In-Operando Evaluation of SOFC Cathodes for Enhanced ORR Activity and Durability

US Department of Energy, National Energy Technology Laboratory, Contract No. FE0026190

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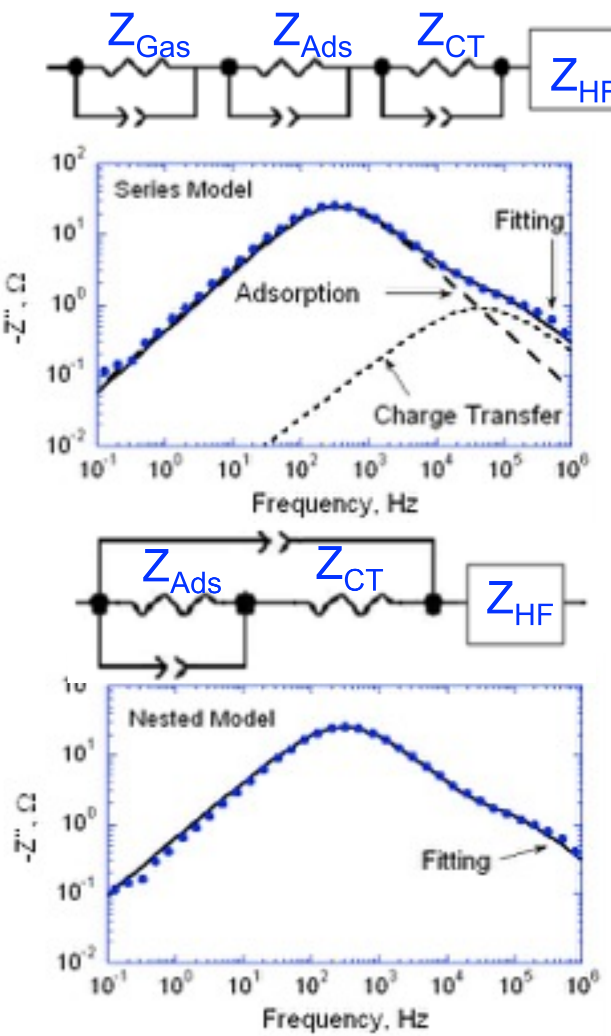
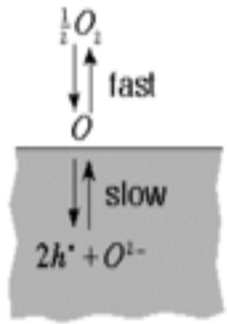
Background - Limitation of ORR from EIS

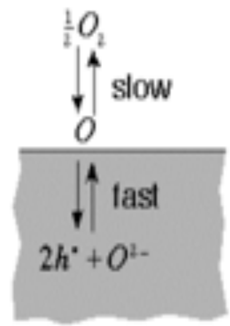


Same!

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

Oxygen exchange limited by vacancy exchange	Oxygen exchange limited by dissociative adsorption





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

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

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

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

Same!

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

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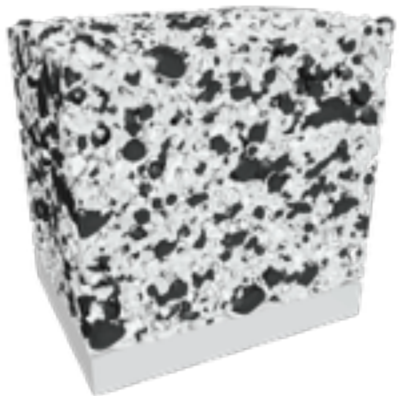
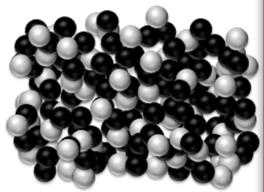
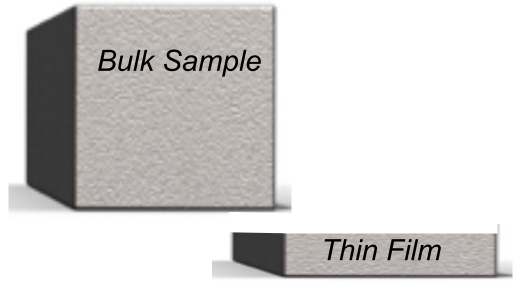
Need to combine multiple techniques to determine mechanism

Background - Experimental vs. Real Microstructures



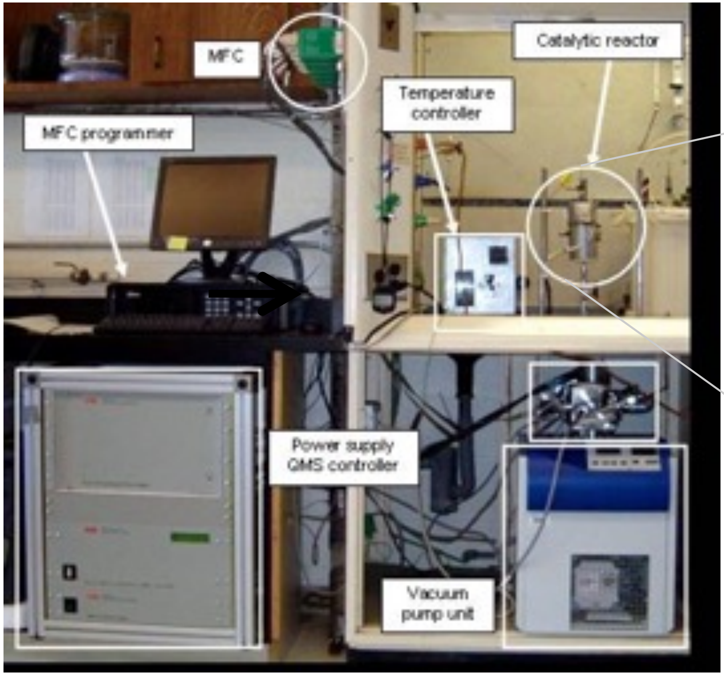


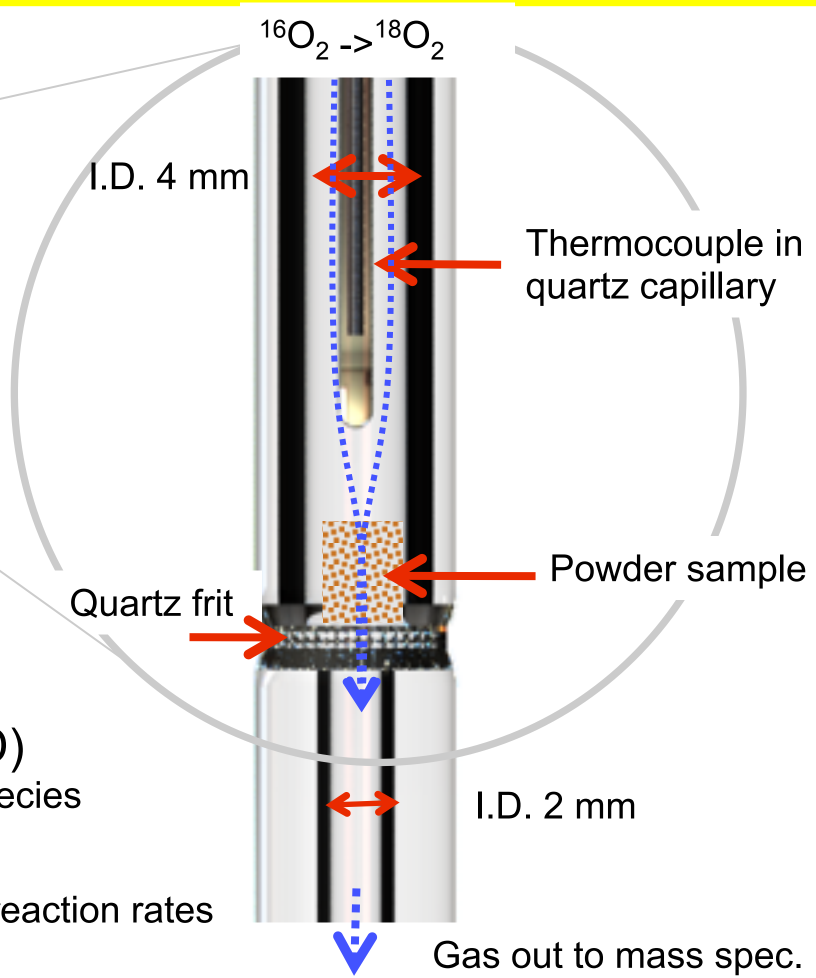


	Real Cathode	Heterogeneous Catalysis	SIMS Depth Profile	Conductivity Relaxation	Heterostructure
Structure/Morphology	• Random crystallographic faces • 3-phase-solid-gas interfaces		• Random (*bulk*) to ordered (*thin film*) crystallographic faces • 2-phase-solid-gas interface		• Single crystal face • 3-phase-solid-gas interface
ORR Kinetics	• Surface controlled		• Bulk samples diffusion controlled • Thin film samples surface controlled but strained		• Surface controlled but strained and only for specific crystallographic orientation
Kinetic Parameters	• k_{ex}, k_{in}, D_{surf}, $D_{b/gb}$	• k_{ex}, k_{in}, D_b, (D_{surf})	• $D_{b/gb}$ (k_{in})	• k_{in}, D_b, (D_{surf})	• k_{in}, D_{surf}, $D_{b/gb}$
Polarization	• Bias current	• OCP	• OCP	• Small current perturbation	• OCP & bias current
***In-Situ* O_2 Exchange Analysis**	• Limited	• Excellent	• Limited	• Limited	• Limited

In-Operando

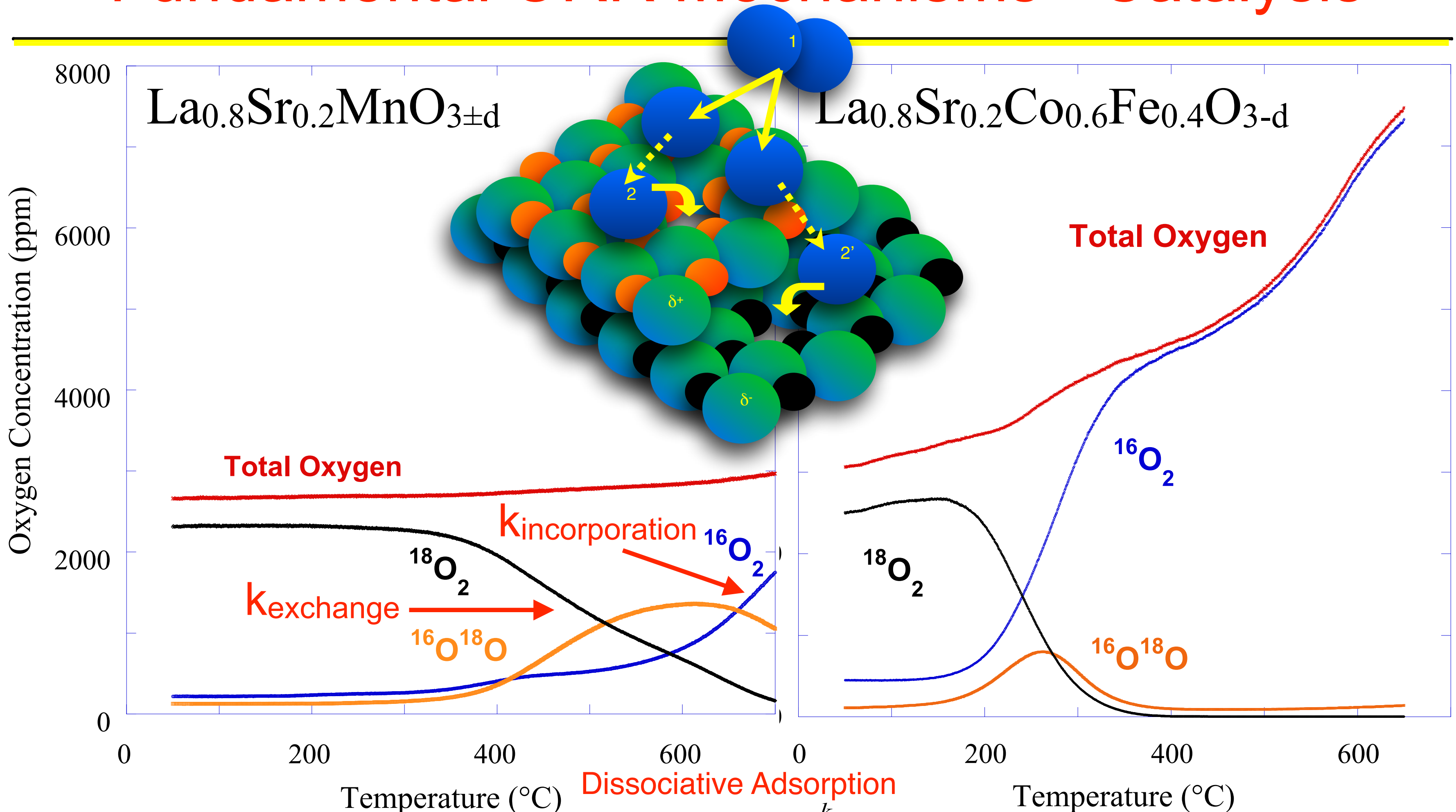
Background - Fundamental ORR Mechanisms





- 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 ORR Mechanisms - Catalysis



