Unraveling Oxygen Reduction Kinetics on SOFC Cathodes Using Patterned Electrodes and X-Ray Techniques

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Phase I accomplishments (mainly focused on LSM):

- Determined that “surface path” is ~4 fold less resistive than “bulk path”.
- Modified the SSM model developed by Mitterdorfer et al. to account for surface potential ($\Delta \chi$) and implemented in Matlab.
- Estimated temperature and pO$_2$ dependence of: $D_s$, $k_{ad}$, $k_{des}$, $k_{f}^{eq}$, $k_{b}^{eq}$, and surface coverage ($\theta$).
- At temperatures below 700 °C was co-limited by diffusion and adsorption. At high temperatures charge transfer contributes significantly to rate.
- Low scatter between samples suggests that samples were successfully fabricated, and model correctly accounts for the geometry changes.
- Used TXRF to measure surface compositions of LSM thin film cathodes.

Work covered in this year’s SECA workshop

- Measurement of Electrode Kinetics on LSCF electrodes using micropatternning

- Surface spectroscopy of LSCF thin films using HAXPES
Necessary first steps:

- Gas Phase Diffusion
- Surface Adsorption
- Dissociation
- Electronation and Incorporation to cathode
- Bulk Diffusion to Electrolyte
- Incorporation into Electrolyte
- Surface Diffusion to Triple Phase Boundary (TPB)
- Electronation and Incorporation to electrolyte at TPB

The “Bulk Path”
La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF-6428)

The “Surface Path”
(La$_{0.87}$Ca$_{0.13}$)$_{0.95}$MnO$_{3\pm\delta}$, (LCM)
LSCF-6428: EIS results $l_{TPB} = 50 \text{ cm}^{-1}$, 800$^\circ$C

$R_M = 23.2 \, \Omega$, $\omega_M = 3.5 \, \text{Hz}$
Primary Evidence of Mixed Conduction LSCF-6428: $1/R_c$ vs. TPB length

Bulk path is more resistive at 800 °C, but less resistive below that temperature.

<table>
<thead>
<tr>
<th>T°C</th>
<th>$R_M$</th>
<th>$R_M^{TPB}$</th>
<th>$R_M^{MIEC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>15</td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>750</td>
<td>66</td>
<td>195</td>
<td>79</td>
</tr>
<tr>
<td>700</td>
<td>189</td>
<td>779</td>
<td>199</td>
</tr>
<tr>
<td>650</td>
<td>488</td>
<td>1113</td>
<td>69</td>
</tr>
<tr>
<td>600</td>
<td>2321</td>
<td>8654</td>
<td>2537</td>
</tr>
</tbody>
</table>

$1/R_M = l_{TPBp}/\rho_M + l_{TPBp}/\rho_M + A_A/R_M^{MIEC}$

$1/R_{TPBp}(\text{cm}^{-1})$
LSCF vs. LCM – far weaker TPB dependence
Goals:

1. Develop model to account for:
   - surface transport
   - bulk transport
   - surface exchange

2. Combine with experimental data to identify influence of each on overall rate.
Use 2-D Model: Geometry
Model Assumptions

- LSCF-6428 has high electron mobility: uniform electron electrochemical potential.

- Overpotential at interface given by Nernst Equation:

  \[ 4F\eta = RT \ln f_{O_2}^{\text{solid}}|_{y=0} - RT \ln p_{O_2} \]
  
  - Where \( f(T,x_v) \) is the fugacity in the solid and \( x_v = \delta/3 \)

- No gas phase limitation

- Oxygen exchange is driven by bulk vacancy concentration changes away from equilibrium with gas phase, but ion exchange across cathode interface considered equilibrated

- Electrolyte resistance and lead wire inductance is subtracted directly from experimental data.
Parameters in model:

\[ R_D = \frac{RT}{8F^2} \frac{(W + H)}{c_0 x_v^o D_v} \quad t_D = \frac{W^2}{A^o D_v} \]

\[ \sigma_M = \omega_M t_D \]

\[ \kappa = \frac{4R_o W}{c_0 x_v^o D_v} \equiv \frac{\text{surface oxygen exchange}}{\text{bulk oxygen diffusion}} \]

\[ \nu = \frac{\Gamma_o \theta_o^o D_{O_s}}{W c_0 x_v^o D_v} \equiv \frac{\text{surface oxygen diffusion}}{\text{bulk oxygen diffusion}} \]

\[ \phi = \frac{A^o}{A_{O_s}^o} \frac{\Gamma_o \theta_o^o}{W c_0 x_v^o} \equiv \frac{\text{surface oxygen storage}}{\text{bulk oxygen storage}} \]

