Degradation of LSM-Based SOFC Cathodes Under Accelerated Testing

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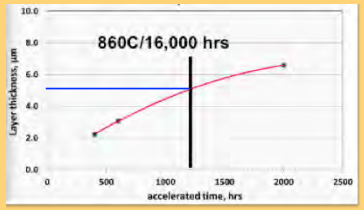
Abstract

After long-term testing (up to 16 kh) under practical operating conditions, SOFC cathodes based on lanthanum strontium manganite (LSM, $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$) exhibit microstructural changes that may be related to loss of cell performance:

- Changes in phase fraction and their distribution across the cathode, particularly densification/ loss of porosity near the cathode-electrolyte interface;
- Changes in (total and active) triple-phase boundary (TPB) density;
- Formation of free manganese oxides (MnO_x); and
- Interfacial chemistry, particularly LSM/YSZ at the cathode/electrolyte interface and in the composite cathode.

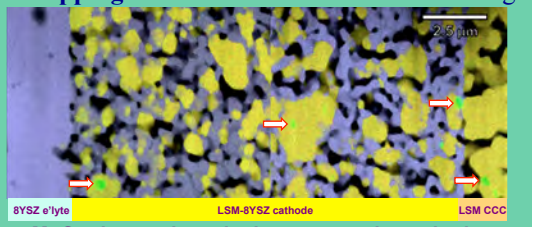
This research program implements an accelerated testing protocol to gather performance data in time frames of e.g. 500 h that are relevant to much longer-term normal cell operation (≥ 5 kh). We present performance data from button cells with a single cathode composition under accelerated conditions at 72 and 500 h. We also present microstructural studies (TEM, EDXS, FIB-SEM, and 3-D reconstruction) on tested cells and an untested, as-reduced cell. We compare these findings to results from prior tests carried out at LG Fuel Cell Systems to see whether similar microstructural and performance differences are seen in these button cells.



Prior results [1] from LGFCS on thickness of densified cathode layer vs. duration of accelerated testing. The vertical black line indicates that 1.2 kh under the accelerated conditions produced the same thickness of densified cathode (5 µm) as was observed after 16 kh of testing under simulated system conditions (horizontal blue line).

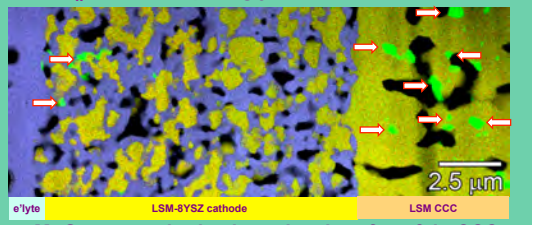
TEM w/EDXS mapping: as-reduced vs. 493 h accel'd testing

As reduced



- MnO_x observed sparingly across entire cathode

493 h accel'd testing

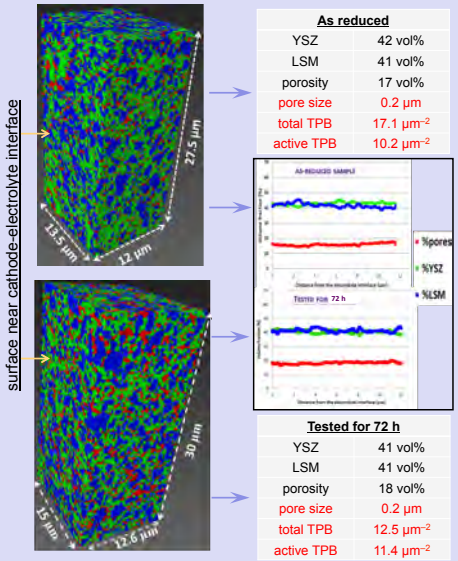


- MnO_x near cathode-electrolyte interface & in CCC
- No obvious densification layer (3DR in progress)

Cell specifications; testing procedures

- Button cells:
  - 8YSZ electrolyte-supported
  - NiO-8YSZ anode (60:40 wt%)
  - LSM:8YSZ (50:50 wt%) cathode
- Accelerated test conditions: same constant temperature, anode and cathode atmospheres, and current density