Dissociative Adsorption

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

Incorporation

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

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

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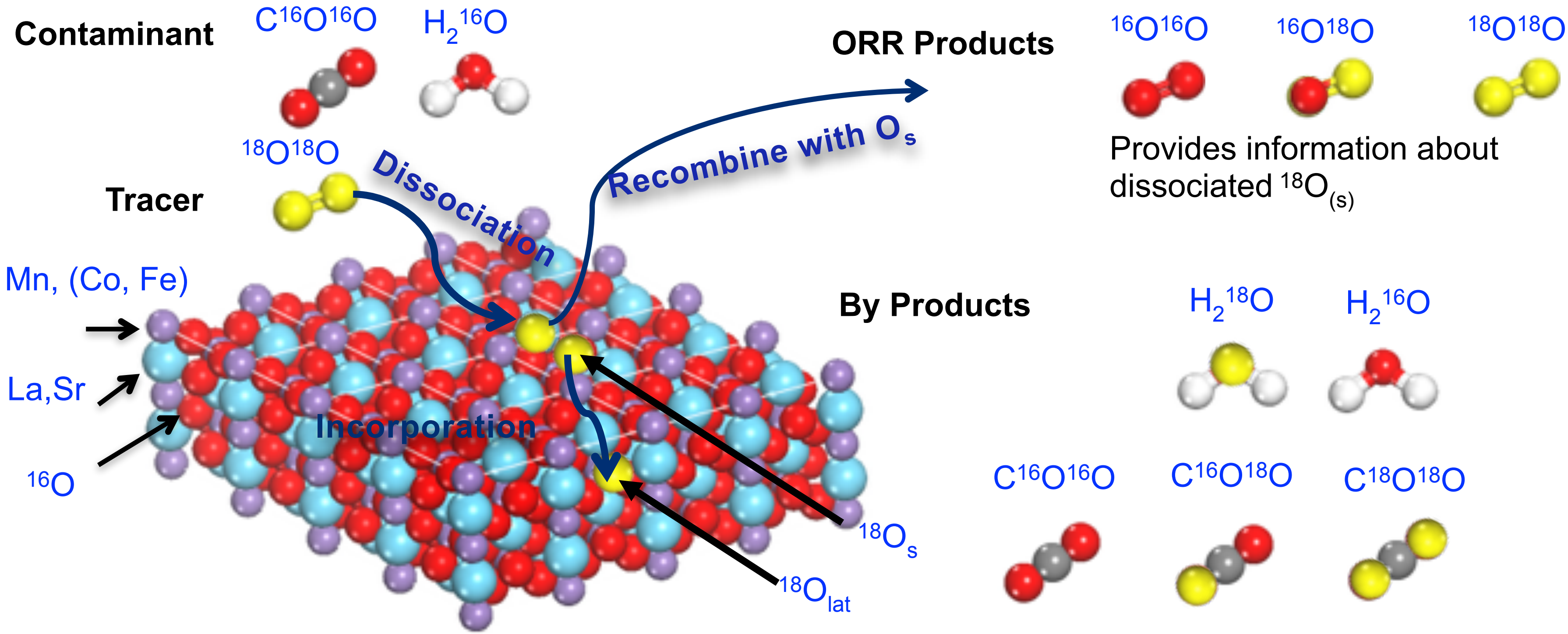
ORR Reaction Mechanisms in Presence of H_2O and CO_2

In situ Isotope Exchange (IIE)

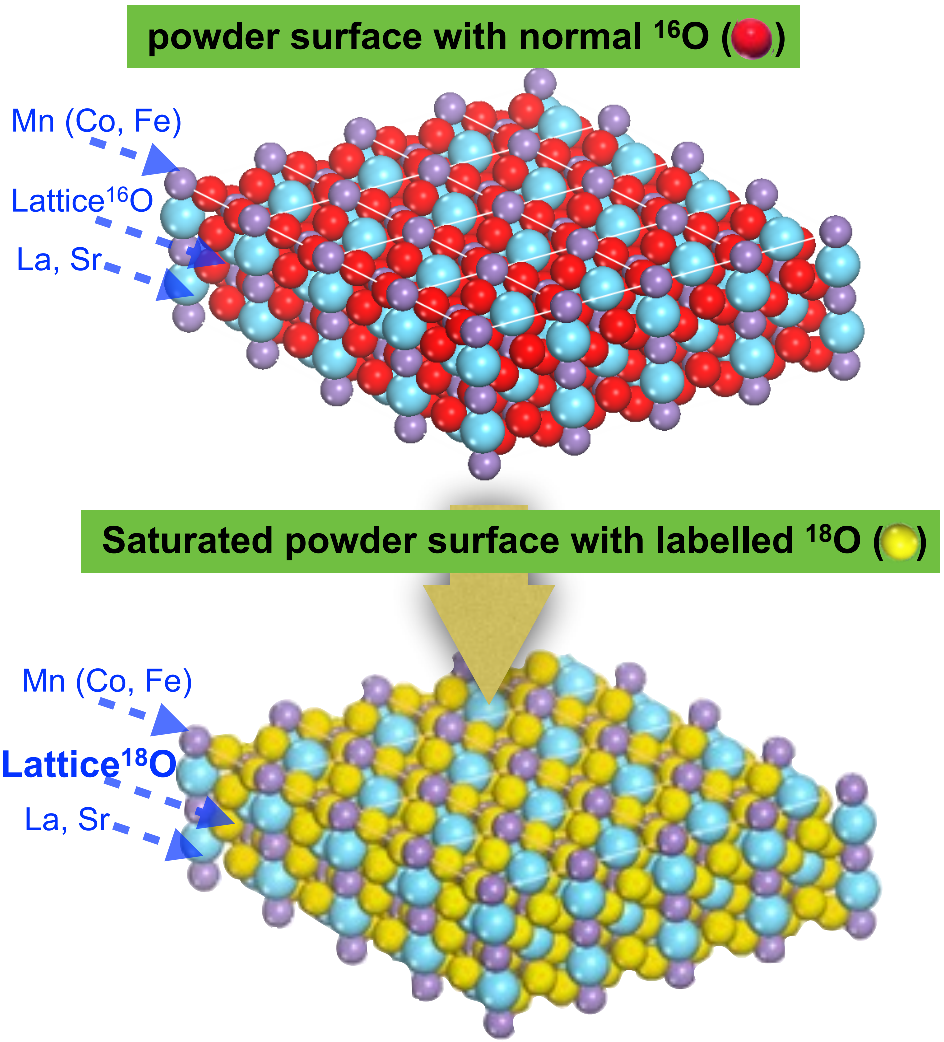


Provide information about surface reaction with contaminants

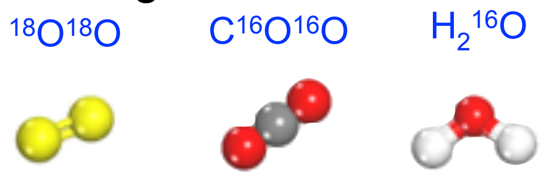
$$S + 1/2O_2 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} O_{ads}$$

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

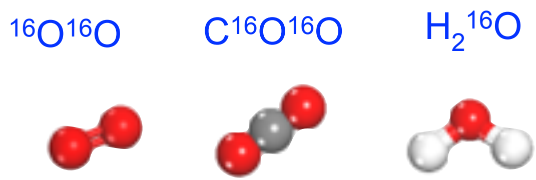
Isotope Saturated Temperature Programmed Exchange (ISTPX)



IIE - Probes the impact of contaminants on gas phase $^{18}O_2$ exchange with cathode surface



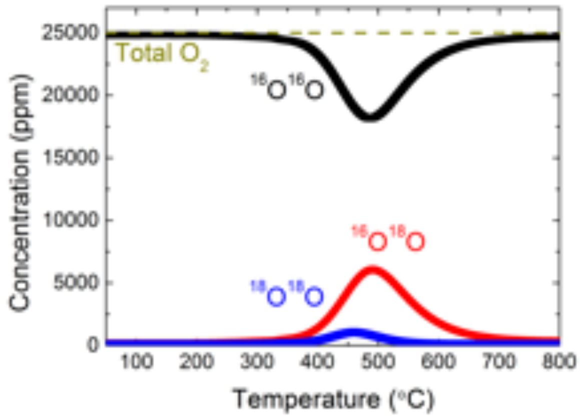
ISTPX - Probes competitive ORR in presence of contaminants on ^{18}O-labeled cathode surface



