Towards a Fundamental Understanding of Cathode Degradation Mechanisms

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Fundamental Mechanisms of SOFC Cathode Reactions

Systematic Approach to Deconvoluting Cathode Polarization:

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

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

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

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

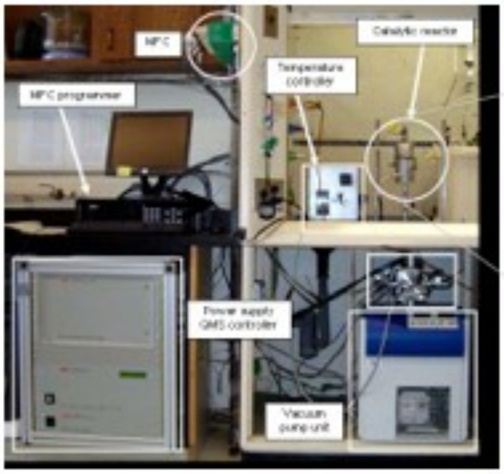
- Microstructure (surface area/volume)
- Kinetics (surface coverage, surface diffusivity)

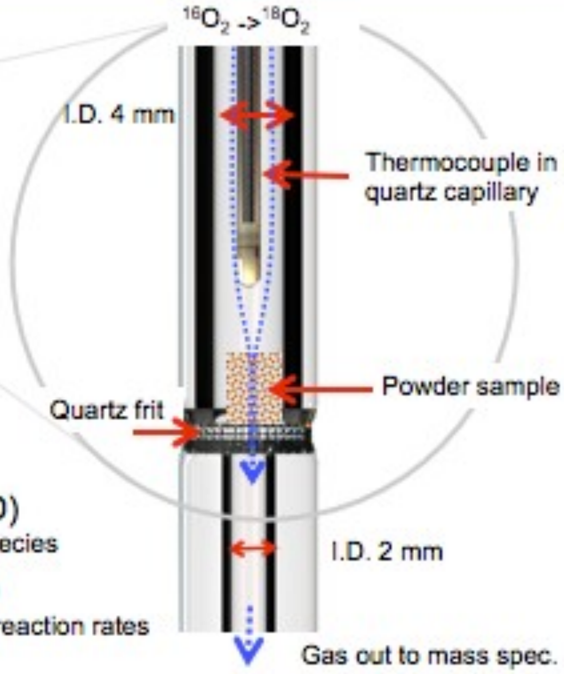
$R_{\text{Charge Transfer}}$ is function of:

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

Integrating EIS, ^{18}O-exchange, and FIB/SEM & STEM/EDS to quantify cathode degradation mechanisms

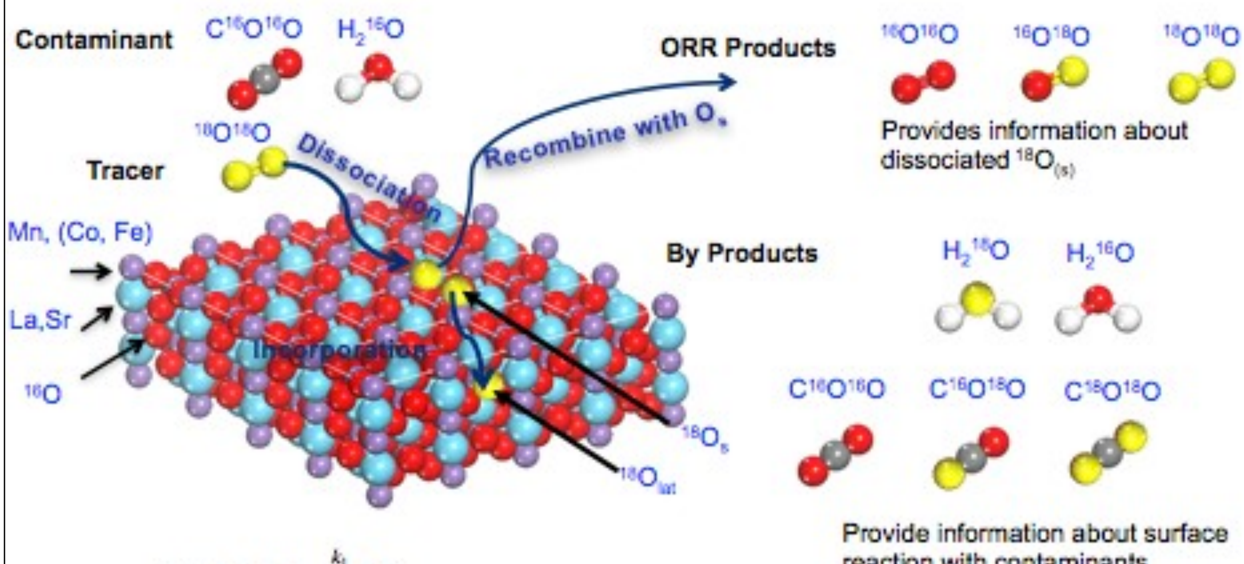
Fundamental Rate Constants - Catalysis





- 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

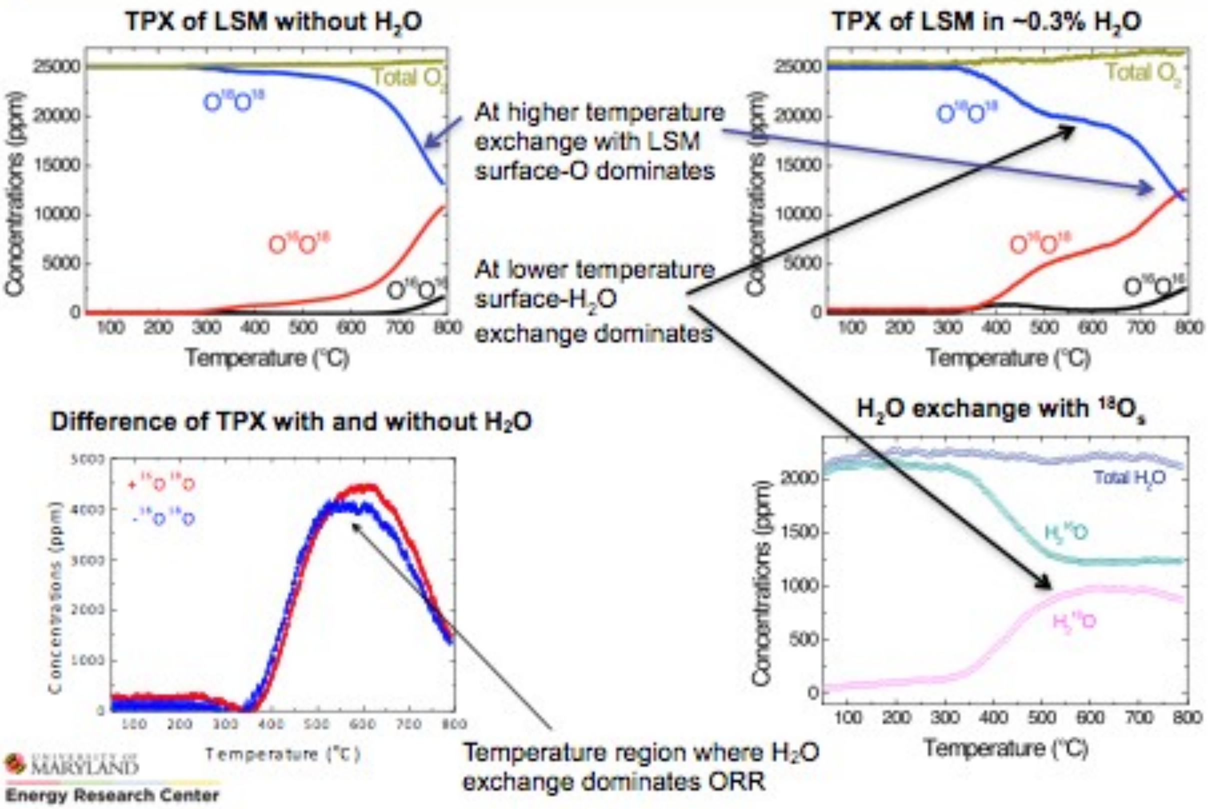
ORR Reaction Mechanisms in Presence of H_2O and CO_2



