In-situ XRD of Anode-Supported SOFC Cathodes
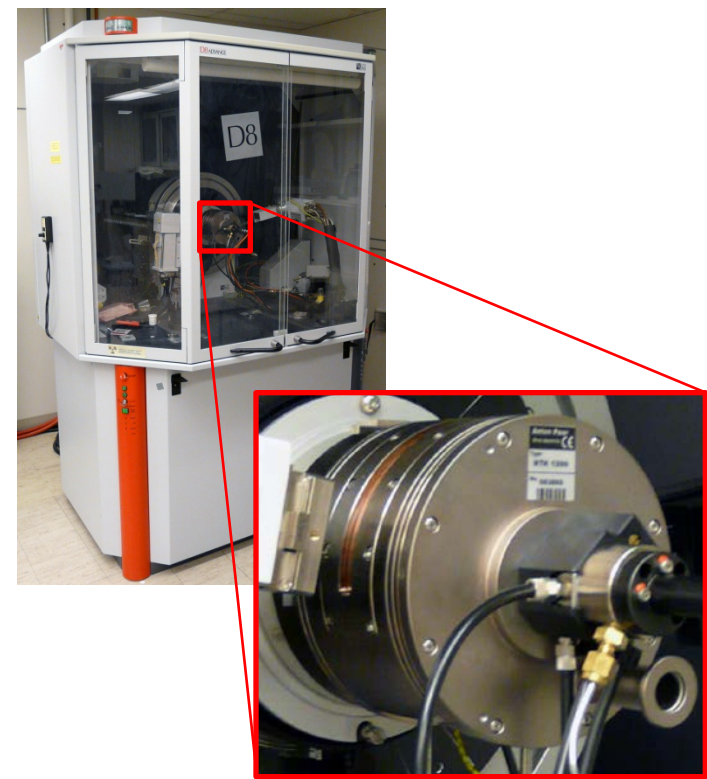
John S. Hardy, Jared W. Templeton, Dan J. Edwards, Zigui Lu, and Jeffry W. Stevenson
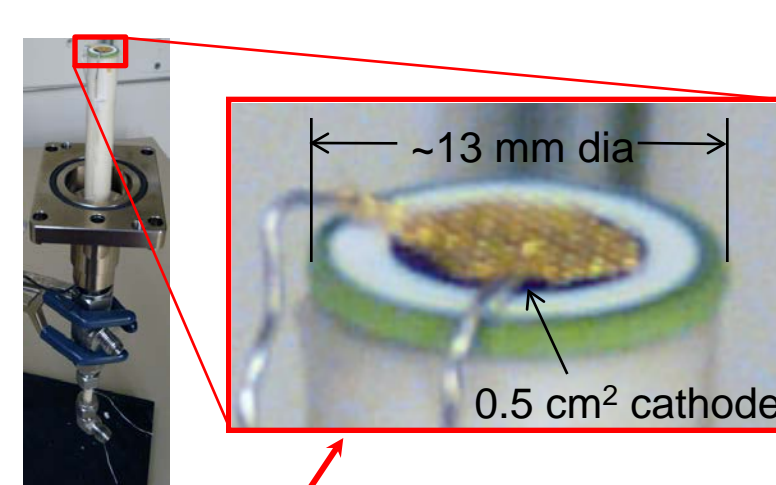
Pacific Northwest
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New SOFC Research Capability was Developed at PNNL
In-situ XRD of Anode-supported SOFCs during Operation