Allows experiment in ambient P_{O2} without saturating mass spectrometer

ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

O_2 exchange with lattice ^{18}O



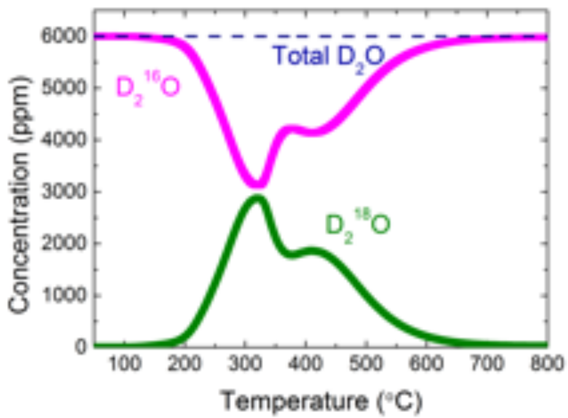
Mass of: $^{18}O = 18$

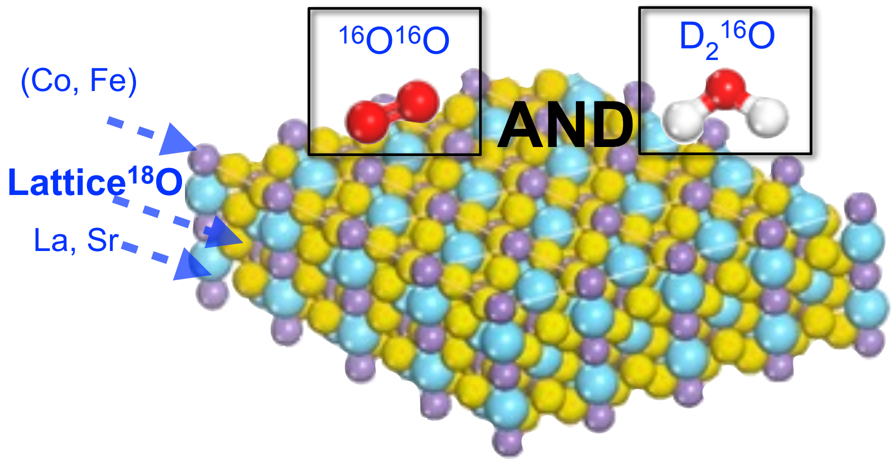
$H_2{}^{16}O = 18$

$D_2{}^{16}O = 20$

$D_2{}^{18}O = 22$

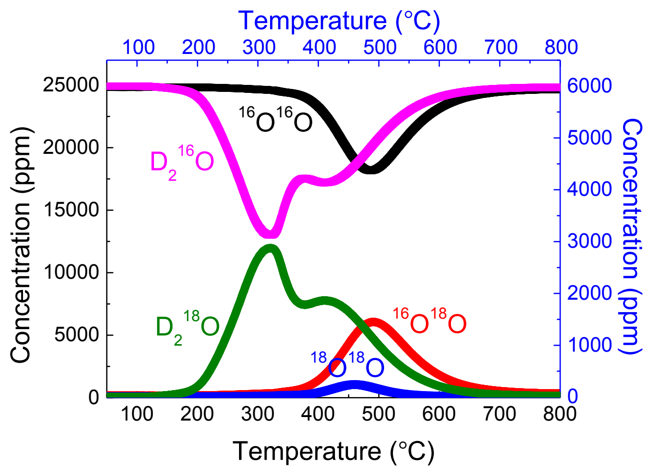
D_2O exchange with lattice ^{18}O

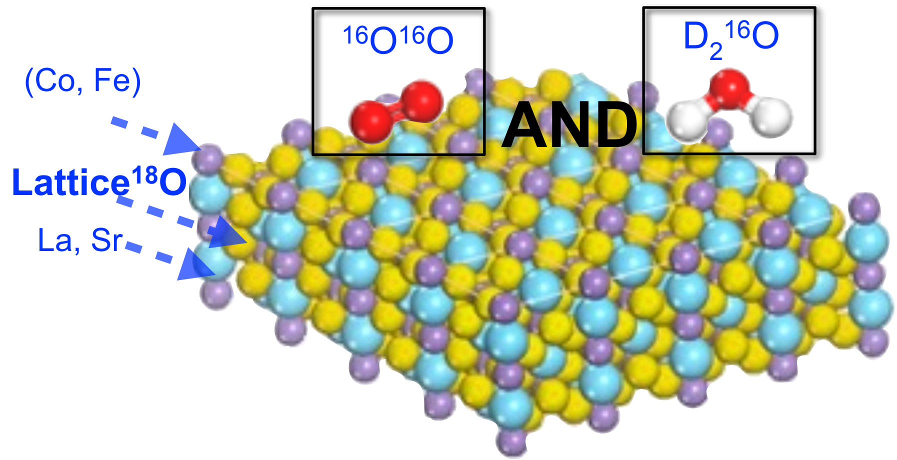




ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

D_2O and O_2 exchange with lattice ^{18}O

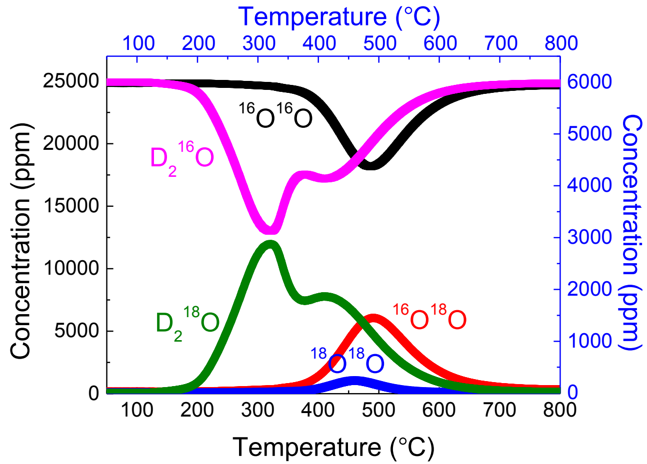


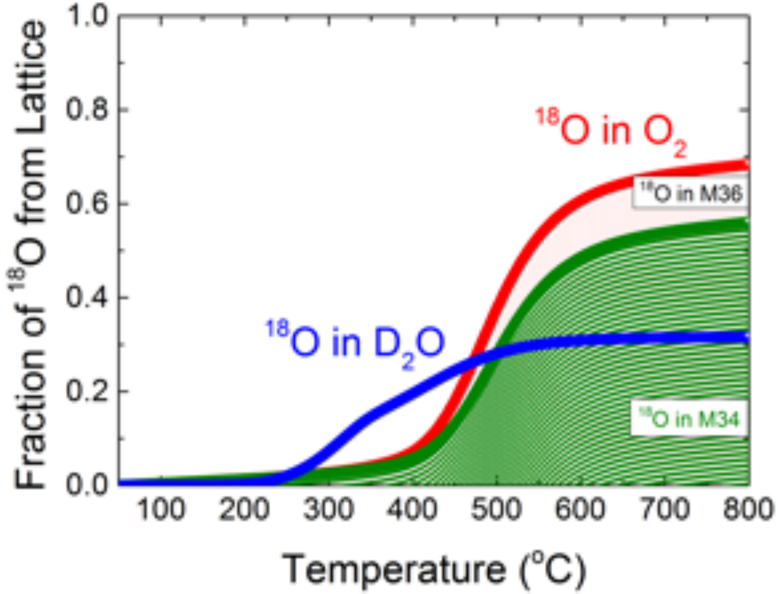


ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

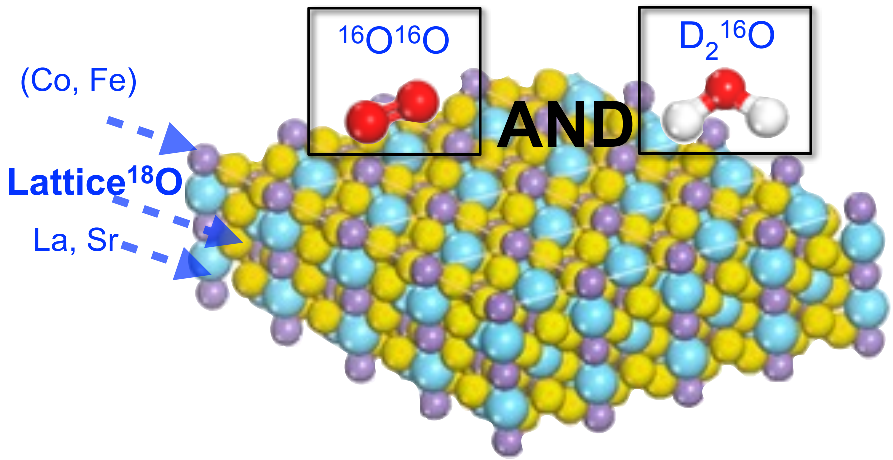
Accumulated Isotopic Fraction exchanged from ^{18}O LSCF

D2O and O2 exchange with lattice 18O





At lower temperature more of the lattice ^{18}O exchanges with water than O_2



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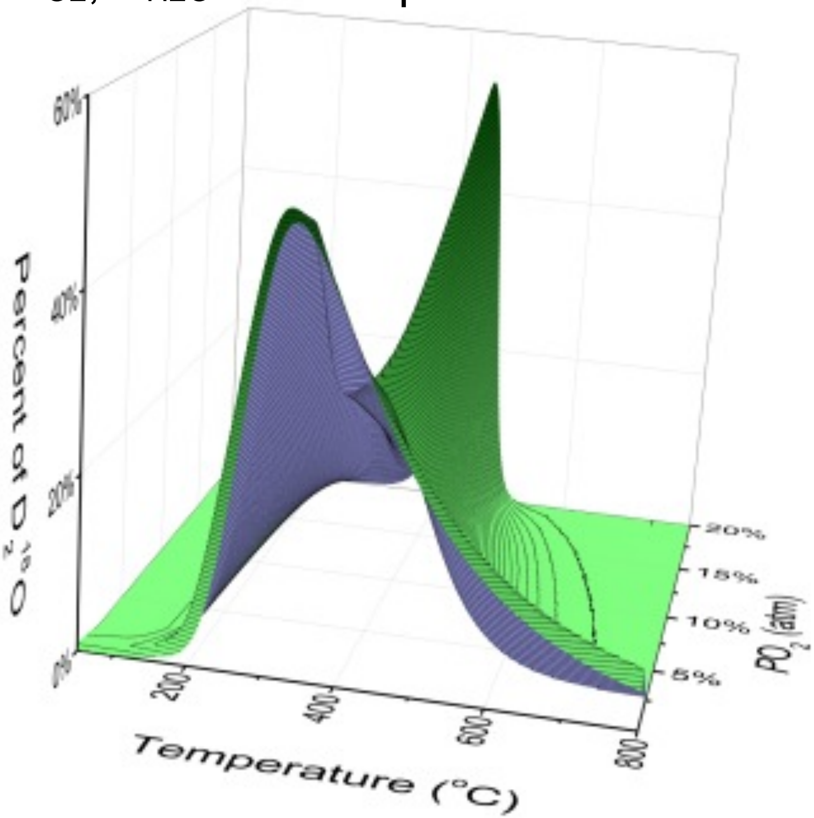
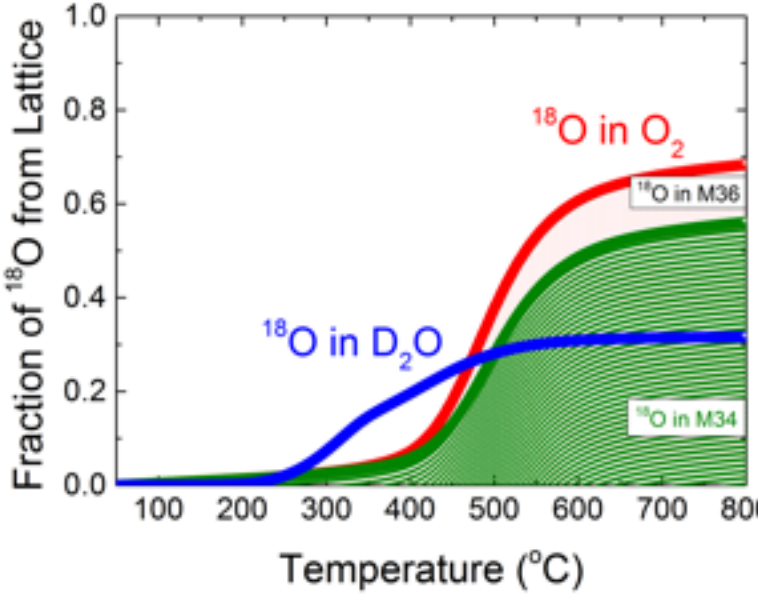
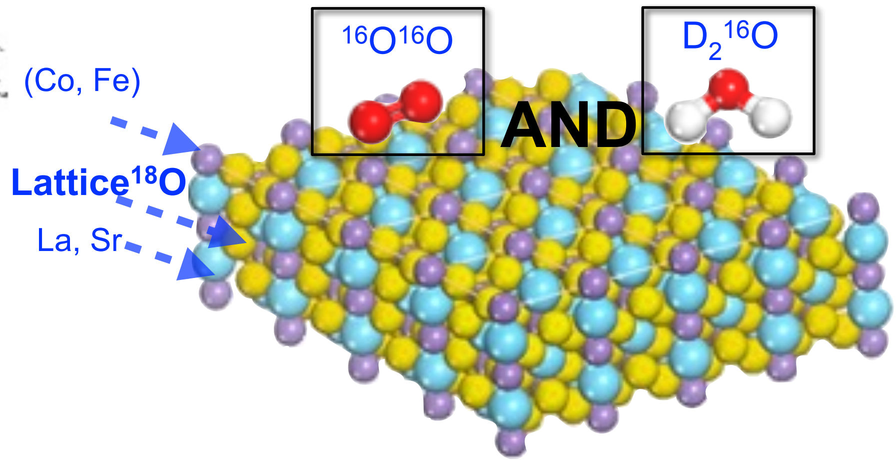
Temperature and PO_2 Dependence of LSCF in D_2O

