Deposition of Nickel Nanoparticles in SOFC Anodes to Improve Performance

Yanchen Lu, Paul Gasper, Boshan Mo, Uday Pal, Srikanth Gopalan and Soumendra Basu

Division of Materials Science and Engineering
Boston University

Motivations for Anode Infiltration

• Incorporation of alternate materials for
  - Sulfur tolerance
  - Coking tolerance

• Ni reduction

• Increase in TPB density
  - decrease in activation polarization
  - Increase in anodic exchange current density
Research Approach

• Ni infiltration of commercial Ni/YSZ cermet anodes
  – Ni/YSZ anodes are already percolating
• Explore liquid phase and vapor phase infiltration
• Only infiltrated Ni particles on YSZ will add to TPB length
  – Quantify added TPB length by SEM study of fracture cross sections
• Additional TPBs will be active only if they have an electrically conducting pathway
  – When are the infiltrated particles part of an electrically conducting pathway?
Characterization of Button Cell Microstructure

**SEM**

- CAL
- YSZ
- AAL
- ACCL

<table>
<thead>
<tr>
<th>Phase</th>
<th>Volume Fraction</th>
<th>TPB density (µm µm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>38.8%</td>
<td></td>
</tr>
<tr>
<td>YSZ</td>
<td>32.5%</td>
<td>2.39</td>
</tr>
<tr>
<td>Pores</td>
<td>28.7%</td>
<td></td>
</tr>
</tbody>
</table>
Liquid Infiltration of Ni-YSZ Anodes

1. Button cell from MRSI
2. Reduce cell (800°C, 2 hours 5% H₂)
3. Weigh cell
4. Reduce cell (800°C, 2 hours 5% H₂)
5. Liquid infiltration in vacuum (<10 mbar)
6. Dry in air (100°C, 20 min), decompose nitrates to NiO in air (320°C, 20 min)
7. N cycles
8. Microstructural/Electrochemical Characterization

Diagram Components:
- Peristaltic pump
- Pressure gauge
- Vacuum pump
- Deposition flask
- Ni nitrate solution with surfactants
For the reduced sample, after 5 cycles, the infiltrated Ni content is:
• 2.33 volume % of anode, or:
• 8.1 volume % of the pores
Liquid infiltration of conventional Ni/YSZ cermet can lead to deposition in the anode active layer.
Challenges of Liquid Infiltration

• Time consuming procedure
• Thermal cycling introduces possibility of electrolyte failure
• Maintaining cell integrity in reduced state during processing steps and electrochemical testing is challenging

Alternate approach:
Vapor phase infiltration of metallic Ni into anode using water vapor and forming gas
Thermodynamics of Ni Vaporization: Effect of T

Calculations conducted in HSC Chemistry 6.0.

- 75% Forming gas (5% H₂, 95% Ar)/25% water vapor
- Unlimited Ni supply

~ $10^4$ reduction in equilibrium partial pressure of Ni-containing vapor species on cooling from 1400°C-900°C.
Vapor phase infiltration of Ni in Ni-YSZ Anodes

Vapor phase deposited Ni nanoparticles

In-situ platinum wire heater brings nickel to 1400°C

Ar-H₂-H₂O passes over nickel source

Vapor phase infiltration of Ni in commercial anodes is feasible

Location of Ni Nanoparticles

• Ni nanoparticles on YSZ grains have rounded shapes
• The shape of the nanoparticles are approximately hemispherical

Ni nanoparticles on YSZ grains will create TPBs
Calculation of Added TPB Density

\[ TPB_{inf} = n \pi \bar{d} \left( \frac{S}{V} \right) \nu \]

- **Additional TPB density in AAL** ($\mu$m/$\mu$m$^3$)
- **Areal particle density in AAL** ($#/\mu$m$^2$)
- **Average particle diameter in AAL** ($\mu$m)
- **Surface area of pores per unit volume of AAL** ($\mu$m$^2$/µm$^3$)
- **Volume fraction of pores in AAL**

