Development of SOFC Cathodes

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July 27-29, 2010

11th Annual SECA Workshop

Pittsburgh, PA

FY10 Research Topics in the Cathode Sub-task

- Importance of Cathode Sintering Temperature Optimization for Cell Performance & Stability
- Enhanced Densification of the SDC Interlayer
- Concentration Polarization in LSCF Cathodes
- Effects of Contamination from Sealing Glass Volatiles on LSM & LSCF Cathodes
- Capability Development: In-situ XRD of an Operating SOFC Cathode*
- Effect of A-site Stoichiometry on LSCF Cathode Performance

* The focus of this talk

Objectives

- To develop the capability to perform *in-situ* XRD measurements on operating SOFC cathodes, including:
  - A test fixture compatible with the XRD.
  - A cell assembly suitable for simultaneous operation and XRD measurements.
- To demonstrate the viability of performing *in-situ* XRD of working cathodes.

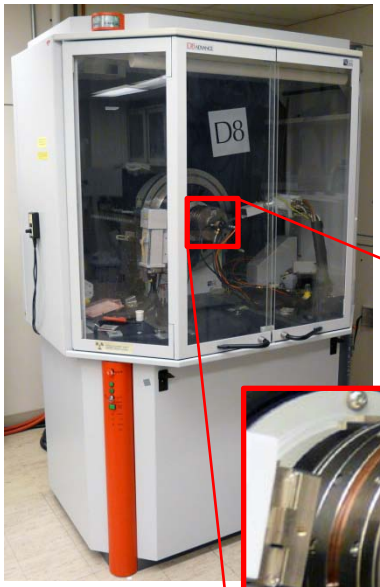
Potential Benefits of *In-situ* XRD Studies

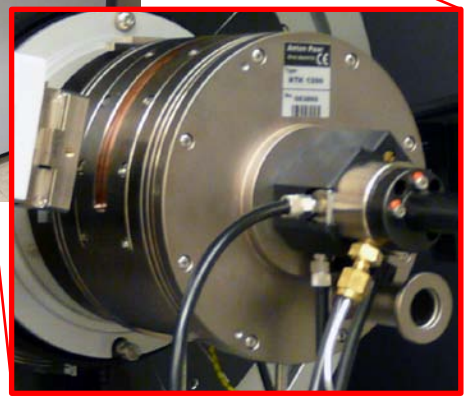
- *In-situ* monitoring of the following during cell operation:
  - Phase composition
  - Phase transitions
  - Lattice strain
  - Crystallite size

- 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 bias voltage, temperature, and oxygen-content/utilization on the cathode
  - The effects of contaminants on LSCF

