Fundamental Characterization and Modeling of Infiltrated SOFC Cathode

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Acknowledgement

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- SECA Program Management Team
  - Dan Driscoll, Shailesh Vora, Briggs White, Joe Stoffa
**Infiltrated SOFC Cathode**

**Principal Assumption:** Infiltrants having high oxygen absorption capabilities enhance oxygen flux into the cathode and thus improve the cathode performance.

![Image showing infiltration](image)

**Strategies:**
1. Catalysts on MIEC
2. IC/EC on EC/IC
3. Self-infiltration to increase TPB

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Fundamental Issues in SOFC Cathode

- Improving the data analysis method for ECR
- Understanding the kinetic parameters obtained from ECR
- Develop ECR application for infiltrated cathode materials
- Infiltrated cathode model
ECR Testing System Setup

Schematic representation of the conductivity relaxation set-up

van der Pauw Method

\[ \sigma = \frac{\ln 2}{a \pi R} \]
Theoretical Background of ECR Method

- Assume a small oxygen partial pressure changing step:

\[
\frac{C(t) - C(0)}{C(\infty) - C(0)} = \frac{\delta(t) - \delta(0)}{\delta(\infty) - \delta(0)} = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} \quad \Delta \log P_{O_2} \leq 1
\]

- Diffusion equation and solution:

\[
\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}
\]

\[-D \frac{\partial C}{\partial x}\bigg|_{x=\pm a} = k[C(\infty) - C(t)]
\]

- \(C(\infty)\): is in equilibrium surface concentration under certain oxygen pressure
- \(C(t)\): real time surface concentration

\[
\frac{C(t) - C(0)}{C(\infty) - C(0)} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n^2Dt/a^2)}{\beta_n^2(\beta_n^2 + L^2 + L)}
\]

\[
L = \frac{ak}{D} = \frac{a}{l_c} = \beta_n \tan \beta_n
\]

Characteristic length
Data Analysis

- **Get initial value of k**

\[
\frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = 1 - \exp\left[ -\frac{k(t-t_0)}{a} \right]
\]

- **Get initial value of D**

\[
\frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[ -\frac{(2n+1)^2 \pi^2 D(t-t_0)}{4a^2} \right]
\]

- **Calculate L**

\[
L = \frac{ak}{D}
\]

*If L > 1, use fitting parameters (D, b_1, t_0)*

*If L <= 1, use fitting parameters (k, b_1, t_0)*

---

Fitting $D$ and $k$

- Problem of the reported method

With 2% noise

<table>
<thead>
<tr>
<th>$D$ [cm$^2$/s]</th>
<th>$k$ [cm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-6}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>$t_0$ [s]</td>
<td>$b_1$ [-]</td>
</tr>
<tr>
<td>0</td>
<td>0.8603</td>
</tr>
<tr>
<td>$a$ [cm]</td>
<td>$L$ [-]</td>
</tr>
<tr>
<td>0.05</td>
<td>1</td>
</tr>
</tbody>
</table>

Multiple local minimums
Improved Method

- Analyze two relaxation data sets

<table>
<thead>
<tr>
<th>D [cm²/s]</th>
<th>k [cm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 × 10⁻⁶</td>
<td>1 × 10⁻⁴</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>t₀ [s]</th>
<th>b₁ [-]</th>
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<table>
<thead>
<tr>
<th>a₂ [cm]</th>
<th>L₂ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>10</td>
</tr>
</tbody>
</table>

\[ f = \sqrt{\frac{F_1^2}{T_1} + \frac{F_2^2}{T_2}} \]

The estimation error for oxygen surface exchange coefficient was decreased by 80% within a 5% variation of minimum error band.
Oxygen Transport in LSCF Cathode

- Testing conditions:
  - Gas flow rate: 400sccm
  - Temperature: 800°C
  - Constant current: 40mA
  - Oxygen partial pressure:
    - 0.20atm~0.018atm
  - Oxygen partial pressure step change: $|\Delta \log P_{O_2}| < 0.1$

