PERFORMANCE ANALYSIS OF SINGLE STEP

CO-FIRED SOLID OXIDE FUEL CELLS (SOFCs)

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Introduction

Single Step Co-firing Process Development

Polarization Modeling

Polarization Analysis

Fuel Utilization Test

Advanced Cathode Investigation

Summary & Future Work
Major Challenges for Commercialization of SOFCs

- High Manufacturing Costs
  (SOFC System Costs per Unit of Power ($/kW))
- Reduced Cell Performance at Low Operating Temperature
  (Interconnects, Sealing, etc.)

- Single Step Co-Firing Process
  with Conventional Material System
- Polarization Modeling: Systematic Analysis of Cell Performance and Polarization Losses

Research Goals

- Manufacture SOFCs with the Lowest Manufacturing Costs
  
  by Single Step Co-Firing of the Entire SOFCs

- Achieve the Highest Cell Performance and Lower Operating Temperature
  
  by Optimization of Materials, Microstructures, and Process Parameters using Polarization Modeling

Minimize $/kW
**Single Step Co-Firing Process**

- **Cathode Current Collector**: Screen Printing
  - Ca-doped LaMnO$_3$ (Porous)

- **Cathode Active Layer**: Screen Printing
  - Ca-doped LaMnO$_3$ + YSZ (Fine & Porous)

- **Electrolyte**: Screen Printing
  - YSZ (Dense)

- **Anode Active Layer**: Screen Printing
  - Ni + YSZ (Fine & Porous)

- **Anode Support**: Tape Casting
  - Ni + YSZ (Porous)

**Co-Firing in Air**
(1300-1330°C)
**PROCESS DEVELOPMENT**

- Lowered Electrolyte Sintering Temperature
  - Density of YSZ: **Without Sintering Aid: ~ 94%, With Sintering Aid: ~ 99+% @1300°C**

- Matched Thermal Expansion Coefficients and Sintering Shrinkages

- Developed Refractory Cathode Composition
  - Doped-(La,Ca)MnO₃

- Optimized **Thickances and Porosities** of Electrodes

- Optimized **Particle Sizes** of Initial Powders

- Evaluated Pore Former Material
  - Carbon Black

- Employed **Cathode Current Collector**
  - (La,Ca)MnO₃: 50μm thick, 50% porous
Temperature: 900°C
H₂+3% H₂O / Air

Power Density (W/cm²) vs. Current Density (A/cm²)

- Cathode Particle Size Optimization
- Cathode Current Collector
- Anode Porosity Optimization
- Pore Former Material Optimization

Cathode Current Collector:
LCM, 50μm thick, 50% porous

Cathode Active Layer:
LCM-YSZ, 30μm thick, 31% porous

Electrolyte:
YSZ, 15μm thick

Anode Support:
Ni-YSZ, 850μm thick, 32% porous
**Baseline Cell: Power Density**

*Test Condition*
- Temperature: 700~800°C
- Fuel: 97% H₂ + 3% H₂O
- Oxidant: Air

Power Density (W/cm²) vs. Current Density (A/cm²)

- Max. = 0.55 W/cm² at 800°C
- Max. = 0.36 W/cm² at 750°C
- Max. = 0.23 W/cm² at 700°C
**Polarization Model: Theory**

\[ E_C = E_0 - i R - \eta_{act} - \eta_{conc} \]

- **Activation Polarization (\(\eta_{act}\))**: 
  \[ i = i_0 \exp\left(\frac{\alpha n_e \eta_{act} F}{RT}\right) - i_0 \exp\left(-\frac{(1-\alpha) n_e \eta_{act} F}{RT}\right) \quad (\alpha=1/2, \, n_e=2) \]

  \[ \eta_{act} = \frac{RT}{F} \ln\left\{\frac{1}{2} \left[\left(\frac{i}{i_0}\right) + \sqrt{\left(\frac{i}{i_0}\right)^2 + 4}\right]\right\} \quad \text{(Anode + Cathode)} \]

