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

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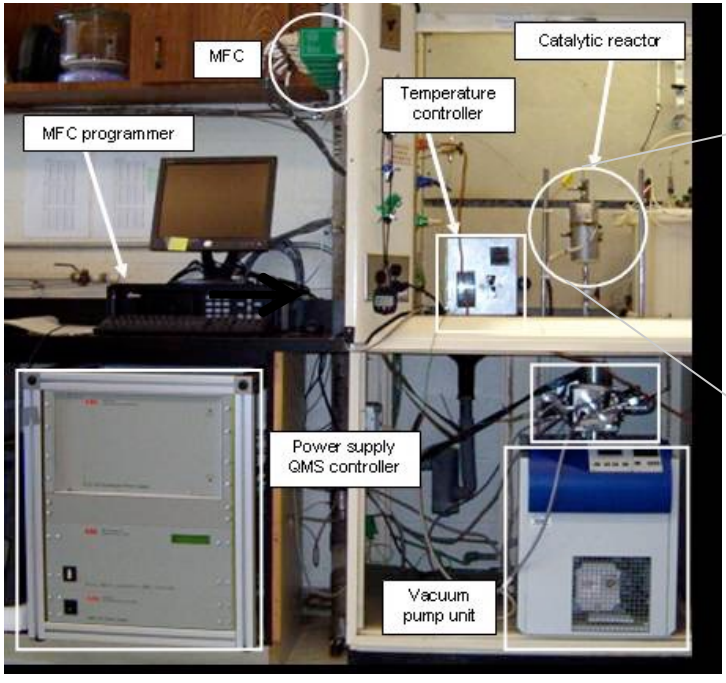
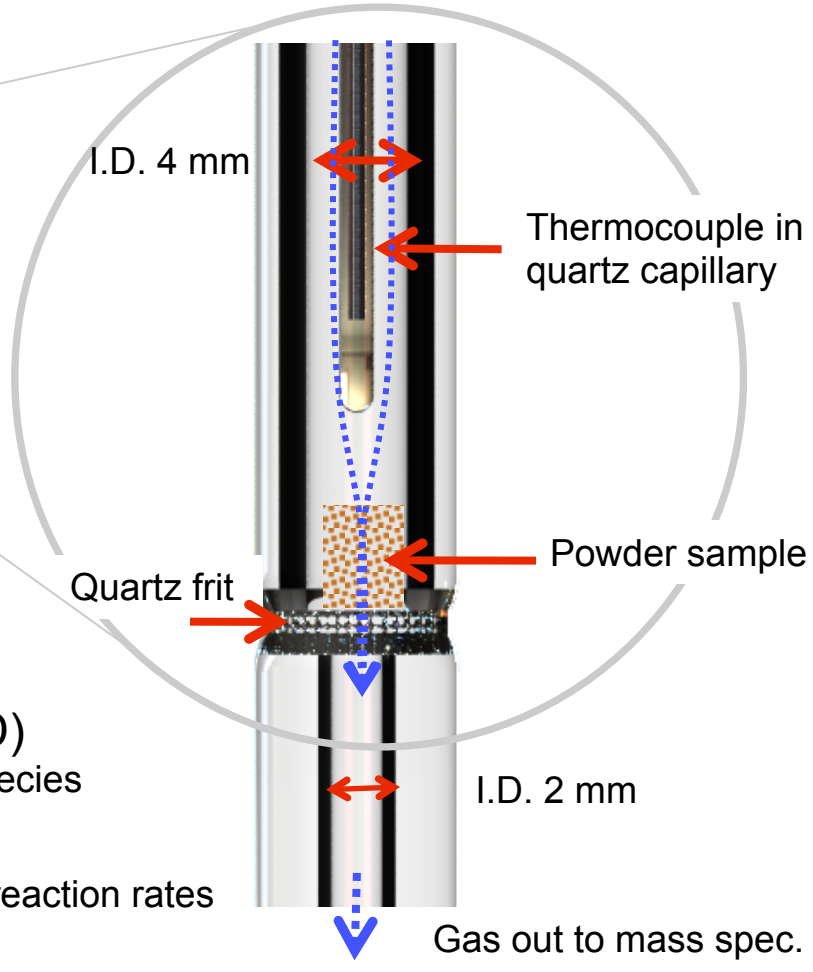
Lourdes Salamanca-Riba, Christopher Pellegrinelli,
Yi-Lin Huang, Joshua Taillon
US Department of Energy, National Energy Technology Laboratory, Contract No. FE0009084
09/01/2012-08/31/2015

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

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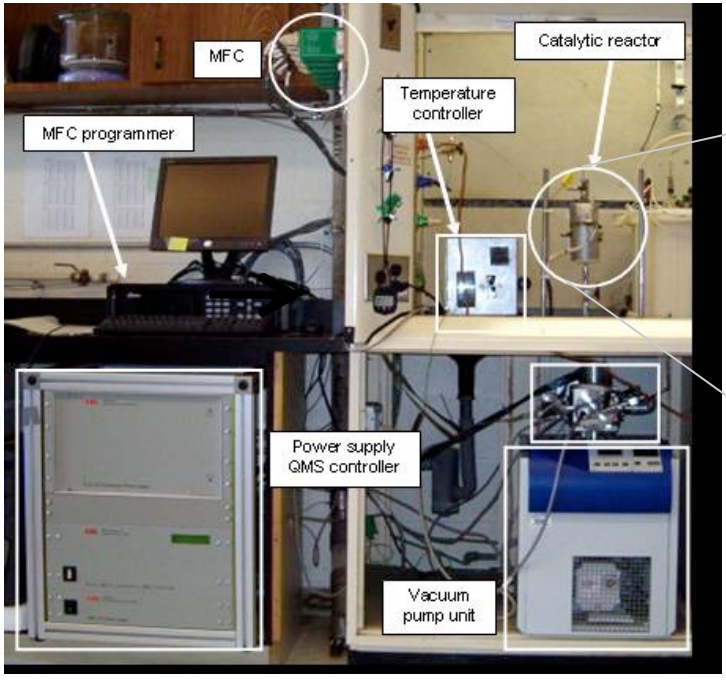

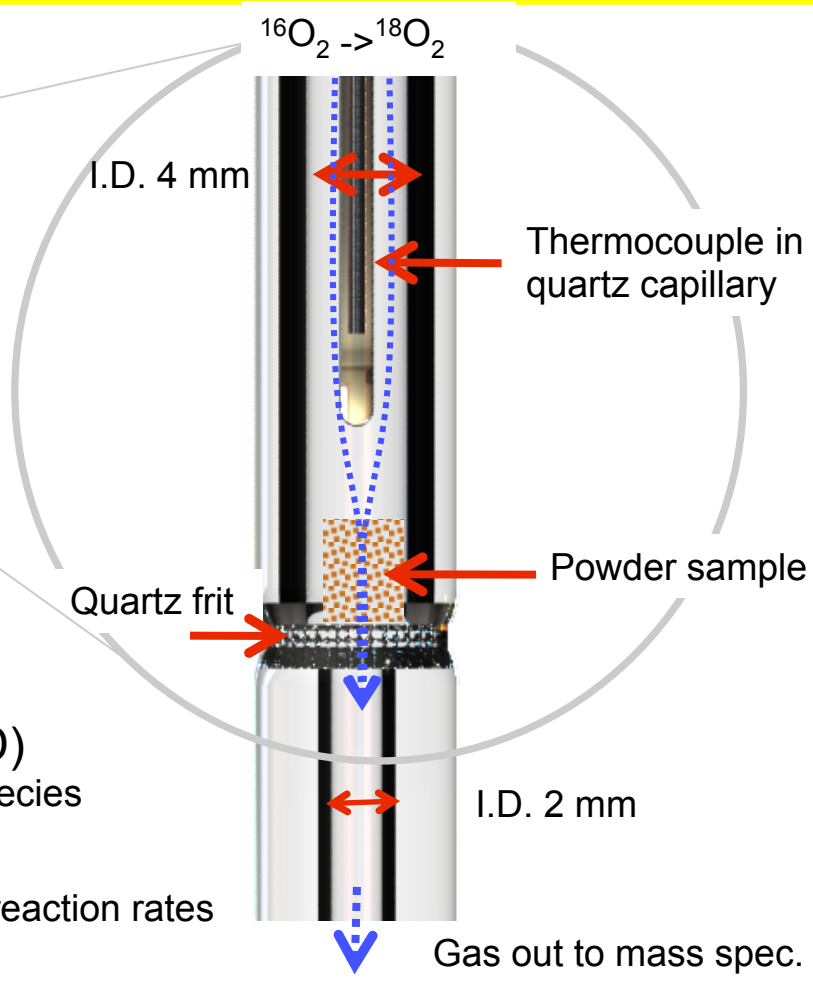

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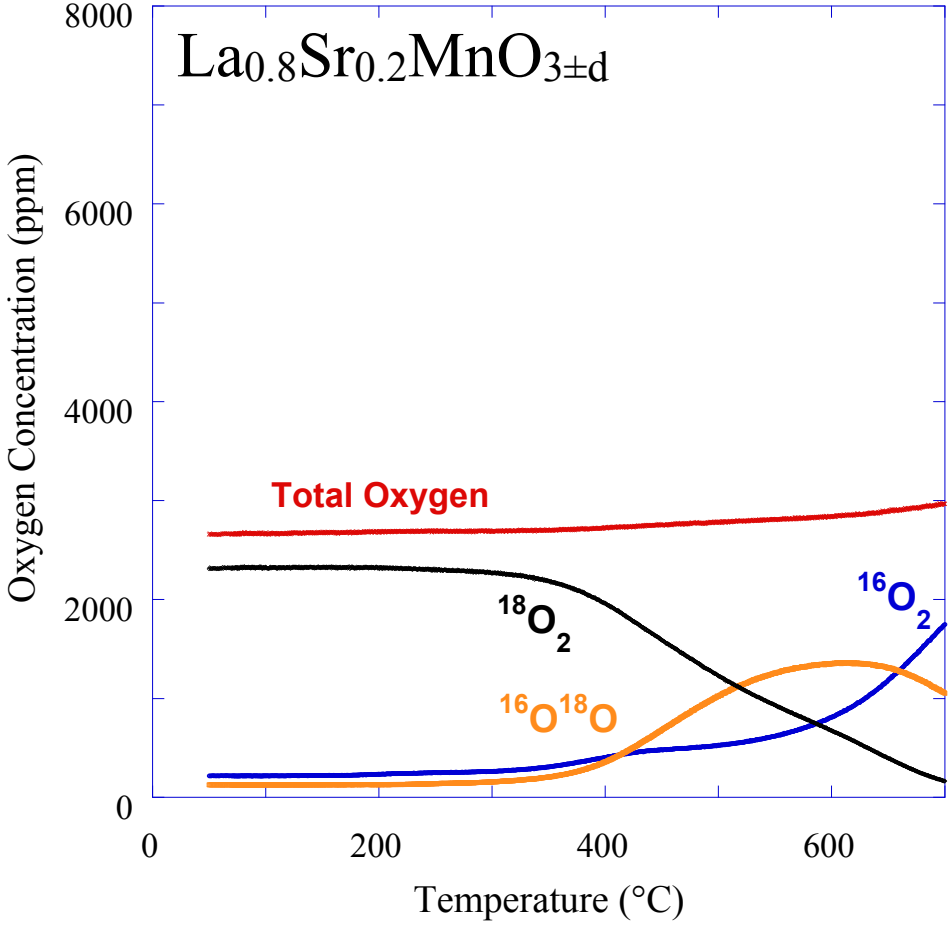
Fundamental ORR Mechanisms - Catalysis



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

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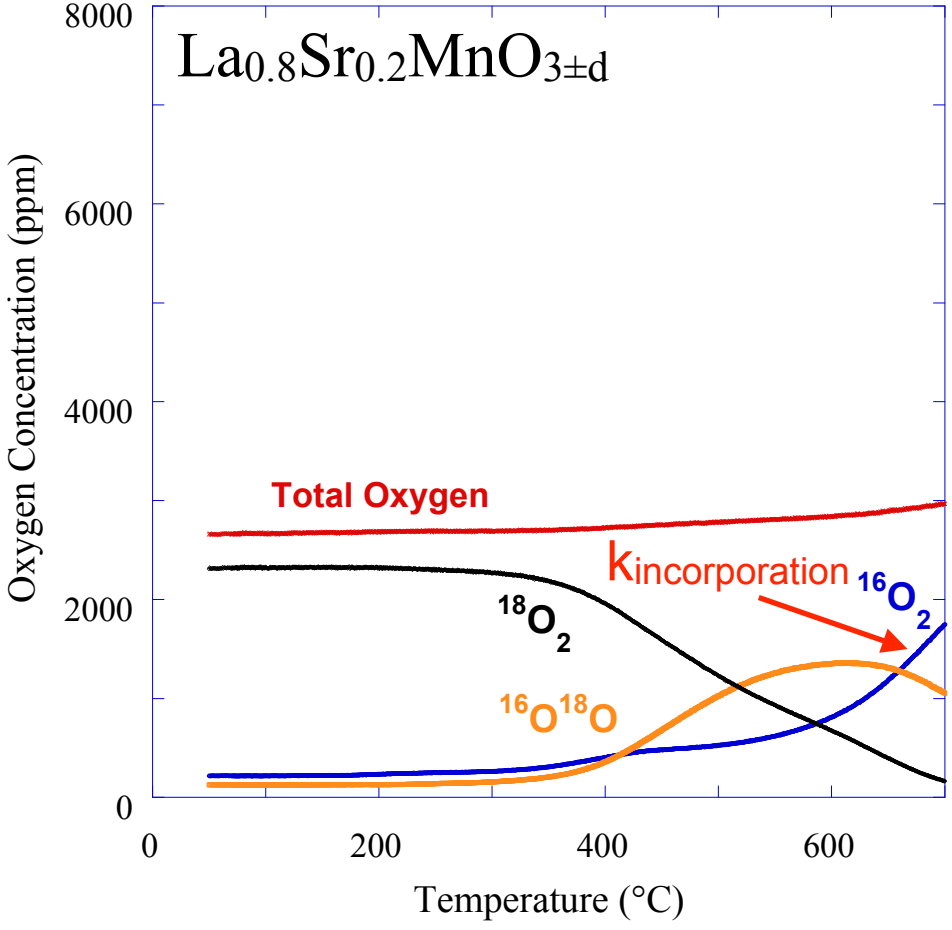

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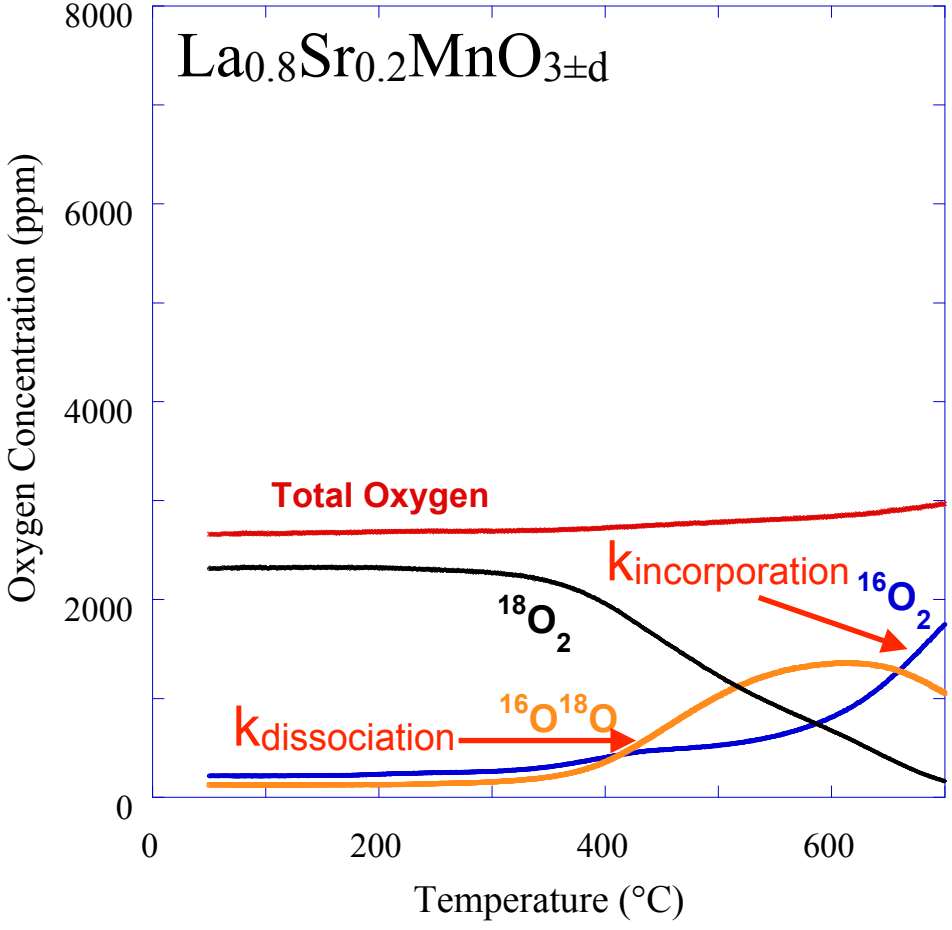

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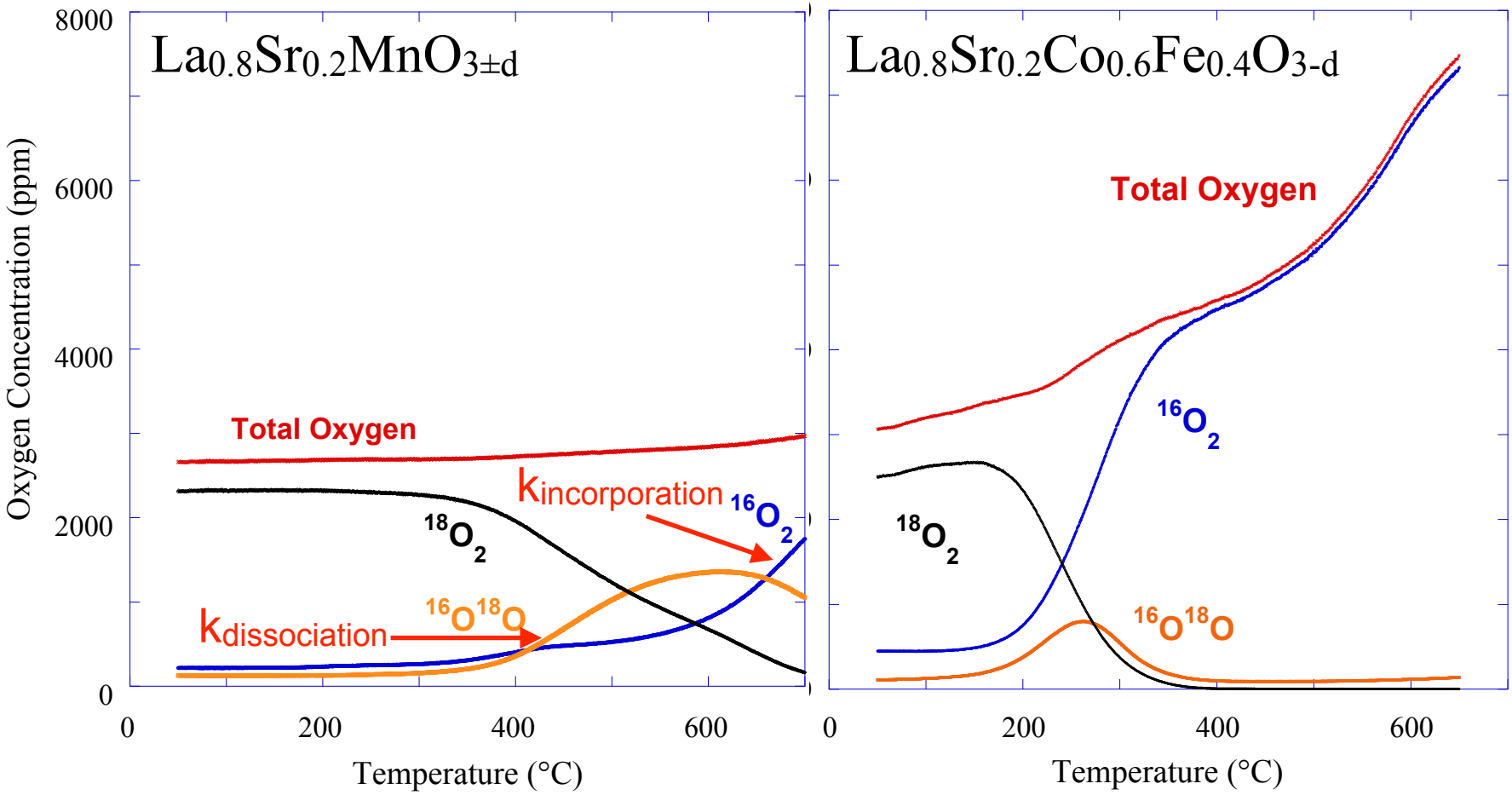

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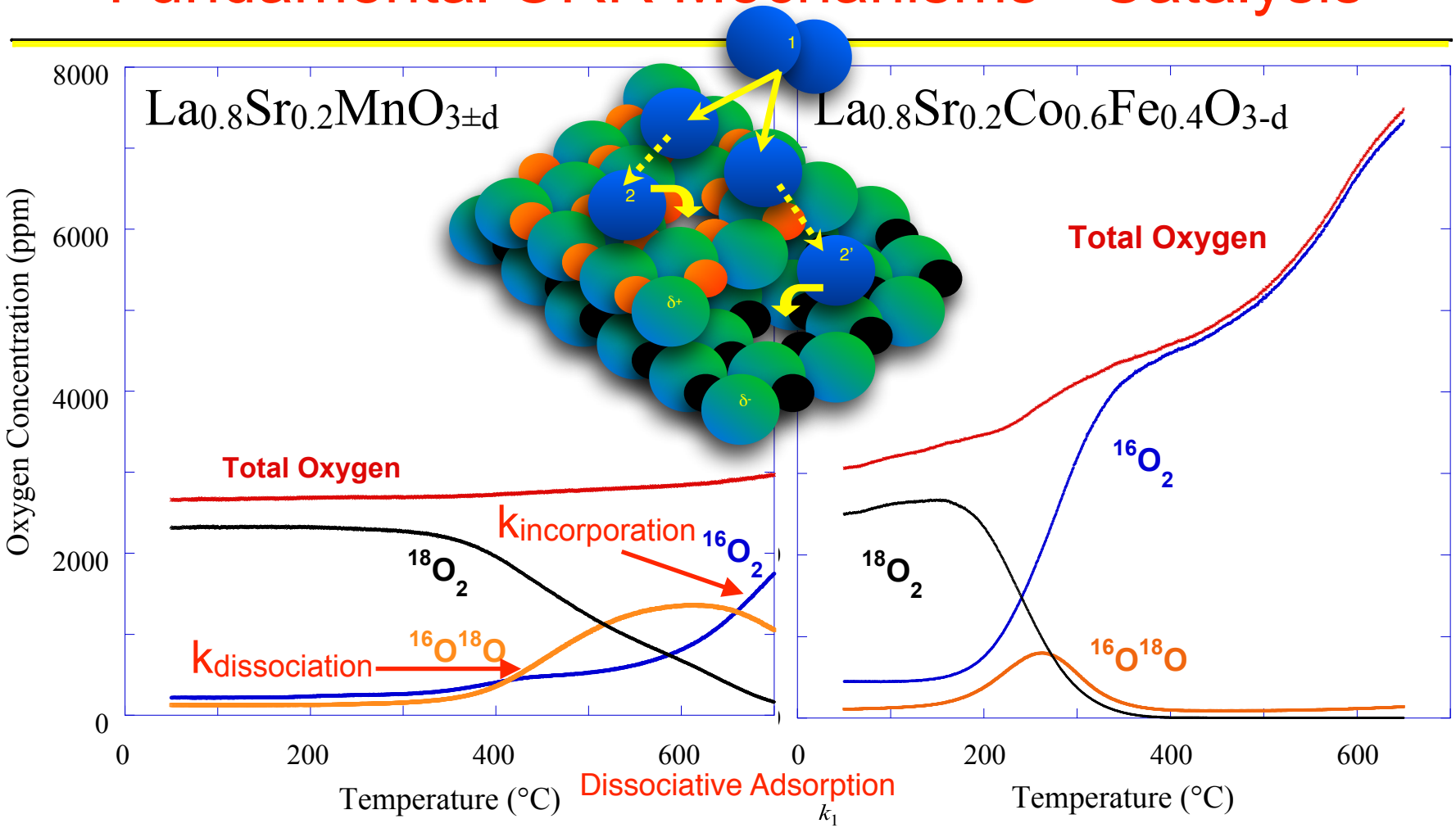


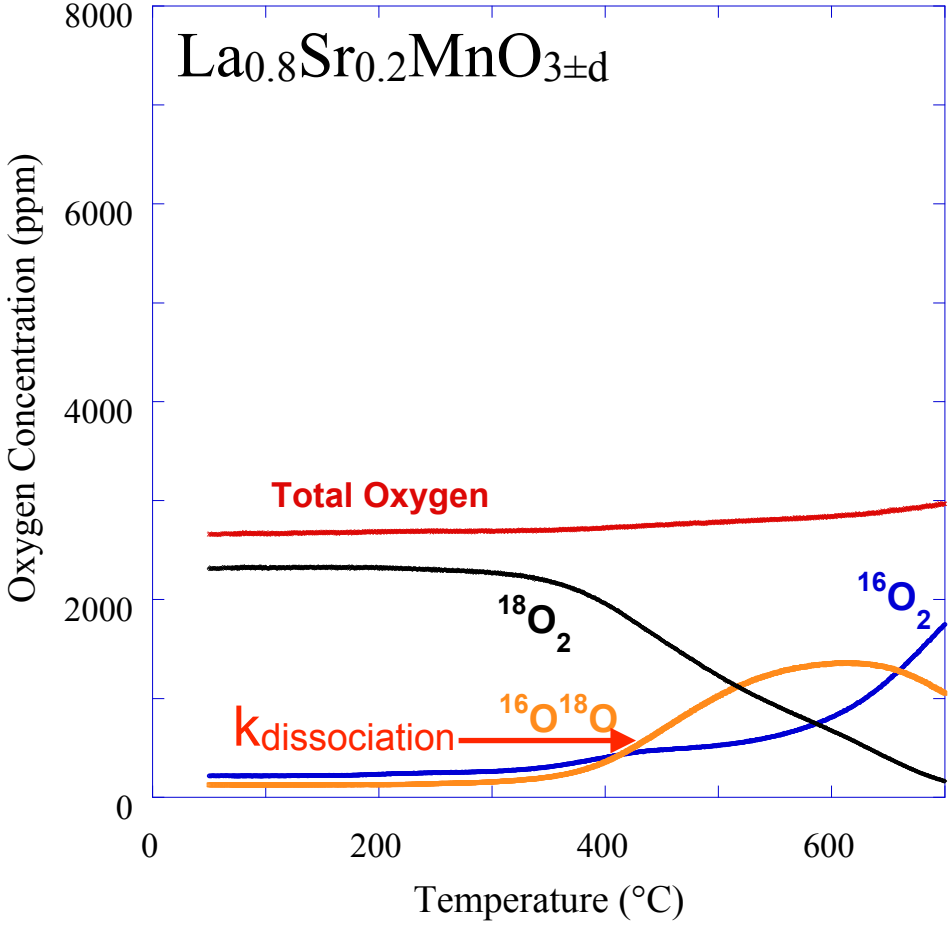
Dissociative Adsorption

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

Incorporation

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

Fundamental ORR Mechanisms - O_2 Dissociation



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Surface Interfaces

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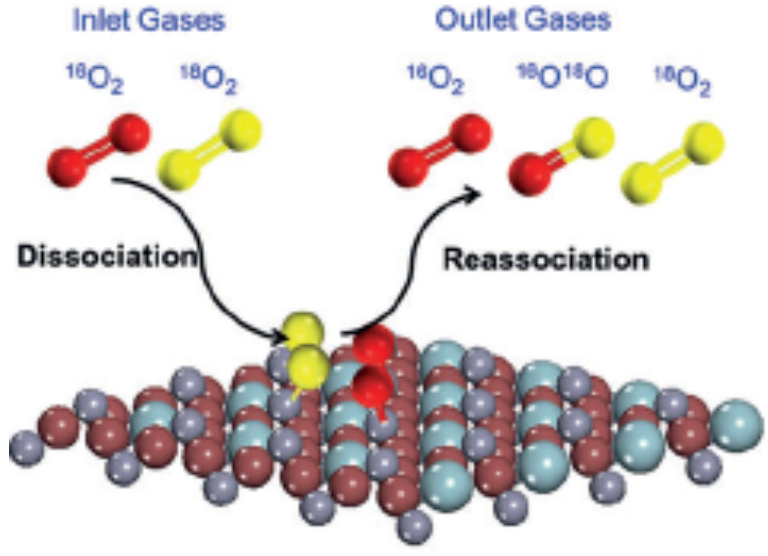
Direct Observation of Oxygen Dissociation on Non-Stoichiometric Metal Oxide Catalysts