Bruker D8 Advance XRD…

XRD-compatible SOFC Test Fixture
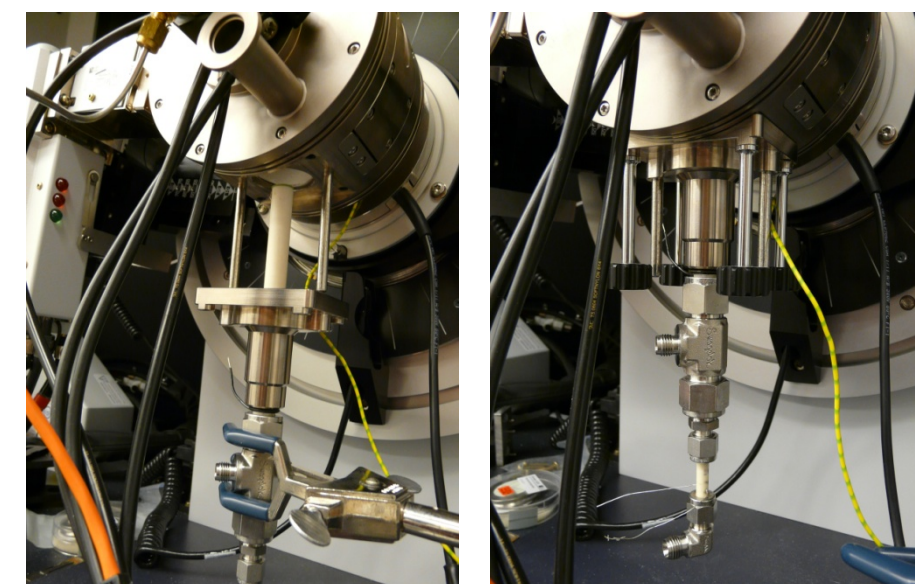
~13 mm dia

0.5 cm² cathode

Small-scale button cell
- LSCF-6428 Cathode on SDC Interlayer
- Ni-YSZ Anode-supported ~10μm YSZ Electrolyte

…with Anton Parr HTK 1200 Heating Chamber

Motivation
Potential Benefits of In-situ XRD Studies

- In-situ monitoring of the following during cell operation:
  - Phase composition
  - Phase transitions
  - Lattice strain
  - Crystallite size

- The above measurements can be made to determine:
  - How LSCF is changing over time at constant current as it degrades
  - The effects of operating parameters such as cell voltage, temperature, and oxygen-content/utilization on the cathode
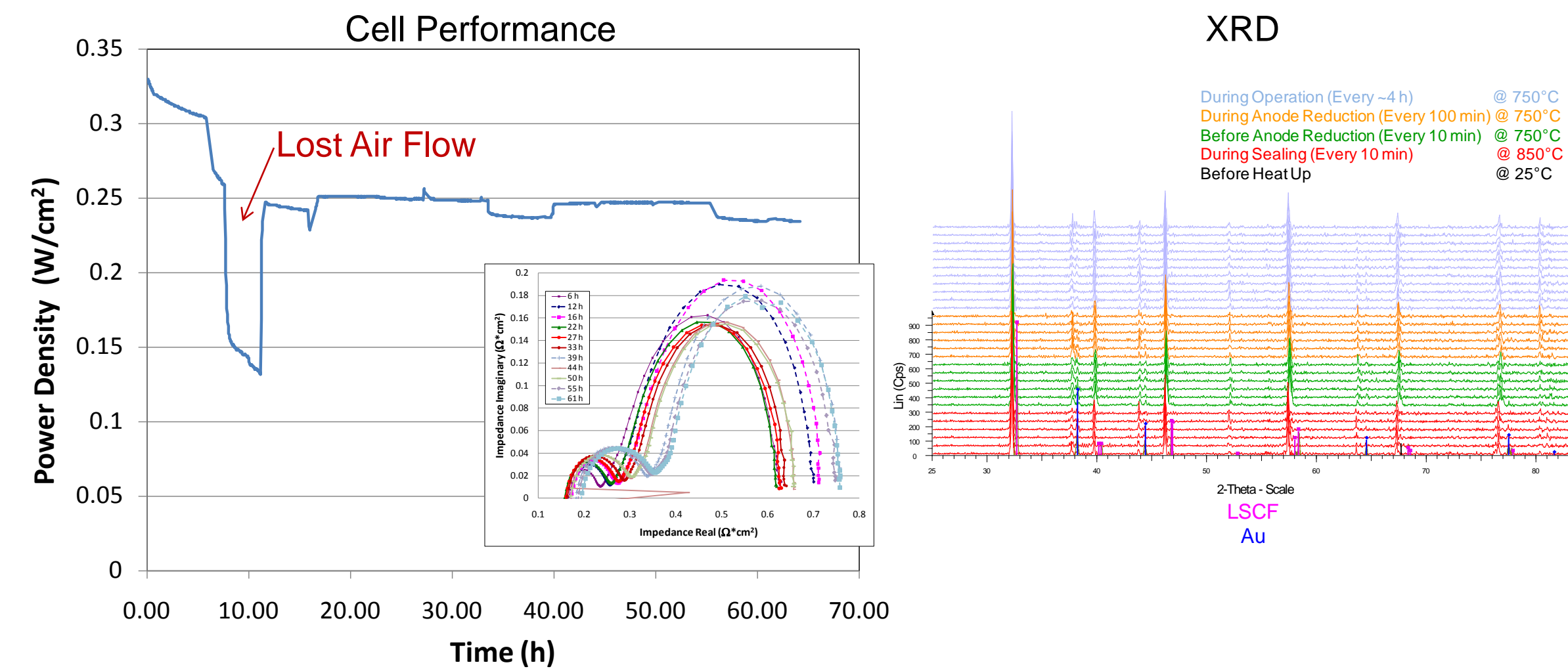 - The effects of contaminants on LSCF

