In-Operando XRD of Anode-Supported LSCF Cathodes at 700 – 800°C for 1000 h

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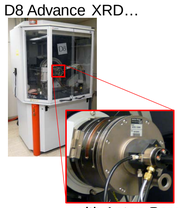
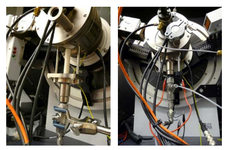
New SOFC Research Capability was Developed at PNNL
In-situ XRD of Anode-supported SOFCs during Operation

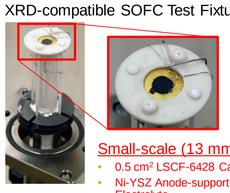
Bruker D8 Advance XRD…



…with Anton Parr HTK 1200 Heating Chamber



XRD-compatible SOFC Test Fixture



Small-scale (13 mm dia) button cell
- 0.5 cm² LSCF-6428 Cathode on SDC Interlayer
- Ni-YSZ Anode-supported ~10µm YSZ Electrolyte

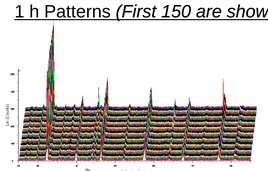
Experimental Parameters for ~1000 hour tests

Cell Tests
- Temperatures: 700, 750, and 800°C
- Operating Cells: Constant Current approximating 800 mV
- Resting Cell: OCV (750°C)
- Feed Gas: Flowing air (cathode) and moist H_2 (anode)

XRD
- Repeated 1 hour scans
- 2θ Range: 25 - 85°
- Step Size: 0.02°
- Time/Step: 1.1 seconds

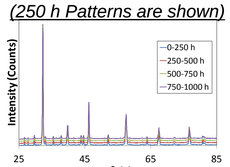
Typical Results & Analysis

1 h Patterns *(First 150 are shown)*

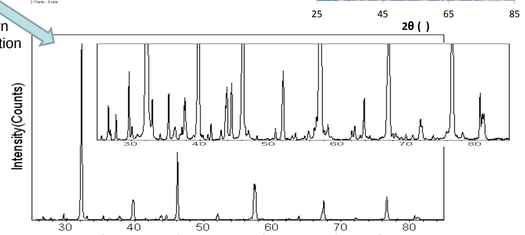


Pattern Summation

Various timeframes are prepared To identify time-dependent changes *(250 h Patterns are shown)*



Pattern Summation



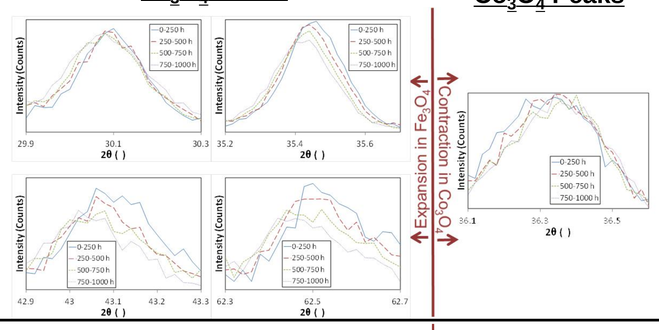
1000 h pattern is prepared to examine minor peaks

Summing 1000 hours of XRD scans made it possible to resolve trace phases

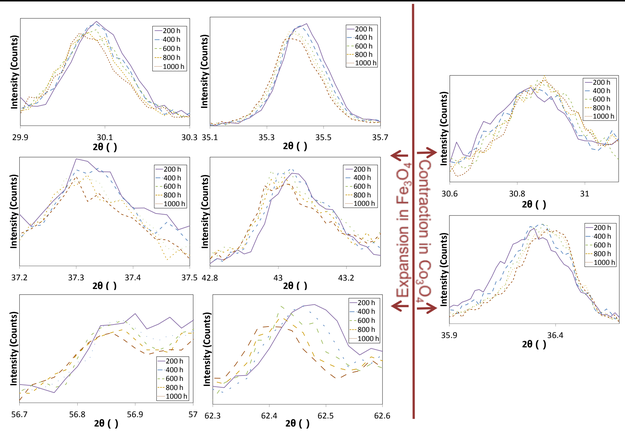
	Sintered Powder	700C Operating	750C OCV	750C Operating	800C Operating
LSCF	99.4 wt%	96.9 wt%	97.3 wt%	91.5 wt%	97.5 wt%
Fe_3O_4	0.4 wt%	2.0 wt%	1.7 wt%	7.7 wt%	0.8 wt%
Co_3O_4	0.2 wt%	1.1 wt%	1.0 wt%	0.8 wt%	1.7 wt%

TIME-DEPENDENT PEAK SHIFTS EXHIBITED BY MINOR PHASES

700°C & ~0.8V: (0.09-0.12 W/cm²)