Repeating exchange experiments as function of P_{O2}, P_{H2O} and temperature



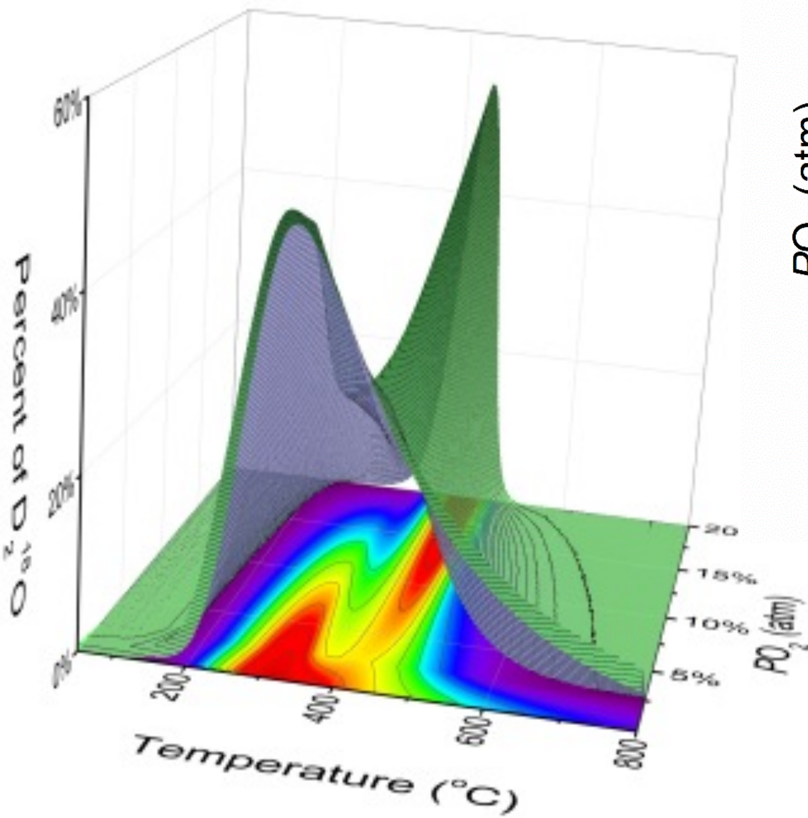
Accumulated Isotopic Fraction exchanged from ^{18}O LSCF

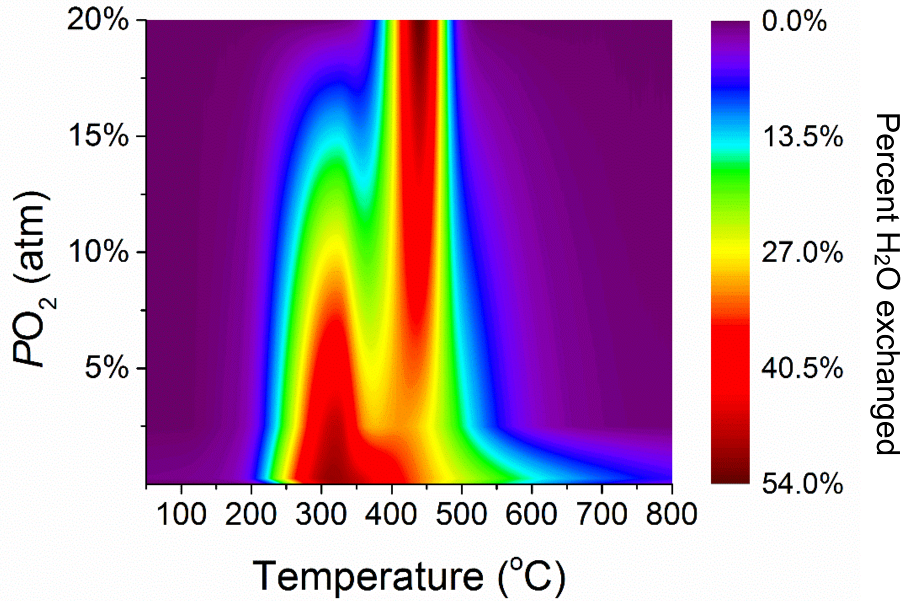




Temperature and PO_2 Dependence of LSCF in D_2O

Exchange as function of P_{O2}, P_{H2O} and temperature





Two Exchange Peaks:
- As PO_2 increases, 300ºC peak decreases
- 450ºC peak still present at high PO_2

- We have now mapped out H_2O (and CO_2) impacts on ORR as function of P_{O2}, temperature, and contaminant concentration

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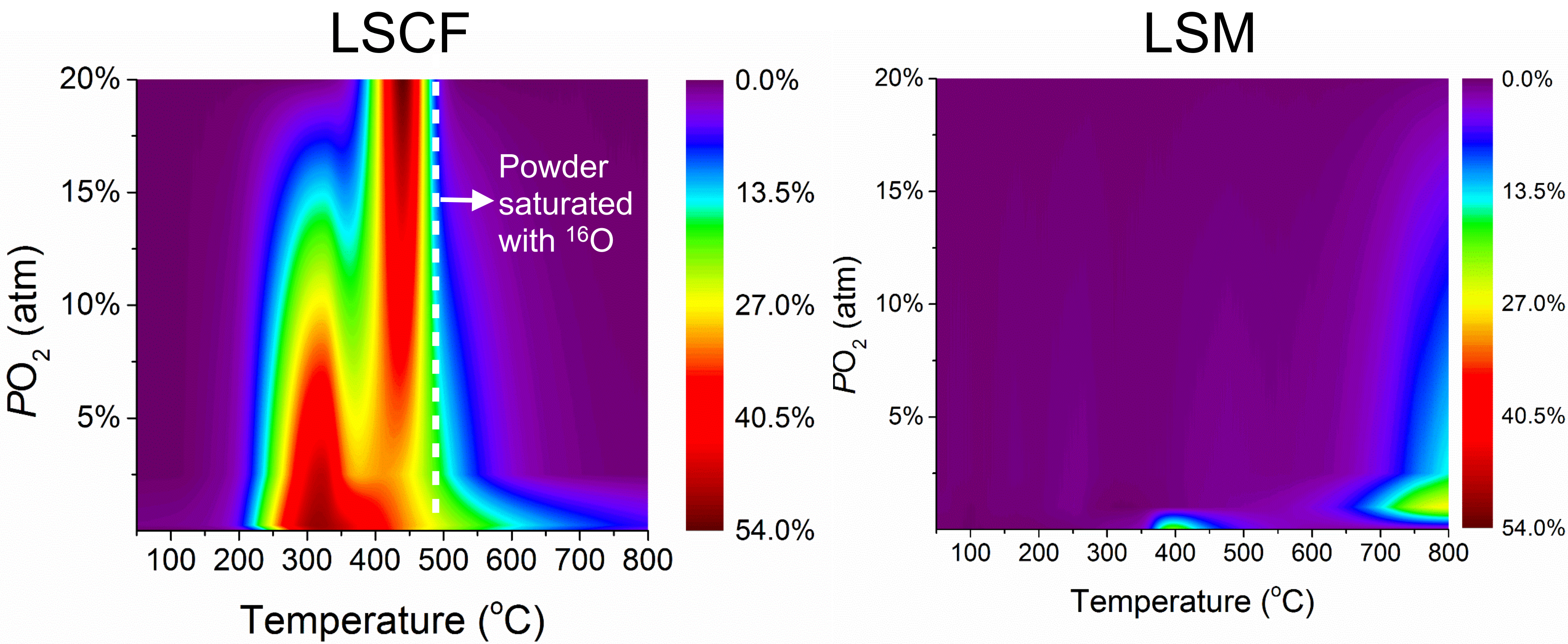
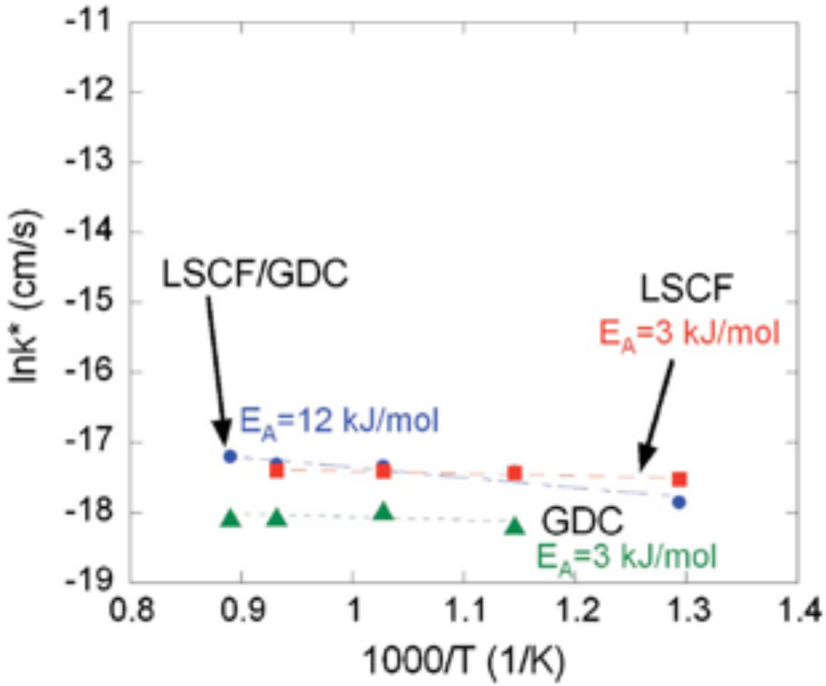
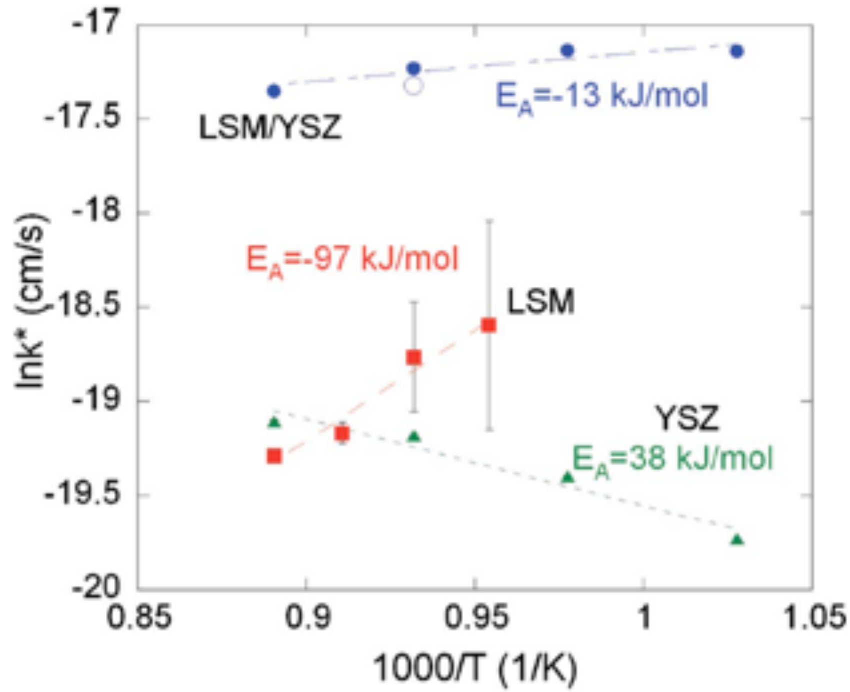
Comparison of LSCF and LSM Temp-PO_2 Dependence in D_2O



- LSCF more active toward water exchange than LSM
- Water exchanges with LSM only at high temp in presence of O_2

Effect of Composite Cathodes on Surface Exchange





- From our previous observation LSCF-GDC and LSCF have similar exchange kinetics due to both having high oxygen vacancy concentration
- While LSM-YSZ is dramatically enhanced relative to LSM indicating greater importance of TPBs and co-existence of O-dissociation and O-incorporation phases

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Surface Exchange Coefficients of Composite Cathode Materials Using In Situ Isothermal Isotope Exchange

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[b]University of Maryland Energy Research Center, University of Maryland, College Park, Maryland 20742, USA

