SECA Core Technology Program - PNNL: Cell Materials Development

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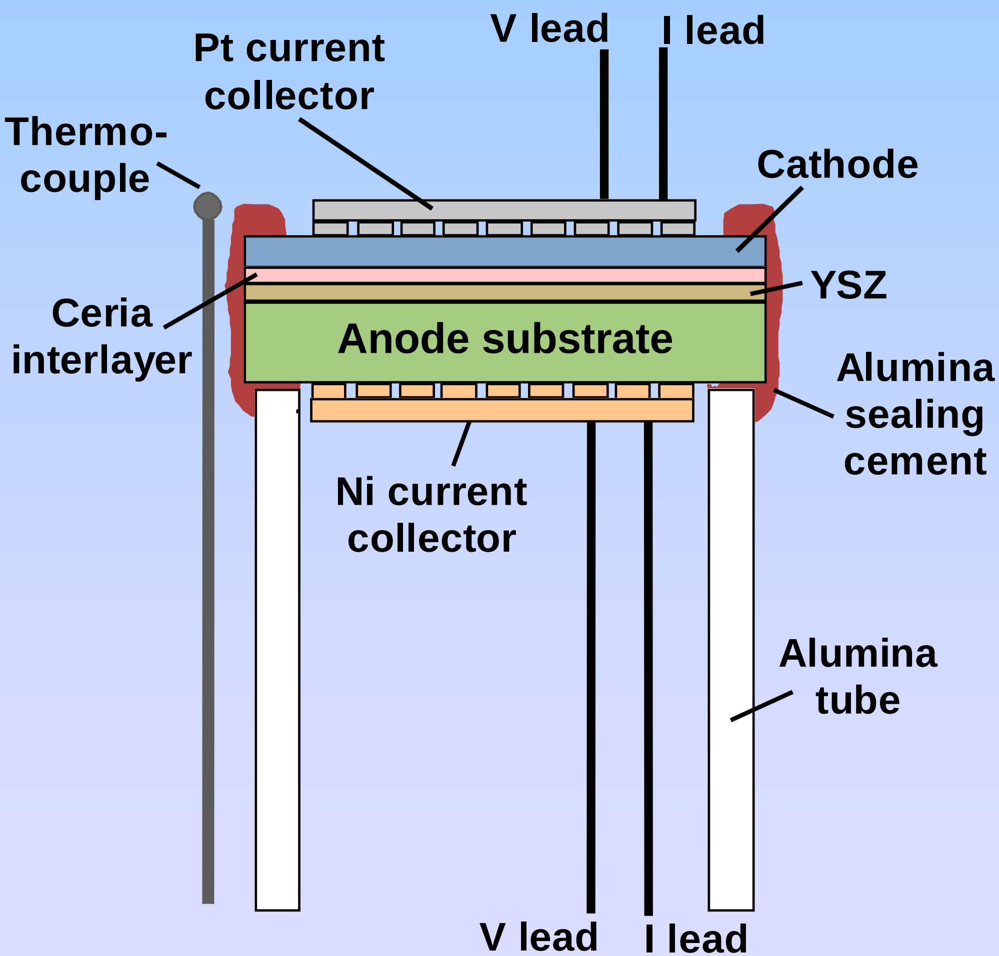
Battelle

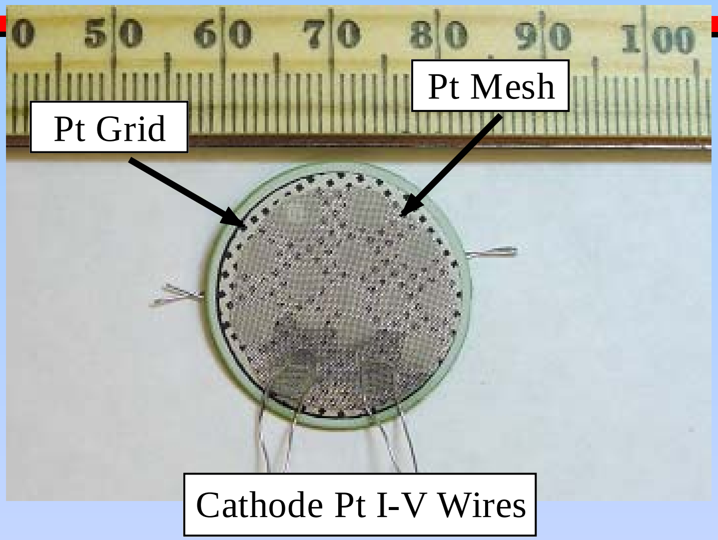
U.S. Department of Energy
Pacific Northwest National Laboratory

