Scalable and Cost Effective Barrier Layer Coating to Improve Stability and Performance of SOFC Cathode

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- Important Factors: K, D, δe, etc.
- Un-settled Issues: ORR Details
- Implications to Industrial Applications

M. Gong, R. Gemmen, X. Liu*, Journal of Power Sources 201 (2012) 204-218
Realistic Composite Cathodes, Effects of Morphology

- Porosity
- Surface area
- Grain size
- Grain boundary
- MIEC/IC ratio
- Etc.

C/Air interface
Ionic current = 0, Electronic potential prescribed, Oxygen concentration prescribed, and flux of all Other species (coverages and vacancies) is zero

C/E Interface
Electronic current = 0, Ionic potential prescribed, YSZ oxygen vacancy is prescribed, All other fluxes are zero
Performance and Durability Implications

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- Chemical reaction with YSZ electrolyte.

\[
La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_{12}(s) \quad SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s)
\]

- Strontium segregation related issues

\[
2Sr^{\prime}_{La} + V_{O,LSCF}^{\bullet\bullet} + 2O^x \leftrightarrow 2SrO(s)
\]

- Poisoning of the cathode (e.g. by chromium species etc.)

\[
SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s) \quad SrO(s) + CO_2(g) \rightarrow SrCO_3(s)
\]

- Etc.
Approaches for Degradation Mitigation

• Microstructural changes (loss effective TPB area)
  o Grain growth
  o Coarsening of the particles
  o Surface re-construction
• No easy solutions

• Chemical reaction with YSZ electrolyte.
• Barrier Layers

• Strontium segregation related issues
• Coating, Infiltration, Sr-free cathodes (maybe)

• Poisoning of the cathode (e.g. by chromium species etc.)
• Interconnect coatings, impurity tolerant cathodes etc.
SOFC Cathode Barrier Layers

• Chemical Compositions (GDC, SDC, etc.)
• Coating Methods (Screen Printing + Sintering)
• Functions
  • Avoid Zirconate Formation
  • Improve ORR
• Current Issues
  • Porosity
  • Thickness
Project Objectives

• **Aim 1:** To develop a scalable and cost-effective electrophoretic deposition (EPD) coating process to achieve a dense barrier layer between an YSZ electrolyte and the cathode in a solid oxide fuel cell (SOFC) to significantly improve both stability and performance of SOFC cathodes

• **Aim 2:** To systematically investigate the interaction between doped ceria barrier layers and (La,Sr)(Co,Fe)O$_3$ (LSCF) cathode and the effects on oxygen reduction reaction (ORR) kinetics, electrochemical performance, and long-term stability of cathodes

• **Aim 3:** To achieve optimal barrier layer thickness.
Aim 1: Electrophoretic Deposition (EPD)

Sketch of EPD Process

Cross-section of EPD (Mn,Co)$_3$O$_4$ coating on 441 stainless steel developed by WVU.

## Aim 1: EPD vs. Other Possible Coating Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Screen Printing</th>
<th>Dip Coating</th>
<th>Spin Coating</th>
<th>Electroplating</th>
<th>Thermal Spray</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Green-body Porosity</strong></td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Coating time (~5μm)</td>
<td>Seconds/minutes</td>
<td>Seconds/minutes</td>
<td>Seconds/minutes</td>
<td>Minutes/hours</td>
<td>Seconds</td>
</tr>
<tr>
<td>Cost</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Scalable</td>
<td>Yes</td>
<td>Yes</td>
<td>Difficult</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Composition Control</td>
<td>Easy</td>
<td>Easy</td>
<td>Easy</td>
<td>Moderate</td>
<td>Easy</td>
</tr>
<tr>
<td>Coating time (~5μm)</td>
<td>Easy</td>
<td>Easy/moderate</td>
<td>Easy/moderate</td>
<td>Moderate</td>
<td>Difficult</td>
</tr>
<tr>
<td>Cost</td>
<td>Difficult</td>
<td>Easy</td>
<td>Moderate</td>
<td>Easy/moderate</td>
<td>Easy</td>
</tr>
<tr>
<td>Scalable</td>
<td>Required</td>
<td>Required</td>
<td>Required</td>
<td>Usually not</td>
<td>Usually not</td>
</tr>
</tbody>
</table>