Both functions of \( D_v \): (intrinsic vacancy diffusivity)

Set equal to zero
Numerical Model:

• Solved using Gauss-Siedel Method, with a tolerance of $10^{-5}$
• Implemented in Matlab, usually converges in about 30 s (per $\sigma$), with mesh size of 200 (width) by 100 (height).
• Boundary conditions: flux/reaction boundary on top and right wall
• Fixed (potential) at cathode/electrolyte interface
• No flux at symmetrical (left wall) boundary.
Model Predictions – Oxygen Vacancy perturbation:

\[ I_{TPB} = 1200 \text{ cm}^{-1} \]

**High Freq. no surf. Diffusion**

\[ \sigma = 10^5, \kappa = 0.1, \nu = 0 \]

**Low Freq. no surf. Diffusion**

\[ \sigma = 100, \kappa = 0.1, \nu = 0 \]

- At high frequency, disturbance limited to interface.
- At low frequency extends through entire cathode.
- With surface diffusion, extends up wall faster
Generate Nyquist Plots from Model:

$$R_M = -R_D \text{ Im}(H(\sigma_M))$$

$$\sigma_M = \omega_M t_D$$

- $\sigma = 0.035, 0.94, 29 \text{ k}$
- $\kappa = 0.1, \nu = 0$
- $\kappa = 317, \nu = 0$
- $\kappa = 0.4, \nu = 1$

**NOTE:**

It is *NOT* practical to fit the *entire* impedance vs. the model because it would take a very long time, instead choose a characteristic resistance, $R_M$, and frequency, $\omega_M$. 
EIS results – $I_{TPB} = 50 \text{ cm}^{-1}$

$T = 800 \, ^\circ\text{C}$

$R_M (\Omega \cdot \text{cm}^2)$, $\omega_M$ (Hz)

$pO_2$ (atm)
Fitting Routine:

Have two known \((R_M \text{ and } \omega_M)\) and 3 fitting parameters \((D_V, \kappa, \text{ and } \nu)\):

\(D_V\) is relatively constant in experimental pO\(_2\) range, so fix it, and fit the other two.
Fitting Results ($I_{TPB} = 430 \, \text{cm}^{-1}$)

Surface Diffusion Contribution increases with $pO_2$ and $T$ –

Surface Exchange Contribution increases with $pO_2$ and $T$ – $R_0$ is roughly constant with $pO_2$ – activation energy is $115 \, \text{kJ/mol}$

dominates rate at all $pO_2$
Conclusions from LSCF-6428:

- Numerical model based on work by Adler’s group but modified to account for entire surface activation, and different geometry.
- First time applied to well-defined patterns: increases confidence in fitting results.
- Surface diffusion is equally (to bulk diffusion) transport path at highest temperatures and pO$_2$: evidence from TPB dependence of 1/R$_M$ and from fitting model results ($\nu > 1$).
- Surface exchange high at all measured T and pO$_2$.

- L.Miara, S.Basu, U.Pal, and S.Gopalan, “2D Numerical Model for Identification of Oxygen Reduction Reaction Mechanisms in Patterned Cathodes of La0.6Sr0.4Co0.2Fe0.8O3-δ”, J.Electrochem.Soc. (In Print)
X-ray spectroscopy techniques
Energy Resolving Fluorescence

- Small energy range corresponds to emission line of specific atomic species
- Window energy range for fluorescence signal.

Diagram showing the interaction of X-rays with a thin film sample, resulting in a fluorescence signal detected by a detector.
Total Reflection X-ray Fluorescence (TXRF)

- Total Reflection X-ray Fluorescence (TXRF) data was taken as a function of angle. Probing with an incident angle larger than the critical angle $\alpha_c$, x-rays penetrate the entire sample and bulk properties are measured.

- $\alpha_c = \lambda \sqrt{\frac{\rho r_0}{\pi}}$

- At low angle the beam is totally reflected, and only the topmost nanometers of the film fluoresce.
LSM on NGO as-deposited

![Graph showing raw counts vs. incident angle for Sr, La, and Mn.]