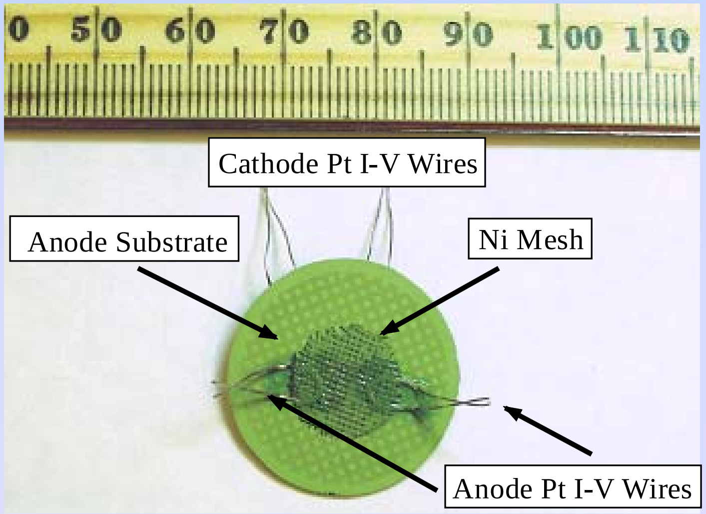
Outline

- Cathodes
  - LSF-based Cathodes
    - Current Collector Effects
    - Performance Degradation
  - LSM-based Cathodes
    - Optimization of Performance
    - Joint GE-PNNL-ANL Cr Degradation Study
- Anodes
  - Current Collector/Contact Materials Development