*Yi-Lin Huang, Chistopher Pellegrinelli, and Eric D. Wachsman**



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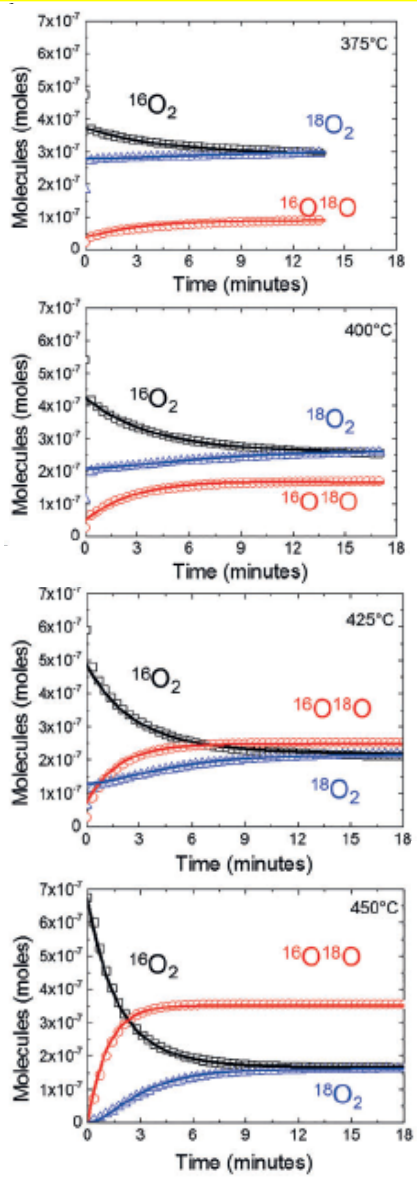
Fundamental ORR Mechanisms - O_2 Dissociation



Increase in [$^{16}O^{18}O$] with temperature until achieves 50%(maximum statistical conversion)

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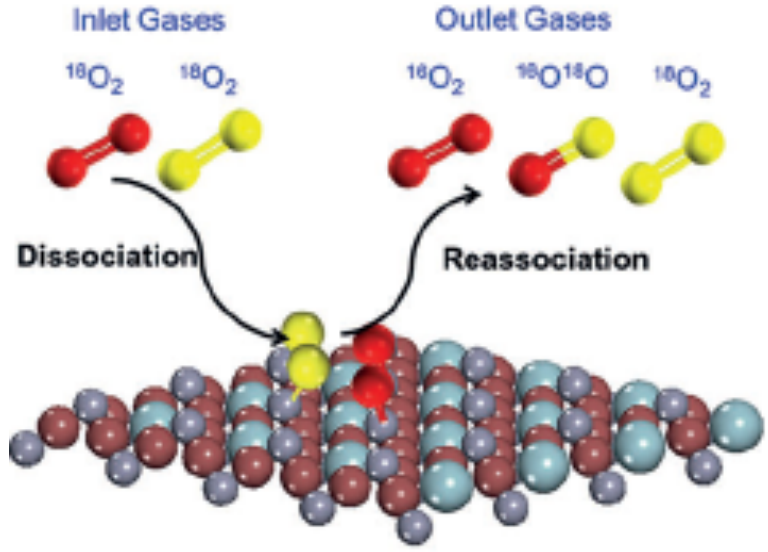

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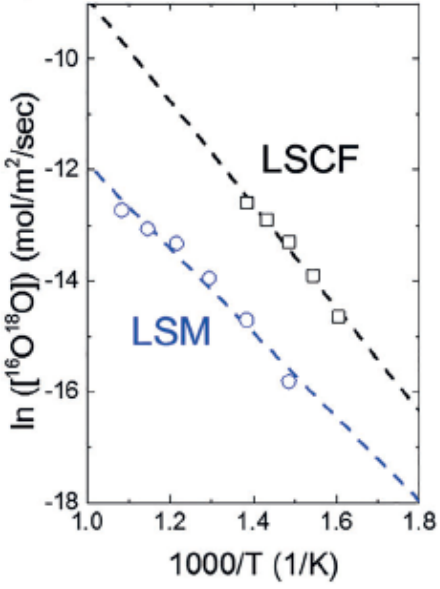
Fundamental ORR Mechanisms - O_2 Dissociation

Providing first ever direct measurement of O_2 dissociation rates



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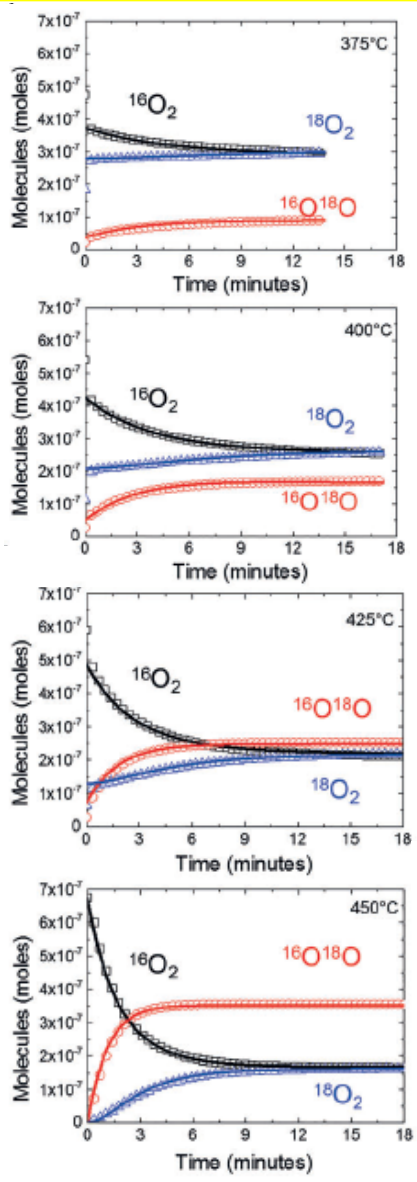

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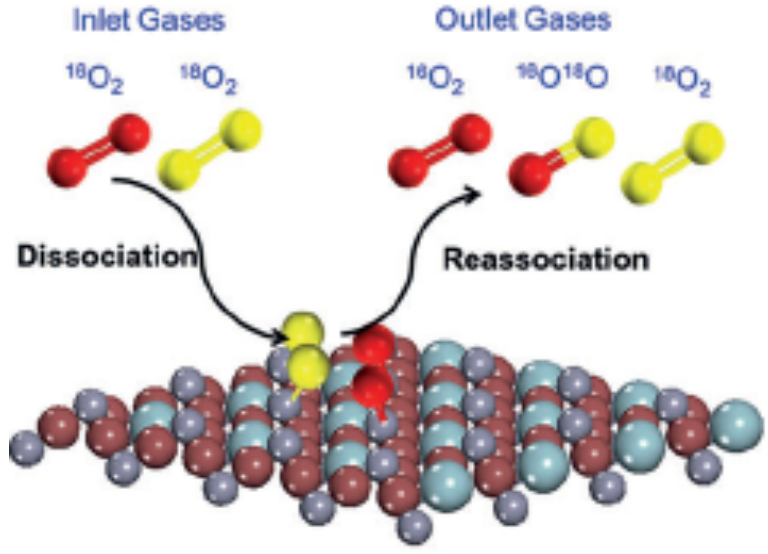

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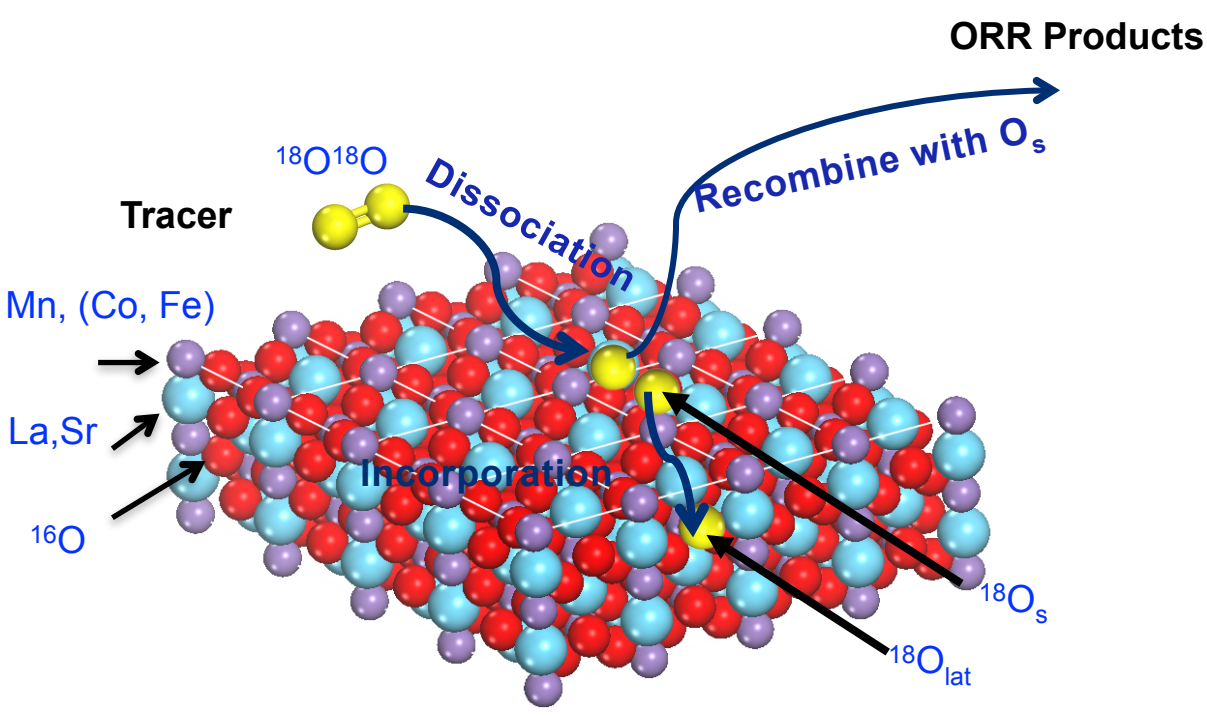
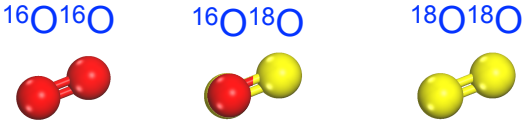
ORR Reaction Mechanisms in Presence of H_2O and CO_2

In situ Isotope Exchange (IIE)





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

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

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

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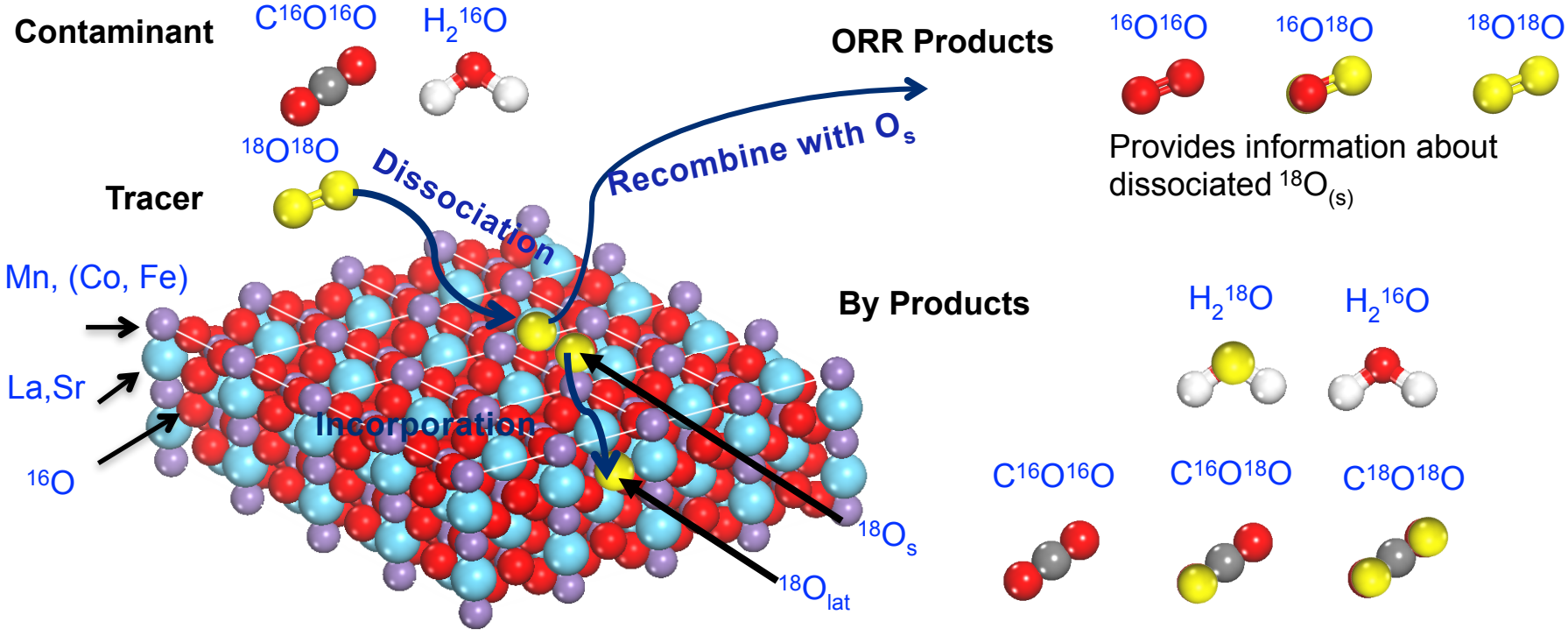

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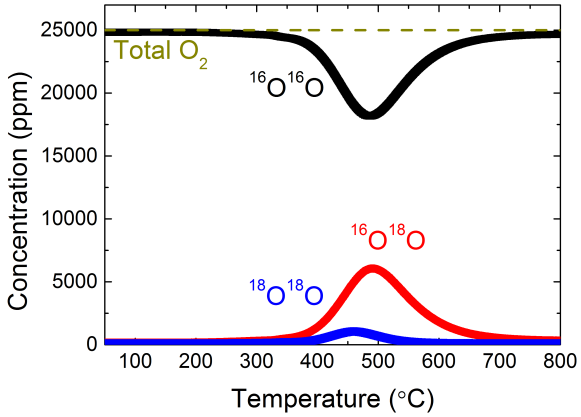
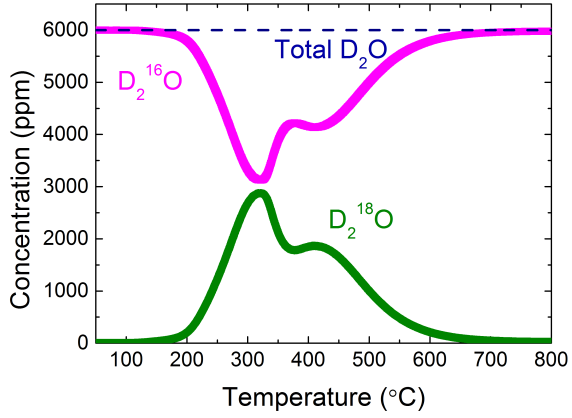
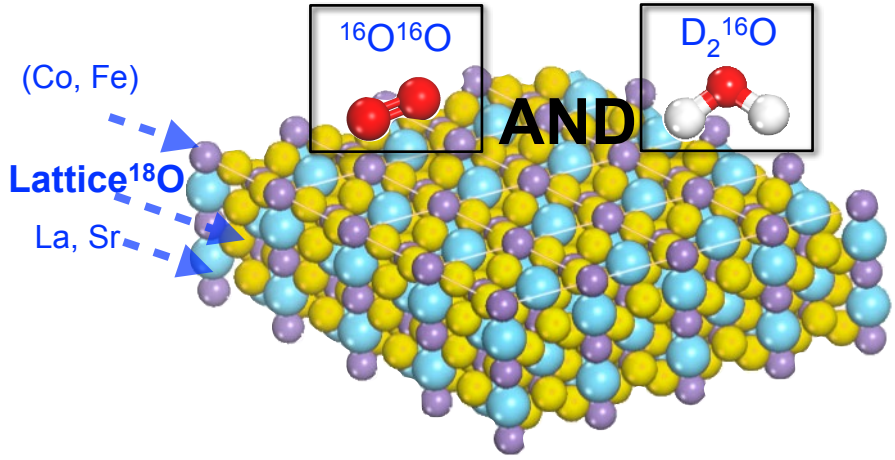
ISTPX of LSCF in 25000ppm O_2 with 6000ppm D_2O

O_2 exchange with lattice ^{18}O



D_2O exchange with lattice ^{18}O





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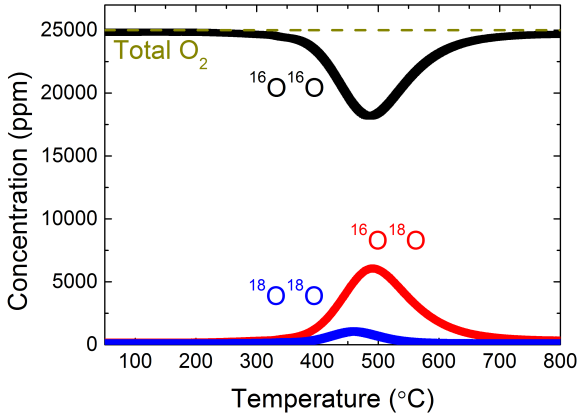
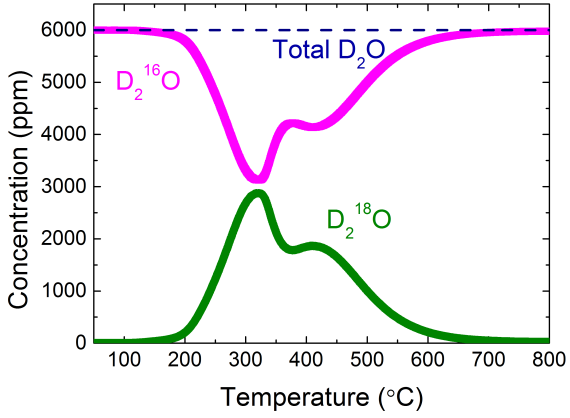
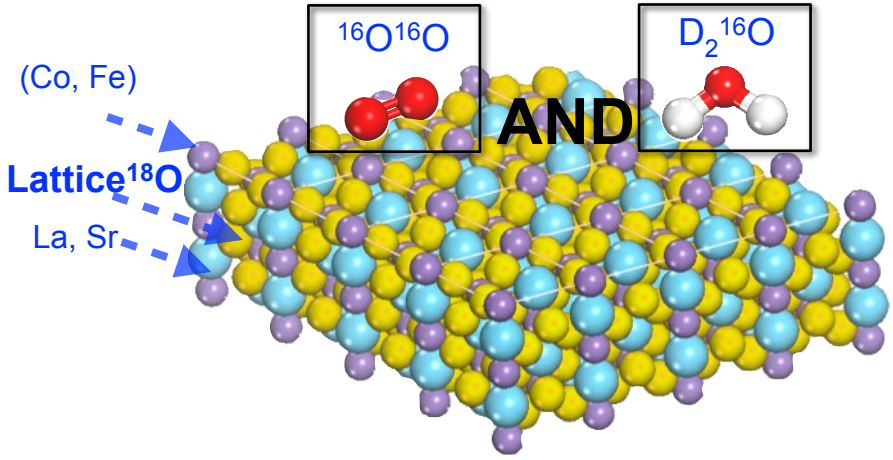


Mass of:
$^{18}O = 18$
$H_2{}^{16}O = 18$
$D_2{}^{16}O = 20$
$D_2{}^{18}O = 22$

D_2O exchange with lattice ^{18}O





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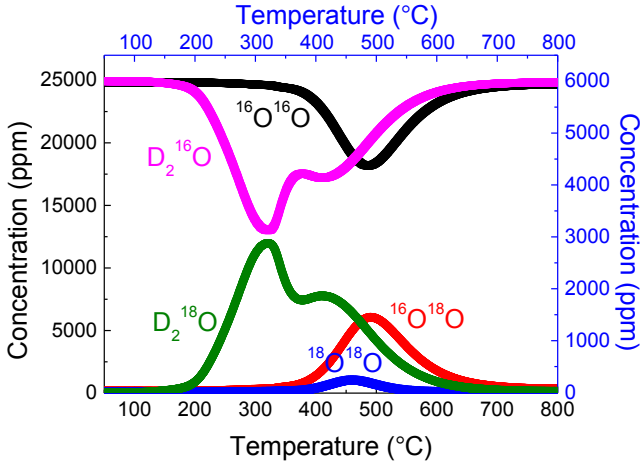
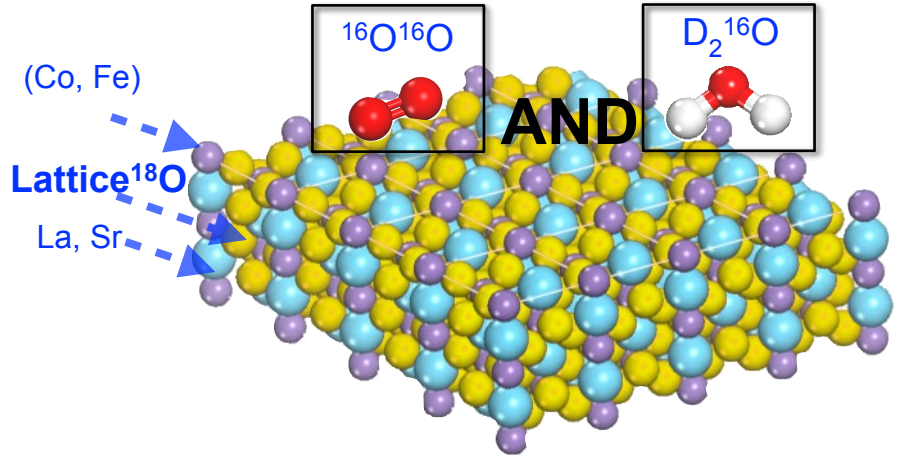
D_2O and O_2 exchange with lattice ^{18}O





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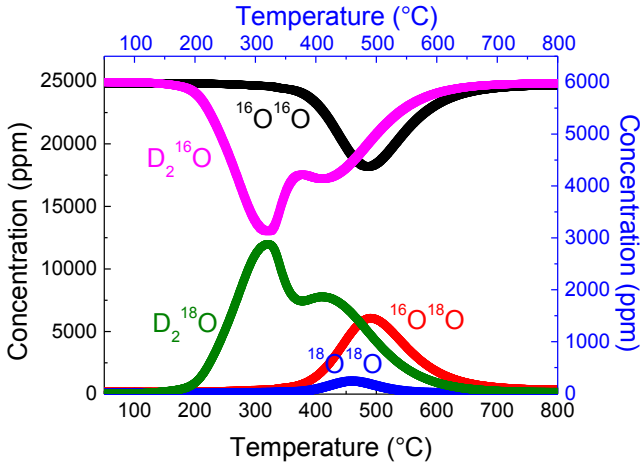
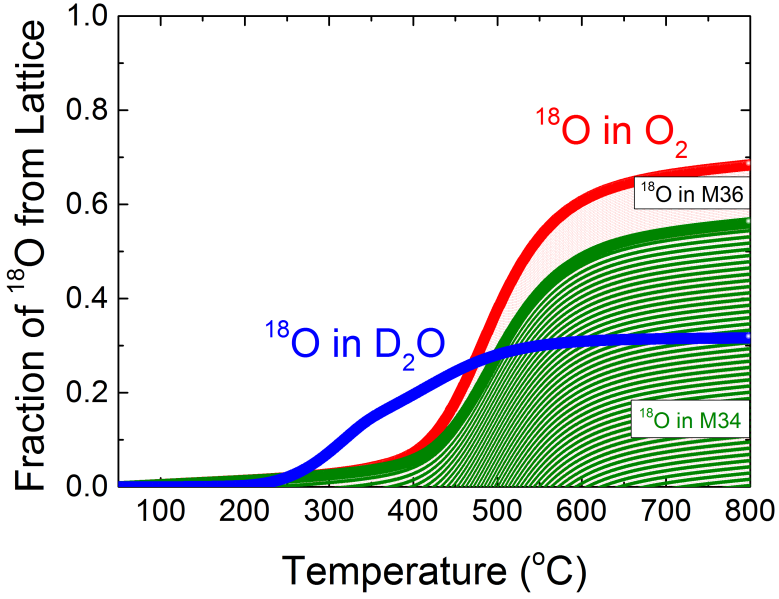
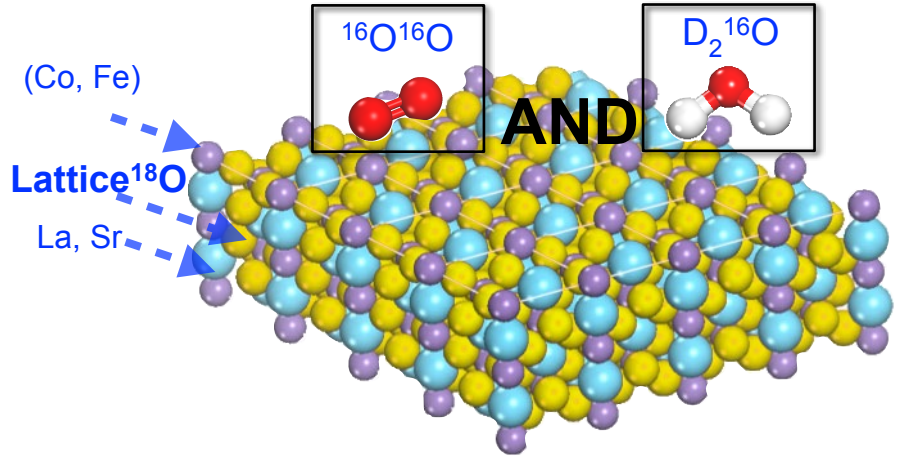


