SOFC Cathode ORR Mechanisms Under Real World Conditions

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University of Maryland Energy Research Center
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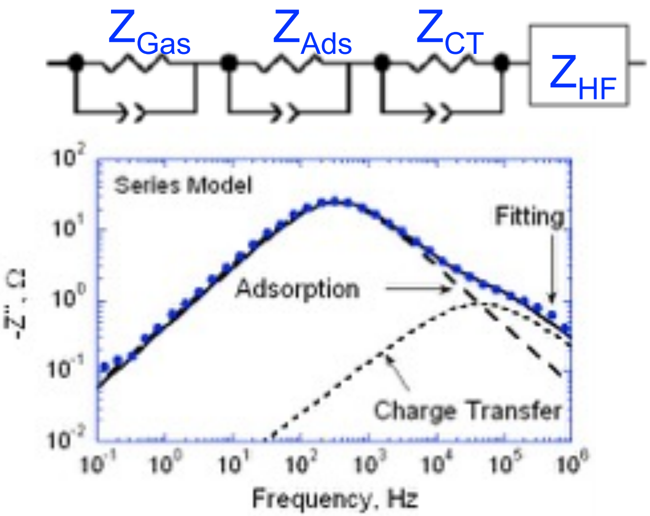
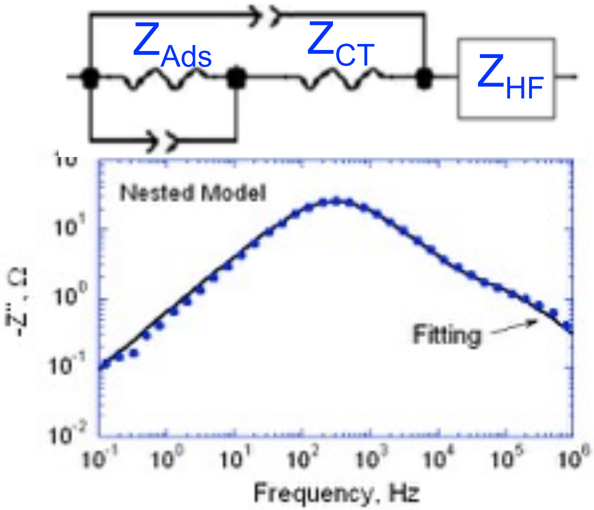
Limitation of ORR from EIS

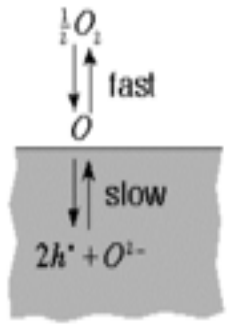




Same!

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

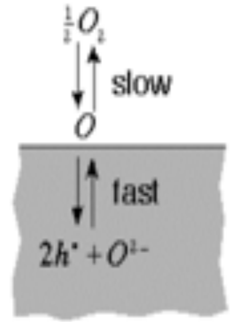
Oxygen exchange limited by vacancy exchange



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

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

Oxygen exchange limited by dissociative adsorption



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

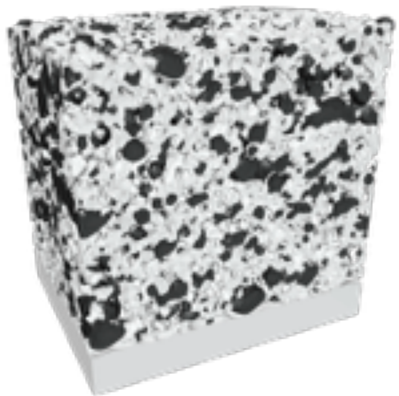
$$r_{exch} = k_1\left(P_{O_2}\right)^{\frac{1}{2}}$$

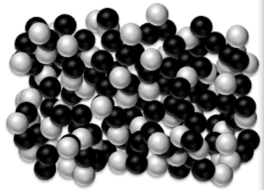
Same!

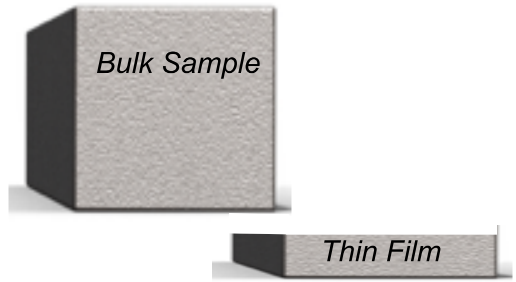
***Stuart Adler**, University of Washington*

Need to combine multiple techniques to determine mechanism

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 (developing *in-operando*)	• OCP	• Small current perturbation	• OCP & bias current
Surface Science Capability	• Limited	• Limited	• Limited	• Amenable	• Multiple approaches

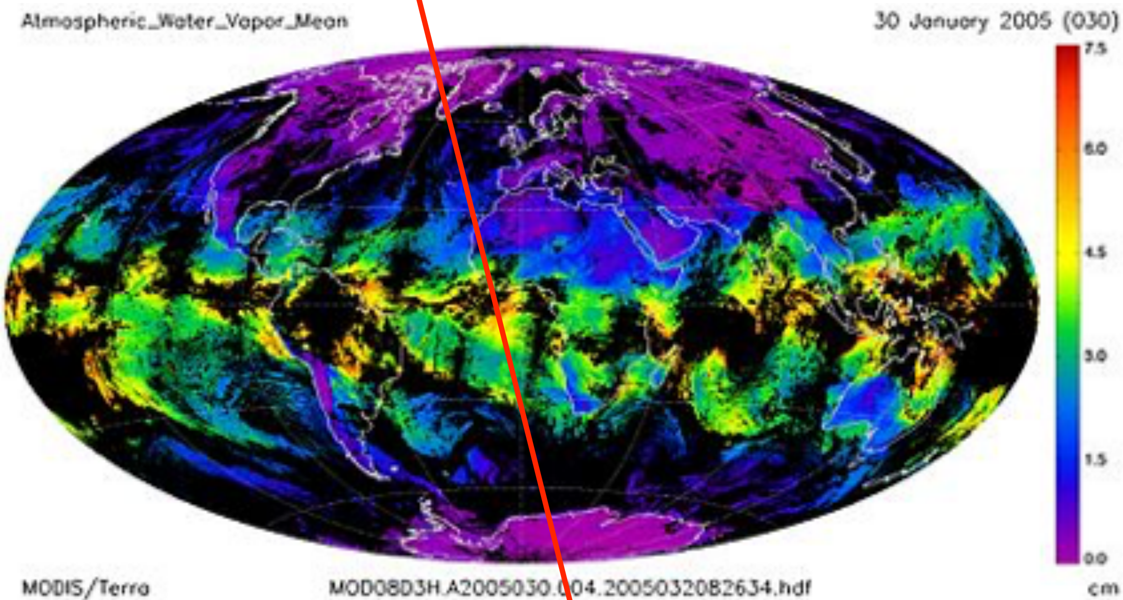
Experimental vs. Real Ambient Air

Linde Synthetic Air

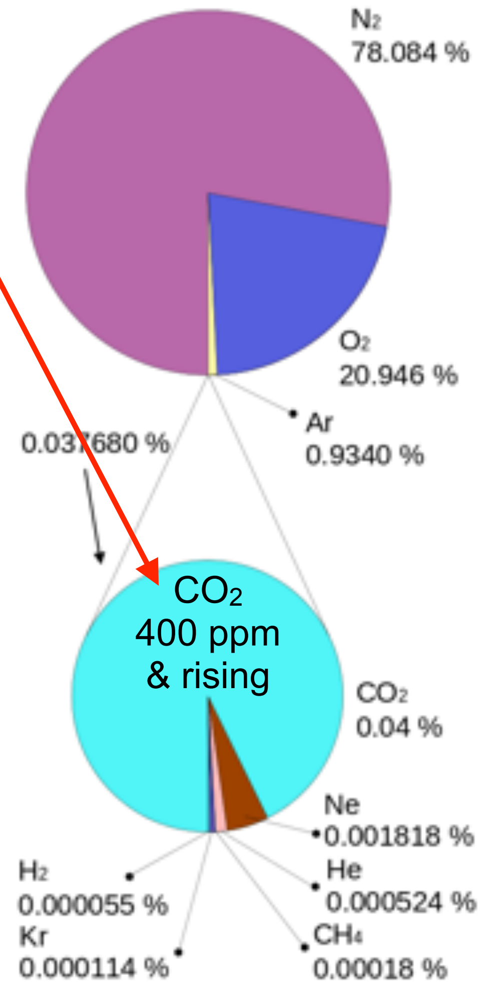
Purity ≥ 99.99%, H_2O ≤5 ppm, No analysis of CO_2, HC's, etc

Purity ≥ 99.999%, H_2O ≤5 ppm & C_nH_m ≤1 ppm, No analysis of CO_2, etc

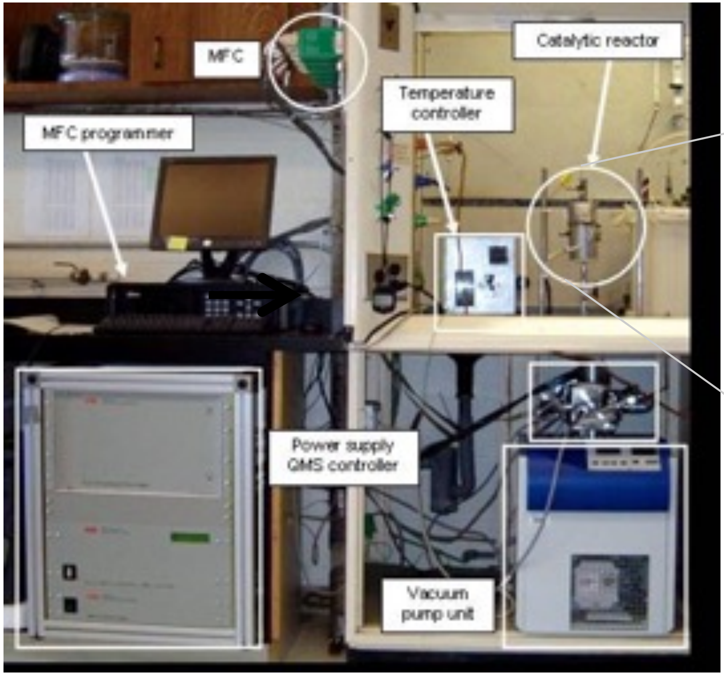
Purity ≥ 99.9995%, H_2O ≤2 ppm C_nH_m ≤0.1 ppm CO ≤1 ppm CO_2 ≤1 ppm

