Mechanistic Enhancement of SOFC Cathode Durability

US Department of Energy, National Energy Technology Laboratory, Contract No. DEFE0009084

Eric D. Wachsman, Yi-Lin Huang, Christopher Pellegrinelli, Joshua Tallion, & Lourdes Salamanca-Riba

University of Maryland Energy Research Center

www.energy.umd.edu

University of Maryland, College Park, USA
Systematic Approach to Developing Low Polarization Cathodes:

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

- \( R_{\text{Gas Diffusion}} \) 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 (LTPB, surface area/volume)
  - Kinetics (Oxygen reduction rate)

Based on Cathode Workshop January 2006, and presented at SECA Workshop, September 2006
Pioneered use of FIB/SEM to quantify cathode microstructures and developed phase contrast for composite cathodes.

Siemens Cathode Sample
Microstructure - Performance Relationship

First direct quantified relationship between cathode microstructure and performance

For the LSM on YSZ cathode reaction:

\[
\frac{1}{2} O_{2,ads} + 2e' + V_{O^{**}}^o \rightarrow O_{O}^x
\]

The current is:

\[
I_0 = k_f [e']^m [O_{2,ads}]^n [V_{O^{**}}^o]^p
\]

The corresponding charge transfer polarization \( (R_{ct}) \) dependence on triple phase boundary length \( (L_{TPB}) \) is:

\[
R_{ct} \sim k_f^{-1} L_{TPB}^{-3.5}
\]
• 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
Oxygen isotope exchange - TPD in 3000 ppm $^{18}O_2$

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

Dissociative Adsorption

$O_{ads} + V_0 \leftrightarrow O_o + S$

Oxygen Concentration (ppm)

Temperature (°C)

$La_{0.8}Sr_{0.2}MnO_3-d$

$La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_3-d$

Fundamental Cathode Kinetic Mechanisms
Oxygen reduction reaction:
1. dissociative absorption
2. incorporation

\[
S + 1 / 2 \text{O}_2 \overset{k_1}{\rightleftharpoons} O_{ads} \\
O_{ads} + V_o \overset{k_2}{\rightleftharpoons} s + O_o^x
\]
Research Plan

• Determine effects of H$_2$O, CO$_2$, and Cr vapor on ORR mechanism
  - Determine surface reaction mechanisms and rates with $^{18}$O- exchange in H$_2$O, CO$_2$, and Cr vapor
  - Determine operating conditions (Temp. & Conc.) where H$_2$O, CO$_2$, and Cr vapor have both major and minor effects on LSM and LSCF cathode performance

• Operate in conditions (Temp. & Conc.) where H$_2$O, CO$_2$, and Cr vapor have major effects on LSM and LSCF cathode performance:
  - Quantify microstructural changes with FIB/SEM
  - Relate microstructural and ORR degradation to cell polarization
  - Test using integrated in situ electrocatalysis

• Develop predictive mechanistic models for cathode degradation and determine operating conditions for maximum durability
$S + 1/2O_2 \xleftrightarrow{k_1} O_{ads}$

$O_{ads} + V_o \xleftrightarrow{k_{-2}} s + O_o^x$

**Oxygen reduction reaction:**
1. dissociative absorption
2. 2. incorporation

---

1: $32\ \left(^{16}O_2\right) = f\left(^{16}O_{\text{lat}}\right) + f\left(k_{-1}^{16}O_{s}^2\right)$

2: $34\ \left(^{16,18}O_2\right) = (k_{-1}^{18}O_s) [^{16}O_s]$)

3: $36\ \left(^{18}O_2\right) = f\left(^{18}O_{2\text{unreactive}}\right) + f\left(k_{-1}^{18}O_s^2\right)$

4: $44\ \left(C^{16}O_2\right) = f\left(C^{16}O_{2\text{unreactive}}\right) + f\left(k_{-1}C^{16}O_s^2\right)$

5: $46\ \left(^{16,18}O_2\right) = (k_{-1}C) [^{18}O_s] [^{16}O_s]$)

6: $48\ \left(^{18}O_2\right) = f\left(k_{-1}C^{18}O_s^2\right)$

7: $\left(^{18}O_{\text{lat}}\right) = f\left(k_{2}^{18}O_s\right)$

---

$\sim 282\ \text{nm}$

---

**18O-Exchange in CO2 to Determine Effect on ORR Mechanism**
Effect of CO\textsubscript{2} on LSCF Temp. Programed \textsuperscript{18}O-Exchange