0.20atm $\rightarrow$ 0.18atm
Conductivity of LSCF

Oxygen Transport in LSCF Cathode

Oxygen Transport in LSCF Cathode

- Oxygen partial pressure effects

Oxygen reduction reaction

\[
\frac{1}{2} O_2 + 2e^- + V_o^\cdot \xrightleftharpoons[k_2]{k_1} O_o^x
\]

Surface exchange coefficient

\[
k = k_1 P_{O_2}^{1/2} [V_o^\cdot] - k_2 C_s = k[C(\infty) - C_s]
\]

\[
k = \frac{k_1 P_{O_2}^{1/2} [V_o^\cdot] - k_2 C_s}{[C(\infty) - C_s]} = k_1 P_{O_2}^{1/2} + \frac{k_1 P_{O_2}^{1/2} [V_o^\cdot] - k_2 C_s}{[C(\infty) - C_s]}
\]

\[
k = k_1 P_{O_2}^{1/2} + \frac{k_2 C(\infty) - k_2 C_s}{[C(\infty) - C_s]} = k_1 P_{O_2}^{1/2} + k_2
\]

\[
[V_o^\cdot] = [V_o^\cdot] + C(\infty) - C_s
\]

\[
k = k_1 P_{O_2}^{1/2} + k_2
\]
Fundamental Issues in SOFC Cathode

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Oxygen transport in Infiltrated SOFC Cathode

- Characterize oxygen exchange coefficient at infiltrated/cathode backbone interface

\[ C_1 - C'_1 = \frac{J}{k_{\text{surface}}} \]

\[ C_2 - C_\infty = \frac{J}{k_{\text{interface}}} \]

\[ C_3 - C_2 = \frac{Ja}{D} \]

\[ \frac{1}{k} = \frac{1}{k_{\text{interface}}} + \frac{1}{k_{\text{surface}}} \]

Total surface exchange coefficient: \(3.3 \times 10^{-4}\) cm/s

Interface exchange coefficient: \(3.7 \times 10^{-4}\) cm/s

Normalized conductivity and fitting curve of spin coated LSC with oxygen partial pressure changing from 0.05 atm to 0.04 atm
Oxygen Transport in Infiltrated SOFCs Cathode

Surface exchange coefficients of single phase LSCF and infiltrated cathodes

$k_{SDC/LSCF} > k_{LSC/LSCF}$

$k_{SDC/LSCF} < k_{LSC/LSCF}$

Fundamental Issues in SOFC Cathode

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**Infiltrated cathode model**
Infiltrated Cathode Modeling

Physical mechanism

\[ O_2 + s \stackrel{k_1}{\rightleftharpoons} O_{2,ad} \]

\[ O_{2,ad} + 2V_{O,1} \stackrel{k_2}{\rightleftharpoons} 2O_{O,1}^x + 4h^0 + s \]

\[ O_{O,1}^x + V_{O,LSCF} \stackrel{k_3}{\rightleftharpoons} V_{O,LSCF} + O_{O,LSCF}^x \]

\[ O_{O,LSCF}^x + V_{O,YSZ} \stackrel{k_4}{\rightleftharpoons} O_{O,YSZ}^x + V_{O,LSCF} \]
Infiltrated cathode modeling

Basic equations

\[ O_2 + s \xleftrightarrow[k_1]{k_1^1} O_{2,ad} \]

\[ O_{2,ad} + 2V_{O,I} \xleftrightarrow[k_2]{k_2^2} 2O_{O,I}^x + 4h^+ + s \]

\[ O_{O,I}^x + V_{O,LSCE} \xleftrightarrow[k_3]{k_3^3} V_{O,I}^x + O_{O,LSCE}^x \]

\[ O_{O,LSCE}^x + V_{O,YSZ} \xleftrightarrow[k_4]{k_4^4} O_{O,YSZ}^x + V_{O,LSCE}^x \]

Governing Equation

\[
\frac{\partial C_{V,LSCE}}{\partial t} = D \frac{\partial^2 C_{V,LSCE}}{\partial x^2} - \frac{\Delta S}{\Delta V} r_3 = D \frac{\partial^2 C_{V,LSCE}}{\partial x^2} - \frac{\Delta S}{\Delta V} r_{3,0} \left( \frac{C_{V,LSCE}}{C_{V,LSCE,eq}} - 1 \right)
\]