At lower temperature more of the lattice ^{18}O exchanges with water than O_2

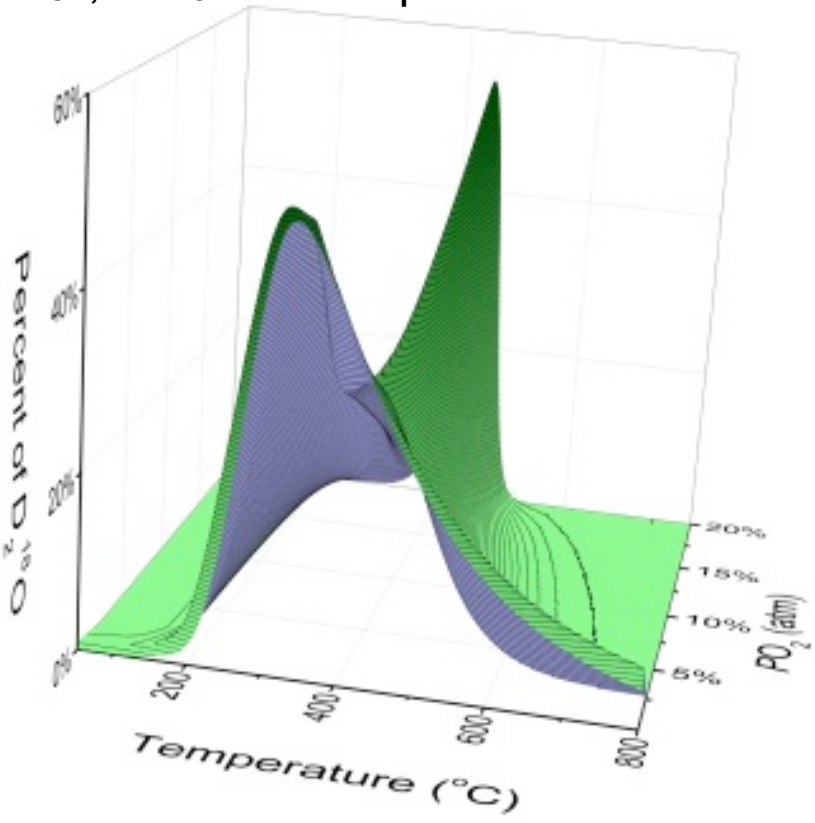
Accumulated Isotopic Fraction exchanged from ^{18}O LSCF





Temperature and PO_2 Dependence of LSCF in D_2O

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



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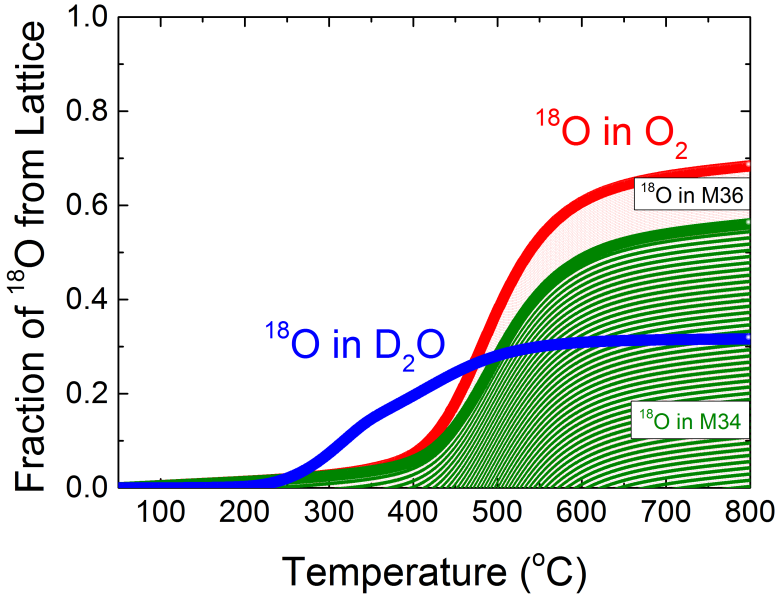

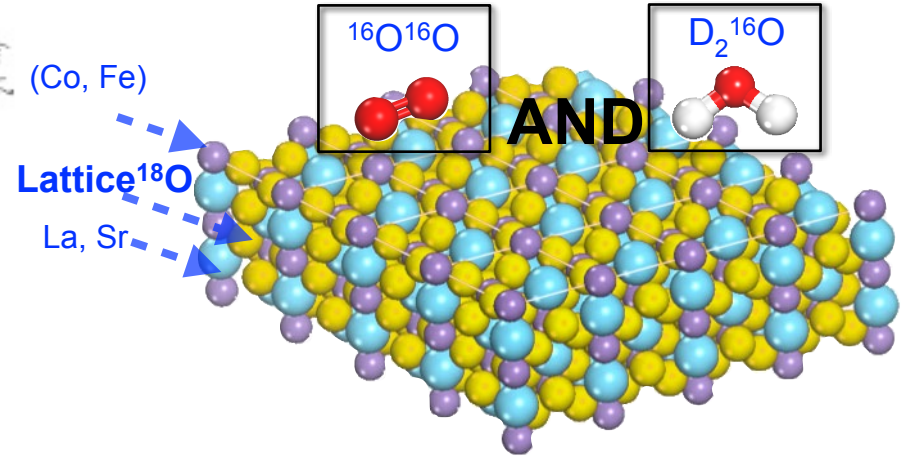

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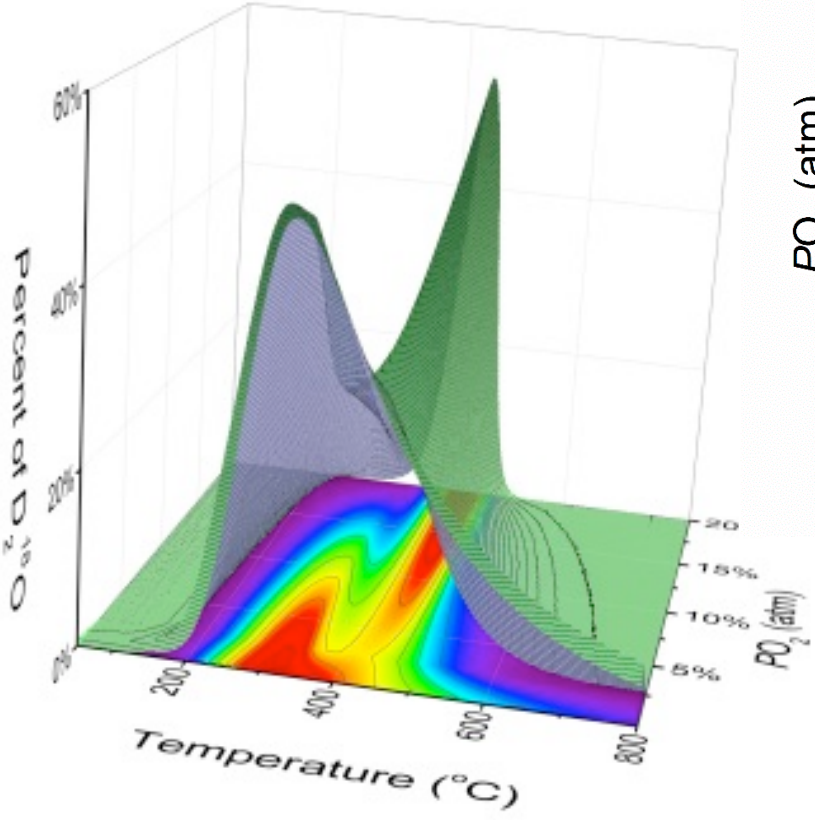

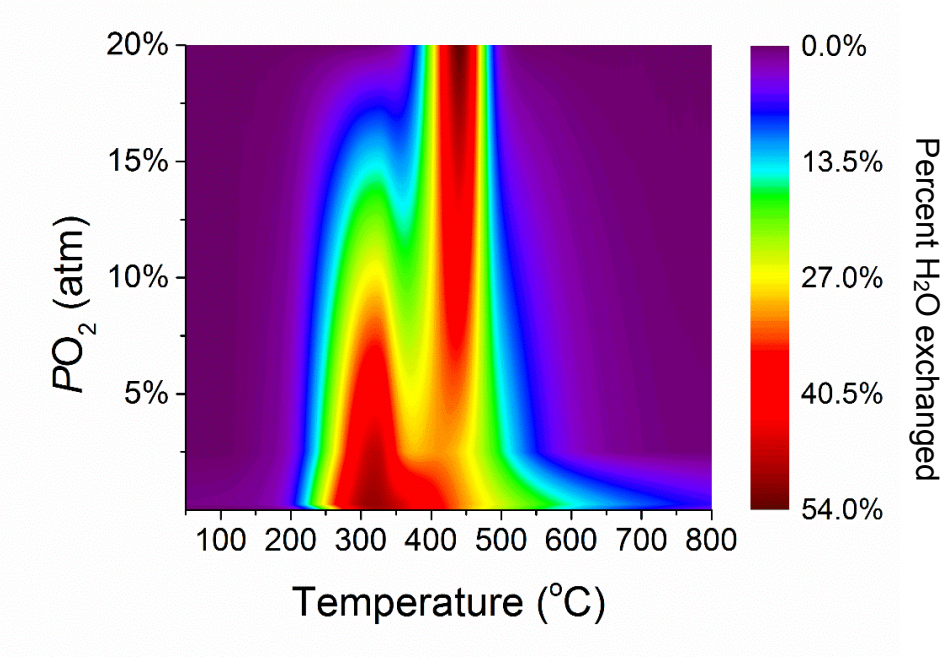

Two Exchange Peaks:
- As PO_2 increases, 300ºC peak decreases
- 450ºC peak still present at high PO_2

- We mapped out H_2O and CO_2 impact on ORR as function of P_{O2}, temperature, and concentration

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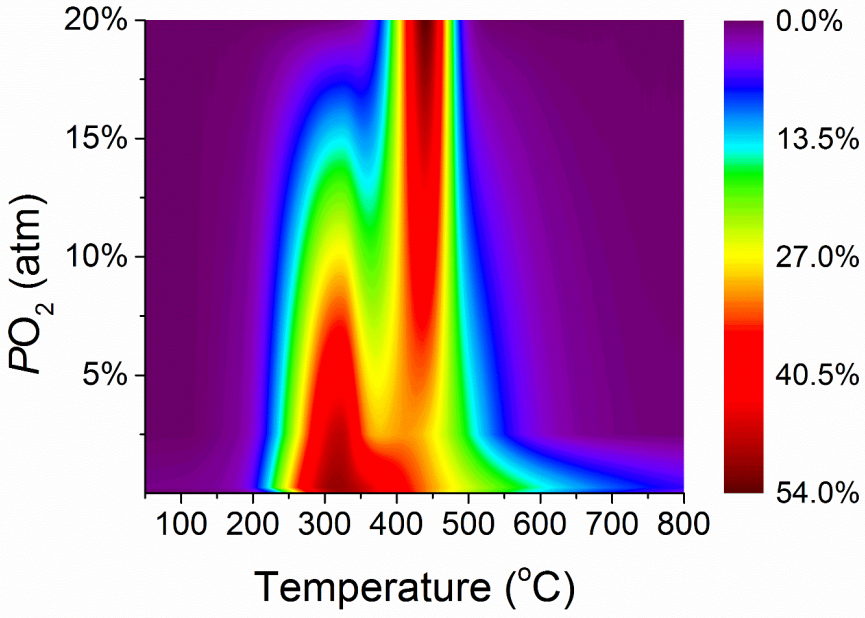
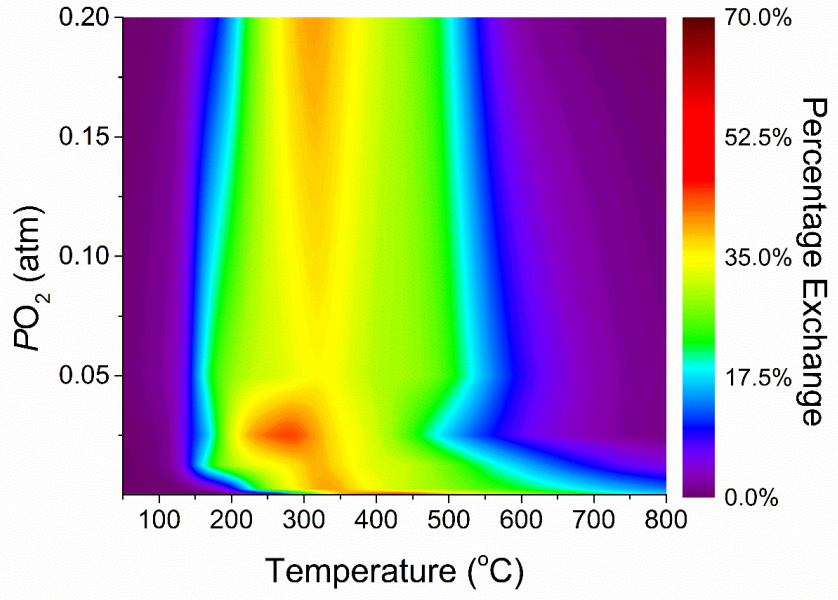
Direct observation of enhanced water and carbon dioxide reactivity on multivalent metal oxides and their composites†

Water Exchange on LSCF vs LSCF-GDC Composite Cathodes

LSCF



LSCF-GDC



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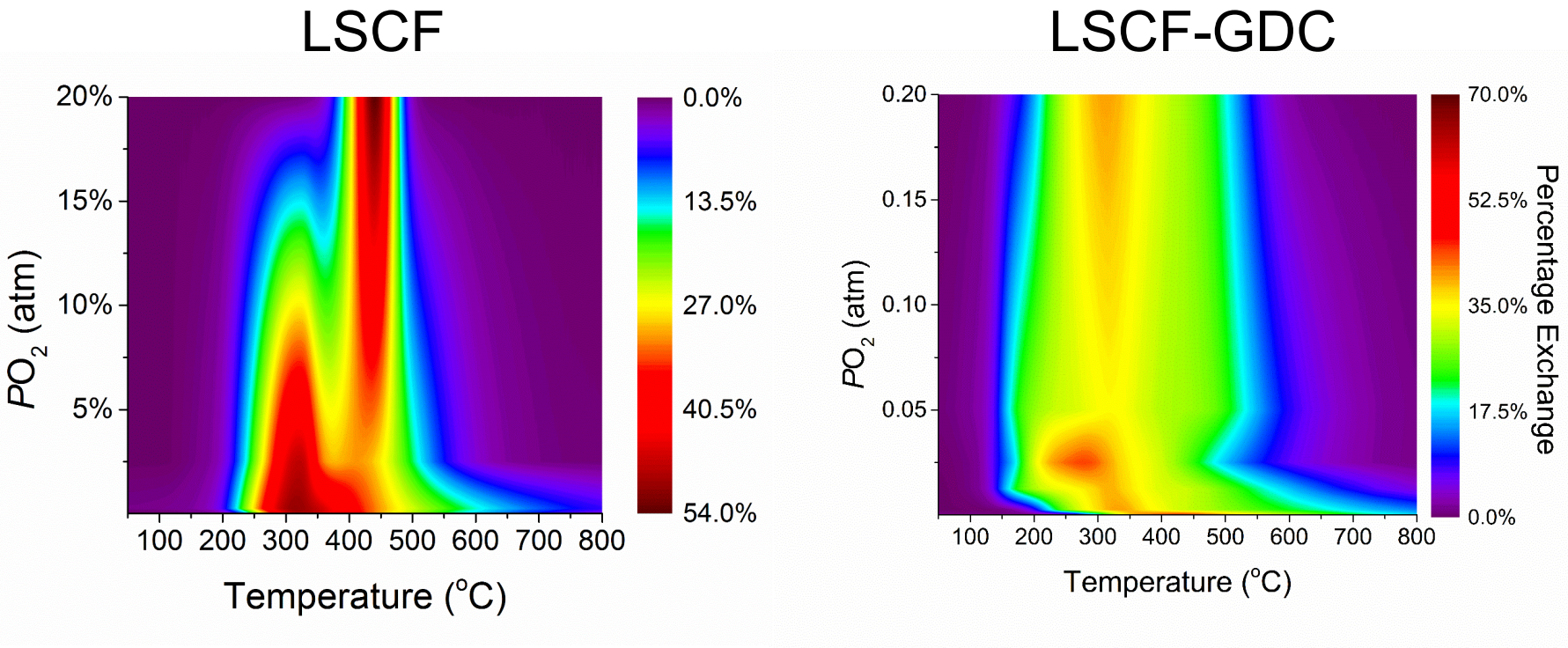

- LSCF composite significantly broadens temperature range of water exchange dominance

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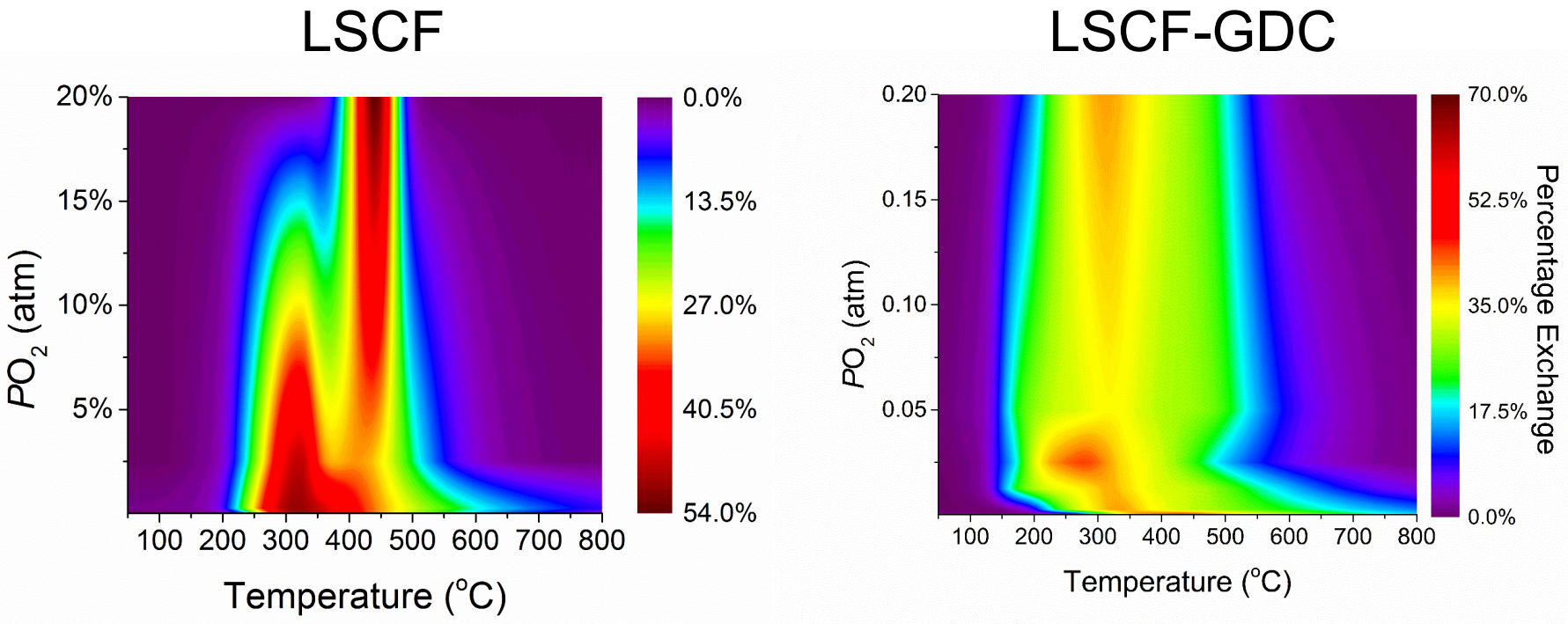

- LSCF composite significantly broadens temperature range of water exchange dominance
- Demonstrating importance of TPBs and co-existence of O-dissociation and O-incorporation phases

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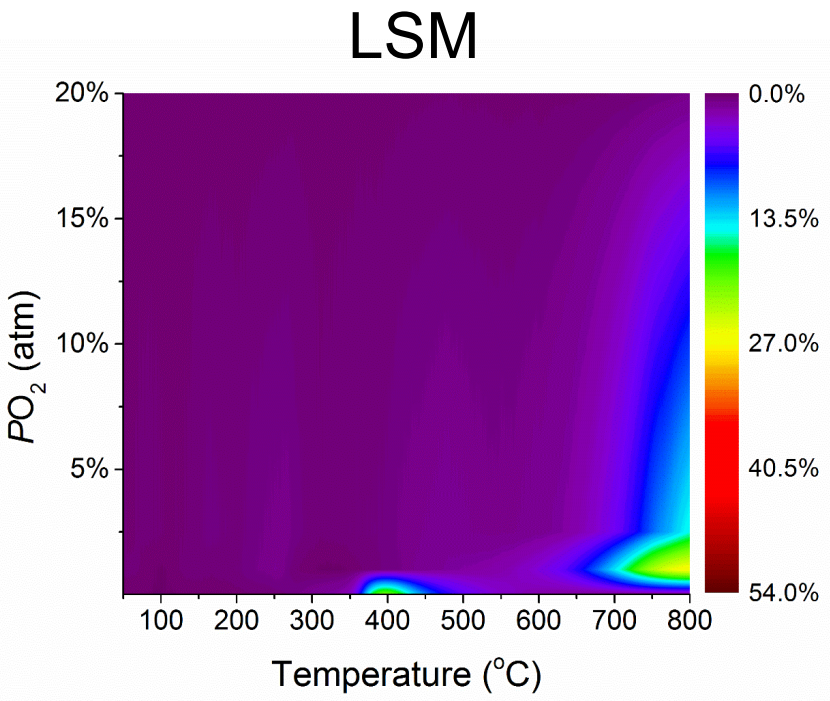
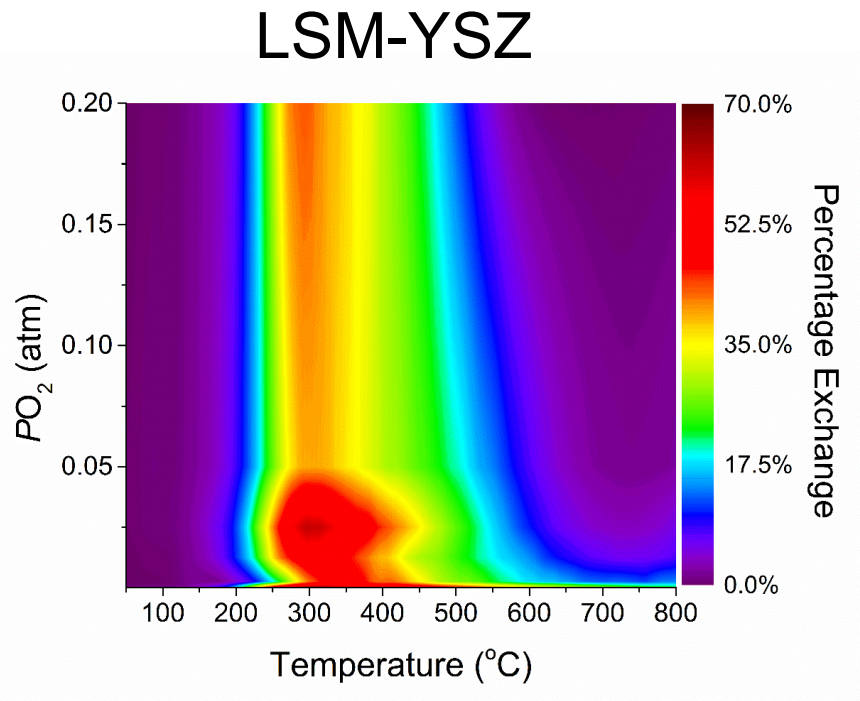
Water Exchange on LSM vs LSM-YSZ Composite Cathodes





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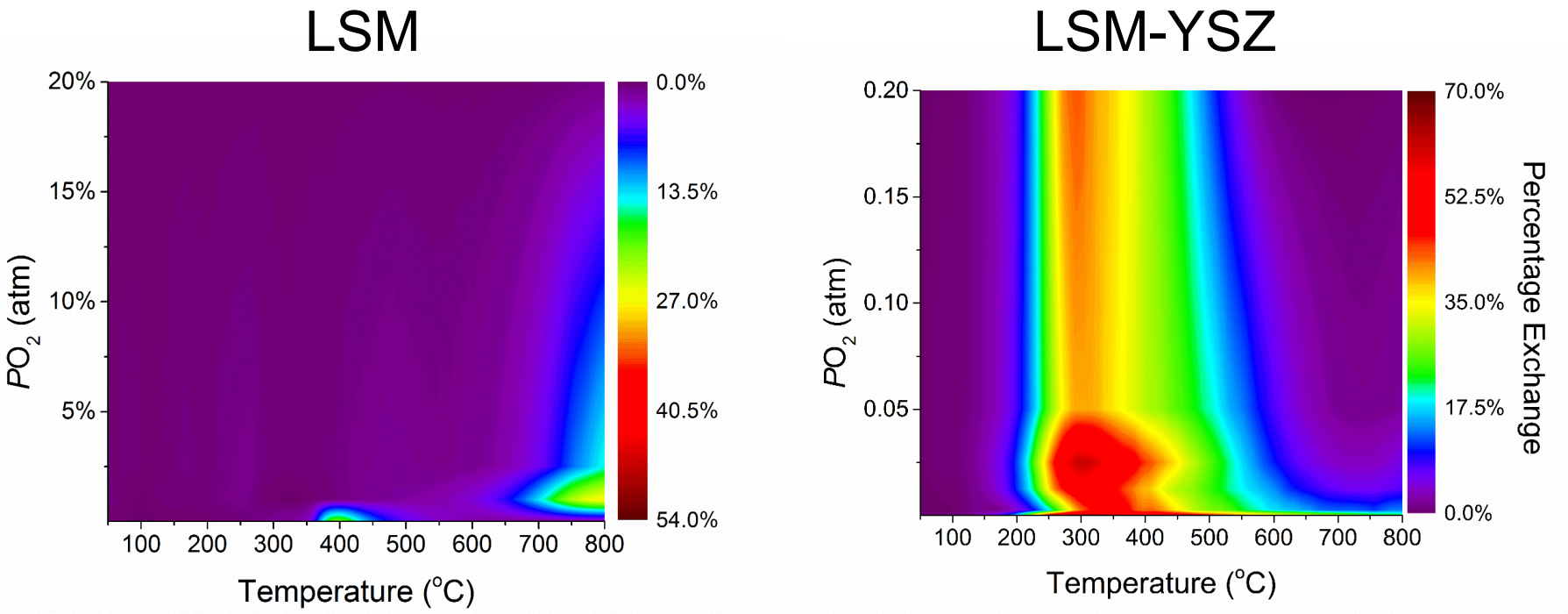