Presence of CO\textsubscript{2}:

- Shifts O\textsubscript{2} peak temperatures
- Reduces O\textsubscript{2} exchange with LSCF lattice
- Indicating that CO\textsubscript{2} participates in surface exchange
Effect of CO$_2$ on Isothermal Isotope Exchange of LSCF

Oxygen exchange without CO$_2$ at 800°C

Oxygen exchange in 2,500ppm CO$_2$ at 800°C
Effect of CO$_2$ on Isothermal Isotope Exchange of LSCF

Presence of CO$_2$:

- Modifies O$_2$ exchange with LSCF surface
- Surface-O is exchanging with CO$_2$
- All of the CO$_2$ dissociates on LSCF surface
Effect of CO$_2$ on IIE of LSCF at Multiple Temperatures

Closed symbol: no CO$_2$
Open symbol: in 2,500ppm CO$_2$

- Decrease in 36 signal indicates CO$_2$ participation
- The O$_2$ in CO$_2$ exchange profile (left, open symbol) has a similar shape to the CO$_2$ exchange profile (right)
- CO$_2$ exchange has lower temperature dependance

- CO$_2$ exchange at 800°C
- CO$_2$ exchange at 700°C
- CO$_2$ exchange at 600°C
CO₂ Concentration Dependence of IIE of LSCF

- As CO₂ concentration increases there are changes in O₂ species concentrations (32, 34, 36)
  - ¹⁸O⁻¹⁸O : final concentration decreases
  - ¹⁶O⁻¹⁸O : final concentration increases

Oxygen exchange in 2500ppm CO₂ at 800°C

Oxygen exchange in 1250ppm CO₂ at 800°C

Oxygen exchange in 5000ppm CO₂ at 800°C
Extracting the Surface Exchange Coefficient from IIE

Switch time (argon tracer)

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

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

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

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

IIE of LSCF  800°C

\(^{18}$O exchange with $^{16}$O lattice

18O Conversion

0.0  0.2  0.4  0.6  0.8  1.0

Time (minutes)

0  5  10  15  20  25  30  35

0  200  400  600  800  1000

Time (Seconds)
Effect of LSCF Surface Exchange on CO₂ Concentration

Fraction of $^{18}$O₂ exchanged with LSCF surface $^{16}$O as function of C$^{16}$O₂ concentration

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>CO₂ Concentration (ppm)</th>
<th>k (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0</td>
<td>9.66E-09</td>
</tr>
<tr>
<td>600</td>
<td>2500</td>
<td>1.38E-08</td>
</tr>
<tr>
<td>700</td>
<td>0</td>
<td>1.06E-09</td>
</tr>
<tr>
<td>700</td>
<td>2500</td>
<td>1.40E-08</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>1.48E-08</td>
</tr>
<tr>
<td>800</td>
<td>1250</td>
<td>1.50E-08</td>
</tr>
<tr>
<td>800</td>
<td>2500</td>
<td>1.54E-08</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>1.64E-08</td>
</tr>
</tbody>
</table>
Effect of LSCF Surface Exchange on CO₂ Concentration

- Oxygen exchange coefficient increases with CO₂ concentration
- Activation energy decreases with increasing CO₂ concentration

CO₂ dependence of surface exchange coefficient

Slope: 3.3E-13

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>CO₂ Concentration (ppm)</th>
<th>k (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0</td>
<td>9.96E-09</td>
</tr>
<tr>
<td>600</td>
<td>2500</td>
<td>1.38E-08</td>
</tr>
<tr>
<td>700</td>
<td>0</td>
<td>1.06E-09</td>
</tr>
<tr>
<td>700</td>
<td>2500</td>
<td>1.40E-08</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>1.48E-08</td>
</tr>
<tr>
<td>800</td>
<td>1250</td>
<td>1.50E-08</td>
</tr>
<tr>
<td>800</td>
<td>2500</td>
<td>1.54E-08</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>1.64E-08</td>
</tr>
</tbody>
</table>

2500ppm CO₂ $E_A=4.11\text{kJ/mol}$

No CO₂ $E_A=15\text{kJ/mol}$
CO$_2$ adsorption peaks at 350ºC
- Gains 0.4% weight during heating
- Maintains 0.1% weight gain at 800ºC possibly due to carbonate formation

➡ Starting LSM $^{18}$O$_2$ in CO$_2$ experiments

- CO$_2$ adsorption peaks at 400ºC
- Gains 0.5% weight during heating
- Weight loss at 800ºC due to decrease in oxygen stoichiometry