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

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

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



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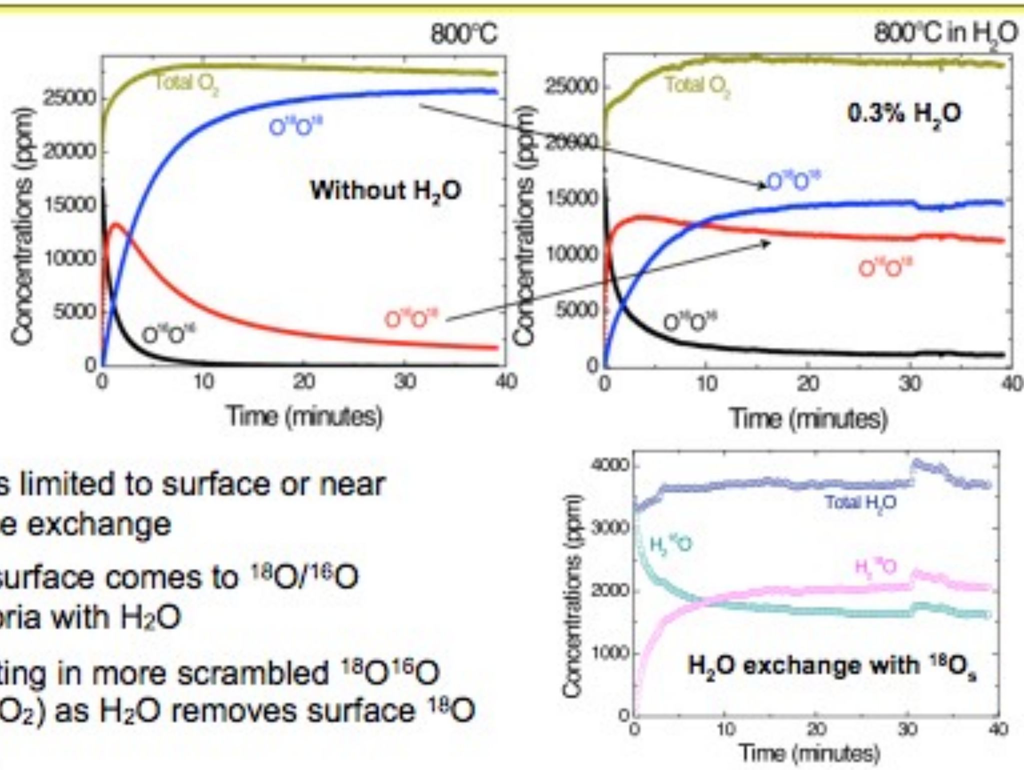
Effect of H_2O on Isothermal Isotope Exchange of LSM



- LSM is limited to surface or near surface exchange
- LSM surface comes to $^{18}O/^{16}O$ equilibria with H_2O
- Resulting in more scrambled $^{18}O^{16}O$ (vs. $^{18}O_2$) as H_2O removes surface ^{18}O

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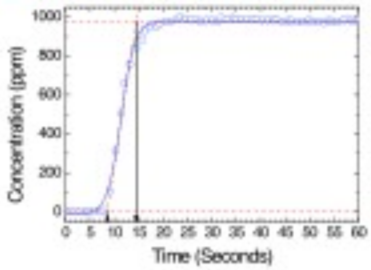
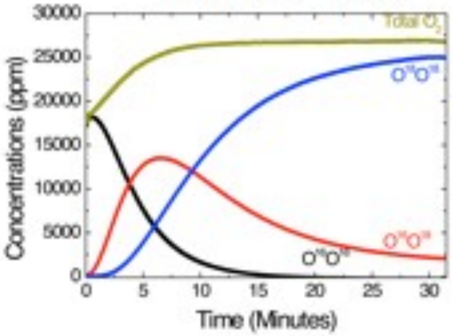
Extracting the Surface Exchange Coefficient from IIE

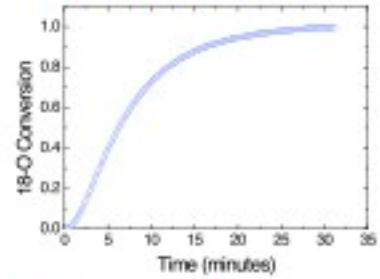




- Use equation below to extract the fraction of ^{18}O that exchanges with lattice ^{16}O
- Can be fit with Crank's solution for sphere

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

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



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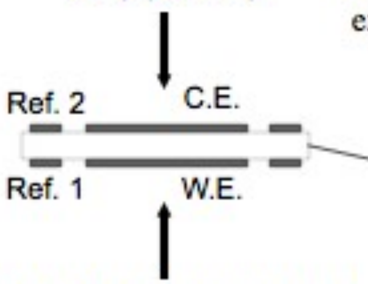
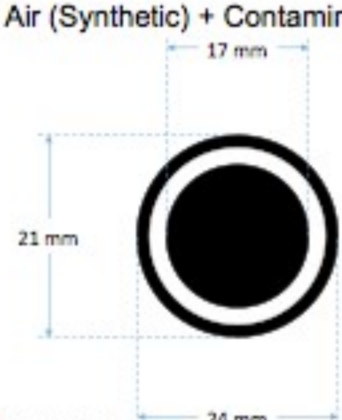
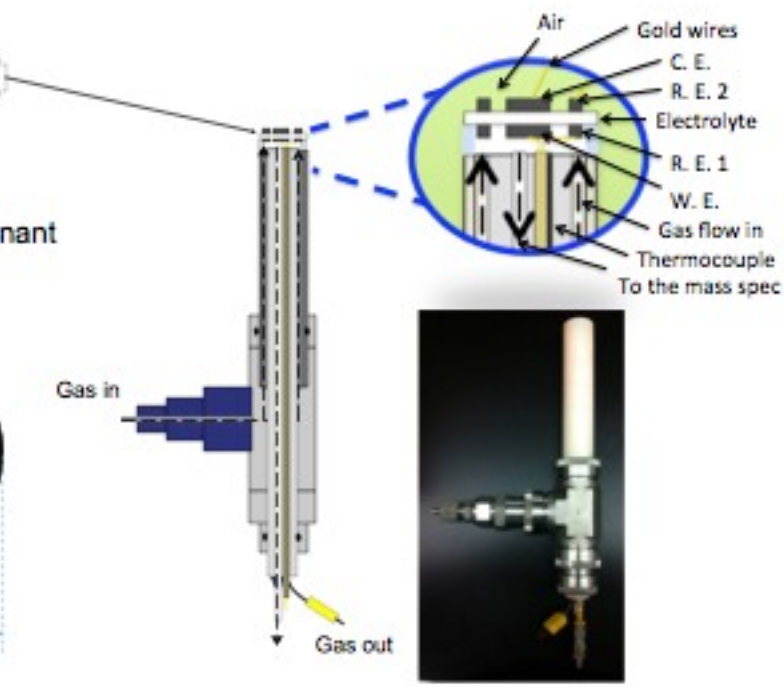
Provides extent and rate of oxygen exchange

Comparison with Symmetric Cell Testing

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







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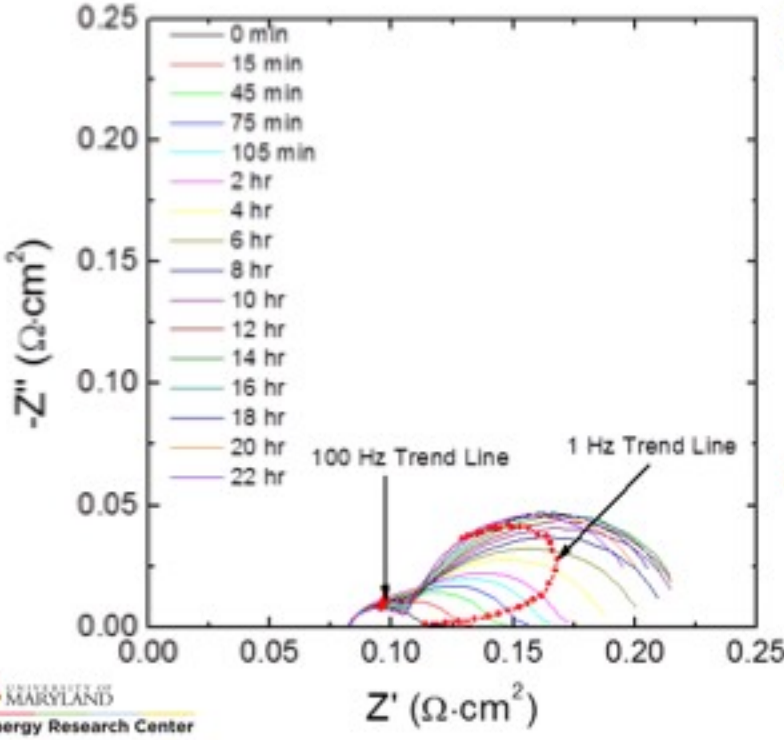
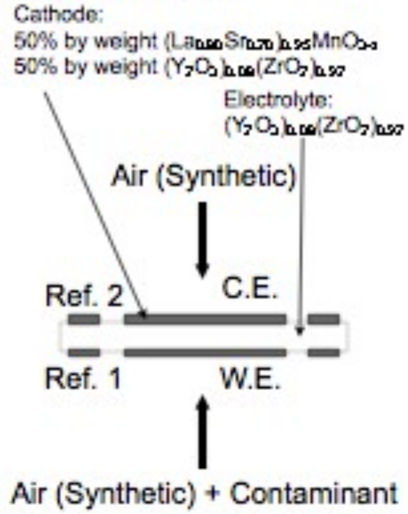
Effect of H_2O on LSM/YSZ Cathode Impedance (EIS)

