Operating Stresses and their Effects on Degradation of LSM-Based SOFC Cathodes

Chenxin Deng,* Andrew Cai, Arthur H. Heuer, and Mark R. De Guire

Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106

*) cxd320@case.edu; 216-225-8404

Abstract

Goals: a) Understand how operating conditions affect the performance of solid oxide fuel cells (SOFCs) with cathodes of lanthanum strontium manganite (LSM, $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$) and yttria-stabilized zirconia (YSZ, $(Zr_{1-z}Y_z)O_{2\pm\delta}$); b) relate the changes in performance to the microstructural changes in the cells after operation.

This project builds on recent studies of performance and microstructural changes in LSM-based SOFC cathodes operated for up to 500 h or more at elevated temperature (1,000 ˚C) and current density (760 mA cm^{-2}). The new studies will add:

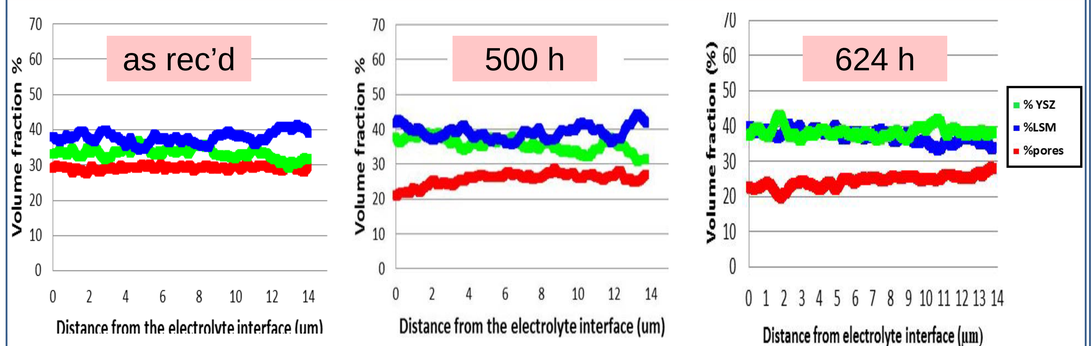
1. *Reduced p_{O_2}* at the cathode, to intensify degradation of cathode performance.
2. *Aging tests:* to study the effects of service temperature and atmosphere at open-circuit voltage *OCV*(*t*) (zero current).
3. *Current load cycling:* to study the effects of *I–V* sweeps and EIS measurements on cell output.

As in the prior work, cells will undergo detailed microstructural characterization, using transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDXS), and three-dimensional reconstruction (3DR), with sample preparation via focused ion-beam scanning electron microscopy (FIB/SEM), focusing on the following phenomena:

1. *Changes in phase fraction and their distribution* across the cathode, particularly densification/loss of porosity near the interfaces of the cathode with the electrolyte and the cathode current collector (CCC);
2. Changes in total and active *three-phase boundary (TPB) density;*
3. Formation and distribution of *manganese oxides (MnO_x)*.

The chosen material sets are currently planned for commercial implementation, and the chosen operating conditions are relevant to operation of cells, stacks, and systems in the field. By elucidating microstructural causes of cell degradation, the new studies have the potential to improve the reliability and lifetime of SOFC technology.

Prior work: 3DR before & after accelerated testing, cathode B



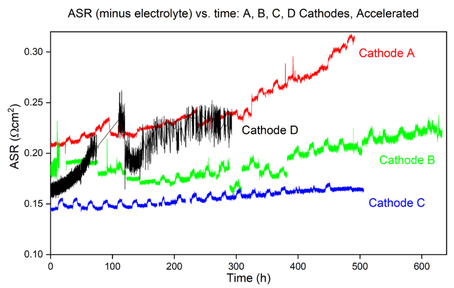
Volume fraction profiles of the YSZ, LSM, and pore phases across the cathode.

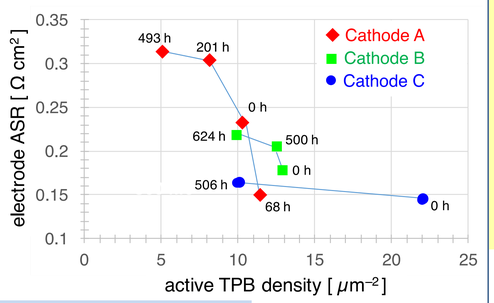
		As received	500h Accel test	624 hrs Accel test
sample volume (µm³)		6300	5096	4550
volume fraction (%)	porosity	29	25	25
	YSZ	33	35	37
	LSM	38	40	38
particle diameter (µm)	porosity	0.38	0.5	0.46
	YSZ	0.45	0.5	0.51
	LSM	**0.65**	**0.7**	**0.72**
normalized surface area (µm^{-1})	porosity	16	13	13
	YSZ	13	12	11
	LSM	9	8	8
Total TPB (µm^{-2})		14.5	14.8	11
Active TPB (µm^{-2})		13.0	12.5	10

Microstructural parameters from 3D reconstructions of cathodes.

