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

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*09/01/2012-08/31/2015*

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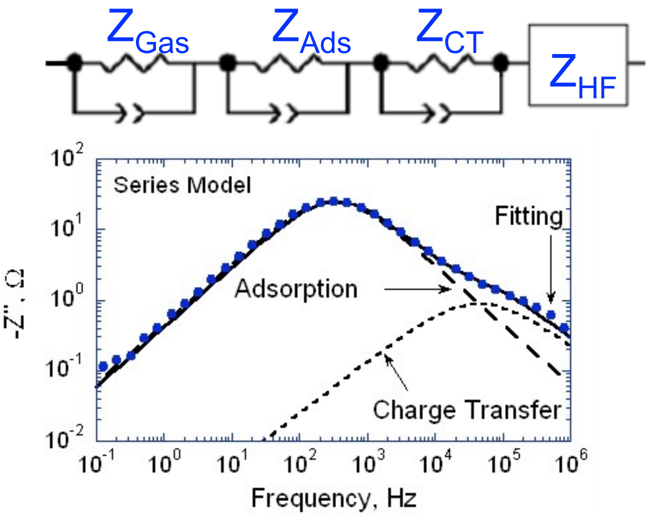
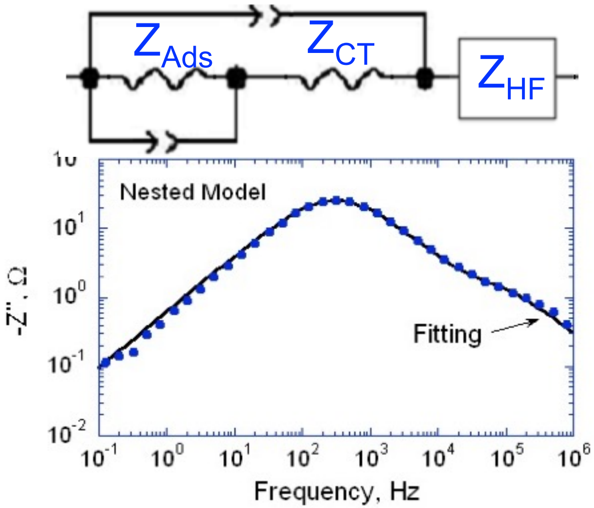
# Background - Limitation of ORR from EIS




Same!

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

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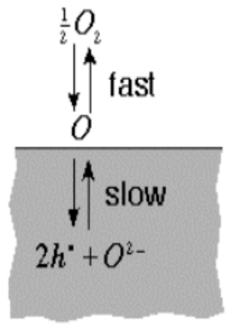
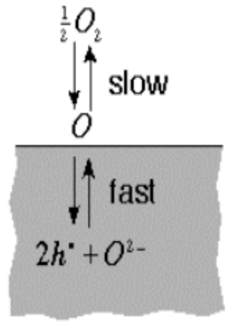
|  |  |





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

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

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

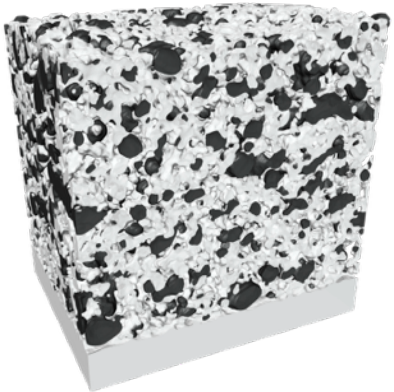
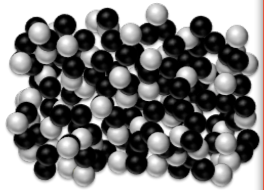
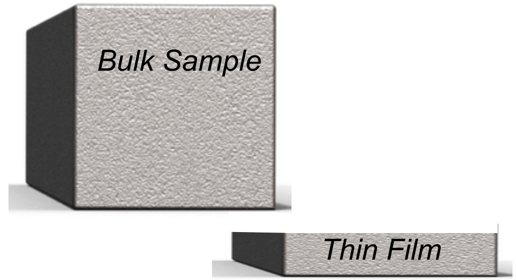
Same!

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

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

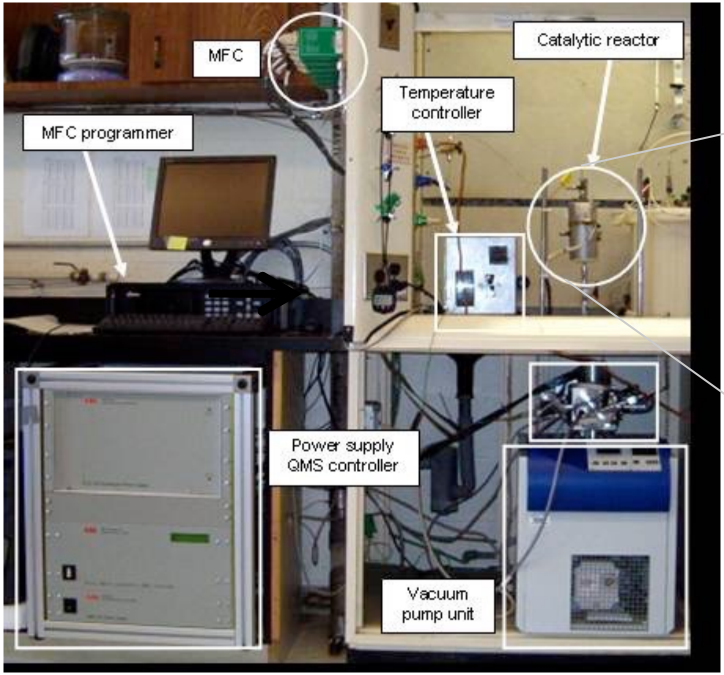
Need to combine multiple techniques to determine mechanism

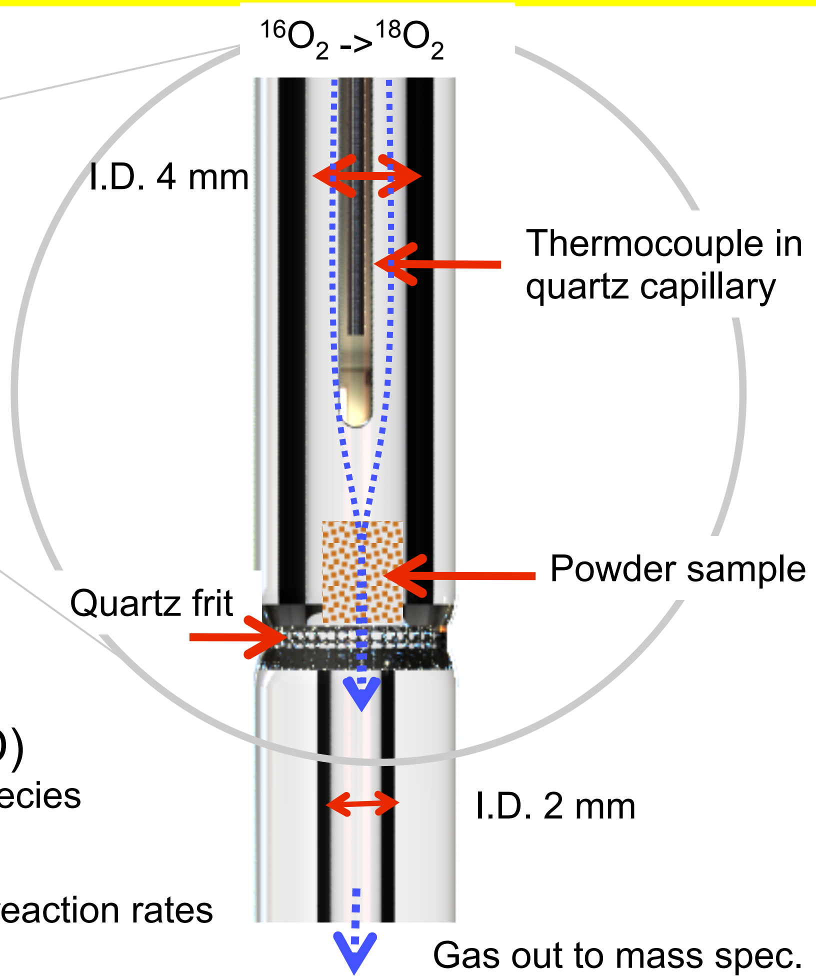
# Background - Experimental vs. Real Microstructures

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

*In-Operando*

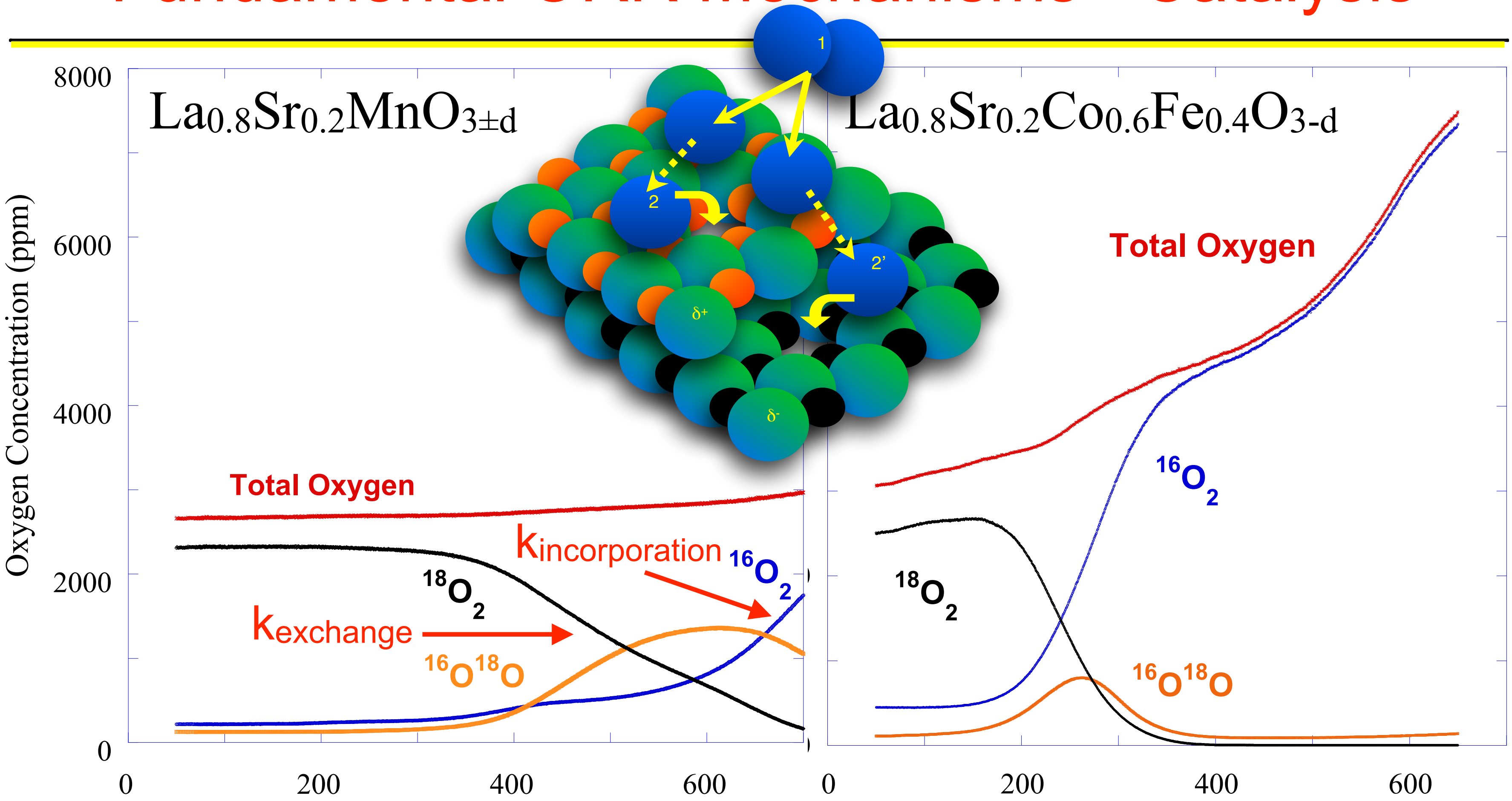
# Background - Fundamental ORR Mechanisms