Experimental Parameters
XRD
- Repeated 10 minute scans from 25 - 85° 2θ
  - 0.05° steps at 0.43 seconds per step

Cell Test
- Constant Current simulating 800 mV at 750°C in flowing air and moist H_2

Experimental Results

Cell Performance

Lost Air Flow

XRD

During Operation (Every ~4 h) @ 750°C
During Anode Reduction (Every 100 min) @ 750°C
Before Anode Reduction (Every 10 min) @ 750°C
During Sealing (Every 10 min) @ 850°C
Before Heat Up @ 25°C

LSCF
Au

Similarity Index
Calculated for XRD Patterns (Individual & Integrated)

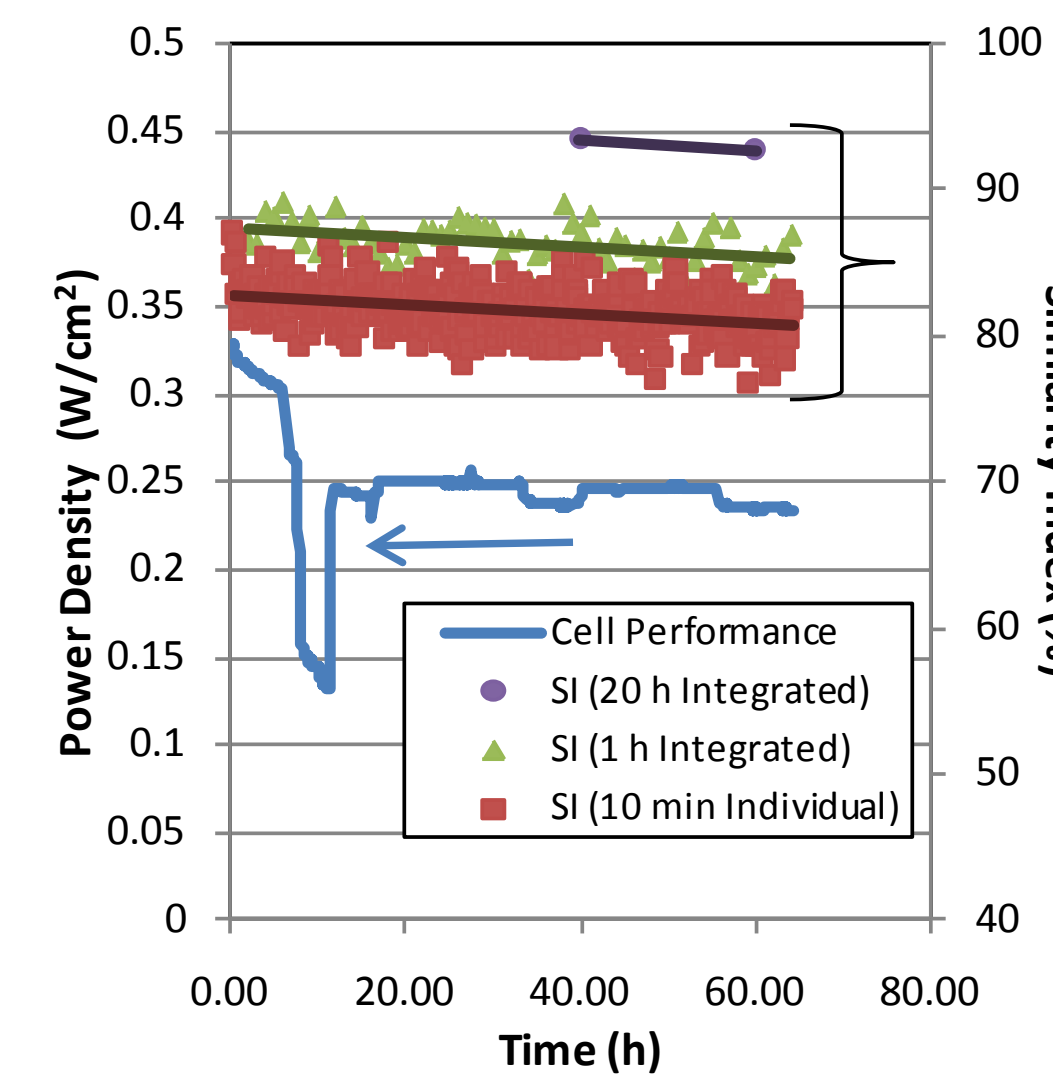The Cluster Analysis add-on module in Jade software [MDI] calculates a similarity index (SI) between XRD patterns using:

Spearman's Rank Order Coefficient(S)

$$S = \frac{\sum (R(a) \times R(b) - Q)}{\sqrt{\sum (R(a)^2 - Q) \times \sum (R(b)^2 - Q)}}$$

Pearson's Correlation Coefficient (P)

$$P = \frac{\sum (I(a) - A) \times (I(b) - B)}{\sqrt{\sum (I(a) - A)^2 \times \sum (I(b) - B)^2}}$$
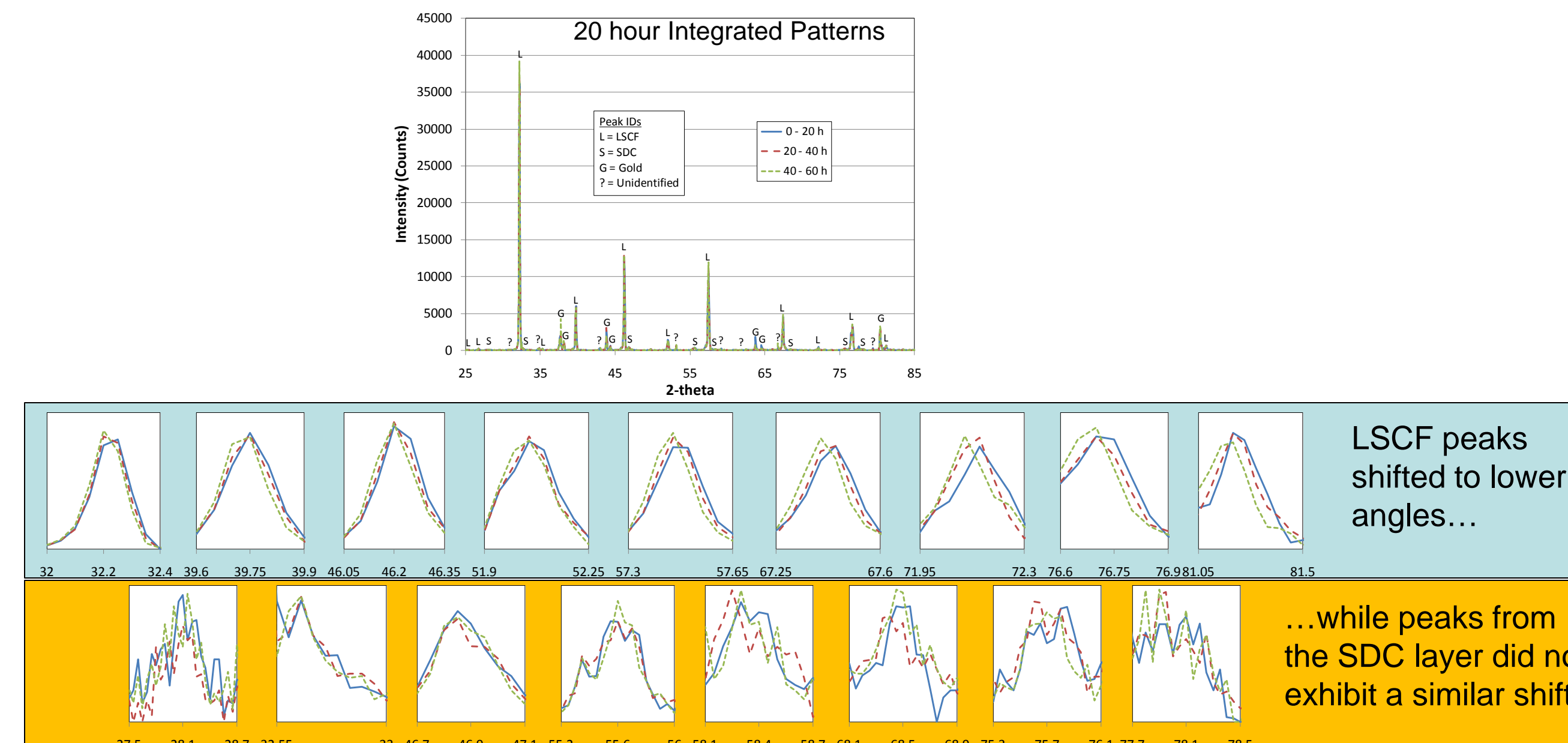
$$SI(\%) = (r \times S + (1-r) \times P) \times 100\%$$