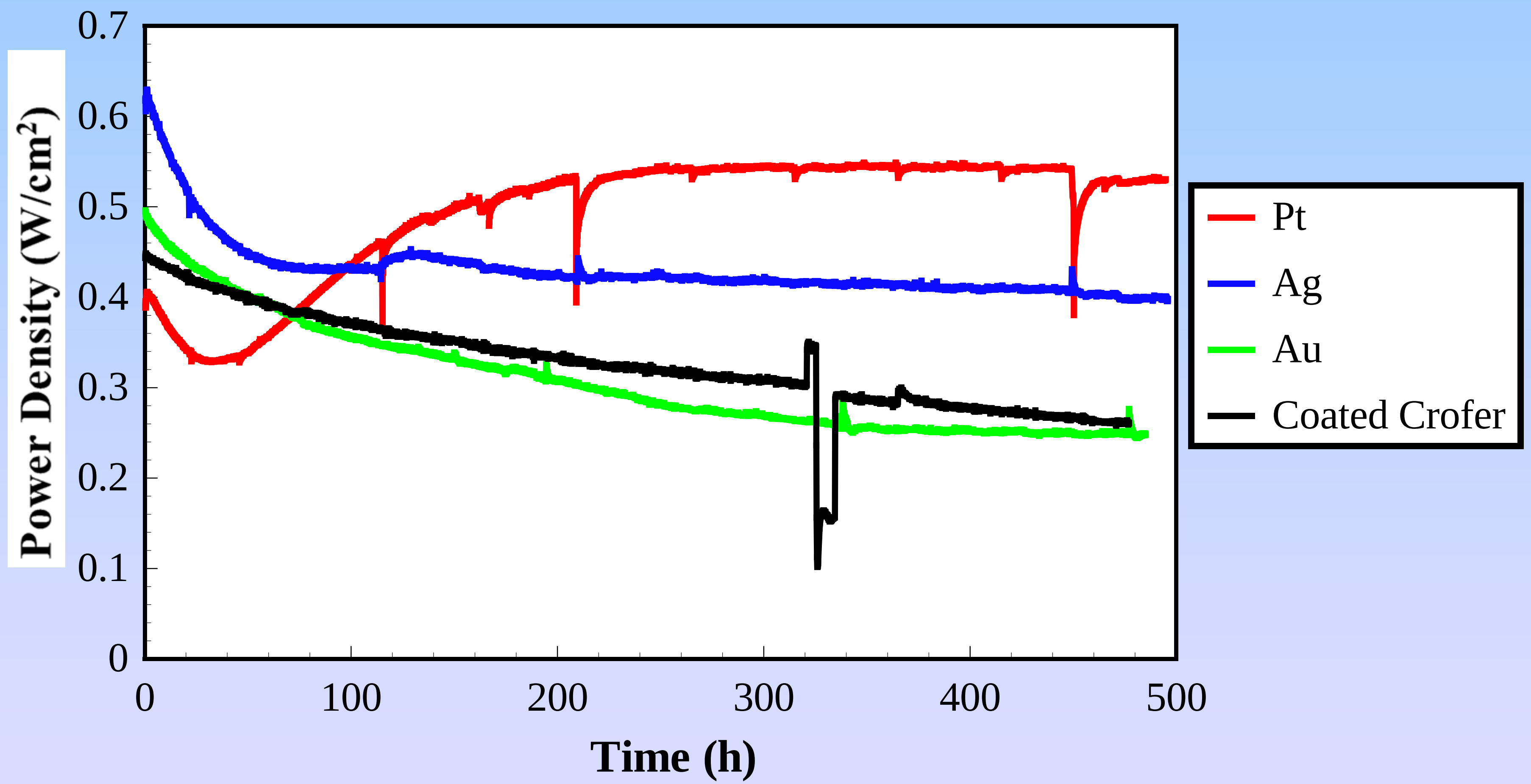
Button Cell Experimental Set-Up





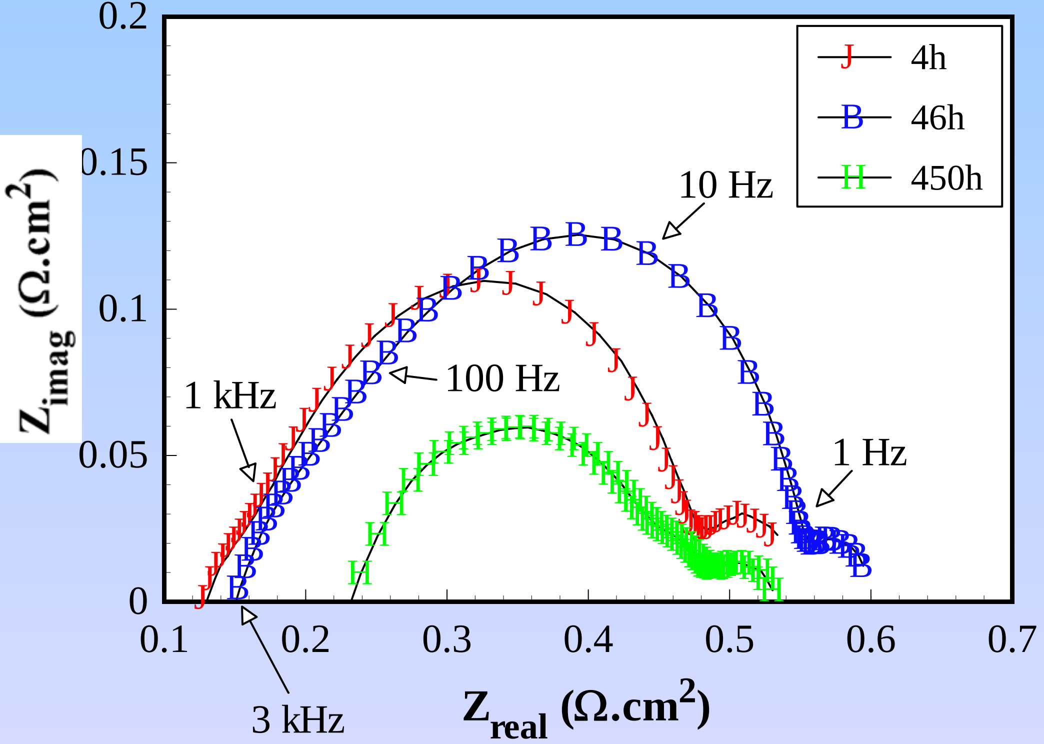


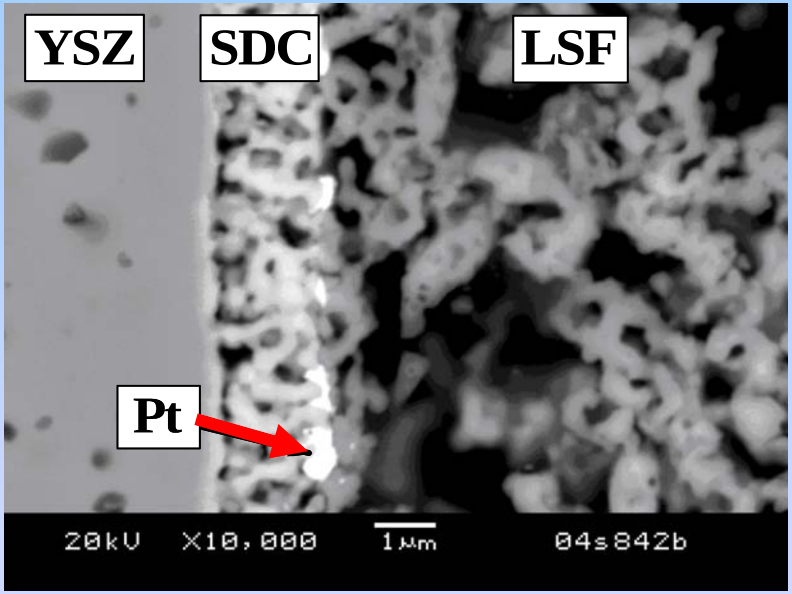
Effect of Current Collector on LSF Performance



Anode supported cells tested on 50/50 H_2/N_2; 750ºC; 0.7 V

LSF - Platinum





- Pt migrates from the current collector to the LSF-SDC interface.
