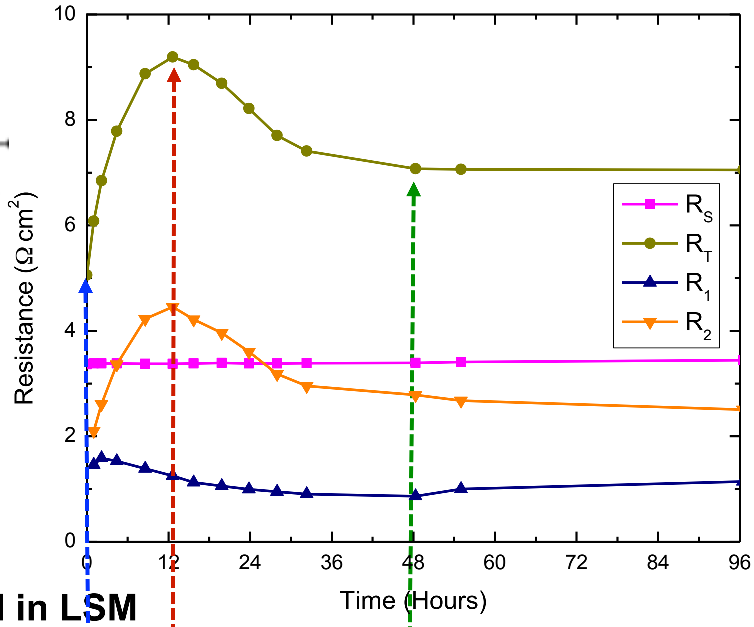




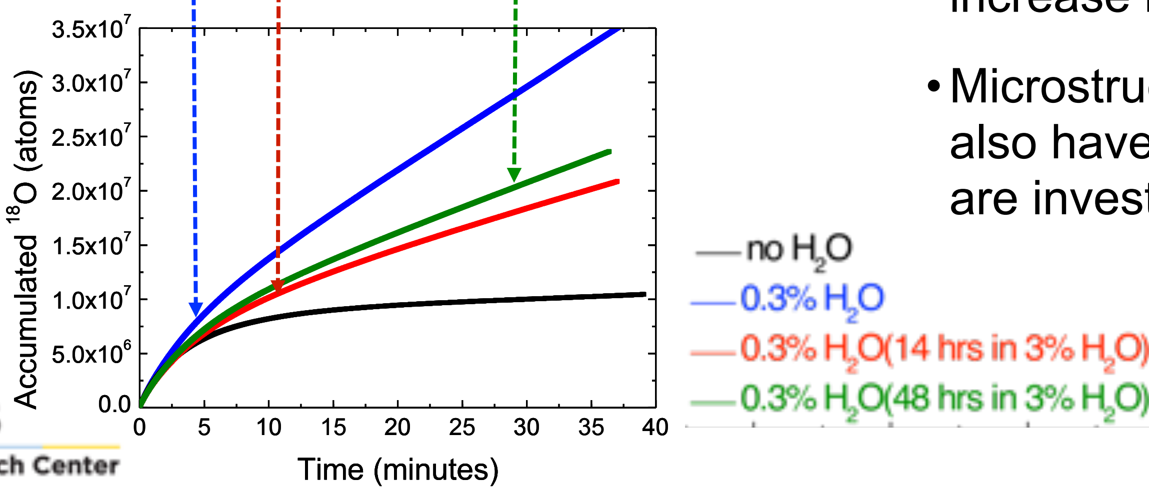
Comparison of LSM Cell Testing and IIE Results

Impedance vs. Cell Run-Time





^{18}O Accumulated in LSM



- Cell and powder aged in 3% H_2O at 800°C
- Increase in non-ohmic electrode impedance from 0 to 14 hrs corresponds to decrease in ^{18}O-exchange
- Subsequent decrease in electrode impedance from 14 to 48 hrs corresponds to increase in ^{18}O-exchange.
- Microstructural changes could also have occurred and we are investigating withFIB/SEM

