Modification of SOFC Anodes and Cathodes by ALD

Raymond J. Gorte, John M. Vohs
University of Pennsylvania
and
Steve McIntosh
Lehigh University

Praveen K. Cheekatamarla
Atrex Energy
Cathode Issues:

1) Performance and stability depends on surface composition
   a) “Surface Catalysts”?
   b) SrO segregation?

2) Also by surface structure.
Infiltration changes composition and structure:

1) LSM, LSF Performance enhanced by infiltration of: YSZ, Pd, SDC, CaO, and K$_2$O

J. Power Sources, 195 (2010) 720

2) Performance affected by surface structure.

SSI, 225 (2012) 146-150

1) What then is the effect of surface composition separate from structure?

2) Can we optimize composition?
Anode Issues:

1) Hydrocarbon tolerance

Ni exposed to 20% CO, 7% H₂ at 550°C.

From M. L. Toebe, et al., Catalysis Today, 2002

2) Sulfur tolerance

Ni-YSZ Anode – 1273 K
H₂ + x ppm H₂S

Goals

- “Engineer” the surface composition of both electrodes.
- Determine the effect of oxide coatings on electrode performance.
- Transfer the most promising technologies to Atrex and test on commercial scale cells.

Technical Approach

- Use atomic layer deposition (ALD) to selectively deposit oxide thin films onto both cathodes and anodes.
- Determine the effect of films on electrode performance.
Atomic Layer Deposition (ALD)

- Allows layer-by-layer control
- Can deposit mixed oxides, including perovskites
- Only surface composition is modified.
1) Commercial equipment not designed for porous materials.
2) Equipment can be very simple and cheap.
   a) Fast pulsing not required! No need for many cycles.
   b) Vacuum (millitorr) more effective than carrier gas.
   c) Easily applied to large cells.
Growth rates:

1) Can be measured gravimetrically
   1-nm of CeO$_2$ on 10 m$^2$/g support is \( \sim 7 \)-wt%

2) Similar for different oxides:
   \( \sim 1 \times 10^{18} \) metal atoms/m$^2$-cycle \( \sim 0.02 \)-nm/cycle

3) 10 ALD cycles \( \sim 1 \) monolayer.
Considerations for Electrode Applications:

Coat support with 1-nm CeO$_2$:

Basis: 10 m$^2$/g support

1 nm = 10$^{-7}$ cm

10$^{-7}$ cm * 10 m$^2$/g * 10$^4$ cm$^2$/m$^2$ = 0.01 cm$^3$ CeO$_2$/g

0.01 cm$^3$ CeO$_2$/g Al$_2$O$_3$ * 7.22 g/cm$^3$ = 0.072 g CeO$_2$/g

= 7-wt% CeO$_2$

If you had a 10-nm film, it would be 42-wt% CeO$_2$!
Why ALD and not simple infiltration?

1) ALD forms uniform films (not particles).
2) ALD does not change the surface area.
3) ALD allows formation of perovskite thin.

STEM, XRD of 0.5-nm, ALD film of LaFeO₃ on MgAl₂O₄
High Sensitivity-Low Energy Ion Scattering:

**LEIS**

- $^3$He$^+$, $^4$He$^+$, Ne$^+$, Ar$^+$
- 1-8 keV

**HS-LEIS**

- Large acceptance angle (360°)
- Parallel Energy Detection
Confirmation of Growth Rates:

LSF cathode with:
- 0 cycles of Co
- 10 cycles of Co
- 40 cycles of Co
The Effect of ZrO$_2$ ALD films on LSF cathodes:

Uniform ZrO$_2$ film effectively blocks adsorption sites

1-nm film!
ALD Films of some oxides *promote* performance:

LSF-YSZ, symmetric cells, 650 °C.

Submonolayer coverages of La or Sr significantly enhances cathode performance.
LSF Cathodes – ALD Modification with A- And B-site Cations

A-site addition – enhances performance
B-Site addition – poisons performance

0.5 monolayer
650 °C
LSF Cathodes – ALD Modification with A- And B-site Cations

Thermodynamic stability of different surface structures

Highly active surfaces are not thermodynamically stable but may be metastable at intermediate temperatures.
LSM also promoted by A-site cations; LSCo is not.
What about “catalyst” addition? Pd

Conclusion: No advantage for adding a catalyst for enhanced O₂ dissociation
Effect of Co ALD

Conclusions:
1) Co addition to LSF makes the surface look like LSCo or LSCF
Modification of Anodes: Grow CaTiO₃ on MgAl₂O₄:

30-wt% CaTiO₃ on MgAl₂O₄:

Surface area comparison (m²/g):

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Bulk CaTiO₃</td>
<td>5</td>
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<tr>
<td>CaTiO₃ ALD-MgAl₂O₄</td>
<td>87</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>118</td>
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Expose Ni/CaTiO$_3$/MgAl$_2$O$_4$ to 10% CH$_4$-He at 800 °C for 12 h

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