- Increased ohmic resistance possibly associated with removal of Pt from the Pt-cathode interface and increased contact resistance.

LSF - Platinum *(Possible Scenario)*

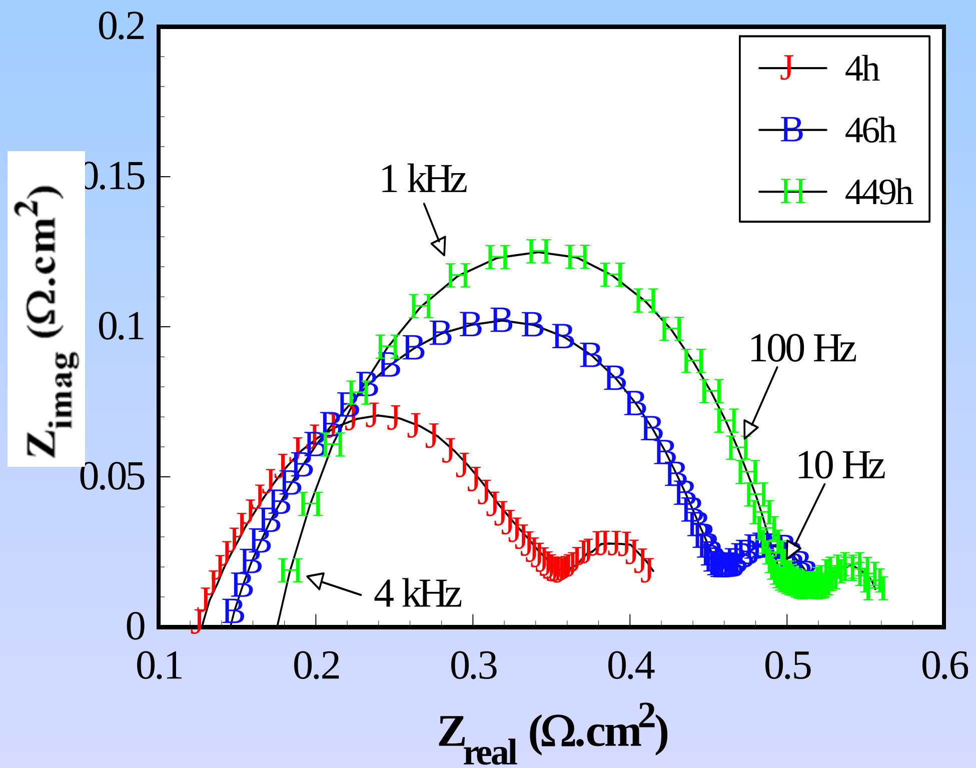
- PtO_2 evaporates and deposits as Pt metal at reduction sites at the LSF-SDC interface