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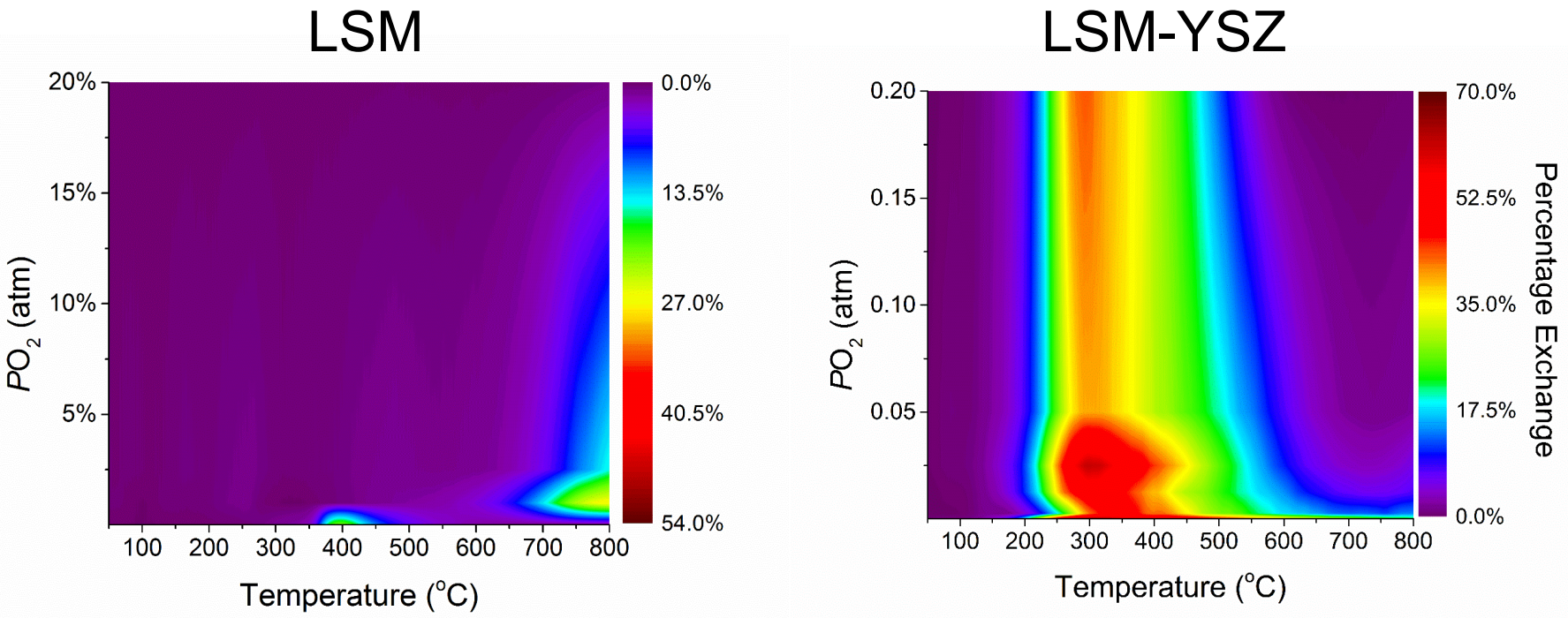

- LSM-YSZ composite demonstrates much greater water exchange than LSM or YSZ at much lower temp
- Composite effect for LSM-YSZ much greater than for LSCF-GDC

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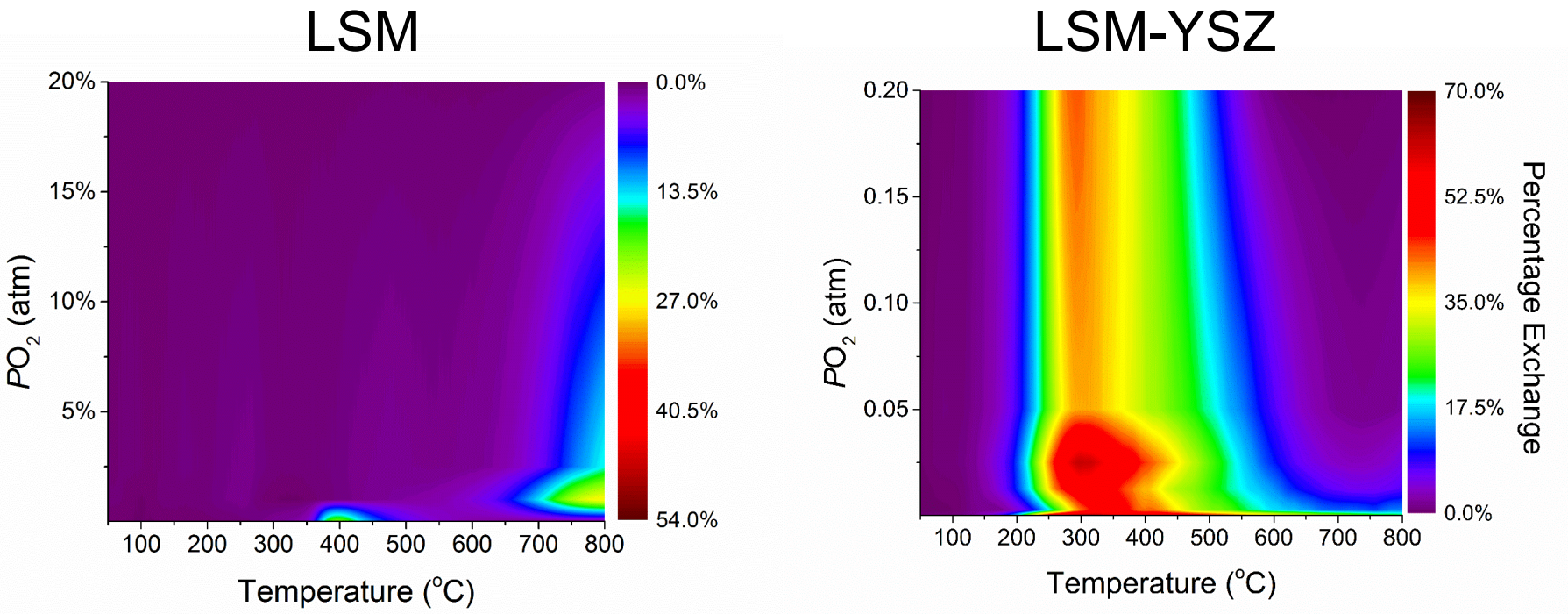
Water Exchange on LSM vs LSM-YSZ Composite Cathodes



- 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

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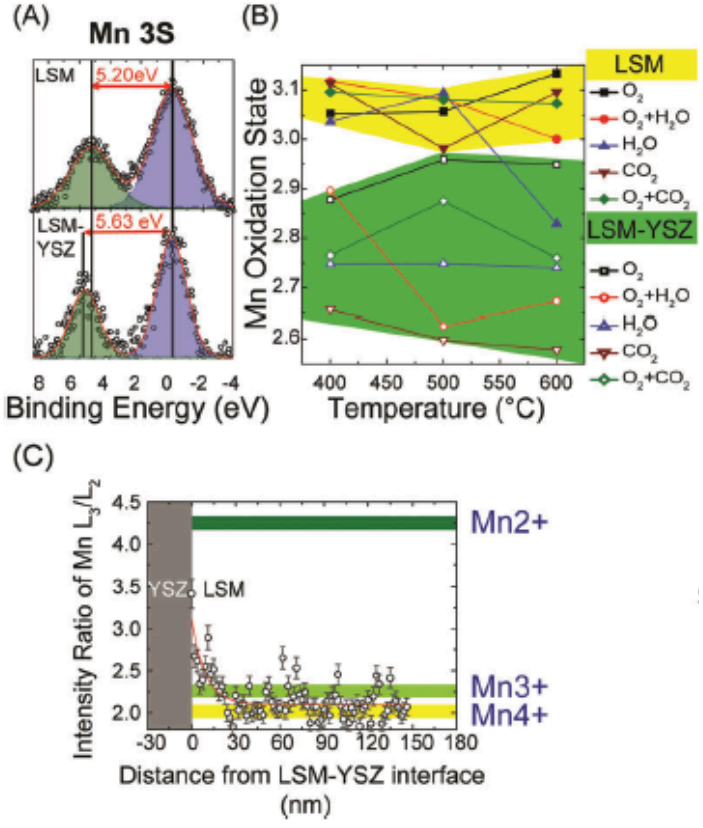
Direct observation of enhanced water and carbon dioxide reactivity on multivalent metal oxides and their composites†

Water & CO_2 Exchange on LSM vs LSM-YSZ Cathodes

- XPS shows LSM-YSZ composite has decreased Mn oxidation state relative to LSM which are compensated for by increase in local V_O concentration
- EELS shows change in Mn oxidation state is localized to LSM-YSZ interface



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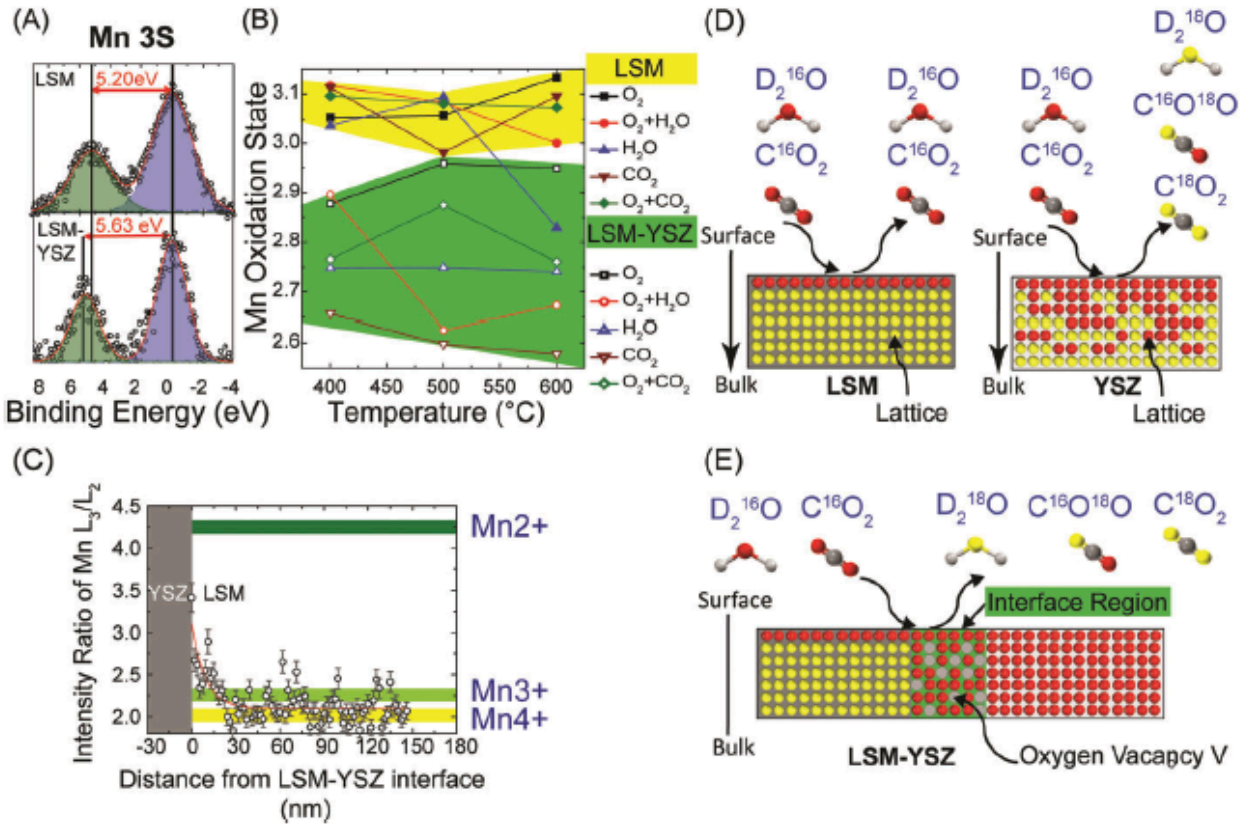

- LSM surface dissociates D_2O and CO_2 but bulk does not incorporate O
- In LSM-YSZ composite dissociated O transports to YSZ interface for incorporation

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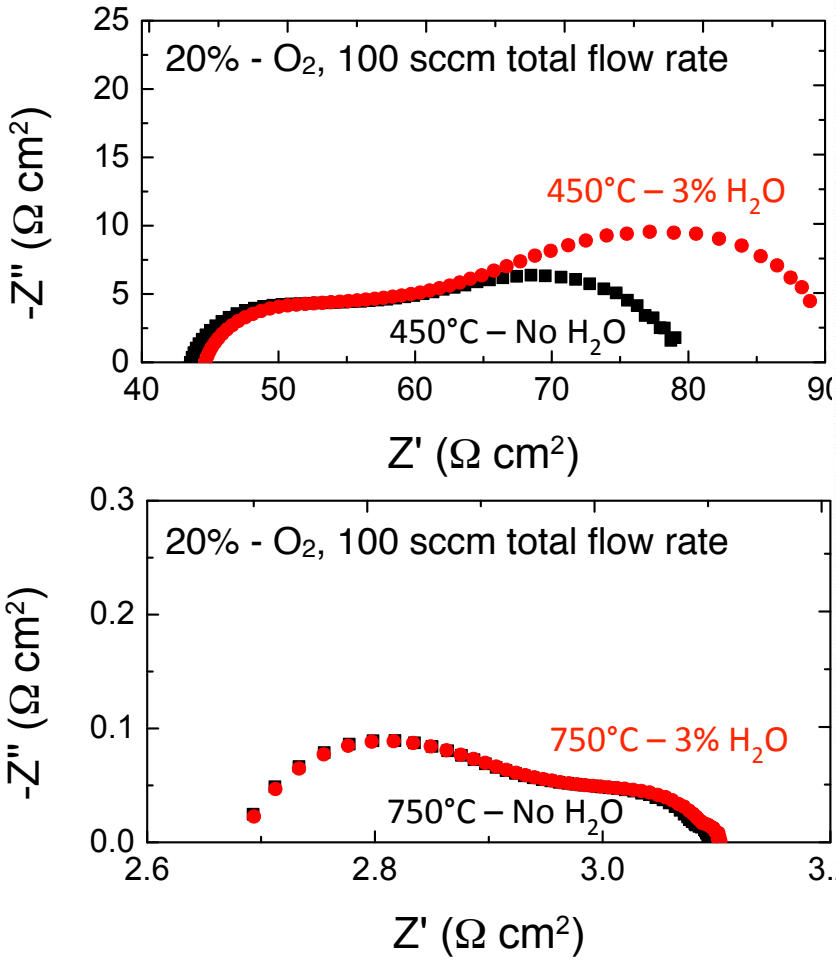
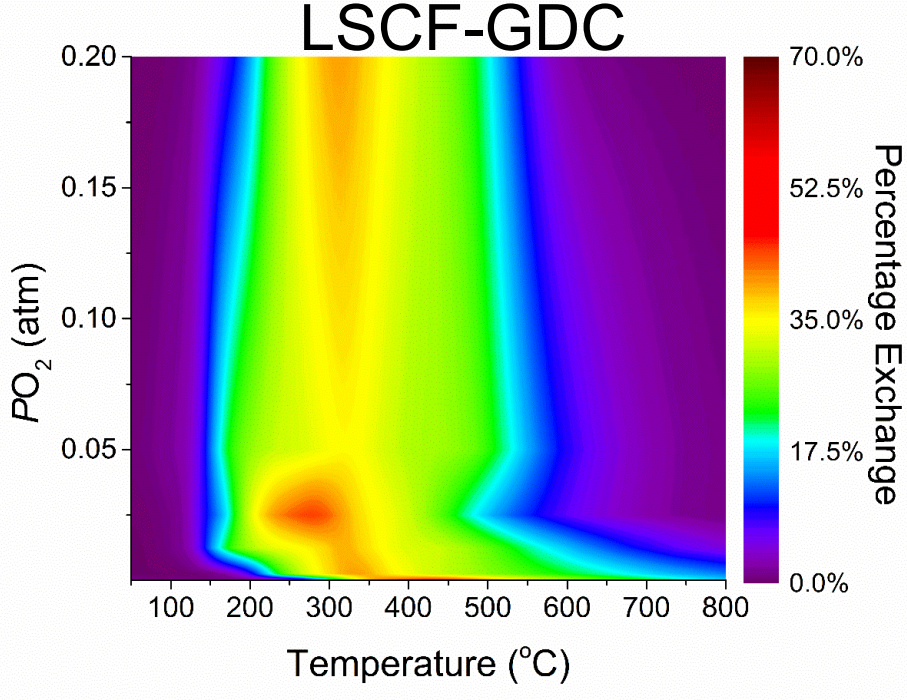
Comparison of ISTPX with EIS for LSCF-GDC in H_2O





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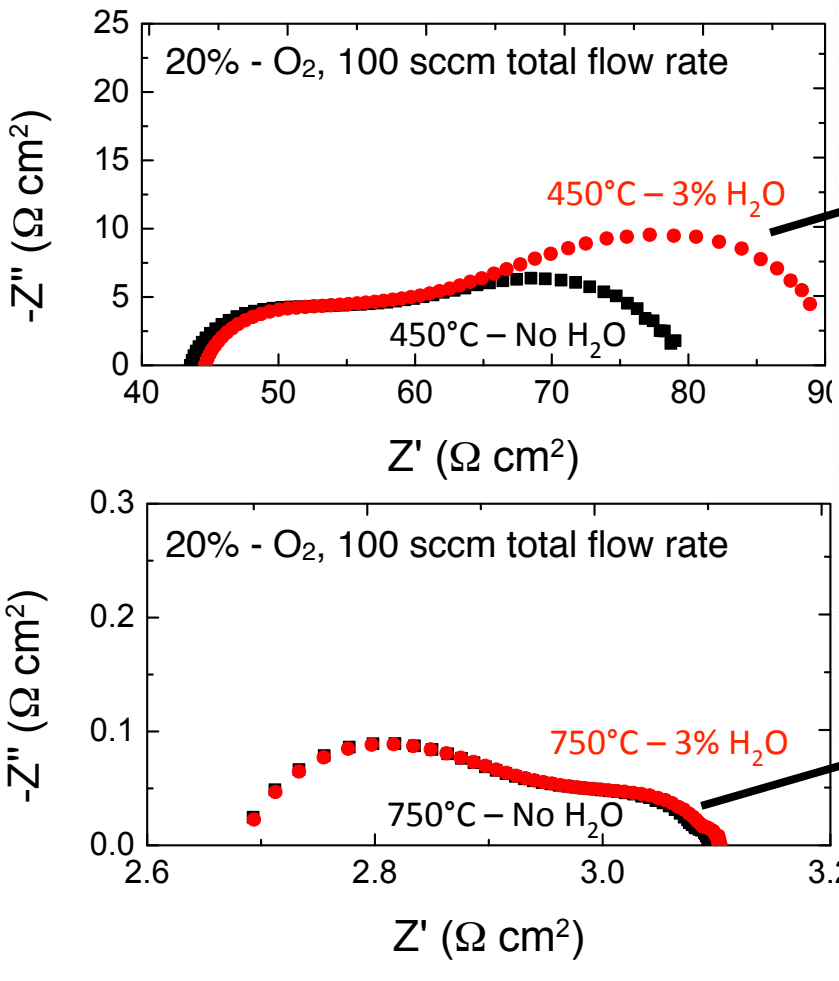

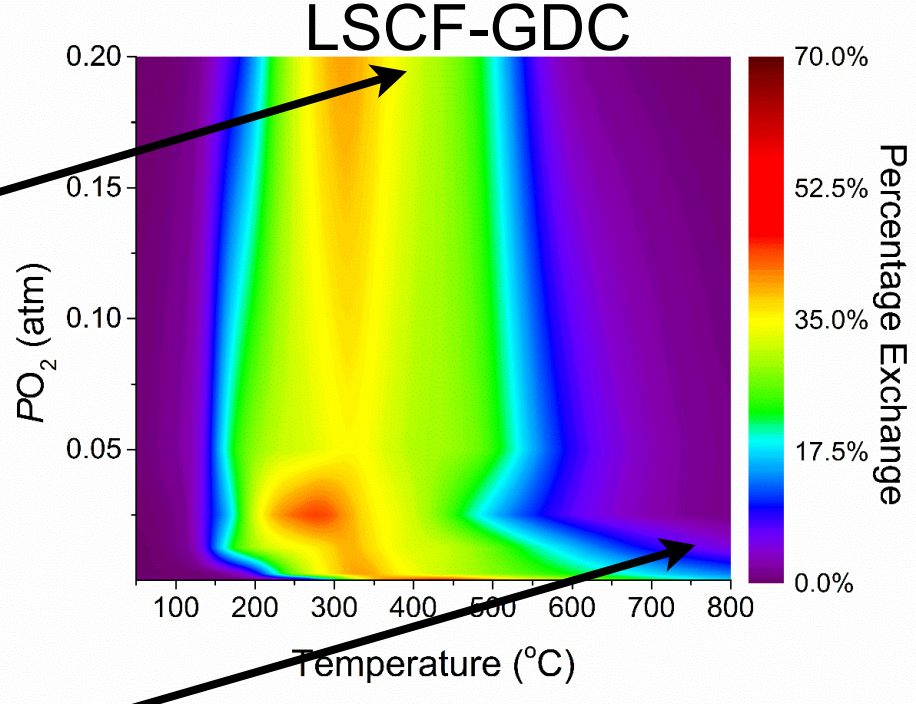

The presence of 3% H_2O effects the low frequency arc at 450ºC but not at 750ºC consistent with the results obtained from ISTPX.

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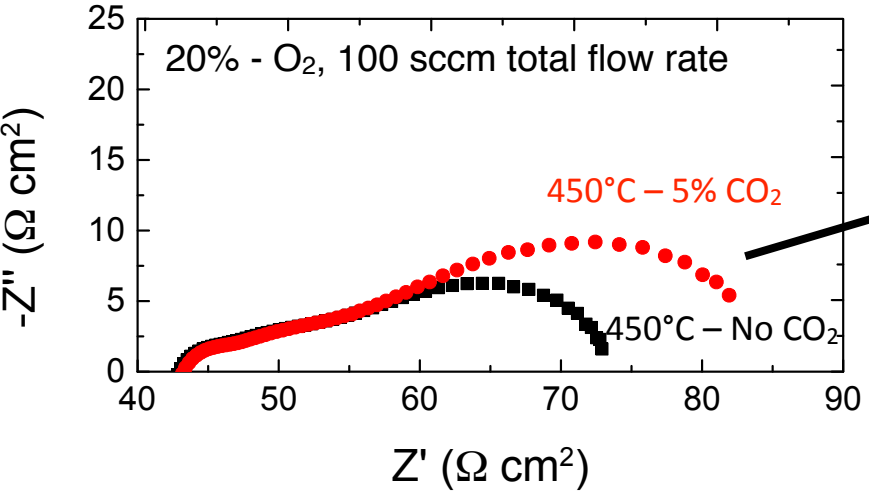
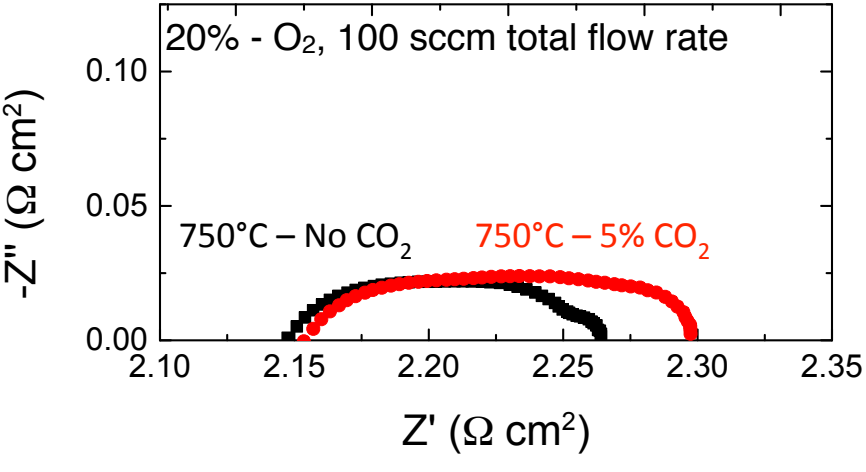
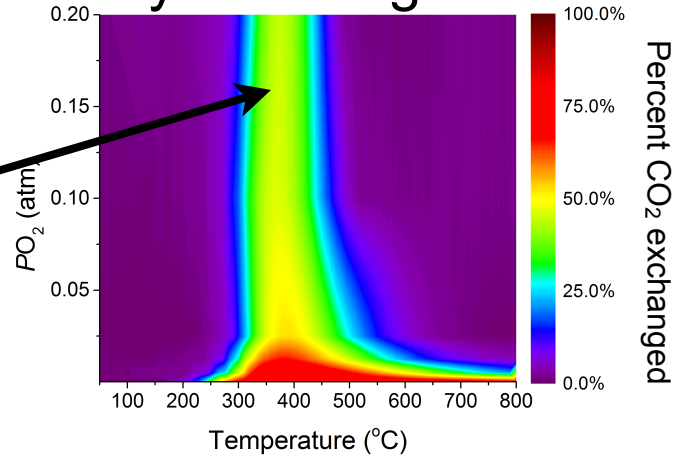




Doubly Exchanged $C^{18}O^{18}O$



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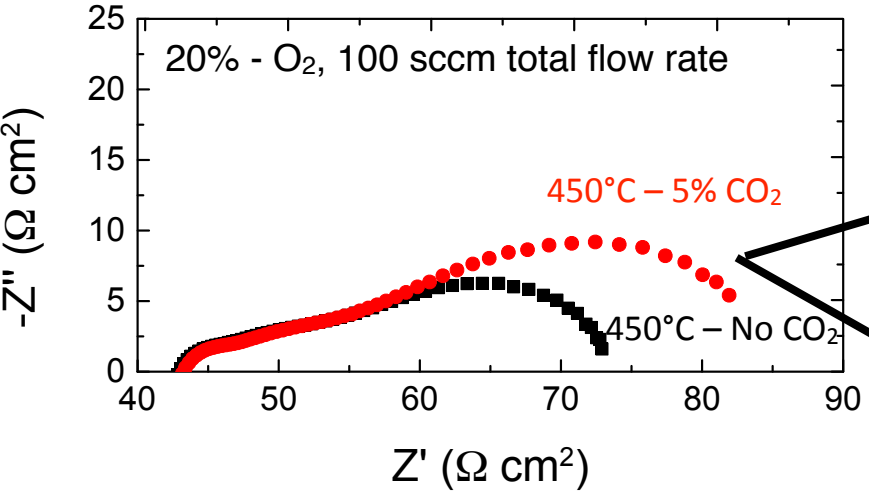

