Degradation of LSM-Based SOFC Cathodes Under Accelerated Testing

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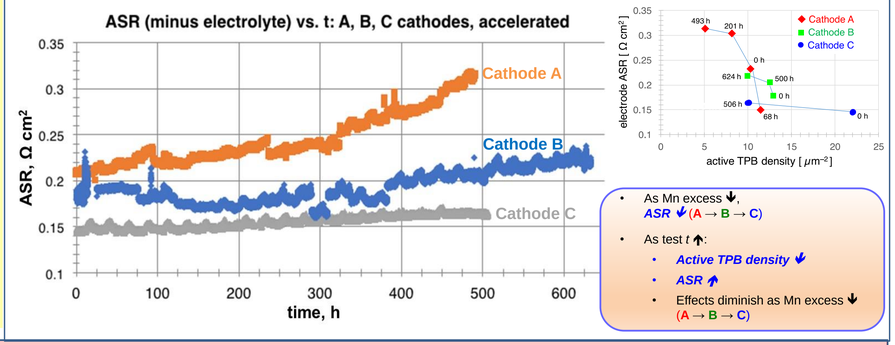
Abstract

To study the effects of composition on performance and microstructural evolution in SOFC cathodes based on lanthanum-strontium manganite (LSM, $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$), button cells with three different LSM compositions were operated for up to 624 h under conventional and accelerated conditions. The cathode compositions differed primarily in the degree of manganese excess (Mn / (La+Sr) > 1). The cells underwent durability testing (voltage versus time at constant current density) with intermittent linear-sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements. Post-test microstructural analysis consisted of transmission electron microscopy (TEM) with energy-dispersive x-ray spectroscopy (EDXS), focused ion-beam scanning electron microscopy (FIB-SEM), and 3-D reconstruction. An LSM composition with an intermediate level of excess manganese gave low increase of area-specific resistance (ASR) over time, and also exhibited high microstructural stability (minimal formation of manganese oxides, little cathode densification, and lowest decrease in three-phase boundary (TPB) density). The LSM composition with the lowest level of excess manganese gave the lowest values of ASR in up to 500 h of testing, but also exhibited significant increases in ASR and in TPB density over time.

Cell specifications; testing procedures

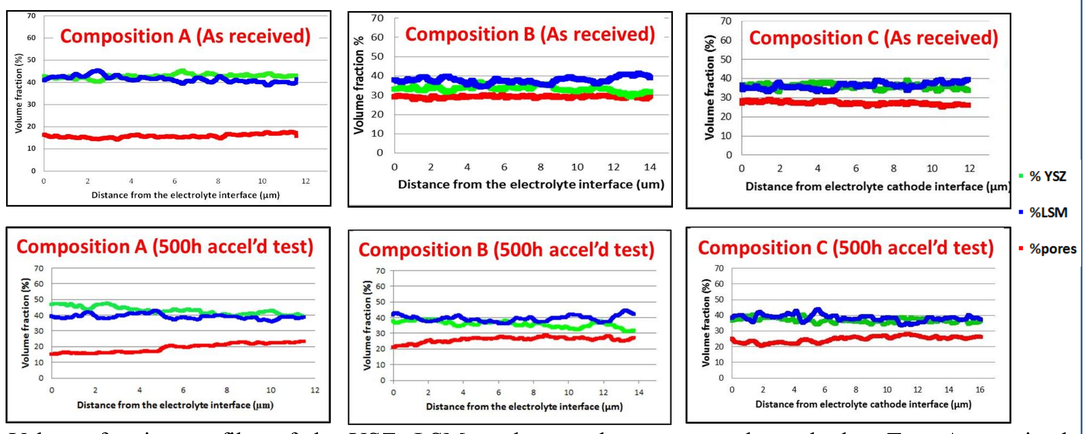
- Button cells:
  - 8YSZ electrolyte • NiO-8YSZ anode
  - Cathodes: LSM + 8YSZ
    - A: $(La_{0.85}Sr_{0.15})_{0.90}MnO_{3\pm\delta}$ *(LSM 85-90)*
    - B: $(La_{0.80}Sr_{0.15})_{0.95}MnO_{3\pm\delta}$ *(LSM 80-95)*
    - C: $(La_{0.80}Sr_{0.15})_{0.98}MnO_{3\pm\delta}$ *(LSM 80-98)*
- Accelerated test conditions: 1000 °C; 760 mA/cm²; ambient air; humidified H_2, 50 sccm

Cell performance versus testing time



- As Mn excess ↓, *ASR* ↓ (A → B → C)
- As test *t* ↑:
  - *Active TPB density* ↓
  - *ASR* ↑
  - Effects diminish as Mn excess ↓ (A → B → C)

3D reconstructions after 500 h accelerated testing



Volume fraction profiles of the YSZ, LSM, and pore phases across the cathodes: Top: As received samples. Bottom: Samples tested for 500 hrs under accelerated conditions.

