Degradation of LSM-Based SOFC Cathodes Under Accelerated Testing

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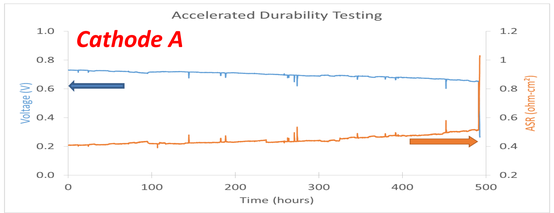
Abstract

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 might lead to a decrease in cell performance:

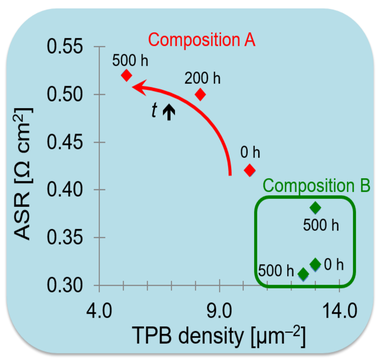
- Changes in phase fraction and their distribution across the cathode, particularly densification/loss of porosity near the cathode-electrolyte interface;
- Changes in (total and active) triple-phase boundary (TPB) density;
- Formation of free manganese oxides (MnO_x); and
- Interfacial chemistry, particularly 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 two cathode compositions under accelerated conditions for 500 h. Post-test analysis using transmission electron microscopy (TEM) with energy-dispersive x-ray spectroscopy (EDXS), focused ion-beam scanning electron microscopy (FIB-SEM) and 3-D reconstruction show the microstructural changes in the tested cells.

Cell performance versus testing time



Voltage and ASR during 500 h of accelerated testing.

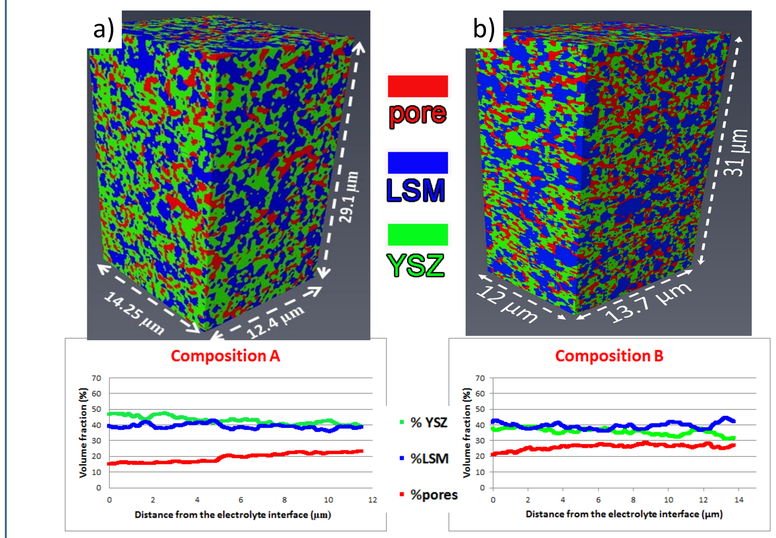


- ***Cathode B*** vs. ***Cathode A*:**
  - Lower ASR
  - Higher TPB density
  - ***Less change during operation***

Cell specifications; testing procedures

- Button cells:
  - 8YSZ electrolyte-supported
  - NiO-8YSZ anode
  - Composition A: YSZ/LSM (10% A site deficient)
  - Composition B: YSZ/LSM (5% A site deficient)
- Accelerated test conditions: same constant temperature, anode and cathode atmospheres, and current density