- **Concentration Polarization (\(\eta_{conc}\))**: 
  \[ \eta_{conc} = -\frac{RT}{4F} \ln(1 - \frac{i}{i_{cs}}) - \frac{RT}{2F} \ln(1 - \frac{i}{i_{as}}) + \frac{RT}{2F} \ln\left(1 + \frac{p_{H_2}^0}{p_{H_2O}^0 i_{as}}\right) \]


**Polarization Modeling: Curve-Fitting (Example)**

- **Test Condition**
  - Temperature: 800°C
  - Fuel: 97% H₂ + 3% H₂O (300cc/min): Fixed
  - Oxidant: 100%, 21%, 8% O₂ + N₂ (1000cc/min)

**Fitting Parameters**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>100% O₂</th>
<th>21% O₂ + 79% N₂</th>
<th>8% O₂ + 92% N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_\text{f}$ (Ω·cm²)</td>
<td>0.082</td>
<td>0.082</td>
<td>0.082</td>
</tr>
<tr>
<td>$i_o$ (A/cm²)</td>
<td>0.52</td>
<td>0.28</td>
<td>0.097</td>
</tr>
<tr>
<td>$i_{as}$ (A/cm²)</td>
<td>5.77</td>
<td>5.77</td>
<td>5.77</td>
</tr>
<tr>
<td>$i_{cs}$ (A/cm²)</td>
<td>-</td>
<td>5.42</td>
<td>1.77</td>
</tr>
</tbody>
</table>

**Assumption:** $i_{cs} >> i_{as}$ and $\eta_{conc,c} << \eta_{conc,a}, \eta_{act}$ with 100% O₂

- **Anode Limiting Current**
  \[ i_{as} = \frac{2 F p^o_{H₂} D_{H₂-H₂O}^{eff}}{R T l_a} \]

- **Cathode Limiting Current**
  \[ i_{cs} = \frac{4 F p^o_{O₂} D_{O₂-N₂}^{eff}}{(p - p^o_{O₂}) R T l_c} \]

<table>
<thead>
<tr>
<th>$D_{H₂-H₂O}^{eff}$</th>
<th>0.23 cm²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{O₂-N₂}^{eff}$</td>
<td>0.037 cm²/s</td>
</tr>
</tbody>
</table>
Various Polarization Losses @800°C with Humidified Hydrogen (3% H₂O) and Air

- Temperature: 800°C
- Fuel: 97% H₂ + 3% H₂O
- Oxidant: Air

Cathodic Limiting Current Density @800°C as a Function of $p_{O_2}$ in Oxidant

- $i_{cs}$ rapidly increases as $p_{O_2}$ increases and approaches 100% O₂

- $\eta_{conc,c} \ll \eta_{conc,a}$ and $\eta_{act}$ except at high current density near $i_{cs}$

- Consistent with assumption that $\eta_{conc,c}$ is negligible compared to other polarization losses when oxygen at the cathode nears 100%
**Polarization Modeling & Impedance Spectroscopy**

- **Activation Polarization Resistance at OCV**
  \[
  R_{act} = \frac{d\frac{d_{act}}{dt}}{d_{act}} = \frac{RT}{F} \cdot \frac{1}{\sqrt{I^2 + 4i_p^2}}
  \]
  \[
  R_{act}|_{i\to0} = \frac{RT}{2Fi_o}
  \]

- **Anodic Concentration Polarization Resistance at OCV**
  \[
  R_{conc,a} = \frac{d\frac{d_{conc,a}}{dt}}{d_{conc,a}} = \frac{RT}{2F} \left[ \frac{1}{i_{as} \left( 1 - \frac{i}{i_{as}} \right)} + \frac{1}{i_{as} \left( 1 + \frac{i_{Hz}^o}{i_{Hz}^0} \right)} \right]
  \]
  \[
  R_{conc,a}|_{i\to0} = \frac{RT}{2F} \cdot \frac{1}{i_{as}} \left( 1 + \frac{p_{Hz}^o}{p_{Hz}^0} \right)
  \]

- **Cathodic Concentration Polarization Resistance at OCV**
  \[
  R_{conc,c} = \frac{d\frac{d_{conc,c}}{dt}}{d_{conc,c}} = \frac{RT}{4F} \cdot \frac{1}{i_{cs} \left( 1 - \frac{i}{i_{cs}} \right)}
  \]
  \[
  R_{conc,c}|_{i\to0} = \frac{RT}{4F} \cdot \frac{1}{i_{cs}}
  \]