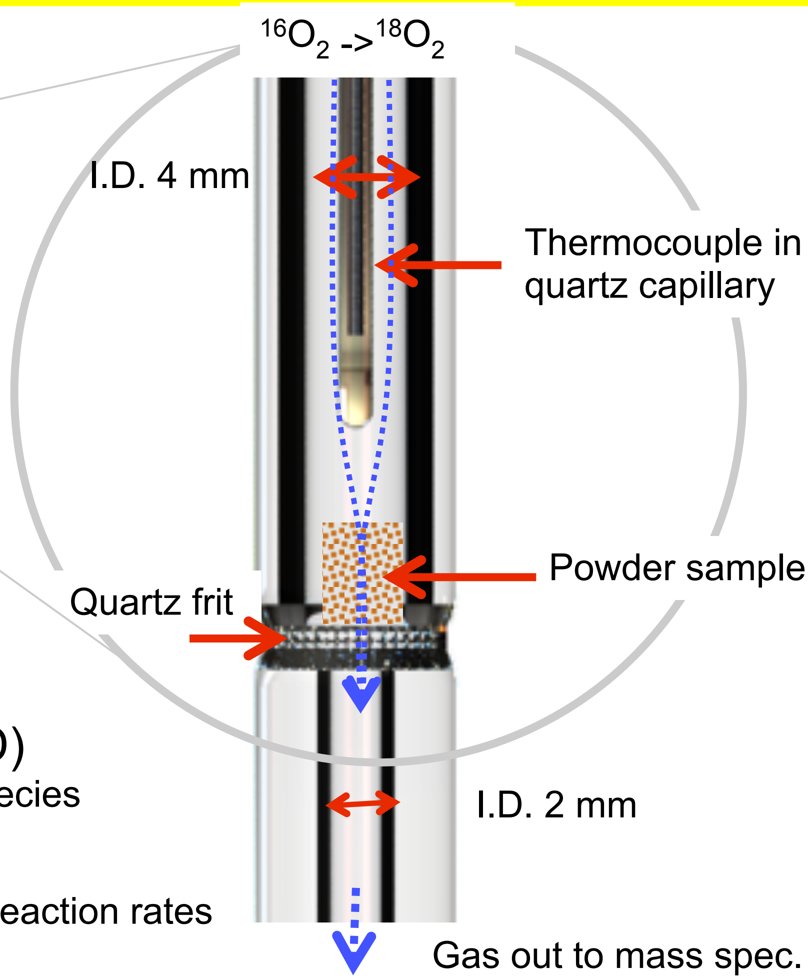


Ambient H_2O 0.001% - 5%
10 ppm to <u>50,000 ppm</u>



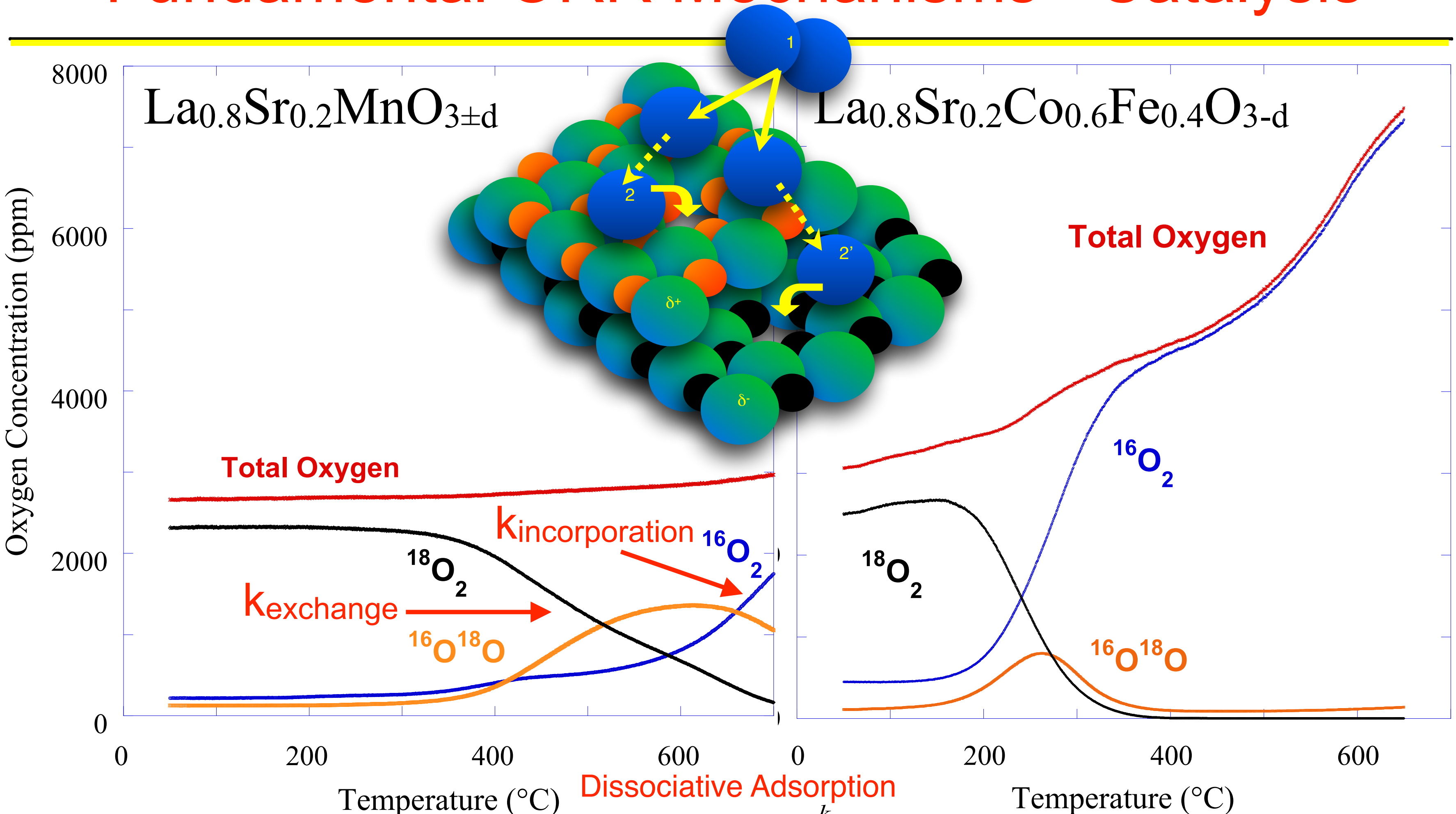
Fundamental ORR Mechanisms - Catalysis





- 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 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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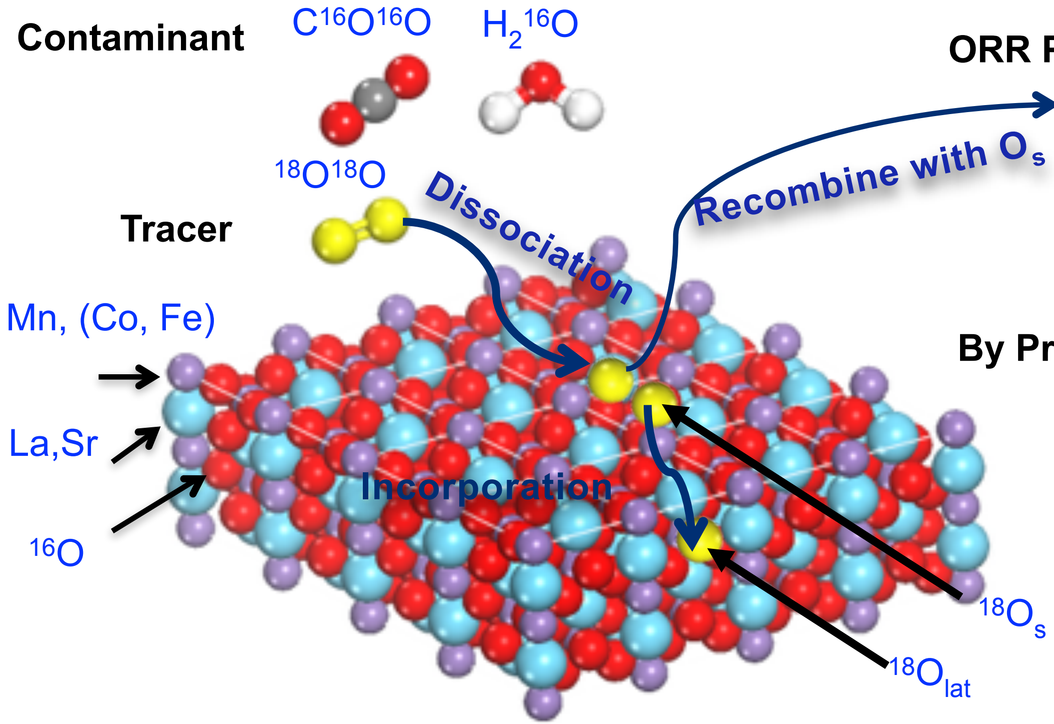
ORR Reaction Mechanisms in Presence of H_2O and CO_2

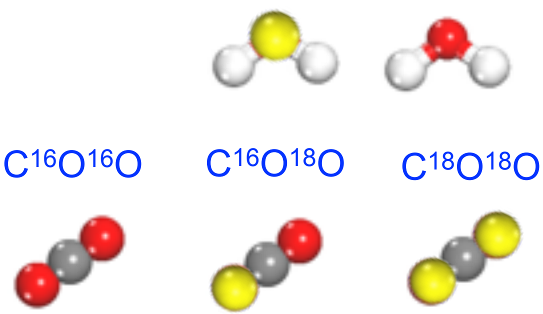
In situ Isotope Exchange (IIE)



ORR Products

Provides information about dissociated $^{18}O_{(s)}$

By Products

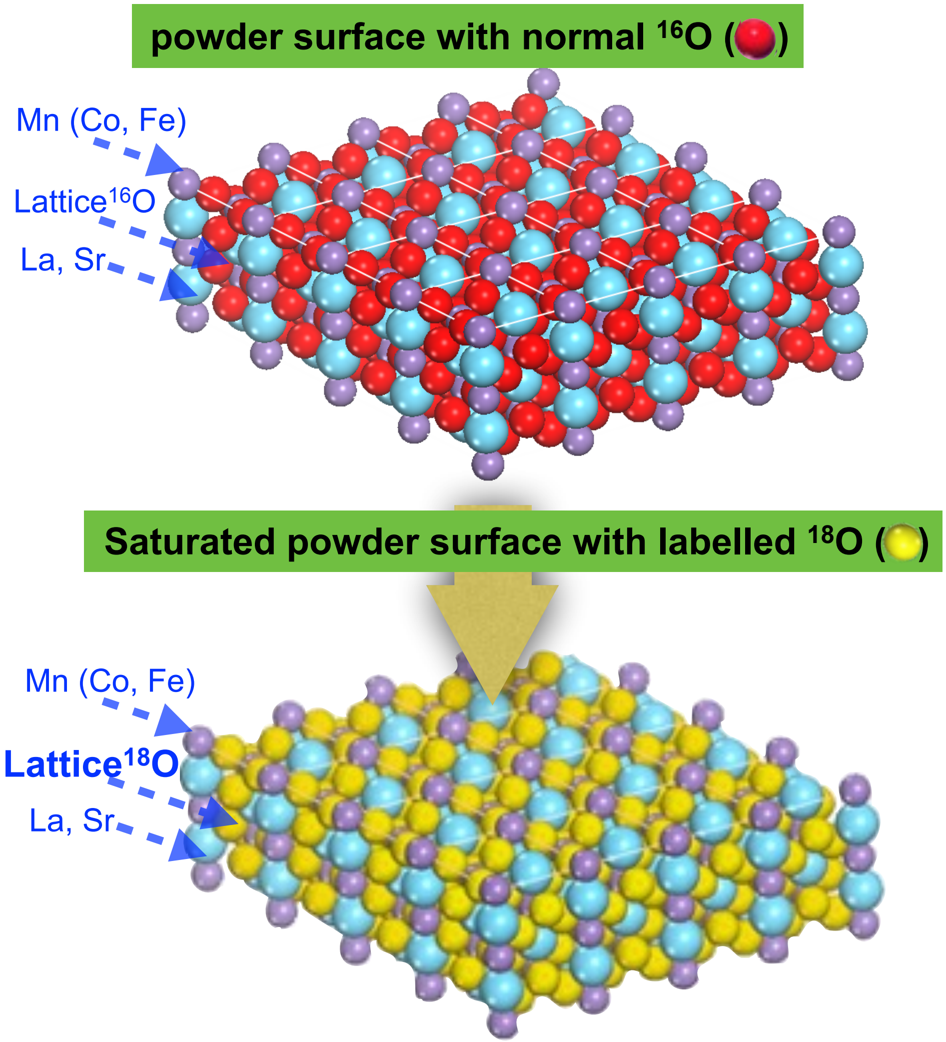


Provide information about surface reaction with contaminants

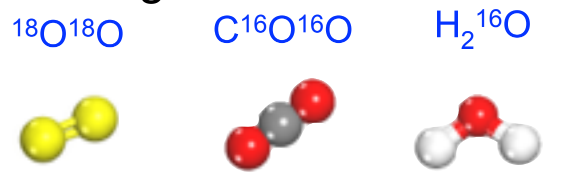
$$S + 1/2O_2 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} O_{ads}$$

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

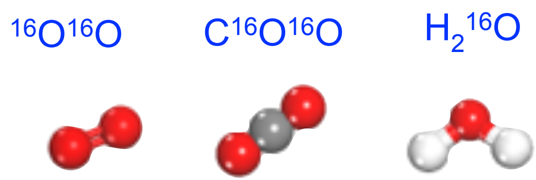
Isotope Saturated Temperature Programmed Exchange (ISTPX)



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



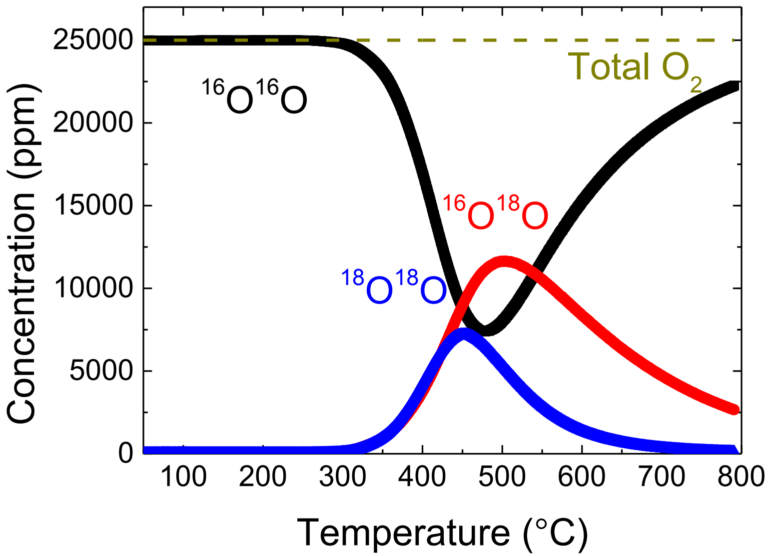
ISTPX - Probes competitive ORR in presence of contaminants on ^{18}O-labeled cathode surface



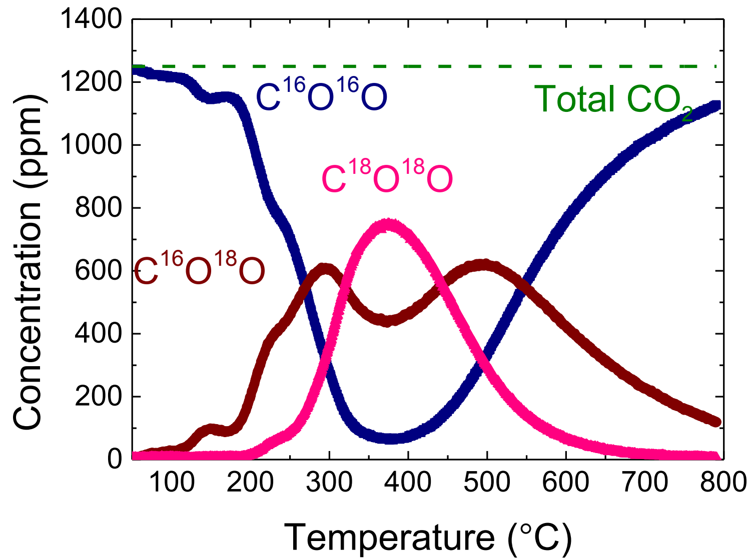
Allows experiment in ambient P_{O2} without saturating mass spectrometer

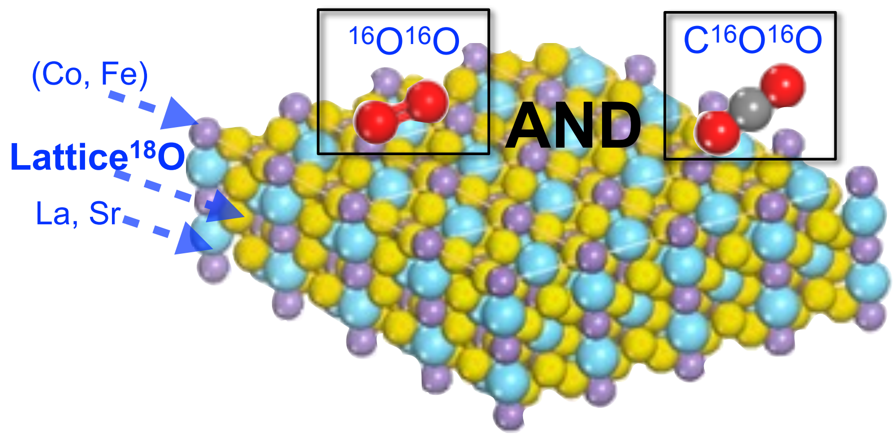
Interaction Between O_2, CO_2 and LSCF Surface

$^{16}O_2$ exchange with lattice ^{18}O



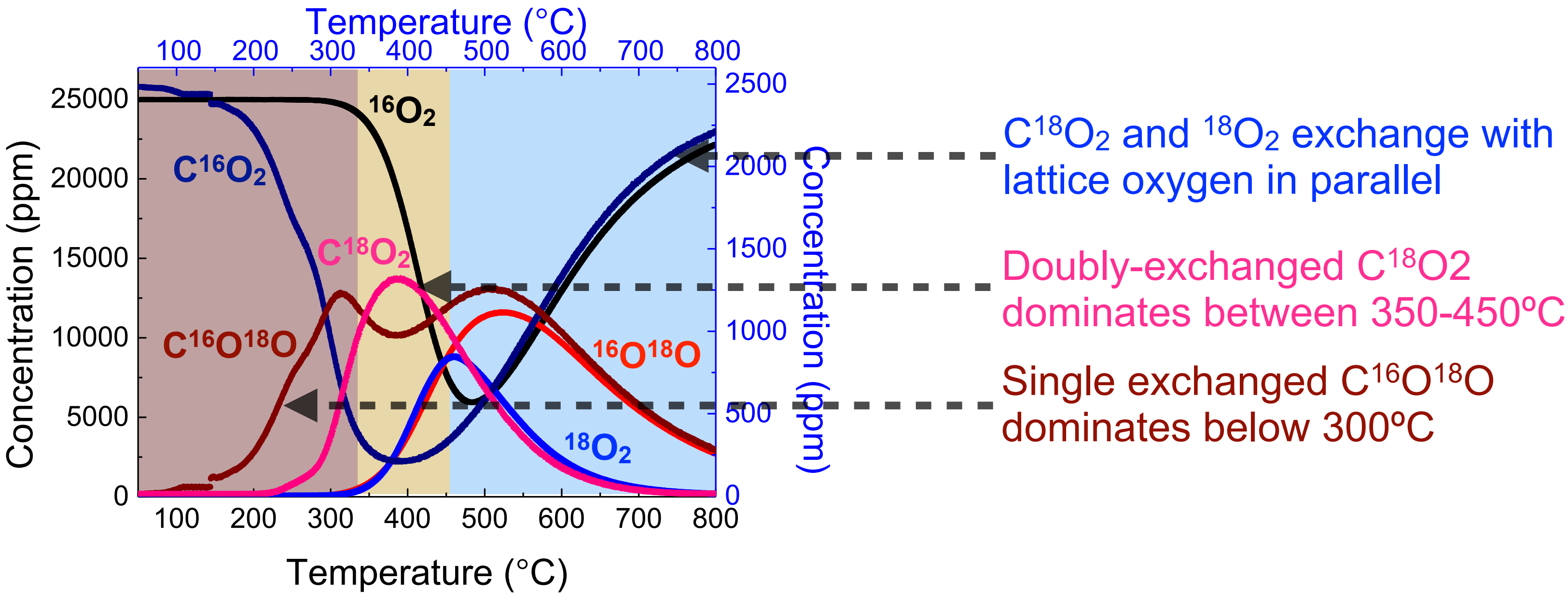
$C^{16}O_2$ exchange with lattice ^{18}O





