THREE DIMENSIONAL MICROSTRUCTURAL CHARACTERIZATION OF CATHODE DEGRADATION IN SOFCs USING FOCUSED ION BEAM AND SEM

Joshua Taillon, Christopher Pellegrinelli, Yilin Huang, Eric Wachsman, and Lourdes Salamanca-Riba
University of Maryland, College Park

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Session A04.3, Room B117
Introduction to Solid oxide fuel cells

- Solid oxide fuel cells (SOFCs) provide a clean, energy-efficient means of energy conversion.
- Low cost, flexible fuels, low emissions, etc.
- Problems?
  - High operating temperature, and limited durability
  - $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{Cr}$ vapor cause losses
  - Adverse effects on polarization, conductivities, and activation
- What is primary cause of these losses?
  - Microstructure!
- Previous work:
  - Quantification in the FIB/SEM:

**Our task:**
Use the FIB/SEM to characterize microstructural changes as cathode degradation occurs, and relate these changes to those in cell performance.

**Our goal:**
Better understanding of the fundamental mechanisms behind cathode degradation.
Outline

• Data acquisition
  • Sample prep and imaging conditions

• Data processing
  • Filters, artefact correction, and segmentation

• Quantification strategies
  • Tortuosity
  • Triple phase boundary
  • Electrochemical activity determination
Experimental - Button cell testing

- Symmetric cathode cells
  - 8-YSZ electrolyte
  - 50 wt. % LSM/YSZ cathode paste
- Sintered at 1000°C for 1hr
- Aged for 250hr at 800°C
  - Polarization was constant 60mA/cm²

- Four conditions compared:
  - Aged – dry air
  - Aged – dry air – cathodic polarization
  - Aged – 3% H₂O – anodic polarization
  - Aged – 3% H₂O – cathodic polarization
Data acquisition

• Our results (and conclusions) can only be so good as our inputs
  • We need good inputs! (GIGO)

• Important considerations:
  • Initial sample preparation (pre-FIB)
  • Sample preparation within the FIB/SEM
  • Slicing resolution (for fidelity of reconstruction)
  • Electron beam parameters - image noise and resolution vs. data acquisition time
  • What is it we need to accentuate?
Pre-FIB sample prep

1. Vacuum impregnation of porous structure
2. Grinding/polishing to 1200 grit
3. Carbon coating and sample mounting

Instrumentation

- FEI Helios 650
  - Part of the Center for Nanoscale Science and Technology (CNST) user facility at NIST
  - Multichem, iFast Developer Kit, etc.
- Auto Slice and View version 1.2
- Avizo Fire + personal Python code
- Tescan Gaia (+ Xeia) at UMD
  - Soon!
Experimental – Electron imaging (detector positioning)

- Positioning of detector and/or energy filtering
  - Careful selection of contrast mechanism
- For SOFC ceramics:
  - Low voltage, elastically scattered BSE provide best contrast between phases

**FEI Helios 660 “In-column” detector (3 kV)**

**Zeiss Crossbeam 540 “EsB” detector (1.5 kV)**

**Tescan Xeia “In-beam BE” detector (5 kV)**
Experimental – post processing of data

• Post-processing done with mix of software:
  • Avizo Fire:
    • Non-local means filtering of data¹ (also Perona–Malik diffusion filter)
    • Watershed segmentation algorithm²
  • ImageJ/Python
    • Intensity gradient correction
    • Fiducial tracking/slice thickness measurement

Results – Surface generation

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air</strong></td>
<td>27.42</td>
<td>23.17</td>
<td>4.64</td>
</tr>
<tr>
<td><strong>Air-cathodic</strong></td>
<td>23.53</td>
<td>27.58</td>
<td>7.28</td>
</tr>
<tr>
<td><strong>H₂O-anodic</strong></td>
<td>24.27</td>
<td>27.58</td>
<td>4.22</td>
</tr>
<tr>
<td><strong>H₂O-cathodic</strong></td>
<td>26.39</td>
<td>19.90</td>
<td>12.10</td>
</tr>
</tbody>
</table>