---

**Impedance Spectroscopy @800°C**

**Graphical Analysis**

- **100% O₂**
- **21% O₂ + 79% N₂**
- **8% O₂ + 92% N₂**

**High Frequency Intercept = \( R_Ω \)**

**Low Frequency Intercept = \( R_{polar} + R_Ω \)**

**Impedance Spectroscopy**

- **Polarization Model**
Polarization Analysis #1: Baseline Cell

- Ohmic Loss (Electrode) + Cathode + Contacts
- Activation Polarization
- Cathodic Concentration Polarization
- Anodic Concentration Polarization

Dominant Polarization Losses
- Ohmic Loss (Electrode)
- Activation Polarization (Cathode)
- Concentration Polarization (Anode)

Temperature: 800°C
H₂-3% H₂O / Air

Voltage (V) vs. Current Density (A/cm²)
**Polarization Analysis #2: Contact Resistance**

- **Cathode Current Collection: Ag Mesh vs. Pt Mesh**

![Graph showing Voltage vs. Current Density for Ag Mesh and Pt Mesh](image)

- Temperature: 800°C
- H₂-3% H₂O / Air

Max. = 0.9 W/cm²

- **Ag Mesh**
  - Max. = 0.55 W/cm²
  - \( T_{in}(Ag) = 961°C \)
  - \( R_{electrode} = 0.067 \, \Omega \cdot \text{cm}^2 \)

- **Pt Mesh**
  - Max. = 0.9 W/cm²
  - \( T_{in}(Pt) = 1772°C \)
  - \( R_{electrode} = 0.156 \, \Omega \cdot \text{cm}^2 \)

- **Ag is softer than Pt at operating temperature.**

  ⇒ Higher Interfacial Contact Area ⇒ Lower Ohmic Electrode Resistance

- **In SOFC stacks, the effect of the contacts between the electrode and interconnects can be substantial.**
Polarization Analysis #3: Cathode Microstructure

- **Sintering Temperature: 1300°C vs. 1330°C**

![Graph showing voltage and current density](image)

- **Temperature**: 800°C H₂-3% H₂O / Air
- **Max. Power Density**: 1.4 W/cm²
- **Max. Voltage**: 0.9 W/cm²

- **1300°C Sintering**
  - Avg. Grain Size = 2.3 μm
  - $i_0 = 0.27 \text{ A/cm}^2$

- **1330°C Sintering**
  - Avg. Grain Size = 3.2 μm
  - $i_0 = 0.16 \text{ A/cm}^2$

- **Impedance Spectroscopy**

- **No Significant Change in Anode Microstructure.**
- **Less Sintering of Cathode ⇒ Low Activation Polarization**
**Polarization Analysis #4: Anode Porosity**

- **Pore Former in Anode: 8 wt% C vs. 5 wt% C**

![Graph showing the comparison of 8 wt% Carbon Black and 5 wt% Carbon Black](image)

- **Increased Anode Porosity**
  - **⇒ Low Anode Concentration Polarization**

**Key Data: 8 wt% Carbon Black**
- **Anode Porosity:** 37%
- **Power Density:** Max. = 1.4 W/cm²
- **Voltage:** Temperature: 800°C, H₂-3% H₂O / Air
- **Current Density:** $i_{as} = 5.77$ A/cm²
- **Effective Diffusion Coefficient:** $D_{eff_{H2-H2O}} = 0.23$ cm²s⁻¹

**Key Data: 5 wt% Carbon Black**
- **Anode Porosity:** 32%
- **Power Density:** Max. = 1.5 W/cm²
- **Voltage:**
- **Current Density:** $i_{as} = 4.97$ A/cm²
- **Effective Diffusion Coefficient:** $D_{eff_{H2-H2O}} = 0.19$ cm²s⁻¹
Temperature: 800°C
97% H₂ + 3% H₂O - Air

Comparable to the State-of-the-Art Cells Fabricated with Multiple Firing Steps
**Fuel Utilization Test: Background**

