Performance and Microstructural Changes in LSM-Based SOFC Cathodes Under Accelerated and Conventional Testing

Mark De Guire,1 Arthur Heuer,1 Zhien Liu,2 Richard Goettler,2 Naima Hilli,1 Minjae Jung,2 Celeste Cooper1

1) Case Western Reserve University
& 2) LG Fuel Cell Systems

17th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting
Pittsburgh, PA • 19–21 July 2016
Outline

• Project objectives and approach
• Accelerated vs. long-term conventional testing
• LSM compositions: role of A-site deficiency
  • Durability testing
  • Cathode microstructural changes
  • ASR and TPB density vs. time
• Summary & conclusions
• Ongoing & future work
Background observations: long-term conventional testing

16 kh, 860 °C:

Cathode densification layer

Segregation of Mn oxides*

Densified layer (between two white lines) is ~5 µm thick (SEM image, courtesy of LGFCS)

(CCC: cathode current collector)

Project Objectives and Approach

- Implement an accelerated testing protocol to replicate long-term microstructural changes in shorter times
- Understand microstructural basis of long-term performance loss in LSM-based SOFC cathodes
- 4 cycles of cathode formulation, testing, and analysis in 3 years
- Develop strategies for optimizing LSM-based cathodes for improved long-term performance and stability
Procedures: button cell specifications

• Fabricated at LGFCS
• Cell details:
  • 8YSZ electrolyte, 32 mm dia.
  • NiO-8YSZ anode (60:40 wt%) 
  • Cathodes: A-site deficient LSM + 8YSZ (50:50 wt%)
    • Comp’n A: (La_{0.85}Sr_{0.15})_{0.90}MnO_{3±δ} (LSM 85-90)
    • Comp’n B: (La_{0.80}Sr_{0.15})_{0.95}MnO_{3±δ} (LSM 80-95)
  • Electrodes: screen printed, 9.5 mm dia., fired separately
Procedures: button cell testing

- Pt mesh and wires attached to both electrodes
- Cell sealed to zirconia tube with fired glass paste
- Anode reduction followed by 24-h burn-in at OCV
- Pre-test protocols: details below
- Durability testing
  - \( \text{H}_2, 50 \text{ sccm} \)
  - Accelerated tests: 1000 °C, 0.760 A cm\(^{-2}\)
  - Conventional tests: 900 °C, 0.380 A cm\(^{-2}\)
  - I-V and EIS scans every 24 or 48 h
Pre-test protocol: temperature parametric study

LSM 80-95 (comp’n B), conventional conditions, $t = 0$
LSM 80-95 (B) durability testing: reproducibility

Two cells, accel’d conditions, 500 h

June 2016    July 2015

Voltage (V)  ASR (Ω·cm²)
Representative V-I & P-I sweeps, 0–624 h

LSM 80-95 (B), accel’d testing
Comparative V-I & P-I sweeps, A vs. B

V-I & P-I Curves

- Comp’n A
- Comp’n B

Voltage (V) vs. Current Density (mA/cm²)

- 493 hrs
- 500 hrs
- 624 hrs

Power Density (mW/cm²)
ASR and changes over time: summary

• In durability testing and EIS: *LSM 80-95* (B) had lower:

  lower:
  • Initial ASR
  • Final ASR
  • $\Delta$ASR over time ($\Omega \text{ cm}^2 \text{ kh}^{-1}$)
Procedures: FIB Slice & View for 3DR

- **FIB Milling**
- **Image Slice Direction**
- **SEM**
- **Fiducial Marks**

Each slice is 150 nm thick.