**SEM of Fracture Cross-Sections**

**FIB-SEM**

**Additional TPB density in AAL**

<table>
<thead>
<tr>
<th>Index</th>
<th>Area</th>
<th>Diameter</th>
<th>Volume</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>488.162</td>
<td>24.93085</td>
<td>4956.764</td>
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<td>2</td>
<td>1240.75</td>
<td>39.74685</td>
<td>16438.43</td>
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<td>3</td>
<td>589.861</td>
<td>27.45056</td>
<td>5388.409</td>
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<td>4</td>
<td>325.442</td>
<td>20.35597</td>
<td>2208.229</td>
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<td>5</td>
<td>447.482</td>
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<td>16</td>
<td>447.482</td>
<td>32.85397</td>
<td>3589.387</td>
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</table>
**Additional TPB Density**

<table>
<thead>
<tr>
<th>TPB in AAL (μm/μm³)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Ni/YSZ cermet</td>
<td>2.39</td>
</tr>
<tr>
<td>Ni nanoparticles</td>
<td>5.99</td>
</tr>
<tr>
<td>Total in infiltrated sample</td>
<td>8.38</td>
</tr>
</tbody>
</table>

**Question?**

Are these TPBs active, i.e., are they a part of an electrically conductive pathway?
Creating Percolating Ni Nanoparticles

Ni-YSZ Contact Angle: Thermodynamic Model

## Cell Nomenclature for I-V Tests

### STUDY 1

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>Cell Nomenclature</th>
<th>Uninfiltrated Cell 1</th>
<th>Infiltrated Cell 1</th>
<th>Infiltrated Cell 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>800° C</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>700° C</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>600° C</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
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</tbody>
</table>

### STUDY 2

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>Cell Nomenclature</th>
<th>Uninfiltrated Cell 2</th>
<th>Infiltrated Cell 3</th>
<th>Infiltrated Cell 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>750° C</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>700° C</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>650° C</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

- Cells were tested in pure O₂ on cathode side under various anode atmospheres and temperatures
- Cathode atmosphere was switched to dry air without cooling and tested under various anode atmospheres and temperatures (results are discussed)
- **STUDY 1**: Cells were tested to high current densities and low potentials (well into concentration polarization conditions).
- **STUDY 2**: Cells were tested to low current densities and high potentials (concentration polarization conditions never reached).
Electrochemical Test Results

Study 1: 800°C

- Infiltrated Cell 1
- Uninfiltrated Cell

Voltage (V)

Current Density (A cm⁻²)

Options: 75% H₂O, 50% H₂O, 3% H₂O
Electrochemical Test Results

Study 1: 800°C

Power Density (W cm$^{-2}$) vs. Current Density (A cm$^{-2}$) for different moisture levels:

- 3% H$_2$O
- 50% H$_2$O
- 75% H$_2$O

Comparison of Uninfiltrated Cell and Infiltrated Cell 1.
Electrochemical Test Results

Study 1: 700°C

- Uninfiltrated Cell
- Infiltrated Cell 2

*Voltage (V) vs. Current Density (A cm⁻²)*

- 75% H₂O
- 50% H₂O
- 3% H₂O
Electrochemical Test Results

Study 1: 700°C

- Uninfiltrated Cell
- Infiltrated Cell 2

Power Density (W cm$^{-2}$) vs. Current Density (A cm$^{-2}$)

- 3% H$_2$O
- 50% H$_2$O
- 75% H$_2$O
Electrochemical Test Results

Study 1: 600°C

Voltage (V)

Current Density (A cm⁻²)

- Uninfiltreated Cell
- Infiltrated Cell 2

50% H₂O
3% H₂O
Electrochemical Test Results

Study 1: 600°C

- Uninfiltrated Cell
- Infiltrated Cell 2

Power Density (W cm\(^{-2}\))

Current Density (A cm\(^{-2}\))