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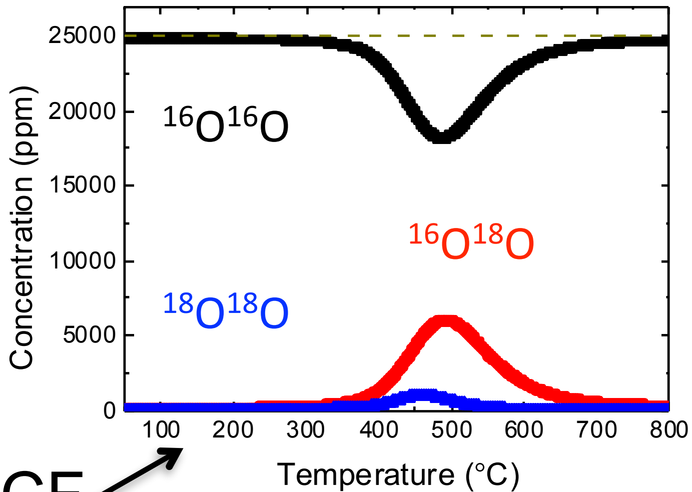
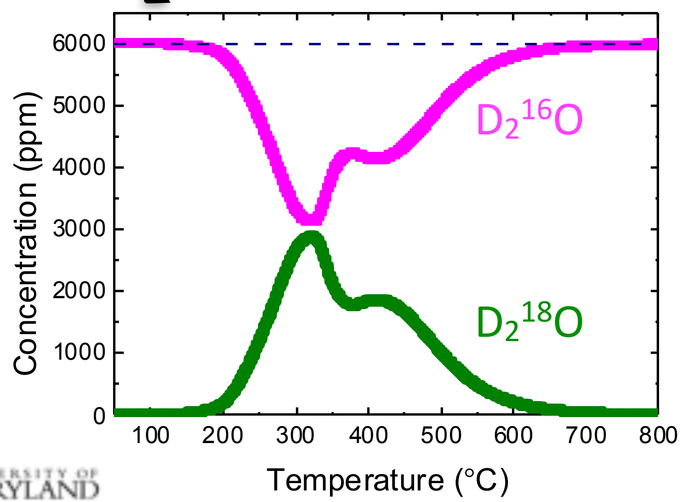
Comparison of LSCF and Composite LSCF-GDC in D_2O

25000ppm O_2 and 6000ppm D_2O



LSCF



Comparison of LSCF and Composite LSCF-GDC in D_2O

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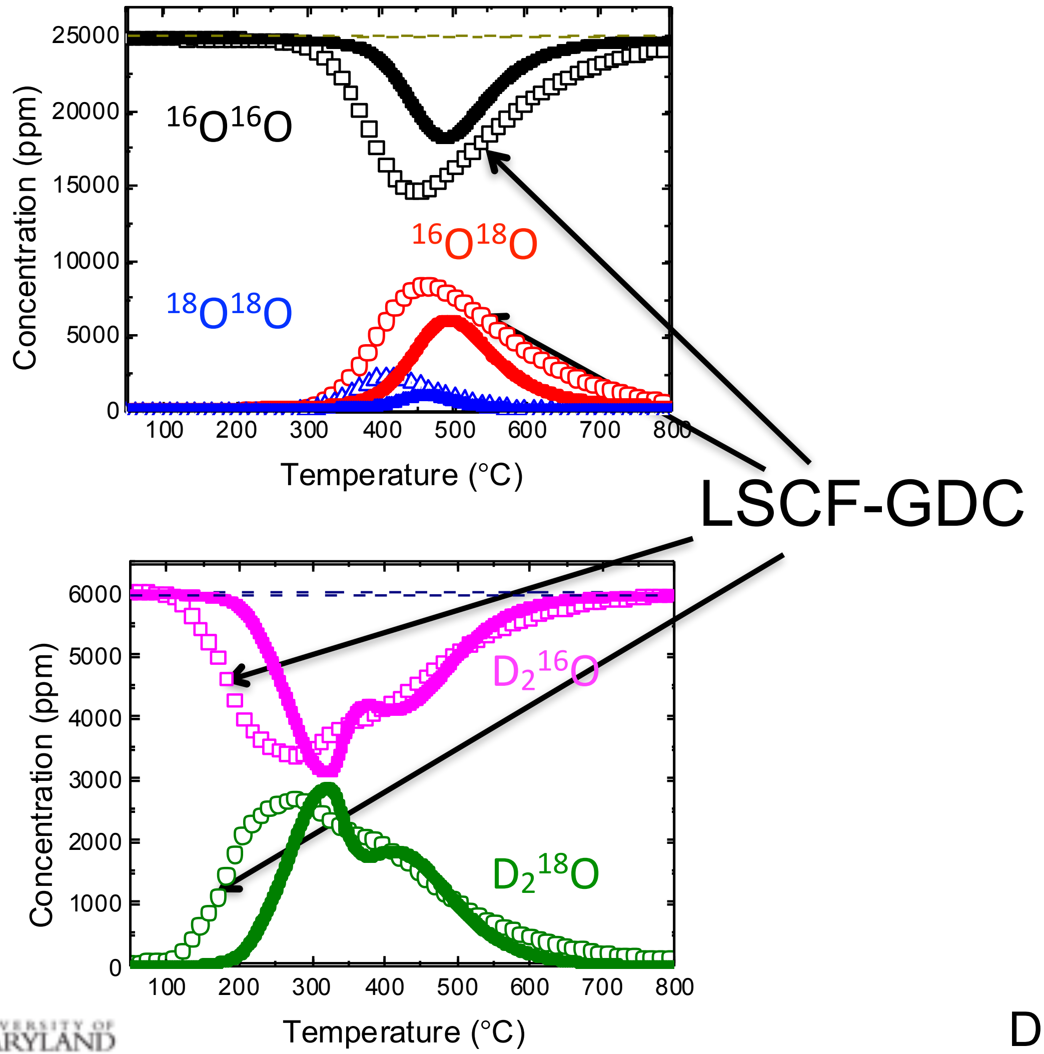
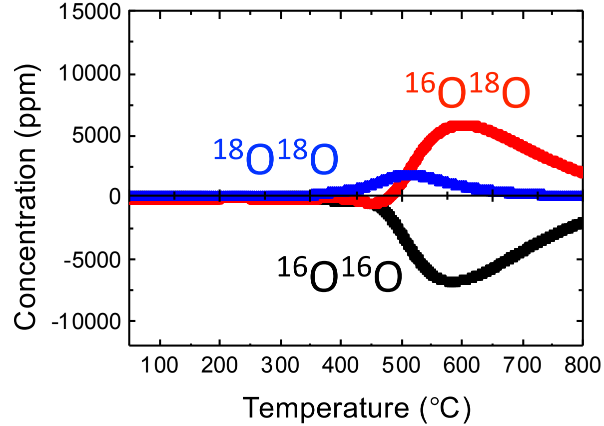
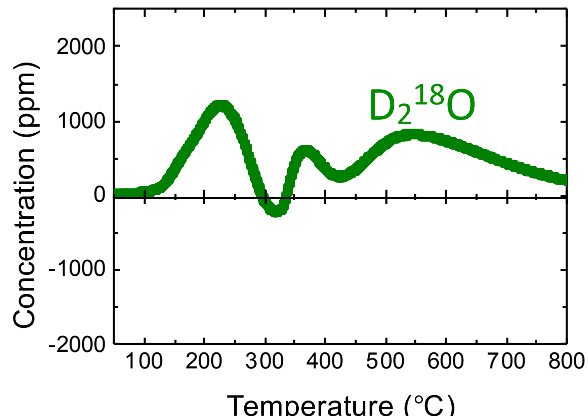


LSCF Subtracted from LSCF-GDC





Difference demonstrates greater D_2O exchange with composite

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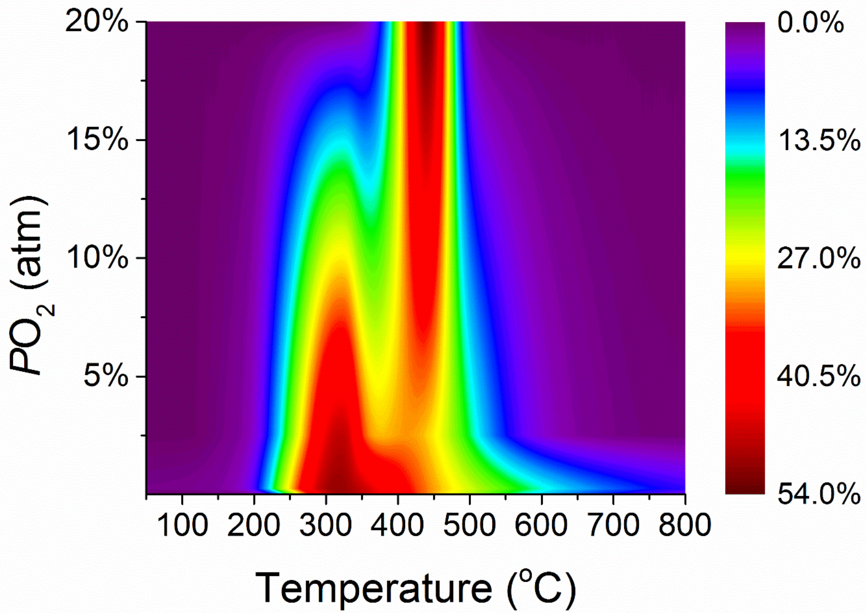
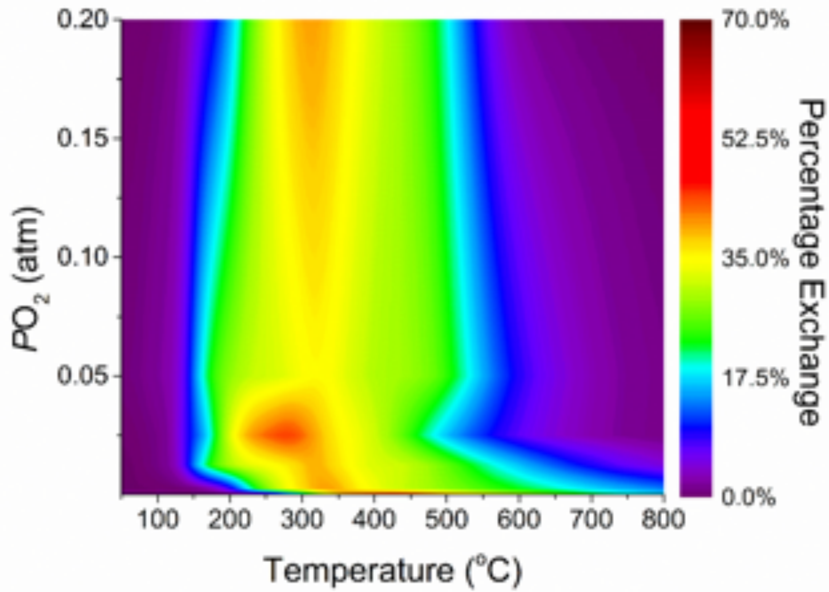
Water Exchange on LSCF vs LSCF-GDC Composite Cathodes