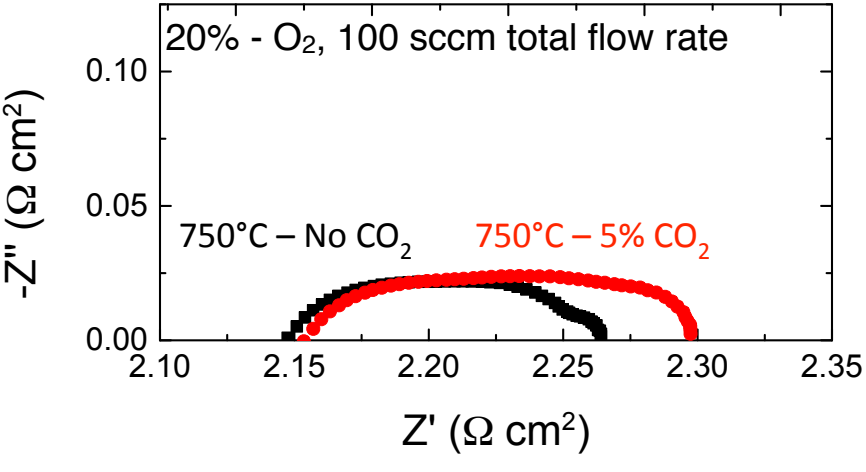

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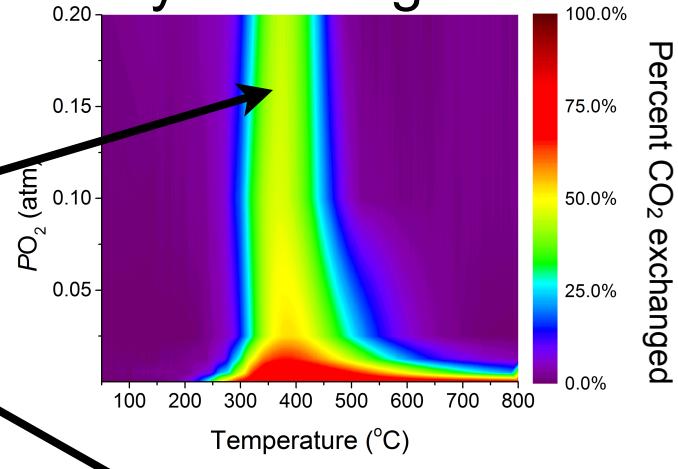

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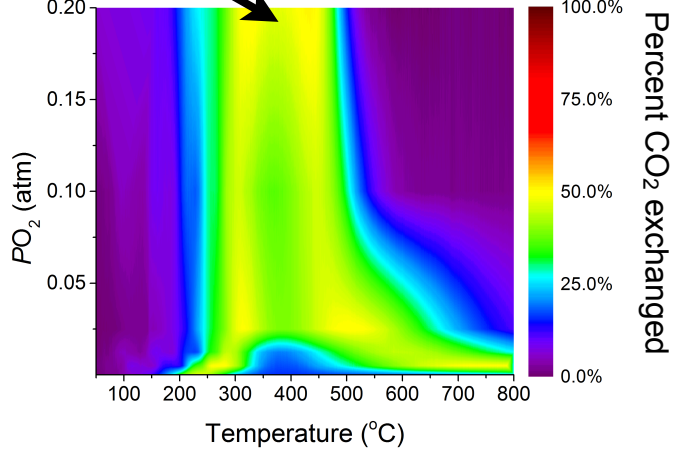

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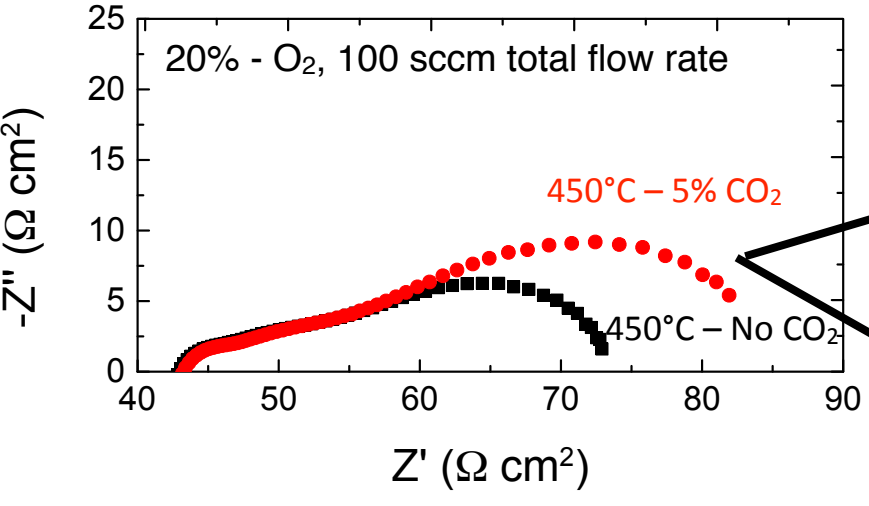

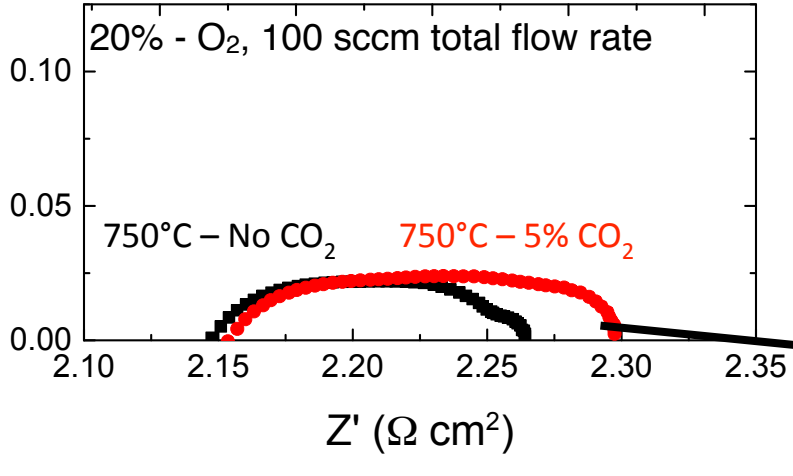

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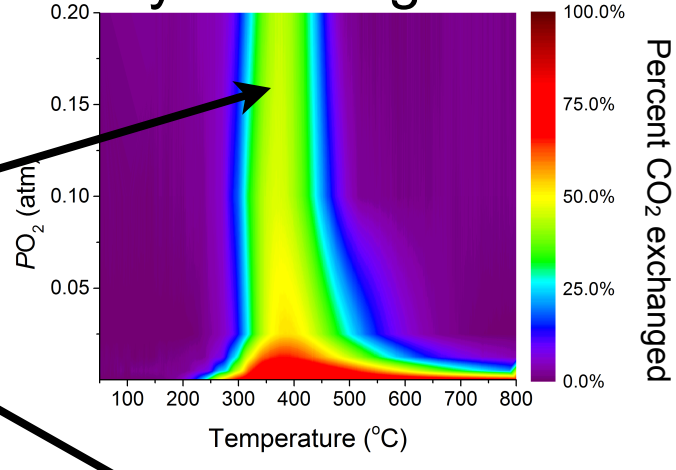

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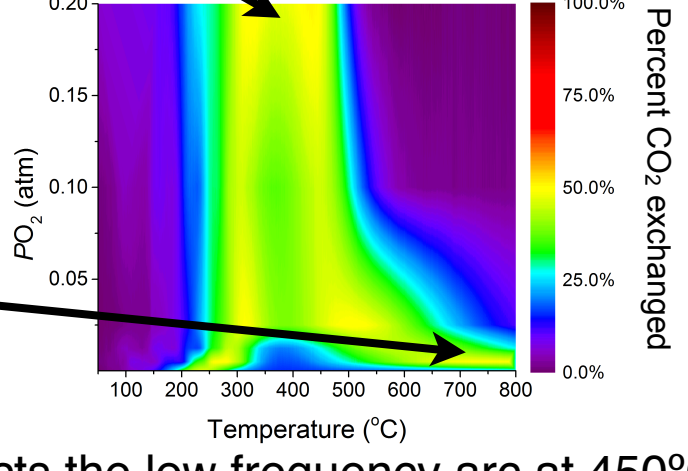

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ORR Reaction Mechanisms in Presence of Cr

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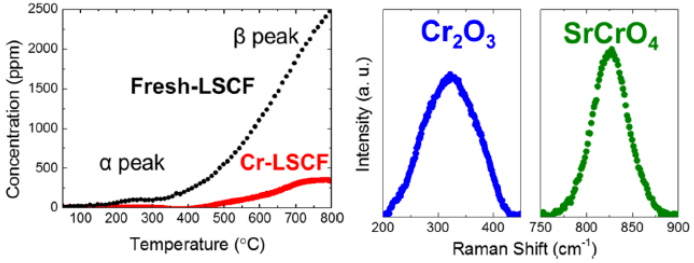

LSCF exposed to air flowing over Crofer 22 for 1 week

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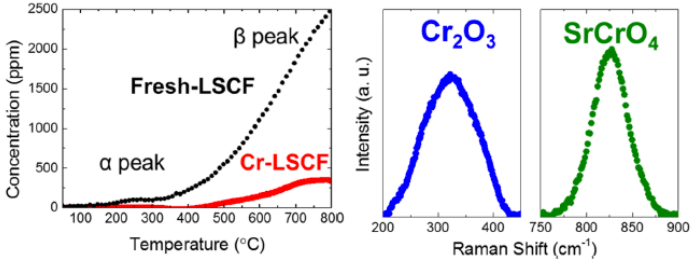

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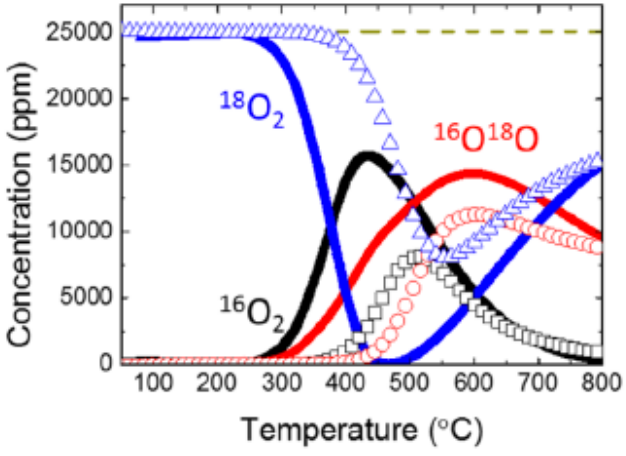

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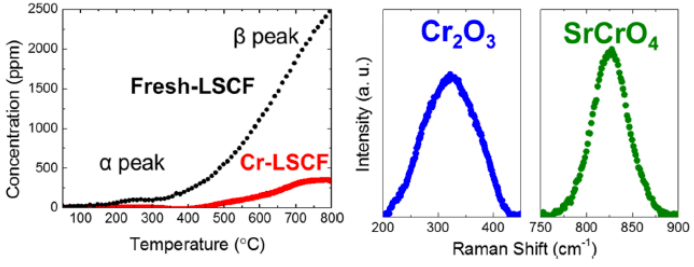

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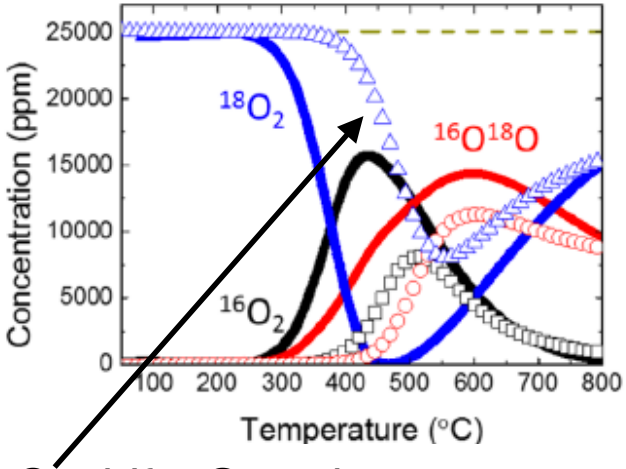

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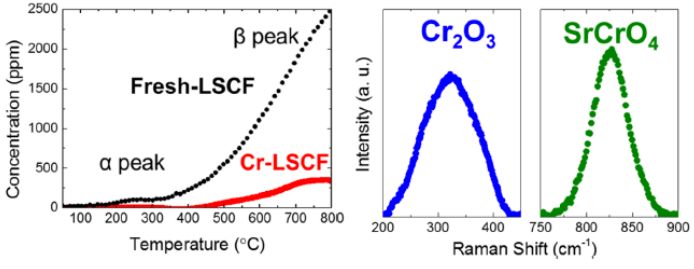

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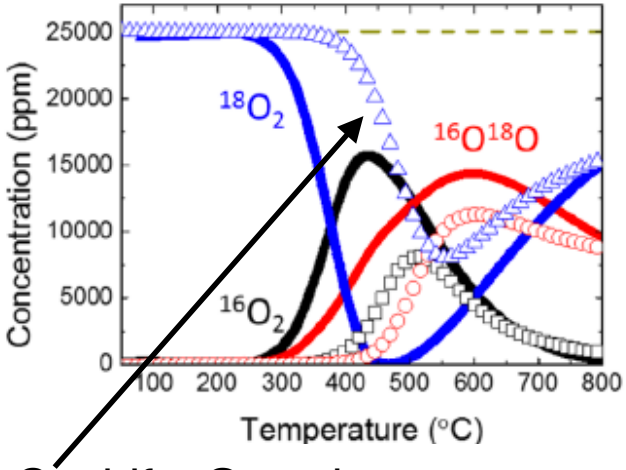

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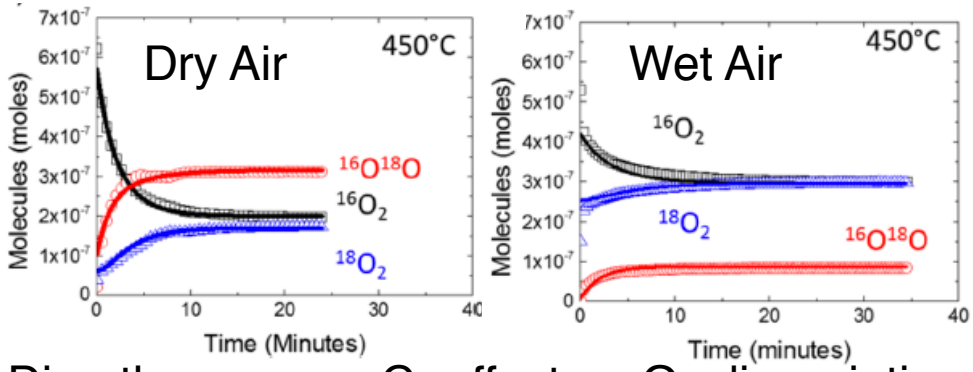

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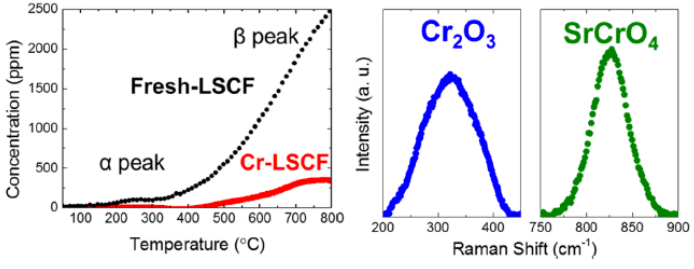

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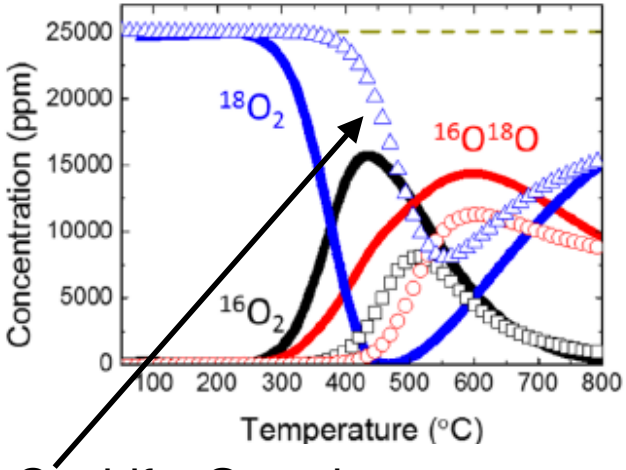

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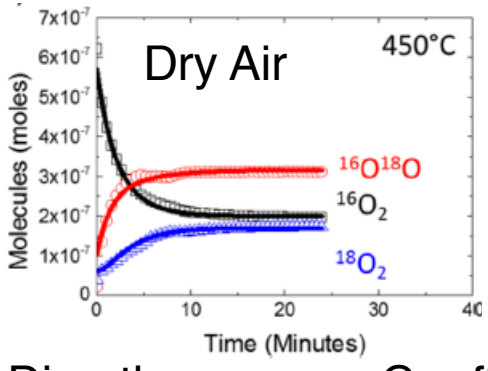

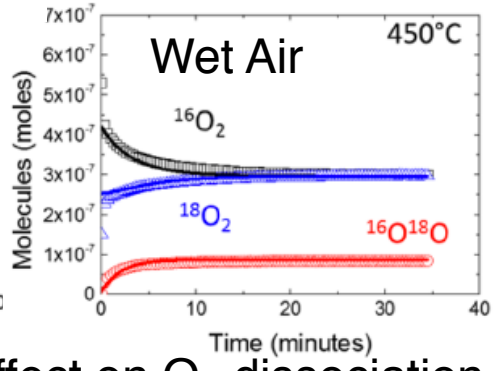

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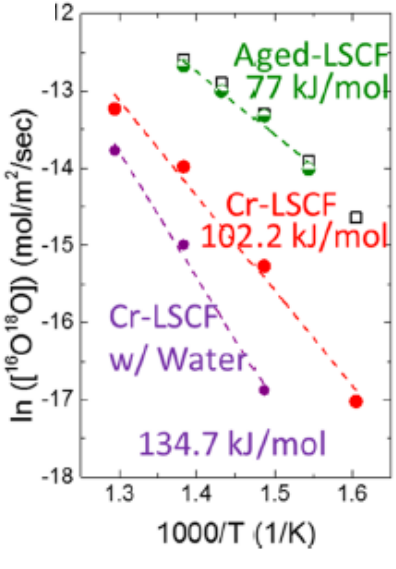

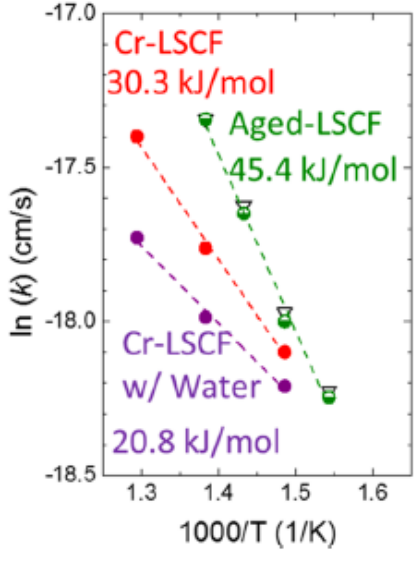

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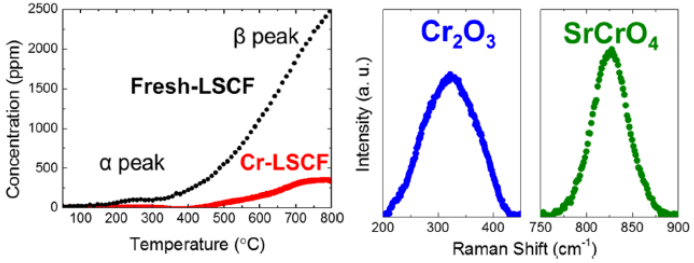

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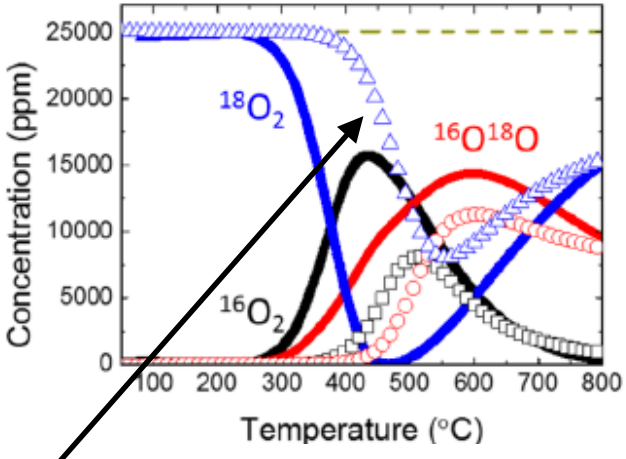

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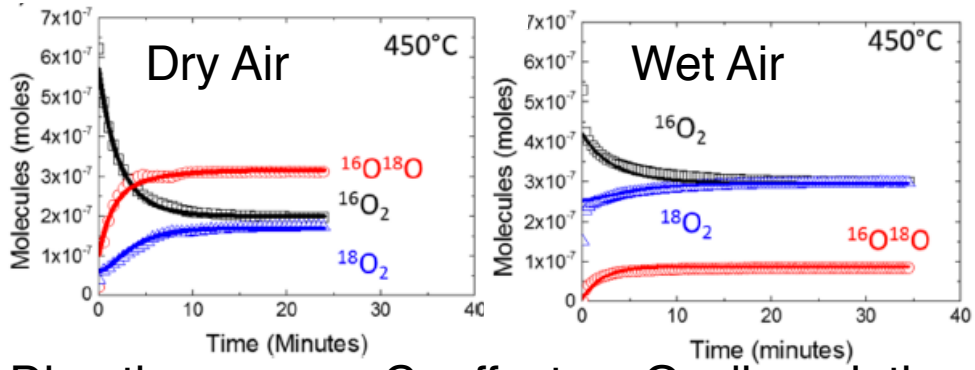

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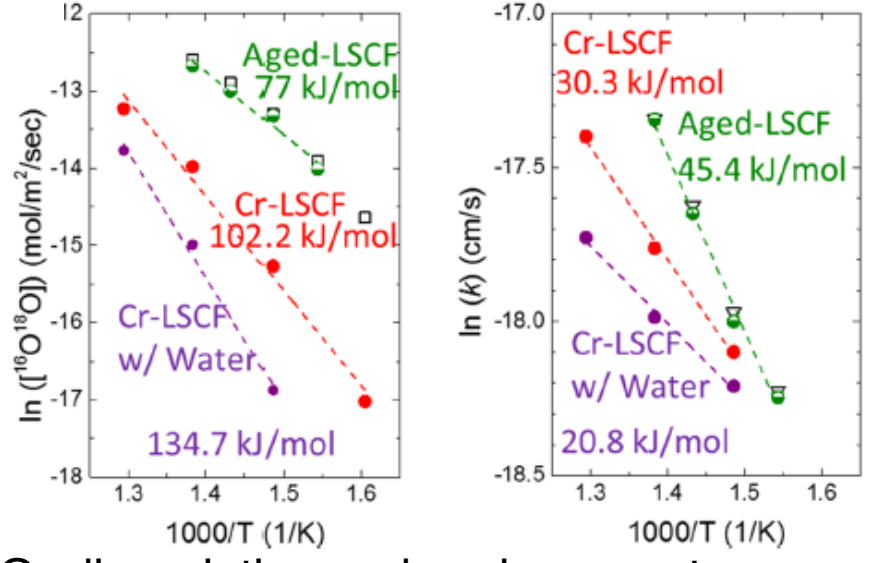

O_2 dissociation and exchange rates decrease upon Cr exposure, worse when wet

In-Situ Conclusions/Outcomes

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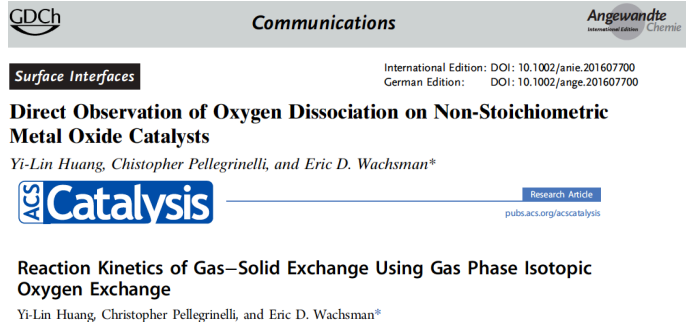

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International Edition: DOI: 10.1002/anie.201607700
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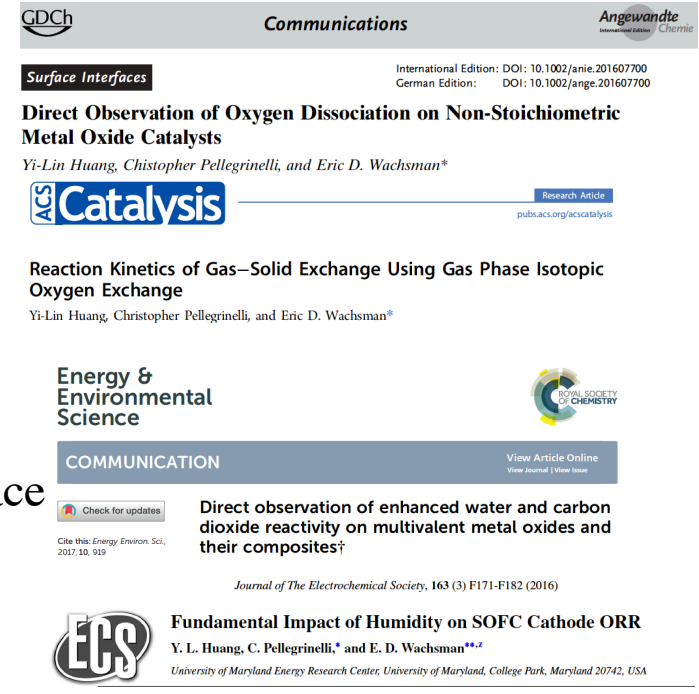

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Journal of The Electrochemical Society, **163** (3) F171-F182 (2016)