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

# Fundamental ORR Mechanisms - Catalysis




Dissociative Adsorption

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

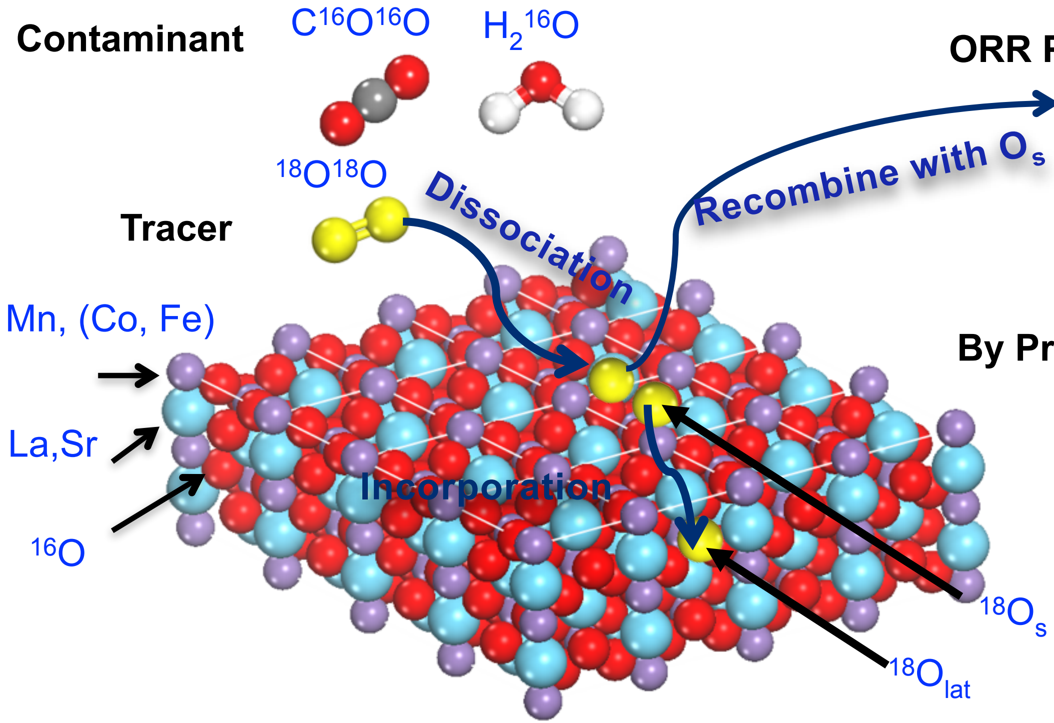
Incorporation

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

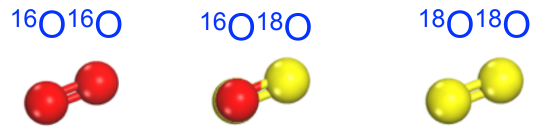
Oxygen isotope exchange - TPD in 3000 ppm $^{18}O_2$

# ORR Reaction Mechanisms in Presence of $H_2O$ and $CO_2$

## *In situ* Isotope Exchange (IIE)

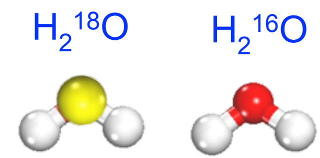


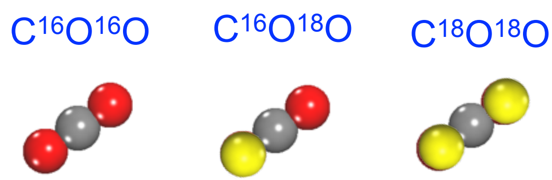

**ORR Products**




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

**By Products**



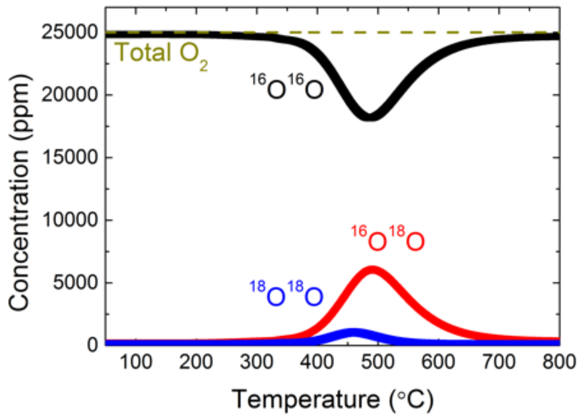

Provide information about surface reaction with contaminants

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

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

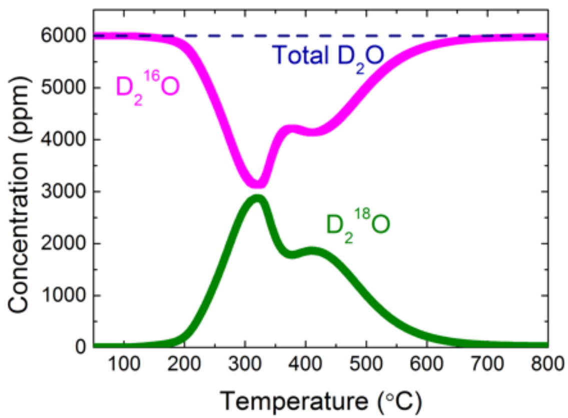
# ISTPX of LSCF in 25000ppm $O_2$ with 6000ppm $D_2O$

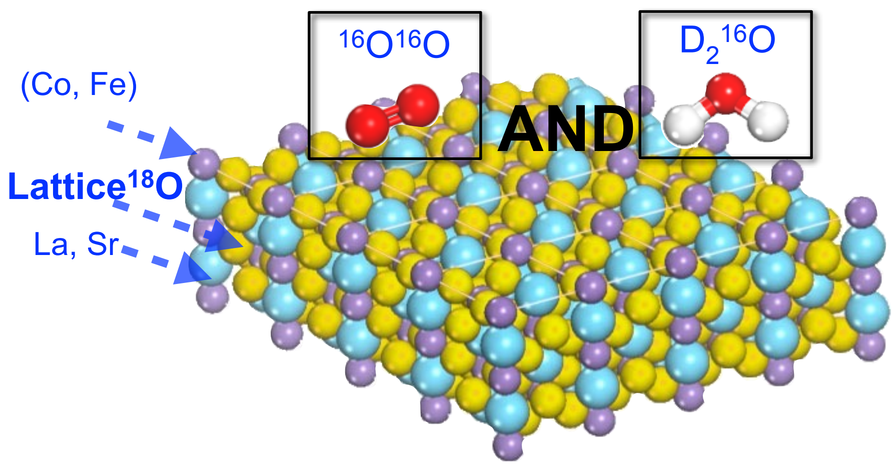
$O_2$ exchange with lattice $^{18}O$




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

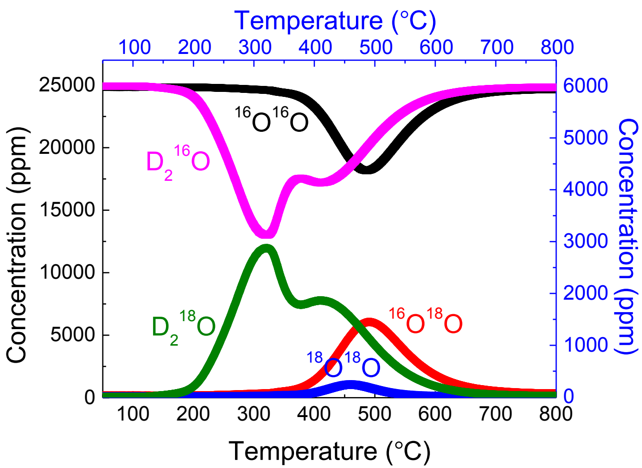
$D_2O$ exchange with lattice $^{18}O$

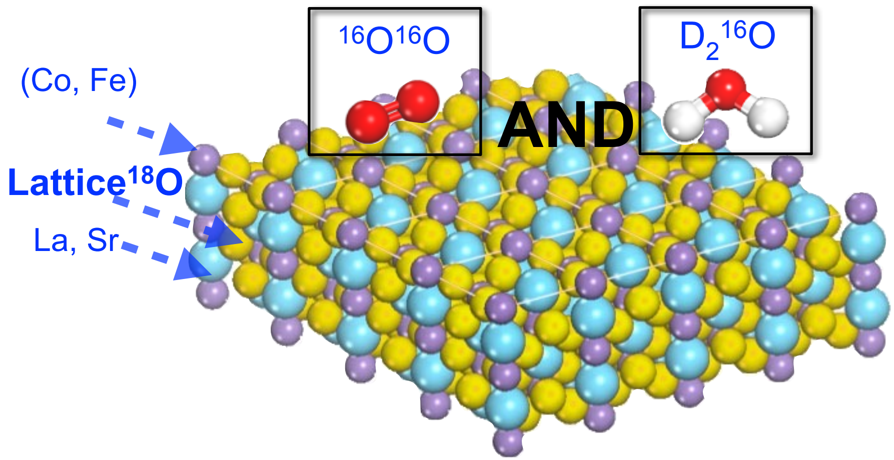


# ISTPX of LSCF in 25000ppm $O_2$ with 6000ppm $D_2O$

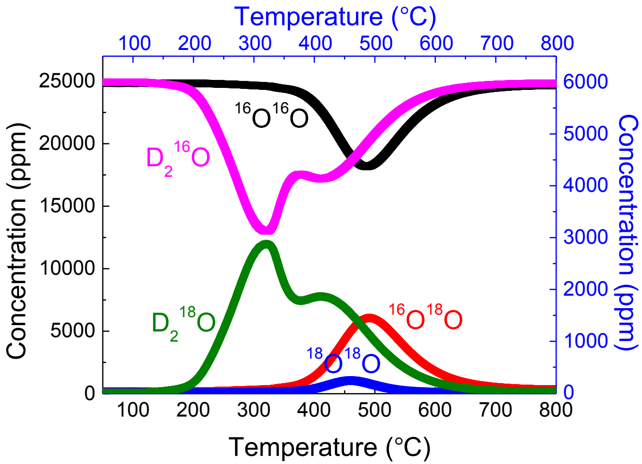
## $D_2O$ and $O_2$ exchange with lattice $^{18}O$