LSCF

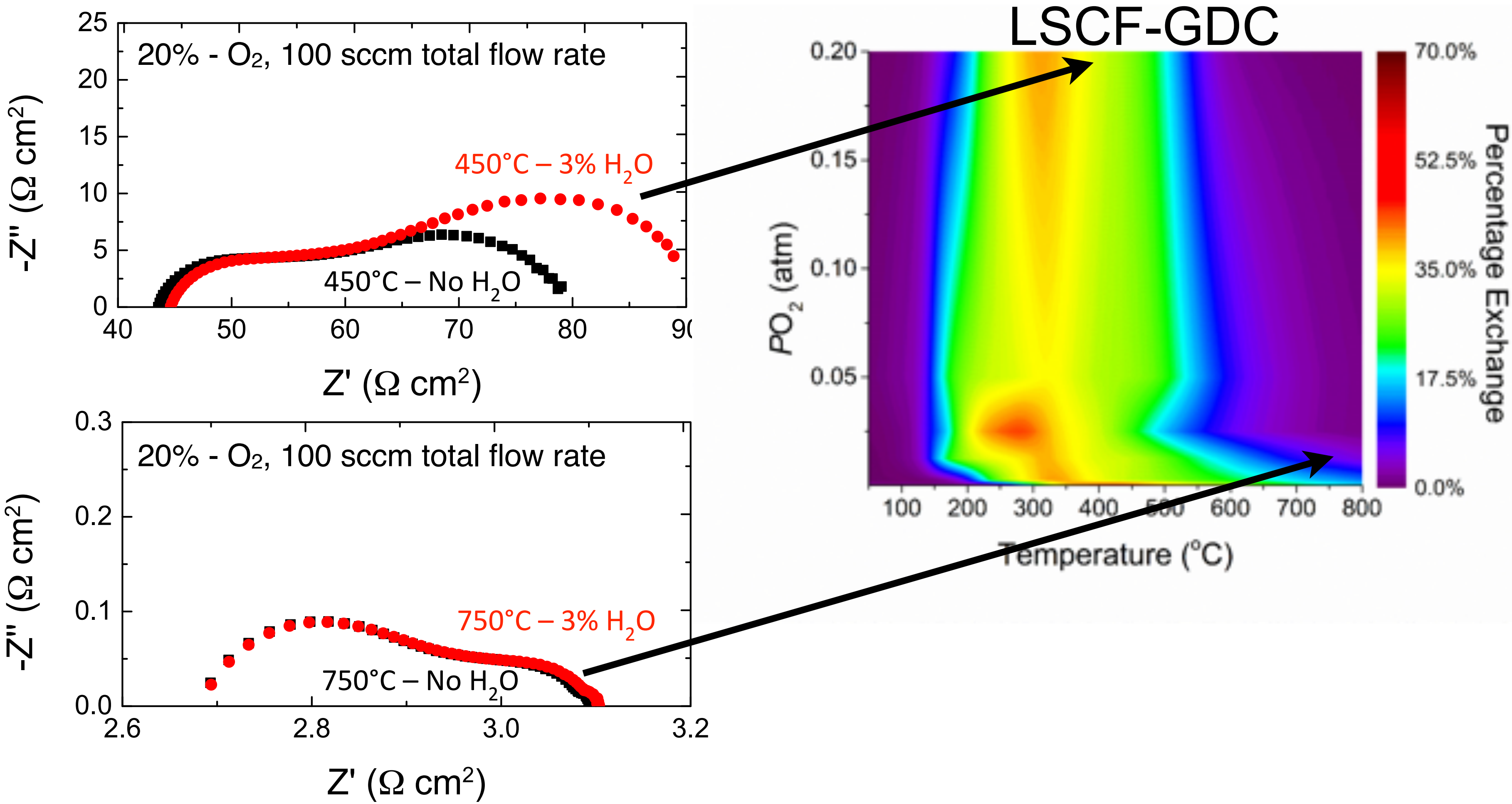


LSCF-GDC



- LSCF composite significantly broadens temperature range of water exchange dominance
- Demonstrating importance of TPBs and co-existence of O-dissociation and O-incorporation phases

Comparison of ISTPX with EIS for LSCF-GDC in H_2O



The presence of 3% H_2O effects the low frequency arc at 450ºC but not at 750ºC consistent with the results obtained from ISTPX.

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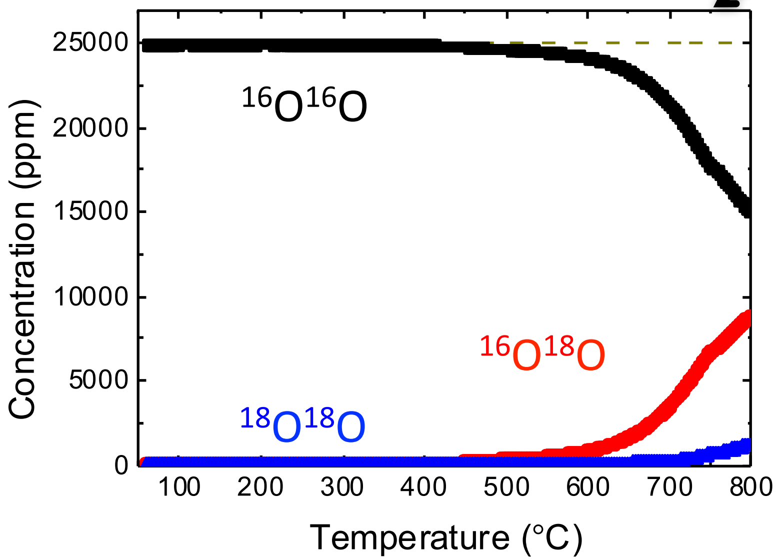
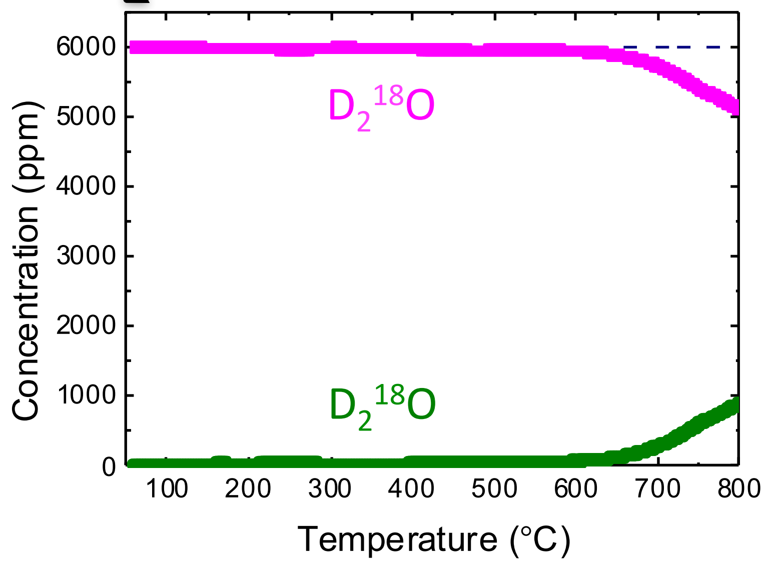
Comparison of LSM and Composite LSM-YSZ in D_2O

25000ppm O_2 and 6000ppm D_2O

LSM

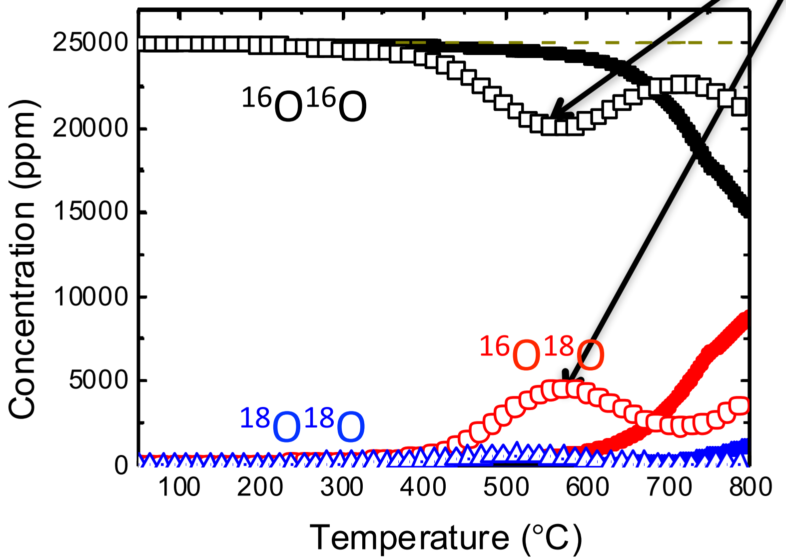


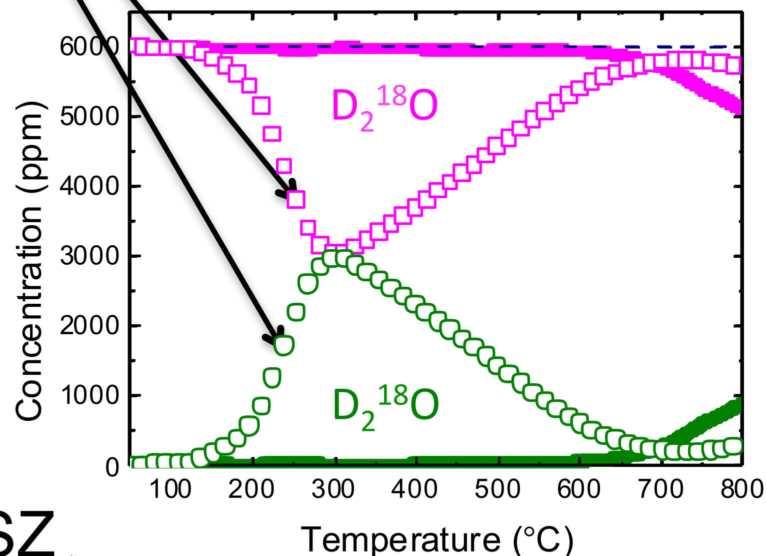


Comparison of LSM and Composite LSM-YSZ in D_2O

25000ppm O_2 and 6000ppm D_2O

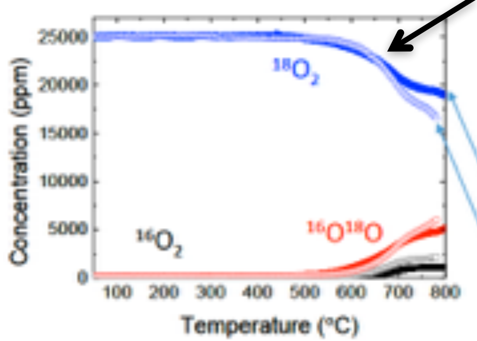
LSM-YSZ





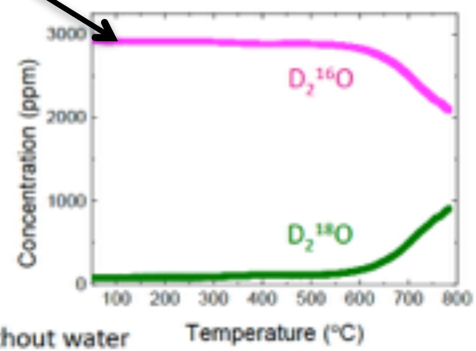
YSZ

Dramatic increase in composite exchange



without water

with water



Increased composite exchange not due to YSZ

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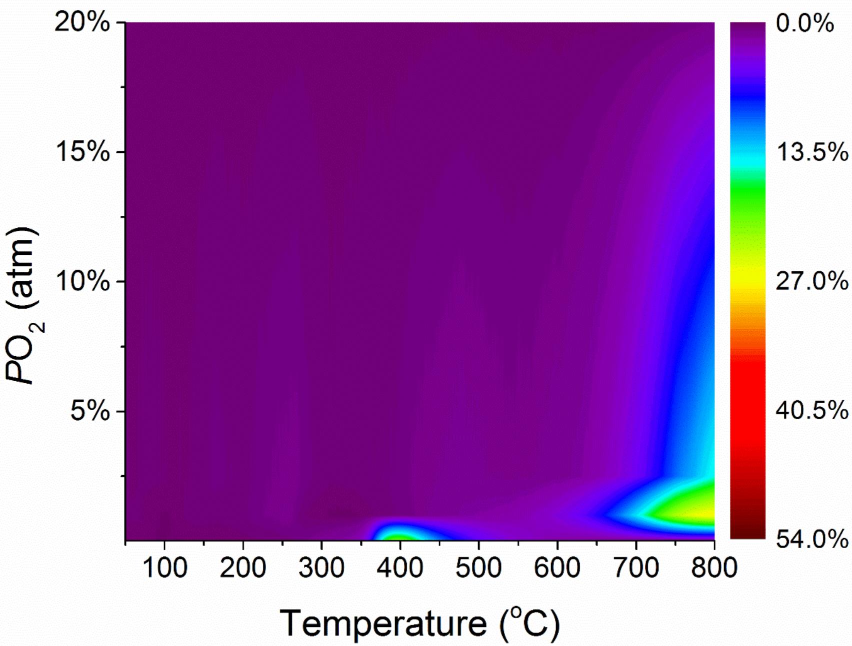
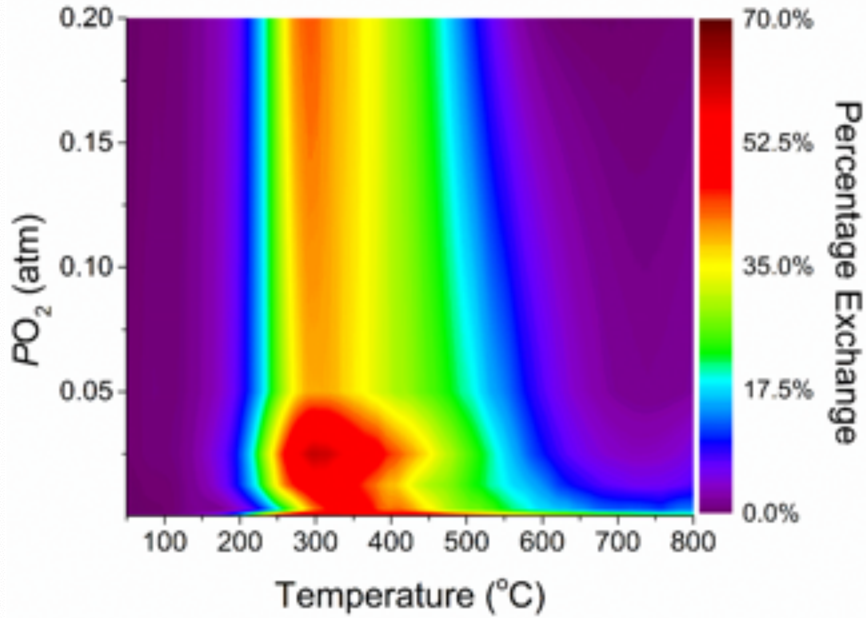
Water Exchange on LSM vs LSM-YSZ Composite Cathodes