50% H\(_2\)O

3% H\(_2\)O
## Summary of Study 1 Results

<table>
<thead>
<tr>
<th>Testing Temperature</th>
<th>Cell</th>
<th>Maximum Power Density (W cm⁻²) at Different Anode Gas Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3% H₂O – 97% H₂</td>
</tr>
<tr>
<td>800 °C</td>
<td>Uninfiltrated</td>
<td>1.078</td>
</tr>
<tr>
<td></td>
<td>Infiltrated Cell 1</td>
<td>1.281</td>
</tr>
<tr>
<td></td>
<td>Change</td>
<td>+18.8%</td>
</tr>
<tr>
<td>700 °C</td>
<td>Uninfiltrated</td>
<td>0.408</td>
</tr>
<tr>
<td></td>
<td>Infiltrated Cell 2</td>
<td>0.606</td>
</tr>
<tr>
<td></td>
<td>Change</td>
<td>+48.5%</td>
</tr>
<tr>
<td>600 °C</td>
<td>Uninfiltrated</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>Infiltrated Cell 2</td>
<td>0.123</td>
</tr>
<tr>
<td></td>
<td>Change</td>
<td>+57.7%</td>
</tr>
</tbody>
</table>
Particle Statistics in Study 1

- **Uninfiltrated Before Testing**: Overall TPB Density: 2.39 µm/µm³
- **Infiltrated Before Testing**: Overall TPB Density: 8.38 µm/µm³, Areal Particle Density: 16.5 #/µm², Average Particle Diameter: 50.29 nm
- **Infiltrated Cell 1 After Testing**: Overall TPB Density: 7.84 µm/µm³, Areal Particle Density: 8.07 #/µm², Average Particle Diameter: 93.48 nm
- **Infiltrated Cell 2 After Testing**: Overall TPB Density: 7.83 µm/µm³, Areal Particle Density: 11.48 #/µm², Average Particle Diameter: 65.63 nm
Electrochemical Test Results

Study 2: 750°C

Voltage (V) vs. Current Density (A cm⁻²)

- 97% H₂ – 3% H₂O
- 75% H₂ – 25% H₂O
- 50% H₂ – 50% H₂O
- 25% H₂ – 75% H₂O

- Uninfiltrated Cell
- Infiltrated Cell 1
Study 2: 700°C

Electrochemical Test Results

Voltage (V) vs. Current Density (A cm$^{-2}$)

- Uninfiltrated Cell
- Infiltrated Cell 2

Gas Compositions:
- 97% H$_2$ – 3% H$_2$O
- 75% H$_2$ – 25% H$_2$O
- 50% H$_2$ – 50% H$_2$O
- 25% H$_2$ – 75% H$_2$O
Electrochemical Test Results

Study 2: 650°C

Voltage

Current Density (A cm⁻²)

97% H₂ – 3% H₂O
75% H₂ – 25% H₂O
50% H₂ – 50% H₂O
25% H₂ – 75% H₂O

Uninfiltrated Cell
Infiltrated Cell 2
Comparison of Study 1 and Study 2 Samples

Performance Ratio at 800 mV
Infiltrated / Uninfiltrated

Temperature (°C)

3% H₂O

Study 1 Samples

Study 2 Samples
Nanoparticle Percolation versus Coarsening

Infiltrated Cell 1 - 700°C (High Current)

Infiltrated cell 3 – 750°C (Low Current)

Nanoparticle connectivity can lead to coarsening
Ni nanoparticles disappeared from the AAL at extremely high current densities.
Conclusions

- **Mechanism**
  - An initial exposure to anodic concentration polarization conditions, followed by normal cell operation should preserve the percolated Ni nanoparticles and maintain improved cell performance.
  - Exposure to very high current densities should be avoided.
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A. Nikiforov, and A. Krupp
Boston University, Boston, MA 02215

S. Markovich, H. Abernathy, S. Vora
NETL, Pittsburgh, PA 15236