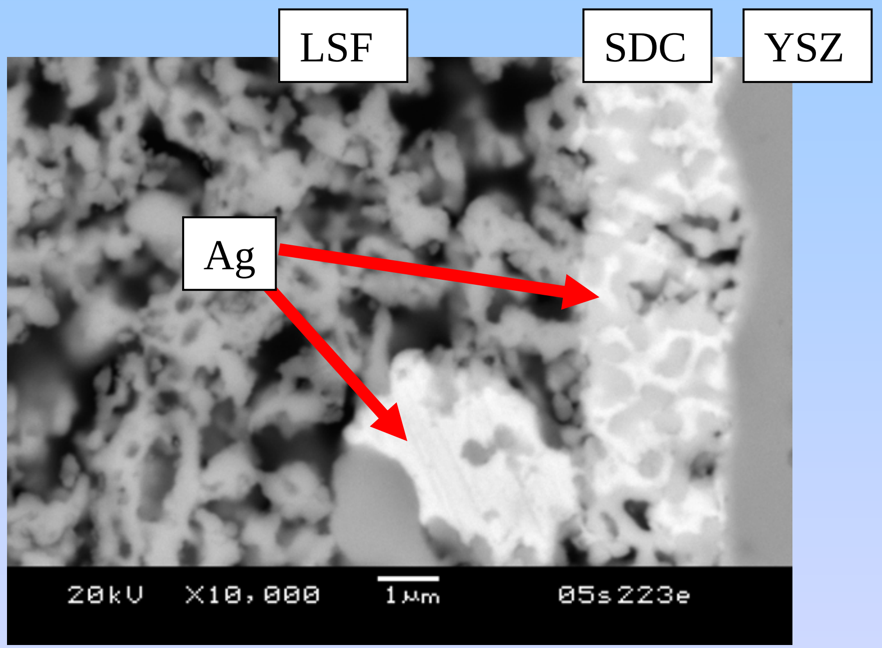
$$PtO_{2(g)} + 4e^{'} + 2V_O^{\bullet\bullet} \rightarrow Pt_{(s)} + 2O_O^x$$

- Pt deposition may catalyze the oxygen reduction reaction, and enhance cell performance.

- Consistent with other studies detailing enhanced catalytic activity of SOFC cathodes by purposefully adding Pt or Pd at the cathode-electrolyte interface.

