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

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Background - SOFC Cathode Degradation

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

\[
2Sr_{La}^+ + V_{O,LSFC}^{**} + 2O_O^x \leftrightarrow 2SrO(s)
\]

- 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.)

\[
SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s) \quad SrO(s) + CO_2(g) \rightarrow SrCO_3(s)
2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4CrO_2(OH)_2(g)
\]
SOFC Cathode Barrier Layers

- Chemical Compositions (GDC, SDC, etc.)
- Coating Methods (Screen Printing, Spray etc.)
- Functions
  - Avoid Zirconate Formation
  - Improve ORR
- Current Issues
  - Porosity
  - Thickness
Research Objectives

- **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.
Major Technical Challenges

- Suspension stability
- Non-conductive YSZ substrate
- Non-shrinking pre-sintered YSZ substrate
Prepare stable suspensions

Develop conductive substrates

**DC EPD**
- Deposition kinetics
- Deposition mechanisms
- Substrate conductivity effects

**AC EPD**
- Deposition mechanisms
- Effect of duty cycles
- Effect of voltages
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
Preparing stable suspension

- 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+)

\[
2\text{CH}_3\text{CH}_2\text{OH}+\text{I}_2 \rightarrow 2\text{CH}_3\text{CHOH}+2\text{HI} \rightarrow 2\text{CH}_3\text{CHOH}+2\text{H}^++2\text{I}^-
\]
In-situ formation of conductive substrate

- In-situ synthesis of polypyrrole
- Easy and commercial

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

APS: ammonium peroxysulfate

Schematic of polypyrrole synthesis process
In-situ formation of conductive substrate

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

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

- The conductivity of PPy is sufficient to carry out EPD experiment
- Deposition rate on PPy is slower than that on graphite

Distance: 1cm
Voltage: 60V

Deposit mass per unit area as a function of time under constant voltage (60 V) by using different cathode
The rate determining step of the deposition on PPy is the charge transfer step.

An H⁺ ion accumulation zone exists near PPy coated YSZ with a decrease of pH.

Initial pH: 3.87

pH near cathode after 10s: 2.09 < 3.87

The reduction of H⁺ at the cathode:

\[
H_{x=\infty}^+ \xrightarrow{\text{transport process}} H_{x=0}^+ \xrightarrow{\text{charge transfer}} \frac{1}{2} H_2
\]

Current as a function of time under constant voltage (60 V) using different cathode.
Increasing resistance

\[ R = \frac{U}{I} = R_1 + R_2 + R_3 = \frac{\rho_s (L - \delta_1)}{S} + \frac{\rho_d \delta_1}{S} + a \delta_2 \]

\[ = \frac{\rho_s L}{S} + \delta_1 \frac{(\rho_d - \rho_s)}{S} + k \delta_2 = C_1 + C_2 \delta_1 + k \delta_2 \]

R is the total resistance, Ω; \( \rho_s, \rho_d \) are the resistivity of suspension and the deposit, respectively, Ω cm, \( \rho_s < \rho_d \); L is the distance between two electrodes, cm; \( \delta_1 \) and \( \delta_2 \) are the thickness of deposit and the ion accumulation zone near cathode, respectively, cm; S is the area of the electrode, cm²; k, a constant, means k Ω for 1 cm ion depletion zone.

\( \delta_1 \) increases with time

Resistance distribution in the EPD cell using PPy coated YSZ as the cathode
Increasing resistance

- The thickness of the ion accumulation zone increases at the beginning, then decreases, finally the ion accumulation zone is replaced by an ion depletion zone.
- The main resistance is from the ion depletion/accumulation zone.

Variation of voltage as a function of time under **constant current** (0.016 A) using PPy coated YSZ as the cathode.

- **A-B**: Charging of the double layer.
- **B-C**: Ion accumulation zone (thickness increases).
- **C-D**: Ion accumulation zone (thickness decreases).
- **Point D**: minimum value (transition point).
- **D-E**: Ion depletion zone.
Schematic of EPD process on PPy coated YSZ

Increasing resistance

No ion accumulation zone

H⁺ ion accumulation zone

No H⁺ ion accumulation zone

Ion depletion zone
DC EPD efficiency

- Deposition rate increases the current density regardless of the conductivity of cathode.