**Method** | **Tape Casting** | **PLD** | **RF Sputtering** | **CVD/ALD** | **EPD**

| **Green-body Porosity**     | High            | Low         | Low          | Low            | Low           |
| Coating time (~5μm)         | Seconds/minutes | Hours       | Hours        | Hours          | Several minutes |
| Cost                        | Low             | High        | High         | High           | Low           |
| Scalable                    | Yes             | No          | Yes          | Yes            | Yes           |
| Composition Control         | Easy            | Moderate    | Moderate     | Moderate       | Easy          |
| Coating time (~5μm)         | Easy            | Moderate    | Moderate     | Easy/moderate  | Easy          |
| Cost                        | Difficult       | Easy/moderate | Easy/moderate | Easy/moderate | Easy/moderate |
| Scalable                    | Required        | Usually not | Usually not  | Usually not    | Required³     |
Aim 1: Major Technical Challenges for EPD

- **Suspension Issues**
  - Conductivity
  - Compatibility with particles & Substrates
  - Stability
- **Non-Conductive Substrates**
- **Sintering Optimization**
  - Sintering Temperature & Atmospheres
  - Sintering Aids
**Aim 1**: Preliminary Results - Suspension

**Substrates**: Stainless Steel, Graphite

**Results**: Dense GDC layer formed on cathodic substrate; GDC particles in ethanol are positively charged
Aim 1: Preliminary Results – Non-Conductive Substrates

Possible Solutions: Carbon Coating vs. Porous Substrates

Preliminary Results: We coated a layer of carbon/graphite on YSZ pellet by spin coating, tap casting, spray, sputtering, but the preliminary results showed the cohesiveness of carbon/graphite layer is very poor and the conductivity is low.

Aim 1: Preliminary Results – Non-Conductive Substrates

Possible Solutions: In-situ forming a conducting Polymer Layer

Aim 1: Preliminary Results – Non-Conductive Substrates

Possible Solutions: In-situ forming a conducting Polymer Layer
Aim 1: Preliminary Results – Reducing Sintering Temperature

Fracture cross sectional SEM images taken after testing of cells with 1 mol% Fe2O3 in the YSZ layers and GDC layers with 1 (a), 2 (b), or 3 (c) mol% Fe2O3.

Voltage and power density versus current density, measured at different temperatures in air and humidified hydrogen.

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

Good performance for YCCC and YCCN

Combination of high electronic conductivity and activity from B site elements.

0.5 \( \Omega \text{cm}^2 \) for YCCC on SSZ at 850\( ^\circ \text{C} \)

Two-arc profiles for all electrodes

Two electrolytes used: YSZ, SSZ \( \rightarrow \) Better performance from SSZ/GDC?

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

Table I. $R$, $C$ and $f_0$ for HF and LF arcs of four electrodes after fitting at 850 °C, and the corresponding $E_a$ as well as reaction order ($n$) in the temperature and $P_{H2}$ ranges used in the work.

<table>
<thead>
<tr>
<th>In wet H$_2$ at 850 °C</th>
<th>$R$ (Ωcm$^2$)</th>
<th>$C$ (F/cm$^2$)</th>
<th>$f_0$ (Hz)</th>
<th>$E_a$ (eV)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF arc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YCCC-YSZ</td>
<td>0.65</td>
<td>5.2×10$^{-5}$</td>
<td>3500</td>
<td>1.0</td>
<td>0.25~0.33</td>
</tr>
<tr>
<td>YCCC-SSZ</td>
<td>0.22</td>
<td>1.1×10$^{-4}$</td>
<td>2300</td>
<td>1.1</td>
<td>0.16~0.30</td>
</tr>
<tr>
<td>YCCN-YSZ</td>
<td>5.2</td>
<td>5.3×10$^{-5}$</td>
<td>530</td>
<td>1.6</td>
<td>0.10~0.16</td>
</tr>
<tr>
<td>YCCN-SSZ</td>
<td>0.96</td>
<td>8.3×10$^{-5}$</td>
<td>1900</td>
<td>1.6</td>
<td>0.10~0.28</td>
</tr>
<tr>
<td>LF arc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YCCC-YSZ</td>
<td>0.33</td>
<td>6.9×10$^{-3}$</td>
<td>70</td>
<td>0.8</td>
<td>0.34~0.50</td>
</tr>
<tr>
<td>YCCC-SSZ</td>
<td>0.27</td>
<td>1.6×10$^{-2}$</td>
<td>70</td>
<td>0.6</td>
<td>0.46~0.60</td>
</tr>
<tr>
<td>YCCN-YSZ</td>
<td>3.2</td>
<td>1.1×10$^{-3}$</td>
<td>45</td>
<td>0.6</td>
<td>0.18~0.37</td>
</tr>
<tr>
<td>YCCN-SSZ</td>
<td>0.66</td>
<td>2.3×10$^{-3}$</td>
<td>100</td>
<td>0.9</td>
<td>0.51~0.70</td>
</tr>
</tbody>
</table>

Table II. Summary of $R$, $C$ and $f_0$ for these four electrodes tested in air at 850 °C, as well as $E_a$ in the temperature range of 650~850 °C.