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

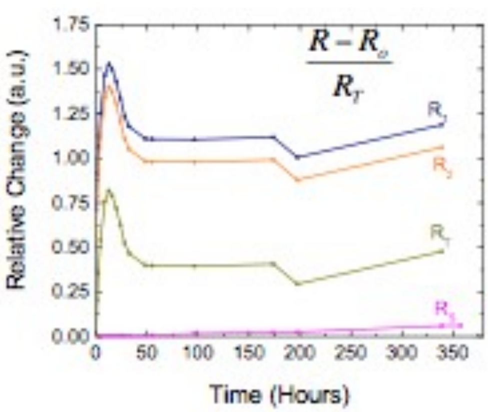




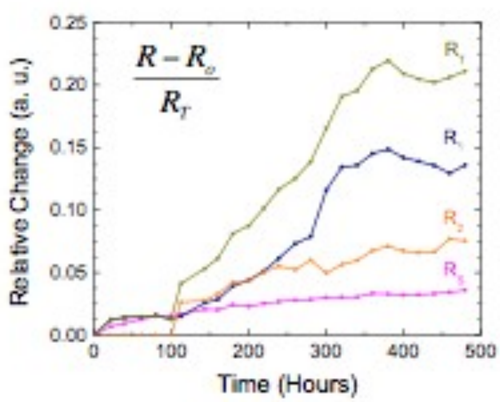
Baseline/aging in H_2O LSM-YSZ/YSZ/LSM-YSZ Cell Testing

Resistance Trends (Relative)

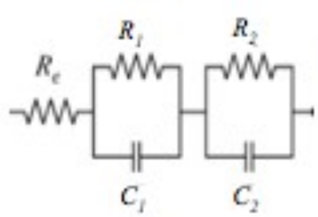
Aging in H_2O



Baseline aging in air

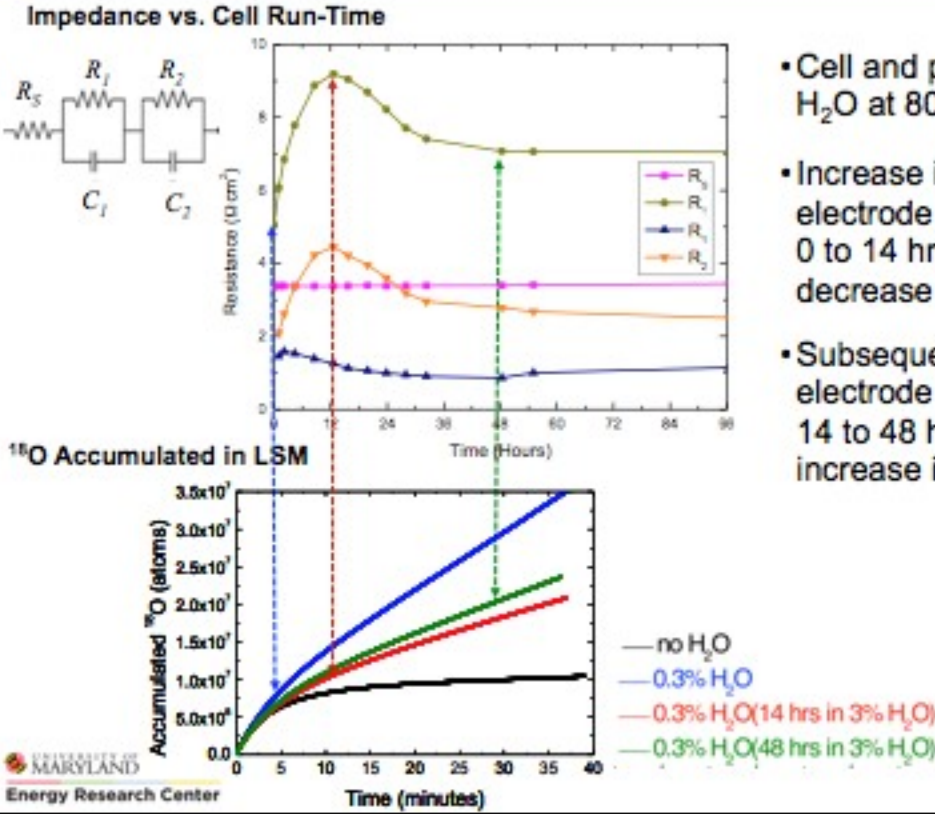


Short time unique H_2O effect



Long term includes aging in air effects

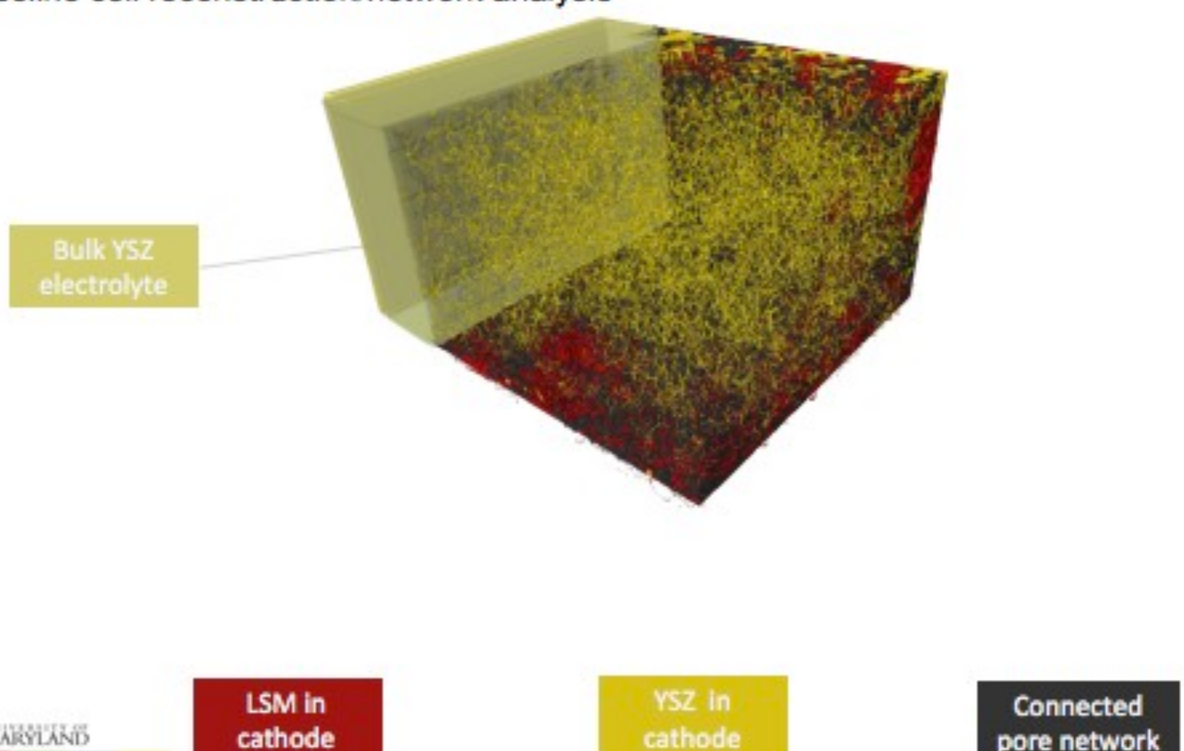
Comparison of LSM Cell Testing and IIE Results



- 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.