ECS

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

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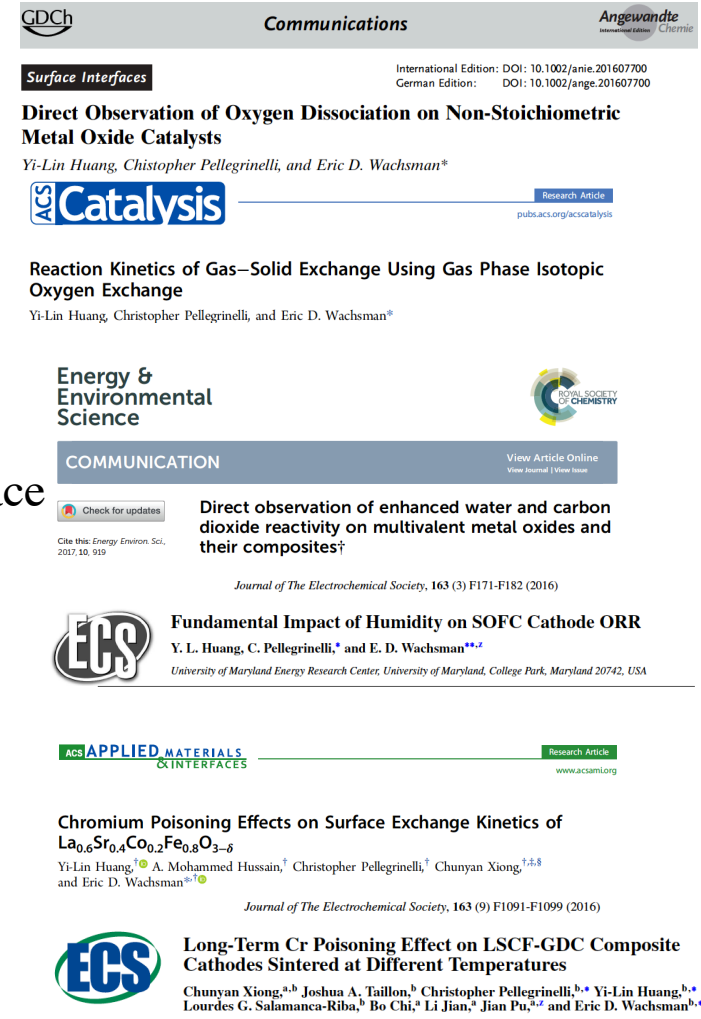
- Demonstrate Cr vapor exposure decreases O_2 dissociation and exchange rate and is made worse in ambient moisture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Long-Term Cr Poisoning Effect on LSCF-GDC Composite Cathodes Sintered at Different Temperatures

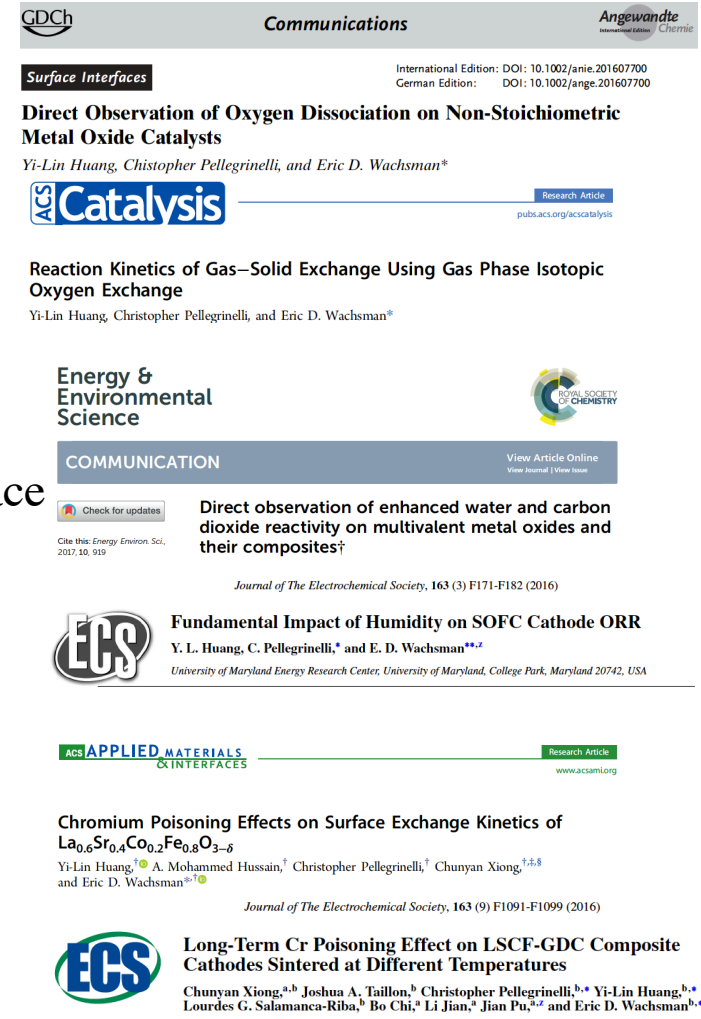
Chunyan Xiong,[a,b] Joshua A. Taillon,[b] Christopher Pellegrinelli,[b,*] Yi-Lin Huang,[b,*] Lourdes G. Salamanca-Riba,[b] Bo Chi,[a] Li Jian,[a] Jian Pu,[a,z] and Eric D. Wachsman[b,*]

In-Situ Conclusions/Outcomes

Developed multiple (IIE, 1:1 IIE, ISTPX) O-isotope exchange techniques that enabled us to:

- Determine fundamental ORR rates for LSCF, LSM, and their composites and for first time was able to directly measure O_2 dissociation

- Demonstrate H_2O and CO_2 actively participate in ORR for both LSCF and LSM and identified temperature and gas composition regions where H_2O dominates O_2 surface exchange and where they are less important
- Identify significant composite cathode effect on surface exchange with H_2O and CO_2
- Demonstrate Cr vapor exposure decreases O_2 dissociation and exchange rate and is made worse in ambient moisture


GDCh Communications Angewandte International Edition Chemie

Surface Interfaces

International Edition: DOI: 10.1002/anie.201607700
German Edition: DOI: 10.1002/ange.201607700

Direct Observation of Oxygen Dissociation on Non-Stoichiometric Metal Oxide Catalysts

Yi-Lin Huang, Chistopher Pellegrinelli, and Eric D. Wachsman*

ACS Catalysis — Research Article — pubs.acs.org/acscatalysis

Reaction Kinetics of Gas–Solid Exchange Using Gas Phase Isotopic Oxygen Exchange

Yi-Lin Huang, Christopher Pellegrinelli, and Eric D. Wachsman*

Energy & Environmental Science — ROYAL SOCIETY OF CHEMISTRY

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Cite this: Energy Environ. Sci., 2017, 10, 919

Direct observation of enhanced water and carbon dioxide reactivity on multivalent metal oxides and their composites†

Journal of The Electrochemical Society, 163 (3) F171-F182 (2016)

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Fundamental Impact of Humidity on SOFC Cathode ORR

Y. L. Huang, C. Pellegrinelli,* and E. D. Wachsman**,z

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

ACS APPLIED MATERIALS & INTERFACES — Research Article — www.acsami.org

Chromium Poisoning Effects on Surface Exchange Kinetics of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

Yi-Lin Huang,† A. Mohammed Hussain,† Christopher Pellegrinelli,† Chunyan Xiong,†,‡,§ and Eric D. Wachsman*,†

Journal of The Electrochemical Society, 163 (9) F1091-F1099 (2016)

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Long-Term Cr Poisoning Effect on LSCF-GDC Composite Cathodes Sintered at Different Temperatures

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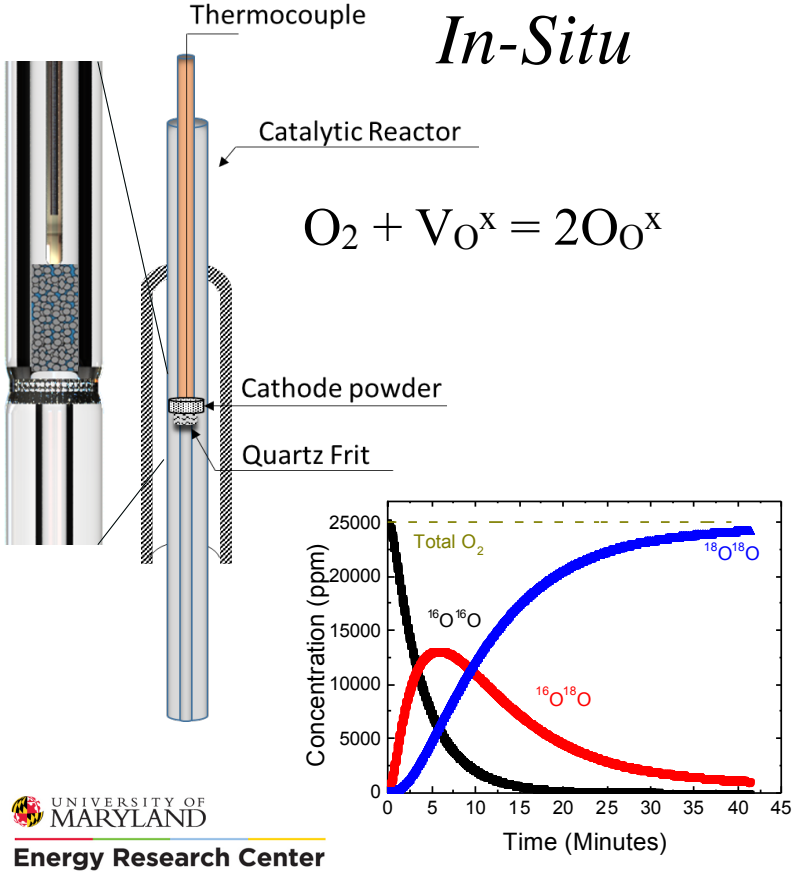
but all done under absence of applied bias with no charge transfer…

Phase 1 *In-Operando* Isotope Exchange System

- Develop *in-operando* apparatus for the study of SOFC cathode oxygen surface exchange properties, under operating conditions of applied voltage / current.
- 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.



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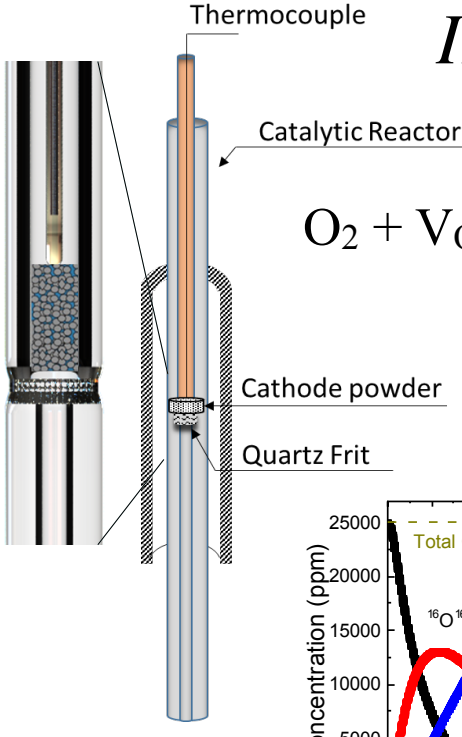
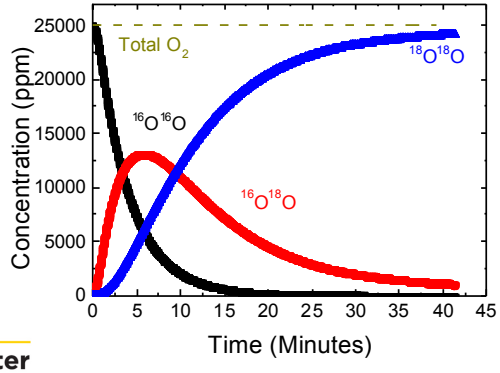
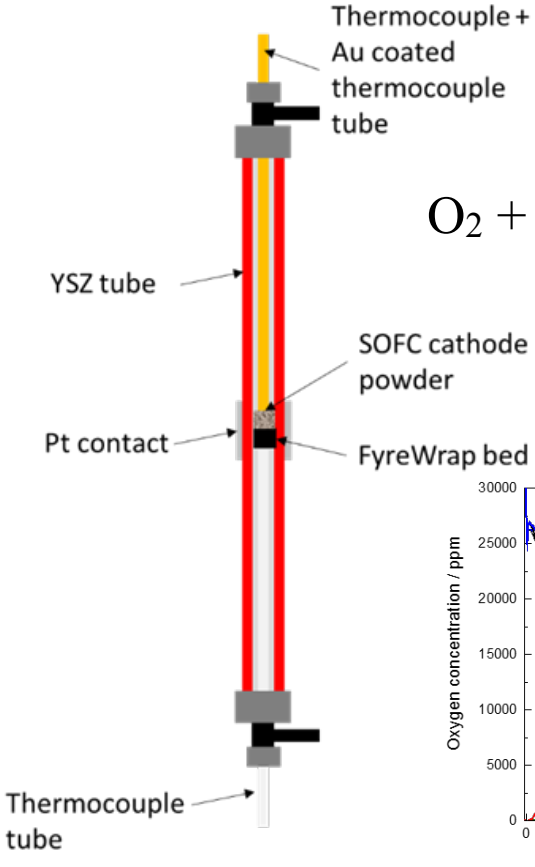
In-Situ



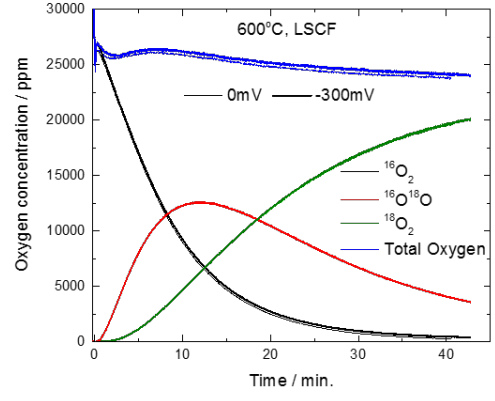
$$O_2 + V_O^x = 2O_O^x$$



In-Operando



$$O_2 + 2V_O^{\bullet\bullet} + 4e' = 2O_O^x$$



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Energy Research Center

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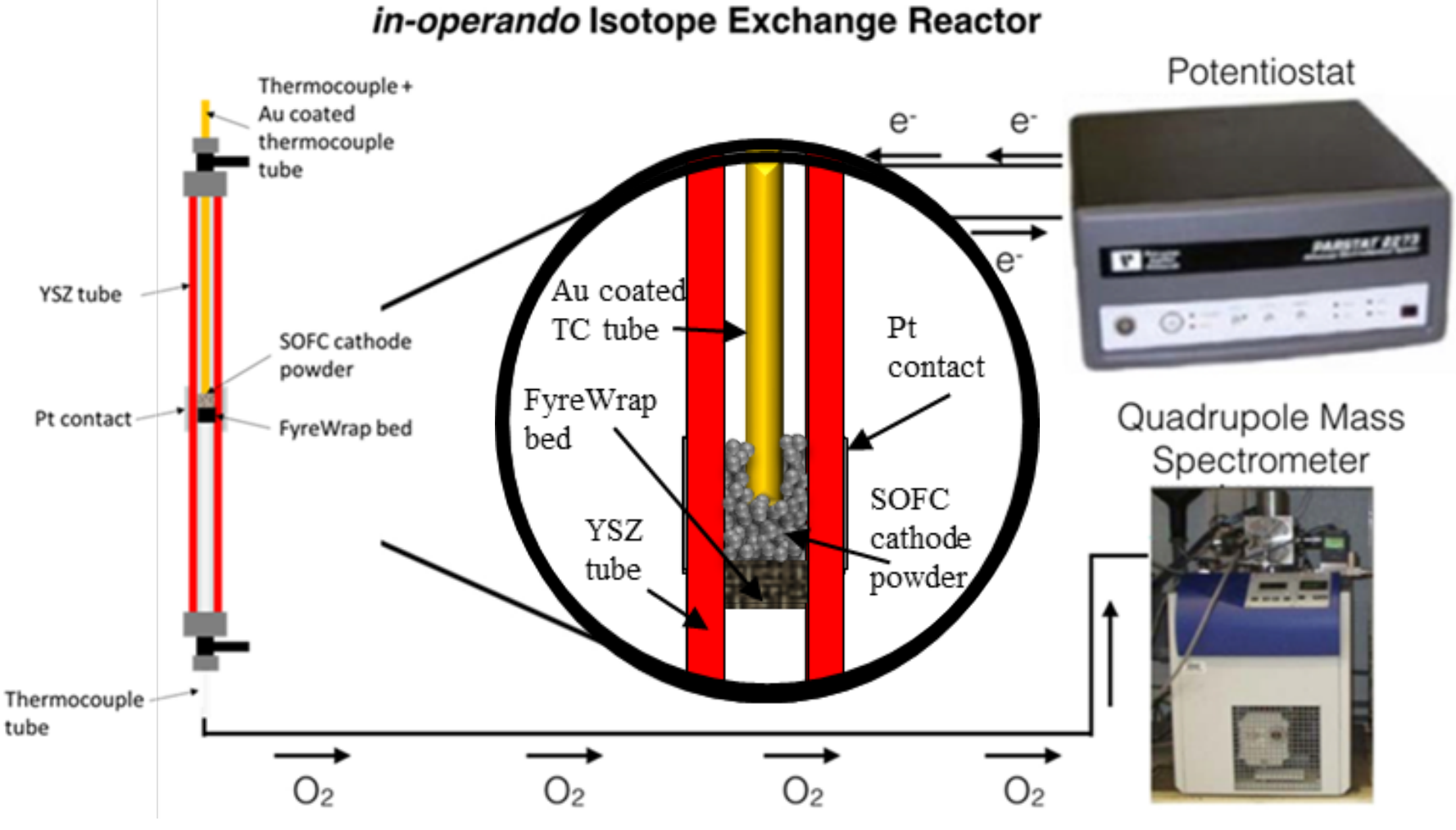

- Convert *in-situ* heterogeneous catalysis set-up to *in-operando* reactor to measure cathode ORR under applied bias

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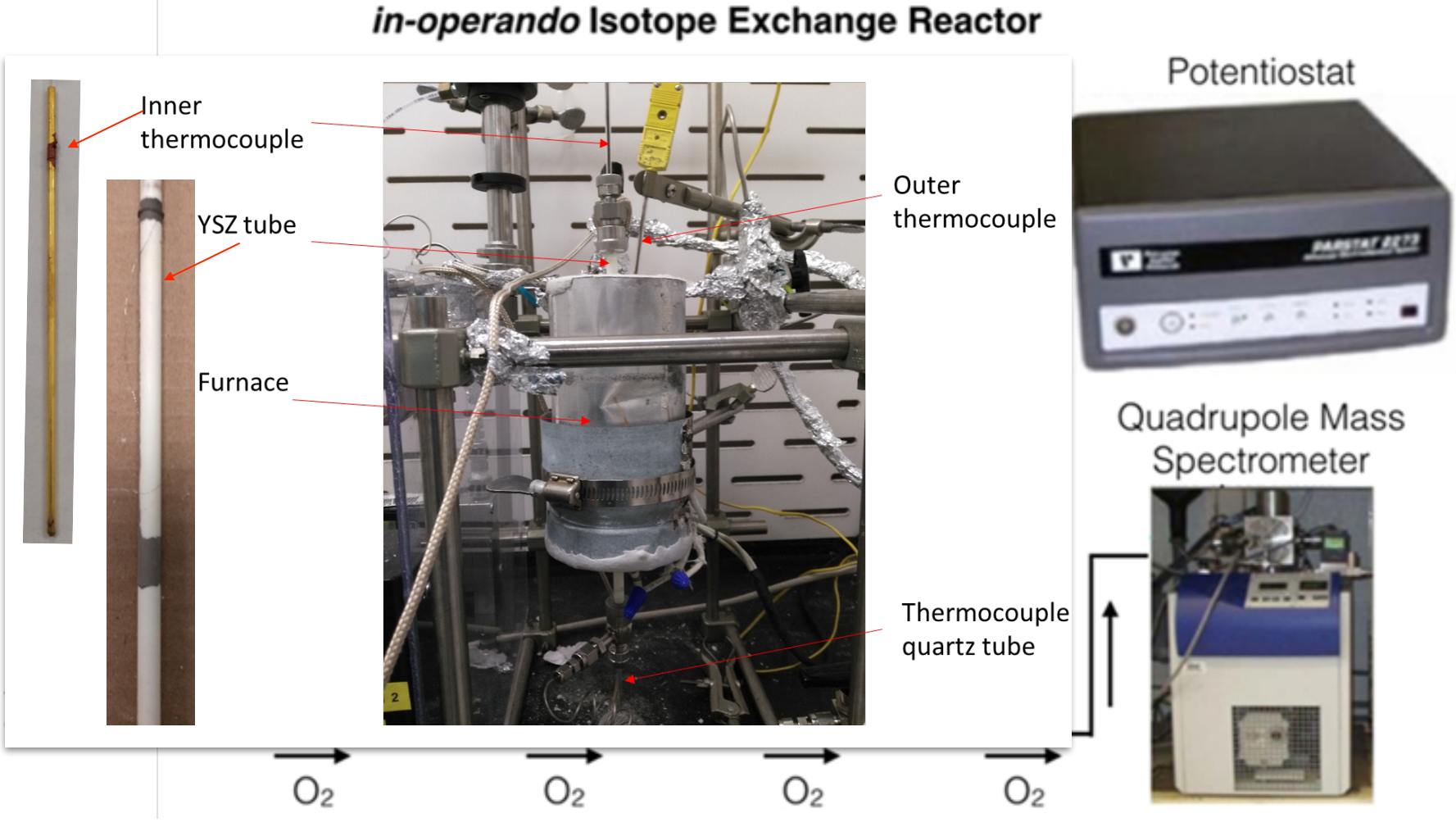

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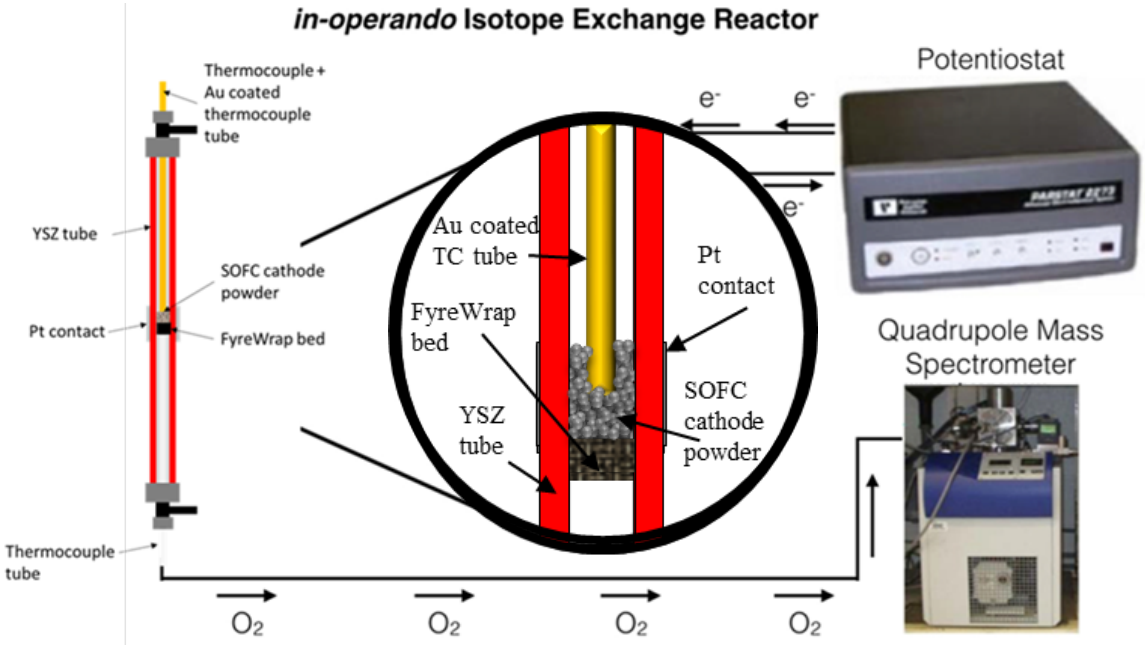
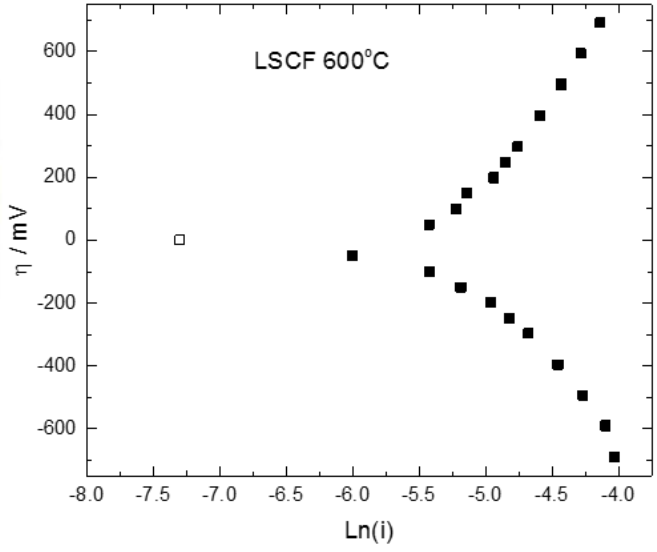
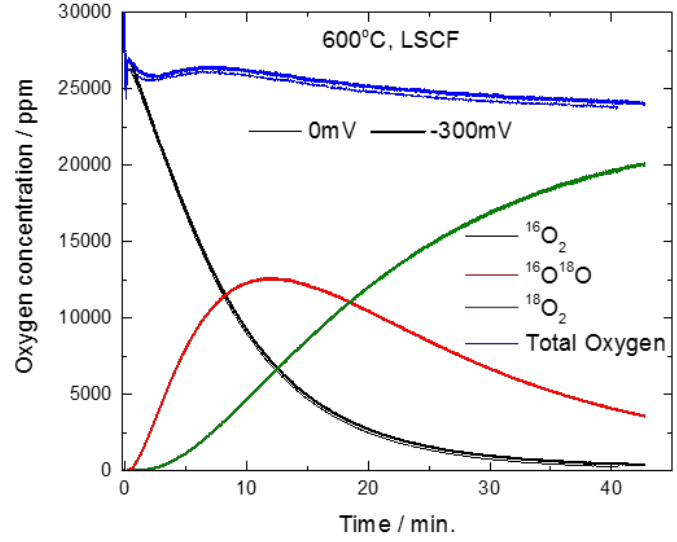




- Now able to *in-operando* determine cathode ORR by simultaneous cell current-voltage behavior under applied bias with *in-situ* heterogeneous ^{18}O-isotope exchange