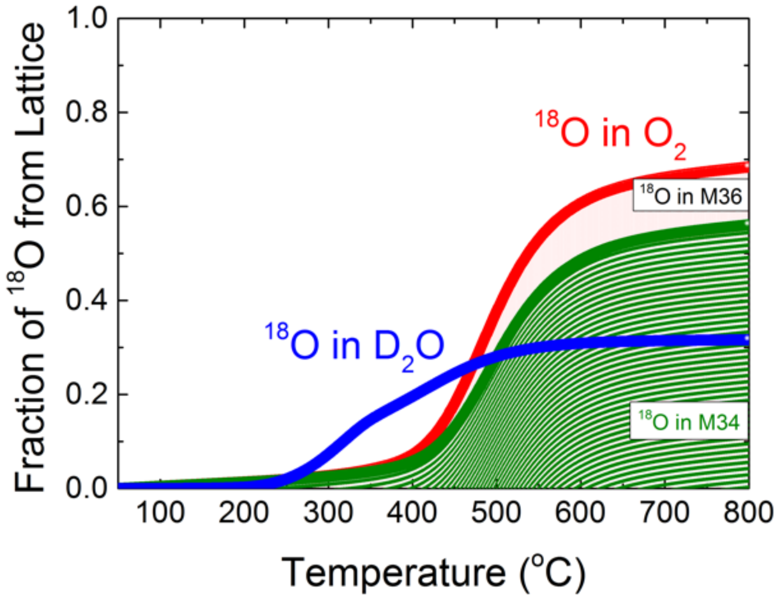



# ISTPX of LSCF in 25000ppm $O_2$ with 6000ppm $D_2O$

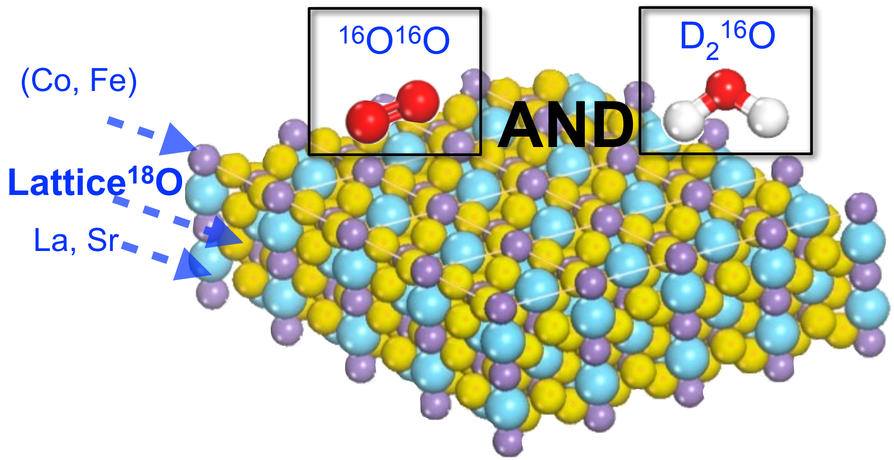
$D_2O$ and $O_2$ exchange with lattice $^{18}O$




Accumulated Isotopic Fraction exchanged from $^{18}O$ LSCF

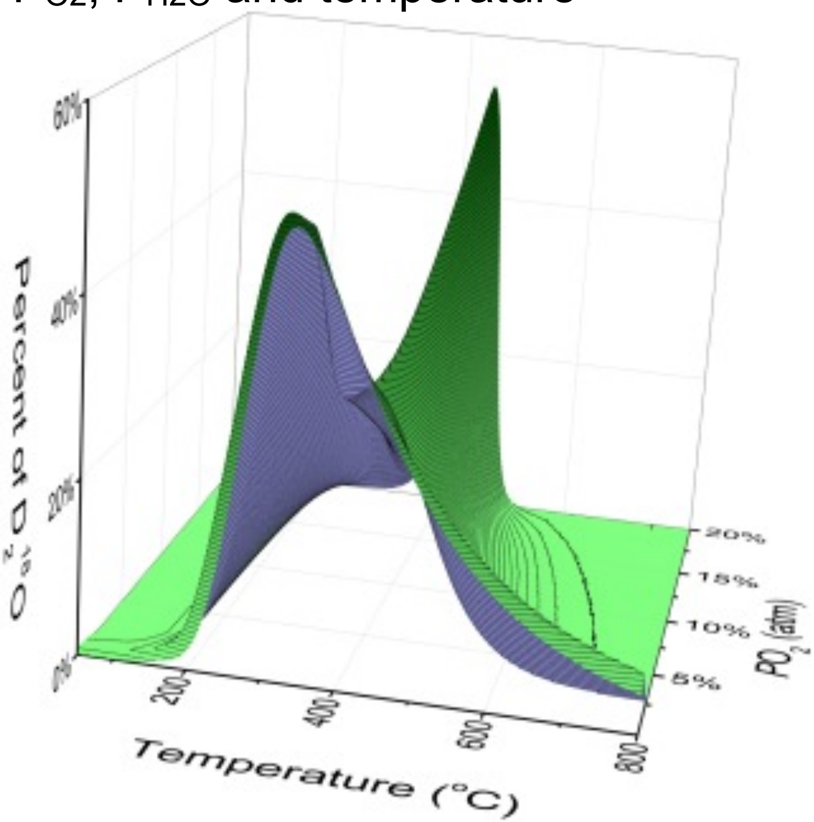



At lower temperature more of the lattice $^{18}O$ exchanges with water than $O_2$

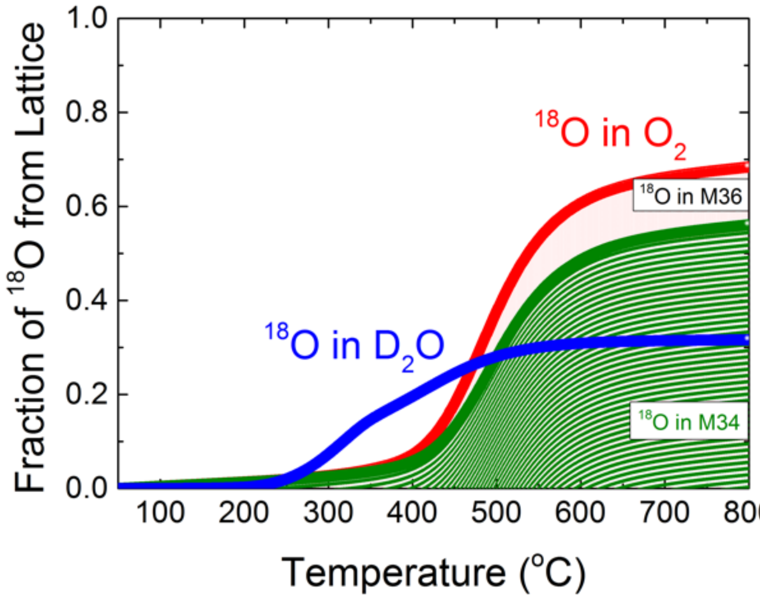


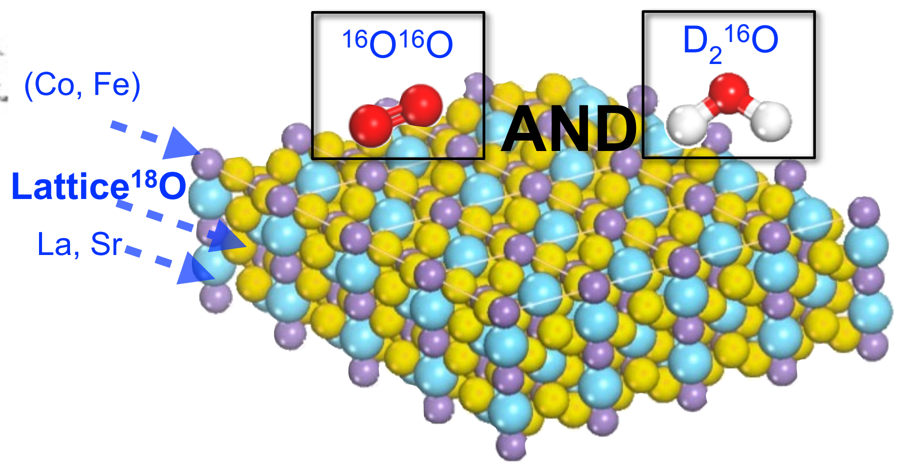
# Temperature and $PO_2$ Dependence of LSCF in $D_2O$