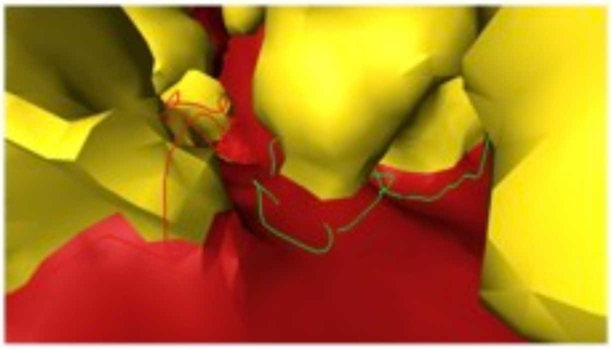
Quantify Microstructural Effects - FIB/SEM

Baseline cell reconstruction/network analysis



Triple Phase Boundary Length Comparison

FIB/SEM reconstruction 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



*Relative to baseline	Baseline	Aged-dry	H2O
Active TPB [norm]	100%	32.5% *	27.5% *
Total ρ_{TPB} [μm/μm³]	19.2	9.69	8.57

- Observe decrease in active L_{TPB} upon aging
- Effect is worse with exposure to 3% H_2O

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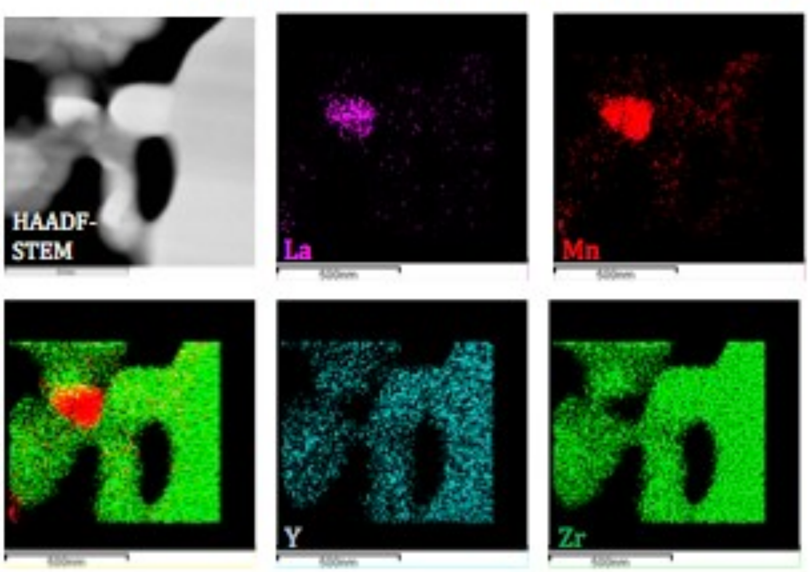
STEM-EDS Maps of LSM-YSZ Aged in Air

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

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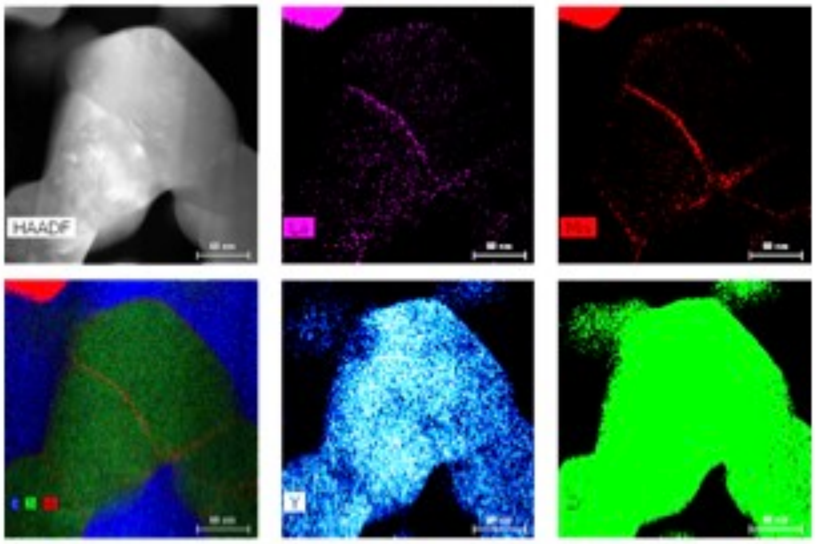
STEM-EDS Maps of LSM-YSZ Aged in Air + H_2O

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

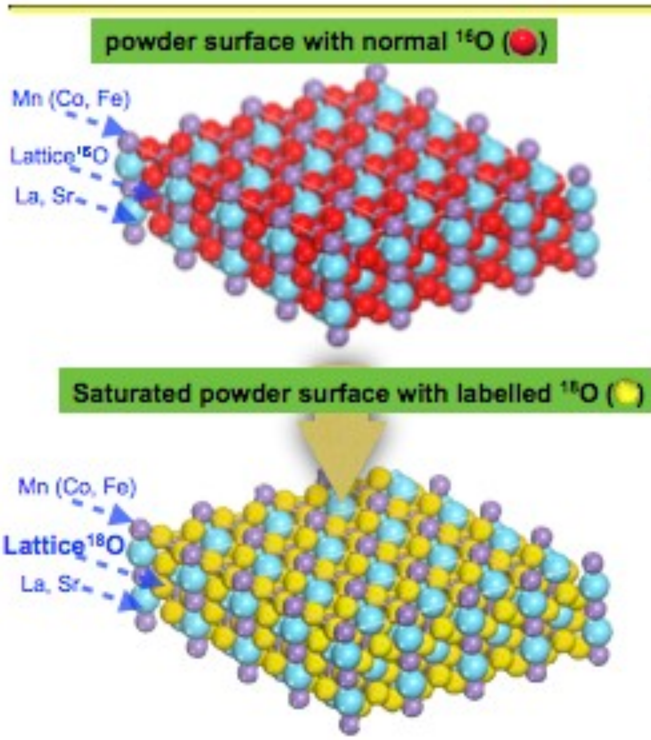


STEM-EDS maps Aged-H_2O SOFC cathode

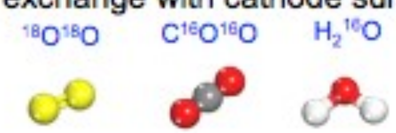
- Distinct particles of LSM and YSZ
- Segregation of La and Mn at YSZ grain boundaries
- Sr is not localized at boundaries

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

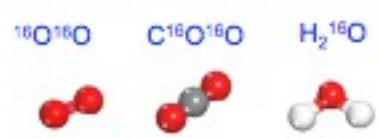
Isotope Saturated Temperature Programmed Exchange (ISTPX)



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



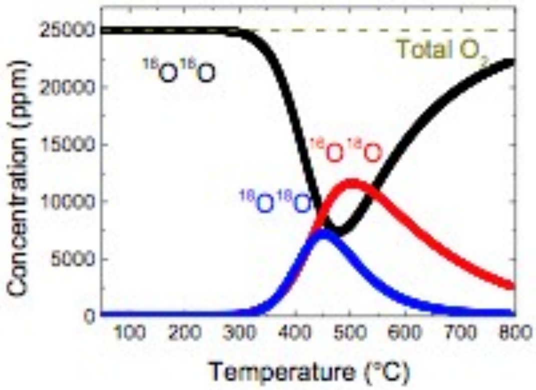
ISTPX - Probes competitive ORR in presence of contaminants on ^{18}O-labeled cathode surface



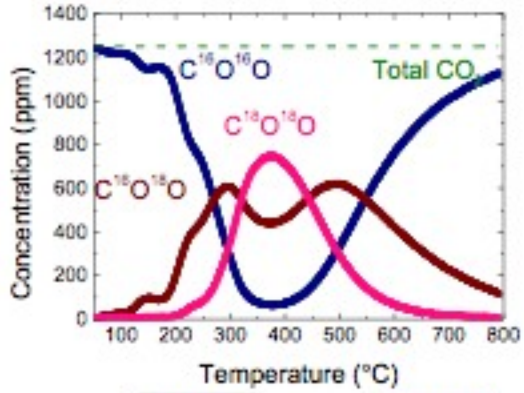
Also allows experiment in ambient P_{O2} without saturating mass spectrometer

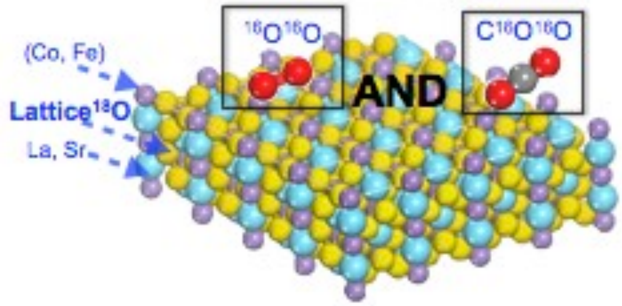
Interaction Between O_2, CO_2 and LSCF Surface