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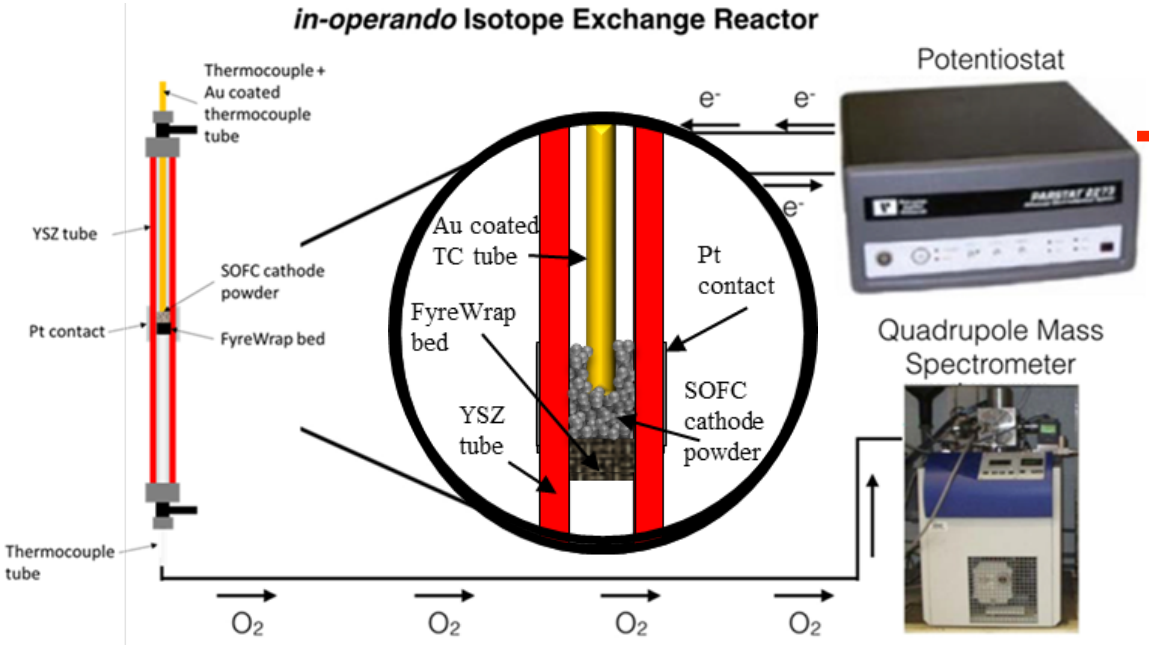

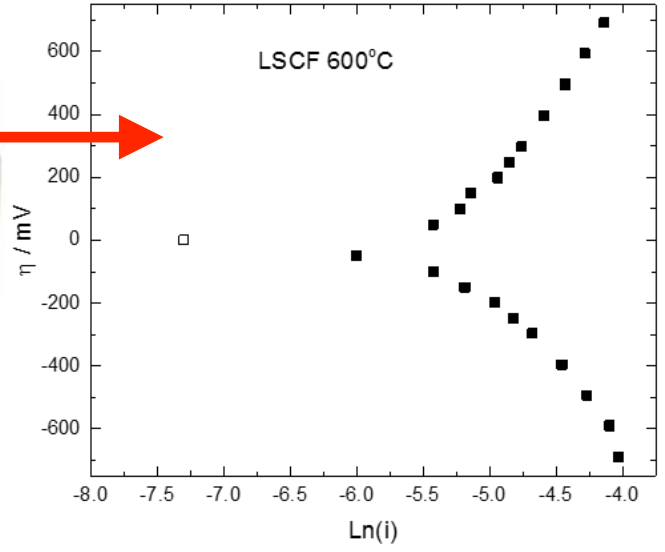

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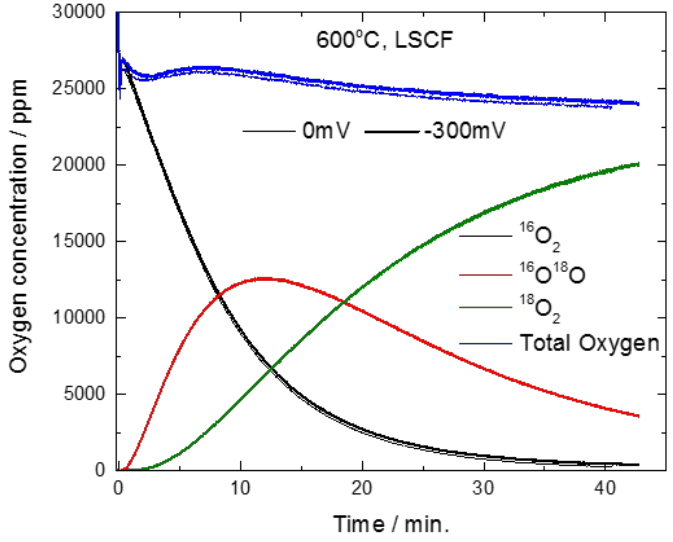

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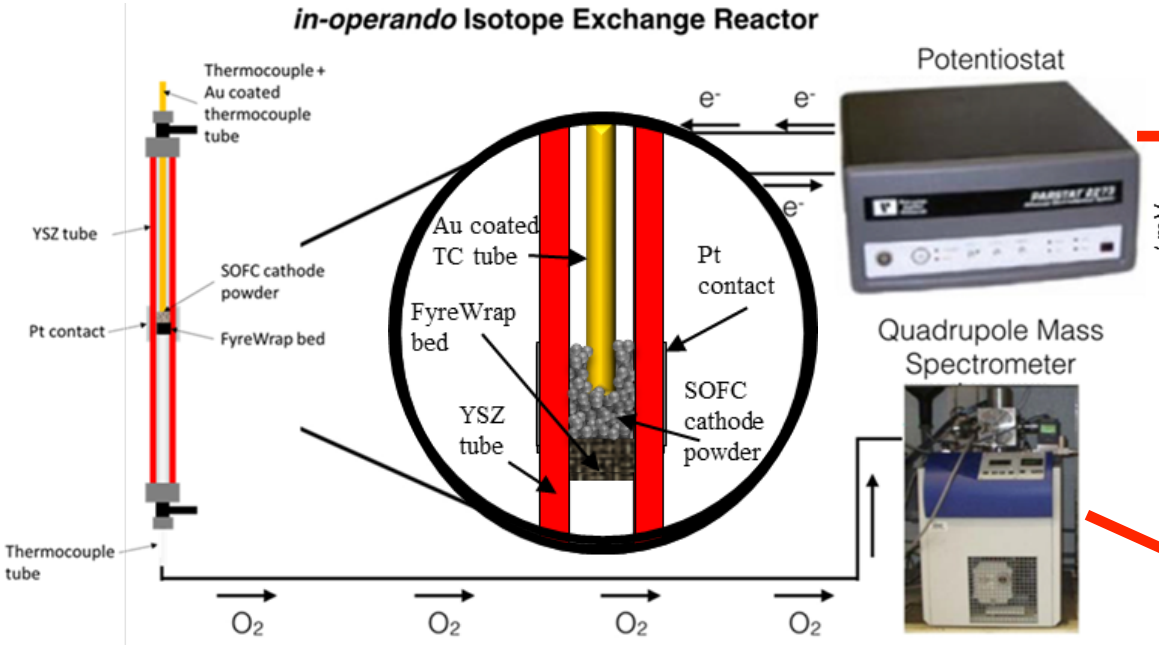

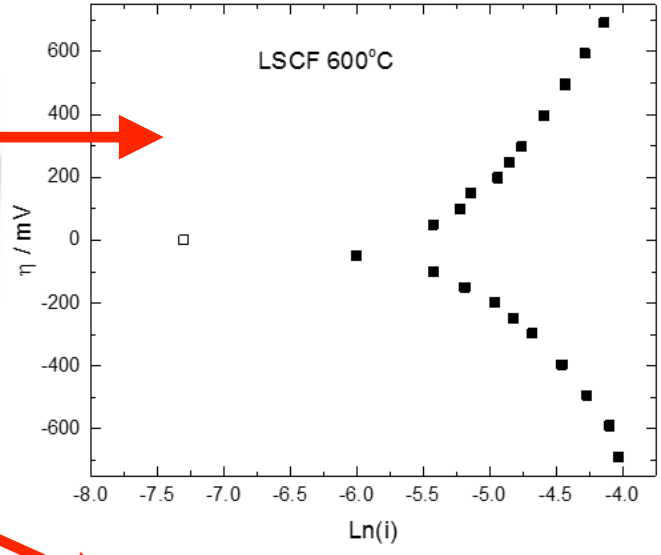

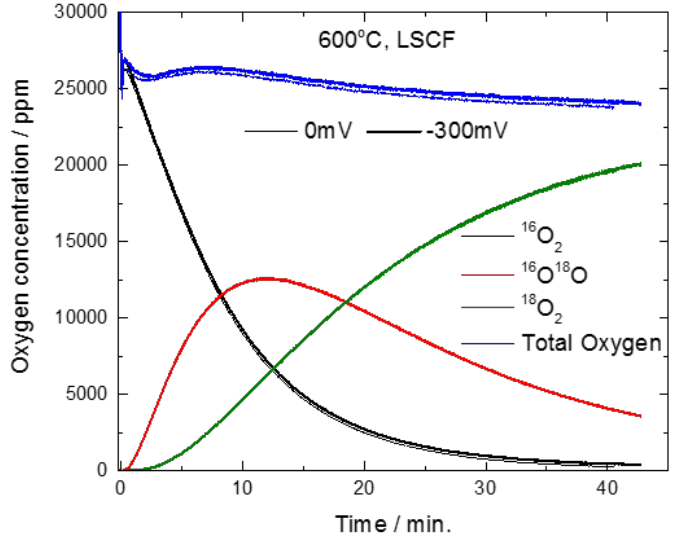

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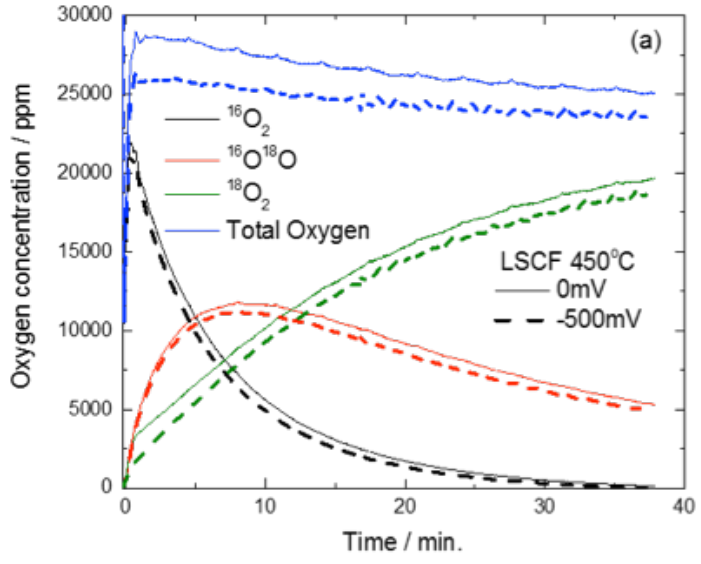
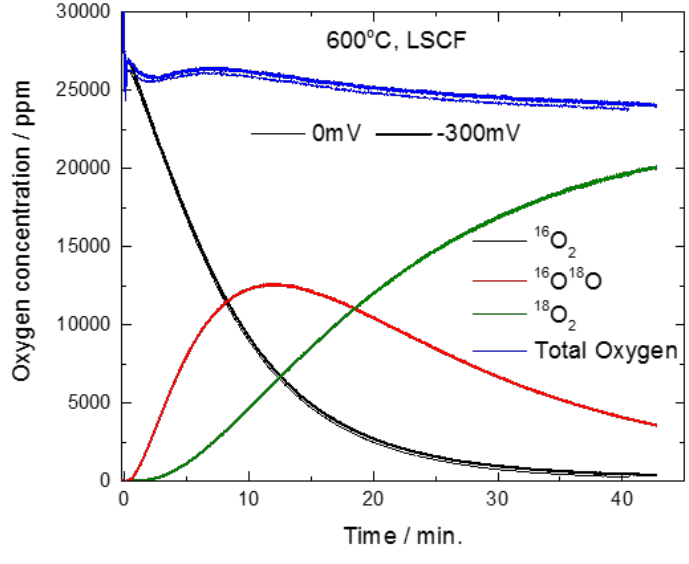
In-Operando Determination of LSCF k_{ex} as Function of Potential





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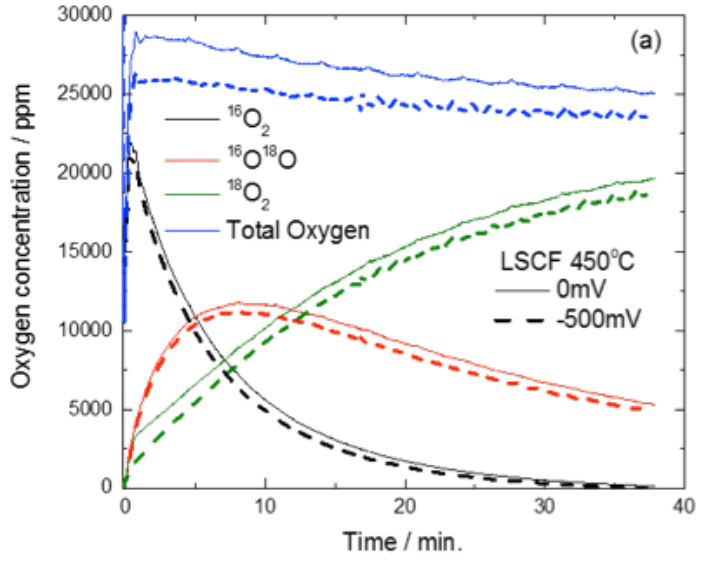
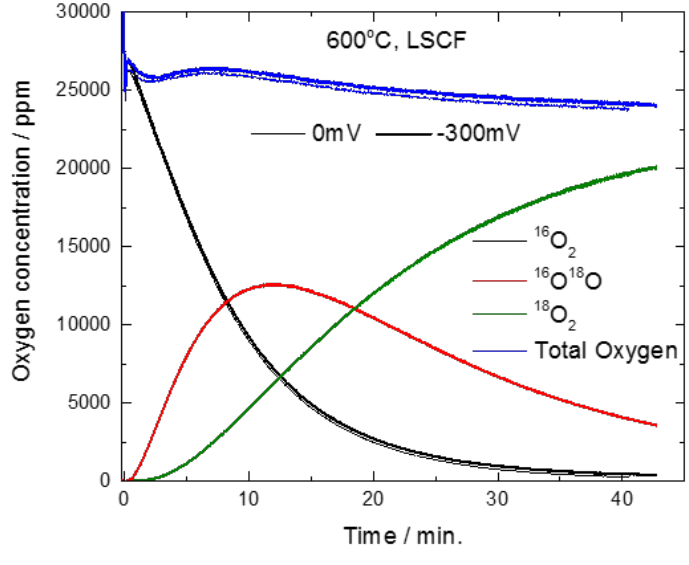
- *In-operando* determination of LSCF surface exchange as a function of cathodic bias





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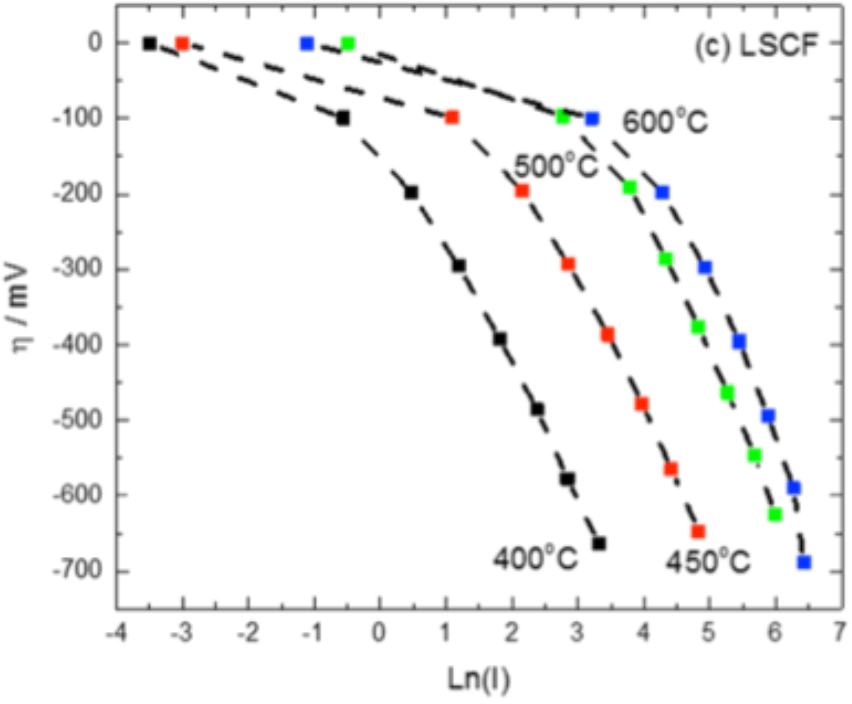
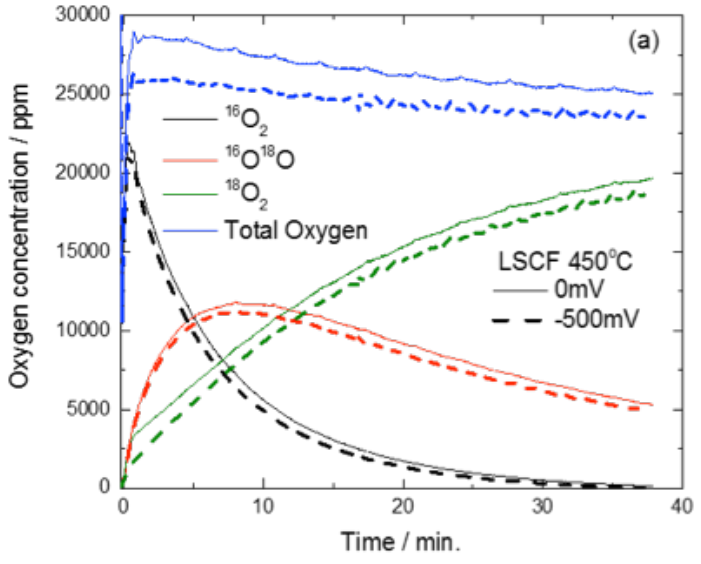
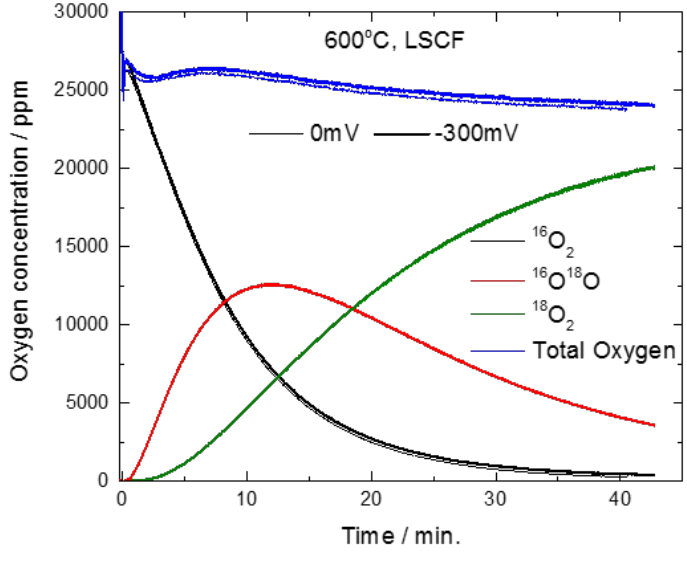
- *In-operando* determination of LSCF surface exchange as a function of cathodic bias
- Follows Tafel relationship (η vs Ln(I))







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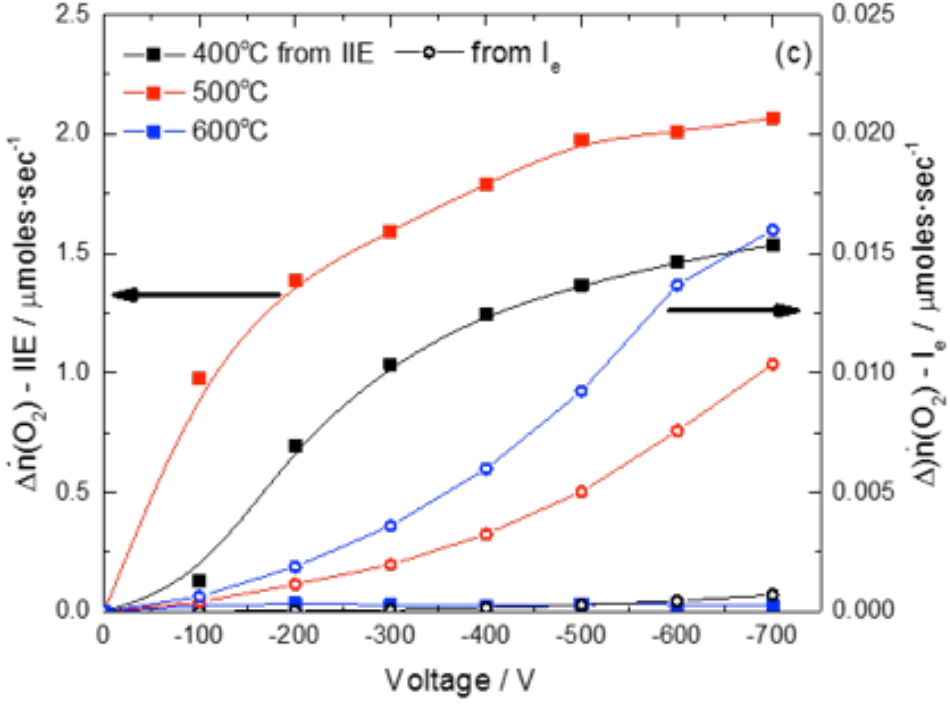

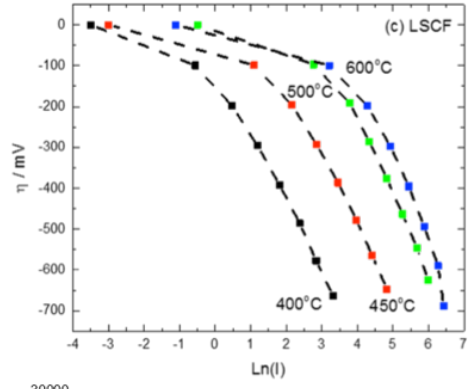

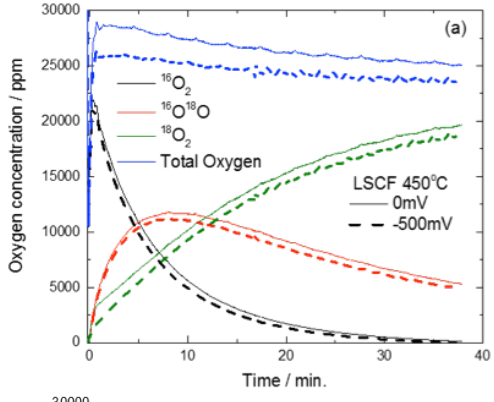

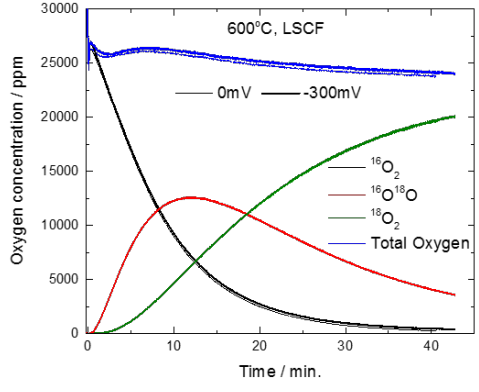

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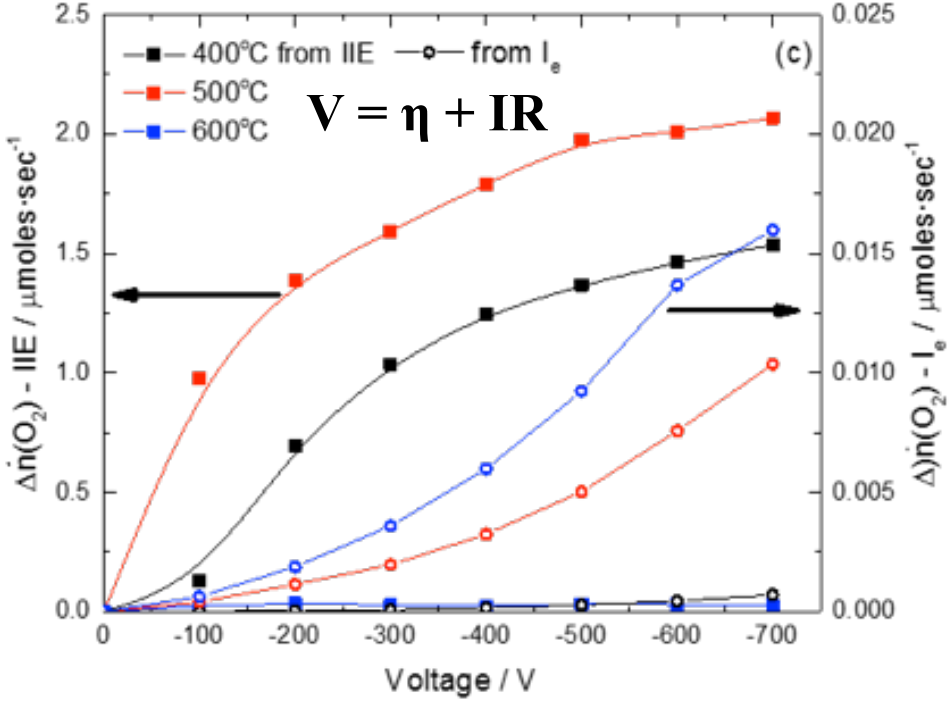

