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

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Background - Limitation of ORR from EIS

Many mechanisms are consistent with $k \sim P_{O_2}^{1/2}$

Oxygen exchange limited by vacancy exchange

\[ r_{ads} = k_1 \left( \frac{f_{surf}}{I_{O_2}} \right)^{1/2} - \left( \frac{f_{surf}}{I_{O_2}} \right)^{1/2} \]

\[ r_{exch} = k_1 \left( P_{O_2} \right)^{1/2} \]

Oxygen exchange limited by dissociative adsorption

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

\[ r_{exch} = k_1 \left( P_{O_2} \right)^{1/2} \]

Same!

Need to combine multiple techniques to determine mechanism

Stuart Adler, University of Washington
Structure/Morphology
- Random crystallographic faces
- 3-phase-solid-gas interfaces

ORR Kinetics
- Surface controlled

Kinetic Parameters
- $k_{\text{ex}}, \, k_{\text{in}}, \, D_{\text{surf}}, \, D_{b/gb}$
- $k_{\text{ex}}, \, k_{\text{in}}, \, D_{b}, \, (D_{\text{surf}})$

Polarization
- Bias current
- OCP

In-Situ $O_2$ Exchange Analysis
- Limited
- Excellent

SIMS Depth Profile
- Random (bulk) to ordered (thin film) crystallographic faces
- 2-phase-solid-gas interface
- Bulk samples diffusion controlled
- Thin film samples surface controlled but strained
- $D_{b/gb} (k_{\text{in}})$
- $k_{\text{in}}, \, D_{b}, \, (D_{\text{surf}})$

Conductivity Relaxation
- OCP
- Small current perturbation
- Limited

Heterostructure
- Single crystal face
- 3-phase-solid-gas interface
- Surface controlled but strained and only for specific crystallographic orientation
- $k_{\text{in}}, \, D_{\text{surf}}, \, D_{b/gb}$
- OCP & bias current
- 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

La$_{0.8}$Sr$_{0.2}$MnO$_3$±d

La$_{0.8}$Sr$_{0.2}$Co$_{0.6}$Fe$_{0.4}$O$_3$-d

Oxygen isotope exchange - TPD in 3000 ppm $^{18}$O$_2$

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

Incorporation

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

Dissociative Adsorption

Total Oxygen

Oxygen Concentration (ppm)

Temperature (°C)
**ORR Reaction Mechanisms in Presence of H$_2$O and CO$_2$**

*In situ* Isotope Exchange (IIE)

Contaminant: Mn, (Co, Fe), La, Sr

Tracer: $^{18}$O$_{lat}$

**Contaminant**
- C$^{16}$O$^{16}$O
- H$_2^{16}$O

**Tracer**
- $^{18}$O$^{18}$O

**ORR Products**
- $^{16}$O$^{16}$O
- $^{16}$O$^{18}$O
- $^{18}$O$^{18}$O

**By Products**
- H$_2^{18}$O
- H$_2^{16}$O
- C$^{16}$O$^{16}$O
- C$^{16}$O$^{18}$O
- C$^{18}$O$^{18}$O

Dissociation
- Provides information about dissociated $^{18}$O$_{(s)}$

Incorporation
- Provide information about surface reaction with contaminants

**Chemical Reactions**

1. $S + 1/2O_2$ $\xleftrightarrow{\kappa_0}$ $O_{ads}$

2. $O_{ads} + V_o$ $\xleftrightarrow{\kappa_2}$ $s + O_o^x$

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ISTPX of LSCF in 25000ppm O₂ with 6000ppm D₂O

**O₂ exchange with lattice \(^{18}\)O**

![Graph showing O₂ exchange with lattice \(^{18}\)O]

**D₂O exchange with lattice \(^{18}\)O**

![Graph showing D₂O exchange with lattice \(^{18}\)O]

Mass of:

- \(^{18}\)O = 18
- H₂\(^{16}\)O = 18
- D₂\(^{16}\)O = 20
- D₂\(^{18}\)O = 22
ISTPX of LSCF in 25000ppm O$_2$ with 6000ppm D$_2$O