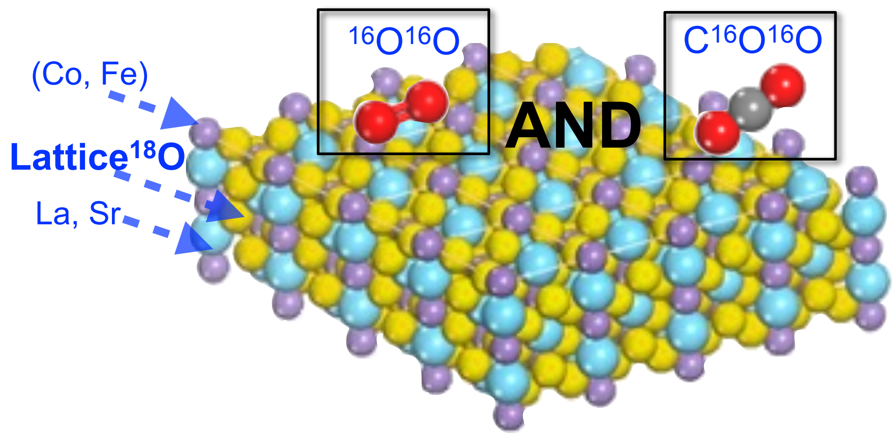
Interaction Between O_2, CO_2 and LSCF Surface

$^{16}O_2$ and $C^{16}O_2$ co-exchanged with lattice ^{18}O



CO_2 exchanges preferentially with lattice at lower temperature:

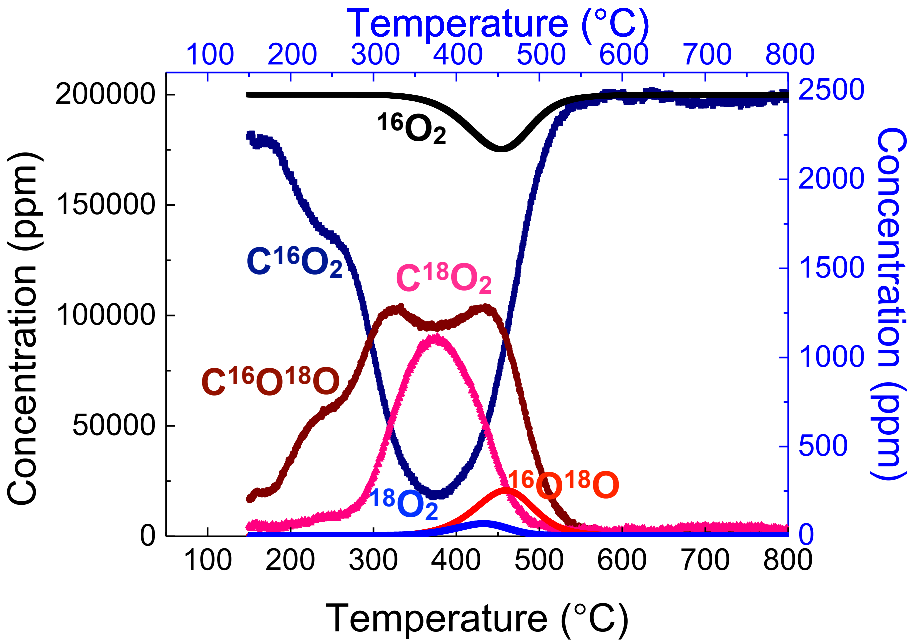
- initially exchanging only single “O” (atomic)
- then both “O” (molecular)
- then at same rate as O_2



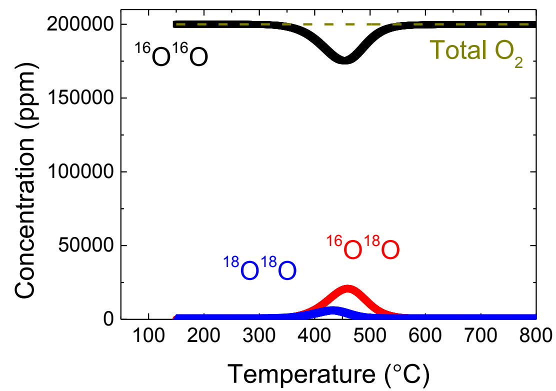
ISTPX of LSCF with 2500ppm CO_2 at ambient PO_2

Competitive exchange of CO_2 vs O_2 with lattice ^{18}O at ambient PO_2

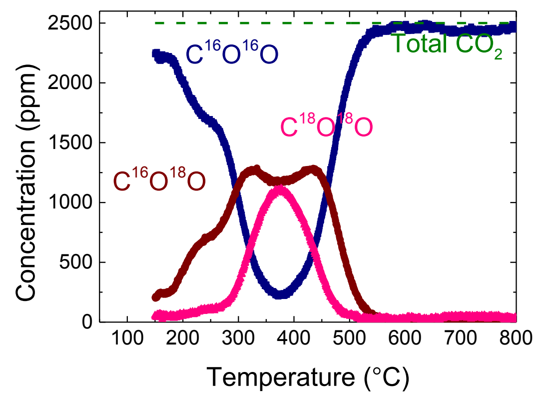
CO_2 and O_2 exchange with lattice ^{18}O in 20% O_2



O_2 exchange with lattice ^{18}O



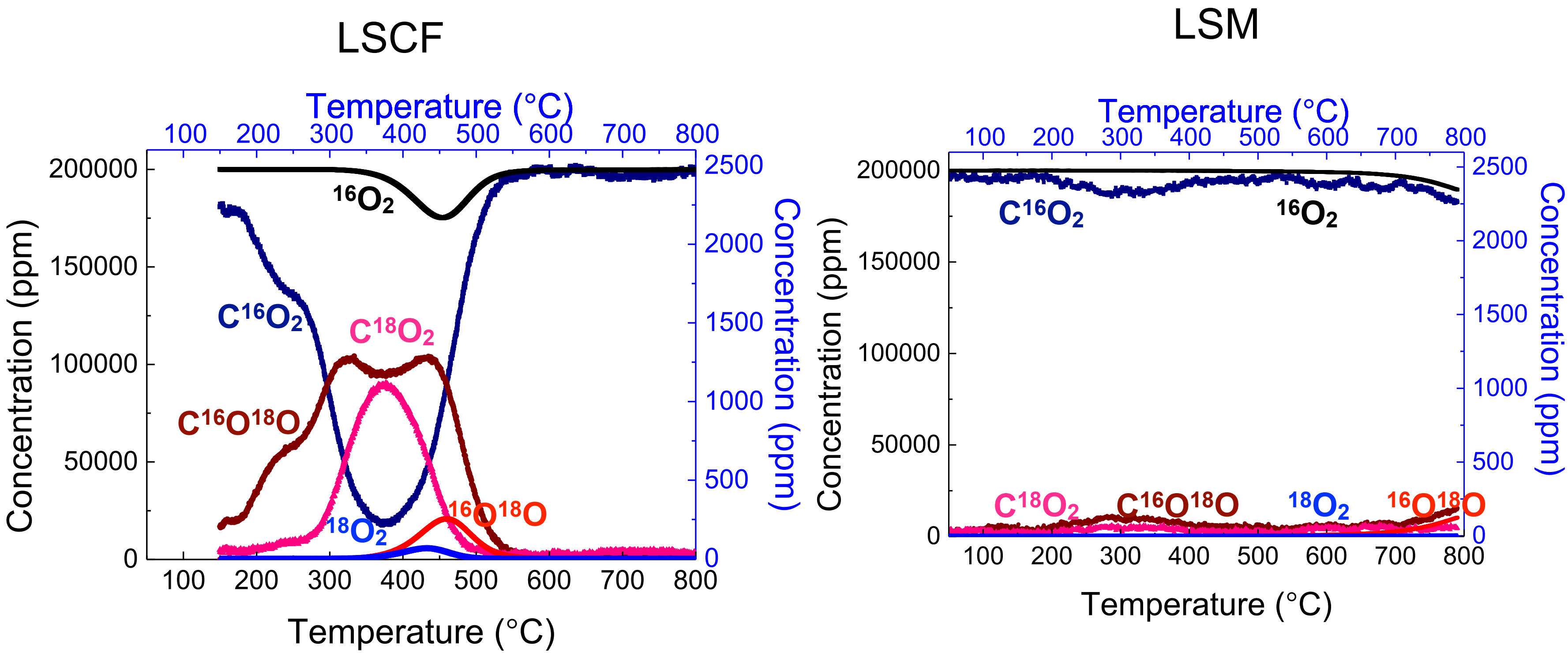
CO_2 exchange with lattice ^{18}O



CO_2 exchanges preferentially even at ambient PO_2

ISTPX of LSCF and LSM with 2500ppm CO_2 at ambient PO_2

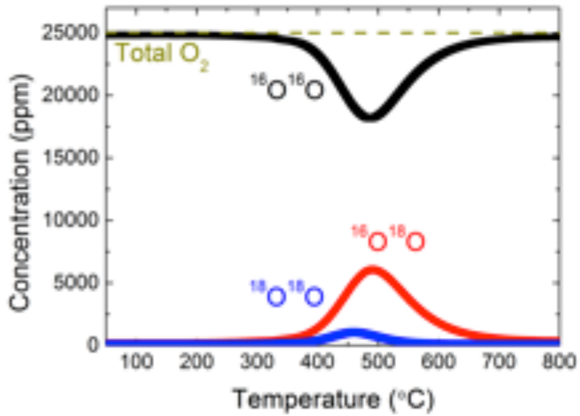
CO_2 and O_2 exchange with lattice ^{18}O in 20% O_2



LSM also has significant CO_2 exchange at low PO_2.
However, for both as PO_2 increases relative CO_2 exchange decreases.

ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

O_2 exchange with lattice ^{18}O



Mass of:

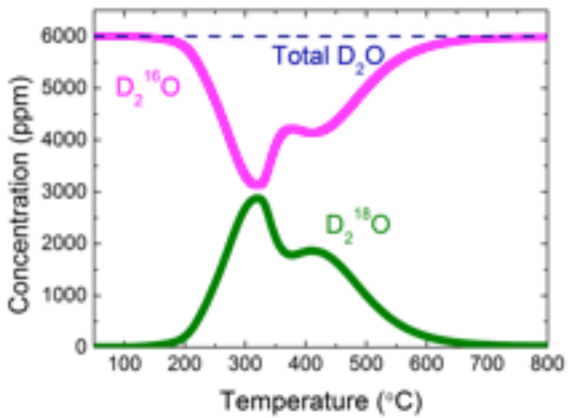
$^{18}O = 18$

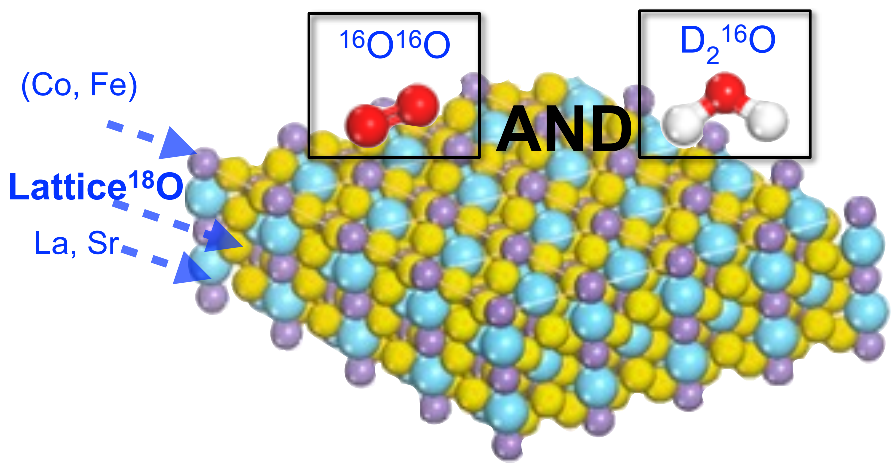
$H_2{}^{16}O = 18$

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

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

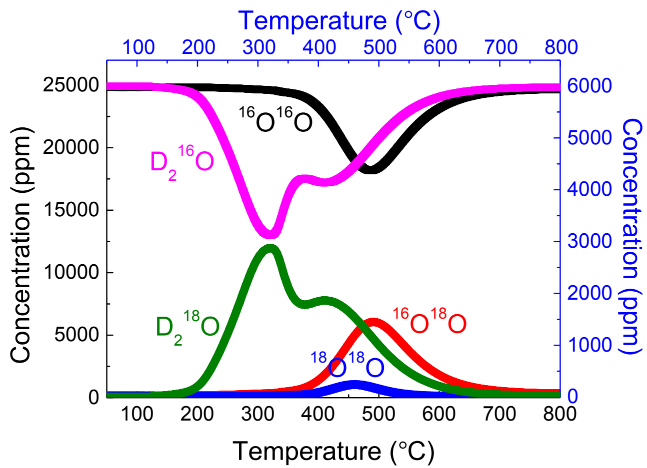
D_2O exchange with lattice ^{18}O

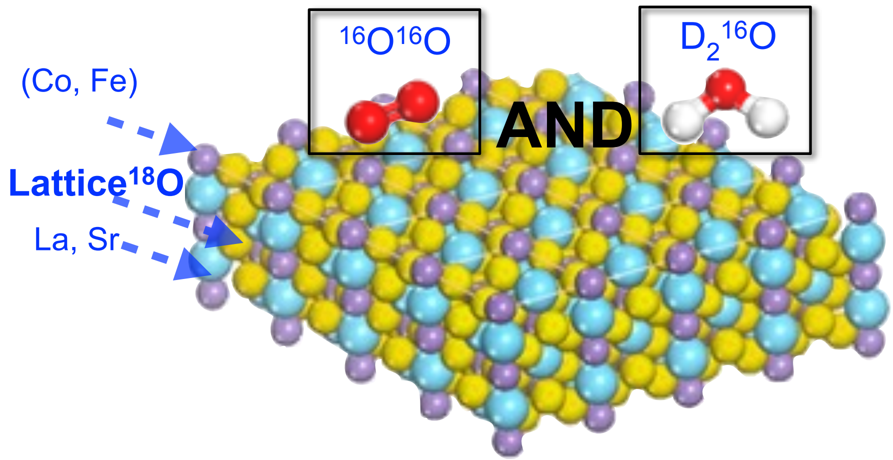




ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

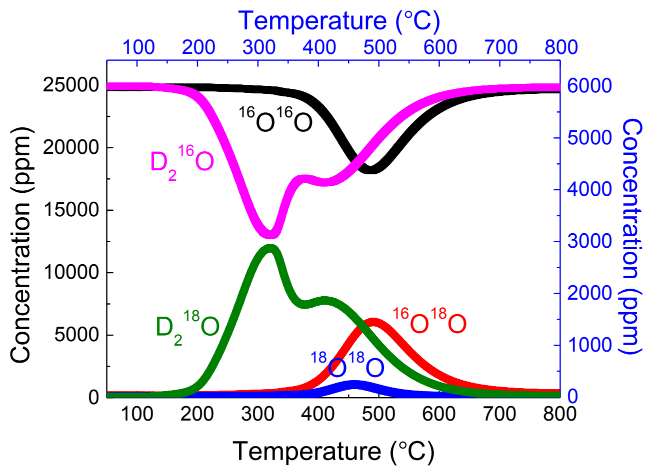
D₂O and O₂ exchange with lattice ¹⁸O





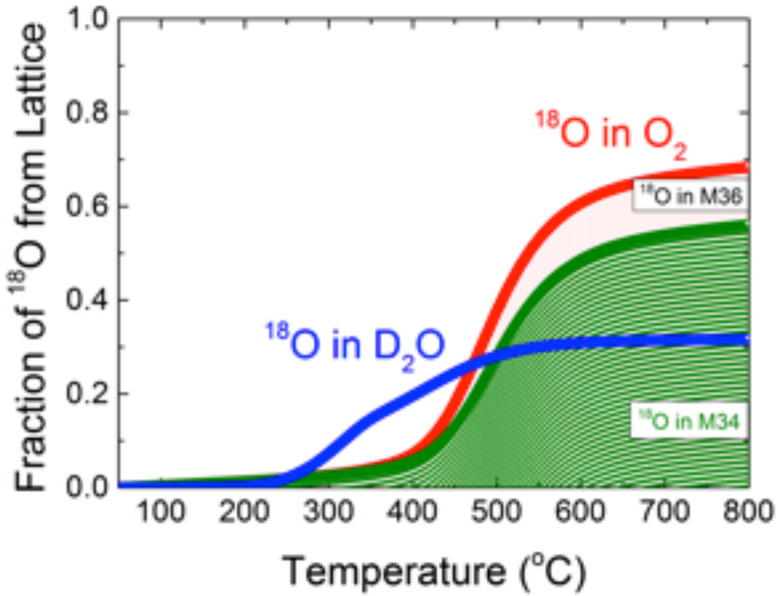
ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