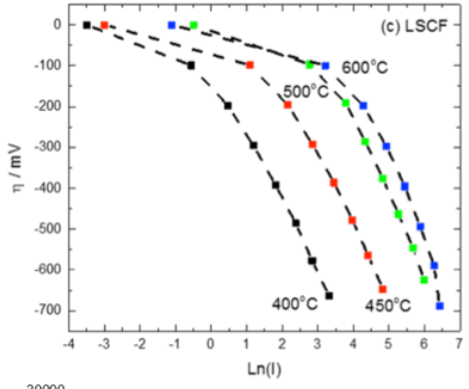

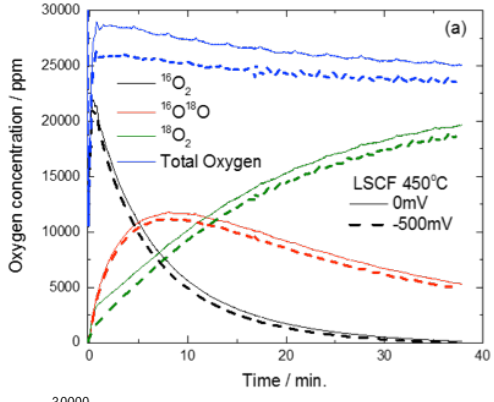

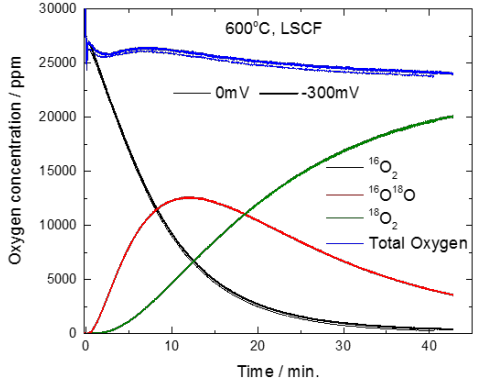

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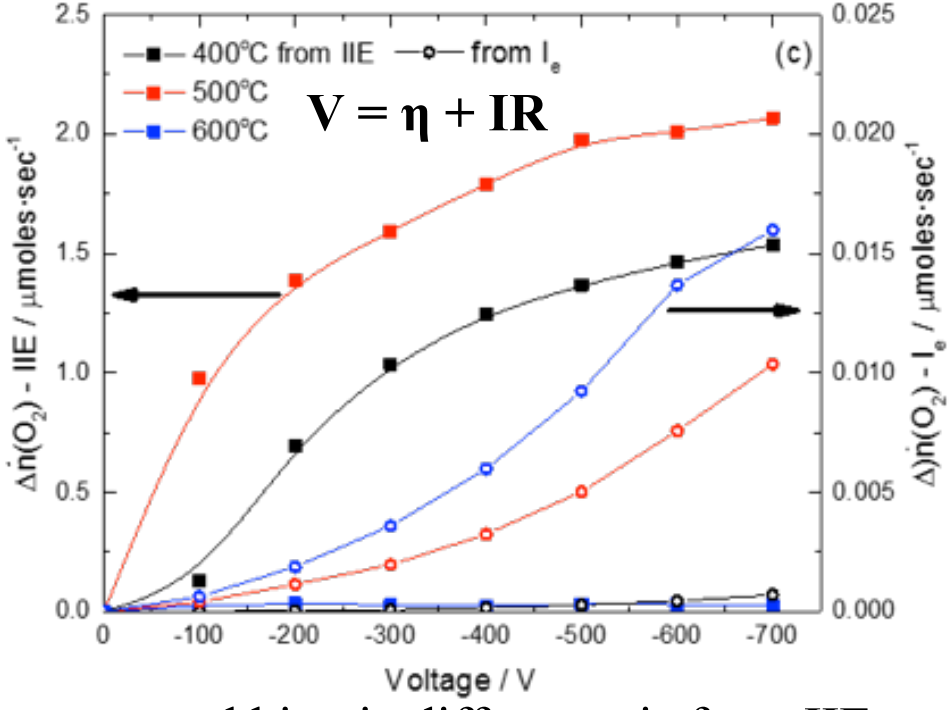
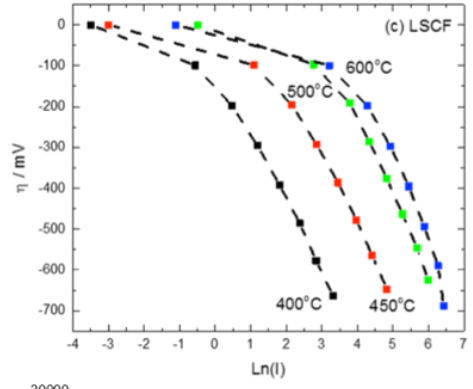
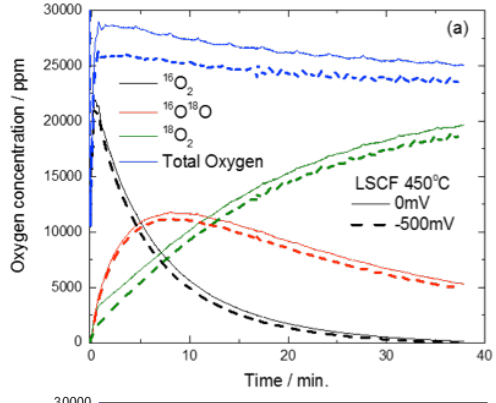
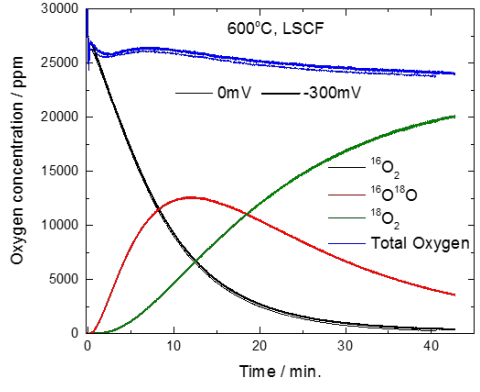


- Demonstrated kinetic difference is from IIE applied potential and not Faradaic O_2 pumping (I_e)







In-Operando Determination of k_{ex} as Function of Potential

Tentative Model

$$O_{2(gas)} \leftrightarrow 2O + 4e^- \leftrightarrow 2O^{2-}$$

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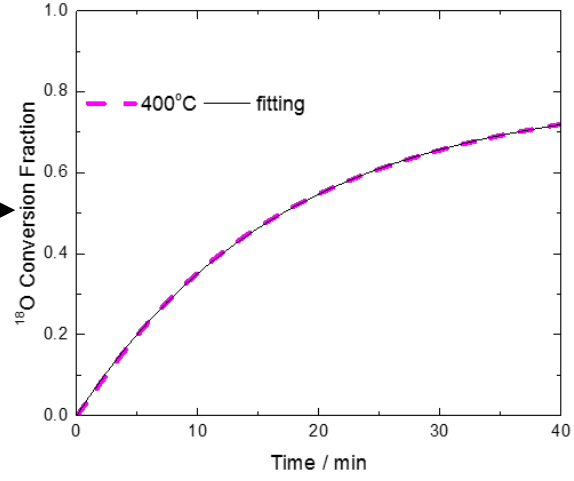
- Under no polarization, the fitting of accumulation profiles to obtain exchange rate (R^*_{ex}):

$$\frac{M(t)}{M_\infty} = 1 - \exp\left(-R^*_{ex} t\right)$$



Gil Cohn, Eric D.Wachsman et al.
Journal of The Electrochemical Society, **163** (2016)

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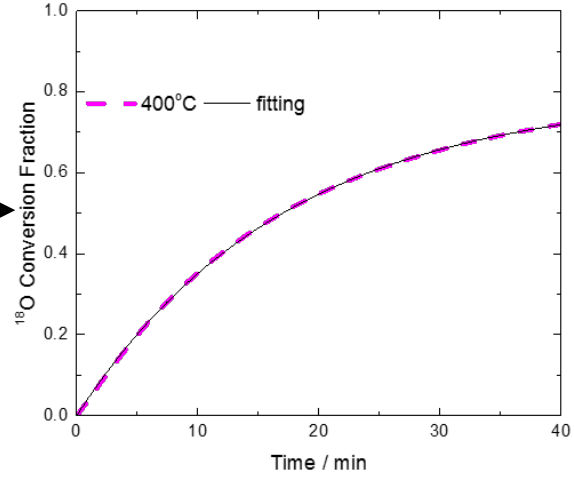

- The 3D exchange rate coefficient, k_{ex}, under polarization (D – particle diameter):

$$k_{ex} = \frac{D}{6}\left(R^*_{ex} - \frac{I}{2FN}\right)$$

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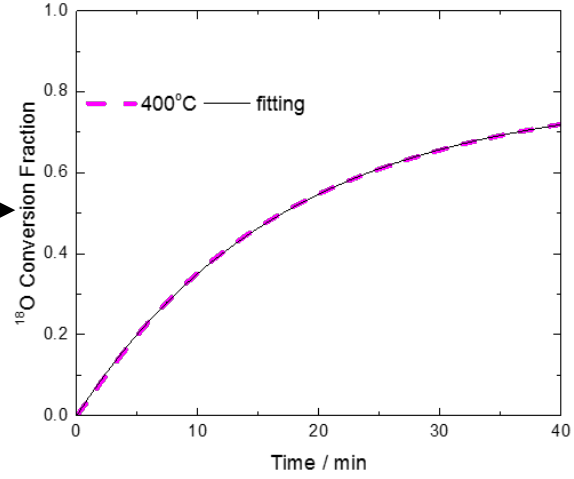

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- Implementing the Tafel relation between I and η:

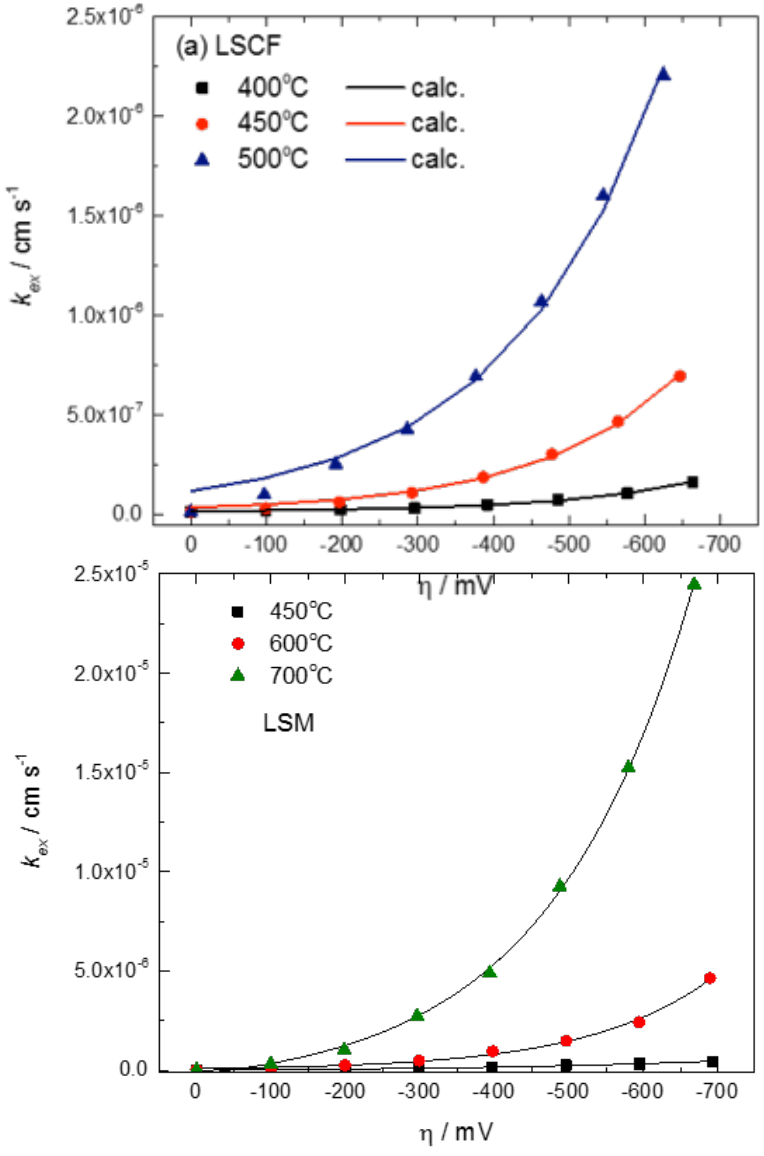
$$I = I_0 \exp(C\eta);\ C = \frac{\alpha ZF}{RT}$$

$$k_{ex} = \frac{D}{6}\left(R^*_{ex} - \frac{I_0 \exp(C\eta)}{2FN}\right)$$

- Relationship between k_{ex} and overpotential

In-Operando Determination of k_{ex} as Function of Potential

- First ever direct *in-operando* measured relationship between surface exchange coefficient and electrochemical overpotential
  - data from *in-operando* experiment and lines are equation
  - demonstrated for both LSCF and LSM



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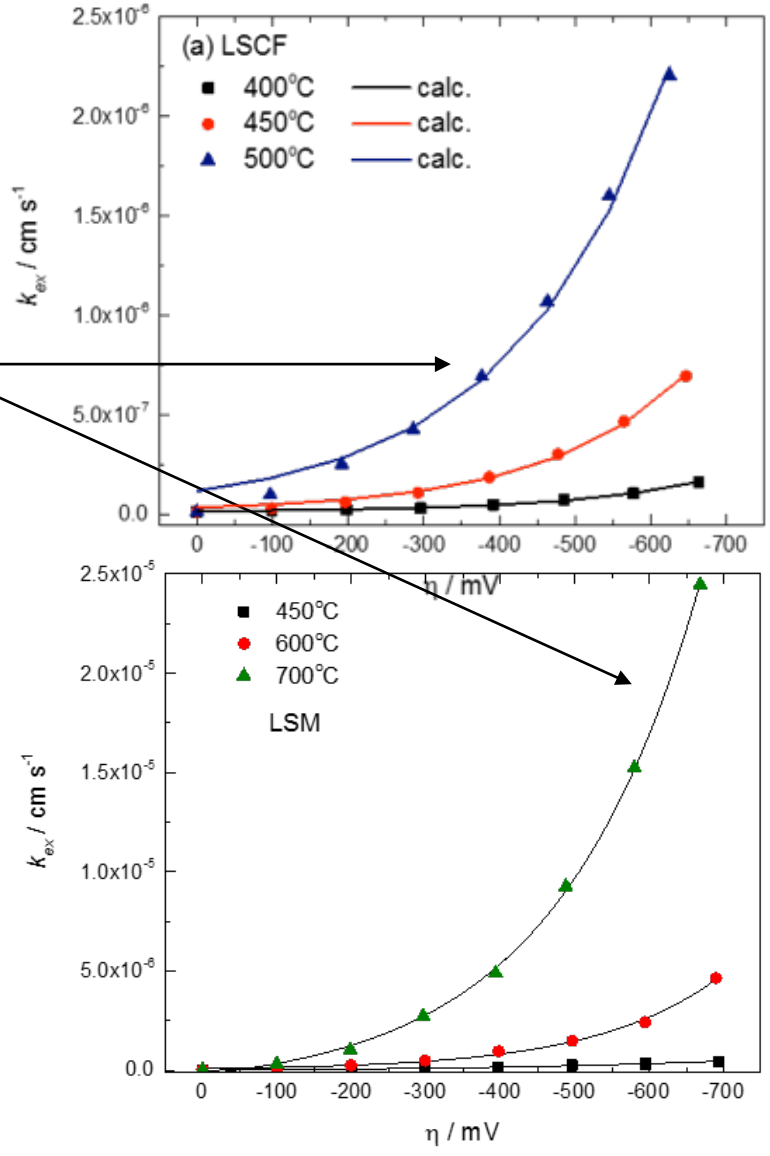

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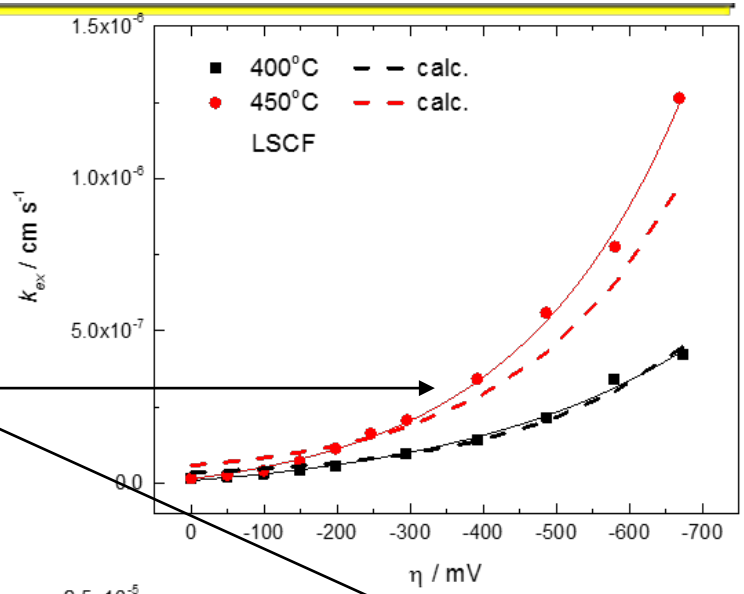
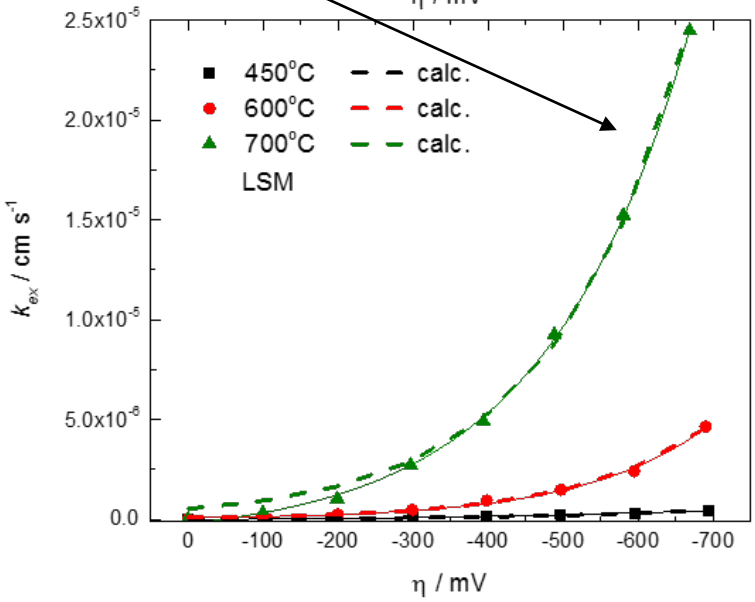
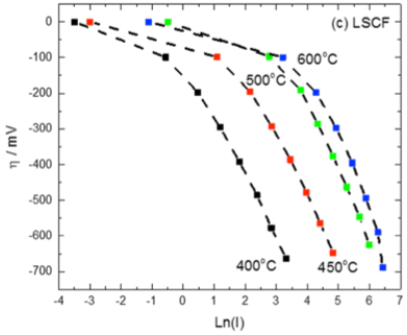






In-Operando Determination of k_{ex} as Function of Potential

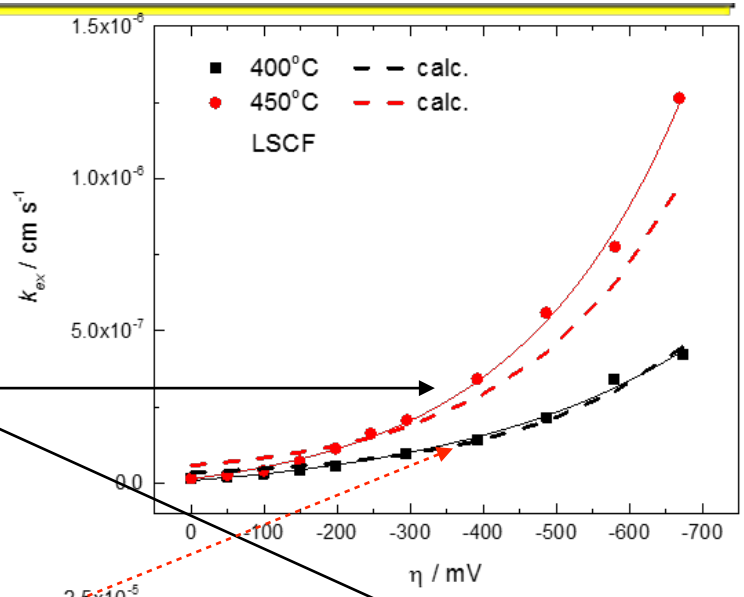
- First ever direct *in-operando* measured relationship between surface exchange coefficient and electrochemical overpotential
  - data from *in-operando* experiment and lines are equation

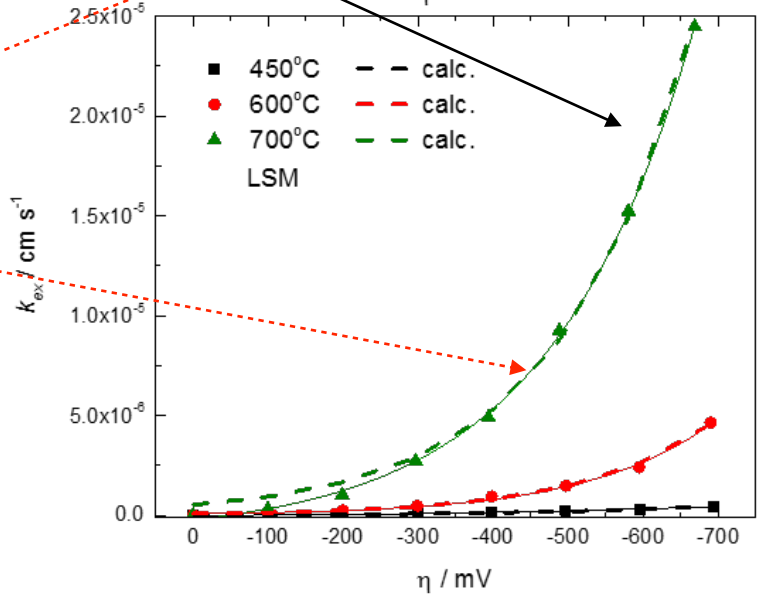
$$k_{ex} = \frac{D}{6}\left(R_{ex}^{*} - \frac{I_0 \exp(C\eta)}{2FN} \right)$$

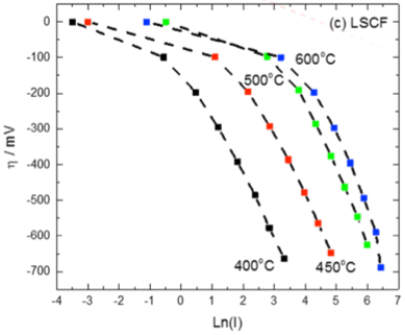
  - demonstrated for both LSCF and LSM

- Potentially first ever unifying theory for k_{ex} between isotope exchange (IIE, IEDP) and electroanalytical (e.g., ECR) techniques
  - dashed lines from equation using open circuit k_{ex} and cell Tafel results

$$I = I_0 \exp(C\eta);\ C = \frac{\alpha ZF}{RT}$$







In-Operando Determination of k_{ex} as Function of Potential

Consistent with Electrochemical Principles:

- At high overpotential best fit is by *logarithmic Tafel* relation

$$I = I_0 \exp\left(\alpha z F \eta / RT\right) = I_0 \exp\left(C\eta\right)$$

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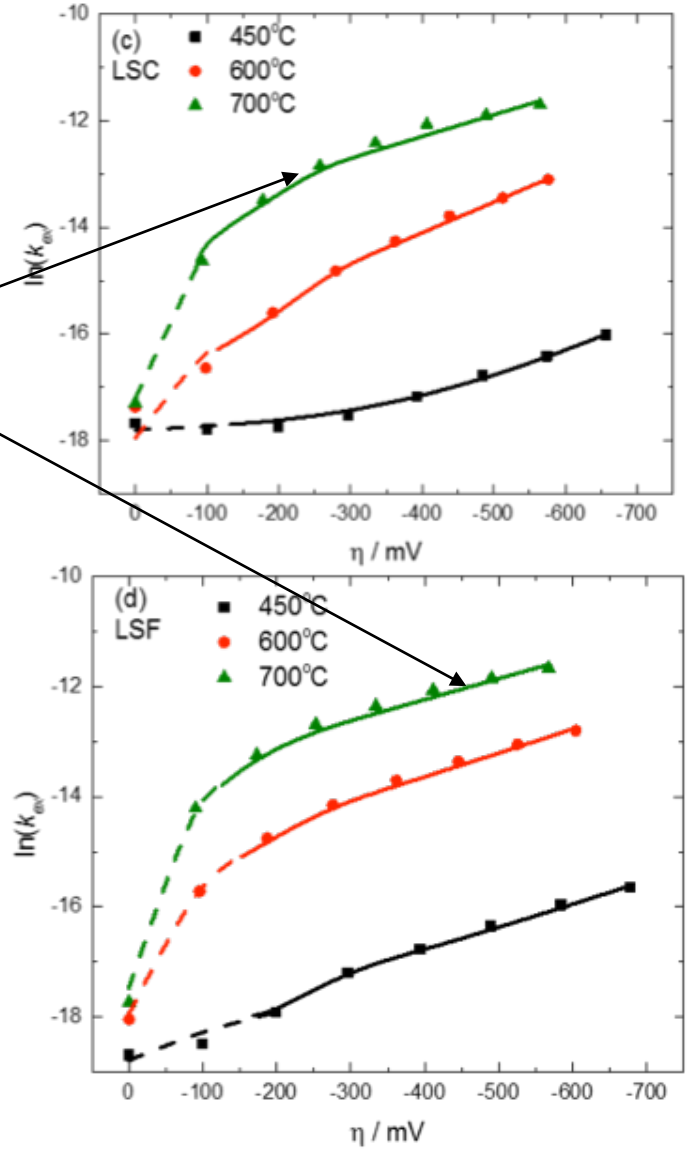

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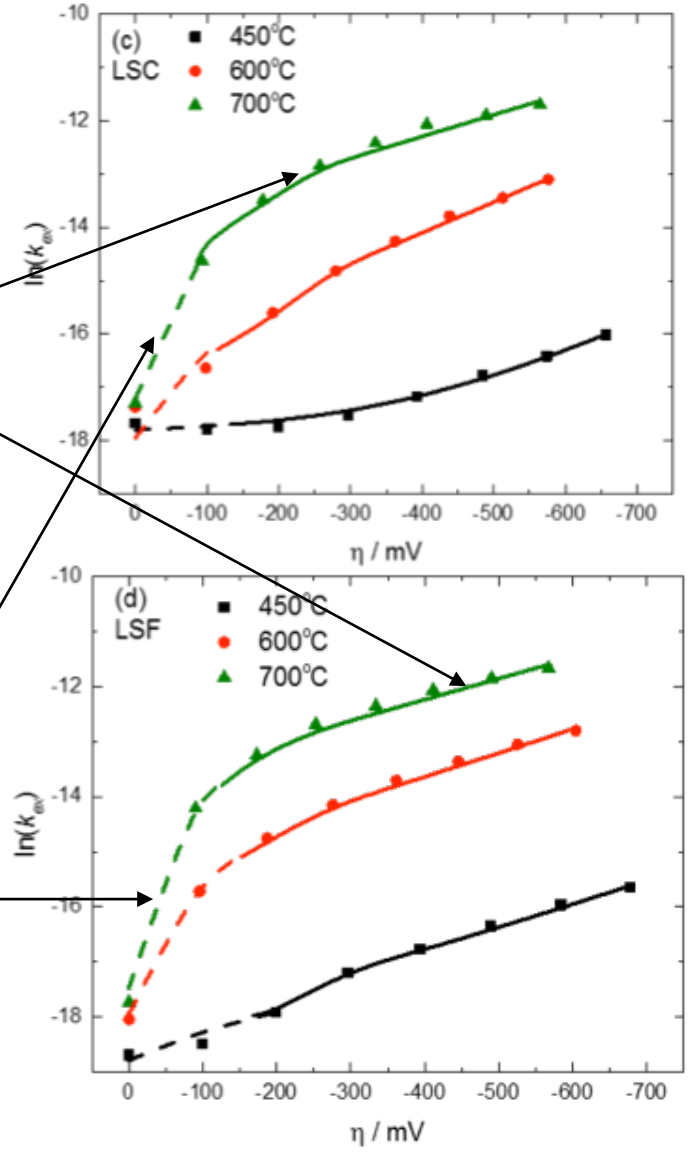
- At low overpotential best fit is by *linear Butler-Volmer* relation

$$I = I_0 \frac{zF}{RT}\left(E - E_{eq}\right) = I_0 \frac{zF}{RT}\eta$$

$$k_{ex} = \frac{D}{6}\left(b - \frac{I_0 \, \mathrm{C}^* \eta}{2FN}\right)$$

$$\mathrm{C}^* = \frac{zF}{RT}$$



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- This technique now enables the direct determination of fundamental ORR mechanisms (such as $k_{dissociation}$ and $k_{exchange}$) and the affect of H_2O, CO_2, and Cr and other contaminants on ORR kinetics and degradation mechanisms as a function of applied polarization