**Fuel Utilization**

\[ U_t = \frac{\text{Molar flow rate of reactants consumed in a cell}}{\text{Molar flow rate of reactants supplied into the cell}} = \frac{\dot{N}_{\text{consumed}}}{N_{in}} \]

**Fuel utilization increases along the flow path over the electrode surface.**

\[ \Leftarrow \text{Fuels are consumed and products are formed along the flow path.} \]

**Cell Performance Loss near Exit (High Fuel Utilization)**

- Loss of Nernst Potential
- Anodic Activation Polarization
- Anodic Concentration Polarization

**Simulate the effect of practical fuel utilization on single cell performance**

by increasing \( H_2O \) content in fuel
**Fuel Utilization Test: Effect of Anode Active Layer**

**With Anode Active Layer**

Temperature: 800°C

- Current Density (A/cm²)
- Power Density (W/cm²)

**Without Anode Active Layer**

Temperature: 800°C

- Current Density (A/cm²)
- Power Density (W/cm²)

**Fuel Compositions**

<table>
<thead>
<tr>
<th>Fuel Compositions</th>
<th>Max. Power Density (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With AAL</td>
</tr>
<tr>
<td>H₂ – 3% H₂O</td>
<td>1.41</td>
</tr>
<tr>
<td>H₂ – 30% H₂O</td>
<td>1.27</td>
</tr>
<tr>
<td>H₂ – 50% H₂O</td>
<td>1.17</td>
</tr>
<tr>
<td>H₂ – 70% H₂O</td>
<td>0.84</td>
</tr>
</tbody>
</table>

**Anode Active Layer**

- Porosity = 26%
- Avg. Grain Size = 1.3 μm
- Avg. Pore Size = 0.7 μm

**Anode Support**

- Porosity = 37%
- Avg. Grain Size = 4.3 μm
- Avg. Pore Size = 2.6 μm
**Fuel Utilization Test: Polarization Modeling**

\[
E_C = E_o - i R_i - \frac{2RT}{F} \ln \left( \frac{1}{2} \left( \frac{i}{i_o} \right) + \sqrt{\left( \frac{i}{i_o} \right)^2 + 4} \right) + \frac{RT}{4F} \ln \left( \frac{i}{i_{ce}} \right) + \frac{RT}{2F} \ln \left( 1 - \frac{i}{i_{as}} \right) - \frac{RT}{2F} \ln \left( 1 + \frac{P^0_{H_2}}{P^0_{H_2O} i_{as}} \right)
\]

- \( R_i \): Independent of Fuel Composition
- \( D_{O_2-N_2}^{\text{eff}} \): Independent of Fuel Composition
- \( D_{H_2-H_2O}^{\text{eff}} \): Independent of \( \text{H}_2/\text{H}_2\text{O} \) ratio (Kinetic Theory of Gases)*

### With Anode Active Layer

<table>
<thead>
<tr>
<th>Fuel Compositions</th>
<th>Exchange Current Density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With AAL</td>
</tr>
<tr>
<td>( \text{H}_2 - 3% \text{H}_2\text{O} )</td>
<td>0.87</td>
</tr>
<tr>
<td>( \text{H}_2 - 30% \text{H}_2\text{O} )</td>
<td>0.84</td>
</tr>
<tr>
<td>( \text{H}_2 - 40% \text{H}_2\text{O} )</td>
<td>0.82</td>
</tr>
<tr>
<td>( \text{H}_2 - 50% \text{H}_2\text{O} )</td>
<td>0.79</td>
</tr>
<tr>
<td>( \text{H}_2 - 60% \text{H}_2\text{O} )</td>
<td>0.75</td>
</tr>
<tr>
<td>( \text{H}_2 - 70% \text{H}_2\text{O} )</td>
<td>0.53</td>
</tr>
</tbody>
</table>

**Fuel Utilization Test: Performance Analysis**

- **Activation Polarization:**
  - At **Low Fuel Utilization** (H₂-3% H₂O)
    - Dominated by **Cathode**
    - (No Difference in Cell Performance and Exchange Current Density due to Anode Active Layer at Low Fuel Utilization)
  
  \[
  \eta_{act} \approx \eta_{act,c} = \frac{2RT}{F} \ln \left\{ \frac{1}{2} \left[ \frac{i}{i_{0,c}} + \sqrt{\left( \frac{i}{i_{0,c}} \right)^2 + 4} \right] \right\}
  \]
  
  \[
  i_{0,a} \gg i_{0,c} \quad i_o \approx i_{0,c}
  \]