LSM

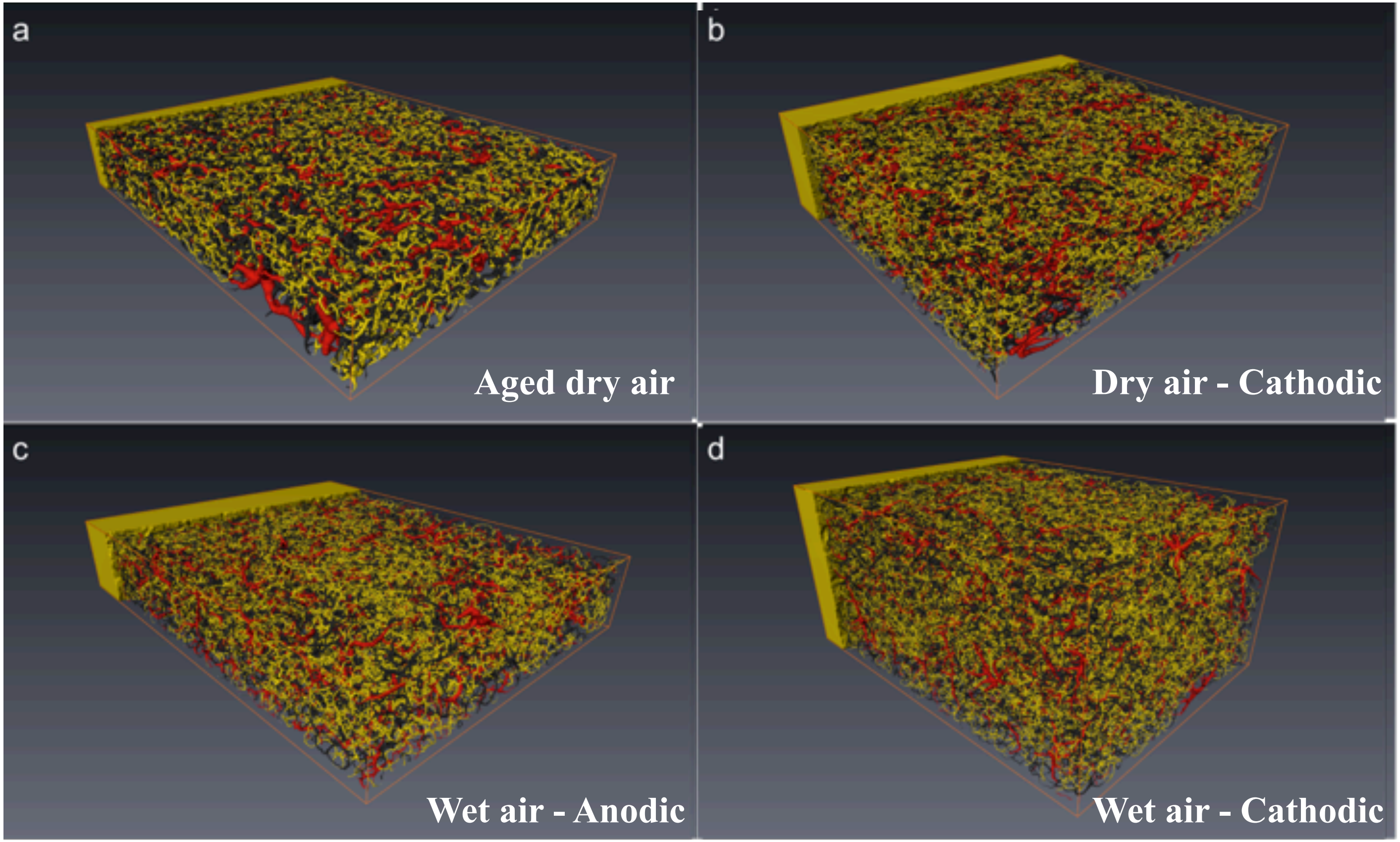


LSM-YSZ



- LSM-YSZ composite demonstrates much greater water exchange than LSM or YSZ at much lower temp
- Composite effect for LSM-YSZ much greater than for LSCF-GDC
- Demonstrating importance of TPBs and co-existence of O-dissociation and O-incorporation phases

H_2O Impact on LSM/YSZ Microstructural Change

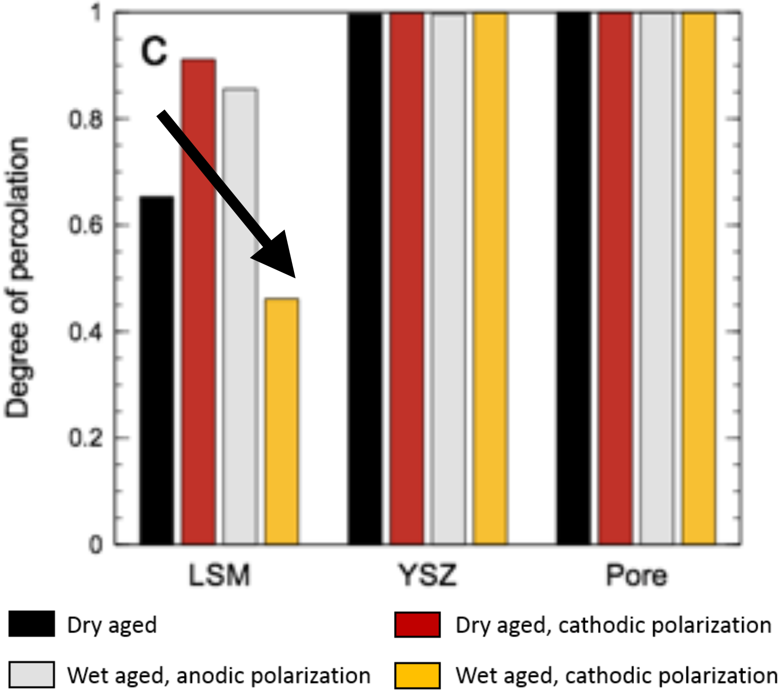


FIB/SEM reconstruction of LSM/YSZ cathodes aged at 800°C for 500 hrs in dry and wet (3% H_2O) air with and without polarization

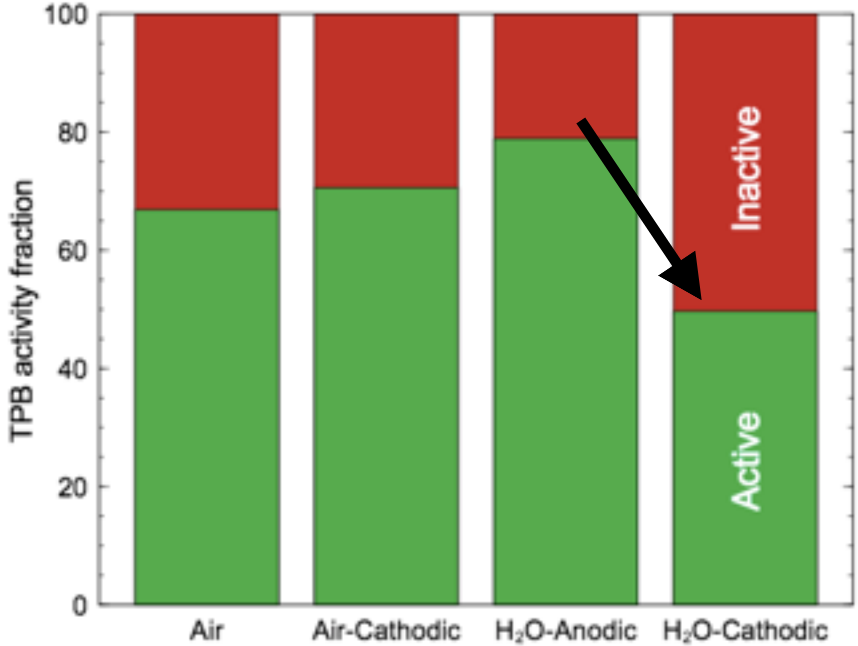
Skeletonization to determine microstructural connectivity

H_2O Impact on LSM/YSZ Microstructural Change

Impact on phase connectivity



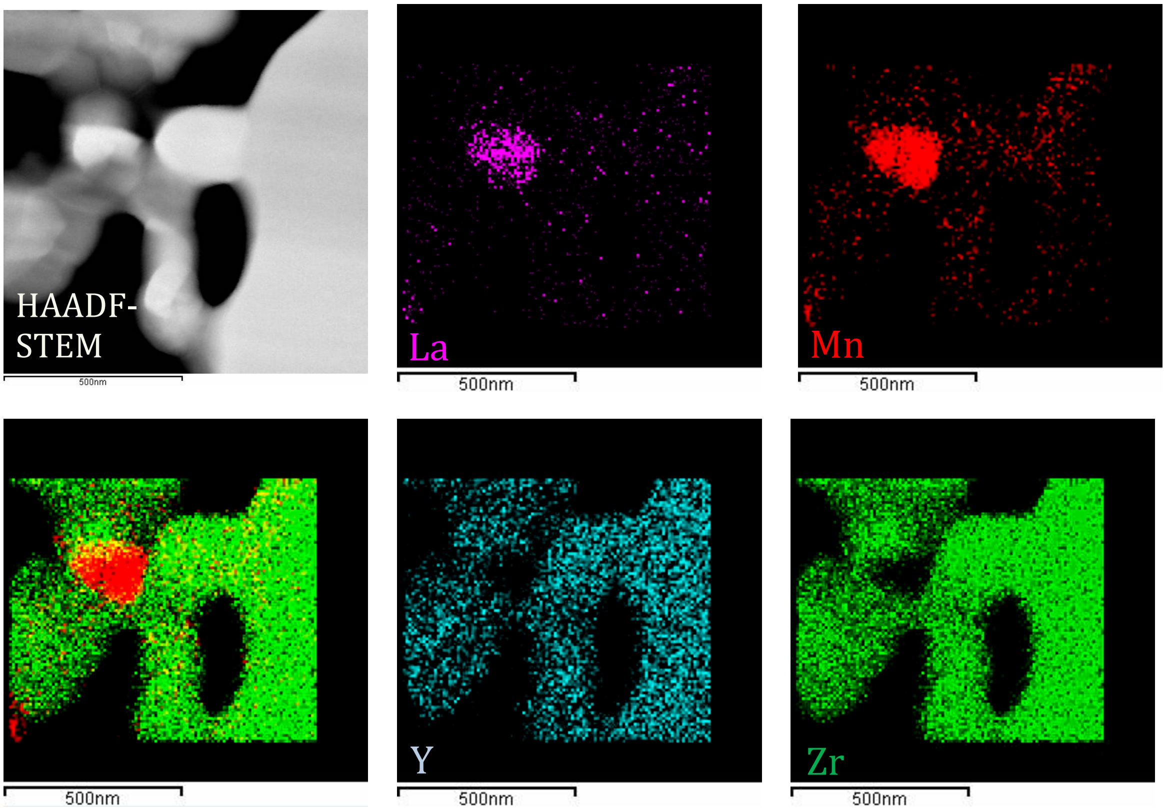
Impact on effective TPB activity



- H_2O under cathodic polarization decreases LSM phase connectivity *(ohmic impedance)*
- H_2O under cathodic polarization decreases fraction of connected “active” TPBs *(non-ohmic impedance)*