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
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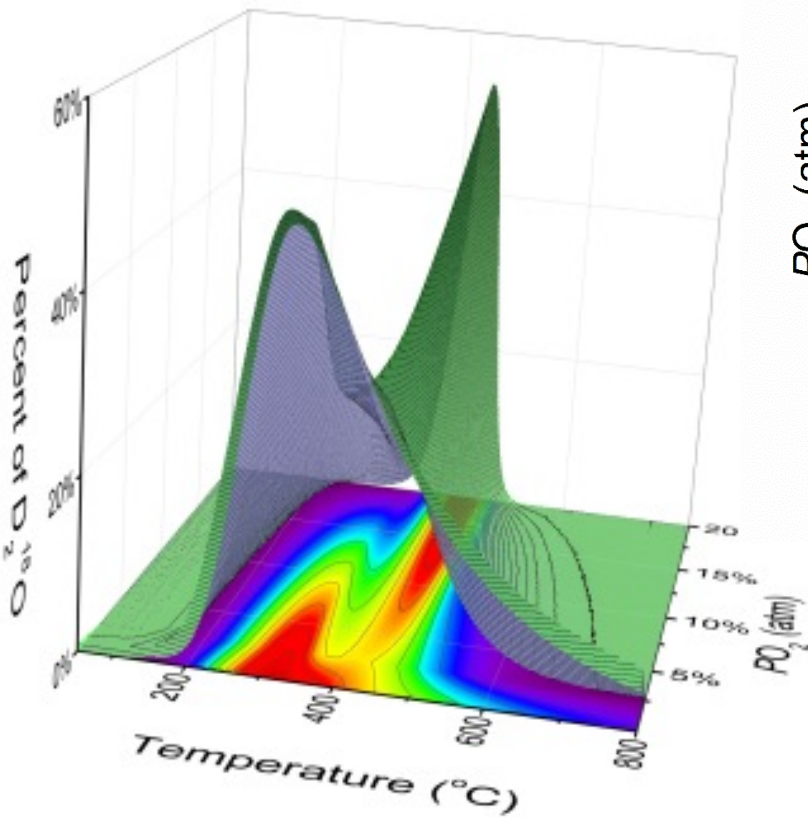
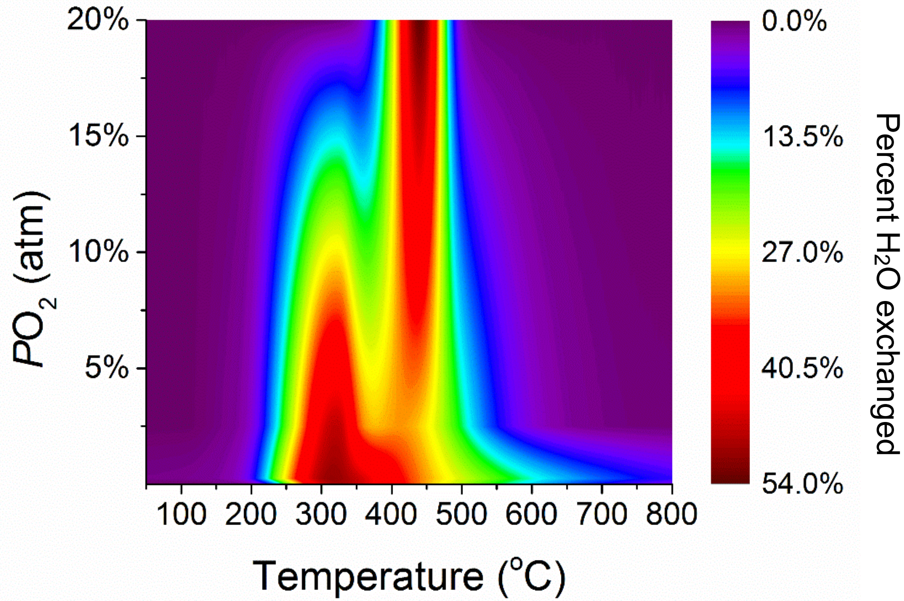
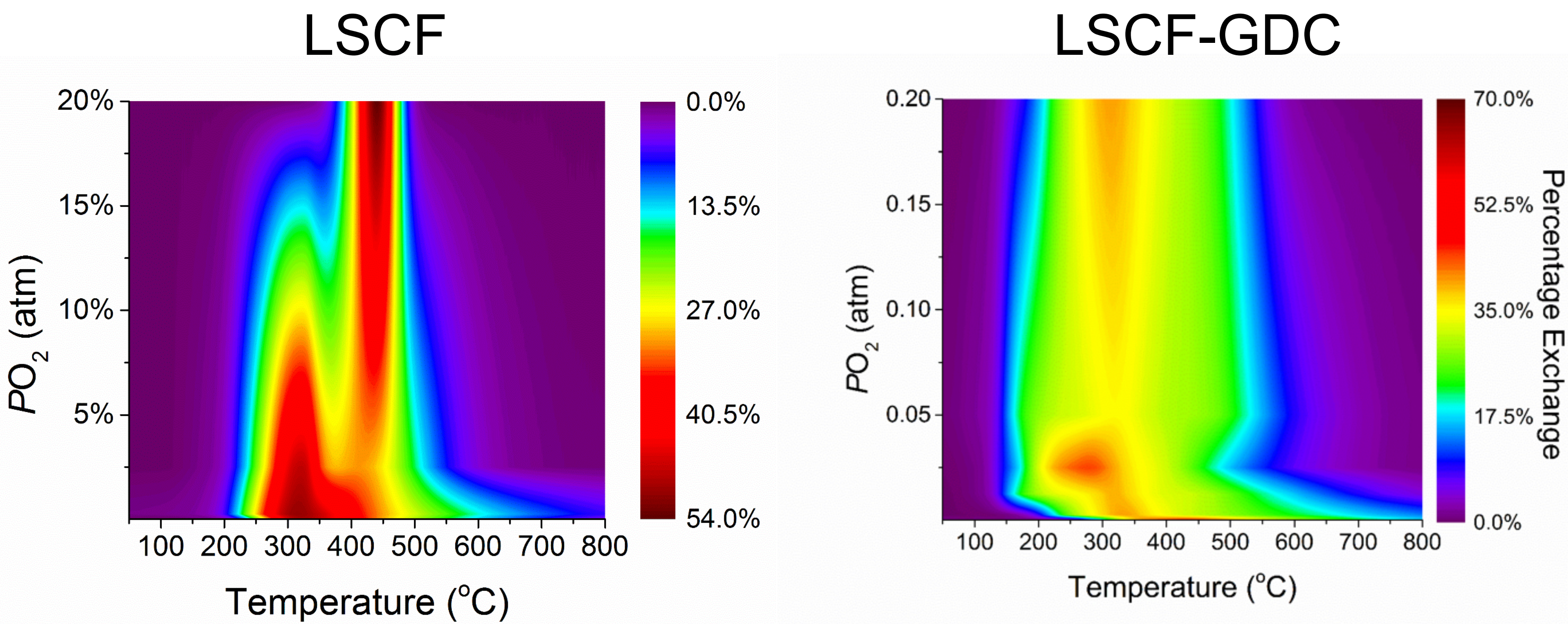



Two Exchange Peaks:
- As $PO_2$ increases, 300ºC peak decreases
- 450ºC peak still present at high $PO_2$

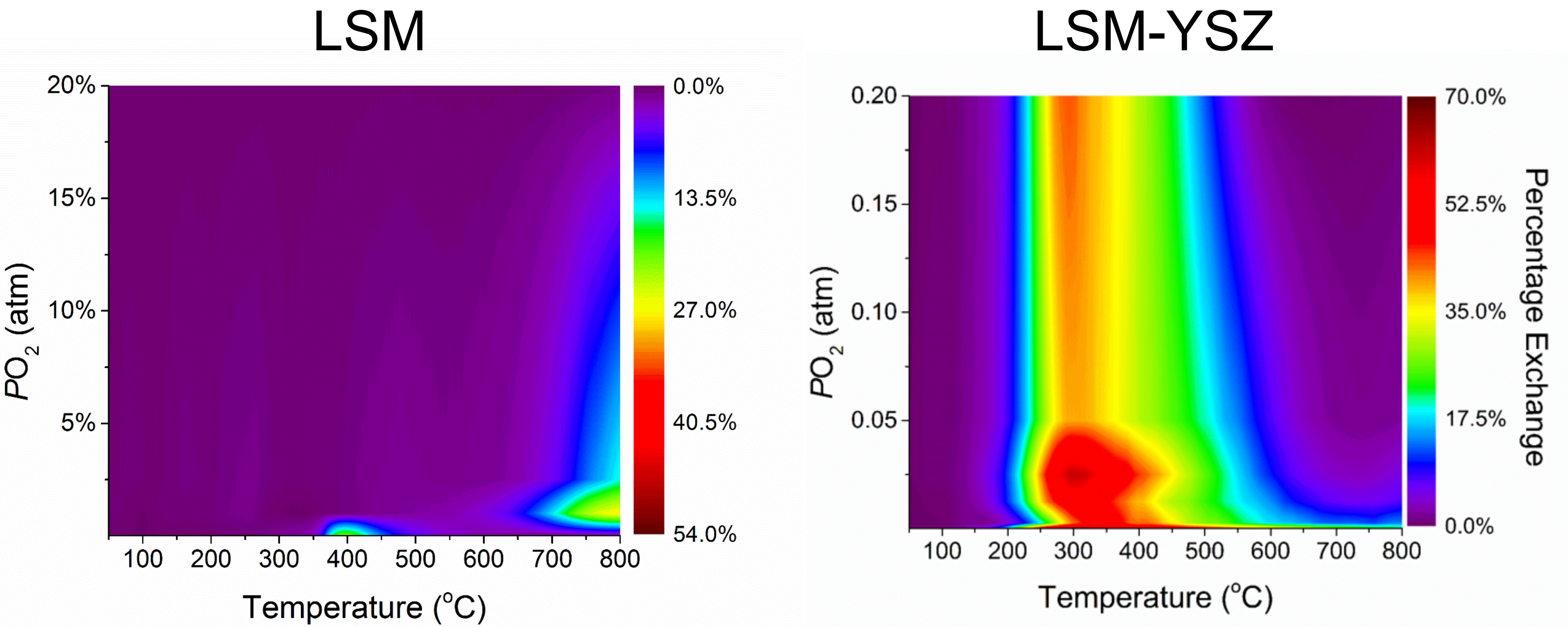
- We have mapped out $H_2O$ (and $CO_2$) impacts on ORR as function of $P_{O2}$, temperature, and contaminant concentration

# Water Exchange on LSCF vs LSCF-GDC Composite Cathodes



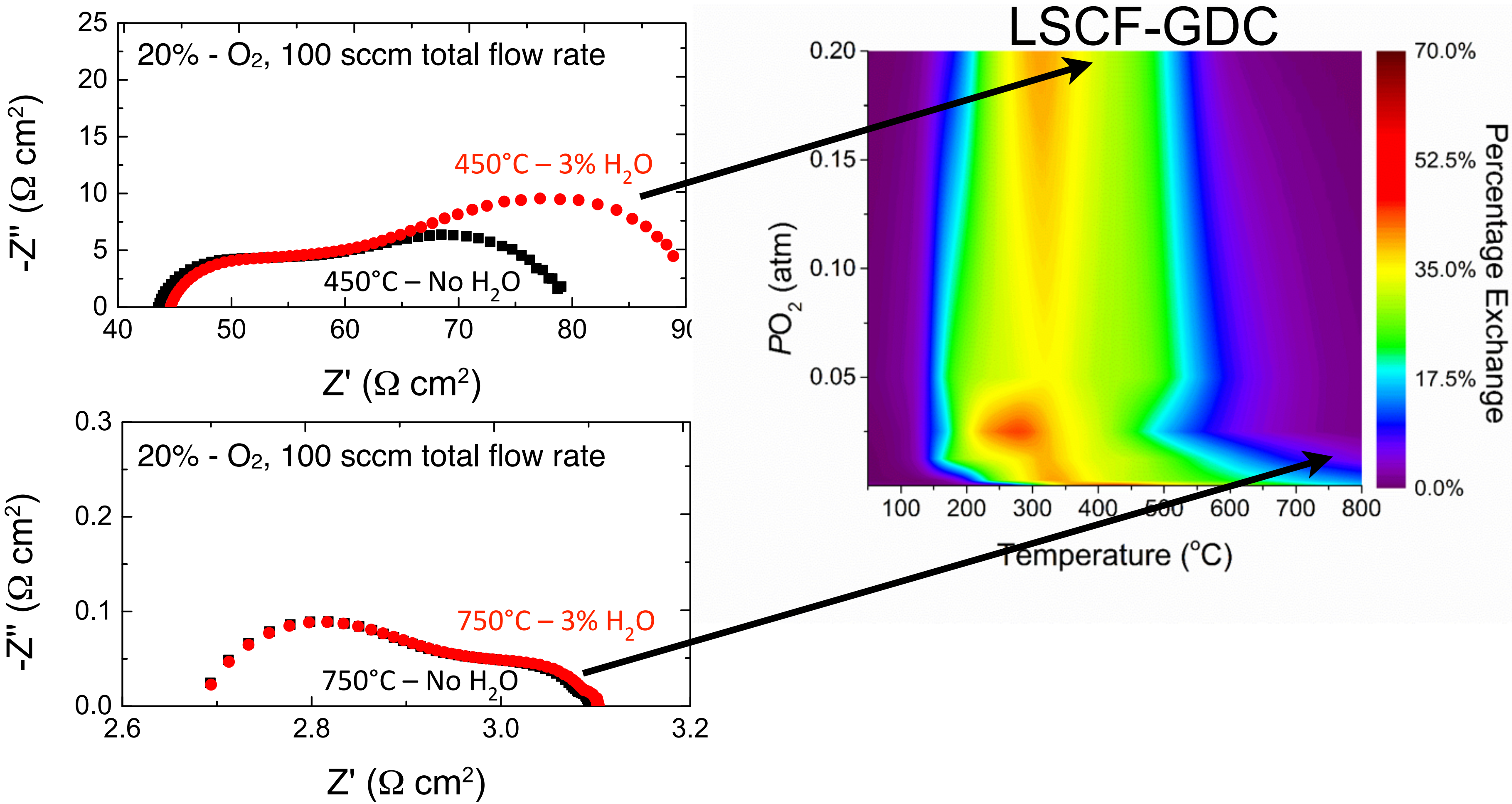

- LSCF composite significantly broadens temperature range of water exchange dominance
- Demonstrating importance of TPBs and co-existence of O-dissociation and O-incorporation phases

