Towards a Fundamental Understanding of Cathode Degradation Mechanisms

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Fundamental Mechanisms of SOFC Cathode Reactions

Systematic Approach to Deconvoluting Cathode Polarization:

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

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

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

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

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

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

- Microstructure ($L_{\text{PN}}$, 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 O₂ gas mixture to determine reaction rates
- Isotope exchange (¹⁶O vs. ¹⁸O)
  - Switch gas to separate solid vs gas species contribution to mechanism

ORR Reaction Mechanisms in Presence of H₂O and CO₂

\[
S + \frac{1}{2} O₂ \leftrightarrow Q_{ads}
\]

\[
Q_{ads} + V_α \leftrightarrow s + O^{x}_α
\]
Effect of H$_2$O on LSM Temp. Programed $^{18}$O-Exchange

TPX of LSM without H$_2$O

At higher temperature exchange with LSM surface-O dominates

At lower temperature surface-H$_2$O exchange dominates

TPX of LSM in ~0.3% H$_2$O

Difference of TPX with and without H$_2$O

Temperature region where H$_2$O exchange dominates ORR

H$_2$O exchange with $^{18}$O$_2$

Effect of H$_2$O on Isothermal Isotope Exchange of LSM

800°C

800°C in H$_2$O

Without H$_2$O

0.3% H$_2$O

• LSM is limited to surface or near surface exchange
• LSM surface comes to $^{18}$O/$^{16}$O equilibria with H$_2$O
• Resulting in more scrambled $^{18}$O$^{16}$O (vs. $^{18}$O$_2$) as H$_2$O removes surface $^{18}$O

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Extracting the Surface Exchange Coefficient from IIE

Switch time (argon tracer)

\[
M(t) = 1 - \sum \frac{6L^t \exp \left(-\beta_i D(t-t_i)\right)}{\beta_i \left(\beta_i + L - L\right)}
\]

\[
M(t) = 2 \times \text{Total Oxygen} - \left(2 \times \text{O}_2^{36} + 34\text{O}_2\right)
\]

Use equation below to extract the fraction of $^{18}\text{O}$ that exchanges with lattice $^{16}\text{O}$.

Can be fit with Crank’s solution for sphere.

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.
Effect of H₂O on LSM/YSZ Cathode Impedance (EIS)

LSM/YSZ Composite in Air + 3% H₂O at 800°C, no bias

Cathode:
50% by weight (La₀·₉₀Sr₀·₁₀MnO₃)
50% by weight (Y₂O₃·₀·₆₅(ZrO₂·₀·₃₅)

Electrolyte:
(Y₂O₃·₀·₆₅(ZrO₂·₀·₃₅

Air (Synthetic)

Ref. 2
C.E.

Ref. 1
W.E.

Air (Synthetic) + Contaminant

Baseline/aging in H₂O LSM-YSZ/YSZ/LSM-YSZ Cell Testing

Resistance Trends (Relative)

Aging in H₂O

Baseline aging in air

Short time unique H₂O effect

Long term includes aging in air effects
Comparison of LSM Cell Testing and IIE Results

- Cell and powder aged in 3% H₂O at 800°C
- Increase in non-ohmic electrode impedance from 0 to 14 hrs corresponds to decrease in ¹⁸O-exchange
- Subsequent decrease in electrode impedance from 14 to 48 hrs corresponds to increase in ¹⁸O-exchange.

Quantify Microstructural Effects - FIB/SEM

Baseline cell reconstruction/network analysis

Bulk YSZ electrolyte

LSM in cathode

YSZ in cathode

Connected pore network
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% H₂O

<table>
<thead>
<tr>
<th>Relative to baseline</th>
<th>Baseline</th>
<th>Aged-dry</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active TPB [norm]</td>
<td>100%</td>
<td>32.5%</td>
<td>27.5%</td>
</tr>
<tr>
<td>Total ρTPB [µm/µm²]</td>
<td>19.2</td>
<td>9.69</td>
<td>8.57</td>
</tr>
</tbody>
</table>

- Observe decrease in active $L_{TPB}$ upon aging
- Effect is worse with exposure to 3% H₂O

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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% H₂O

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
**STEM-EDS Maps of LSM-YSZ Aged in Air + H₂O**

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% H₂O

- STEM-EDS maps Aged-H₂O 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

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**Isotope Saturated Temperature Programmed Exchange (ISTPX)**