$R(x)$ = rank of a data point in pattern x
$I(x)$ = square root of a data point in pattern x
X = average of $I(x)$'s
$Q = n(n+1)^2/4$ where n = number of datapoints
r = Spearman-Pearson mix

Cell Performance
SI (20 h Integrated)
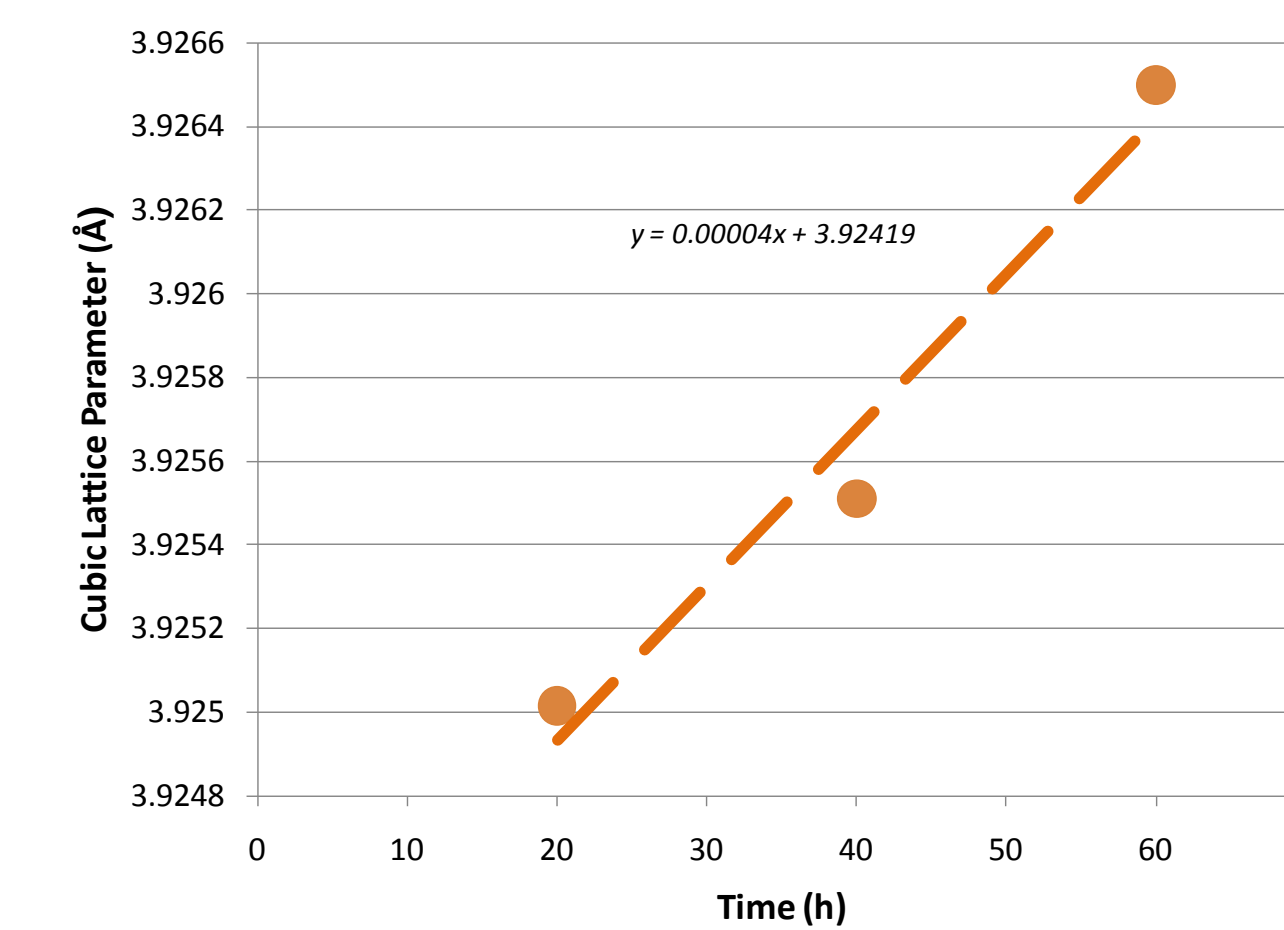SI (1 h Integrated)
SI (10 min Individual)

