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

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SOFC Cathode Barrier Layers

• Chemical Compositions (GDC, SDC, etc.)
• Coating Methods (Screen Printing + Sintering)
• Functions
  • Avoid Zirconate Formation
  • Improve ORR
• Current Issues
  • Porosity
  • Thickness
Electrolyte/Barrier Layer Effect on ORR Kinetics

Having no effect on reaction occurring here

\[
\text{Oxygen exchange:} \quad \text{O}_2 + 2\text{V}^{**}_{\text{O LSCF}} + 4e \leftrightarrow 2\text{O}^X_{\text{O LSCF}}^{**}
\]

3PB charge transfer:

\[
\text{V}^{**}_{\text{0 electrolyte}} + \text{O}^X_{\text{ads}} + e \leftrightarrow \text{O}^X_{\text{0 electrolyte}}^{**}
\]

Interface ion transfer:

\[
\text{V}^{**}_{\text{0 electrolyte}} + \text{O}^X_{\text{0 LSCF}} \leftrightarrow \text{O}^X_{\text{0 electrolyte}} + \text{V}^{**}_{\text{O LSCF}}
\]

2PB contribution

In wet H₂ @850°C


affect these two reactions
Aim 1 - Develop a scalable and cost-effective electrophoretic deposition (EPD) coating process to form a dense barrier layer between a YSZ electrolyte and the cathode in a SOFC.

Aim 2 - Characterize the Sr diffusion/distribution across barrier layer with the aim to determine optimum barrier layer thickness.
## EPD vs. Other Possible Coatings

<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>
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<tbody>
<tr>
<td>Green-body Porosity</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
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<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>
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<tr>
<td>Cost</td>
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<td>Low</td>
<td>Low</td>
<td>Medium</td>
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<tr>
<td>Scalable</td>
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<td>Yes</td>
<td>Difficult</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>Composition Control</td>
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<td>Easy</td>
<td>Easy</td>
<td>Moderate</td>
<td>Easy</td>
</tr>
<tr>
<td>Thickness Control (~5μm)</td>
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<td>Easy/ moderate</td>
<td>Easy/ moderate</td>
<td>Moderate</td>
<td>Difficult</td>
</tr>
<tr>
<td>Coat on non-flat surface</td>
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<td>Easy</td>
<td>Moderate</td>
<td>Easy/moderate</td>
<td>Easy</td>
</tr>
<tr>
<td>Sintering</td>
<td>Required</td>
<td>Required</td>
<td>Required</td>
<td>Usually not</td>
<td>Usually not</td>
</tr>
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</table>

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<thead>
<tr>
<th>Method</th>
<th>Tape Casting</th>
<th>PLD</th>
<th>RF Sputtering$^1$</th>
<th>CVD/ALD</th>
<th>EPD$^2$</th>
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<td>Low</td>
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<td>Low</td>
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<tr>
<td>Coating time (~5μm)</td>
<td>Seconds/minutes</td>
<td>Hours</td>
<td>Hours</td>
<td>Hours</td>
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<tr>
<td>Cost</td>
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<td>Low</td>
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<tr>
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<td>Moderate</td>
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<td>Usually not</td>
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<td>Required$^3$</td>
</tr>
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Movement of Particles during EPD

Driving force:
The interaction of the surface charge with the electric field (accelerate particle)

Drag forces:
1 Viscous drag from the liquid
2 The force exerted by the electric field on the counter-ions in the double layer
3 When a particle moves, the distortion in the double layer caused by a displacement between the center of the negative and positive charge
- Suspension: 100ml ethanol + 1.5g GDC + 1g iodine
- Zeta-potential: 18 mV
- Substrates: Stainless steel
- Voltage: 50V
- Time: 2min
- Distance: 1cm

- GDC Particles are positively charged (absorbed H+)

\[ 2\text{CH}_3\text{CH}_2\text{OH} + \text{I}_2 \rightarrow 2\text{CH}_3\text{CHOH} + 2\text{HI} \rightarrow 2\text{CH}_3\text{CHOH} + 2\text{H}^+ + 2\text{I}^- \]
Conductive Substrate

- In-situ synthesis of polypyrrole
- Easy and industrial viable

Schematic of polypyrrole synthesis process

NDA: 2-6-naphthalene-difulfonic acid disodium salt

APS: ammonium peroxydisulfate
Possible Solutions: In-situ forming a conducting Polymer Layer
Results in 2016 – Conductive Polymer

- Uniform layer of Ppy
- Thickness less than 1μm
- Conductivity is about 9 S/cm

(a) Cross-section and (b) microstructure of polypyrrole coated on YSZ before sintering

(a) WVUSRF 20.0kV 12.0mm x4.50k SE(M) 10.0μm
(b) WVUSRF 20.0kV 12.0mm x4.50k SE(M) 10.0μm
Results in 2016 - Deposited GDC by EPD

Microstructure of deposited GDC before sintering

Cross-section and (b) surface morphology of GDC layer before sintering
The hydrogen gas bubble will impair the density of GDC layer

Two type of $H^+$: free $H^+$; absorbed $H^+$

$H^+$ can pass through GDC deposit to cathode and reduced under DC electric field

Note: hydrogen gas pass through the GDC deposit and impair the density and adhesion between GDC and YSZ
Optimal Voltage

- Uniformness and thickness of deposit depends on applied voltage

The deposit for 10 mins as a function of applied voltage (a) 60V, (b) 80V, (c) 100V, (d) 120V, (e) 140V and (f) 160V
• Good adhesion between GDC and YSZ after sintering when voltage is not larger than 100V

Cross-sectional morphology of the deposit for 10 mins as a function of applied voltage (a) 60V, (b) 80V, (c) 100V, (d) 120V, (e) 140V and (f) 160V
Rate-Determining Step