# 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

# Comparison of ISTPX with EIS for LSCF-GDC in $H_2O$




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

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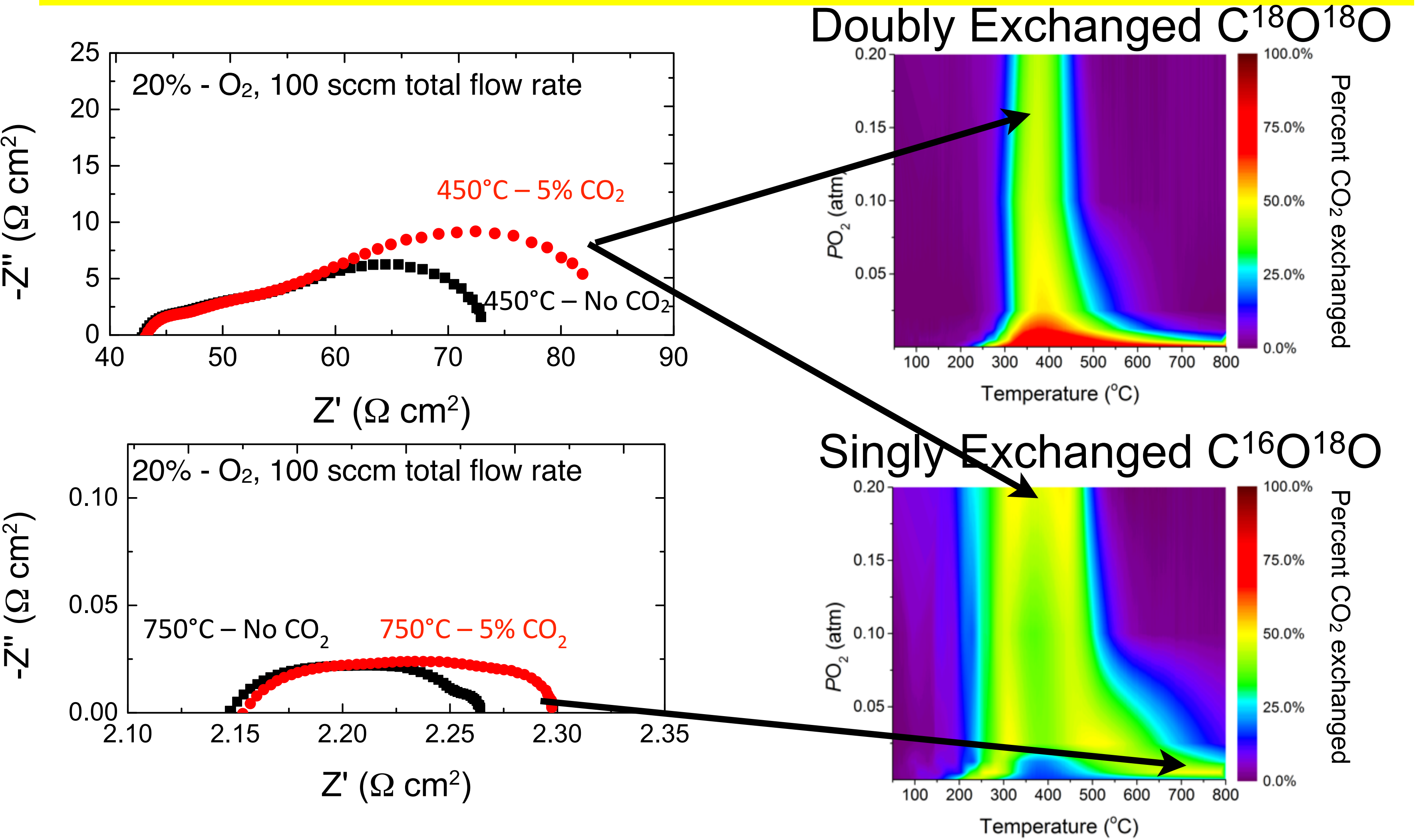
# Comparison of ISTPX with EIS for LSCF-GDC in $CO_2$




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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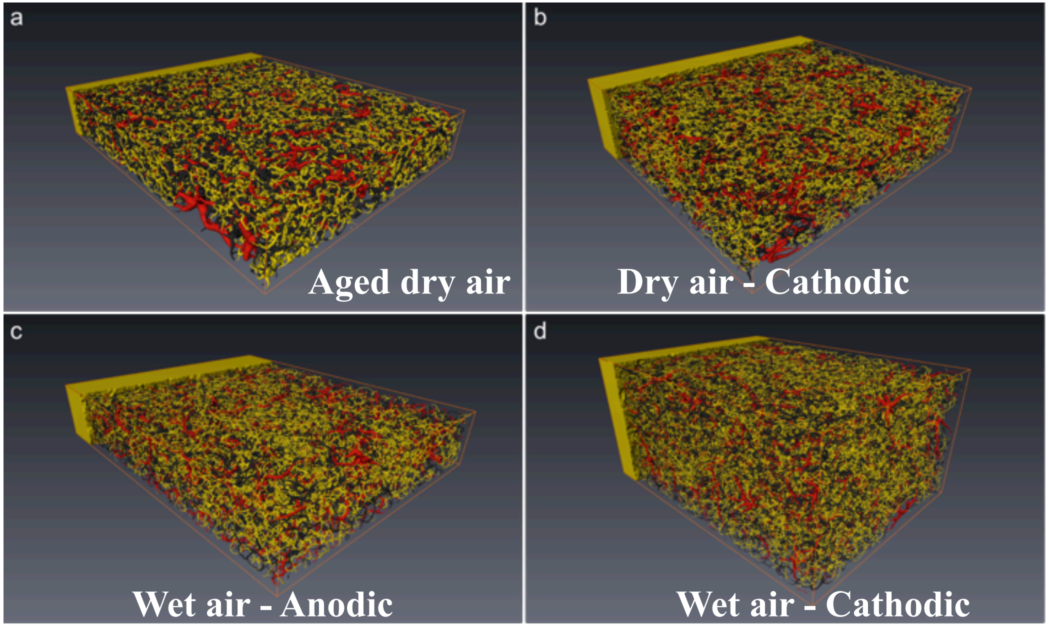
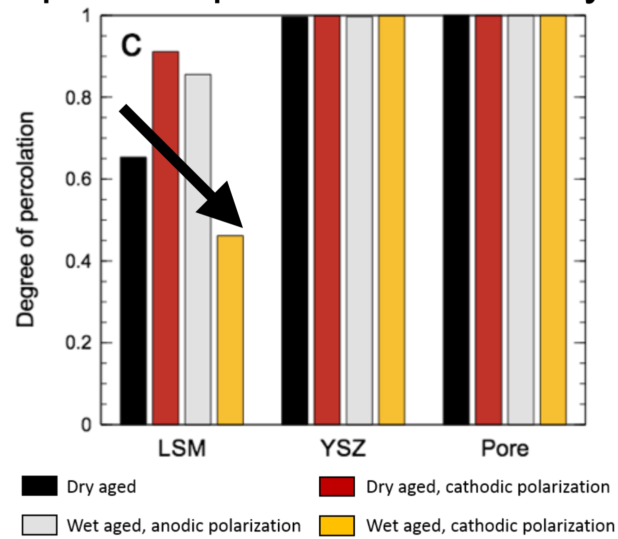
# $H_2O$ Impact on LSM/YSZ Microstructural Change

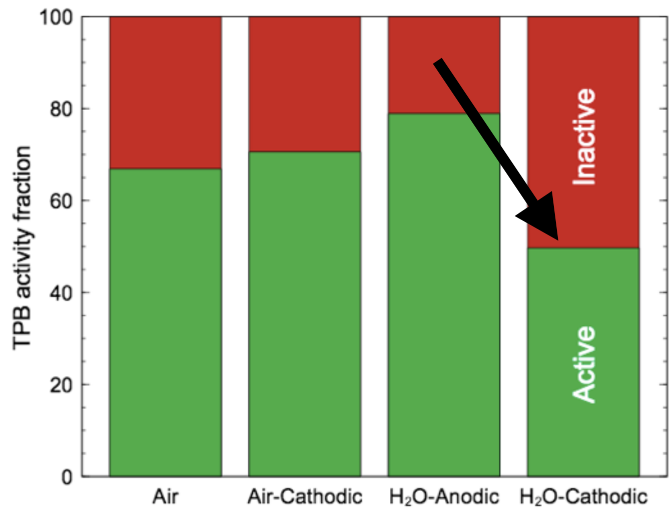
Microstructural degradation under $P_{H2O}$ identified by isotope exchange conditions




Impact on phase connectivity




Impact on effective TPB




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

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# *In-Situ* Conclusions/Outcomes

- Integrated heterogeneous catalysis, polarization, and microstructural characterization to provide fundamental understanding of cathode ORR and degradation mechanisms
- Demonstrated LSCF is more active than LSM and has different ORR mechanism
- $H_2O$ (and $CO_2$) actively participate in ORR for both LSCF and LSM
- Identified temperature and gas composition regions where $H_2O$ dominates $O_2$ surface exchange mechanism and where they are less important
- Identified composite cathode effect on $O_2$ surface exchange with $H_2O$
- Ambient humidity has a direct impact on LSM/YSZ cathode microstructural and compositional changes that degrades ohmic and non-ohmic ASR