- At **High Fuel Utilization**
  - Anodic Activation Polarization Increases
  - Cathodic Activation Polarization: Independent of Fuel Composition

  \[
  \eta_{act,a} \approx \eta_{act} - \eta_{act,c} = \frac{2RT}{F} \ln \left\{ \frac{1}{2} \left[ \frac{i}{i_{0,a}} + \sqrt{\left( \frac{i}{i_{0,a}} \right)^2 + 4} \right] \right\}
  \]
Anodic Activation Polarization:

\[ \eta_{\text{act},a} = \frac{2RT}{F} \ln \left\{ \frac{1}{2} \left( \frac{i}{i_{0,a}} \right) + \sqrt{\left( \frac{i}{i_{0,a}} \right)^2 + 4} \right\} \]

With Anode Active Layer

- 30% H₂-70% H₂O
- 40% H₂-60% H₂O
- 50% H₂-50% H₂O
- 60% H₂-40% H₂O
- 70% H₂-30% H₂O
- Curve-fitted

Without Anode Active Layer

- 30% H₂-70% H₂O
- 40% H₂-60% H₂O
- 50% H₂-50% H₂O
- 60% H₂-40% H₂O
- 70% H₂-30% H₂O
- Curve-fitted

<table>
<thead>
<tr>
<th>Fuel Compositions</th>
<th>Anodic Exchange Current Density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With AAL</td>
</tr>
<tr>
<td>H₂ – 30% H₂O</td>
<td>26.73</td>
</tr>
<tr>
<td>H₂ – 40% H₂O</td>
<td>15.68</td>
</tr>
<tr>
<td>H₂ – 50% H₂O</td>
<td>9.47</td>
</tr>
<tr>
<td>H₂ – 60% H₂O</td>
<td>6.02</td>
</tr>
<tr>
<td>H₂ – 70% H₂O</td>
<td>1.55</td>
</tr>
<tr>
<td>Cathodic Exchange Current Density (A/cm²)</td>
<td>0.87</td>
</tr>
</tbody>
</table>
**Fuel Utilization Test: Performance Analysis**

- **Anodic Concentration Polarization:**

  \[
  \eta_{\text{conc},a} = \frac{RT}{4F} \ln \left( \frac{p_{o2}^{i,a}}{p_{o2}^{0,a}} \right)
  \]

  - \(p_{o2}^{i,a}\): Oxygen partial pressure at anode-electrolyte interface
  - \(p_{o2}^{0,a}\): Oxygen partial pressure outside anode surface

  **Determined by Local \(H_2-H_2O\) Equilibrium:**

  \[
  p_{o2} = \frac{p_{H_2O}^i}{Kp_{H_2}^2}
  \]

**Calculation of \(p_{o2}^{i,a}\)**

In Steady State,

\[
|U_{H_2}| = |U_{H_2O}| = \frac{i}{2F} \quad J_{H_2} + J_{H_2O} = 0
\]

\[
\begin{align*}
I_{H_2} &= -D_{H_2-H_2O}^{\text{eff}} V_{H_2} = -D_{H_2-H_2O}^{\text{eff}} \frac{p_{H_2}^i - p_{H_2}^0}{RTl_\alpha} \\
I_{H_2O} &= -D_{H_2-H_2O}^{\text{eff}} V_{H_2O} = -D_{H_2-H_2O}^{\text{eff}} \frac{p_{H_2O}^0 - p_{H_2O}^i}{RTl_\alpha}
\end{align*}
\]

\[
\begin{align*}
p_{H_2}^i &= p_{H_2}^0 - \frac{RTl_\alpha}{2FD_{H_2-H_2O}^{\text{eff}}}i \\
p_{H_2O}^i &= p_{H_2O}^0 + \frac{RTl_\alpha}{2FD_{H_2-H_2O}^{\text{eff}}}i
\end{align*}
\]
**Anodic Concentration Polarization:**

\[
\eta_{\text{conc,a}} = \frac{RT}{4F} \ln \left( \frac{p_{02}^{i,a}}{p_{02}^0} \right)
\]

\[
= \frac{RT}{2F} \ln \left[ \frac{1}{p_{H2}^0} + \frac{\frac{RTl_a}{2FD_{H2-H2O}^{\text{eff}}} i}{p_{H2}^{0,a}} \right] \left( 1 + \frac{\frac{RTl_a}{2FD_{H2-H2O}^{\text{eff}}} i}{p_{H20}^{0,a}} \right)
\]