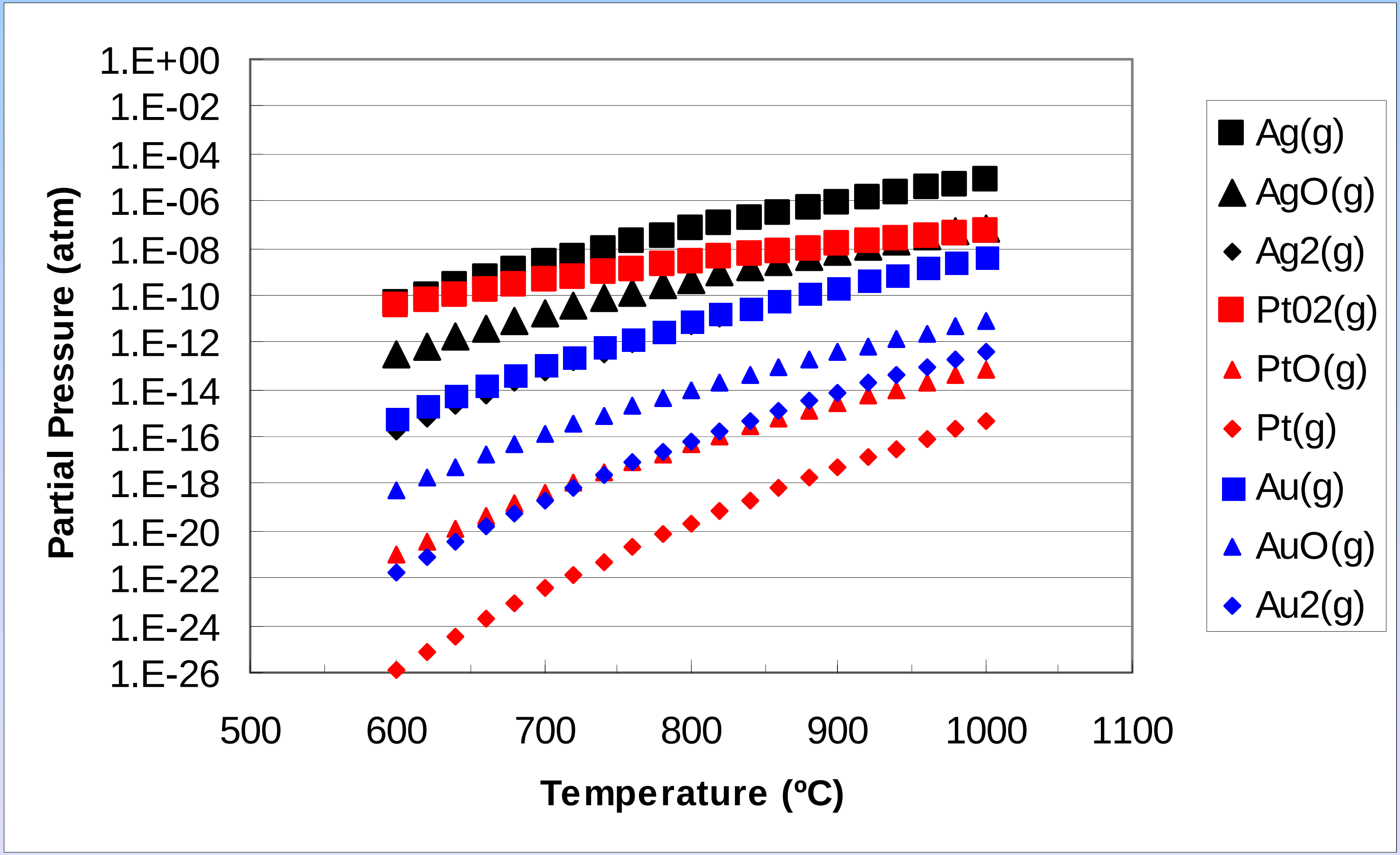
LSF - Silver



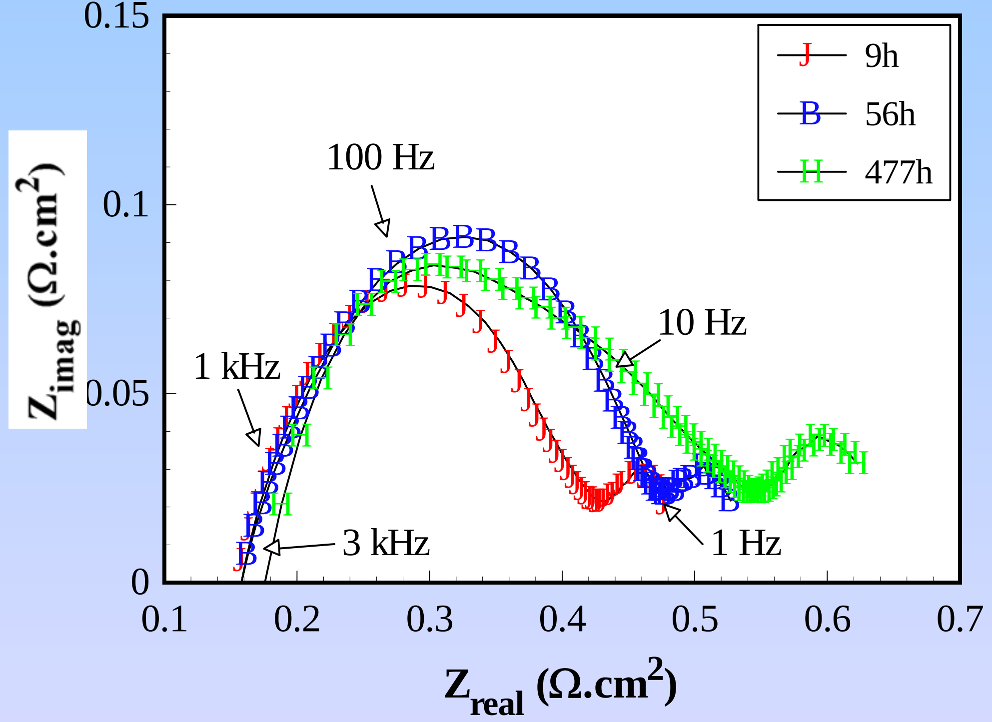


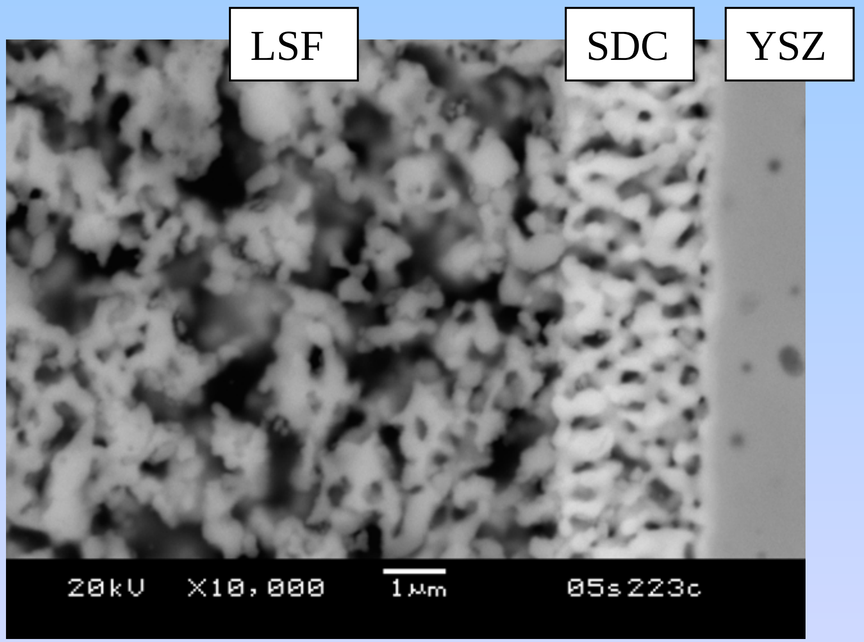
- Silver deposition different to Pt ➔ Ag not limited to interface – may indicate a different mechanism.
- Ag (and possibly AgO) vaporize and deposit at the LSF-SDC interface and within the SDC pores.