D$_2$O and O$_2$ exchange with lattice $^{18}$O

![Diagram showing exchange between D$_2$O and lattice $^{18}$O with various temperatures and concentrations.](image)

(Co, Fe) AND

Lattice $^{18}$O

La, Sr
ISTPX of LSCF in 25000ppm O₂ with 6000ppm D₂O

D₂O and O₂ exchange with lattice ¹⁸O

At lower temperature more of the lattice ¹⁸O exchanges with water than O₂

Accumulated Isotopic Fraction exchanged from ¹⁸O LSCF

(18O in O₂, 18O in D₂O, 18O in M36, 18O in M34, 16O16O, D₂16O, (Co, Fe), Lattice18O, La, Sr)
Temperature and PO$_2$ Dependence of LSCF in D$_2$O

Repeating exchange experiments as function of P$_{O_2}$, P$_{H_2O}$ and temperature

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

- $^{18}$O in O$_2$
- $^{18}$O in D$_2$O
- $^{18}$O in M36
- $^{18}$O in M34

(Co, Fe) $^{16}$O$^{16}$O

AND

Lattice$^{18}$O

La, Sr $D_2^{16}$O

(Underlying lattice structure with atoms labeled)

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

Exchange as function of $PO_2$, $P_{H2O}$ and temperature

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

- We have mapped out $H_2O$ (and $CO_2$) impacts on ORR as function of $PO_2$, 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
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\textsubscript{2}O

The presence of 3% H\textsubscript{2}O effects the low frequency arc at 450ºC but not at 750ºC consistent with the results obtained from ISTPX.
The presence of 5% CO₂ effects the low frequency arc at 450°C and at 750°C consistent with the results obtained from ISTPX.
H$_2$O Impact on LSM/YSZ Microstructural Change

Microstructural degradation under $P_{H_2O}$ identified by isotope exchange conditions

- H$_2$O under cathodic polarization decreases LSM phase connectivity (ohmic impedance)
- H$_2$O under cathodic polarization decreases fraction of connected “active” TPBs (non-ohmic impedance)
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$_2$O (and CO$_2$) actively participate in ORR for both LSCF and LSM
- Identified temperature and gas composition regions where H$_2$O dominates O$_2$ surface exchange mechanism and where they are less important
- Identified composite cathode effect on O$_2$ surface exchange with H$_2$O
- Ambient humidity has a direct impact on LSM/YSZ cathode microstructural and compositional changes that degrades ohmic and non-ohmic ASR

5. “Enhancement of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ Activity by Ion Implantation for Low-Temperature SOFC Cathodes,” J. of Electrochem. Soci., 162, 9, F965-970, (2015).
16. “Reaction Kinetics and CO$_2$-O$_2$ Co-Exchange on Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$”, in preparation.
17. “Chromium Poisoning Effects on Surface Exchange Kinetics of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$”, 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**

\[ \text{O}_2 + \text{V}_{O^x} = 2\text{O}_{O^x} \]

*In-Operando*

\[ \text{O}_2 + 2\text{V}_{O^{xx}} + 4e' = 2\text{O}_{O^x} \]

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**Graphs**

[Graph showing concentration of various isotopes over time.]
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

- $k_{ex}$ 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 ($R^*_{ex}$):
  \[ \frac{M(t)}{M_\infty} = 1 - \exp(-R^*_{ex} t) \]

- 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 $\eta$:
  \[ I = I_0 \exp(C\eta); \quad C = \frac{\alpha ZF}{RT} \]
  \[ k_{ex} = \frac{D}{6} \left( R^*_{ex} - \frac{I_0 \exp(C\eta)}{2FN} \right) \]

- 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
    \[
    k_{ex} = \frac{D}{6} \left( R^*_e - \frac{I_0 \exp(C\eta)}{2FN} \right)
    \]
  - demonstrated for both LSCF and LSM
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

  \[ I = I_0 \exp(C\eta); \quad C = \frac{\alpha ZF}{RT} \]
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* \(^{18}\text{O}\)-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.