H_2O Impact on LSM/YSZ Compositional Change

STEM-EDS of symmetric cell aged at 800°C for 500 hrs with one side in dry air and the other in air with 3% H_2O



STEM-EDS maps of Aged-dry SOFC cathode near electrolyte interface

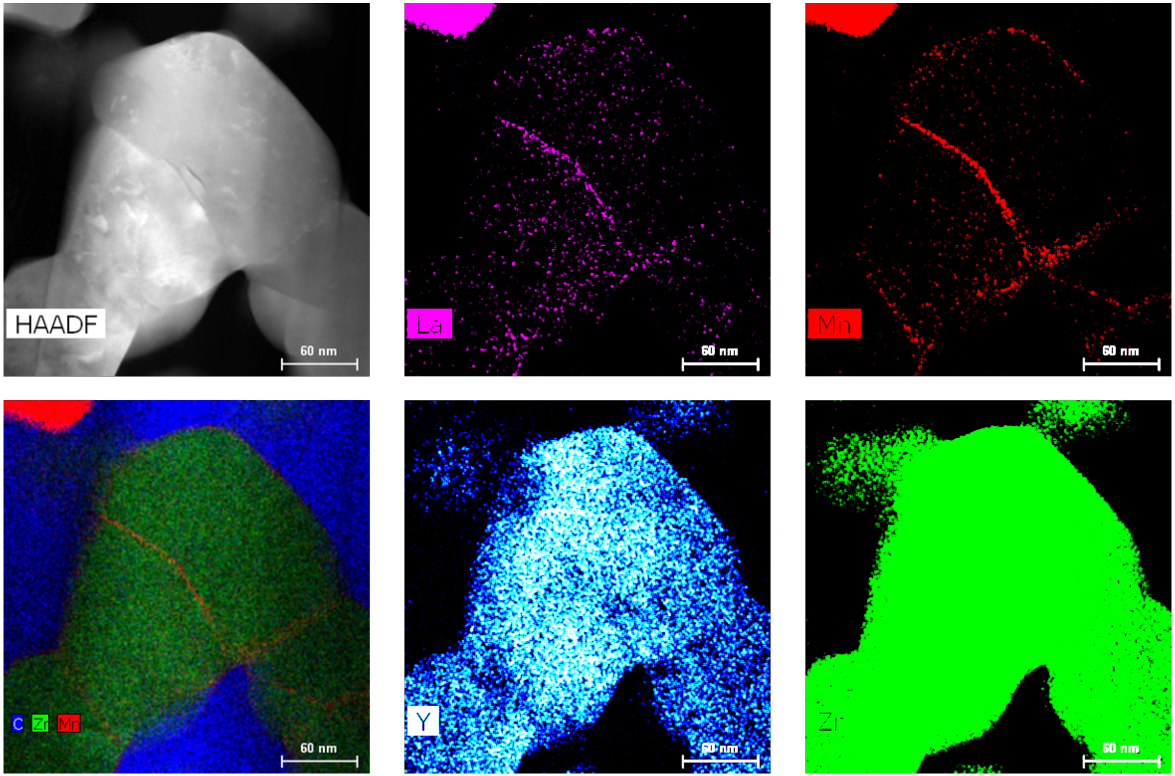
- Still distinct particles of LSM and YSZ

- Perhaps more Mn distributed throughout YSZ

While morphological changes in dry air, no observed chemical change

H_2O Impact on LSM/YSZ Compositional Change

STEM-EDS of symmetric cell aged at 800°C for 500 hrs
with one side in dry air and the other in air with 3% H_2O



STEM-EDS maps Aged-H_2O SOFC cathode

- Distinct particles of LSM and YSZ
- Segregation of La and Mn at YSZ grain boundaries
- Sr is not localized at boundaries

Observed segregation of La and Mn to YSZ grain boundaries for wet aged LSM/YSZ

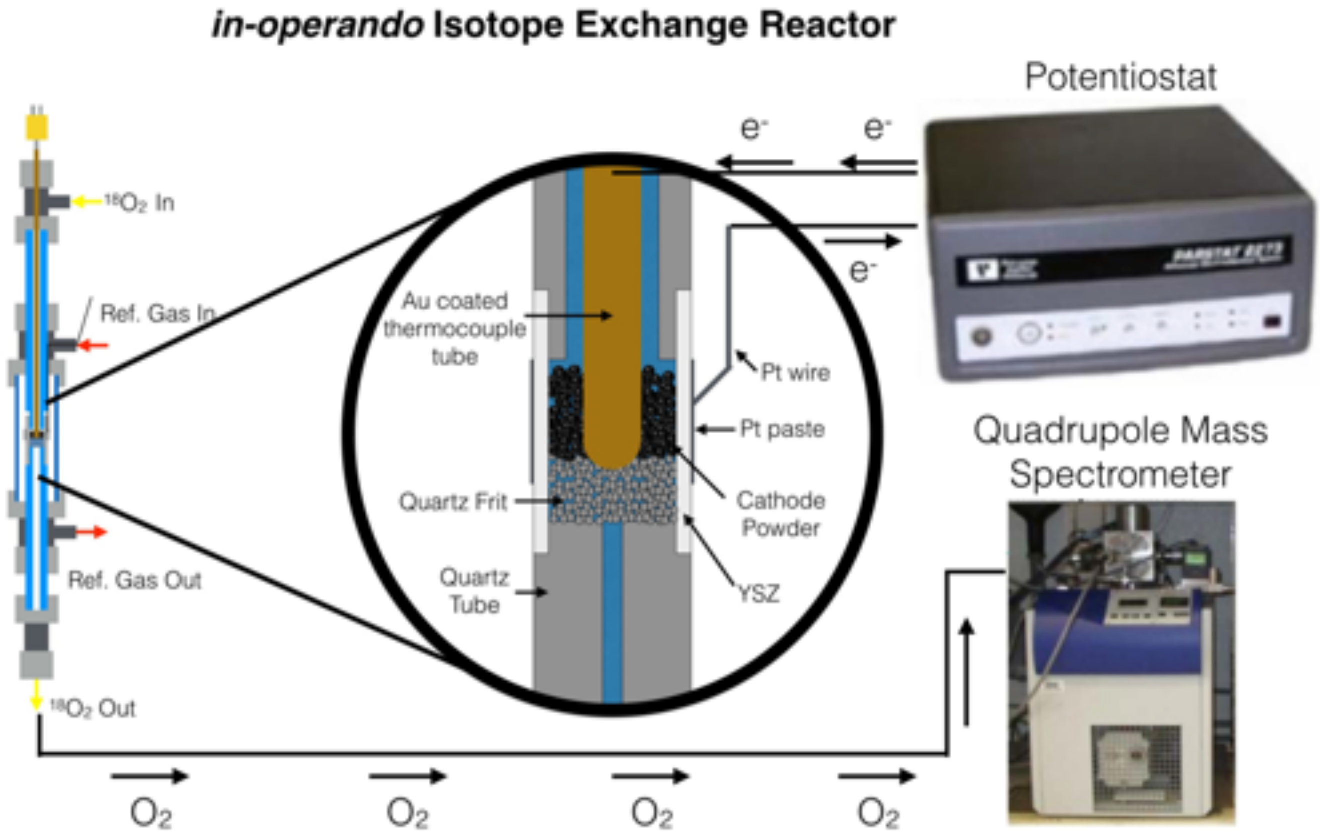
Technical Approach - Phase 1

Task 1 - Project Management and Planning

- Project Management, planning and reporting in accordance with the Project Management Plan to meet all technical, schedule and budget objectives and requirements

Technical Approach - Phase 1

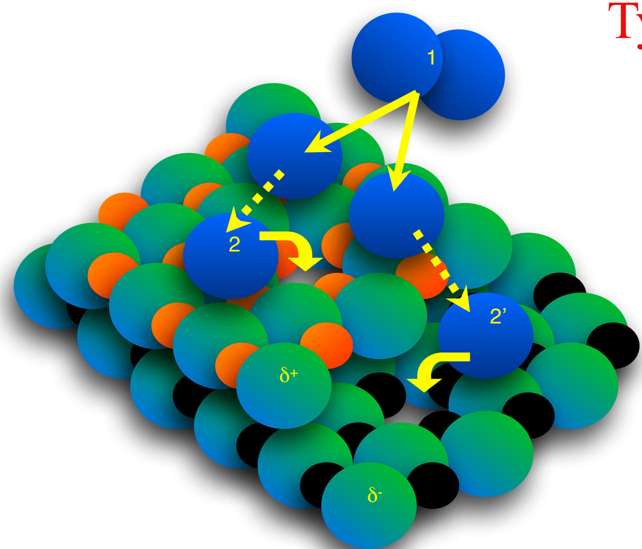
Task 2 - Develop *In-Operando* Apparatus for Oxygen Isotope Exchange of Cathode Materials

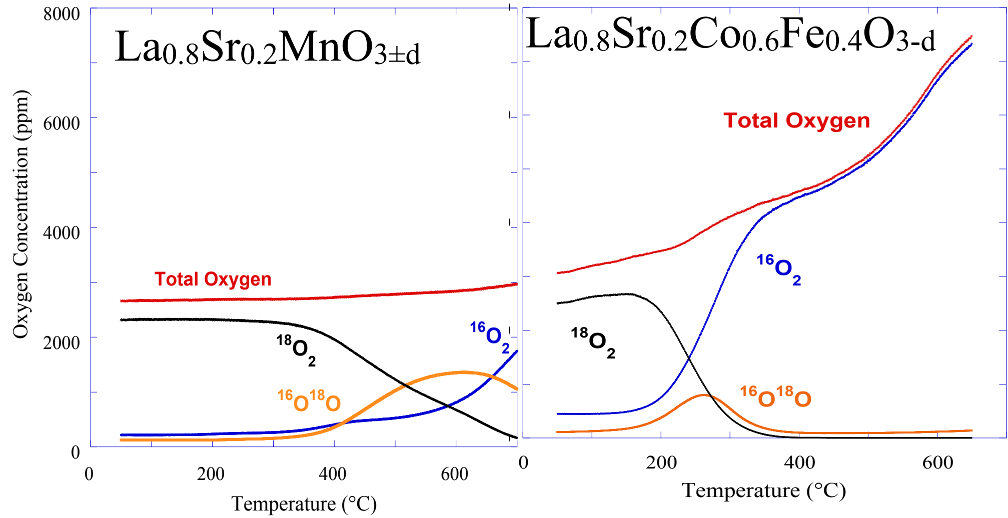


- Convert *in-situ* heterogeneous catalysis set-up to *in-operando* reactor to measure cathode ORR under applied bias

Technical Approach - Phase 1

Task 3 - Determine Effect of A and B-site stoichiometry and Dopant Type on Cathode ORR





- Use our specially designed system to study the changes in ORR kinetics under cathodic polarization for a wide range of A/B site ratios in LSM and LSCF, as well as dopant types (e.g., Ca for Sr or Mn for Co/Fe), and ratio of LSM and LSCF to YSZ and GDC.
- Materials investigated will be both commercial and laboratory-synthesized compositions, in order to find the most suitable composition for most stable and fastest ORR.

Project Objectives

1. Develop *in-operando* apparatus for the study of SOFC cathode oxygen surface exchange properties, under operating conditions of applied voltage / current.
2. Determine surface exchange mechanisms and coefficients using *in-operando* ^{18}O-isotope exchange of LSM and LSCF powders, and their composites with YSZ and GDC.