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



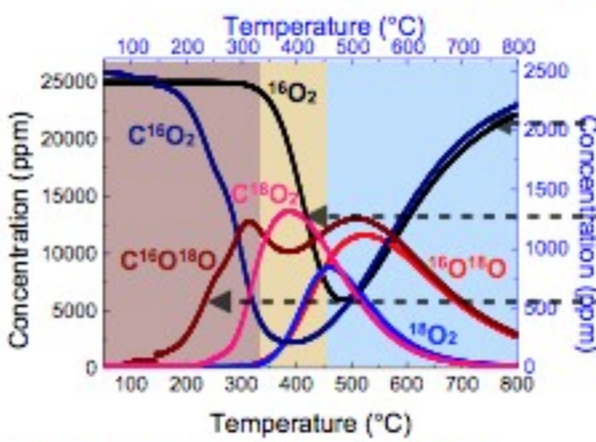
$C^{16}O_2$ exchange with lattice ^{18}O





Interaction Between O_2, CO_2 and LSCF Surface

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



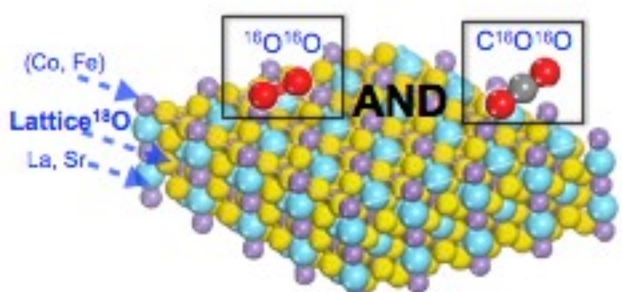
$C^{18}O_2$ and $^{18}O_2$ exchange with lattice oxygen in parallel

Doubly-exchanged $C^{18}O2$ dominates between 350-450ºC

Single exchanged $C^{16}O^{18}O$ dominates below 300ºC

CO_2 exchanges preferentially with lattice at lower temperature:

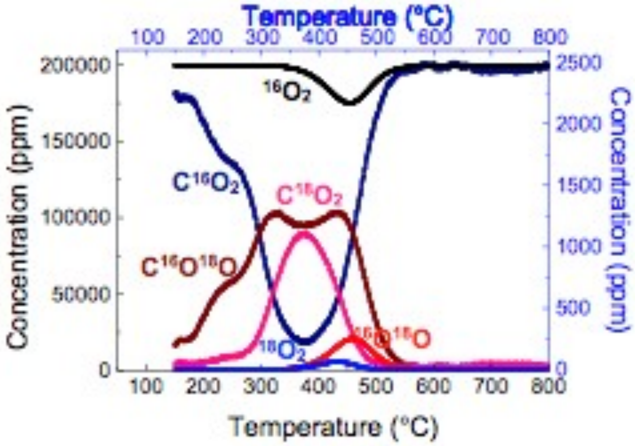
- initially exchanging only single "O" (atomic)
- then both "O" (molecular)
- then at same rate as O_2



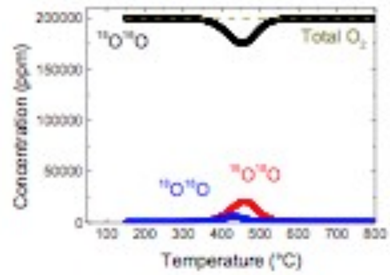
ISTPX of LSCF with 2500ppm CO_2 at ambient PO_2

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

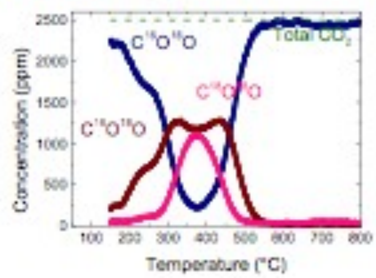
CO₂ and O₂ exchange with lattice ¹⁸O in 20% O₂



O₂ exchange with lattice ¹⁸O



CO₂ exchange with lattice ¹⁸O



CO_2 exchanges preferentially even at ambient PO_2

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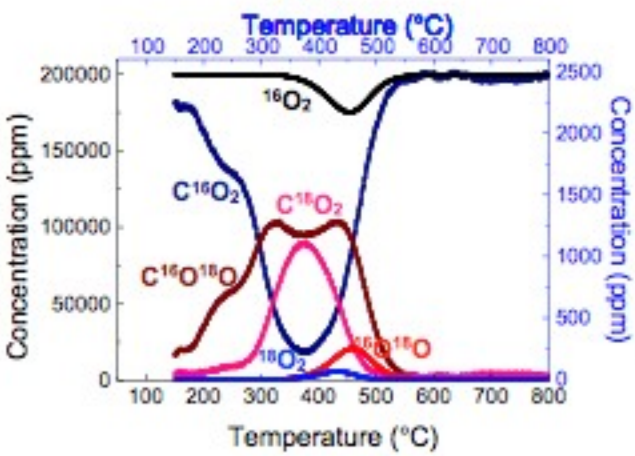
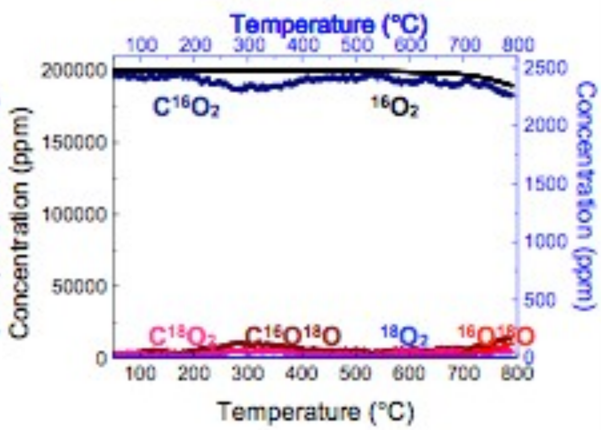
ISTPX of LSCF and LSM with 2500ppm CO_2 at ambient PO_2

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

LSCF



LSM



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

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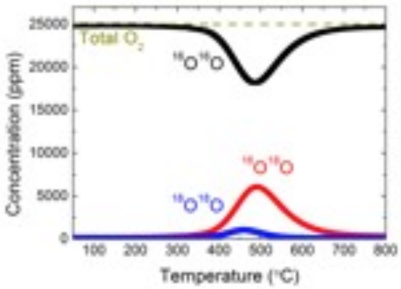
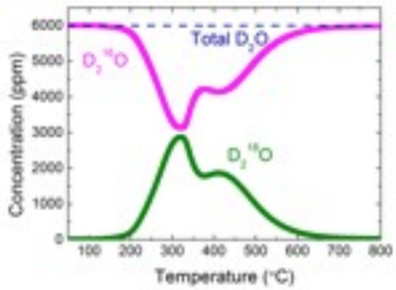
ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

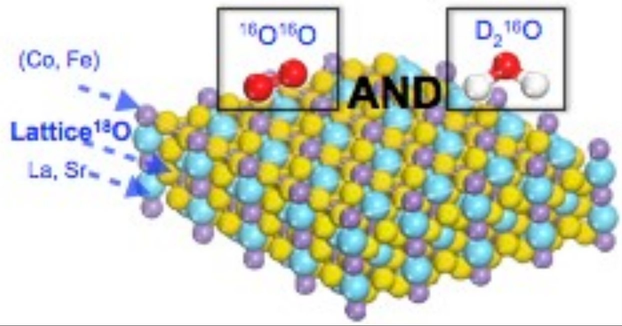
O_2 exchange with lattice ^{18}O



D2O exchange with lattice ^{18}O

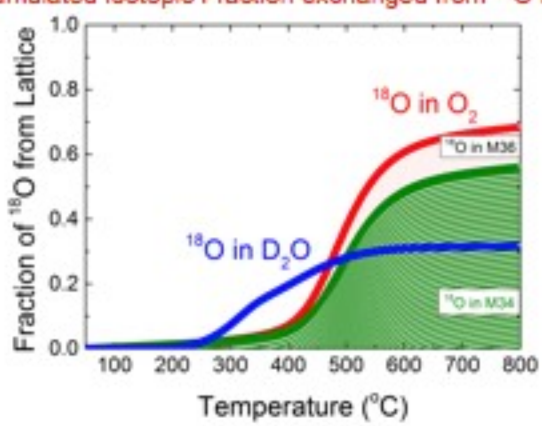


Mass of: ^{18}O = 18
$H_2{}^{16}O$ = 18
$D_2{}^{16}O$ = 20
$D_2{}^{18}O$ = 22

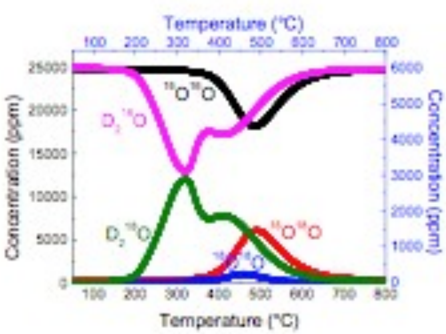


ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

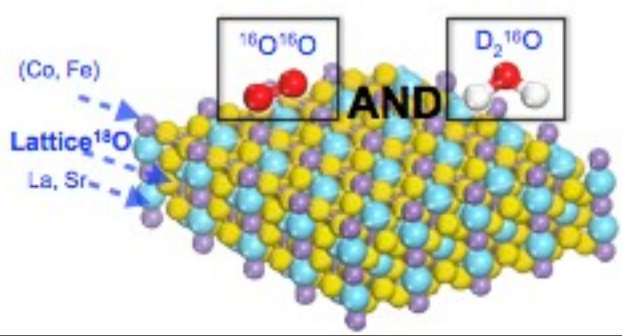
Accumulated Isotopic Fraction exchanged from ^{18}O LSCF



