In-Operando XRD of LSM/YSZ Cathodes in Combined H₂O + CO₂ during 1000+ h SOFC Tests John S. Hardy, Christopher A. Coyle, Nathan L. Canfield, and Jeffry W. Stevenson

New SOFC Research Capability was Developed at PNNL In-situ XRD of Anode-supported SOFCs during Operation

Bruker D8 Advance XRD...







nall-scale (13 mm dia) button cell 0.5 cm² LSM/YSZ Cathode Ni-YSZ Anode-supported ~10um YSZ Electrolyte

...with Anton Parr HTK 1200 Heating Chamber



Experimental Parameters for 1000+ hour tests

Cell Operation

- Temperature: 775°C
- Electrical: Constant Current approximating 800 mV
- Cathode Gas: Flowing air with no contaminants; or 3% H_2O ; or 3% H_2O + 12% CO_2
- Fuel: Moist H₂

XRD Parameters

- Repeated 1 hour scans
- 20 Range: 25 85°
- Step Size: 0.02°
- Time/Step: 1.1 seconds

Typical Results & Analysis







CONTAMINANTS CAUSED PERFORMANCE DEGRADATION



TIME-DEPENDENT PEAK SHIFTS EXHIBITED BY LSM **Rietveld refinement finds that contaminants cause expansion**



AVERAGE PHASE COMPOSITION (wt%)

	0% H ₂ O + 0% CO ₂	3% H ₂ O + 0% CO ₂	3% H ₂ O + 12% CO ₂
LSM	45.7 +/- 1.1	46.4 +/- 1.1	45.2 +/- 2.2
YSZ	43.3 +/- 1.2	45.0 +/- 1.0	45.1 +/- 2.4
Tet-YSZ	0.6 +/- 0.1	1.0 +/- 0.5	1.1 +/- 0.8
Mn ₃ O ₄	3.0 +/- 0.2	2.3 +/- 0.2	2.1 +/- 0.4
MnO ₂	3.5 +/- 0.3	2.0 +/- 0.2	ND
MnO	2.1 +/- 0.2	1.1 +/- 0.1	6.0 +/- 0.9
La ₂ O ₃	1.8 +/- 0.2	1.9 +/- 0.2	0.3 +/- 0.1
La ₂ Zr ₂ O ₇	<0.1	<0.1	0.1 +/- 0.1

Summing 1000+ hours of XRD scans enables resolution of trace phases



NO SIGNIFICANT DIFFERENCES IN SEM/EDS

No Contaminants

H₂O Only



WHAT COULD LEAD TO MEASURED LSM EXPANSION IN CONTAMINANTS?

Loss of Sr or O causes expansion in LSM

Rate of Sr loss that correlates to the measured rate of expansion

	۸ ³ /հ	A^3/x in La _{1-x} Sr _x MnO ₃		v /h		
	A / 11	min	max	~ / 11		
	0.0006	20.540*	24.036*	3×10 ⁻⁵		
Effects of Sr on Unit Cell Volume referenced from:						

• Moriche, et al., J. Power Sources, 252, 43 (2014).

• Millini, et al., J. Mater. Sci., 29, 4065 (1994).

• Hammouche, et al., Mater. Res. Bull., 24, 367 (1989).

Corresponding values for O were not available.

SUMMARY

- Tetragonal YSZ, Mn oxides, La oxide, and trace amounts of La zirconate pyrochlore form during sintering of LSCF cathodes.
- Power density decreased with increasing cathode air contaminants.
- In air with no added contaminants, the LSM/YSZ cathode exhibited stable performance, while in contaminants, it degraded - at nearly the same rate with and without CO_2 .
- In air with no added contaminants, the LSM crystal lattice contracted, while in contaminants, it expanded at similar rates with and without CO_2 . • A loss of ~0.00003 Sr/h from the chemical formula of LSM could cause the expansion
- experienced during exposure to contaminants in cathode air.
- No significant differences in cathode microstructure or chemistry due to contaminant exposure were observed in SEM/EDS.