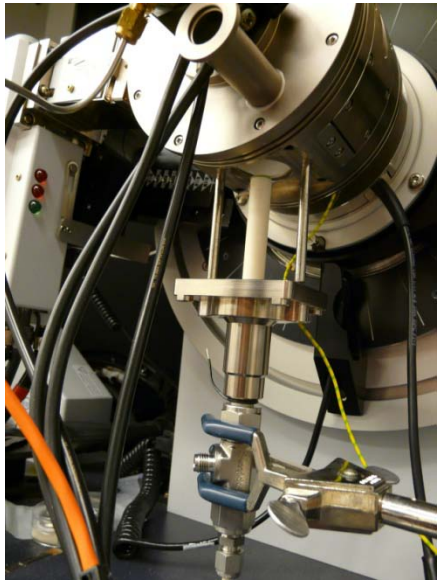
Instrument & Apparatus

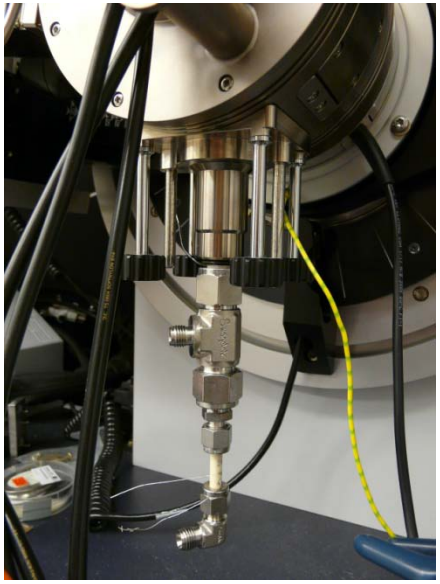
Bruker D8 Advance XRD…



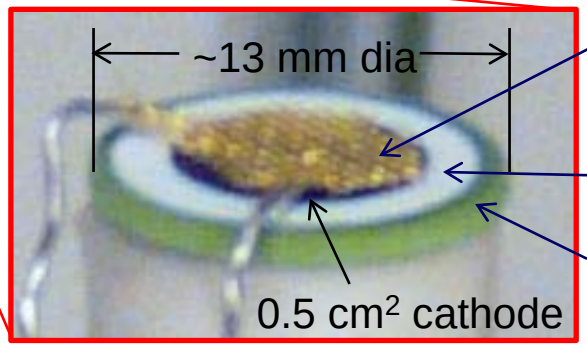


…with Anton Parr HTK 1200 Heating Chamber





SOFC Test Fixture for XRD



LSCF Cathode under Au mesh & paste current collector

SDC Interlayer

Anode-supported electrolyte bilayer

Small-scale button cell

Challenges

- Sealing
  - Should avoid burning out organics in XRD heating chamber
  - Modifications required for a load to be applied during sealing

    (Additional Consideration: Load must not shield cathode from x-rays)

  - Comparison of Candidate Sealing Materials

Aremco Ceramabond 569 & 685	PNNL G-18 Barium Calcium Aluminosilicate Glass
Organics removed during 100C curing heat treatment	Organics must be burned out at 500-600C
Bond is strong enough for handling after curing	Not much strength for handling after burn out
Seals reliably without a load	Hit or miss on sealing without a load
Not a great seal (typical OCV ~1.04 V)	Good seal (typical OCV ~1.1 V)

- Cathode Current Collection
  - Require adequate current collection without shielding cathode from impinging x-rays