1. "A Model for Extracting Fundamental Kinetic Rates of SOFC Cathode Materials from Oxygen Isotope Exchange Experiments," *ECS Transacions*, **9** (May 2014).
2. "Three Dimensional Microstructural Characterization of Cathode Degradation in SOFCs Using Focused Ion Beam and SEM," *ECS Transactions*, **9** (May 2014).
3. "Towards a Fundamental Understanding of the Cathode Degradation Mechanisms," *ECS Transactions*, **9** (May 2014).
4. "A Study of SOFC Cathode Degradation in $H_2O$ Environments," *ECS Transactions*, **10** (Oct 2014).
5. "Enhancement of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ Activity by Ion Implantation for Low-Temperature SOFC Cathodes," *J. of Electrochem. Soci.*, **162**, 9, F965-970, (2015).
6. "Three Dimensional Microstructural Characterization of Cathode Degradation in SOFCs Using FIB/SEM and TEM," *Microscopy and Microanalysis* **S3**, 2161 (Aug 2015).
7. "Investigating the Relationship Between Operating Conditions and SOFC Cathode Degradation," *ECS Transactions,* (2015).
8. "Fundamental Impact of Humidity on SOFC Cathode ORR", *J. of Electrochem. Soc.*, **163** (3), F171-F182, (2016).
9. "Investigation of Long-Term Cr Poisoning Effect on LSCF-GDC composite cathodes", accepted, *J. of Electrochem. Soc*,
10. "Comprehensive Quantification of Porous LSCF Cathode Microstructure and Electrochemical Impedance", submitted *J. of Electrochem. Soc.*
11. "Reaction Kinetics of Gas-Solid Exchange Using Gas Phase Isotopic Oxygen Exchange", submitted *ACS Catalysis*.
12. "$CO_2$ $O_2$ Co-Exchange on Multivalent Metal Oxides", submitted *The Journal of Physical Chemistry*.
13. "Water and $CO_2$ gas-solid Exchange on Multivalent Metal Oxides and Their Composites", in preparation.
14. "Direct Observation of Oxygen Dissociation on Metal Oxides", in preparation.
15. "Concurrent Heterogeneous Reactions on Perovskites Using Gas Phase Isotopic Oxygen Exchange", in preparation.
16. "Reaction Kinetics and $CO_2$-$O_2$ Co-Exchange on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$", in preparation.
17. "Chromium Poisoning Effects on Surface Exchange Kinetics of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$", in preparation.
18. "Effect of Gas Contaminants on LSCF-GDC Composite Cathodes", in preparation
19. "Mechanisms Governing Water Exchange on LSM and Composite LSM-YSZ Cathodes", in preparation.
20. "Oxygen Reduction Kinetics on LSM and LSM-YSZ Composite", in preparation.


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

# *In-Operando* Project Objectives

## Phase 1

- 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.

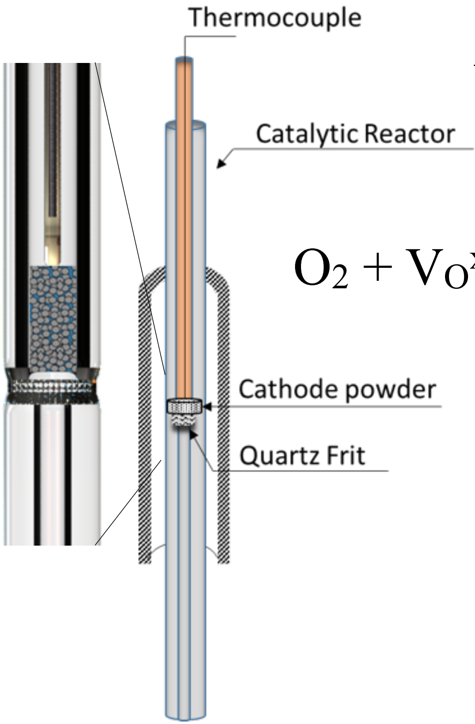
## Phase 2

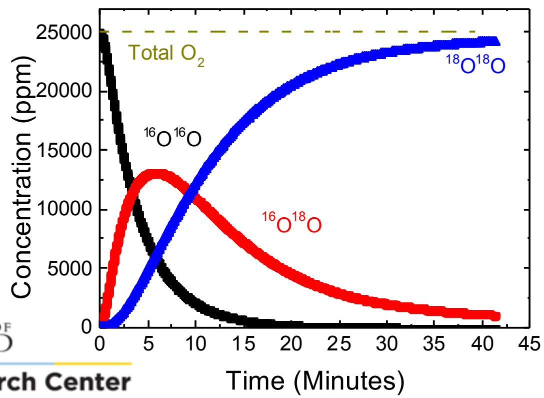
- Determine effect of microstructure, macrostructure and composition on the cathode performance, $O_2$ surface exchange mechanism and coefficient.
- Integrate results and identify cathode composition/structures and operational conditions to reduce ASR and enhance durability.
- Develop unifying theory for the numerous surface exchange processes obtained by ECR, IIE, IEDP, etc.
- Apply the model results on existing surface exchange coefficient data, and identify cathode compositions and structures with enhanced activity and durability.

# Develop *In-Operando* Isotope Exchange System

## *In-Situ*

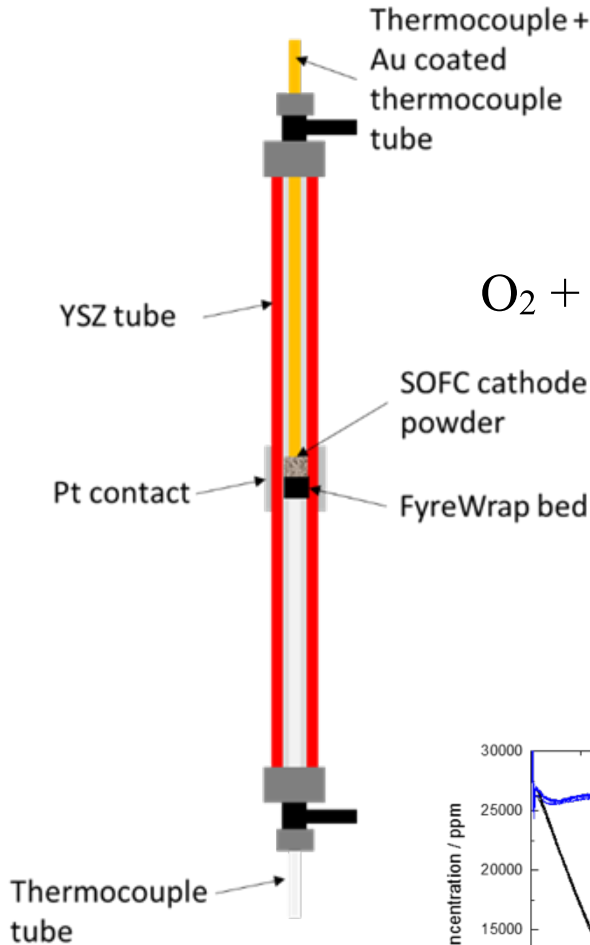
$$O_2 + V_O^x = 2O_O^x$$

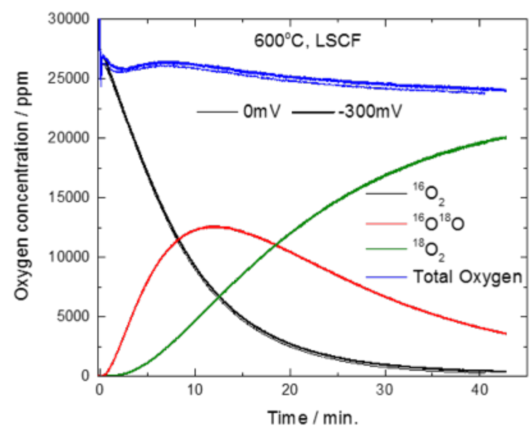



## *In-Operando*

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

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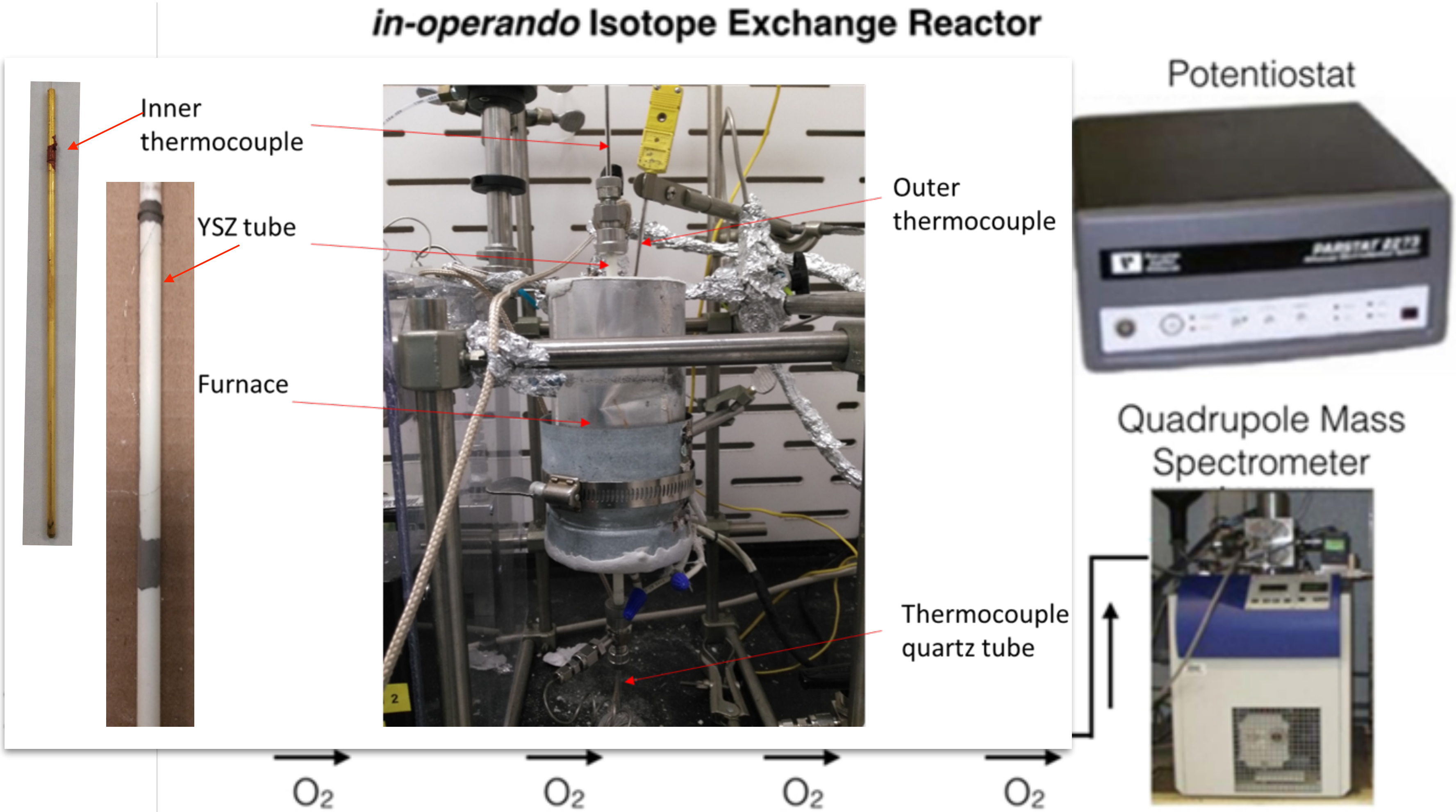
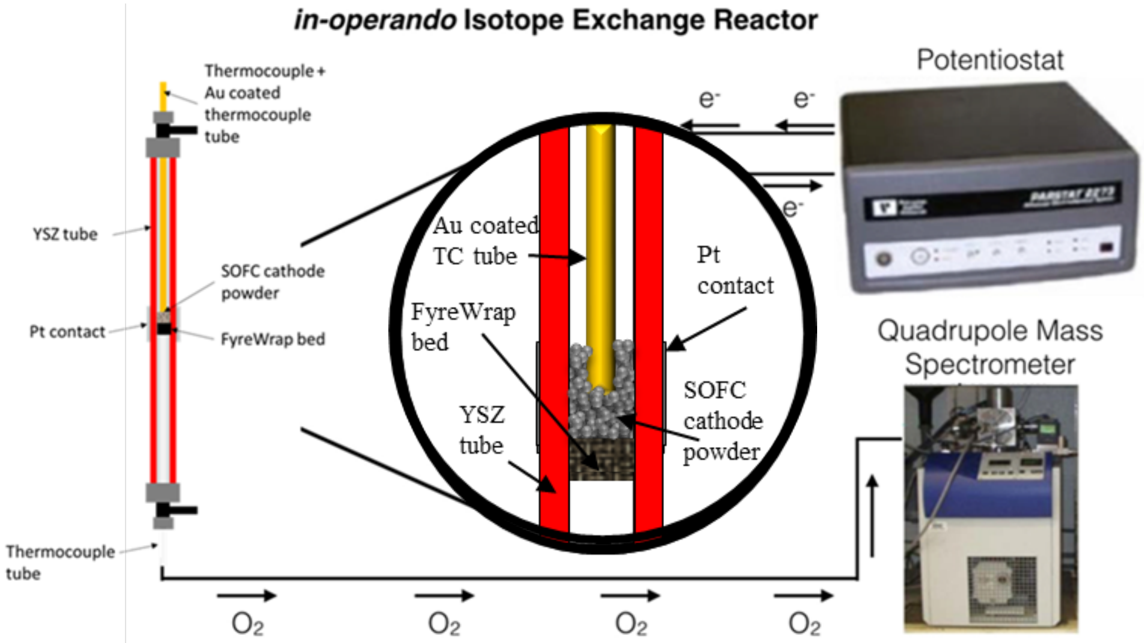
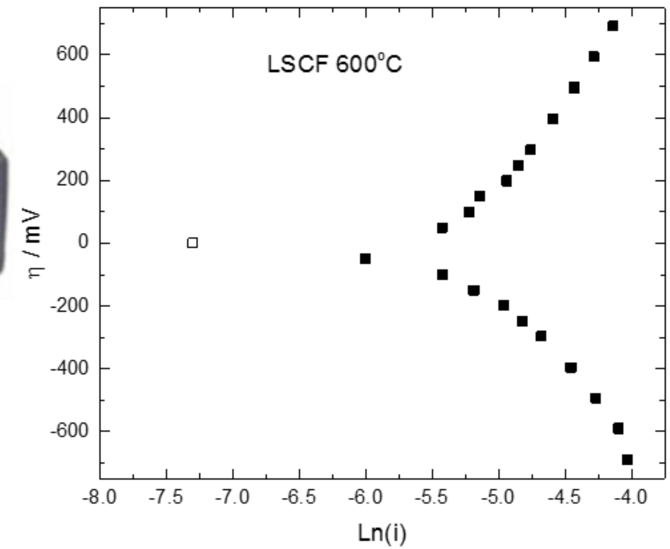
# Develop *In-Operando* Isotope Exchange System