**Average deposition rate and current as a function of time under constant voltage (60 V) when using (a) graphite and (b) PPy coated YSZ as the cathode.**
\( \frac{m}{m_0} Z e = Q_{ab} \)

\[ Q = \int I dt \]

Anode: \( 2H_2O - 4e^- \rightarrow 4H^+ + O_2 \)

Cathode: \( 2H^+ + 2e^- \rightarrow H_2 \)

or \( 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \)

\( \frac{m}{m_0} Z e = Q_{ab} = f Q_T \)

\( m \) is the deposit mass, g; \( m_0 \) is the average mass of a single particle, g; \( Z \) is the valence of a charged particle which is proportional to the zeta potential; \( e \) is the electronic charge, C; \( Q_{ab} \) is the charge quantity transferred resulted from the reduction of \( H^+ \) ions which desorbed from the particles, named as “absorbed \( H^+ \) ions”; \( Q_T \) is the total charge amount transferred during EPD process, C; \( f \), EPD efficiency, is the percentage of total charge transferred resulted from the reduction of absorbed \( H^+ \) ions, with a range from 0 to 1.
DC EPD efficiency

- $f$ is in the range from 0 to 0.5

1. The primary charge carriers are free ions.

2. Free $H^+$ ions moves faster than absorbed $H^+$ ions.

Schematic of EPD process

- Absorbed $H^+$ ion
- Free $H^+$ ion
- GDC particle

suspension deposit
DC EPD efficiency

- $f$ decreases with the increase of voltage or current density
- $f$ decreases with the increase of the conductivity of cathode due to hydrogen evolution

Same $Q_T$
Different $I$
Constant current

Cathode: $2H^+ + 2e^- \rightarrow H_2$

or $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Deposit mass per area as a function of current density under constant current and same total charges by using PPy coated YSZ and graphite as the cathode
• 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
Morphology of GDC layer

- a uniform layer of GDC can be formed by EPD

SEM top view of (a) green, (b) sintered GDC surface, and cross-sectional view of (c) green, (b) sintered GDC layer.
Morphology of GDC layer

- 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

Morphology of GDC with 2 mol% Fe$_2$O$_3$ formed by EPD after sintering at 1300°C
To minimize the bubble evolution during coating, to decrease the densification temperature, AC signal was used to avoid the electrochemical reaction.

\[ V_1, V_2: 0-100V \]
\[ D (duty cycle): 0-100\% \]
\[ f: 0\sim 400 \text{ kHz} \]

Equivalent circuit of electric double layer
- R\(_1\) is the resistance of the suspension;
- R\(_2\) is the resistance to faradaic current at the electrode surface;
- C\(_1\) is the differential capacity of the double layer.

f sufficiently high $\rightarrow$ No current flows through R\(_2\) $\rightarrow$ No electrochemical reaction or bubble evolution

Very low f $\rightarrow$ No current flows through C\(_1\) $\rightarrow$ electrochemical reaction occurs
AC frequency effect

- The deposition rate increases when the frequency increases from 10 Hz to 500 Hz, while decreases when further increases the frequency to 5000 Hz.

![Graph showing deposition mass as a function of frequency with peak at 500 Hz and decrease at 5000 Hz.

Deposit mass as a function of frequency of the AC power supply with a fixed $V_1/V_2$ ratio of 100/80 and a fixed duty cycle of 50% when using graphite as the cathode.
The deposition rate increases with the increase of voltage ratio.
The deposition rate increases with the increase of duty cycle.

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Deposit mass as a function of voltage ratio of the AC power supply with a fixed duty cycle of 50% and a fixed frequency of 500 Hz.

Deposit mass as a function of duty cycle of the AC power supply with a fixed $V_1/V_2$ voltage ratio of 100/80 and a fixed frequency of 500 Hz when using graphite as the cathode.
AC-EPD mechanism--desorption

- The deposit mass decreases a little when reversing the DC direction because of the bubble evolution derived from the electrolysis of water.
- Desorption of absorbed charge carrier is irreversible.