D2O and O2 exchange with lattice ^{18}O

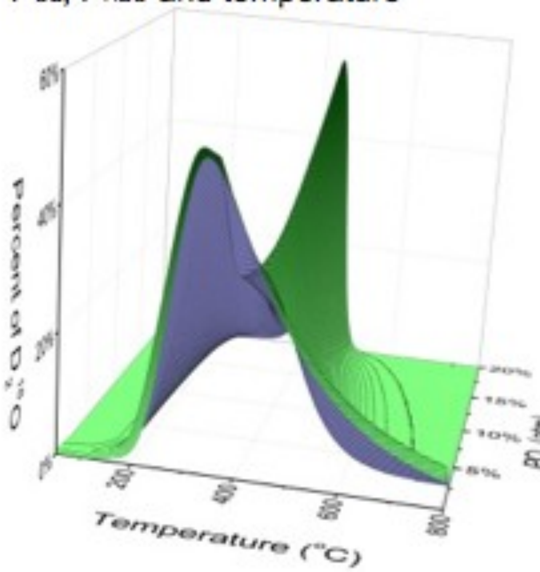


At lower temperature more of the lattice ^{18}O exchanges with water than O_2

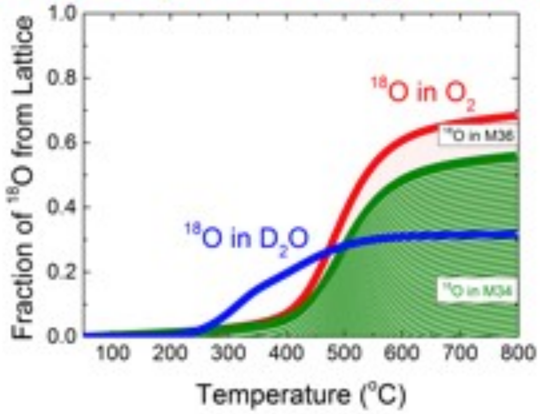


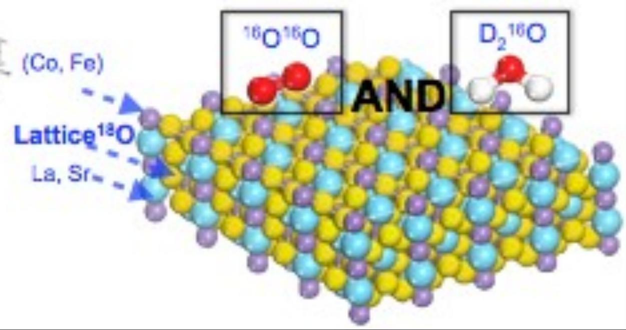
Temperature and PO_2 Dependence of LSCF in D_2O

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



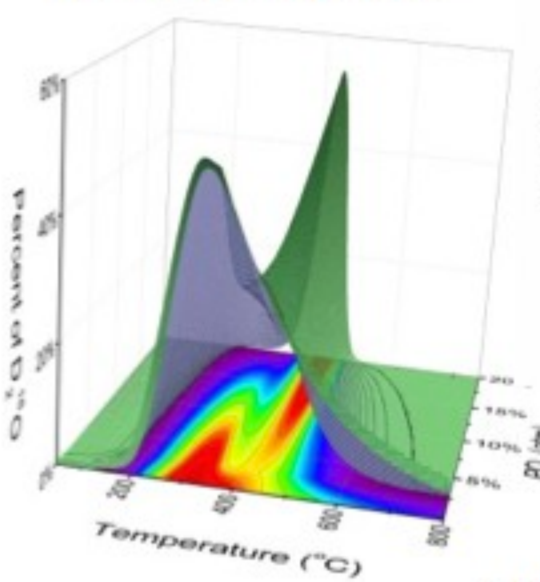
Accumulated Isotopic Fraction exchanged from ^{18}O LSCF

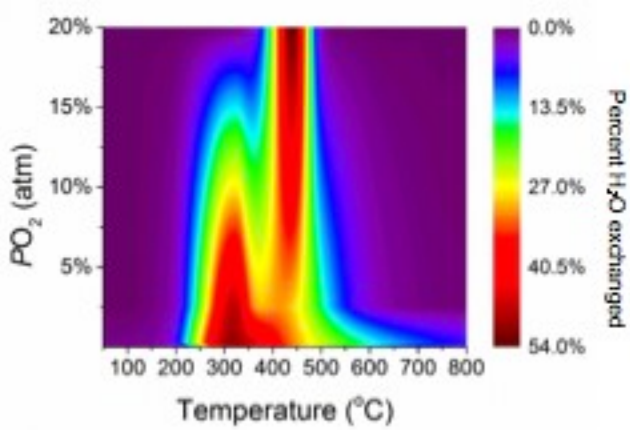




Temperature and PO_2 Dependence of LSCF in D_2O

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

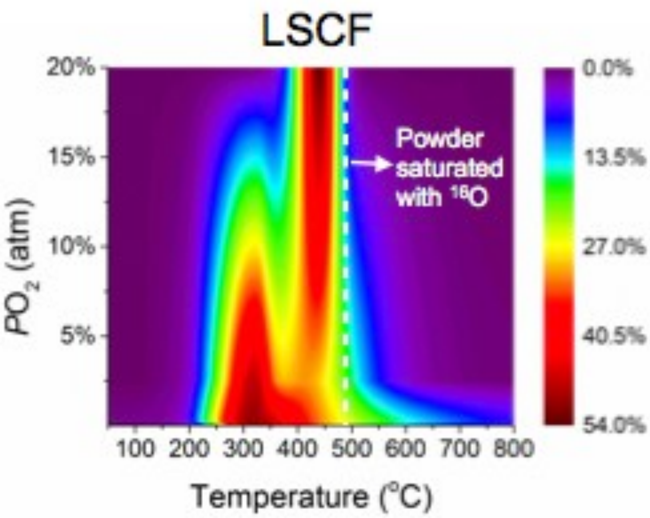


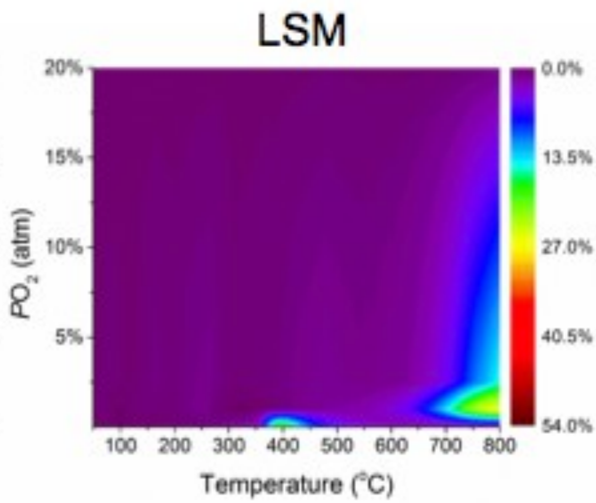


Two Exchange Peaks:
- As PO_2 increases, 300°C peak decreases
- 450°C peak still present at high PO_2

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

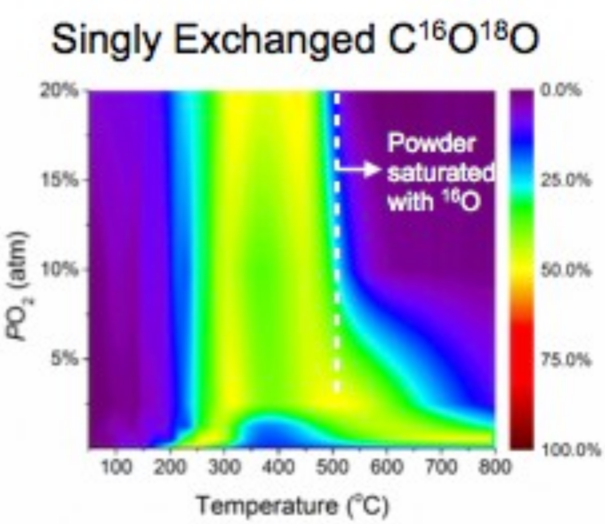
Comparison of LSCF and LSM Temp-PO_2 Dependence in D_2O