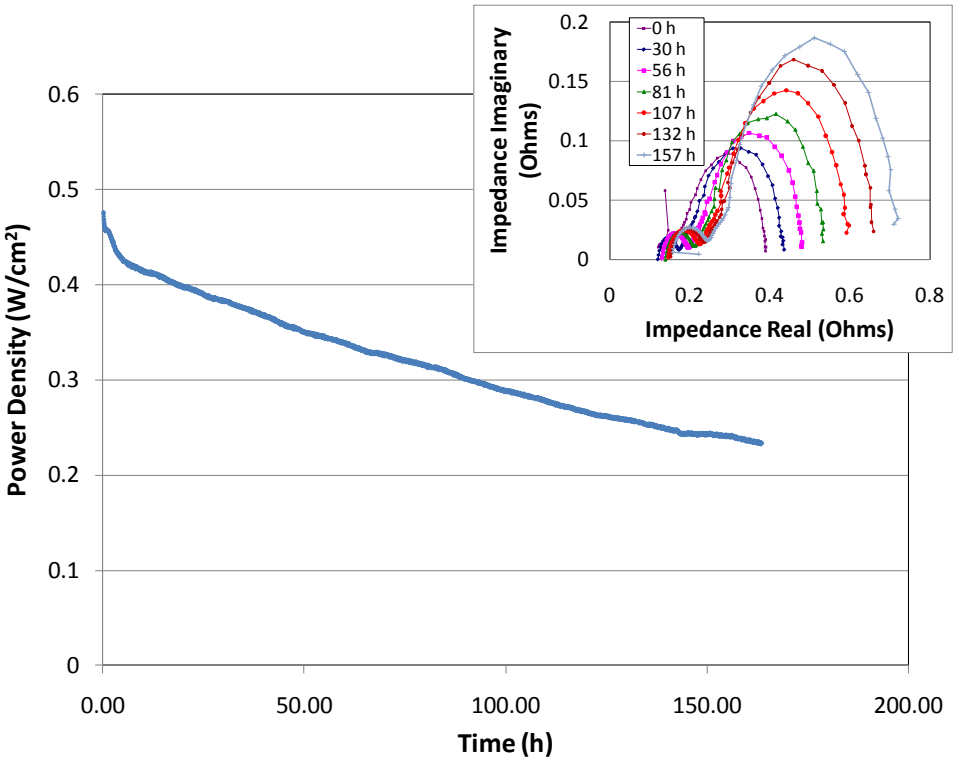
Experimental Parameters

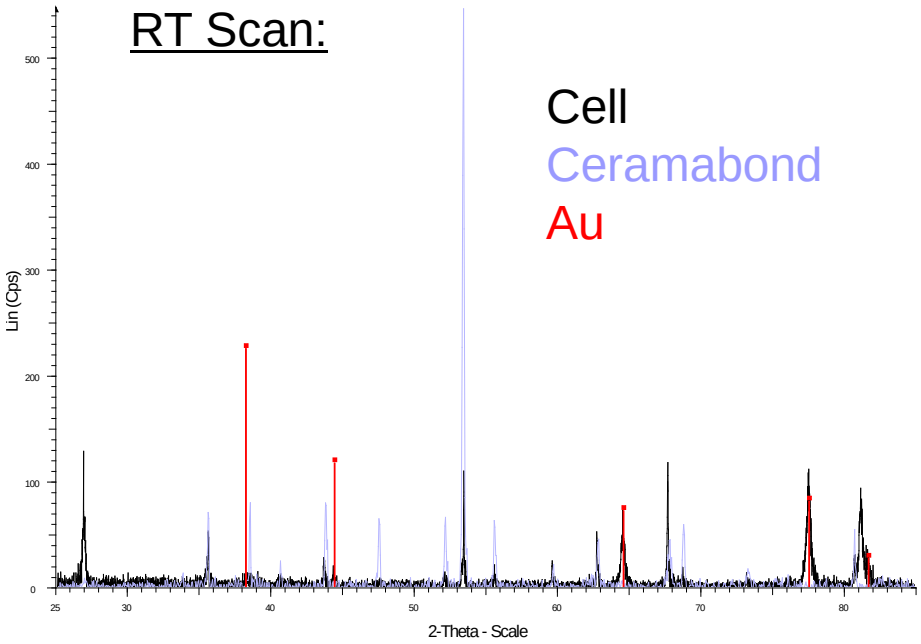
- XRD
  - All XRD scans cover a 2θ range of 25 - 85°
  - Room temperature scans:
    - 0.01° steps for 2 seconds/step (~3.5 hour scan)
  - Elevated temperature scans
    - 10 minute scans to be repeated through isothermal dwell
      - 0.05° steps for 0.43 seconds/step
    - Higher resolution scans will be run intermittently
      - 0.01° steps for 0.52 seconds/step (~1 hour scan)
      - These scans will be run in sets of three back-to-back

- Cell Operation Targets
  - 750ºC
  - Constant Current approximating 0.8 V operation
  - Air
  - H_2 with 3% H_2O

Initial Cell Test Results

Seal Material:	Current Collector	OCV
Ceramabond	Fine Au mesh rolled to <40 µm thick with gold paste contact points	1.04 V