<table>
<thead>
<tr>
<th>Reversed EPD parameters</th>
<th>Deposit mass before reversed EPD/g</th>
<th>Deposit mass after reversed EPD/g</th>
<th>Decrease of deposit mass/g</th>
<th>Ratio of decrease/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 V, 5 min</td>
<td>0.1395</td>
<td>0.1344</td>
<td>0.0051</td>
<td>3.6559</td>
</tr>
<tr>
<td>80 V, 8 min</td>
<td>0.1385</td>
<td>0.1336</td>
<td>0.0049</td>
<td>3.5379</td>
</tr>
<tr>
<td>80 V, 10 min</td>
<td>0.1489</td>
<td>0.1437</td>
<td>0.0052</td>
<td>3.4923</td>
</tr>
<tr>
<td>80 V, 12.5 min</td>
<td>0.1481</td>
<td>0.1431</td>
<td>0.005</td>
<td>3.3761</td>
</tr>
<tr>
<td>50 V, 8 min</td>
<td>0.1621</td>
<td>0.1577</td>
<td>0.0044</td>
<td>2.7144</td>
</tr>
<tr>
<td>100 V, 8 min</td>
<td>0.1555</td>
<td>0.1505</td>
<td>0.005</td>
<td>3.2154</td>
</tr>
</tbody>
</table>

Note: the graphite along with preformed deposit and a new graphite plate were used as anode and cathode, respectively. An DC was used to supply electric field.
AC frequency effect

- The density of the GDC layer increases when the frequency increases from 10 Hz to 500 Hz. Further increase of frequency does not increase the density any more.

**Corresponding cross-sectional morphology of GDC layer formed on PPy coated YSZ after sintering at 1350°C for 4h.**
Coating Morphology

- Dense GDC layer on non-shrinking substrate can be obtained by AC-EPD + sintering @ 1250°C

Morphology of GDC layer on Ppy coated YSZ formed by (a) DC-EPD and (b) AC-EPD after sintering at 1250°C
Performance of Symmetric cell

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

EIS at 750°C and (b) 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 2: Characterization of Diffusions in GDC Barrier Layers in SOFCs

§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
§Averaged elemental intensities from SEM-EDS maps versus distance perpendicular to the LSCF/GDC/YSZ interfaces.

§The LSCF cathodes were fired at 1200 °C

§GDC thicknesses were 1.5 µm, 3.0 µm, 4.5 µm, or 6.0 µm

§Increased Sr intensity can be seen at the interface for 1.5 and 3.0 µm
Effect of LSCF Firing Temperature

§ 1.5 micron thick GDC

§ Sr segregation to YSZ/GDC interface detected for 1200 and 1100 °C, not 1000 °C
Summary of Sr Interfacial Amounts

Integrated intensity of interfacial Sr from SEM-EDS data

Tabulated versus firing temperature and GDC thickness

<table>
<thead>
<tr>
<th>GDC thickness / Temp</th>
<th>1000 °C</th>
<th>1100 °C</th>
<th>1200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0 µm</td>
<td>&lt;0.1</td>
<td>&lt; 0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>4.5 µm</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>3.0 µm</td>
<td>&lt;0.1</td>
<td>0.15</td>
<td>0.3</td>
</tr>
<tr>
<td>1.5 µm</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
§ Cross-sectional bright field (a) and HAADF (b) images

§ From a 1.5 µm GDC electrolyte layer with LSCF fired at 1200 °C

§ EDS line scans taken along the lines indicated

§ Zirconate forms where Sr can transport across GDC pores and/or grain boundaries
$\text{SrZrO}_3$ detected in selected areas of GDC/YSZ interface
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
Barrier layers by EPD (early)
LSCF Fired at 1000 C: SEM-EDS

- 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
EPD is an effective method to deposit GDC on non-shrinking YSZ electrolyte
- DC EPD coating can be densified @ 1300C
- AC EPD coating can be densified @ 1250C

4.5-6 microns dense GDC seems to be enough as barrier layer
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