Volatility of Noble Metal Species



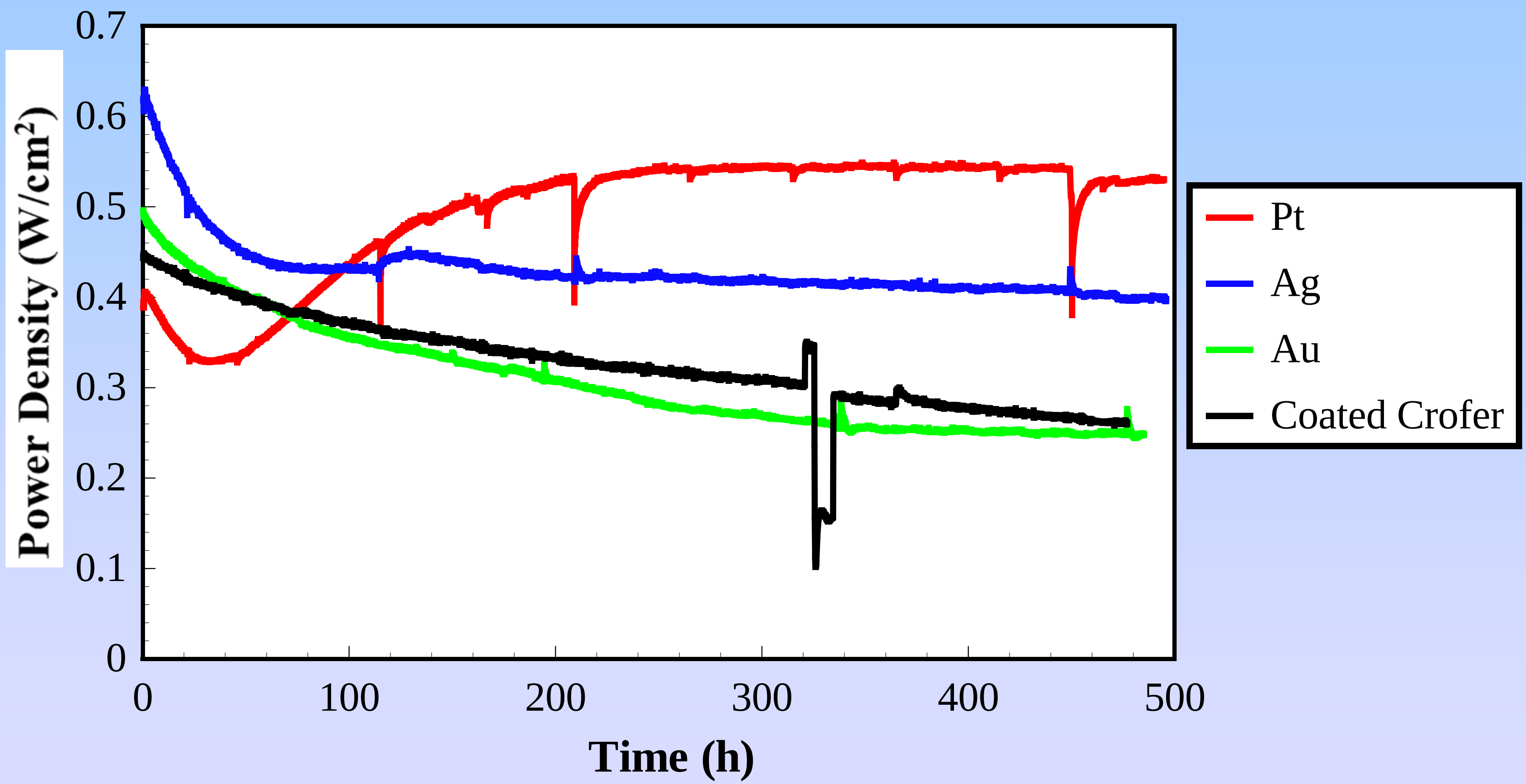
LSF - Gold





- No detectable gold migration to the LSF-SDC interface or within the bulk cathode.
- Cell indicates continued degradation during 500 hour test.
- Only slight increase in ohmic resistance – Au-cathode contact maintained due to lack of Au volatility