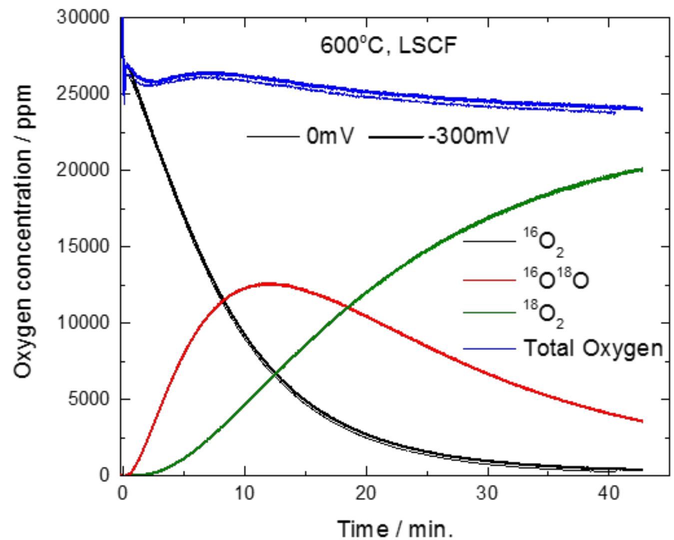



- Convert *in-situ* heterogeneous catalysis set-up to *in-operando* reactor to measure cathode ORR under applied bias

# Develop *In-Operando* Isotope Exchange System

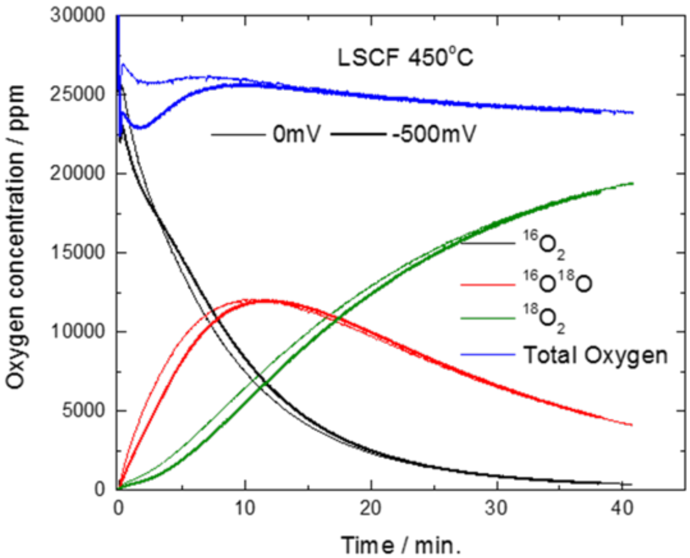


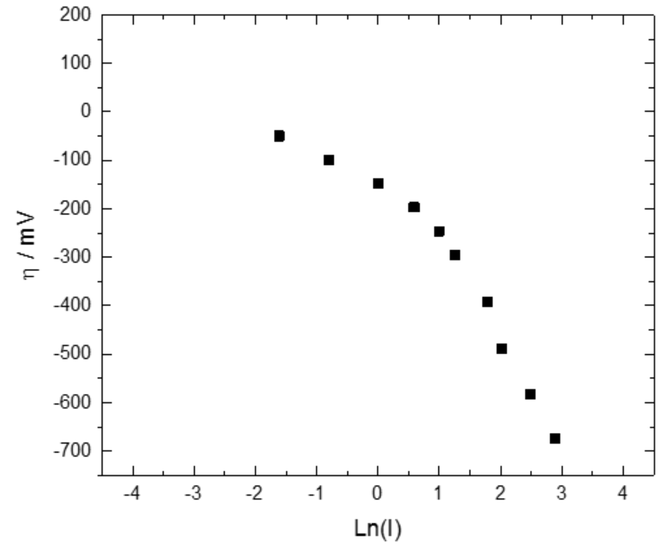




- Now able to *in-operando* determine cathode ORR by simultaneous cell current-voltage behavior under applied bias with *in-situ* heterogeneous $^{18}O$-isotope exchange

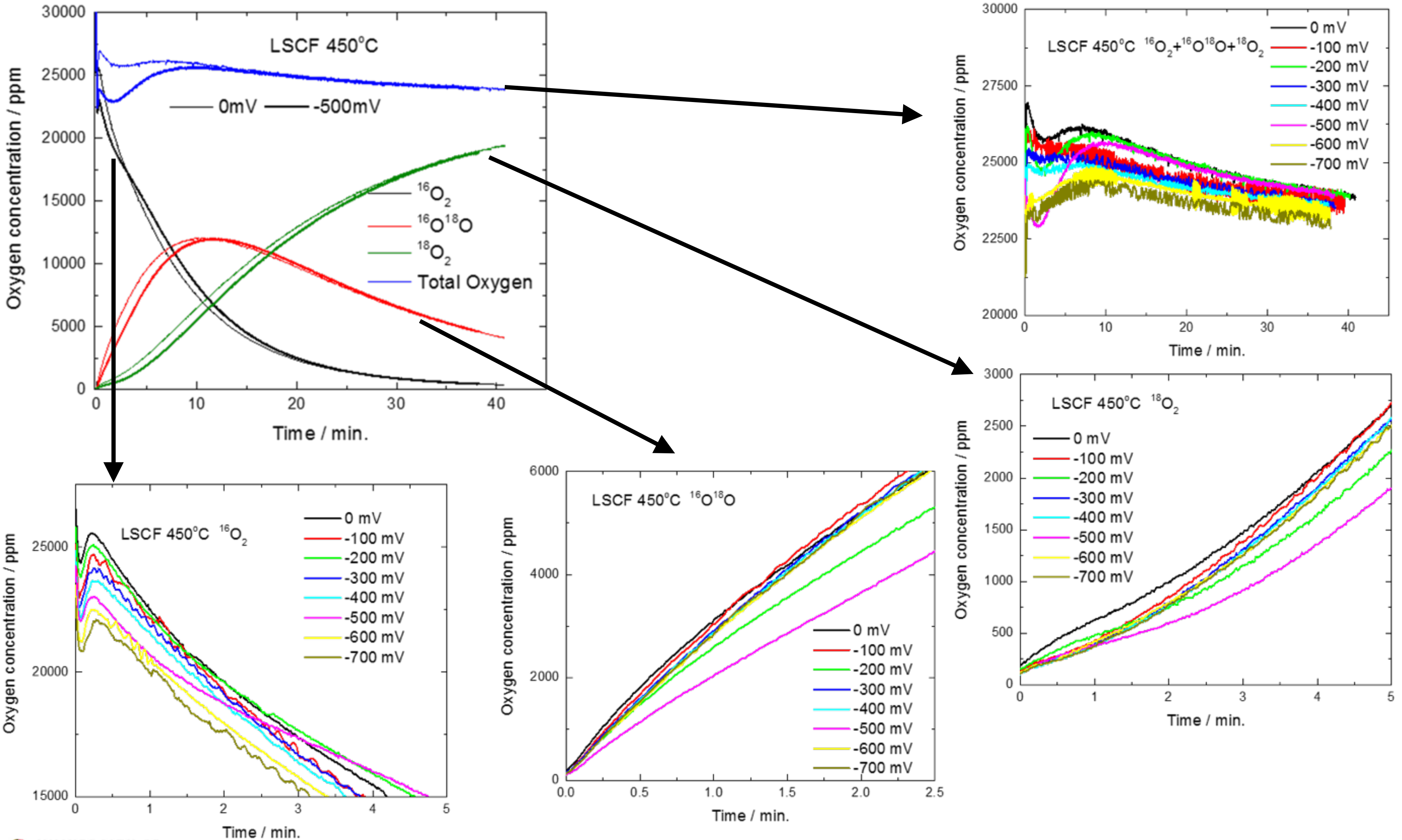
# *In-Operando* Determination of LSCF $k_{ex}$ as Function of Potential




