Tuning Surface Stoichiometry of SOFC Electrodes at the Molecular and Nano-Scale for Enhanced Performance and Durability

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7/20/2020

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Project Objectives

• Control the surface stoichiometry of electrodes (cathode and anode)
• Correlate the catalytic activity with the surface defect chemistry
• Develop surface modification techniques to modify the surface stoichiometry of electrodes
• Prevent the phase segregation such as strontium carbonate / strontium oxide formation in common cathodes and advanced ceramic anodes
• Develop novel approaches utilizing different cost-effective and mass producible surface modification techniques
• Identify the optimal surface modification process that yields the best initial performance and long-term stability on the modified electrodes
• Quantify degradation rates/performance and reveal the underlying mechanisms on tuned stoichiometric electrodes
• Integrate the optimized cathode and anode to full cell level
## Project Schedule

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<td>Develop ALD coating techniques</td>
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<td>Task 3</td>
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<td>Apply and test developed process on anodes</td>
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<td>Complete performance characterization of button cells integrated with modified anodes and cathodes</td>
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<td>MS 5.2</td>
<td>Complete post-testing characterization on surface modified SOFCs</td>
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• Determined Factors that Control Cation Segregation on Cathodes

• Developed Surface Modification Technique
  - Developed ALD Coating Technique
  - Developed Solution Infiltration Technique

• Enhanced SOFC Cathode Performance/Durability

• Enhanced SOFC Ceramic Anode Activity
Surface Segregation is Driven by Thermodynamics and Kinetics

Determined key factors that control surface cation segregation

1. Temperature
2. Aging time at different temperature
3. Oxygen partial pressure (chemical potentials)
4. CO$_2$
5. A-site Stoichiometry
6. Different perovskite compositions
Temperature Effect on Surface Segregation of LSCF

Aging of Dense LSCF Surface in Synthetic Air for 25 hrs

- The increase in temperature promotes surface cation precipitation (size, numbers)
- Temperature activates SrO segregation
- Different mechanism is observed at higher temperatures (> 850 °C), porous surface and grain orientation dependence.
Aging of Dense LSCF Surface at 700 °C in Synthetic Air

Aging time increases SrO particle nucleation and growth at 700 °C
Time Effect on Surface Segregation of LSCF

Aging of Dense LSCF Surface at 800 °C in Static Air

- Different grains are highlighted using different colors
- Segregation Process: Likely to nucleate at grain boundaries and then migrate to the grain center.
**$pO_2$ Effect on Surface Segregation of LSCF**

Aging of Dense LSCF Surface at **700 °C** for 25 hrs

- The increase in $pO_2$ first promotes SrO segregation.
- Above 21% further increase in $pO_2$ suppresses SrO segregation.
- Likely correlates to defect chemistry of LSCF
$pCO_2$ Effect on Surface Segregation of LSCF

700 °C for 25 hrs, balanced with N$_2$

- Increase in $pCO_2$ decreases the precipitated particle size and increases particle number.
- CO$_2$ promotes nucleation and suppress particle migration/growth.
A-site Stoichiometry Effect

\[(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3\] in \(\text{N}_2/\text{O}_2\) Mixture

- A-site deficient suppresses SrO segregation
- A-site deficient does NOT help prevent CO\(_2\) induced SrO segregation

In 50% CO\(_2\) (20%O\(_2\), 30%N\(_2\))
Different Surface Segregation Mechanism on Different Cathodes

Surface Segregation of PBSCF and SSC

10% CO$_2$

PBSCF

SSC

5µm

5µm
Composition Analysis on Surface Segregation of Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC)

- Study of the light-colored grains indicates they were rich in Sm instead of Sr.
- This was unexpected and is further evidence of a different cation segregation mechanism in SSC.
Temperature Effect on Cation Segregation in SSC

Aging of Dense SSC Surface in Synthetic Air for 25 hrs

- As with LSCF, when SSC undergoes cation segregation, there is also nucleation of distinct particles that seem to start at the grain boundaries and agglomerate.
- Unlike LSCF, SSC exhibited discolored grains prior to particle segregation. These grains appear in multiple aging conditions.
Oxygen Effect on Cation Segregation in SSC

Aging of Dense SSC Surface at 700°C for 25 hrs

- SSC appears to be more stable in higher $pO_2$ environments.
- Light-colored regions appear to be the first step in cation segregation in SSC.
- These observations suggest a different mechanism for cation segregation in SSC compared to LSCF.
Cathode Surface Modification

1. Development of ALD coating technique

2. Development of solution infiltration technique

3. Performance/Durability Enhancement of Surface Modified Cathode
Electrochemical Performance of ALD Modified LSCF-GDC

ALD films of TiO$_2$ and ZnO were found to improve electrochemical performance of LSCF-GDC cathode symmetric cells.

