Kinetics of Oxygen Reduction in LSM and LSCF

Division of Materials Science and Engineering, Boston University
Motivation:

Power plant design: IGFC Concept

SOFC Stack: current collection, thermal management, interconnects.

Single Cell: degradation, mass and thermal transport

Electrodes: Reaction Kinetics, Oxygen Transport, Material and Geometry effects
The Oxygen Reduction Reaction:

Where does this take place:

• On the surface?
• In the bulk?
• On the electrolyte?
• At the three phase boundary?
• At the cathode/electrolyte interface?
• Does it depend on the material?

What processes are important?

\[ \text{O}_2(g) + 4\text{e}^- \rightarrow 2\text{O}^{2-} \]
What processes are important for oxygen reduction?

**Kinetics and Rate Laws:**
Is one rate determining?

**Surface Diffusion:**
What are the mechanisms?

**Bulk Diffusion:**
When is it important?

\[ \text{O}_2 + 2s \leftrightarrow 2\text{O}^\text{ad} \text{ surface} \]

\[ \text{ TPB } \]

\[ 2\text{O}^\text{ad} + 2V_\text{YSZ} \rightarrow \text{2O}_x^\text{YSZ} + 2h + 2s \]

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Replay  Stop


J.D. Ferguson et al., *Advanced Materials* V. 23, Issue 10, p 1226–1230

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Apply Current
BU Cathode Project...

Experimental Data:

- Heteroepitaxial Thin-Films
- Patterned Cathodes on YSZ

Surface Science:
- Crystal structure
- Electronic structure
- Bonding sites/Bonding Species

Electrochemistry:
- Electrochemical impedance spectroscopy (EIS)

Modeling:
- Diffusion coefficients, kinetic rate constants, rate-determining steps
X-ray Techniques

• Surface Composition [TXRF]

• Local Electronic Structure [EXAFS], [XANES]
Energy Resolving Fluorescence

- Small energy range corresponds to emission line of specific atomic species
- Window energy range for fluorescence signal.
There is manganese enrichment at the surface during annealing.

Quenched and cooled sample are similar.

Suggests surface composition developed at high temperature is preserved.

Experiments at high temperature are not done yet.
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:
\[ [O_0^x] + [V_0] = 3 \]

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:
\[ K_S = [V_0]^3 \cdot [V_A''] \cdot [V_B''] \]

Redux reaction:
\[ K_r = \frac{[Mn_B^x] \cdot [V_0] \cdot PO_{2}^{1/2}}{[Mn_B] \cdot [O_0^x]} \]

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

Solved Concentrations

For a given $x$, $y$, $K_s$, $K_r$, $K_i$ can generate relevant concentrations versus $T$ and $P_{O_2}$.

TXRF provides specific information about $x$ and $y$ on the surface. Next step is to calculate the Brouwer diagram of LSM surface.
Kinetic Measurements Using Polycrystalline Thin Film Electrodes
2 Pathways for Oxygen Reduction Reaction...

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)
Experimental – LCM Patterned Cathodes:

Known to have low ionic conductivity, can we find evidence of “Surface Path?”

Generate Patterns:
- TPB length = 450 – 1600 cm cm$^{-2}$
- Cathode/electrolyte area = constant

$$R_p \,(\Omega\text{-cm}^2) = \text{Nyquist} \,(L_{f_{\text{intercept}}} - H_{f_{\text{intercept}}}) \times \text{Area}$$
LCM – Evidence of Surface Path:

Two parallel paths:

\[ \frac{1}{R_p} = \frac{1}{R_{TPB}^P} + \frac{A_A}{R_{p}^{MIEC}} \]

Where:

- TPB due to pores
- Pattern TPB

\[ R_{TPB}^P = \frac{\rho_p}{l_{TPB}}, \quad l_{TPB} = l_{TPB_p} + l_{TPB_o} \]

“Surface Path”: direct reduction of \( O_2 \) at TPB or by surface diffusion

Total Polarization scales inversely with TPB

LCM – Evidence of Surface Path:

\[
\frac{1}{R_p} = \frac{l_{\text{TPB}_p}}{\rho_p} + \frac{l_{\text{TPB}_0}}{\rho_p} + \frac{A_A}{R_p^{\text{MIEC}}}
\]

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<th>T °C</th>
<th>R_p</th>
<th>R_p^{(TPB)}</th>
<th>R_p^{(miec)}</th>
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<td>15</td>
<td>19</td>
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<tr>
<td>600</td>
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<td>290</td>
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</table>