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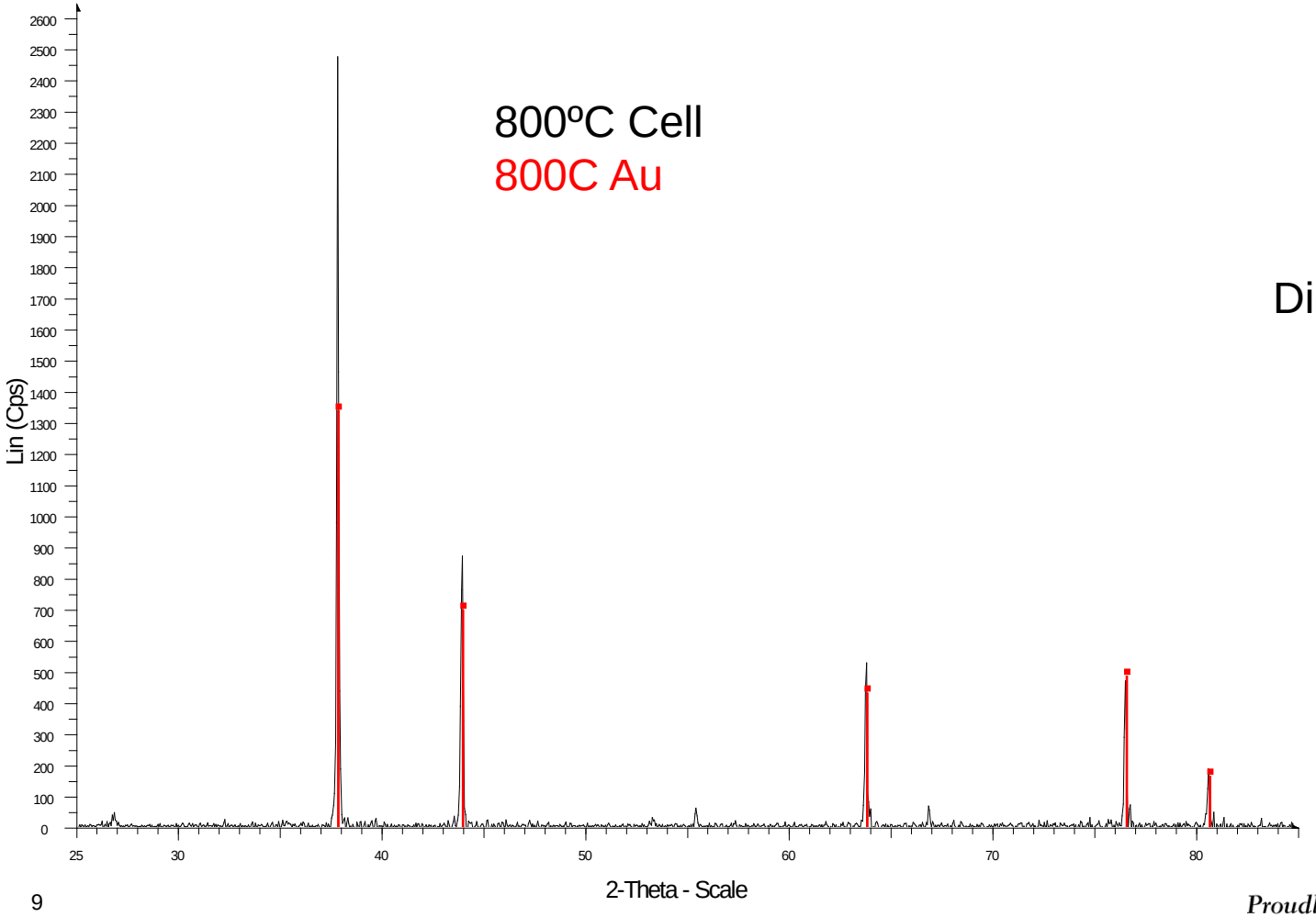
Cell Test Results – Changed Current Collector

Seal Material:	Current Collector	OCV
Ceramabond	Full coverage with thin Au screen print. Gold mesh ring contacting perimeter of print.	1.03 V



Did not operate cell

Cell Test Results – Sealing Problems

Seal Material:	Current Collector	OCV
Ceramabond	Gold mesh ring around perimeter of cathode with gold paste contact points	0.850 V
G-18 Paste around edge of cell and tube	Gold mesh ring around perimeter of cathode with gold paste contact points	0.07 V, G-18 melted and ran down tube
G-18 Paste with Ceramabond painted over G-18	Gold mesh ring around perimeter of cathode with gold paste contact points	0.60 V
G-18 Paste with Ceramabond painted over it and G-18 tape between cell and tube	Gold mesh ring around perimeter of cathode with gold paste contact points	1.01 V but not stable
G-18 Paste and G-18 tape	Gold mesh ring around perimeter of cathode with gold paste contact points	Not Measured – No bubbling in exhaust line