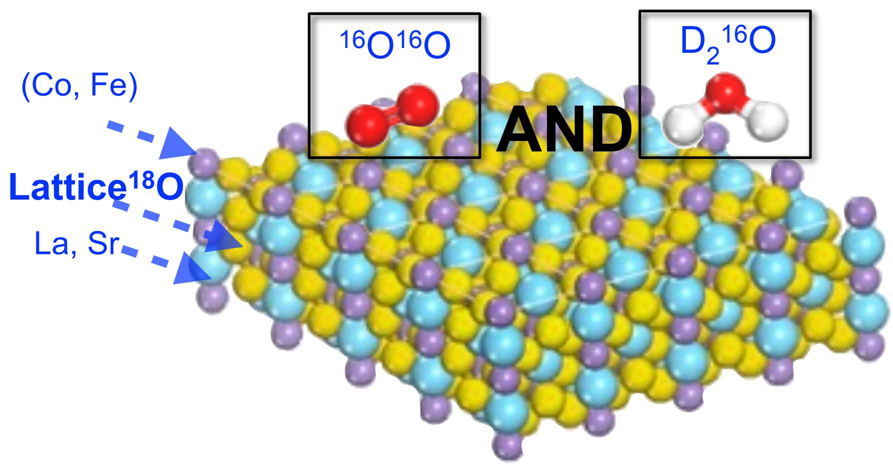
D₂O and O₂ exchange with lattice ¹⁸O



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

Accumulated Isotopic Fraction exchanged from ^{18}O LSCF





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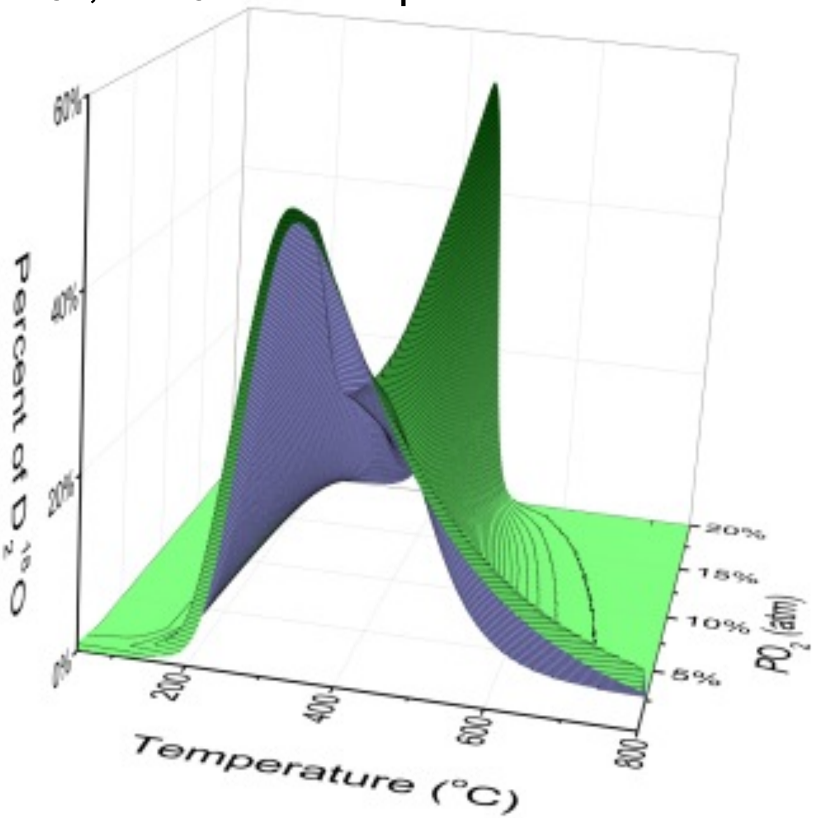
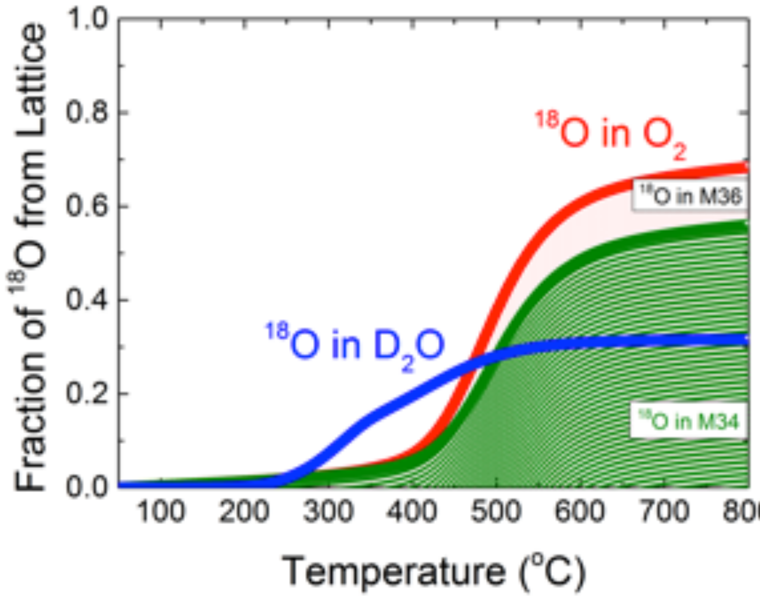
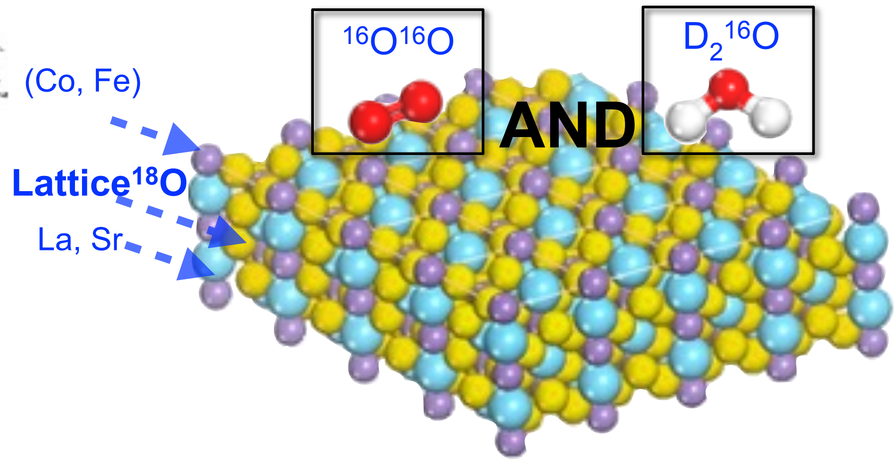
Temperature and PO_2 Dependence of LSCF in D_2O

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



Accumulated Isotopic Fraction exchanged from ^{18}O LSCF





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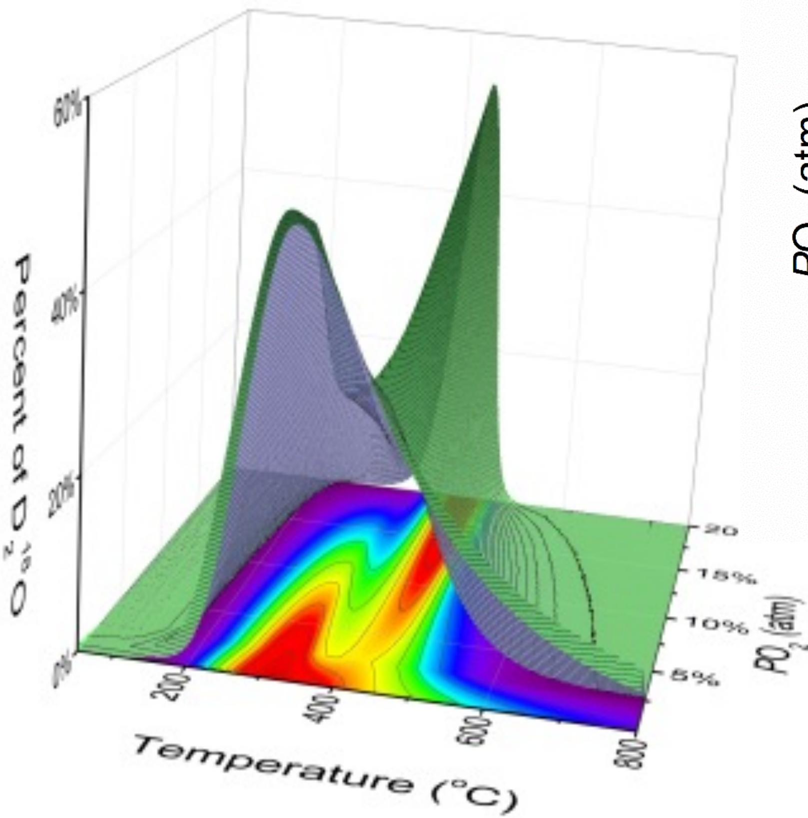
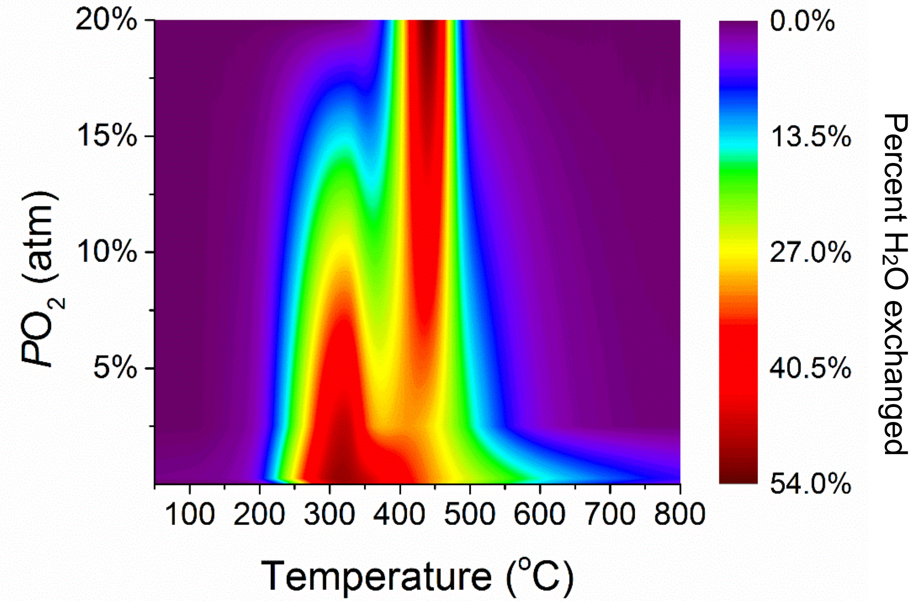
Temperature and PO_2 Dependence of LSCF in D_2O

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 can now map out H_2O and CO_2 impacts on ORR as function of P_{O2}, temperature, and contaminant concentration

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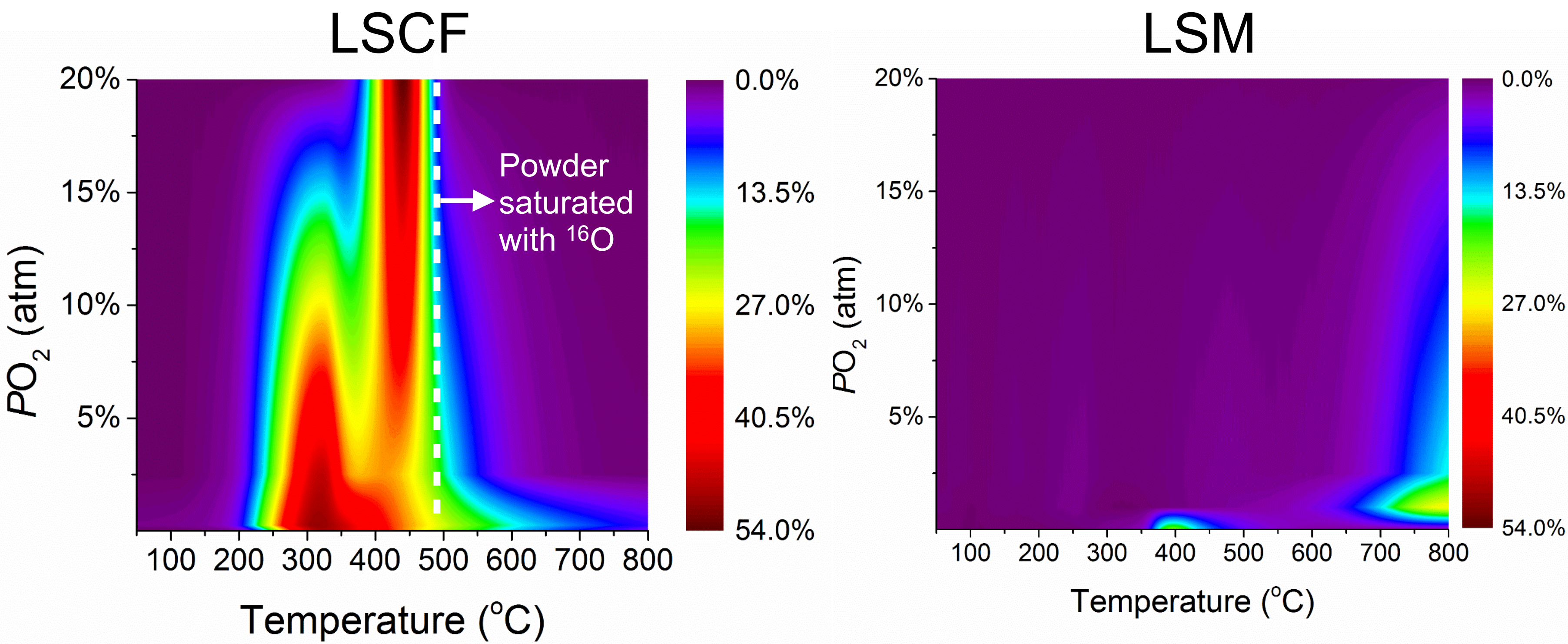
Comparison of LSCF and LSM Temp-PO_2 Dependence in D_2O