- Anodic concentration polarization is low when the fuel is in the intermediate \( H_2O \) partial pressure region.

- Anode active layer had no significant effect on anodic concentration polarization.
**Fuel Utilization Test: Polarization Analysis**

- Anodic Electrode Polarization Loss:
  - With Anode Active Layer
  - Without Anode Active Layer

**Activation Polarization: Dominant Loss at High Fuel Utilization**

⇒ Significantly Reduced by Anode Active Layer
Advanced Cathode Investigation: Background

- Cathode Polarization Loss: Major Difficulty in Lowering the Operating Temperature

- A site-doped Lanthanum Cobaltite
  - High Catalytic Activity and Mixed Electronic-Ionic Conductivity
  - High Thermal Expansion Coefficient
  - Solid State Reaction with YSZ at Low Temperature

- A site-doped Lanthanum Ferrite
  - High Catalytic Activity and Mixed Electronic-Ionic Conductivity
  - Adjustable Thermal Expansion
  - No Solid State Reaction with YSZ up to 1400°C
  - Diffusion of Zr$^{4+}$ into Lanthanum Ferrite: Doped Ceria Interlayer

- Calcium-doped Lanthanum Ferrite
  - Defect Model $\rho_{O_2}$ - Weight Relationship
  - Thermogravimetry Measurements $\Rightarrow$ Equilibrium Defect Concentration
  - Electrical Conductivity Measurements $\Rightarrow$ Hole Mobility
Point Defect Model for $(La_{0.8}Ca_{0.2})_{0.95}FeO_{3-\delta}$

<table>
<thead>
<tr>
<th>A-site</th>
<th>B-site</th>
<th>O-site</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La_{La}^{x}$</td>
<td>$Fe_{Fe}^{x}$</td>
<td>$O_{O}^{x}$</td>
</tr>
<tr>
<td>$Ca_{La}'$ = 0.2×0.95</td>
<td>$Fe_{Fe}^{*}$</td>
<td>$V_{O}^{**}$</td>
</tr>
<tr>
<td>$V_{La}'''$ = 0.05</td>
<td>$Fe_{Fe}^{*}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Fe_{Fe}^{*}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Fe_{Fe}^{*}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$V_{Fe}'''$ = 0</td>
<td></td>
</tr>
</tbody>
</table>

- **Oxygen Incorporation Reaction**
  \[ V_{O}^{**} + 2Fe_{Fe}^{x} + \frac{1}{2}O_2 \leftrightarrow O_{O}^{x} + 2Fe_{Fe}^{*} \]
  \[ K_{ox} = \frac{[O_{O}^{x}][Fe_{Fe}^{2}]}{[V_{O}^{**}][Fe_{Fe}^{x}]^{1/2}p_{O_2}^{1/2}} \]

- **Charge Disproportionation Reaction**
  \[ 2Fe_{Fe}^{x} \leftrightarrow Fe_{Fe}^{*} + Fe_{Fe}^{*} \]
  \[ [Fe_{Fe}^{*}] \approx 0 \ @ \ 0.001\text{atm} \leq p_{O_2} \leq 1\text{atm} \]

- **Schottky Equilibrium Reaction**
  \[ n\Omega \leftrightarrow V_{La}^{III} + V_{Fe}^{III} + 3V_{O}^{**} \]
  \[ [V_{Fe}^{III}] \approx 0 \]
### Charge Neutrality Condition

\[
2[V_0^{••}] + [\text{Fe}^{••}_{\text{Fe}}] = [\text{Ca}^{•}_{\text{La}}] + 3[V_{\text{La}}^{•••}] \quad \Rightarrow \quad [\text{Fe}^{••}_{\text{Fe}}] = [\text{Ca}^{•}_{\text{La}}] + 3[V_{\text{La}}^{•••}] - 2[V_0^{••}] = 0.2 \times 0.95 = 0.19
\]