- **powder surface with normal ^{16}O (●)**
  - Mn (Co, Fe)
  - Lattice^{16}O
  - La, Sr

- **Saturated powder surface with labelled ^{18}O (●)**
  - Mn (Co, Fe)
  - Lattice^{18}O
  - La, Sr

IIE - Probes the impact of contaminants on gas phase ^{18}O₂ exchange with cathode surface

- \(^{18}O^{18}O\)
- \(^{16}O^{18}O\)
- \(^{18}O^{16}O\)
- \(^{16}O^{16}O\)

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

- \(^{16}O^{16}O\)
- \(^{15}O^{16}O\)
- \(^{16}O^{16}O\)

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 $^{18}O$

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

CO$_2$ exchanges preferentially with lattice at lower temperature:
  - initially exchanging only single "O" (atomic)
  - then both "O" (molecular)
  - then at same rate as $O_2$

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ISTPX of LSCF with 2500 ppm CO₂ at ambient PO₂

Competitive exchange of CO₂ vs O₂ with lattice ¹⁸O at ambient PO₂

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

- O₂ exchange with lattice ¹⁸O
  - Temperature (°C)
  - Concentration (ppm)

- CO₂ exchange with lattice ¹⁸O
  - Temperature (°C)
  - Concentration (ppm)

CO₂ exchanges preferentially even at ambient PO₂

ISTPX of LSCF and LSM with 2500 ppm CO₂ at ambient PO₂

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

- LSCF
  - Temperature (°C)
  - Concentration (ppm)

- LSM
  - Temperature (°C)
  - Concentration (ppm)

LSM also has significant CO₂ exchange at low PO₂.
However, for both as PO₂ increases relative CO₂ exchange decreases.
ISTPX of LSCF in 25000ppm O₂ with 6000ppm D₂O

O₂ exchange with lattice ¹⁸O

Mass of:
- ¹⁸O = 18
- H₂¹⁶O = 18
- D₂¹⁶O = 20
- D₂¹⁸O = 22

D₂O exchange with lattice ¹⁸O

(Left) Accumulated Isotopic Fraction exchanged from ¹⁸O LSCF

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

(Co, Fe) Lattice¹⁸O
La, Sr

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Temperature and PO₂ Dependence of LSCF in D₂O

Repeating exchange experiments as function of PO₂, P H₂O and temperature

Accumulated Isotopic Fraction exchanged from ¹⁶O LSCF

Temperature (°C)

- ¹⁸O in O₂
- ¹⁸O in D₂O
- ¹⁸O in M36
- ¹⁷O in M34

Lattice ¹⁸O
La, Sr

(Co, Fe)

AND

D₂ ¹⁶O

Two Exchange Peaks:
- As PO₂ increases, 300°C peak decreases
- 450°C peak still present at high PO₂

- We can now map out H₂O and CO₂ impacts on ORR as function of PO₂, temperature, and contaminant concentration
Comparison of LSCF and LSM Temp-PO₂ Dependence in D₂O

- LSCF more active toward D₂O exchange than LSM
- D₂O exchanges with LSM only at high temp in presence of O₂

Temperature and PO₂ Dependence of LSCF in CO₂

- Singly Exchanged C¹⁶O¹⁸O
- Doubly Exchanged C¹⁸O¹⁸O
Comparison of LSCF and LSM Temp-PO₂ Dependence in CO₂

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
Comparison of LSCF and Composite LSCF-GDC in D₂O

25000 ppm O₂ and 6000 ppm D₂O

LSCF subtracted from LSCF-GDC

Difference demonstrates greater D₂O exchange with composite

Comparison of LSCF and Composite LSCF-GDC in CO₂

25000 ppm O₂ and 2500 ppm CO₂

LSCF subtracted from LSCF-GDC
Comparison of LSM and Composite LSM-YSZ in D$_2$O

- LSM-YSZ composite demonstrates much greater exchange than LSM at much lower temp for D$_2$O
- Composite effect for LSM-YSZ much greater than for LSCF-GDC

Comparison of LSM and Composite LSM-YSZ in 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% H₂O and changes in O₂ 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.

- CO₂ and H₂O actively participate in ORR for both LSCF and LSM
  - Most likely influences literature k_{ex} results.

- Identified temperature and gas composition regions where CO₂ and H₂O dominate O₂ 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 O₂ surface exchange with CO₂ and H₂O.
  - Particularly dramatic for LSM/YSZ.