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

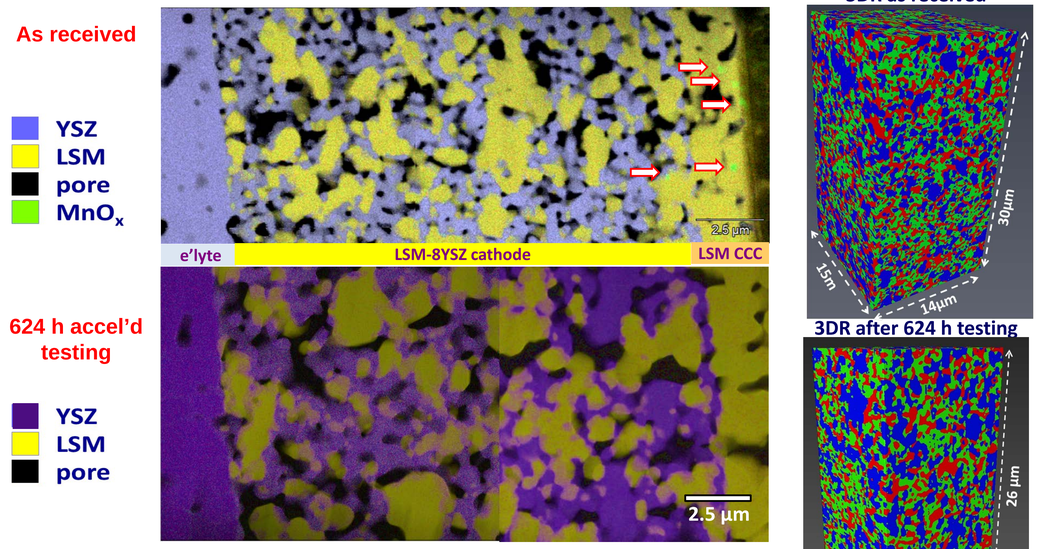
Prior work: Durability tests; ASR vs. TPB density





- As Mn excess decreases, ***ASR decreases*** (A → B → C)
- As test *t* increases, ***active TPB decreases*** and ***ASR increases***
- Effects diminish as Mn excess decreases (A → B → C)

Prior work: TEM & 3DR before & after 624 h accel'd testing, cathode B

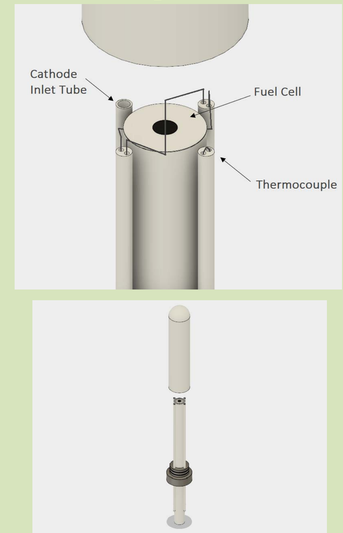


- All as-received cathodes had uniform microstructure across their thickness.
- 624 h, cathode B: No MnO_x; slight coarsening and loss of interfacial area for all phases; less porosity near electrolyte.

Cell details; test conditions

- 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: $(La_{0.80}Sr_{0.20})_{0.95}MnO_{3\pm\delta}$ *(LSM 80-95)*
    - C: $(La_{0.80}Sr_{0.20})_{0.98}MnO_{3\pm\delta}$ *(LSM 80-98)*
- Accelerated test conditions: 1000 °C; 760 mA/cm^2; ambient air; humidified H_2, 50 sccm

Low-p_{O_2} test fixture



Stresses and applicable stress levels for single-cell testing[1]

stress	stress level range	aging / failure	additional impact
high temperature	900 … 1050°C	interdiffusion agglomeration densification / sintering decomposition	
low temperature	400 … 650°C	phase changes electrode poisoning carbon deposition	
high current density	depends on cell	Ni-agglomeration	temperature fuel utilization
fuel utilization	< 100%	Ni-agglomeration	
fuel humidity ($p(H_2O)$)	< 90%	Ni-agglomeration	fuel humidity
air utilization	< 100%	cathode decomposition	oxidant composition
oxidant composition	$p(O_2) > 0.1\%$	cathode decomposition	
C_mH_n-content (m>1)	ppm to %	carbon deposition metal dusting	
S-content (H_2S, SO_x)	<< 1%	catalyst deactivation electrode poisoning	fuel utilization

1) A. Weber, J. Szasz, S. Dierickx, C. Endler-Schuck, and E. Ivers-Tiffee, "Accelerated Lifetime Tests for SOFCs," *ECS Transactions*, **68** [1] pp. 1953–1960 (2015).

New aspects of current project

- Possible outcomes from ***testing at low cathode p_{O_2}:***[1]
  - Higher ASR in durability testing
  - Higher cathode overpotentials (higher cathode peaks in Bode plots)
  - More MnO_x near electrolyte
  - Faster loss of TPD density
  - Role of Mn excess
- ***Aging tests versus durability tests***[1]
  - Independent variables
    - Time at temperature
    - Air versus low p_{O_2}
    - Operation (durability tests) versus OC
    - Mn excess
  - Dependent variables
    - Loss of TPB density
    - MnO_x formation
    - Change in OCV over time (baseline degradation rate)
- Possible outcomes from ***current load cycling***[1]
  - Step changes in ASR
  - Step changes in OCV
  - Faster degradation
  - Corresponding changes in microstructure

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