In-Operando XRD of LSCF Cathodes in Humid Air during 700+ h Anode-Supported SOFC Tests

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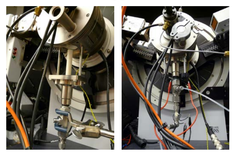
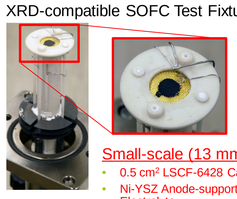
New SOFC Research Capability was Developed at PNNL
In-situ XRD of Anode-supported SOFCs during Operation

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

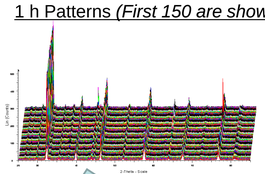
Experimental Parameters for 700+ hour tests

Cell Tests
- Temperatures: 650ºC for humid air test; 700, 750, and 800ºC for dry air tests.
- Operating Cells: Constant Current approximating 800 mV
- Resting Cell: OCV (750ºC)
- Feed Gas: Flowing air with 0% or 3% H_2O (cathode) and moist H_2 (anode)

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

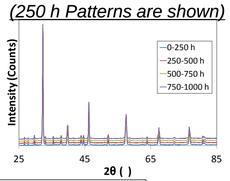
Typical Results & Analysis

1 h Patterns *(First 150 are shown)*

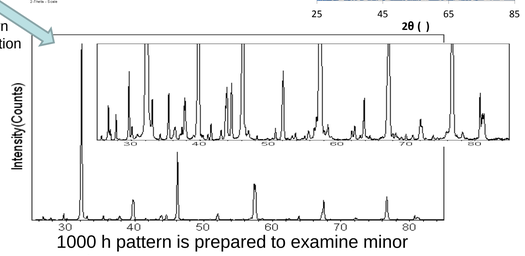


Pattern Summation

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



Pattern Summation

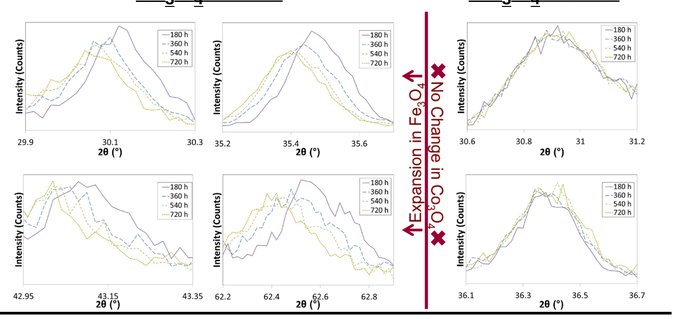


1000 h pattern is prepared to examine minor peaks

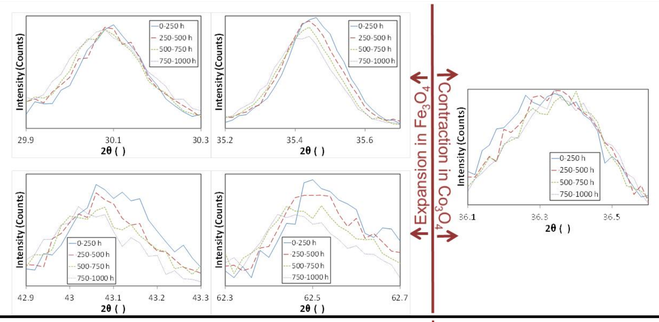
TIME-DEPENDENT PEAK SHIFTS EXHIBITED BY MINOR PHASES

Fe_3O_4 Peaks | Co_3O_4 Peaks

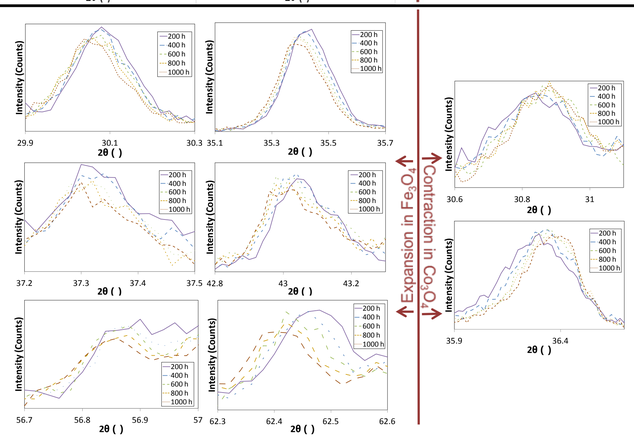
HUMID 650ºC & ~0.8V: (0.09-0.10 W/cm²)



DRY 700ºC & ~0.8V: (0.09-0.12 W/cm²)



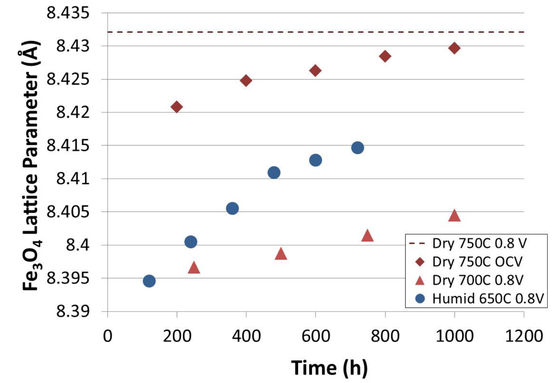
DRY 750ºC & OCV: (1.08-1.09 V)



- 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

DRY 750-800ºC & ~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	Steam in Cathode Air	Time-dependent Changes in XRD
650ºC	~0.8 V	3%	Expanding Fe_3O_4 & Stable Co_3O_4
700ºC	~0.8 V	0%	Expanding Fe_3O_4 & Contracting Co_3O_4
750ºC	OCV	0%	Expanding Fe_3O_4 & Contracting Co_3O_4
750ºC	~0.8 V	0%	None
800ºC	~0.8 V	0%	None

Phase Composition

	Humid 650ºC ~0.8 V	Dry 700ºC ~0.8 V	Dry 750ºC OCV	Dry 750ºC ~0.8 V	Dry 800ºC ~0.8 V
LSCF	94.4 wt%	94.2 wt%	94.7 wt%	90.6 wt%	97.6 wt%
Fe_3O_4	1.9 wt%	1.4 wt%	1.2 wt%	5.3 wt%	0.6 wt%
Co_3O_4	0.9 wt%	0.8 wt%	1 wt%	1 wt%	1.5 wt%
La_2CoO_4	1.2 wt%	1.7 wt%	1.6 wt%	1 wt%	0.2 wt%
$LaCoO_3$	0.8 wt%	1.4 wt%	1.2 wt%	2.2 wt%	ND
Co_2O_3	0.4 wt%	0.2 wt%	0.1 wt%	ND	0.1 wt%
La_2O_3	0.3 wt%	0.3 wt%	0.2 wt%	ND	<0.1 wt%

Summing 700+ hours of XRD scans enables resolution of trace phases

SUMMARY

- Fe/Co spinels form during sintering of LSCF cathodes.
- In dry air at 700ºC and 0.8V or 750ºC and OCV, the lattice parameters of Fe/Co spinels gradually change.
- In humid air at 650ºC and 0.8V in humid air, the lattice of the Fe-rich spinel expands more quickly than in dry air while the Co-rich spinel is stable.
- In dry air at 750 - 800ºC and 0.8V, Fe/Co spinels equilibrate too quickly for observation with laboratory XRD.
- Spinel lattice parameter changes suggest Fe & Co are mobile during long term operation of LSCF cathodes at low temperature.