**Image resolution:** 4096*3536 pixels

**Imaging mode:** backscattered (Immersion detector)
**LSM 85-90 (A) microstructural evolution: 3D reconstruction**

<table>
<thead>
<tr>
<th>LSM 85-90 cathode:</th>
<th>as-received</th>
<th>after 200 h accel’d testing</th>
<th>after 493 h accel’d testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>pore size (µm)</td>
<td>0.20</td>
<td>0.34</td>
<td>0.42</td>
</tr>
<tr>
<td>pore tortuosity</td>
<td>2</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>normalized pore surface area (µm⁻¹)</td>
<td>26</td>
<td>17.4</td>
<td>14.2</td>
</tr>
<tr>
<td>total TPB (µm⁻²)</td>
<td>17.1</td>
<td>9.6</td>
<td>5.86</td>
</tr>
<tr>
<td>active TPB (µm⁻²)</td>
<td>10.3</td>
<td>8.2</td>
<td>5.13</td>
</tr>
</tbody>
</table>

---

**Coarsening of pores, loss of pore area and TPB**

**Other observations —**

- Phase fraction profiles: flat across cathode
- Densification at cathode-electrolyte interface? Inconclusive
Accumulation of MnO\textsubscript{x} at cathode-electrolyte interface

Other observations —

- LSM and YSZ composition profiles: flat across cathode
- Densification at cathode-electrolyte interface? Inconclusive
• As received: \( \text{MnO}_x \) ( ) only in CCC

• 500 h accel’d testing: occasional small \( \text{MnO}_x \) grains near electrolyte interface

**LSM 80-95 (B) microstructural evolution: TEM**
A – B comparison: TEM

- More MnO$_x$ observed in LSM 85-90 (untested and tested)
- Larger MnO$_x$ particles in LSM 85-90 CCC
- More pores in LSM 80-95 cathode post-testing
In contrast to LSM 85-90 (A), **LSM 80-95 (B)** shows:
- Pore refinement (!?) and increasing area and tortuosity
- **Stabler TPB** (total and active)
A – B comparison: ASR and TPB density

- **LSM 85-90**, as $t \uparrow$:
  - active TPB density $\downarrow$
  - ASR $\uparrow$

- **LSM 80-95**:
  - Higher active TPB density
  - Lower ASR

- Overall: inverse correlation between ASR and TPB density
Summary & Conclusions

During accelerated testing up to 500 h:

• **LSM 85-90** (A) cathode:
  • Pore coarsening
  • MnO_x segregation at electrolyte-cathode interface
  • Microstructure–performance trend over time:
    • TPB density ↓  • ASR ↑

• **LSM 80-95** (B) cathode:
  • Stabler microstructure  • Less A-site deficient → less MnO_x
  • Higher TPB, lower ASR than LSM 85-90
  • Not yet observed:
    • Cathode densification at electrolyte  • Mn depletion at electrolyte

*Inverse TPB – ASR relationship is emerging*
Ongoing & Future Work

• Continue reproducibility studies

• 624-h accelerated test: microstructural analysis underway; look for densification layer

• Thermodynamic studies to predict conditions for MnO$_x$ formation

• MnO$_x$ formation: symptom, or cause, of degradation?

• Continue to explore relationship between TPB and ASR
  • vs. LSM composition  
  • Accelerated vs. conventional testing

• Composition C cells fabricated; testing & analysis are underway
Acknowledgments

• Funding: DoE SECA Core Technology Program (DE-FE0023476)
• NETL program manager: Patcharin Burke
• Mirko Antloga, Craig Virnelson (CWRU)

Disclaimer: This research is based in part upon work supported by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
3DR in SOFCs: Triple phase boundaries (TPB)

- YSZ: **100% ionic** conductor
- LSM (cathode) and Ni (anode): **100% electronic** conductors
- For TPB to be **active electrochemically**, it must have percolation paths:
  - **Ionic conductor** must connect to electrolyte
  - **Electronic conductor** must connect to **current collector**
  - **Pore** must connect to **external atmosphere**

3DR can definitively determine whether TPB is **active**, or may be **inactive**
LSM 80-95 durability testing: 624 h