### A-site Restriction

\[
[\text{La}^x_{\text{La}}] + [\text{Ca}^{•}_{\text{La}}] + [V_{\text{La}}^{•••}] = 1
\]

### B-site Restriction

\[
[\text{Fe}^x_{\text{Fe}}] + [\text{Fe}^{••}_{\text{Fe}}] = 1 \quad \Rightarrow \quad [\text{Fe}^x_{\text{Fe}}] = 1 - [\text{Fe}^{••}_{\text{Fe}}] = 1 - [\text{Ca}^{•}_{\text{La}}] - 3[V_{\text{La}}^{•••}] + 2[V_0^{••}] = 0.2 \times 0.95 = 0.19
\]

### O-site Restriction

\[
[O_0^{••}] + [V_0^{••}] = 3 \quad \Rightarrow \quad [O_0^{••}] = 3 - [V_0^{••}]
\]

### Mass Action Coefficient for Oxygen Exchange Reaction

\[
K_{\text{ox}} = \frac{[O_0^{••}][\text{Fe}^{••}_{\text{Fe}}]^2}{[V_0^{••}][\text{Fe}^x_{\text{Fe}}]^2 p_{O_2}^{1/2}}
\]

\[
K_{\text{ox}} = \frac{(3 - [V_0^{••}])([\text{Ca}^{•}_{\text{La}}] + 3[V_{\text{La}}^{•••}] - 2[V_0^{••}])^2}{[V_0^{••}](1 - [\text{Ca}^{•}_{\text{La}}] - 3[V_{\text{La}}^{•••}] + 2[V_0^{••}])^2} \cdot \frac{1}{p_{O_2}^{1/2}}
\]
Relationship between $p_{O_2}$ and Weight of $(La_{0.8}Ca_{0.2})_{0.95}FeO_{3-\delta}$

\[ K_{Ox} = \frac{(3 - [V_0^{\bullet\bullet\bullet}])([Ca_{La}'] + 3[V_{La}''''] - 2[V_0^{\bullet\bullet}])^2}{[V_0^{\bullet\bullet\bullet}](1 - [Ca_{La}'] - 3[V_{La}''''] + 2[V_0^{\bullet\bullet}])^2} \cdot \frac{1}{p_{O_2}^{1/2}} \]

\[ M_{LCF} = n \times m_{LCF} = n \times [(0.8 \times m_{La} + 0.2 \times m_{Ca}) \times 0.95 + m_{Fe} + (3 - \delta) \times m_{O}] \]

\[ \delta = [V_0^{\bullet\bullet\bullet}] = 13.56 - 0.0625 \times \frac{M_{LCF}}{n} \]

\[ p_{O_2} = \frac{1}{K_{Ox}^2} \times \frac{(-10.56 + 0.0625 \times \frac{M_{LCF}}{n})^2}{(13.56 - 0.0625 \times \frac{M_{LCF}}{n})^2} \left( -26.78 + 0.125 \times \frac{M_{LCF}}{n} \right)^4 \]
Thermogravimetry Measurements

\[
p_{O_2} = \frac{1}{K_{ox}^2} \times \left( \frac{-10.56 + 0.0625 \times \frac{M_{ICE}}{n}}{13.56 - 0.0625 \times \frac{M_{ICE}}{n}} \right)^2 \left( \frac{-26.78 + 0.125 \times \frac{M_{ICE}}{n}}{27.78 + 0.125 \times \frac{M_{ICE}}{n}} \right)^4
\]

\[n = 0.00049\text{ mol}\]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>850°C</th>
<th>800°C</th>
<th>750°C</th>
<th>700°C</th>
<th>650°C</th>
<th>600°C</th>
<th>550°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{ox})</td>
<td>186</td>
<td>235</td>
<td>317</td>
<td>376</td>
<td>504</td>
<td>630</td>
<td>813</td>
</tr>
</tbody>
</table>
**Advanced Cathode Investigation: Defect Equilibrium**

- **Equilibrium Defect Concentration**
  - **High** $p_{O_2}$ range
    - $[V_0^{\cdot\cdot\cdot}]$: low
    - Charge neutrality is maintained by hole formation.
  - **Low** $p_{O_2}$ range
    - $[V_0^{\cdot\cdot\cdot}]$: high
    - Hole concentration decreases.