16 cycles of TiO$_2$ ALD was found to be optimum for enhancing performance.
Electrochemical Performance of ALD Modified LSCF-GDC

- All ALD modified samples had similar $pO_2$ dependence except for 9 cycles of TiO$_2$. 
Electrochemical Performance of ALD Modified LSCF-GDC

Effect of ALD Oxidizer and $N_2$ Annealing on Electrochemical Performance

- It was hypothesized that tuning the non-stoichiometry of the ALD films could enhance kinetics, so the effect of different oxidizers (and pulse times) were tested.
- Annealing in pure $N_2$ for 1 hour at 400°C was also used to tune non-stoichiometry.
- Annealing significantly lowered total ASR below 650°C.
• TiO$_x$ modified cell shows a lower ASR in all tested temperature region.

• In contrast, VO$_x$ modified cell shows an opposite trend with an increase in ASR.

• For $pO_2$ dependence, unmodified cell has a slope of 0.22. TiO$_x$ modified cell has a lower ASR across all $pO_2$ range with a decrease in the slope.
Solution Infiltration Procedure

a. Micropipette
b. Nitrate precursor containing catalyst
c. Vacuum Chamber
d. 450 °C in furnace
e. End Result
Electrochemical Performance of Surface Modified SSC

Screening over multiple elements

Pr modified SSC shows promising electrochemical performance
Impact of CO$_2$ on Cathode Performance

Cathode ASR as a function of CO$_2$

*Open Symbols: SSC-GDC
Closed Symbol: Surface Modified SSC-GDC

- CO$_2$ has much less impact on modified cathodes
- Modified cathodes show high stability in 1% CO$_2$
Surface Modified SOFC Performance

Baseline Cell: **SSC-GDC/GDC/Ni-GDC**

Cathode Modified Cell

Modified SSC-GDC
The surface modification technique can apply widely to different cathodes

- Determined via Symmetric Cell Configuration
  1. Area specific resistance (ASR) decreases an order of magnitude after modification
  2. Modified cathode shows improved stability

- Static air, 600 °C

- LSCF-GDC
- Modified LSCF-GDC
Surface Modified SOFC Performance/Stability

Baseline Cell: LSCF-GDC/GDC/Ni-GDC

Cathode Modified Cell

Cell Configuration
- Cathode (~20-30 µm)
- GDC (~20 µm)
- Ni-GDC (~500 µm)

100 SCCM H2, 3% H2O | lab air 600 °C
Anode Surface Modification

1. Development of Ceramic Anodes
   - increase intrinsic surface activity by particle exsolution

2. ALD modified Ceramic Anodes

3. Solution Infiltration Modified Ceramic Anodes

4. Performance/Durability Enhancement of Surface Modified Anodes
**Sr(Fe,Ni,Mo)O$_{3-\delta}$ Phase Characterization**

**SFNM composition**

- 100
- 955
- 811
- 522
- 333
- 244
- 144
- 055

**Sr(Fe,Ni,Mo)O$_{3-\delta}$ Conductivity**

- Temperature (°C)
- 650 600 550 500 450
- Conductivity (S cm$^{-1}$)
- 10$^{-2}$ 10$^{-1}$ 100 101 102

After Calcination (in air)

- Intensity (a.u.)

After Reduction (H$_2$) (operating condition)

- Intensity (a.u.)

2-theta (°)

- Increased doping stabilizes phase from perovskite to double perovskite.
- Highly doped SFNM is stabilized in reducing conditions with minor Ruddlesden-Popper secondary phase formation.
- Heavily doped compositions retain their phase while also increase in charge carrier concentration. $\sigma > 35$ S/cm from 450-650°C
Exsolution Morphology & Composition

Surface Morphology

- Reduced at 600 °C for 24 hrs in H₂
- Exsolved particle size and spatial density are controlled by parent material composition

Surface Chemistry Analysis - XPS

XPS: Exsolved particles contain metallic Ni and Fe (slight Mo, depending on the SFNM composition)

TEM: Exsolved particles have Fe-rich shell.
SFNM Composition Effects on Cell Performance

- Determined using GDC electrolyte supported cells
- Performance strongly depends on parent perovskite and exsolved particle properties

**Cell Configuration**

- Cathode (~20-30 µm)
- GDC (~100 µm)
- SFNM-GDC (~20-30 µm)
Development of SFNM Ceramic Anode Supported Cells

Cell structure: good anode-electrolyte interface

- **Image:** Shows a microscopic view of the cell structure with a good anode-electrolyte interface. The darker grains represent SFNM, while the brighter grains represent GDC.