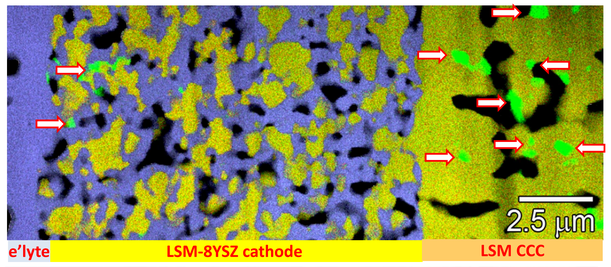
		Gen A		Gen B			Gen C	
		As received	493h Accel test	As received	500h Accel test	624 hrs Accel test	As received	500h Accel test
sample volume (μm³)		4350	4525	6300	5096	4550	4100	5012
volume fraction (%)	porosity	17	18	29	25	25	28	25
	YSZ	41	43	33	35	37	37	37
	LSM	41	38	38	40	38	35	38
particle diameter (μm)	porosity	0.23	0.42	0.38	0.5	0.46	0.28	0.44
	YSZ	0.52	0.46	0.45	0.5	0.51	0.32	0.46
	LSM	**0.59**	**0.61**	**0.65**	**0.7**	**0.72**	**0.26**	**0.71**
normalized surface area (μm^{-1})	porosity	26	14	16	13	13	21	14
	YSZ	12	13	13	12	11	18	13
	LSM	10	10	9	8	8	13	8
Total TPB (μm^{-2})		17.1	5.9	14.5	14.8	11	21.7	11.1
Active TPB (μm^{-2})		10.3	5.1	13.0	12.5	10	20.0	10.2

Microstructural parameters from 3D reconstructions of cathodes.

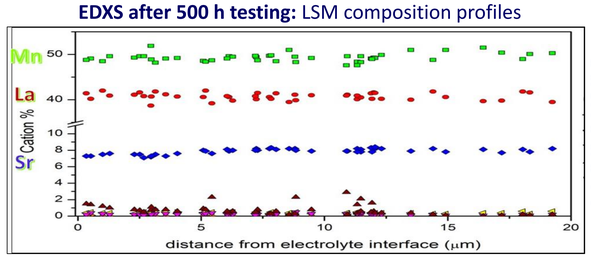
- All three cathodes developed porosity gradients after 500 h of accelerated testing, exhibiting lower porosity at the cathode / electrolyte interface than at the cathode / cathode current collector interface.
- Cathode B shows less pore coarsening, less loss of pore area, and stabler TPB (total and active).

TEM w/EDXS after 500 h accelerated testing

Cathode A — 493 h accel'd testing

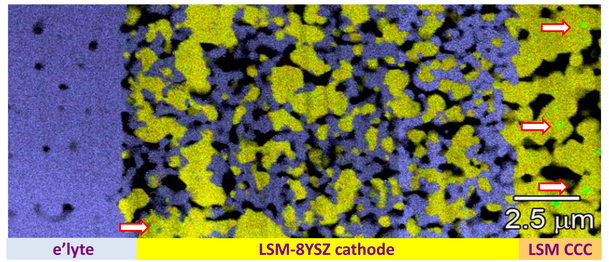


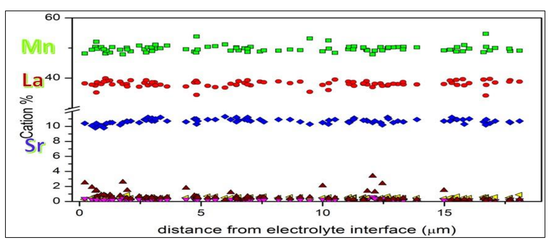
EDXS after 500 h testing: LSM composition profiles



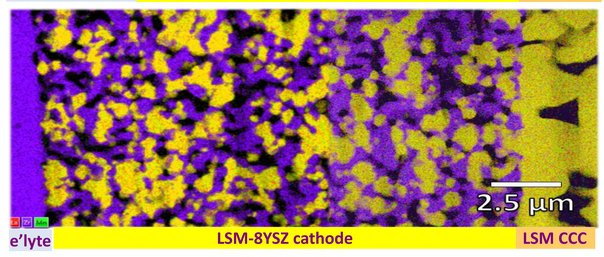
Cathode B — 500 h accel'd testing

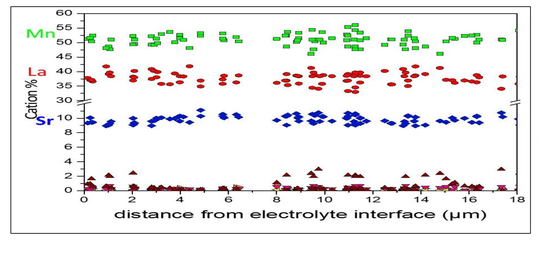
YSZ
LSM
pore
MnO_x





Cathode C — 500 h accel'd testing





- More MnO_x was observed in cathode A, both at the electrolyte interface and in the cathode current collector (CCC).
- MnO_x was absent in cathode C close to the electrolyte / cathode interface and in the CCC.
- In all three cathodes, the LSM composition remained uniform across the cathodes and the CCC after 500 h of testing.

Summary

After 500 h of accelerated testing:

- Cathode A exhibited higher rates of ASR rise than cathode B and C.
- Cathode A showed more MnO_x near the electrolyte and in the cathode current collector; no MnO_x was observed in cathode C.
- Cathodes B and C had higher porosity than cathode A at all stages of testing.
- Cathode B showed less pore coarsening and stabler TPB (total and active).
- All three cathodes developed porosity gradients after 500 h of accelerated testing, exhibiting lower porosity at the cathode / electrolyte interface than at the cathode / cathode current collector interface.
- As testing proceeds, active TPB density decreases and ASR increases. These trends diminish as Mn excess decreases.