- **$\text{ln}(K_{ox})$ vs. $1/T$**
  - Linear Fit
  - Slope = $-\Delta H_{ox}^o / R$

### Equations

\[
\text{ln}(K_{ox}) = \frac{-\Delta H_{ox}^o}{RT} + \frac{\Delta S_{ox}^o}{R}
\]

- $\Delta H_{ox}^o = -37.5 \text{ kJ mol}^{-1}$
- $\Delta S_{ox}^o = 10.6 \text{ J mol}^{-1} \text{ K}^{-1}$
**Electrical Conductivity Measurements**

- **Conductivity vs. Temperature**
  
  - $\sigma_t = \sigma_e + \sigma_i \approx \sigma_e$

- **Mobility vs. Temperature**

  - $\mu = \frac{[\text{Fe}^4\text{Fe}]^*}{q}$

- **Key Points**
  - $p_0^2 \uparrow \Rightarrow \sigma_e \uparrow$: $\rho$-type conductor
  - Lower Temperature: Thermally Activated Behavior (Small Polaron Hopping)
  - High Temperature: Decrease in Hole Concentration
  - $p_0^2 \downarrow$, $T \uparrow \Rightarrow [\text{Vo}^-] \uparrow$
  - Hopping Conduction Via Fe$^{4+}$-O-Fe$^{3+}$ Chain
  - Vo$: Scattering Centers or Random Traps for Electrons
Advanced Cathode Investigation: Conduction Mechanism

- Adiabatic Small Polaron Hopping

\[
\mu_p = \frac{(1 - [\text{Fe}^*_F \text{e}])q_a^2v}{kT} \exp \left( - \frac{E_A}{kT} \right)
\]

- Non-adiabatic Small Polaron Hopping

\[
\mu_p = \frac{(1 - [\text{Fe}^*_F \text{e}])q_a^2v}{kT} P \exp \left( - \frac{E_A}{kT} \right)
\]

\[P = \frac{I^2}{2\hbar} \left( \frac{e}{E_d kT} \right)^{1/2}\]

### Table: Activation Energy and R² Values

<table>
<thead>
<tr>
<th>(P_{O_2}) (atm)</th>
<th>Adiabatic Case</th>
<th>Non-adiabatic Case</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activation Energy (eV)</td>
<td>(R^2)</td>
</tr>
<tr>
<td>1</td>
<td>0.108</td>
<td>0.99353</td>
</tr>
<tr>
<td>0.21</td>
<td>0.111</td>
<td>0.99344</td>
</tr>
<tr>
<td>0.05</td>
<td>0.195</td>
<td>0.99423</td>
</tr>
<tr>
<td>0.001</td>
<td>0.272</td>
<td>0.98927</td>
</tr>
</tbody>
</table>
**SUMMARY**

- Successfully developed single-step un-constrained co-firing of the solid oxide fuel cell @ 1300°C.
- Modeled cell performance.
- Achieved maximum power density of 1.50 W/cm² at 800°C and 0.87 W/cm² at 700°C with humidified hydrogen (3% H₂O) and air.
- Simulated the effect of practical fuel utilization on single cell performance.
- Improved cell performance at high fuel utilization by employing anode active layer.
- Investigated defect chemistry and electrical conduction mechanism of novel cathode material (calcium-doped lanthanum ferrite).

**FUTURE WORK**

- Employ advanced cathode material in co-firing process.
- Analyze performance at low operating temperature (600-700°C).
Publication List

Journal Papers


5. Kyung Joong Yoon, Peter Zink, Larry Pederson, Srikanth Gopalan, Uday B. Pal, “Defect Chemistry and Electrical Properties of $(La_{0.8}Ca_{0.2})_{0.95}FeO_3$,” in preparation (2009).

Conference Proceedings


Thank you!