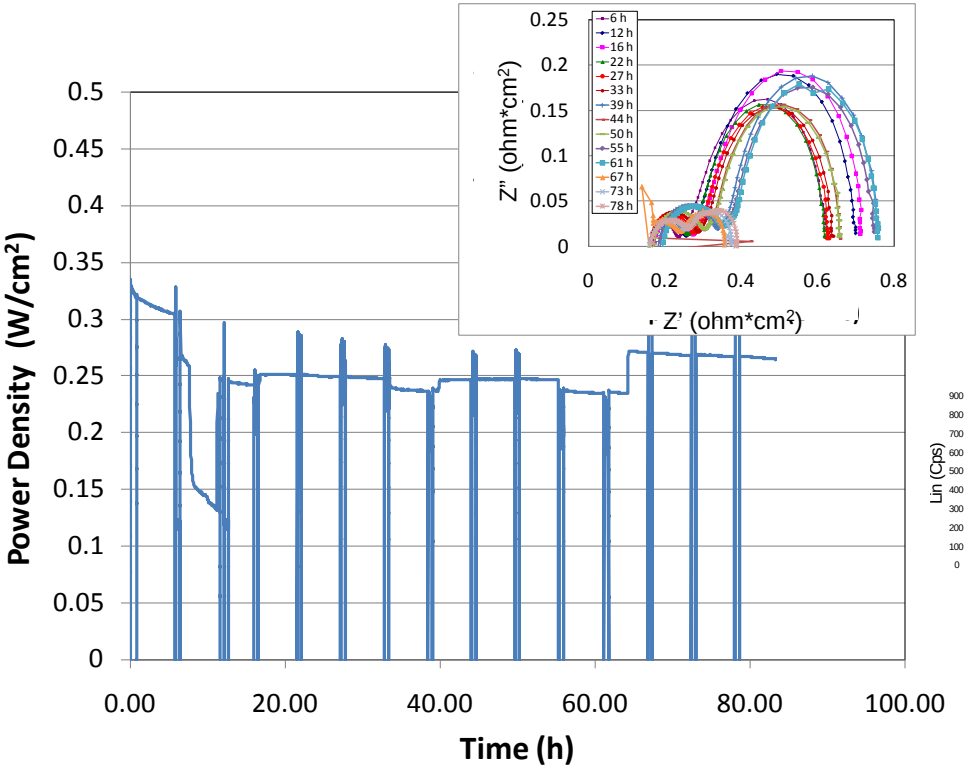
Subsequent tests found that the cell was 50°C hotter than expected

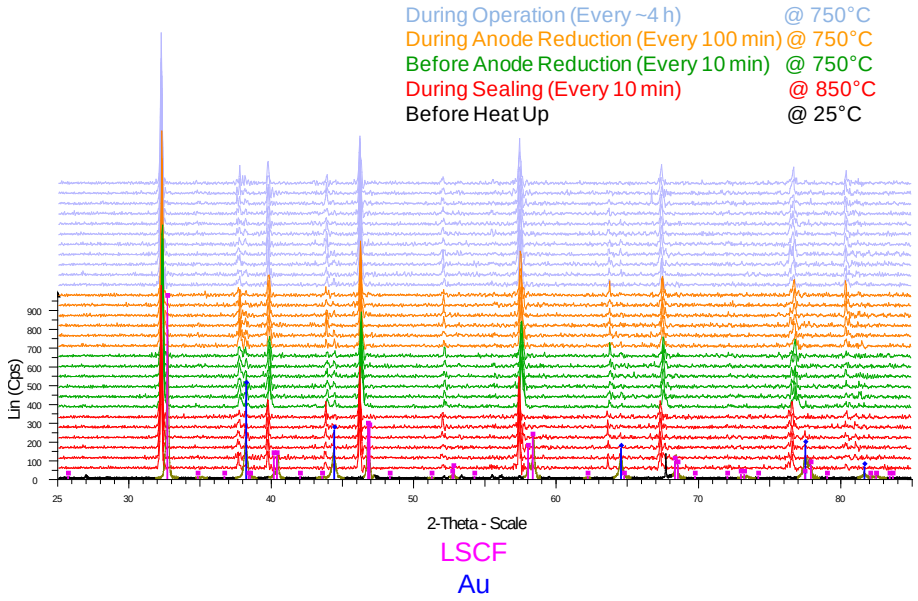
Water was condensing & plugging the vent line

- In subsequent tests, target temperatures were adjusted to compensate for ΔT.
- Vent line was blown out and a moisture trap installed to keep line clear.