26% ASR rise

$\Delta \text{ASR} = 0.034 \text{ cm}^2$

$y = 0.0000708x + 0.2713034$

- Voltage
- ASR
- Linear (ASR)
Cathode B: 500-hr Conventional Test

Durability Testing

Voltage (V)

ASR (Ω-cm²)

Time (hours)

0-24hr: 6.2%

24-165hr: -21.6%

165-506hr: 15.2%
Representative Bode plots, 0–624 h

LSM 80-95 (B), accel’d testing
Representative Nyquist plots, 24–400 h

Figure showing Nyquist plots for different time periods (24, 200, 300, and 400 hours) labeled as ASR_{200h}. The plots are for LSM 80-95 (B), accelerated testing. Points on the plots correspond to different time intervals. The plots are derived from a simple equivalent circuit model (R_s, R_p, C_p).
Cathode B: 500-hr Conventional Test

Bode Plot

Frequency (Hz)

$Z''$
Cathode B: 500-hr Conventional Test

Nyquist Plot

![Graph showing Nyquist plots for different times: 0 hr, 24 hr, 43 hr, 70 hr, 98 hr, 114 hr, 139 hr, 165 hr, 189 hr, 207 hr, 233 hr, 258 hr, 283 hr, 304 hr, 331 hr, 357 HR, 375 hr, 422 hr, 449 hr, 478 hr, and 500 hr. The graph displays the impedance spectra over time, with markers at each time point.](image)
## Microstructural studies

Progress as of 2016-03-08

<table>
<thead>
<tr>
<th></th>
<th>GenA button cell</th>
<th>GenB button cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEM</td>
<td>3D</td>
</tr>
<tr>
<td><strong>As-received</strong></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>72 h accelerated</strong></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>200 h accelerated</strong></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>500 h accelerated</strong></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>500 h conventional</strong></td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
TEM w/EDXS mapping

- As reduced (0 h)
  - \( \text{MnO}_x \) (red arrows) observed sparingly across entire cathode

- 72 h and 493 h accelerated testing
  - \( \text{MnO}_x \) near cathode/electrolyte interface
  - \( \text{MnO}_x \) also observed in LSM cathode current collector (CCC) for 500 h

- Smaller pores, but no obvious densification layer
TEM w/EDX of bulk LSM composition

72 h

493 h

cathode  CCC

- Uniform LSM composition across cathode and CCC
- Same composition as in as-reduced cell (not shown)
TEM w/EDXS of bulk 8YSZ composition

- Uniform YSZ composition across cathodes
- 4 - 5 cat% Mn
Overview: 3D Reconstruction Process

1: Sample Preparation
- Impregnate with epoxy
- Mount with SOFC layers exposed on two sides
- Polish specimen
- Coat with Pd

2: Preparing Area of Interest
- Deposit Pt to protect area of interest
- Focused Ga-ion beam (FIB): prepare two side trenches, one front trench

3: Data Collection
- Iteratively “slice and view”:
  - FIB sections, 150 nm thick
  - Each section imaged in SEM

4: Data Processing
- Phase segmentation
- Synthesize stack of 2D images
- Calculate:
  - volume fractions
  - particle diameters
  - tortuosity
  - triple phase boundary (TPB) density
Making steps 1 through 4 appear one at a time could be helpful here. Otherwise the slide is a bit overwhelming at first sight. Before you leave this slide, you should briefly point out what aspects of your sample preparation were not routine, or for which you deviated from standard practice in ways that improved your analyses.