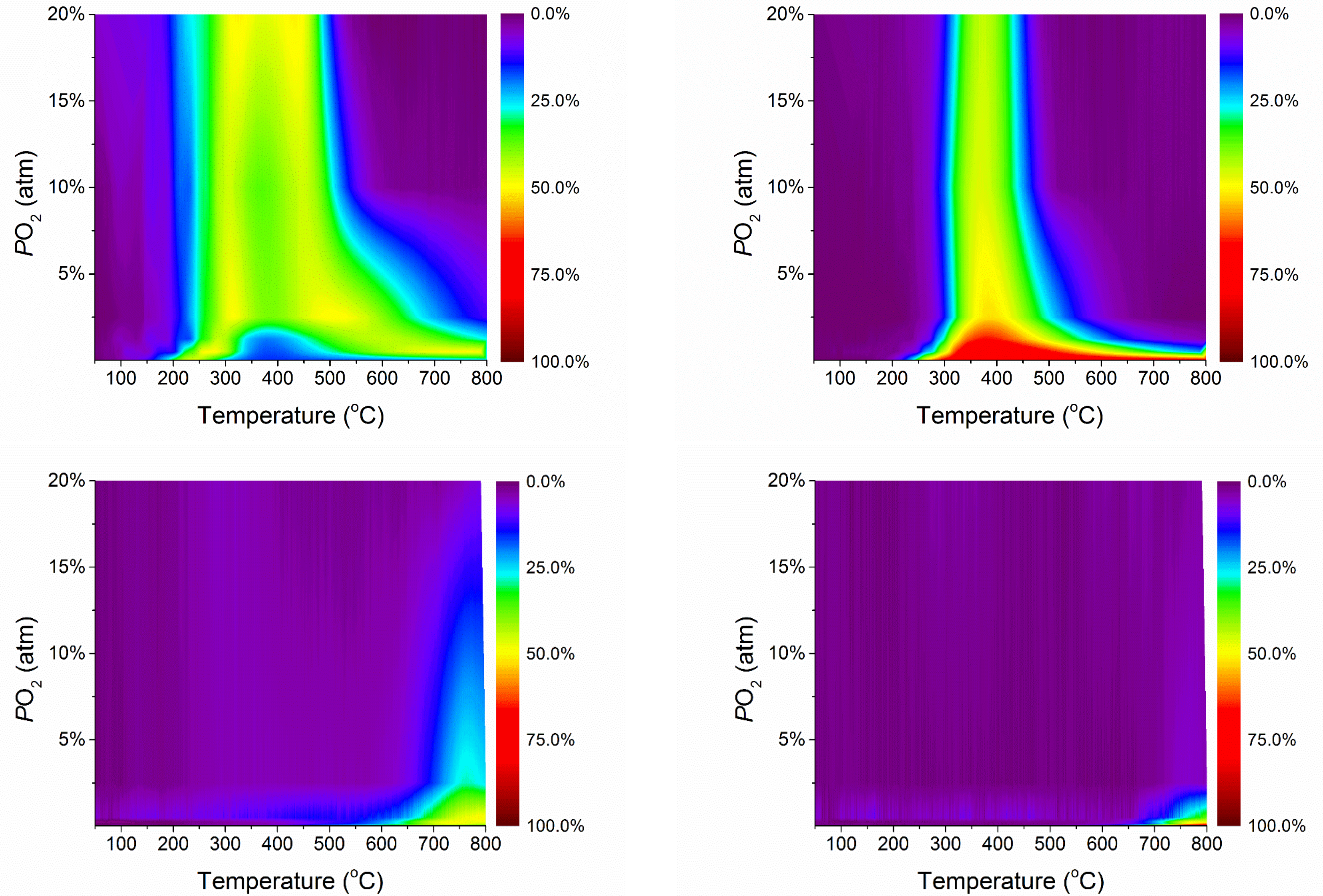
- LSCF more active toward D_2O exchange than LSM
- D_2O exchanges with LSM only at high temp in presence of O_2

Comparison of LSCF and LSM Temp-PO_2 Dependence in CO_2

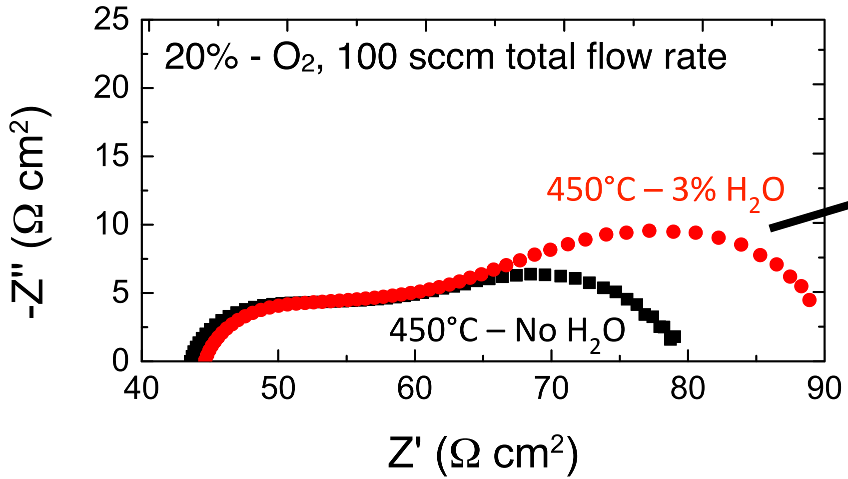
Singly Exchanged $C^{16}O^{18}O$ | Doubly Exchanged $C^{18}O^{18}O$

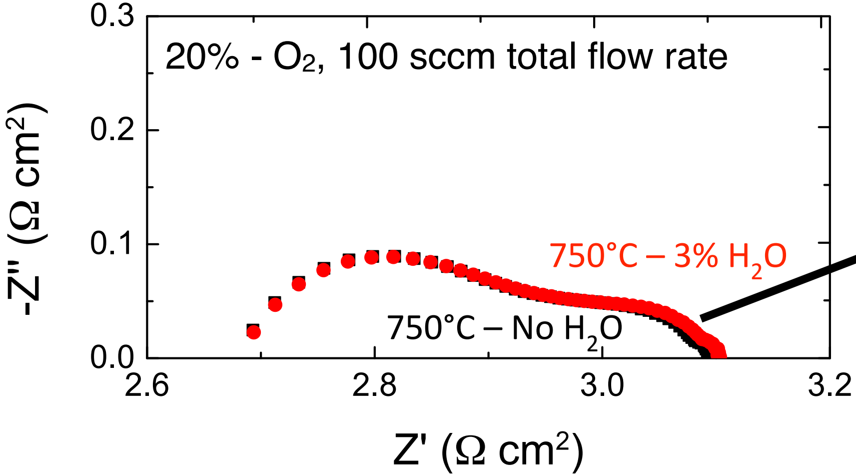
LSCF

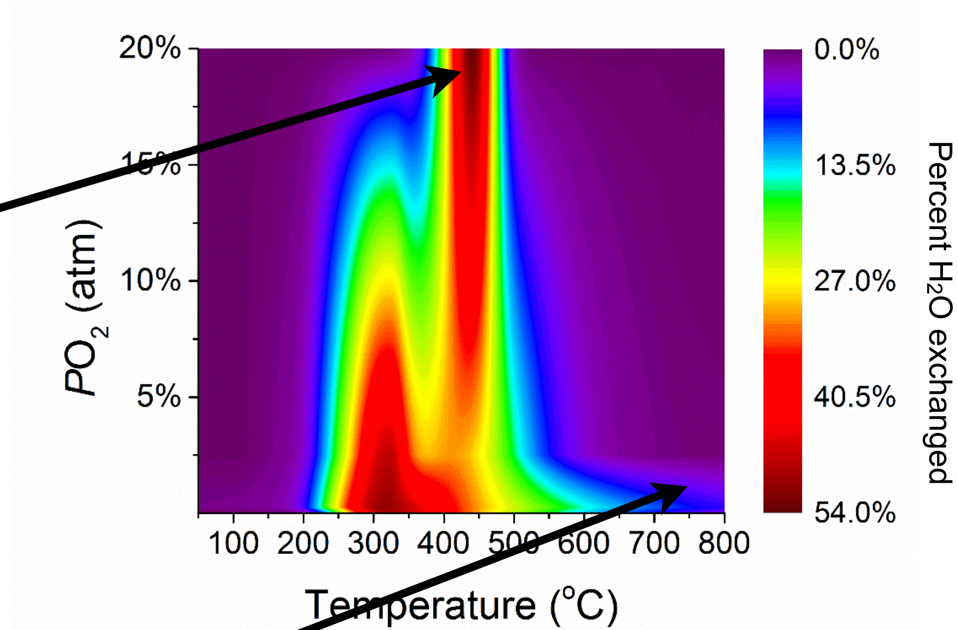
LSM



Comparison of ISTPX with EIS for LSCF-GDC in H_2O





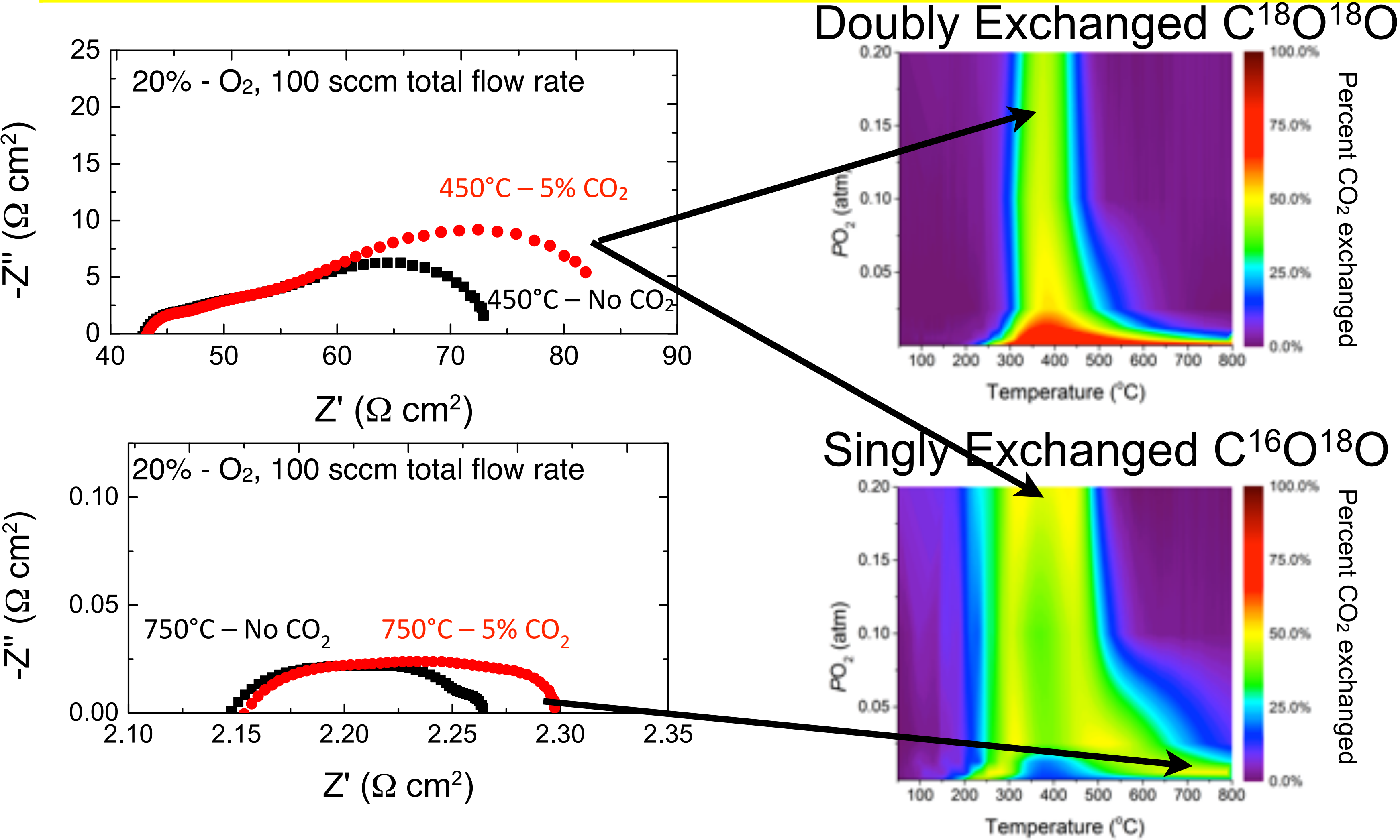


Two Exchange Peaks:

- As PO_2 increases, 300ºC peak decreases
- 450ºC peak still present at high PO_2

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

Comparison of ISTPX with EIS for LSCF-GDC in CO_2



The presence of 5% CO_2 effects the low frequency arc at 450°C and at 750°C consistent with the results obtained from ISTPX.

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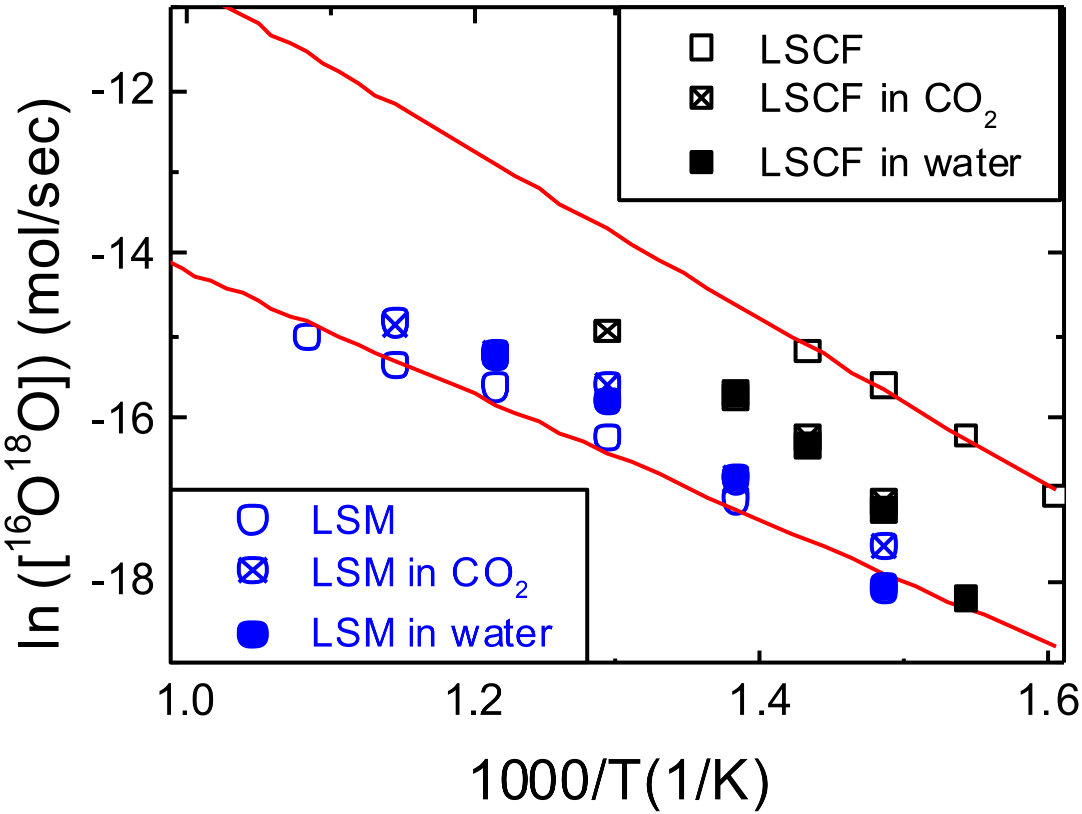
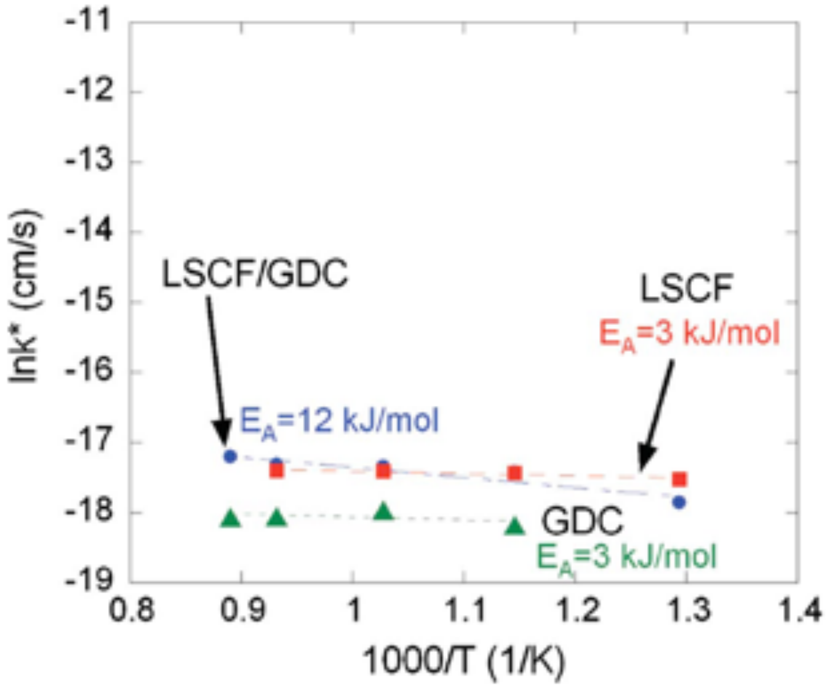
Effect of CO_2 and H_2O on Catalytic Activity for O_2 Dissociation