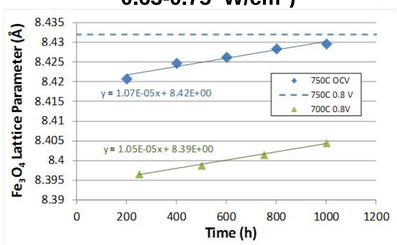
750°C & OCV: (1.08-1.09 V)



- No significant changes detected in LSCF peaks over time
- Secondary phases of Fe_3O_4 and Co_3O_4 exhibited peak shifts
  - Lattice parameters were diverging from one another

750-800°C & ~0.8V: (0.2-0.3 W/cm² & 0.63-0.75 W/cm²)

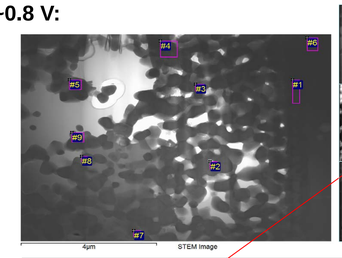
No time-dependent changes in the XRD patterns were significant enough to be identified

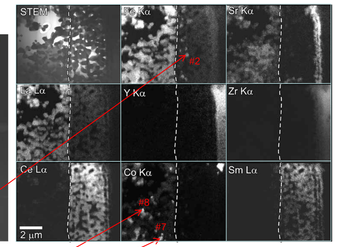


Temperature	Cell Voltage	Time-dependent Changes in XRD
700ºC	~0.8 V	Divergent Fe_3O_4 and Co_3O_4 peak shifts
750ºC	OCV	Divergent Fe_3O_4 and Co_3O_4 peak shifts
750ºC	~0.8 V	None
800ºC	~0.8 V	None

POST-MORTEM SEM/EDS MAPPING

750°C & ~0.8 V:

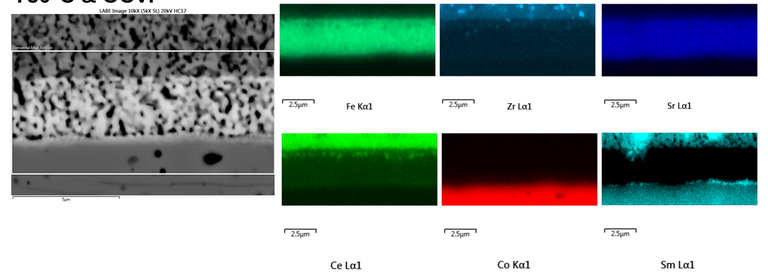




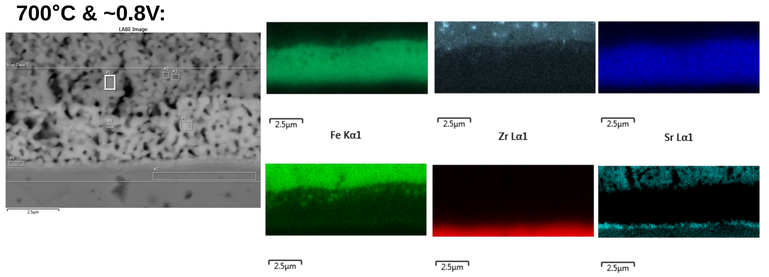
Spectrum	O	Fe	Co	Sr	Y	Zr	La	Ce	Sm
Sum Spectrum	34.51	10.38	2.96	6.36	2.79	15.25	9.36	14.50	3.87
#1	6.87	3.09	0.00	29.21	4.89	43.84	0.98	4.43	6.68
#2	45.16	20.18	3.16	3.11	0.00	0.00	4.61	8.50	15.28
#3	49.14	7.18	1.39	2.37	0.00	0.00	5.97	25.30	8.66
#4	30.89	25.63	7.36	6.39	0.29	0.00	23.36	1.93	4.15
#5	33.89	27.54	9.16	6.01	0.00	0.00	23.41	0.00	0.00
#6	4.37	1.63	36.10	0.00	8.66	47.97	0.00	0.00	1.26
#7	51.12	8.98	34.10	1.40	0.00	0.00	4.40	0.00	0.00
#8	44.75	11.50	35.10	4.82	0.00	0.00	3.83	0.00	0.00
#9	43.68	22.34	2.93	4.65	0.00	0.00	26.40	0.00	0.00

All results in atomic%

750°C & OCV:



700°C & ~0.8V:



SUMMARY

- During sintering, Sr migrates to SDC/YSZ interface and Fe/Co spinels form.
- At 700ºC and 0.8V or 750ºC and OCV, the lattice parameters of Fe/Co spinels gradually change.
- At 750ºC and 0.8V or 800ºC and 0.8V, Fe/Co spinels equilibrate too quickly for observation with laboratory XRD.
- SEM suggests that
  - Fe-rich spinels are predominantly in the SDC layer.
  - Co-rich spinels are predominantly in the LSCF cathode.
- Spinel lattice parameter changes suggest Fe & Co exchange with LSCF.

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