Mark De Guire, 10/28/2014
3DR of cathode A — accelerated testing

- No obvious densification layer — consistent with TEM
surfaces near cathode-electrolyte interface
<table>
<thead>
<tr>
<th></th>
<th>Gen A</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as received</td>
<td>200 h accel.</td>
<td>493 h accel.</td>
</tr>
<tr>
<td><strong>sample volume (µm^3)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>≈ 4350</td>
<td>≈ 4620</td>
<td>≈ 4525</td>
</tr>
<tr>
<td><strong>volume fraction (%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample volume (µm^3)</td>
<td><strong>porosity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>17</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td><strong>YSZ</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>41</td>
<td>43.2</td>
</tr>
<tr>
<td></td>
<td><strong>LSM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>42</td>
<td>38.4</td>
</tr>
<tr>
<td><strong>particle diameter (µm)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>porosity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>0.2</strong></td>
<td><strong>0.34</strong></td>
<td><strong>0.42</strong></td>
</tr>
<tr>
<td></td>
<td><strong>YSZ</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.6</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td><strong>LSM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>tortuosity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>porosity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td><strong>YSZ</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.43</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td><strong>LSM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>1.35</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>normalized surface area (µm^{-1})</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>porosity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>17.4</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td><strong>YSZ</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td><strong>LSM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.6</td>
<td>9.88</td>
</tr>
<tr>
<td><strong>Total TPB (µm^{-2})</strong></td>
<td><strong>17.1</strong></td>
<td><strong>9.6</strong></td>
<td><strong>5.86</strong></td>
</tr>
<tr>
<td><strong>Active TPB (µm^{-1})</strong></td>
<td><strong>10.3</strong></td>
<td><strong>8.3</strong></td>
<td><strong>5.12</strong></td>
</tr>
<tr>
<td></td>
<td>Gen A</td>
<td>Gen B</td>
<td>Gen B</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>---------------</td>
</tr>
<tr>
<td></td>
<td>as reduced</td>
<td>493 h accel.</td>
<td>as received</td>
</tr>
<tr>
<td>sample volume (µm³)</td>
<td>≈ 4350</td>
<td>≈ 4525</td>
<td>≈ 6300</td>
</tr>
<tr>
<td>volume fraction (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>porosity</td>
<td>17</td>
<td>18.4</td>
<td>29</td>
</tr>
<tr>
<td>YSZ</td>
<td>42</td>
<td>43.2</td>
<td>33</td>
</tr>
<tr>
<td>LSM</td>
<td>41</td>
<td>38.4</td>
<td>38</td>
</tr>
<tr>
<td>particle diameter (µm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>porosity</td>
<td>0.2</td>
<td>0.42</td>
<td>0.46</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.5</td>
<td>0.46</td>
<td>0.47</td>
</tr>
<tr>
<td>LSM</td>
<td>0.6</td>
<td>0.6</td>
<td>0.67</td>
</tr>
<tr>
<td>tortuosity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>porosity</td>
<td>2</td>
<td>1.6</td>
<td>1.34</td>
</tr>
<tr>
<td>YSZ</td>
<td>1.5</td>
<td>1.3</td>
<td>1.32</td>
</tr>
<tr>
<td>LSM</td>
<td>1.3</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>normalized surface area (µm⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>porosity</td>
<td>26</td>
<td>14.2</td>
<td>13</td>
</tr>
<tr>
<td>YSZ</td>
<td>12</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>LSM</td>
<td>10</td>
<td>9.88</td>
<td>8.9</td>
</tr>
<tr>
<td>Total TPB (µm⁻²)</td>
<td>17.1</td>
<td>5.86</td>
<td>14.5</td>
</tr>
<tr>
<td>Active TPB (µm⁻²)</td>
<td>10.3</td>
<td>5.13</td>
<td>13.0</td>
</tr>
</tbody>
</table>
Total TPB – ASR relationship

Calculated from Continuous ASR Data

ASR (Ω·cm²)

Total TPB (μm²)

- 0 hr
- 200 hr
- 500 hr

0.1 0.2 0.3 0.4 0.5 0.6

0 2 4 6 8 10 12 14 16 18
Active TPB – ASR relationship

Calculated from Continuous ASR Data

- Active TPB (μm²)
- ASR (Ω-cm²)

0 hr, 200 hr, 500 hr points on the graph.