- *In-operando* determination of LSCF surface exchange coefficient $k_{ex}$ as a function of cathodic bias

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





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- $k_{ex}$ as a function of cathodic bias is most sensitive at short time

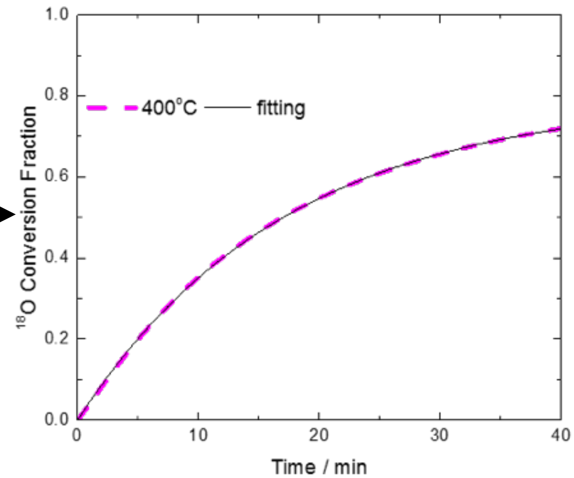
# *In-Operando* Determination of $k_{ex}$ as Function of Potential

**Tentative Model**

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

- 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)

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

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

- Implementing the Tafel relation between $I$ and $\eta$:

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

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

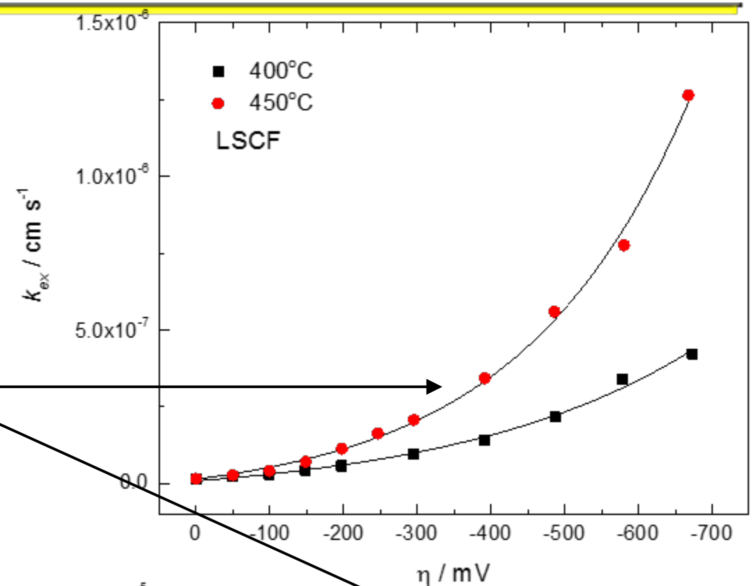
- Relationship between $k_{ex}$ and overpotential

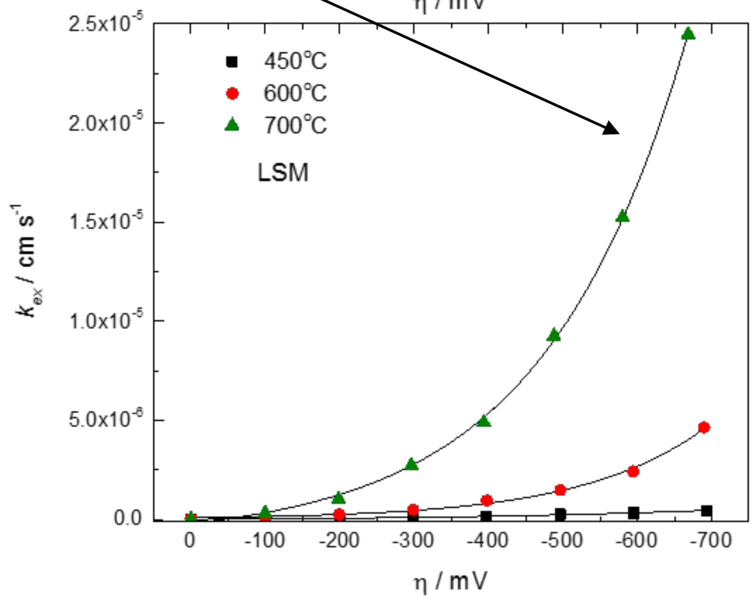
# *In-Operando* Determination of $k_{ex}$ as Function of Potential

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

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

  - demonstrated for both LSCF and LSM



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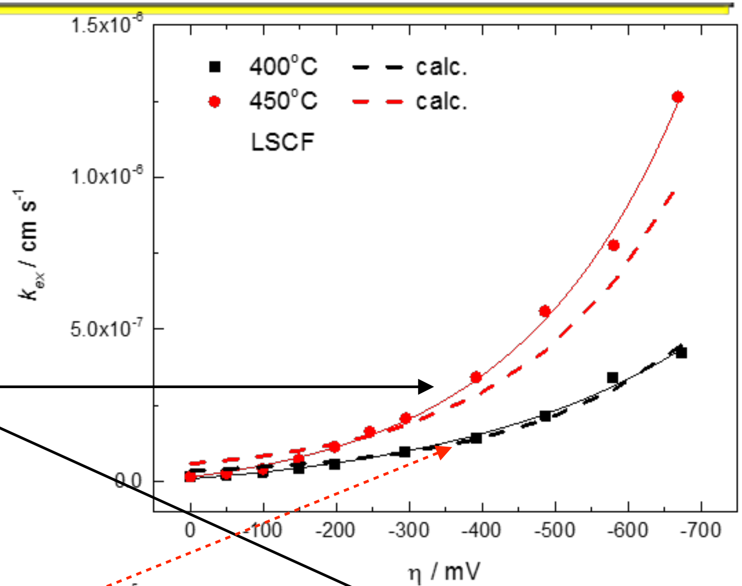
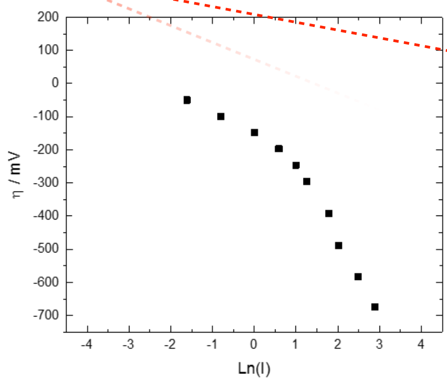
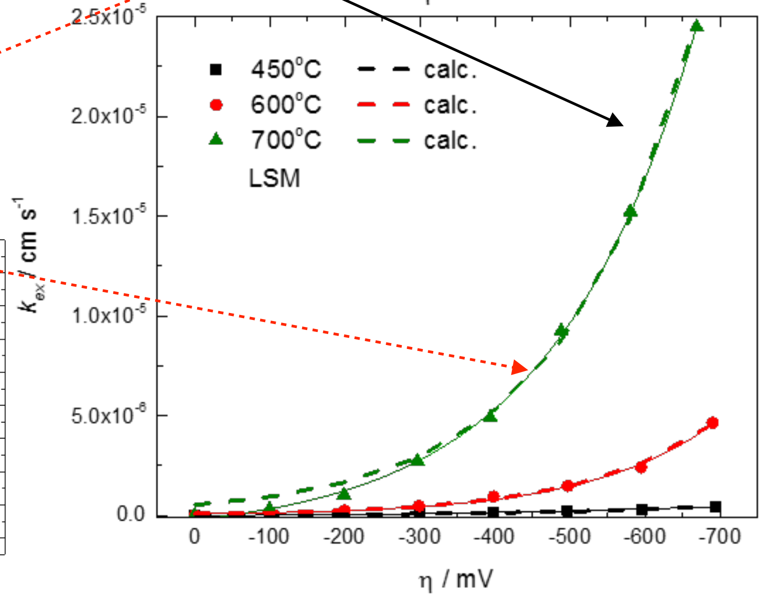



- Potentially first ever unifying theory for $k_{ex}$ between isotope exchange (IIE, IEDP) and electroanalytical (e.g., ECR) techniques
  - dashed lines from equation using open circuit $k_{ex}$ and cell Tafel results

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



# Summary/Conclusions

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

- For the first time determined the oxygen surface exchange coefficient ($k_{ex}$) *in-operando* as a function of applied electric potential with *in-situ* $^{18}O$-isotope exchange

- Developed direct relationship between electrochemical (I-V) performance and $k_{ex}$ as well as unifying theory to relate isotope exchange obtained $k_{ex}$ to other electroanalytic (e.g., ECR) techniques

# Future Work

- Determine in-operando $k_{ex}$ for varying A/B site ratios in LSM and LSCF and their composites with YSZ and GDC and determine how changes under degradation

## If Phase 2 Awarded

- Develop and validate *in-operando* button cell apparatus
- Extend to effect of microstructure, macrostructure and composition on cathode performance, $O_2$ surface exchange mechanism and coefficient.
- Integrate results and identify cathode composition/ structures and operational conditions to reduce ASR and enhance durability.
- Apply the model results on literature $k_{ex}$ data, to identify cathode compositions and structures with enhanced activity and durability.

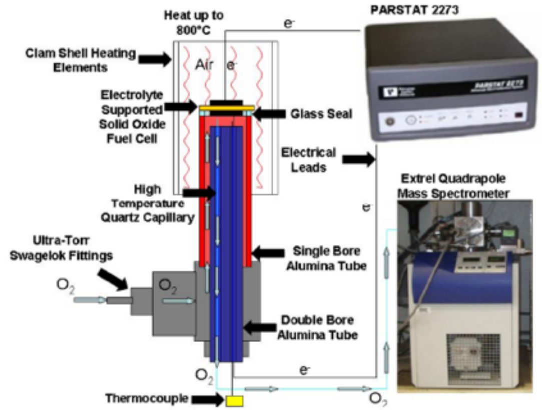



*Fig. 9. In-operando cell testing system (ICTS) consisting of custom cell, flow system, furnace, potentiostat and mass*

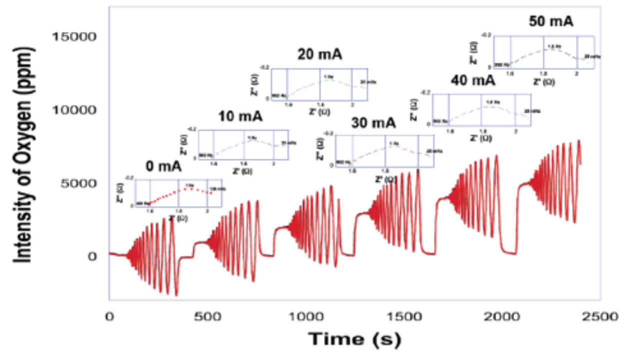



***Fig. 10.*** *Example of ICTS results, measured $^{18}O_2$ concentration as a function of transient cell voltage during galvanostatic impedance measurements, demonstrating ability to measure rapid gas concentration changes with EIS voltage sweep at static applied current steps.*

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