TGA of LSCF and LSM in 30% CO$_2$
18O-Exchange in H2O to Determine Effect on ORR Mechanism

0.5 SCCM 100% 18O2 balanced in 19.5 SCCM He + 0.3% H2O

1: 32 (16O2)=f(16O_{lat})+f(k_{-1}[16O_s]^2)

2: 34 (16,18O2 )=(k_{-1} [18O_s] [16O_s])

3:36 (18O2)=f(18O_{2\text{unreactive}})+f(k_{-1}[18O_s]^2)

4:18( H_2^{16}O)=f(H_2^{16}O_{unreactive})+f(k_{-1}H_2 [16O_s])

5:20( H_2^{18}O)=f(k_{-1}H_2 [18O_s])

6:[18O_{lat}]=f(k_2 [18O_s])
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

$^{18}$O-Exchange

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

Difference of TPX with and without H$_2$O

Temperature region where H$_2$O exchange dominates ORR
Effect of H$_2$O on Isothermal Isotope Exchange of LSM

Fraction of $^{18}$O exchanged with $^{16}$O lattice

$K = 1.6 \times 10^{-8}$ cm/s

LSM surface comes to $^{18}$O/$^{16}$O equilibria with H$_2$O
LSM is limited to surface or near surface exchange

Much smaller exchange at lower temperature

$^{16}\text{O}$ in $^{16}\text{O}^{18}\text{O}$ from H$_2$O or LSM surface oxygen

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

- Without H$_2$O
- 0.3% H$_2$O
Effect of H$_2$O on IIE of LSM Powder Aged in 3% H$_2$O

Aging in 3% H$_2$O decreases $^{18}$O-exchange
Comparison with Symmetric Cell Testing

Direct comparison of cathodes with and without exposure to contamination with same thermal history.
Effect of H$_2$O on LSM/YSZ Cathode Impedance (EIS)

LSM/YSZ Composite in Air + 3% H$_2$O at 800°C, no bias

Cathode:
50% by weight (La$_{0.80}$Sr$_{0.20}$)$_{0.95}$MnO$_{3-x}$
50% by weight (Y$_2$O$_3$)$_{0.08}$(ZrO$_2$)$_{0.92}$

Electrolyte:
(Y$_2$O$_3$)$_{0.08}$(ZrO$_2$)$_{0.92}$

Air (Synthetic) + Contaminant

- Z' (Ω·cm$^2$)
- Z'' (Ω·cm$^2$)

1 Hz Trend Line
100 Hz Trend Line

Ref. 1
W.E.

Ref. 2
C.E.
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 $^{18}$O-exchange
- Subsequent decrease in electrode impedance from 14 to 48 hrs corresponds to increase in $^{18}$O-exchange.
- Microstructural changes could also have occurred and we are investigating with FIB/SEM
Effect of H$_2$O on LSM/YSZ Cathode

LSM/YSZ Composite in Air + 3% H$_2$O at 800°C, no bias

Visible discoloration of cathode exposed to H$_2$O after 380 hours indicating degradation
3D reconstruction of degraded electrode will be compared with electrode on other side, same thermal history but no H$_2$O exposure.
Conclusions

- CO$_2$ actively participates in O$_2$ surface exchange with LSCF
  - CO$_2$ increases surface exchange coefficient and decreases activation energy

- H$_2$O actively participates in O$_2$ surface exchange with LSM
  - Between 350°C and 700°C H$_2$O exchange with dissociated surface-O dominates
  - Above 700°C O$_2$ exchange with LSM surface dominates

- Demonstrated direct correlation between LSM/YSZ cathode impedance changes during aging in 3% H$_2$O and changes in O$_2$ surface exchange of LSM
Integrated *In situ* Electrocatalysis

Heat up to 800°C

- Clam Shell Heating Elements
- Electrolyte Supported Solid Oxide Fuel Cell
- High Temperature Quartz Capillary
- Ultra-Torr Swagelok Fittings
- Single Bore Alumina Tube
- Double Bore Alumina Tube
- Glass Seal
- Electrical Leads
- Extrel Quadrupole Mass Spectrometer

**PARSTAT 2273**
Acknowledgement

US Department of Energy - SECA

Isotope exchange and impedance:
  Yi-Lin Huang & Christopher Pellegrinelli

FIB/SEM characterization:
  Joshua Tallion & Prof. Lourdes Salamanca-Riba