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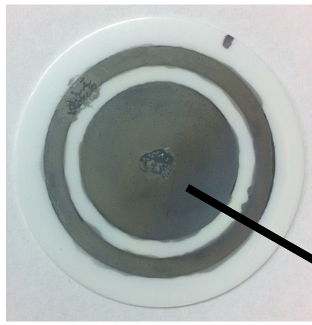
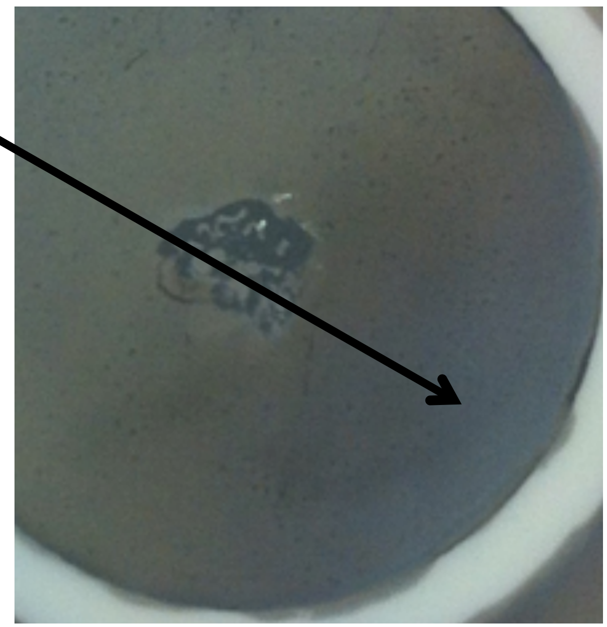
Effect of H_2O on LSM/YSZ Cathode

LSM/YSZ Composite in Air + 3% H_2O at 800°C, no bias

Air

Air +3% H_2O

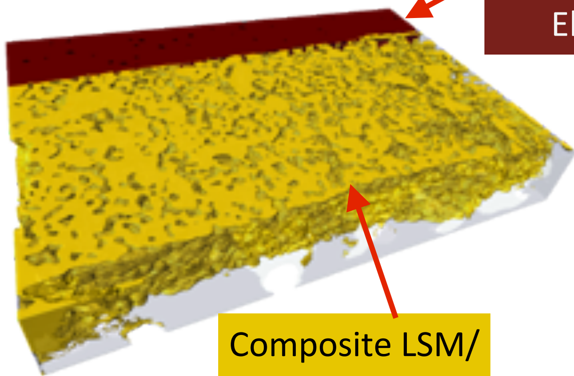




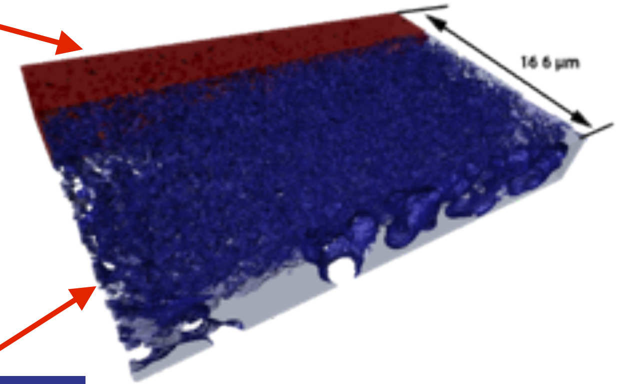
Visible discoloration of cathode exposed to H_2O after 380 hours indicating degradation

3D Reconstruction of Degraded LSM/YSZ Cell

3D Image of LSM/YSZ Cathode



3D Image of Pore Network

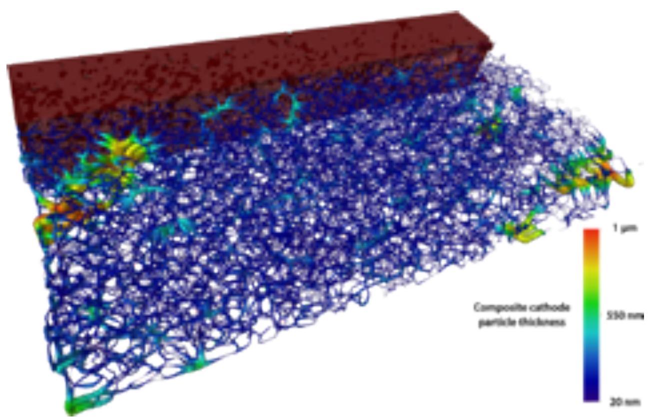


Dense YSZ Electrolyte

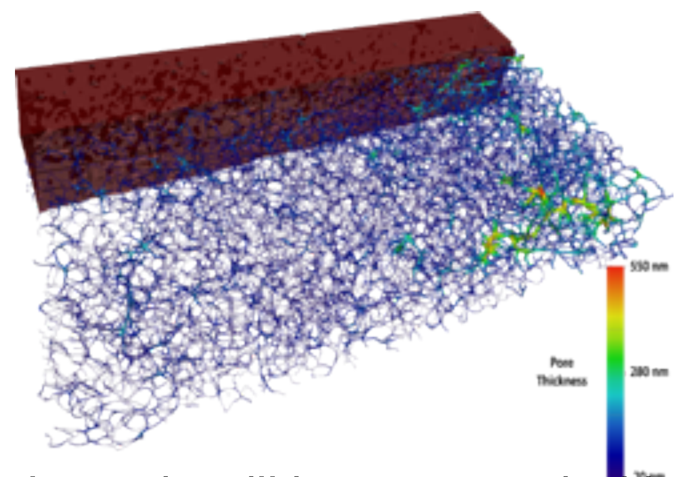
Composite LSM/ YSZ Cathode

Pore Network

Composite Cathode Skeleton



Pore Skeleton



3D reconstruction of degraded electrode will be compared with electrode on other side, same thermal history but no H_2O exposure