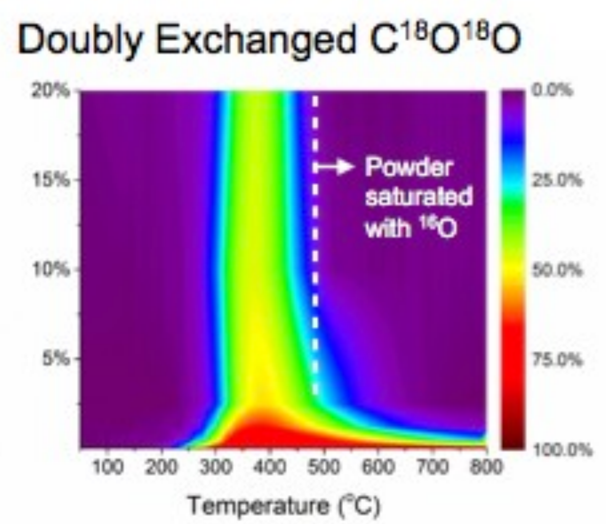




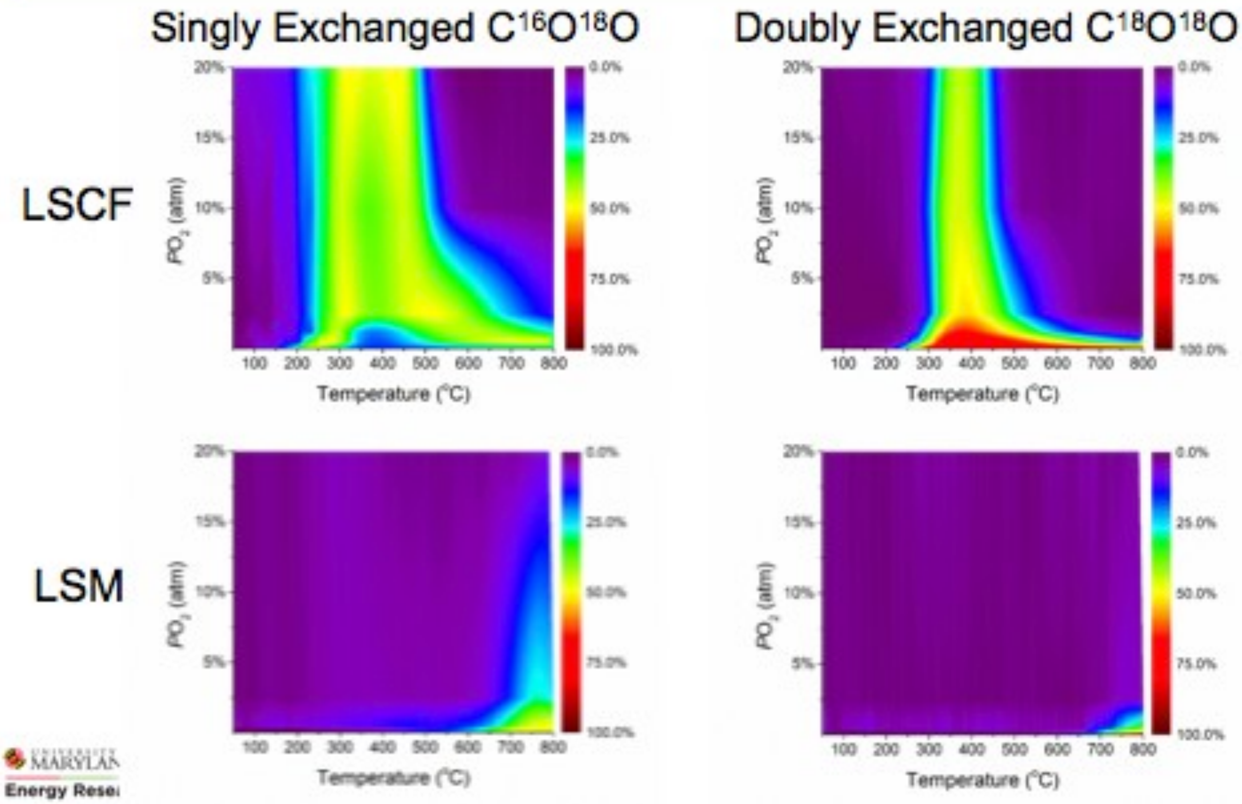
- LSCF more active toward D_2O exchange than LSM
- D_2O exchanges with LSM only at high temp in presence of O_2

Temperature and PO_2 Dependence of LSCF in CO_2

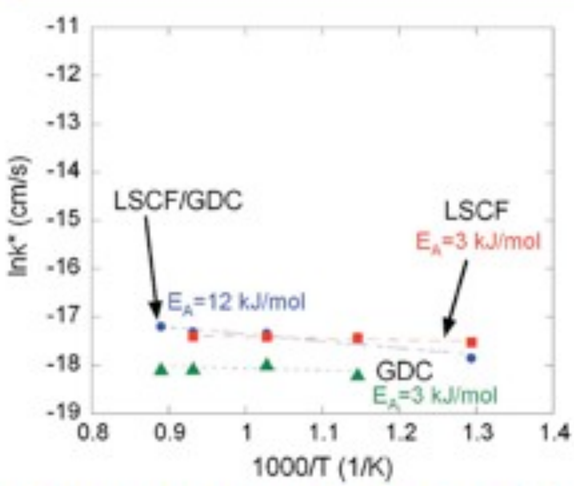


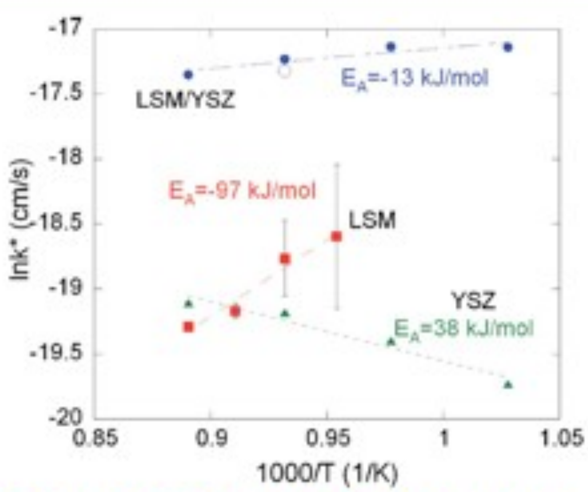


Comparison of LSCF and LSM Temp-PO_2 Dependence in CO_2



Effect of Composite Cathodes on Surface Exchange





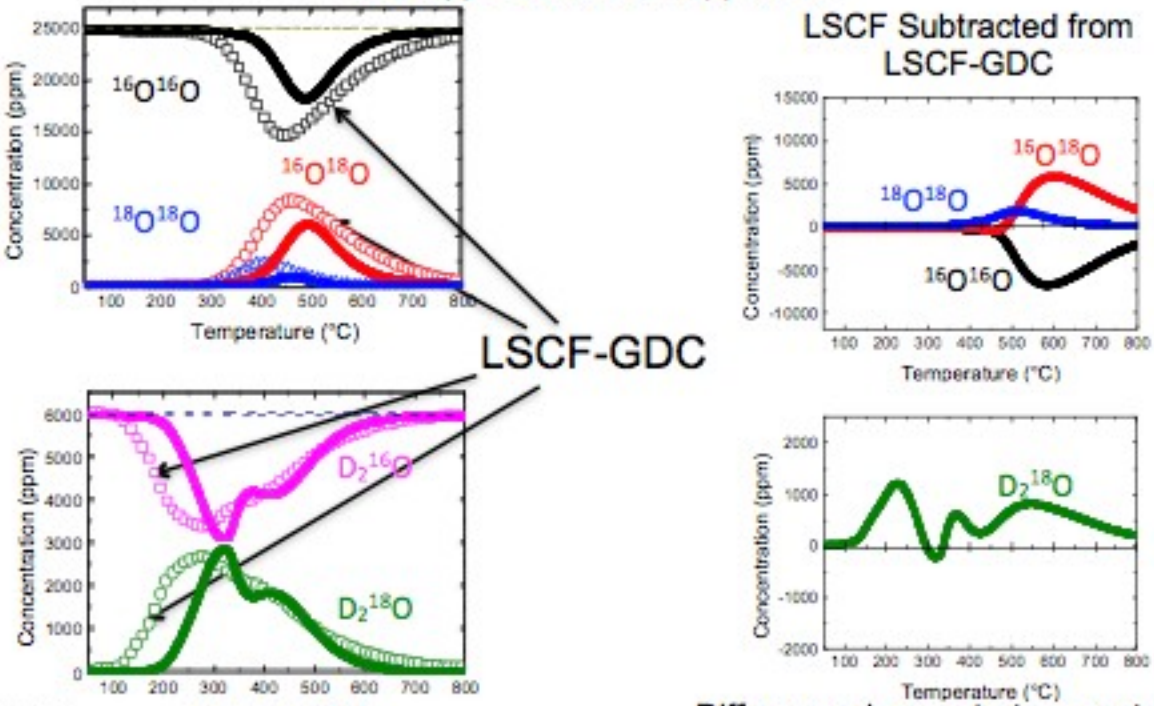
- From our previous observation LSCF-GDC and LSCF have similar exchange kinetics due to both having high oxygen vacancy concentration
- While LSM-YSZ is dramatically enhanced relative to LSM indicating greater importance of TPBs and co-existence of O-dissociation and O-incorporation phases