On average **TPB path** is ~4 fold less resistive, and thus the most likely path

“Surface Path”: direct reduction of O_2 at TPB or by surface diffusion

Total Polarization scales inversely with TPB
Goals:

1. Derive a model incorporating dominant processes.
2. Simulate impedance data to extract relevant kinetic parameters.
3. Determine rate limiting steps.
Model: Reaction Scheme

Dissociative Adsorption: \[ \text{O}_2 + 2s \xleftrightarrow{k_{\text{ad}}/k_{\text{des}}} 2\text{O}^{\text{ad}} \]

Surface Diffusion:
\[ \frac{d[\text{O}^{\text{ad}}]}{dt} = D_s \frac{d^2[\text{O}^{\text{ad}}]}{dz^2} \]

Reduction/Incorporation Reaction:
\[ 2\text{O}^{\text{ad}} + 2\text{V}^{\text{YSZ}} \xleftrightarrow{k_1/k_{-1}} 2\text{O}^{x-\text{YSZ}} + 2h + 2s \]

Define:
\[ \theta = \frac{[\text{O}^{\text{ad}}]}{\Gamma} \text{ and } s = \Gamma \cdot (1 - \theta) \]
\[ \Gamma = \text{Total # of oxygen adsorption sites} \]

Mass balance at TPB:
\[ \frac{d\theta}{dt} = 2k_{\text{ad}}P_{\text{O}_2}\Gamma(1 - \theta)^2 - 2k_{\text{des}}\Gamma\theta^2 - k_1[V_{\text{O}^{\text{YSZ}}}]\theta + k_{-1}[O^{x-\text{YSZ}}](1 - \theta) \]

Charge Balance:
\[ I_F = 2\Gamma F A_a[k_{-1}[O^{x-\text{YSZ}}](1 - \theta) - k_1[V_{\text{O}^{\text{YSZ}}}]\theta] \]

Surface Mass Transport:

- Incorporated using 1D Finite-Difference Method
- Compartments are smallest closest to TPB (expand geometrically away) to capture the higher gradient at the interface.
- The concentration of $O^{\text{ad}}$ is considered uniform in a given compartment
- Surface is discretized to $6\delta$, where $\delta$ is the penetration depth determined by:

$$2\pi^{-1/2} = \frac{\delta \sqrt{\omega_{\text{max}}}}{2D_S}$$

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Block $\omega$: Final block, ad/des rxn. Flux: out

Blocks $i$: ad/des rxn. Flux: in/out

Block 1: TPB compart, Flux in, red./incorp. rxn.
Initial and Boundary Conditions:

• Initial Condition: $\theta(z,0) = \theta_0$
  
  – Where: $\frac{\theta_0}{1 - \theta_0} = K\sqrt{pO_2}; \text{ with } K = \sqrt{\frac{k_{ad}}{k_{des}}}$

• Boundary conditions:
  
  • Infinitely far away (i.e. $6\delta$): $\theta(\infty,t) = \theta_0$
  
  • At the TPB interface:
    
    – The current equals the charge balance
    
    – The electron transfer reaction only takes place in this compartment
Dependence of kinetic Parameters on:

Temperature:

\[ k_{ad} = k_{ad}^0 \exp \left( \frac{-E_{ad}}{RT} \right) \quad k_{1}^{eq} = k_{1}^{eq} \exp \left( \frac{-E_{fc}}{RT} \right) \]

\[ k_{des} = k_{des}^0 \exp \left( \frac{-E_{des}}{RT} \right) \quad k_{-1}^{eq} = k_{-1}^{eq} \exp \left( \frac{-E_{bc}}{RT} \right) \]

Electrode Potential:

Where:

\[ k_{1} = k_{1}^{eq} \exp \left( -\frac{\beta F}{RT} (\Delta \chi) \right) \quad k_{-1} = k_{-1}^{eq} \exp \left( \frac{(1 - \beta) F}{RT} (\Delta \chi) \right) \]

\[ \Delta \chi = 2\eta - \frac{RT}{F} \ln \left( \frac{\theta}{1 - \theta} \frac{1 - \theta_{o}}{\theta_{o}} \right) \]

\[ \eta = \text{applied overpotential at cathode/electrolyte interface} \]

And:

\[ \frac{\theta_{o}}{1 - \theta_{o}} = K\sqrt{pO_2}; \text{ with } K = \sqrt{\frac{k_{ad}}{k_{des}}} \]
Final form for Simulink:

Final Block ($\omega$):

\[
\frac{d\theta_\omega}{dt} = 2k_{ad}p_0 \Gamma (1 - \theta_\omega)^2 - 2k_{des} \Gamma \theta_\omega^2 \frac{\theta_\omega}{1 + q} - \frac{(2q + 1)\theta_\omega}{1 + q} + \theta_0
\]

Adsorption/Desorption

Block $i$:

\[
\frac{d\theta_i}{dt} = 2k_{ad}p_0 \Gamma (1 - \theta_i)^2 - 2k_{des} \Gamma \theta_i^2 + \frac{1}{T_i} \left( \frac{\theta_{i-1}}{1 + q} - \theta_i + \frac{\theta_{i+1}}{1 + q} \right)
\]

Diffusion

TPB Block (1):

\[
\frac{d\theta_1}{dt} = 2k_{ad}p_0 \Gamma (1 - \theta_1)^2 - 2k_{des} \Gamma \theta_1^2 - k_f^{eq} \exp \left( -\frac{\beta F}{RT} \Delta \chi \right) \theta_1 + k_b^{eq} \exp \left( \frac{(1 - \beta)F}{RT} \Delta \chi \right) (1 - \theta_1) + \frac{1}{T_1} \left( -\frac{\theta_1}{1 + q} + \frac{\theta_2}{1 + q} \right)
\]

Charge Transfer/Incorporation

* $T_i = \Delta z_i^2 / 2D$; $q$ = geometric factor expanding block size
Typical Simulation Results:

\[ f(p) = 1.2 \]
\[ \theta = 0.17 \]
\[ k_{ad} = 4.6 \times 10^5 \text{m}^2 \cdot (\text{s mol atm})^{-1} \]
\[ k_{des} = 2.3 \times 10^6 \text{m}^2 \cdot (\text{s mol})^{-1} \]
\[ D_S = 2.1 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1} \]
\[ k_f_{eq} = 7 \times 10^2 \text{m}^3 \cdot (\text{mol s})^{-1} \]
\[ k_b_{eq} = 1.3 \text{ m}^3 \cdot (\text{mol s})^{-1} \]
\[ Q_o = 3.53 \times 10^{-4} \text{F} \]

\[ T = 700^\circ \text{C}, \ P_{O_2} = 0.21, \ \text{TPB Length} = 7.0 \text{ m} \]

Least-Squares minimization to the equation:

\[ \min |Z_{sim}(i) - Z_{exp}(i)|^2 \]
Surface Coverage:

Equilibrium surface coverage increases with pO$_2$. Little scatter between samples shows experimental reliability.

The surface coverage increases away from TPB, and then plateaus (Dirichelet condition).

$\Delta \chi$ decreases to a max of $2\eta$ as $\theta \rightarrow \theta_o$.
Surface Diffusivity:

Surface diffusivity is flat at low coverage: \( D_s \approx D_s^0 \) (intrinsic diffusivity).

At high coverage need thermodynamic factor, \( A(\theta) \):
\[ D_s = A(\theta)D_s^0, \]
to account for repulsive interactions between adatoms.

Activation energy is very high. Surface migration was estimated to have activation energy of \(~194\ \text{kJ/mol}\) from DFT calculations (Kotomin et al. *Phys. Chem. Chem. Phys.*, 2008, 10, 4644-4649).
Adsorption and Desorption Coefficients

$E_{ad} = 24 \text{ kJ mol}^{-1}$

$pO_2 = 0.21 \text{ atm}$

$E_{des} = 121 \text{ kJ mol}^{-1}$

$pO_2 = 0.21 \text{ atm}$
Surface processes:

700°C – $P_{O_2} = 0.21$ atm

Bode Plot Analysis:

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\begin{equation}
Z_G = R_{chem} \sqrt{\frac{1}{1 - j\omega t_{chem}}}
\end{equation}
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“Gerischaer” shaped indicates – co-limitation
Rate Determining Steps:

Surface Processes

Charge Transfer

\( P_{O_2} = 0.21 \text{ atm} \)
Conclusions from LCM patterned Cathodes:

- 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: $D_s$, $k_{ad}$, $k_{des}$, $k_{feq}$, $k_{beq}$, and surface coverage ($\theta$).
- At temperatures below 700 °C was co-limited by diffusion and adsorption. At high temperatures incorporation reaction contributions to total polarization increase significantly.
- Low scatter between samples suggests that the model correctly accounts for the geometry changes.
LSCF vs. LCM – far weaker TPB dependence
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