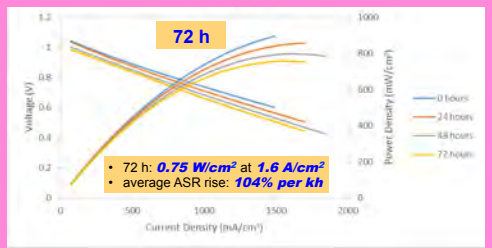
3-D reconstruction: 0 & 72 h accel'd testing

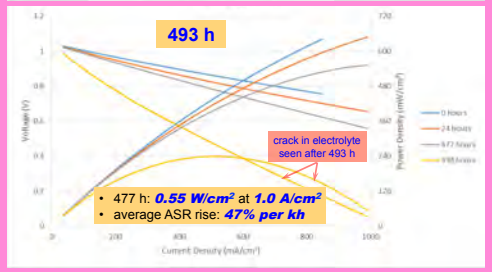


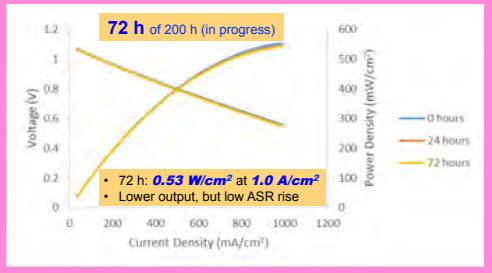
As reduced	
YSZ	42 vol%
LSM	41 vol%
porosity	17 vol%
pore size	0.2 µm
total TPB	17.1 µm^{-2}
active TPB	10.2 µm^{-2}

Tested for 72 h	
YSZ	41 vol%
LSM	41 vol%
porosity	18 vol%
pore size	0.2 µm
total TPB	12.5 µm^{-2}
active TPB	11.4 µm^{-2}

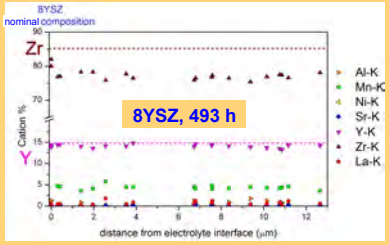
V–I & P–I curves: accelerated testing



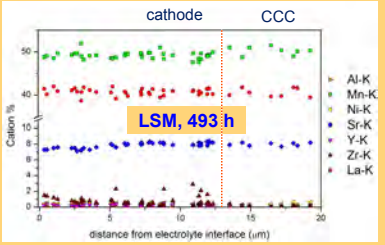




EDXS after 493 h testing: 8YSZ and LSM composition profiles



- Compositions and profiles ~same as in as-reduced cell
- Uniform across cathode
- 4–5 cat% Mn



- Uniform composition across cathode and CCC
- Slight Sr depletion at cathode–electrolyte interface, vs. as-reduced cell

Summary

- The accelerated test protocol leads to much higher rates of degradation (ca. 50–100% ASR rise per kh) than normal cell testing (target ≤1% per kh).
- 72 h of accelerated testing led to coarsening of pores, and some loss in total TPB density, but no conspicuous changes in phase fractions or phase distribution nor densification at the cathode-electrolyte interface, compared to the as-reduced, untested cell.
- After 493 h of accelerated testing:
  - MnO_x was confined to the cathode-electrolyte interface and the cathode current collector.
  - No obvious densification layer was observed at the cathode-electrolyte interface. 3-D reconstruction (in progress) will provide a more conclusive and quantitative analysis.
  - 8YSZ and LSM compositions and profiles were largely unchanged compared to the as-reduced, untested cell.

These studies should help clarify whether correlations exist between MnO_x formation, localized cathode densification, and performance loss.

Reference: [1] M. R. De Guire, A. H. Heuer, and Z. Liu, "Long-Term Degradation of LSM-Based SOFC Cathodes: Use of a Proven Accelerated Test Regimen." Poster at 15th SECA Workshop, Pittsburgh, PA, 22-23 July 2014.

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