- **Sr**
- **La**
- **Mn**

**Incident Angle (Degrees)**

**Raw Counts**

- Range: 0 to 2500000
- Scale: 0.4, 0.2, 0.0, -0.2, -0.4
\[ N(\theta) \propto I(\theta) \]

- \( N_{Sr} = \alpha I_{Sr} \), \( N_{La} = \beta I_{La} \), \( N_{Mn} = \gamma I_{Mn} \)

- Want \( \frac{N_{Sr}}{N_{Sr} + N_{La}} \), \( \frac{N_{Sr} + N_{La}}{N_{Mn}} \)

\[ R_1 = \frac{N_{Sr}}{N_{Sr} + N_{La}} = \frac{I_{Sr}}{I_{Sr} + \frac{\beta}{\alpha} I_{La}} \quad \text{Define } C_1 = \frac{\beta}{\alpha} \]

\[ C_1 = \frac{I_{Sr}(1 - R_1)}{R_1 I_{La}} \quad \text{For } \theta > \alpha_c, R_1 = 0.21 \]

Can now plot \( R_1 \) for all angles.
LSM – TXRF *in-situ* measurements

A-site to B-site for LSM. Change upon anneal. Quenched agrees with high T.
LSCF – TXRF *in-situ* measurements

Above the critical angle the bulk value is unchanging. Below the critical angle an increase in the ratio value indicates a higher strontium content. At 800°C the surface is still evolving over eight hours.
Understanding TXRF compositional changes

• We assume that the near-surface behaves in a bulk-like way that allows for a bulk defect model explanation.

• Using the Defect model to relate surface concentration changes to defect concentration.
LSM-20 Defect Chemistry Model for an Electronic Conductor

Electroneutrality:
\[ 2[V_0^{-}] + [Mn_B^+] = [Mn_B^{-}] + [Sr_A^+] + 3[V_A^{''''}] + 3[V_B^{''''}] \]

A-site balance:
\[ [La_A^{x^+}] + [Sr_A^+] + [V_A^{''''}] = 1 \]

B-site balance:
\[ [Mn_B^{-}] + [Mn_B^{x^+}] + [Mn_B] + [V_B^{''''}] = 1 \]

O-site balance:
\[ [O_0^{5-}] + [V_0^{-}] = 3 \]

Metal contents:
\[ \frac{[La_A^{x^+}]}{[Sr_A^+]} = \frac{1 - x}{x} \]
\[ \frac{[La_A^{x^+}] + [Sr_A^+]}{[Mn_B^{-}] + [Mn_B^{x^+}] + [Mn_B]} = y \]

Shottky-reaction:
\[ K_S = [V_0^{-}]^3 \cdot [V_A^{''''}] \cdot [V_B^{''''}] \]

Redox reaction:
\[ K_r = \frac{[Mn_B^{x^+}] \cdot [V_0^{-}] \cdot P_{O_2}^{1/2}}{[Mn_B] \cdot [O_0^{x^+}]} \]

Charge disproportionation:
\[ K_i = \frac{[Mn_B^{-}] \cdot [Mn_B]}{[Mn_B^{x^+}]^2} \]

Direct measurement from TXRF

Direct measurement from HAXPES

X-Ray Photoelectron Spectroscopy

$E_{\text{Binding}} = h\nu - \phi - E_{\text{Kinetic}}$

Thin film sample

Kinetic Energy [eV]

Counts [a.u.]

X-rays in

X-rays out

Ejected Core Electrons

Incoming angle $\theta$
Hard X-ray Photoelectron Spectroscopy HAXPES

• Overcomes surface contamination problems of soft x-ray spectroscopies.
• Tunable penetration depth.
• Identify Cation states as a function of probing depth.
• Apply defect model to Cation states.
LSCF Sr3p

Incident photon energy of 3000eV compared to 2140eV.
AFM Surface Evolution

As Deposited

RMS Surface Roughness 0.68nm

800°C 5 hours Quench

RMS Surface Roughness 9.4nm
Summary

• Using TXRF to do composition analysis of surfaces versus bulk

• Using HAXPES to probe electronic structure of surfaces versus bulk

• Goal – converge on a complete picture of the defect chemistry of the structure versus the bulk

• Correlate results with the kinetics of oxygen reduction measured on patterned thin films
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