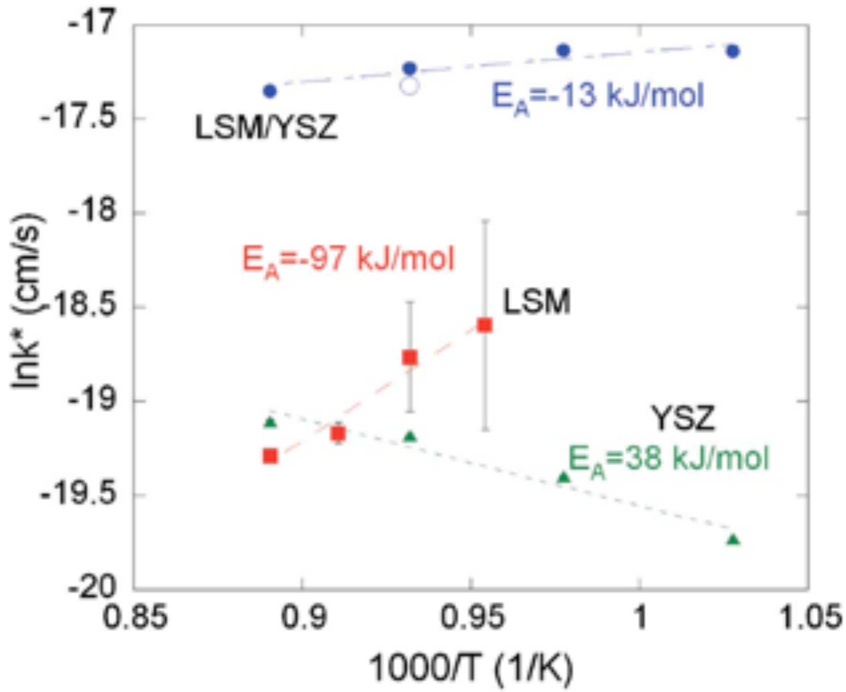
Arrhenius Plot of Steady State Concentration [$^{16}O^{18}O$] to Reciprocal Temperature



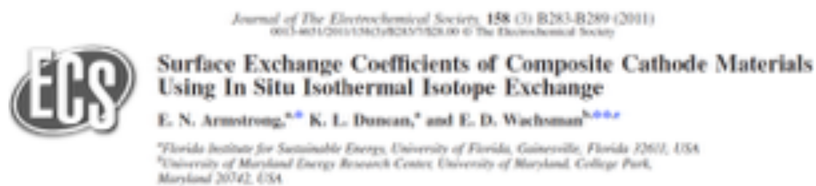
- LSCF has greater rate of O_2 dissociation than LSM
- CO_2 and H_2O decrease the rate of O_2 dissociation on LSCF
- But CO_2 and H_2O increase O_2 dissociation on LSM

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


Journal of The Electrochemical Society, 158 (3) B283-B289 (2011)

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

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University of Maryland Energy Research Center, University of Maryland, College Park, Maryland 20742, USA

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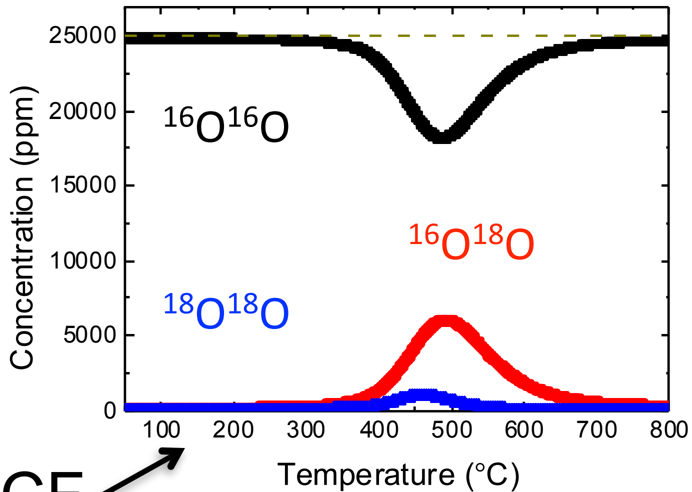
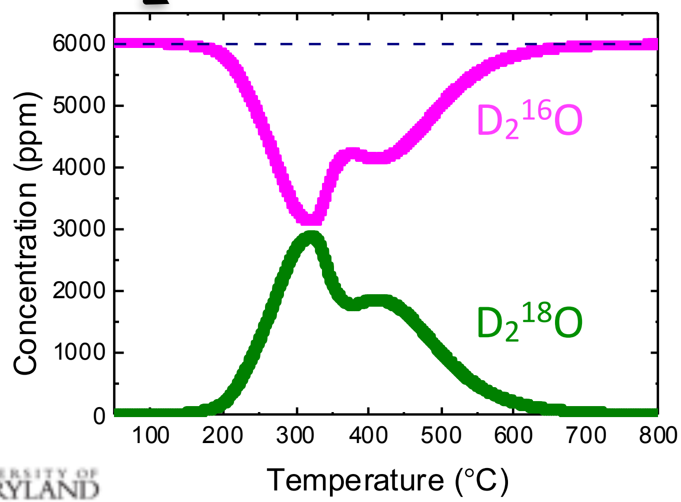
Comparison of LSCF and Composite LSCF-GDC in D_2O

25000ppm O_2 and 6000ppm D_2O



LSCF



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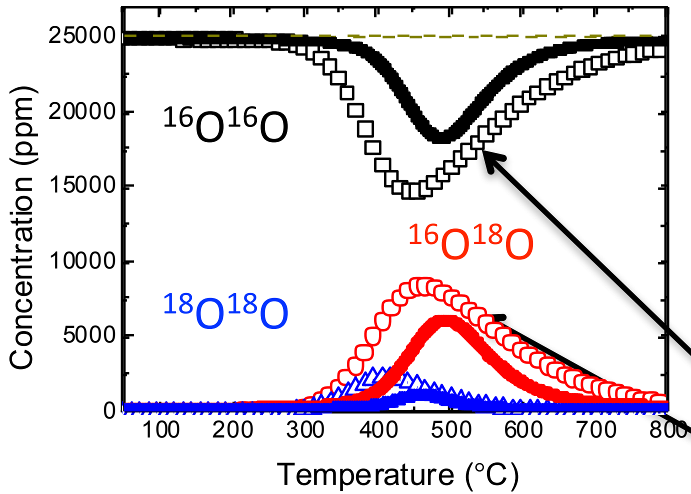
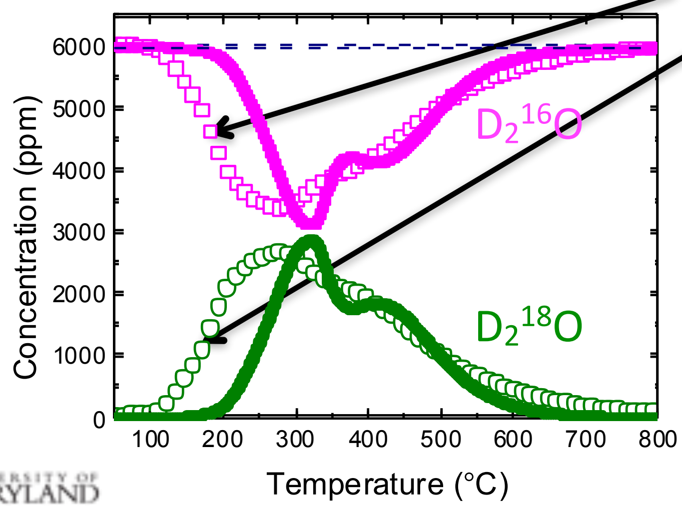
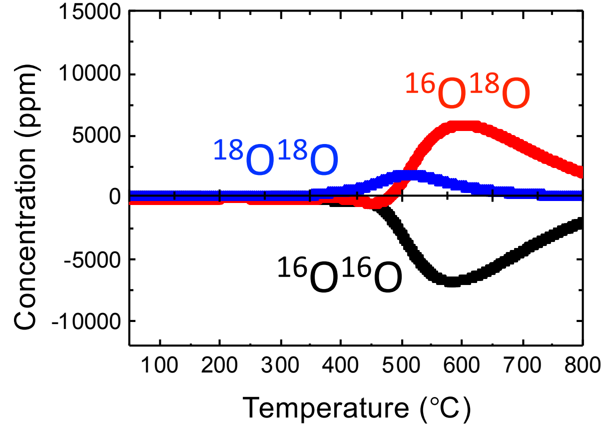
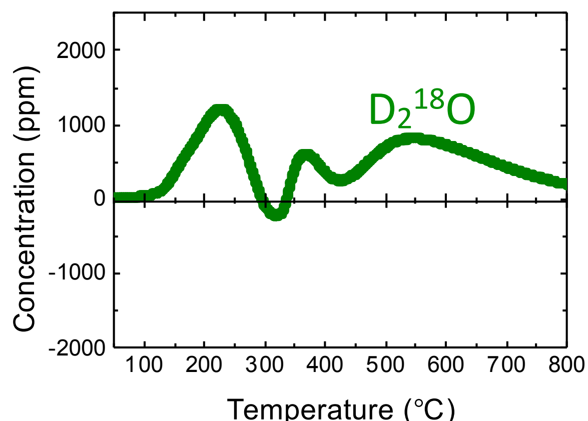


LSCF-GDC



LSCF Subtracted from LSCF-GDC



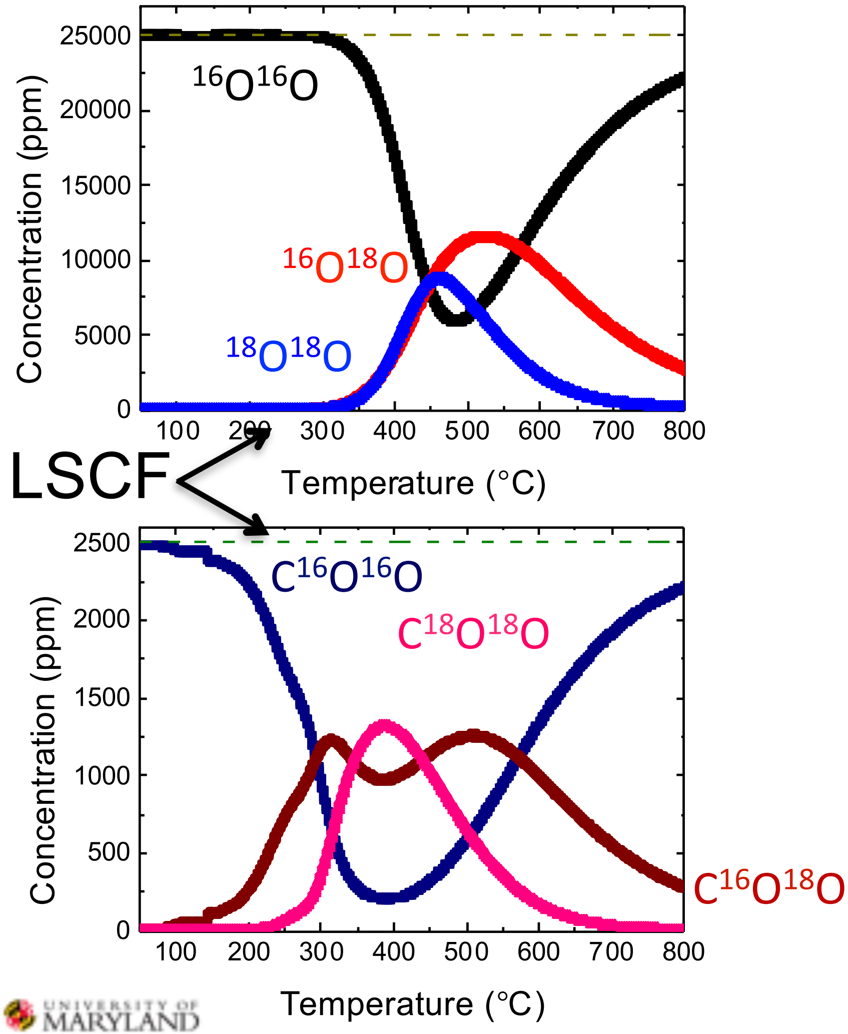


Difference demonstrates greater D_2O exchange with composite

University of Maryland Energy Research Center

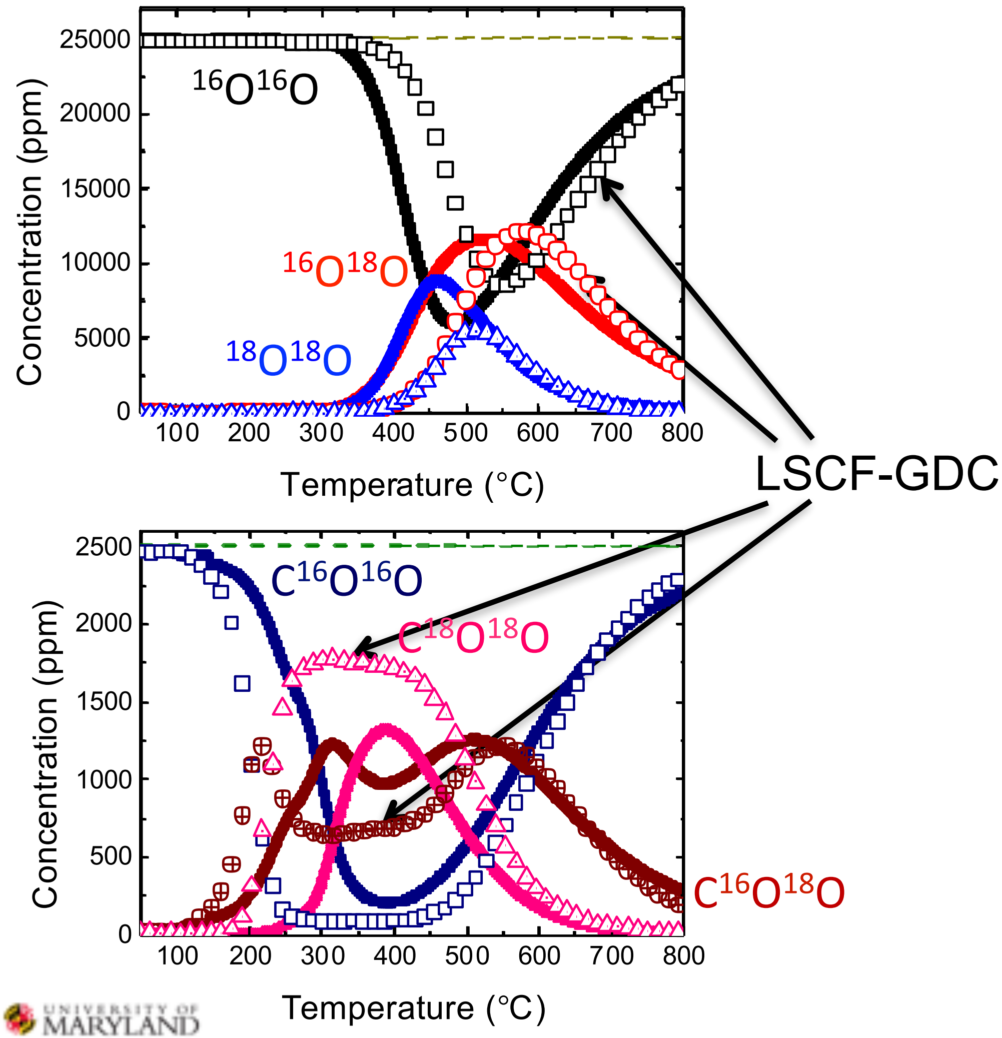
Comparison of LSCF and Composite LSCF-GDC in CO_2