Bounding box dimensions (µm):

- **Air**: 27.42 µm x 23.17 µm x 4.64 µm
- **Air-cathodic**: 23.53 µm x 27.58 µm x 7.28 µm
- **H₂O-anodic**: 24.27 µm x 27.58 µm x 4.22 µm
- **H₂O-cathodic**: 26.39 µm x 19.90 µm x 12.10 µm
Results – Phase fraction and surface quantification

- Overall porosity decreases upon exposure to H$_2$O
- Phase solid fractions remain similar to expected values (from source materials)
  - Except for H$_2$O-cathodic
  - Will impact diffusivity estimates

<table>
<thead>
<tr>
<th></th>
<th>Exp. YSZ</th>
<th>Exp. LSM</th>
<th>Obs. YSZ</th>
<th>Obs. LSM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aged air</td>
<td>0.52</td>
<td>0.48</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>Air-cathodic</td>
<td>0.52</td>
<td>0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O-anodic</td>
<td>0.51</td>
<td>0.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O-cathodic</td>
<td>0.59</td>
<td>0.41</td>
<td></td>
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</tr>
</tbody>
</table>
Results – Tortuosity

- Tortuosity is comparison of:
  \[ \tau = \lim_{L_G \to \infty} \left( \frac{\text{Geodesic distance}}{\text{Euclidean distance}} \right) \]

- Geodesic distance calculated with “fast marching method”
  - scikit-fmm Python library

Results – Tortuosity

• Effective diffusion coefficient is dependent on volume fraction and tortuosity\(^*\):

\[
D_{\text{eff}} = D \left( \frac{V_p}{\tau} \right)
\]

• \(V_p/\tau\) relatively constant, except slightly larger for YSZ in H\(_2\)O samples
• Agrees with slight performance enhancement

Results – Phase percolation

- Comparison of longest section of each phase to overall network
  - Used 5 longest components

- Result:
  - YSZ and pore completely interconnected
  - LSM is limiting transport
Triple phase boundary ($L_{TPB}$) determination

- Intersection of three phases is necessary for the oxygen reduction reaction to occur:
  - ORR: $\frac{1}{2}O_2 + 2e^- \leftrightarrow O^2-$
  - This quantity can be directly related to cell performance

- Within analysis volume, a phase and boundary site can be described as active, inactive, or unknown
- Labels depend on connection to edges
  - Unknown have at least 1 border with edges (dead-end)
  - Active have two borders across a dimension (transverse)
  - Inactive networks have no intersection with an edge (isolated)

- Collaboration with Scientific Applications and Visualization Group at NIST
  - Implemented edge-counting more accurate than morphological expansion (current trend in literature)
Results – Triple phase boundaries

- Total $\rho_{TPB}$ relatively constant (except H$_2$O-anodic, which has low sampling volume)
- H$_2$O-cathodic has significant decrease in active TPB density, suggesting drop in active sites for ORR
Results – Impact of aspect ratio?

- $\text{H}_2\text{O}$ Cathodic has less active TPB
  - Real result, or artefact of measurement?
  - Our classification depends on analysis of volume boundaries
Summary

Conclusions

• We have developed and refined methods using both Avizo Fire and external calculations to quantify 3D microstructure of solid oxide fuel cell cathodes
• At the conditions tested, subtle changes in microstructure occur; which agree with subtle changes in cell performance
• $\rho_{TPB,active}$ decreases when aged under $H_2O$ contamination and cathodic polarization
• Segregation of La and Mn to YSZ grain boundaries in $H_2O$-cathodic (but not Sr)

Upcoming Work

• Analyze and quantify composition of segregation products using TEM/EELS
• Further correlation with EIS data from same samples
• Investigation of LSCF/GDC composite cathode degradation
Acknowledgements

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HyperSpy
OpenCV
ImageJ/Fiji
THANK YOU

Questions and comments?

Email:

jtaillon@umd.edu
and/or
riba@umd.edu