<table>
<thead>
<tr>
<th>In air at 850 °C</th>
<th>$R$ (Ωcm$^2$)</th>
<th>$C$ (F/cm$^2$)</th>
<th>$f_0$ (Hz)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YCCC-YSZ</td>
<td>Single arc</td>
<td>1.2</td>
<td>1.1×10$^{-3}$</td>
<td>112</td>
</tr>
<tr>
<td>YCCC-SSZ</td>
<td>Single arc</td>
<td>1.0</td>
<td>1.4×10$^{-3}$</td>
<td>50</td>
</tr>
<tr>
<td>YCCN-YSZ</td>
<td>Single arc</td>
<td>36.7</td>
<td>1.5×10$^{-4}$</td>
<td>30</td>
</tr>
<tr>
<td>YCCN-SSZ</td>
<td>HF arc</td>
<td>12.6</td>
<td>3.8×10$^{-4}$</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>LF arc</td>
<td>8.7</td>
<td>1.2×10$^{-3}$</td>
<td>5</td>
</tr>
</tbody>
</table>
Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

Having no effect on reaction occurring here

Oxygen exchange

\[ \text{O}_2 + 2V_{\text{O}_{\text{LSCF}}}^{\text{**}} + 4e \leftrightarrow 2O_{\text{O}_{\text{LSCF}}}^{\text{X}} \]

3PB charge transfer

\[ V_{\text{O}_{\text{electrode}}}^{\text{**}} + O_{\text{ads}}^{2-} + e \leftrightarrow O_{\text{O}_{\text{electrode}}}^{X} \]

2PB contribution

Electrolyte

Interface ion transfer

\[ V_{\text{O}_{\text{electrode}}}^{\text{**}} = O_{\text{O}_{\text{LSCF}}}^{X} \leftrightarrow O_{\text{O}_{\text{electrode}}}^{X} + V_{\text{O}_{\text{LSCF}}}^{\text{**}} \]

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

How electrolyte improve the non-charge transfer processes?

B-V eqn. for charge transfer at cathode side:

\[ j_{ct} = j_{ct}^0 \left( \frac{c_{O^-}}{c_{O^-}^0} \right) \exp(-\alpha \eta) - \exp[(1-\alpha)f\eta] \]

- Increased charge transfer exchange current
- Under the same overpotential, more \( O^- \) is consumed
- Lowered concentration of \( O^- \) species right outside electrolyte

**YSZ**→**SSZ/GDC**

- Gradient increases
- More areas are activated in \( O^- \) adsorption and diffusion processes
- Gradient of \( O^- \) spread far away to recover reduction of \( O^- \)
- Gradient increases

Current is steady but bigger at last

Not only charge transfer is increased, but active site for surface processes is also increased

**Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics**

![Graph showing the effect of electrolyte on ORR kinetics]

**Improved charge transfer and surface processes on SSZ/GDC electrolyte**

Aim 3: Optimized Barrier Layers Thickness

Diffusion profile observed in GDC that had been annealed at 1200°C for 115 h with LSF [Ref. 1].

Bulk diffusivities as function of temperature [Ref. 2].


Aim 3: Optimized Barrier Layers Thickness

Objectives: Understand Cation diffusion & Zirconate formation kinetics in the vicinity of barrier layer as function of temperature, overpotential, barrier layer thickness etc.

Approaches: Secondary Ions Mass Spectroscopy (SIMS)

Cross-sectional transmission electron microscopy (XTEM)

3-D Atom-Probe Tomography (3-D APT)

*In operando* EIS
Summary & Future Work

We have
- Demonstrated the feasibility of EPD barrier layer on YSZ
- Demonstrated the beneficial effect of sintering aids to reduce sintering temperature
- Started the investigation on ORR kinetics at Cathode/Barrier layer interface
- Initiated the characterization of cation diffusion profile in barrier layer

We are going to
- Optimize the EPD process
- Quantify the cation diffusion & zirconate formation kinetics as function of operation parameters and barrier layer thickness
- Test in industrial setting
Acknowledgement

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