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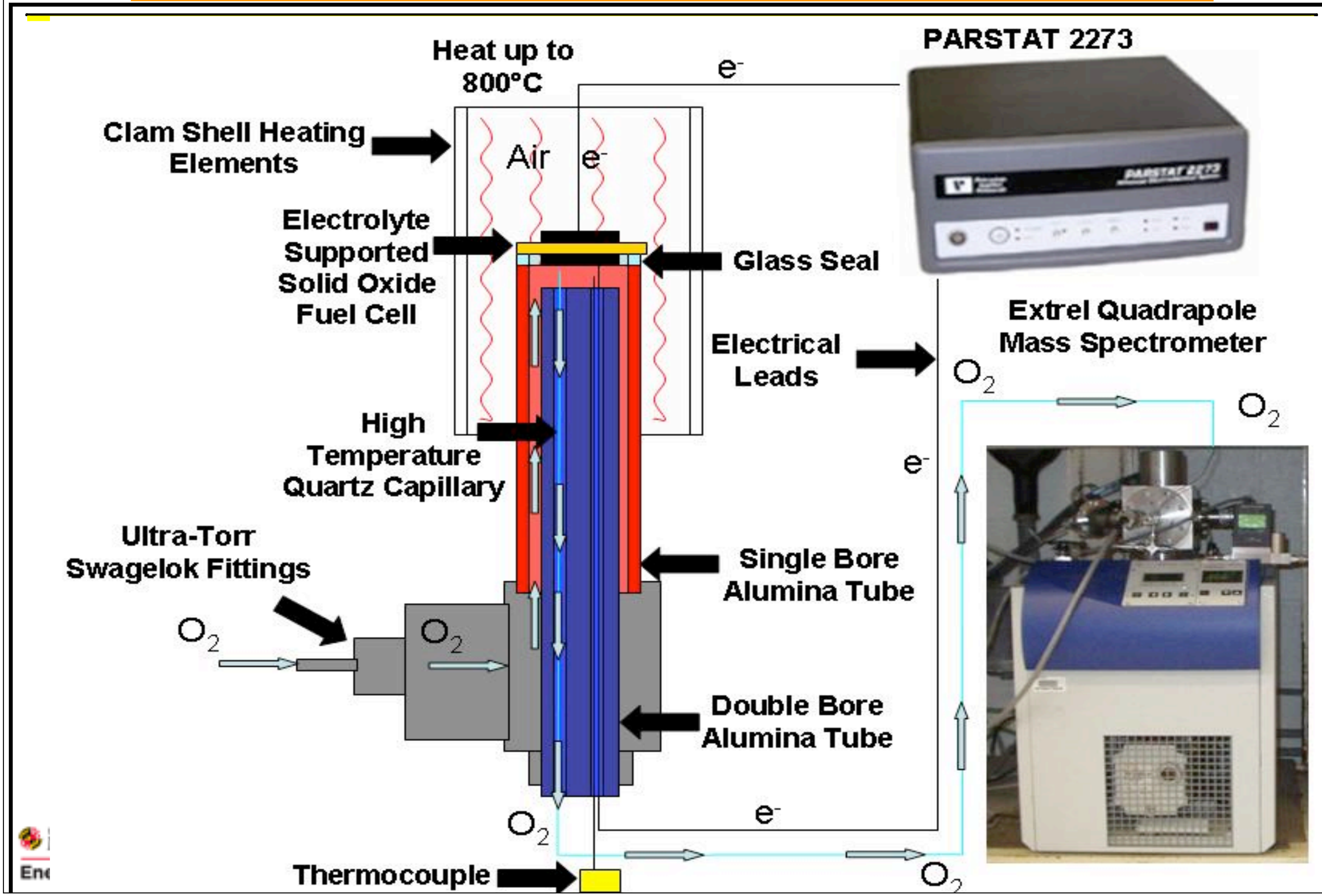
Conclusions

- CO_2 actively participates in O_2 surface exchange with LSCF
  - CO_2 increases surface exchange coefficient and decreases activation energy
- H_2O actively participates in O_2 surface exchange with LSM
  - Between 350°C and 700°C H_2O exchange with dissociated surface-O dominates
  - Above 700°C O_2 exchange with LSM surface dominates
- Demonstrated direct correlation between LSM/YSZ cathode impedance changes during aging in 3% H_2O and changes in O_2 surface exchange of LSM

Integrated *In situ* Electrocatalysis



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