- **Graphs:**
  - A graph showing potential vs. current density with an inset indicating in situ surface modification (exsolution).
  - Another graph showing power density vs. time, highlighting OCV and operating voltage.

- **Text:**
  - *Initial 2 hr reduction* indicates the time period for the reduction process.
  - *600, H₂* denotes the operating conditions with hydrogen gas.

**Notes:**
- The images and graphs demonstrate the effectiveness of the SFNM ceramic anode in producing good anode-electrolyte interfaces, which is crucial for high performance in fuel cells.
- The in situ surface modification (exsolution) is a critical aspect for improving the cell's performance and durability.
- The power density and time graphs show stable performance with minor fluctuations, indicating robust operation under the specified conditions.
Ni-GDC Co-infiltrated SFCM Anode

**Pretreatment Temperature Effect**

- **H₂ 550 °C**

**Loading Effect**

- Optimization of solution infiltration into SFCM anode
- Both loading and reduction temperature affect the performance
- Shows a peak power density over 0.6 W/cm² at 550 °C
VO$_x$ ALD on SFCM-GDC Ceramic Anode

- Vanadium ALD modified SFNM ceramic anode with Ni/GDC co-infiltration
- Shows peak power density of 0.21 W/cm$^2$ at 550 °C
SFCM Performance in Methane

- Screened anode infiltrates
- Shows peak power density over 0.4 W/cm² at 600 °C in methane
Modified Ceramic Anode shows:
- Peak power density over 0.7 W/cm² at 550 °C in H₂
- Peak power density over 0.45 W/cm² at 550 °C in CH₄
- Continuous operation over 500 hours in CH₄/H₂ at 550 °C
Conclusions

Control Surface Segregation

- **Temperature**: different segregation mechanisms are observed at different temperature regimes
- **Time**: revealed the surface segregation process—(1) nucleation at grain boundaries, (2) surface migration, (3) particle growth
- $pO_2$ : Defect chemistry of LSCF can either promote or suppress SrO segregation.
- $pCO_2$ : Promotes the nucleation step, and suppress the particle growth
- **A-site Stoichiometry**: Suppress SrO segregation but no impact on preventing CO$_2$ induced phase segregation
- **Perovskite Composition**: Significantly affected segregated cations and mechanism

ALD Modified Cathodes

- Different elements show different effects on the cathode electrochemical performance
- Ti improved LSCF cathode ASR but V coated cell does not show any improvement
- Annealing conditions of ALD coatings affect electrochemical performance
- Demonstrated the ALD impact on both cathode and anode modification
Conclusions

Solution Infiltrated Cathodes

- The non-ohmic area specific resistance can be reduced by ~1 order of magnitude.
- The increase in surface electrocatalyst loading could result in the blocking effect.
- Modified cathodes show enhanced performance and durability (over 2000 hrs in full cells).
- Also increases CO$_2$ tolerance.

Self Assembled Exsolved Nanoparticles on Ceramic Anodes

- The parent material SFNM composition directly controls the exsolved particle size/density/composition.
- A core/shell structure of exsolved particles can be achieved by tuning material composition.
- Shows promising performance < 600 °C

Solution Infiltrated Anodes

- Demonstrated multiple factors can affect the properties of infiltrated ceramic anodes.
- Peak power density over 0.7 W/cm$^2$ at 550 °C in H$_2$
- Peak power density over 0.45 W/cm$^2$ at 550 °C in methane
- Stability increased over 500 hours
Future Work

• Integrate the optimized cathode and anode to full cells
  - We demonstrated promising full cell results and plan to optimize the modification process.

• Post-testing characterization on surface modified SOFCs
  - We will perform post-modern chemical, structural characterization to provide feedback on the surface modified electrodes.
Publications & Presentations


“Understanding Strontium Segregation on La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$,” E. Ostrovskiy, Y.L. Huang, E.D. Wachsman, in preparation, (2020).