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

E. N. Armstrong, K. L. Duncan, and E. D. Wachsman

Comparison of LSCF and Composite LSCF-GDC in D_2O

25000ppm O_2 and 6000ppm D_2O



Difference demonstrates greater D_2O exchange with composite

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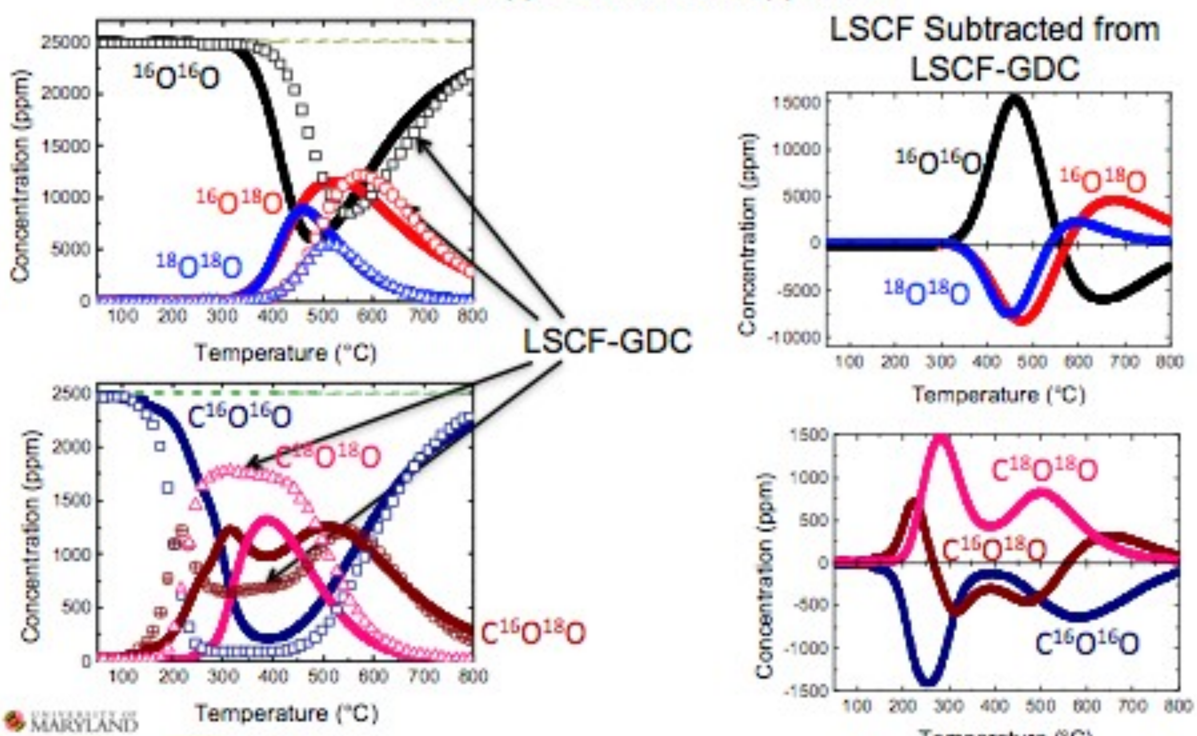
Comparison of LSCF and Composite LSCF-GDC in CO_2

25000ppm O_2 and 2500ppm CO_2



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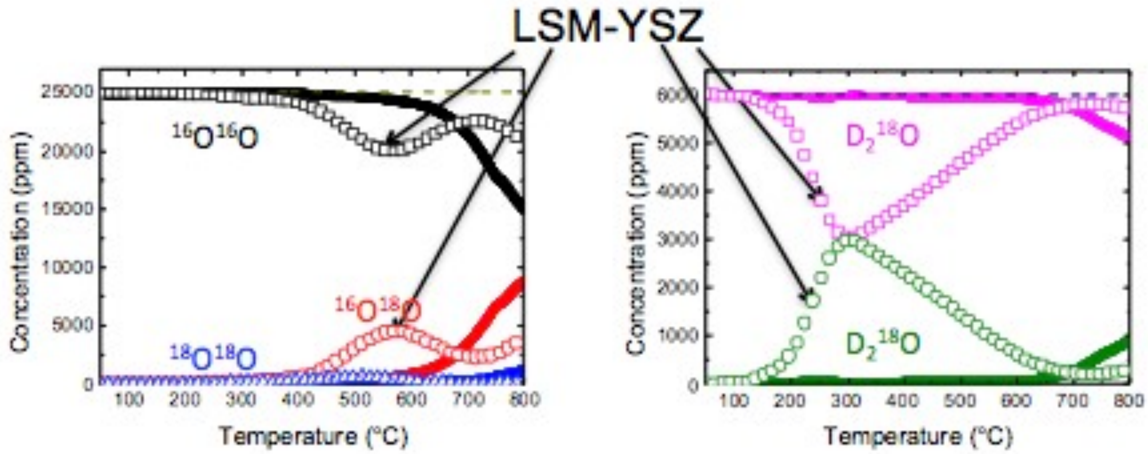
Comparison of LSM and Composite LSM-YSZ in D_2O

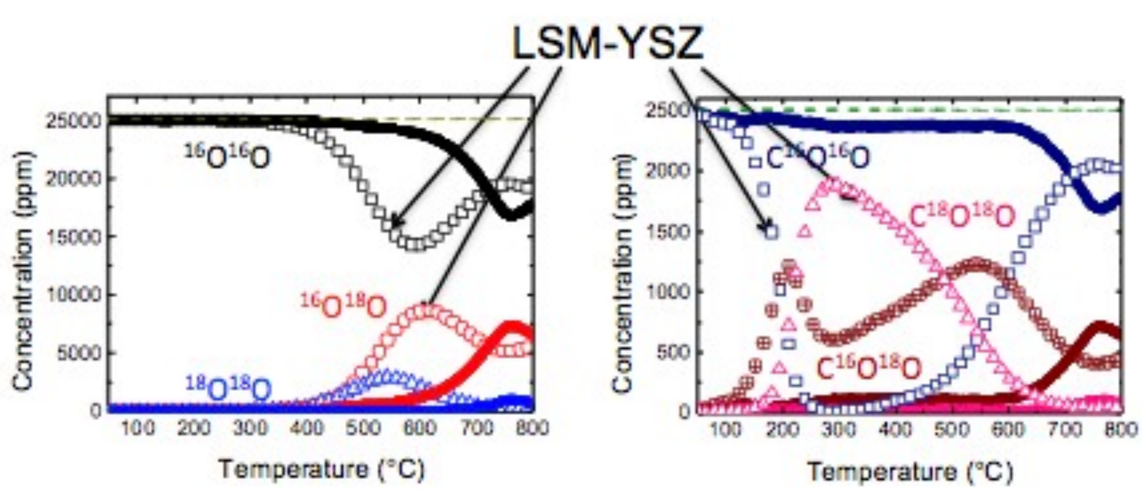
25000ppm O_2 and 6000ppm D_2O



- LSM-YSZ composite demonstrates much greater exchange than LSM at much lower temp for D_2O
- Composite effect for LSM-YSZ much greater than for LSCF-GDC

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

Conclusions

- We are integrating polarization measurements (EIS) with microstructural characterization (FIB/SEM) and heterogeneous catalysis (IIE & ISTPX) to provide fundamental understanding of cathode ORR and degradation mechanisms
- Demonstrated direct correlation between LSM/YSZ cathode impedance changes during aging in 3% H_2O and changes in O_2 surface exchange of LSM and LSM/YSZ microstructural and compositional changes
- O^{18}- 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