• Constant current under constant voltage  
  constant deposition rate
• H+ accumulation zone near cathode
• The reduction of H+ is the rate-determining step

(a) current and (b) pH near the cathode as a function of time under constant voltage
• The thickness of deposit is proportional to time

Thickness as a function of time for a GDC/ethanol suspension, under constant-voltage conditions (100V) when using polypyrrole coated YSZ as the cathodic electrode
AC EPD of GDC

- A uniform layer of GDC can be formed by EPD
- AC-EPD can improve the density

Microstructure of pure GDC layer formed by (a, b) DC and (c) AC-EPD after sintering at 1300°C; (d) schematic of symmetric AC signal
Effect of Sintering Aid

- Iron oxide can be used as sintering aid to improve the density of GDC
- Dense GDC layer can be obtained at 1300°C by DC-EPD
- AC-EPD can decrease the densification temperature to 1250°C

![Figure 12](image1.png)
Fig. 12 (a) cross-section and (b) surface morphology of GDC layer with 2mol% FeO$_{1.5}$ after sintering at 1300°C

![Figure 13](image2.png)
Fig. 13 cross-section of GDC layer with 2mol% FeO$_{1.5}$ formed by (a) DC and (b) 100kHz AC EPD after sintering at 1250°C
LSCF fired at 1000°C

- No Sr diffusion to YSZ

Fig. 17 EDAX analysis of LSCF/GDC/YSZ before after long-time stability test
Performance of Symmetric cell

- Compared with spin coating, the total Ohmic resistance of symmetric cell with GDC formed by EPD is smaller.

![Graphs showing performance comparisons](image)

**EIS at 750°C and temperature dependence of Ohmic resistance of symmetric cell with GDC layer with sintering aid formed by spin coating and EPD**

Cross-section micrograph of symmetric cell formed by (a) spin coating and (b) EPD.
Aim 1 - Summary

1. 100V is the optimal voltage for the suspension. The rate-determining step is the reduction of H\(^+\).

2. A uniform layer of GDC can be formed by EPD with a constant deposition rate under 100V.

3. Dense GDC layer can be obtained at 1300\(^\circ\)C by DC-EPD, densification temperature can be decreased to 1250\(^\circ\)C by AC-EPD.

4. Compared with spin coating, the total Ohmic resistance of symmetric cell with GDC formed by EPD is smaller.
Aim 2: Characterization of GDC Barrier Layers

§ Co-fired GDC/YSZ bi-layer electrolytes
   – Cross-sectional SEM-EDS, TEM-EDS
   – Atom-probe tomography

§ GDC barriers made by WVU
   – Cross-sectional SEM-EDS
§ Reduced firing temperature yields fairly dense thin GDC layers with little GDC/YSZ interdiffusion
  – GDC thicknesses varied from 1.5 to 6.0 microns
§ LSCF layer applied
  – Fired at 1000, 1100, or 1200 °C
§ Aim: explore interdiffusion effect over range of conditions
§ 1.5 micron thick GDC
§ Sr segregation to YSZ/GDC interface detected for 1200, not 1000 or 1100 C
§ Little Sr at typical LSCF firing temperature of 1100 C
§ Apparent Sr in YSZ layer due to Sr/Y peak overlap
§ Thicker GDC layer appears to prevent Sr diffusion even at 1200°C.
Effect of GDC Pores

Defects in GDC layer allow Sr diffusion to GDC/YSZ interface

Example shown is a 3 micron thick GDC layer
Transmission Electron Microscopy

Above results show limited Sr at GDC/YSZ interface for 1.5 micron, 1200 C case
TEM with energy dispersive x-ray spectroscopy (EDS) used to explore at higher resolution
§SrZrO$_3$ detected in selected areas
- No SrZrO3 detected at void-free location
Thick SrZrO$_3$ layer detected near GDC void
- Barrier layer shows limited porosity
- No evidence of Sr accumulation at GDC/YSZ interface
  - Apparent Sr in YSZ layer is an artifact of peak overlap (with Y)
LSCF Fired at 1100 C: SEM-EDS

- Clear evidence of Sr segregation to GDC/YSZ interface
- La, Fe, and Co also appear to be present
LSCF Fired at 1200 C

- More pronounced Sr segregation, along with La, Fe, and Co
Aim 2: Summary and Conclusions

§ Reduced-temperature co-firing yields reasonably dense GDC barrier with minimal GDC/YSZ interdiffusion
  – Even a 1.5 micron co-fired barrier provides good protection for 1100°C firing
  – 1200°C causes considerable zirconate formation, unless a thicker GDC layer is used
  – Zirconate forms at defects/pores in the GDC layer

§ WVU GDC layer shows greater porosity but is thicker
  – Effective as a barrier layer at 1000°C, but some zirconate formation at 1100 & 1200°C
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Stefan Megel, Fraunhofer-IKTS
James Swistock, Penn Cara Energy
SOFC Cathode Degradation

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction

- Strontium segregation related issues
  \[ 2Sr_{La}^* + V_{O,LSCF}^{**} + 2O_O^x \leftrightarrow 2SrO(s) \]

- Chemical reaction with YSZ electrolyte.
  \[ La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_3(s) \quad SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s) \]

- Poisoning of the cathode (e.g. by CO\(_2\), chromium species etc.)
  \[ SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s) \quad SrO(s) + CO_2(g) \rightarrow SrCO_3(s) \]
  \[ 2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4CrO_2(OH)_2(g) \]
**Atom Probe Tomography**

**Sr:**
- Present at ~ 0.2% in YSZ/GDC
- Higher concentration at boundary
- Depleted around boundary

**Co**
- Present only near boundary

**Fe:**
- Used as sintering aid at 0.2%
- Strongly segregated at boundary