25000ppm O_2 and 2500ppm CO_2

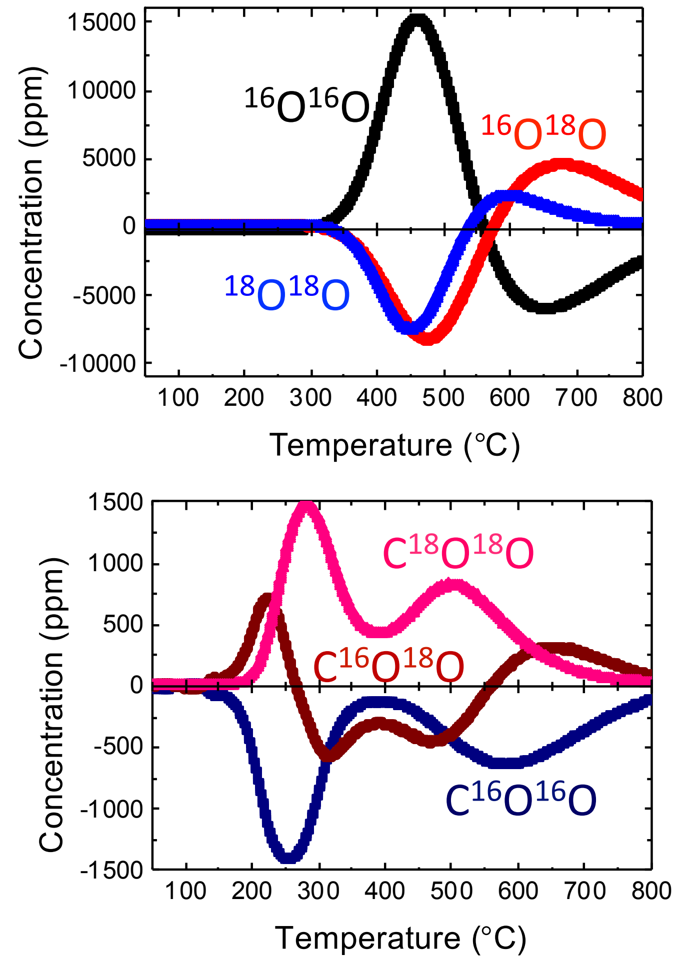


Comparison of LSCF and Composite LSCF-GDC in CO_2

25000ppm O_2 and 2500ppm CO_2



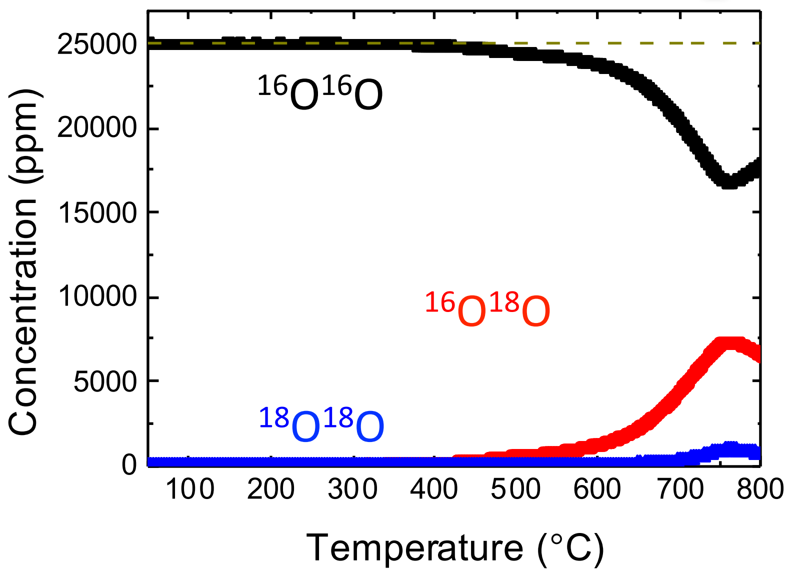
LSCF Subtracted from LSCF-GDC

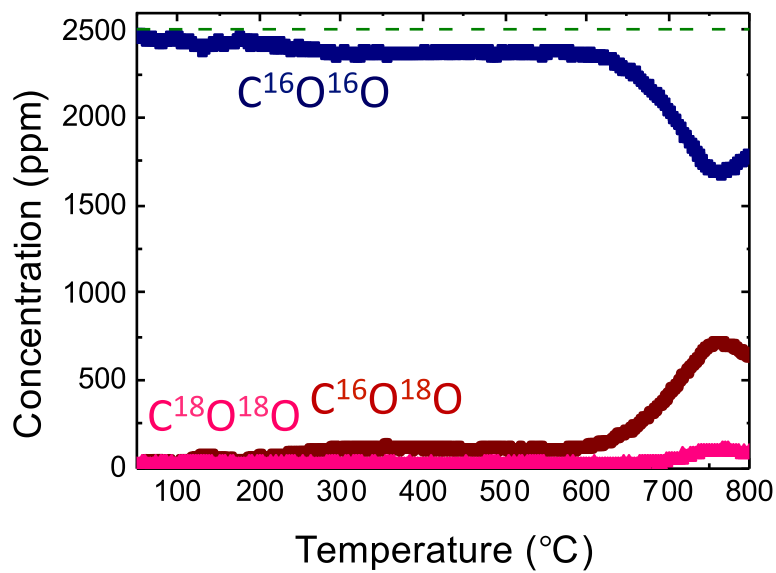


Comparison of LSM and Composite LSM-YSZ in CO_2

25000ppm O_2 and 2500ppm CO_2

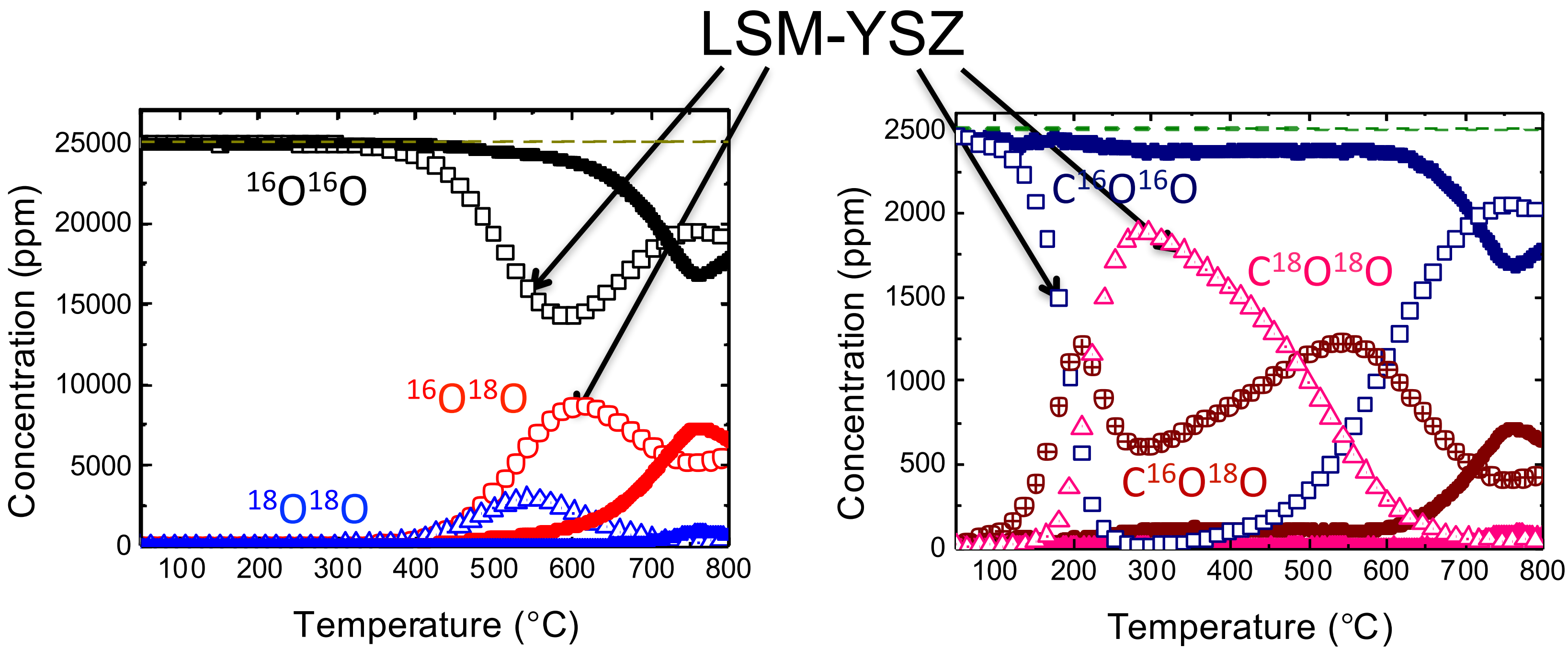
LSM





Comparison of LSM and Composite LSM-YSZ in CO_2

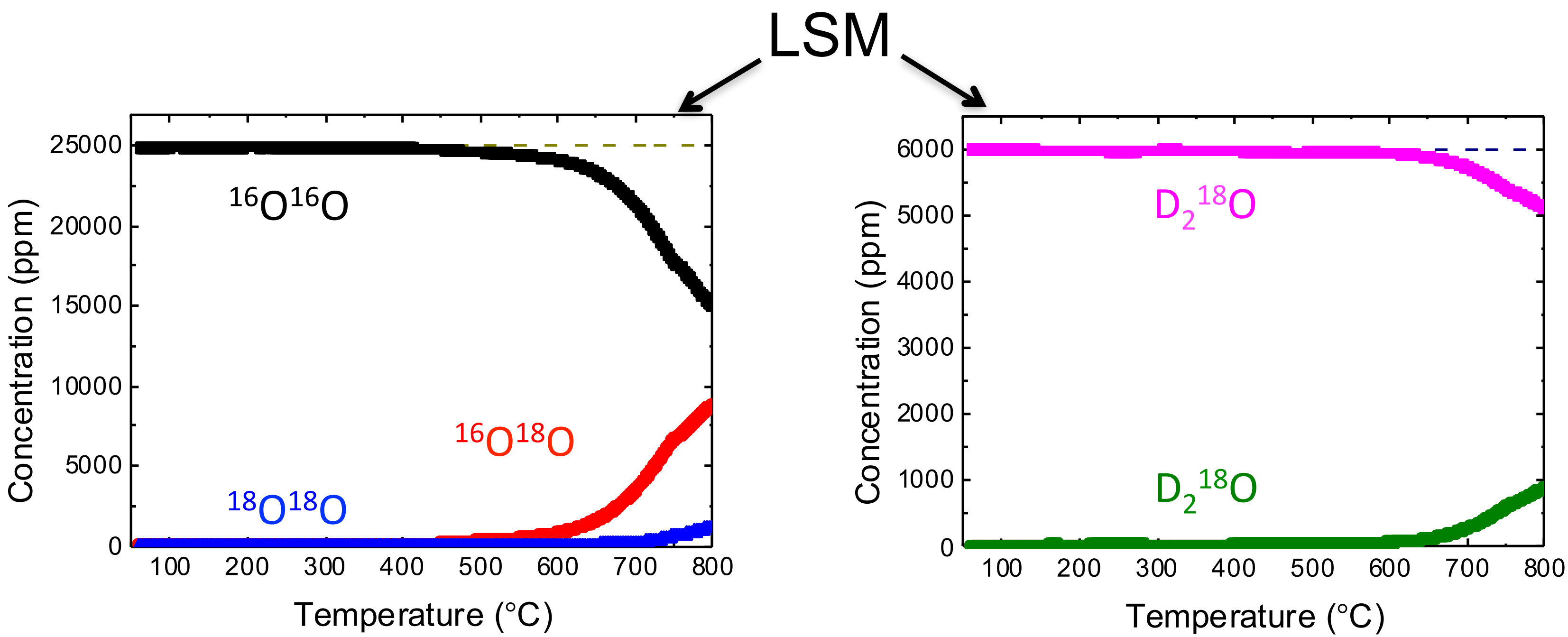
25000ppm O_2 and 2500ppm CO_2



- LSM-YSZ composite demonstrates much greater exchange than LSM at much lower temp for CO_2
- Composite effect for LSM-YSZ much greater than for LSCF-GDC

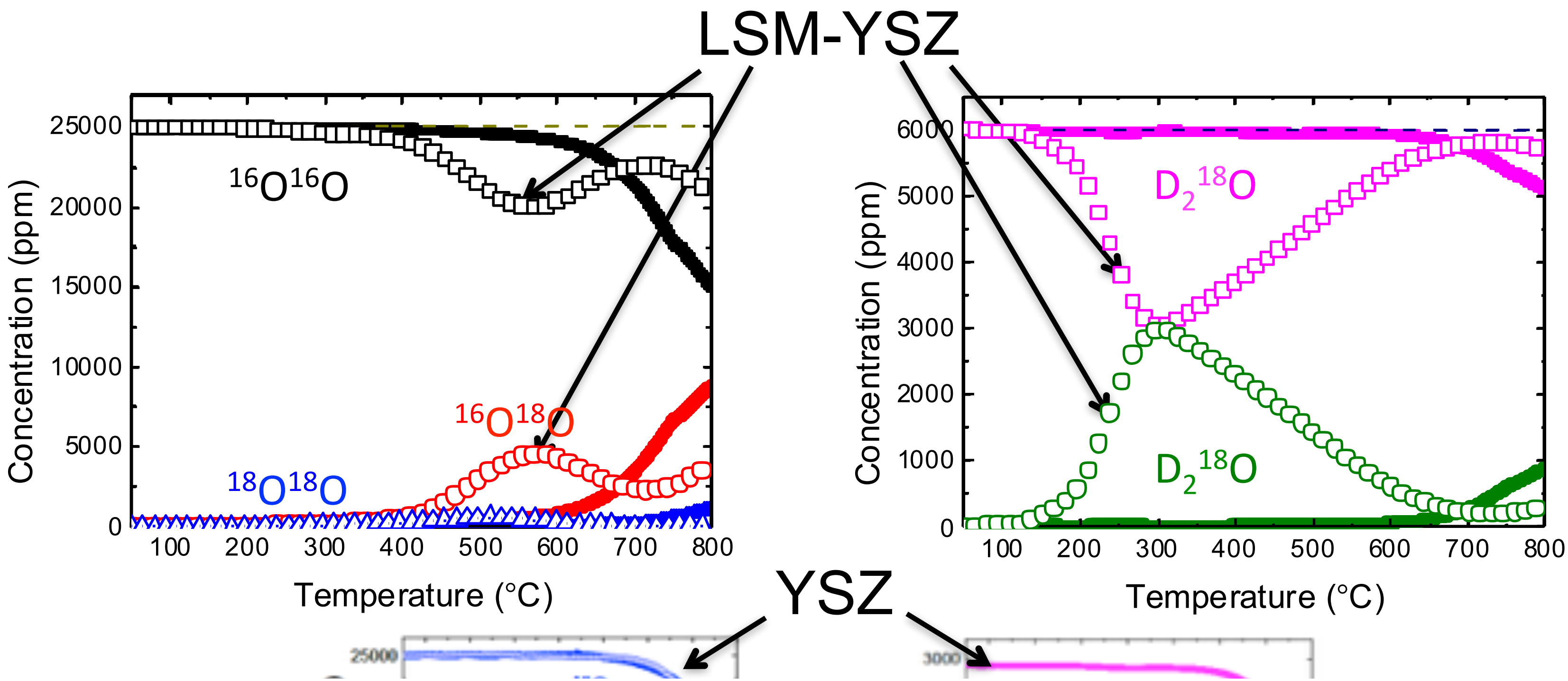
Comparison of LSM and Composite LSM-YSZ in D_2O