Over the course of cell operation, the XRD patterns gradually became less similar to the initial pattern in 3 different time frames

What Gradual Changes in XRD were Reflected by the Similarity Index?

20 hour Integrated Patterns

Peak IDs
L = LSCF
S = SDC
G = Gold
? = Unidentified

0 - 20 h
20 - 40 h
40 - 60 h

LSCF peaks shifted to lower angles…

…while peaks from the SDC layer did not exhibit a similar shift

Rietveld Refinement of 20 hour Integrated XRD Patterns

$y = 0.00004x + 3.92419$

During SOFC operation, the lattice parameter of the LSCF cathode expanded at a rate of:

~0.00004 Å per hour

What Compositional Changes could Account for this Expansion?

Sr loss

Tai et al., *Solid State Ionics*, **75** 273-283 (1995):
~0.06 Å per *x* in $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-\delta}$ → **Losing ~0.0007 Sr per hour**

Mineshige et al., *Solid State Ionics*, **176** 1145-1149 (2005):
~0.09 Å per *z* in $La_{0.6}Sr_{0.4-z}Co_{0.2}Fe_{0.8}O_{3-\delta}$ → **Losing ~0.0004 Sr per hour**
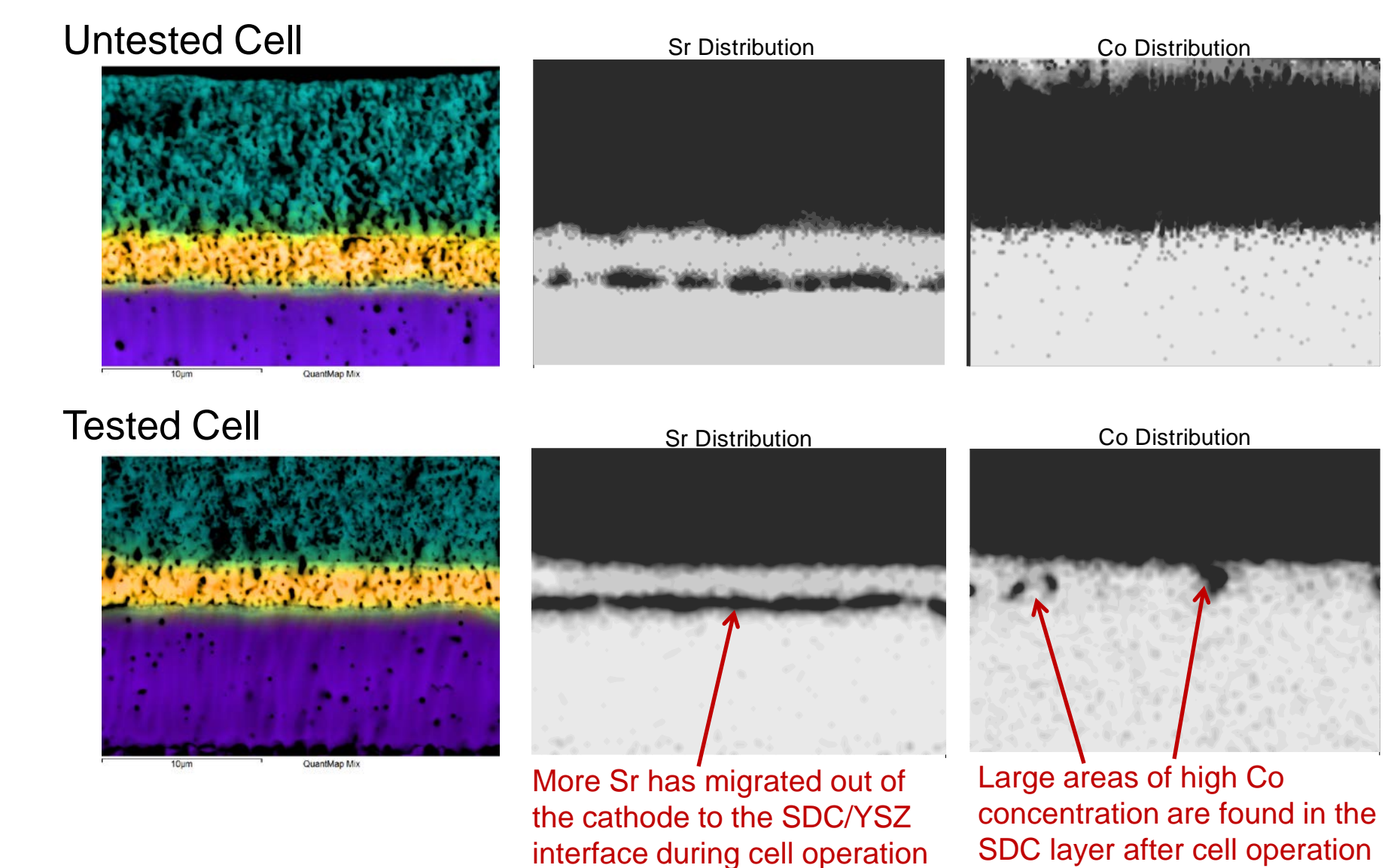
Co loss

Hashimoto et al., *Solid State Ionics*, **186**[1] 37-43 (2011):
~0.06 Å per *y* in $La_{0.6}Sr_{0.4}Co_yFe_{1-y}O_{3-\delta}$ → **Losing ~0.0007 Co per hour**

Kuhn et al., *Catal Lett*, **121** 179-188 (2008):
~0.12 Å per *y* in $La_{0.6}Sr_{0.4}Co_yFe_{1-y}O_{3-\delta}$ → **Losing ~0.0003 Co per hour**

SEM Analysis
Comparison of Tested Cell to Duplicate Untested Cell

Untested Cell

Sr Distribution

Co Distribution

Tested Cell

Sr Distribution

Co Distribution

More Sr has migrated out of the cathode to the SDC/YSZ interface during cell operation

Large areas of high Co concentration are found in the SDC layer after cell operation

Summary:
- XRD of an operating SOFC cathode detected gradual expansion of the LSCF lattice.
- This expansion was correlated to reported lattice strain due to Sr- and Co-removal from LSCF.
- SEM found that increased amounts of Sr and Co had migrated into the SDC layer during cell operation.

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