Initial Condition

\[ t=0, \quad C_{V,LSCE} = 1 \times 10^{-4} \text{ mol/cm}^3 \]

Boundary conditions

\[ x=0 \]

\[ D \frac{\partial C_{V,LSCE}}{\partial x} = -r_4 = -r_{4,0} \left[ \exp(-2\alpha_{2PB}f \eta) - \frac{C_{V,LSCE}}{C_{V,LSCE,eq}} \exp[2(1 - \alpha_{2PB})f \eta] \right] \]

\[ x=l_c \]

\[ \frac{\partial C_{V,LSCE}}{\partial x} = 0 \]
Infiltrated Cathode Modeling

- **ECR measurement application**

\[
O_{O,I}^x + V_{O,LSCF}^\rightarrow \xrightarrow{k_3} V_{O,I}^\rightarrow + O_{O,LSCF}^x
\]

\[
r_3 = k_3 C_{V,LSCF} - k_3^C V_{I}\]

\[
k_{interface}(C_{V,LSCF} - C_{V,LSCF,eq}) = k_3 C_{V,LSCF} - k_3^C V_{I}\]

\[
r_{3,0} = k_3 C_{V,LSCF,eq} = k_3^C V_{I}\]

\[
r_{3,0} = k_3 C_{V,LSCF,eq} = k_3^C V_{I} = k_{interface} C_{V,LSCF,eq}\]

\[
k_{interface} = \frac{k_3 C_{V,LSCF} - k_3^C V_{I}}{C_{V,LSCF} - C_{V,LSCF,eq}}\]

\[
k_3^C V_{I} \frac{C_{V,LSCF}}{C_{V,LSCF,eq}} - k_3^C V_{I}\]

\[
= \frac{k_3^C V_{I}}{C_{V,LSCF,eq}}\]
Over-potential effects

\[ r_{3,0} \text{ (mol/cm}^2\text{·s)} = 3 \times 10^{-8} \]

(a)-0.05V (b) -0.1V (c) -0.2V (d) -0.3V (e) -0.4V (f) 0.05V (g) 0.1V

Exchange current = 0.14A/cm²
Cathode backbone effects

\[ \eta = -0.2 \text{V} \]

\[ r_{3,0} \text{ (mol/cm}^2\cdot\text{s) value is: (a) } 1 \times 10^{-8} \text{ (b) } 2 \times 10^{-8} \]
\[ (c) 3 \times 10^{-8} \text{ (d) } 4 \times 10^{-8} \text{ (e) } 5 \times 10^{-8} \]

\[ C_{v,eq} \text{ (mol/cm}^3\) = 1 \times 10^{-4} \]

\[ C_{v,eq} \text{ (mol/cm}^3\) = 1 \times 10^{-5} \]
➤ Improve ECR data fitting method
  • Fix the initial relaxation time by assuming the reactor is an ideally stirred tank reactor
  • Using weight average error function to fitting two data sets together

➤ Investigate oxygen transport in LSCF
  • Oxygen surface exchange coefficient depends on the final oxygen partial pressure following the law
  • Deduce oxygen reduction reaction constants and the results revealed that it is easier for oxygen to enter LSCF lattice than to leave at 800° C

➤ Develop ECR technique for Infiltrated SOFCs cathode
  • LSC infiltrated cathode materials possess higher oxygen surface exchange rate compared to single phase LSCF material

➤ Cathode Modeling
  • The characteristic length of the cathode decreased with the increasing interface oxygen ion exchange rate.
Take Home Message

- Infiltrants
  - Surface Exchange Rate Limiting Step
  - Strain Effect
  - Size vs. Characteristic Length
- Hetero-Interface
  - Nature of the Interface
  - Oxygen Transport Mechanisms
- Stability Issues
  - Backbone
  - Reaction between Backbone and Infiltrants
  - Infiltrants growth
- Overall ORR Kinetics
THANK YOU