Successfully Operated Cell and Measured Strong Cathode Diffraction Peaks

Seal Material:	Current Collector	OCV
Ceramabond	Gold mesh ring around perimeter of cathode with gold paste contact points	1.04 V





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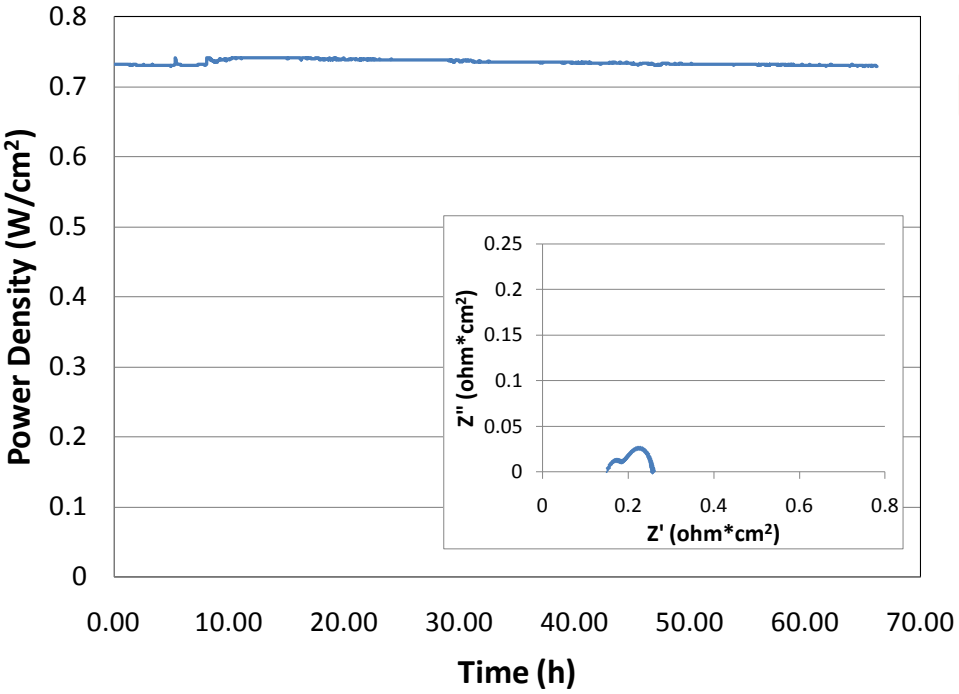
Further Improvements Underway

- Modify the test fixture to add spring loading to facilitate use of G-18 glass seal to improve OCV.
- Add air delivery tube that blows incoming air directly on the cathode to decrease concentration polarization resistance.
- Fabricate an insert that will narrow the x-ray beam to impinge only on the cathode and not the surrounding current collector for a cleaner XRD pattern.

Duplicate of XRD Cell in Button Cell Test Stand

- 0.5 cm^2 cathode printed on standard 25 mm dia button cell.
- Au current collector only around perimeter of cell.
- G-18 seal.
- Incoming air impinges directly on cathode.



- High power density means:
  - Perimeter current collector is adequate
  - Planned improvements should have significant impact of performance of cells in XRD test fixture.

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Conclusions

- Developed a new resource to aid in studying SOFC cathodes.
- Successfully operated an SOFC while simultaneously performing XRD on the cathode.
- Have identified further improvements & demonstrated their potential benefits.

Acknowledgements

- The summarized work was funded under the U.S. Department of Energy's Solid State Energy Conversion Alliance (SECA) Core Technology Program.
- Helpful Discussion and Guidance from NETL

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