3D reconstructions after 500 h accelerated testing



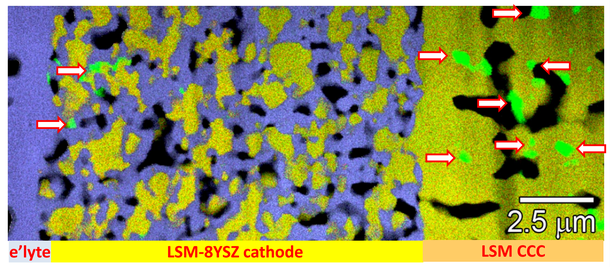
Data from cathodes after 500 h of accelerated testing. Left: composition A; right: composition B. Top: 3-D reconstructions. The front left face is adjacent to the electrolyte. Bottom: Volume fraction profiles of the YSZ, LSM, and pore phases across the cathodes.

		cathode A			cathode B		
		as received	500 h conventional test	493 h Accelerated test	as received	500 h conventional test	500 h Accelerated test
sample volume (μm³)		4350	3700	4525	6300	5000	5096
volume fraction (%)	porosity	17	21.9	18.4	29	26	26
	YSZ	42	42.6	43.2	33	35.5	35
	LSM	41	35.5	38.4	38	38.5	39
particle diameter (μm)	porosity	0.20	0.40	0.42	0.46	0.45	0.38
	YSZ	0.50	0.50	0.46	0.47	0.42	0.51
	LSM	0.60	0.65	0.60	0.67	0.65	0.70
normalized surface area (μm^{-1})	porosity	26	15.7	14.2	13	13.3	15.9
	YSZ	12	11.5	13	13	14	11.9
	LSM	10	8.9	9.9	8.9	9.26	8.5
Total TPB (μm^{-2})		17.1	11.0	5.86	14.5	14.2	14.8
Active TPB (μm^{-2})		10.3	9.5	5.13	13.0	13.0	12.5

Microstructural parameters from 3D reconstructions of cathodes.

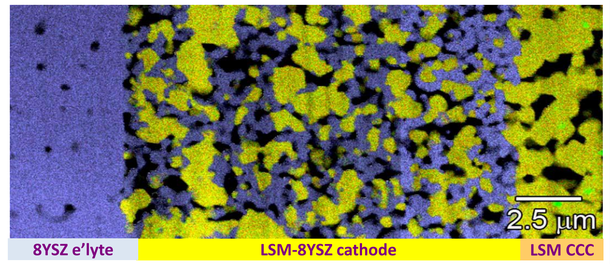
TEM w/EDXS after 500 h accelerated testing

Cathode A
493 h accel'd testing



Cathode B
500 h accel'd testing

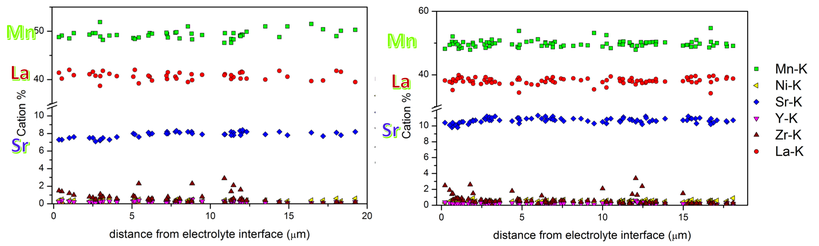
YSZ
LSM
pore
MnO_x



- More MnO_x was observed in cathode A, both at the electrolyte interface and in the cathode current collector (CCC).
- Cathode B was more porous than cathode A at all stages of testing.

EDXS after 500 h testing: LSM composition profiles

Cathode A **Cathode B**



- In both cathodes A and B, LSM composition was uniform across the cathodes and the CCC

Summary

After 500 h of accelerated testing:

- Cathode A exhibited higher rates of ASR rise than cathode B.
- Cathode A showed more MnO_x near the electrolyte and in the cathode current collector.
- Cathode B was more porous than cathode A at all stages of testing.
- Loss of porosity near the electrolyte, seen in cells tested under conventional conditions for >8 kh, was not observed.
- TPB (total and active) decreased steadily in cathode A, but did not change significantly in cathode B.

Overall, a pattern of microstructural stability, absence of MnO_x formation, and high TPB density coincided with lower ASR in cathode B, in contrast with cathode A.