25000ppm O_2 and 6000ppm D_2O



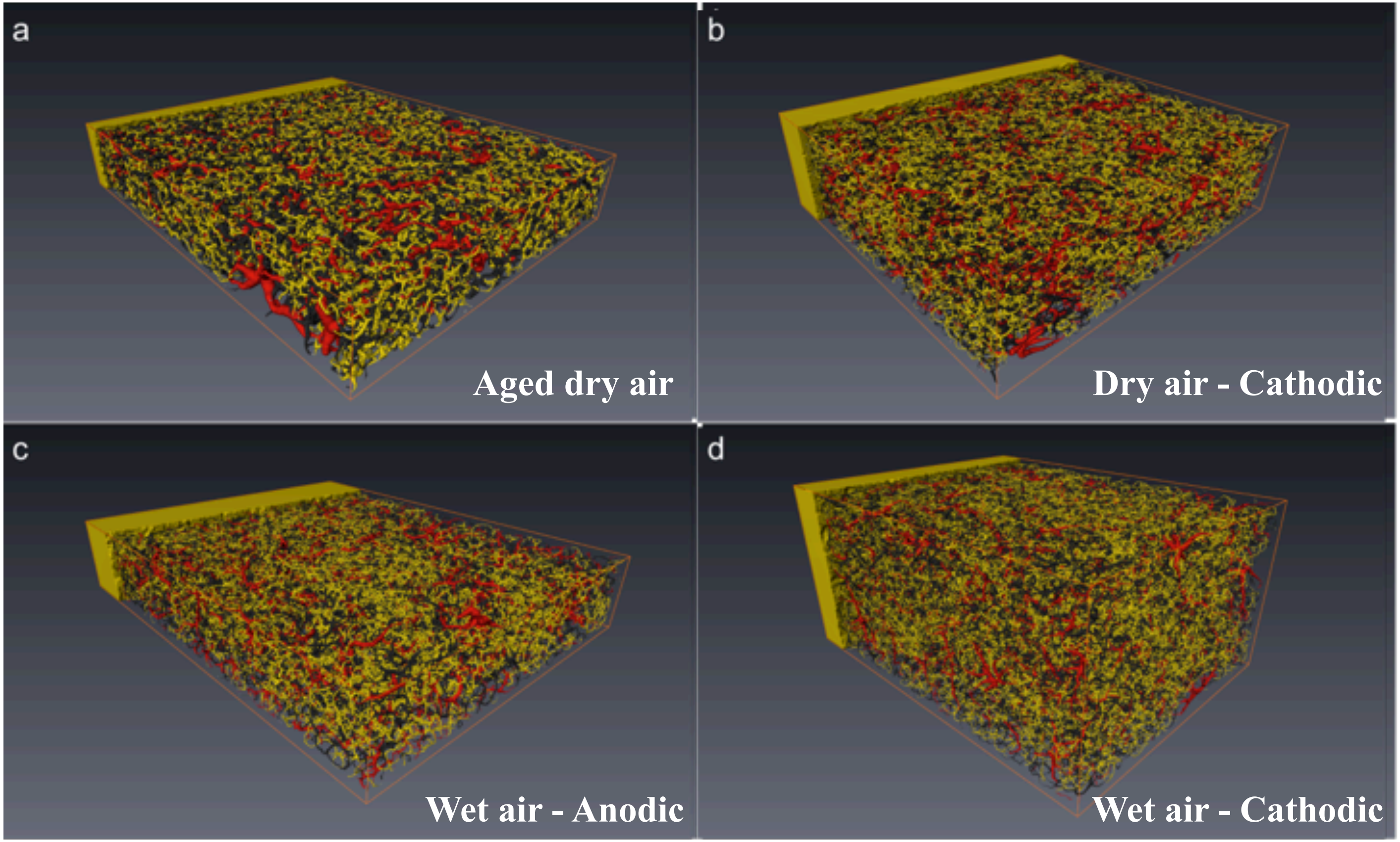
Comparison of LSM and Composite LSM-YSZ in D_2O

25000ppm O_2 and 6000ppm D_2O



- LSM-YSZ composite demonstrates much greater exchange than LSM or YSZ at much lower temp for D_2O
- 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

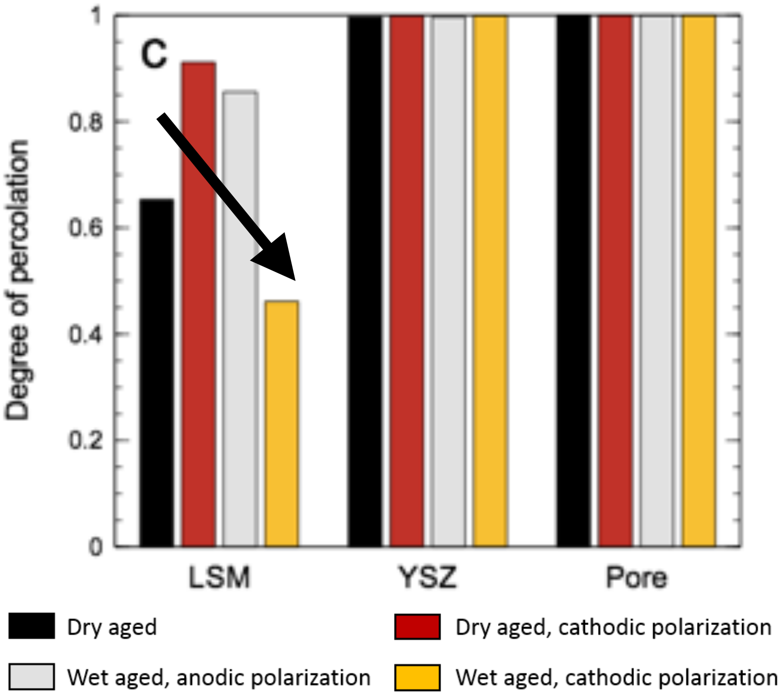


FIB/SEM reconstruction of LSM/YSZ cathodes aged at 800°C for 500 hrs in dry and wet (3% H_2O) air with and without polarization

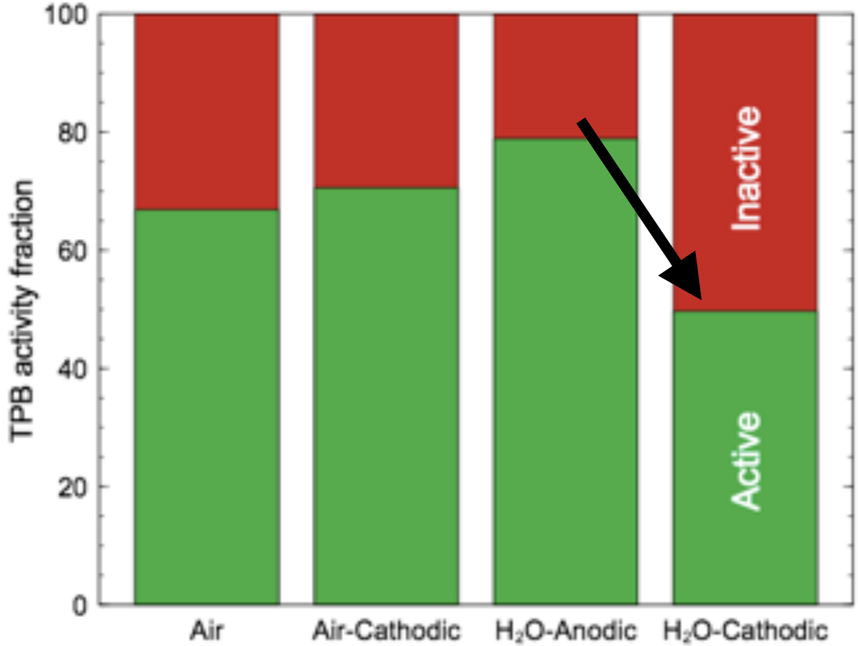
Skeletonization to determine microstructural connectivity

H_2O Impact on LSM/YSZ Microstructural Change

Impact on phase connectivity



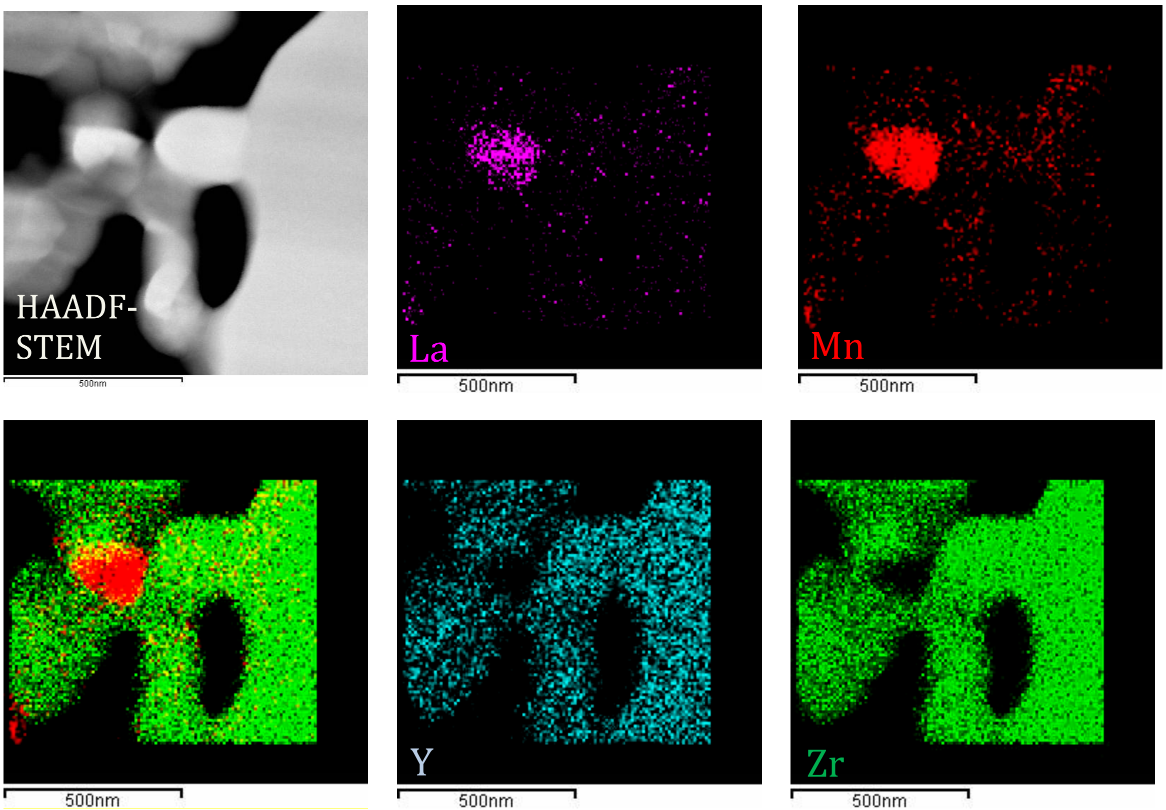
Impact on effective TPB activity



- 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



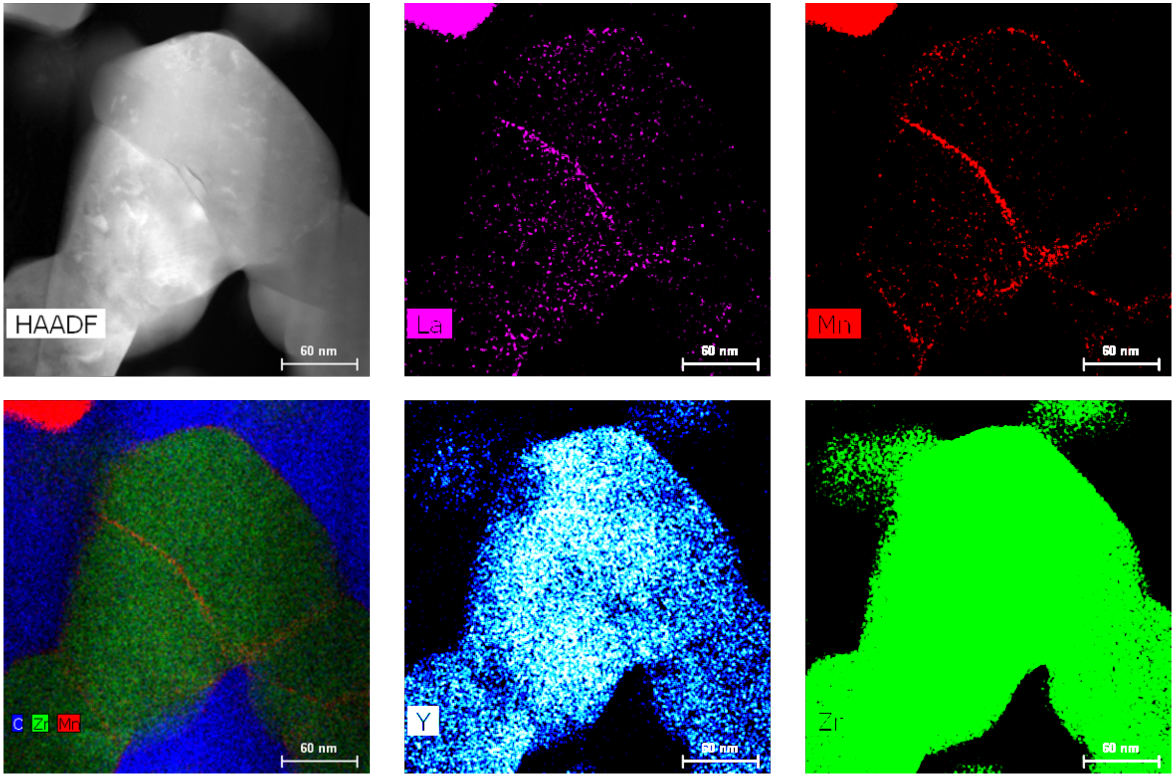
STEM-EDS maps of Aged-dry SOFC cathode near electrolyte interface

- 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

Conclusions/Summary

- ^{18}O-exchange demonstrates LSCF is more active than LSM and has different ORR mechanism
- CO_2 and H_2O actively participate in ORR for both LSCF and LSM
  - Most likely influences literature k_{ex} results
- Identified temperature and gas composition regions where CO_2 and H_2O dominate O_2 surface exchange mechanism and where they are less important
  - Needs to be taken into consideration when selecting cathodes and operating conditions
- Identified composite cathode effect on O_2 surface exchange with CO_2 and H_2O
  - Particularly dramatic for LSM/YSZ
  - Indicates microstructure (e.g., TPB's) plays important role
- Ambient humidity has a direct impact on LSM/YSZ cathode microstructural and compositional changes (currently characterizing LSCF/GDC) that degrades ohmic and non-ohmic ASR
- Heterogeneous catalysis (IIE & ISTPX), polarization measurements (EIS), and microstructural characterization (FIB/SEM) are being integrated to provide fundamental understanding of cathode ORR and degradation mechanisms

- Have recently started investigating effect of Cr