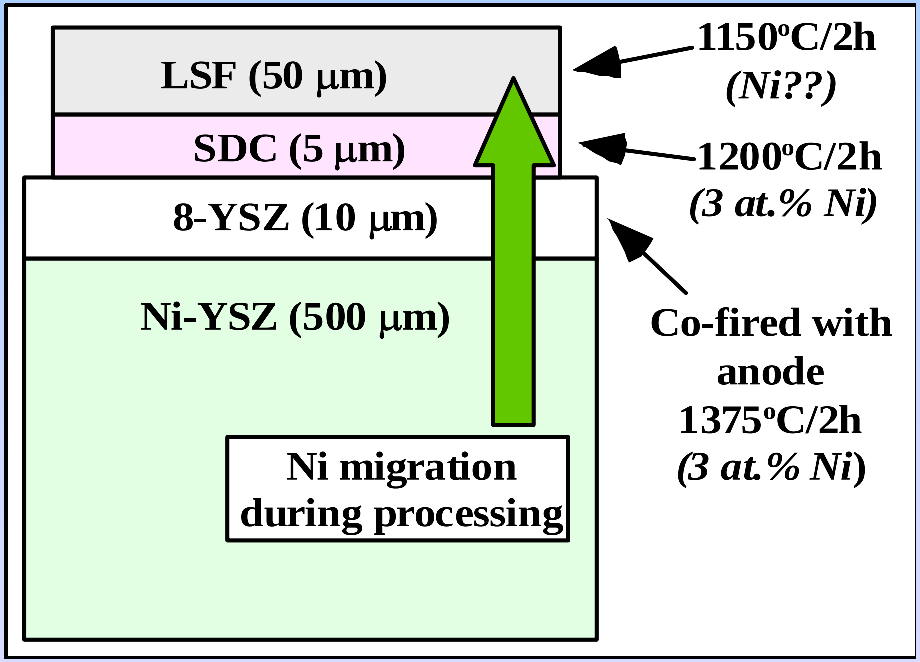
Effect of Current Collector on LSF Performance

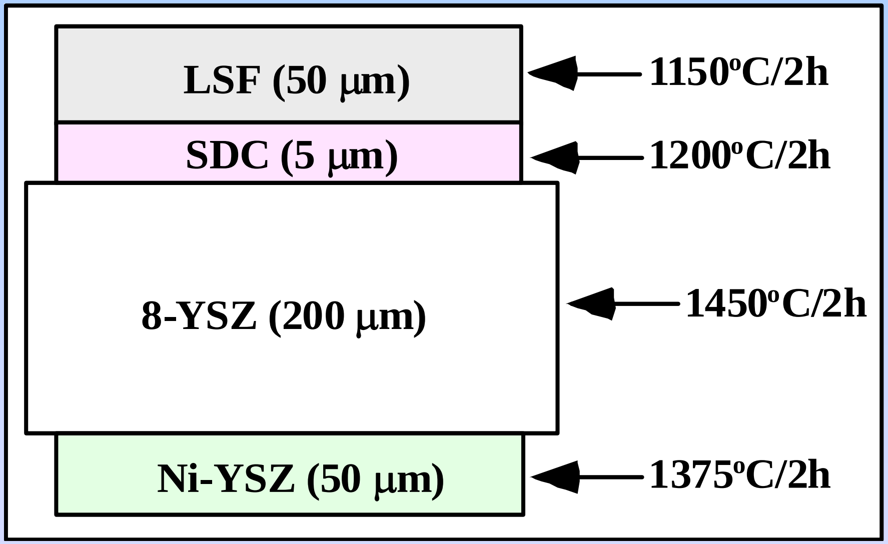


Anode supported cells tested on 50/50 H_2/N_2; 750ºC; 0.7 V

LSF Degradation – Role of Ni?

- Is the degradation of LSF (with inert Au current collector) intrinsic to LSF or due to the combination of LSF with an anode-supported cell geometry ➔Ni migration.

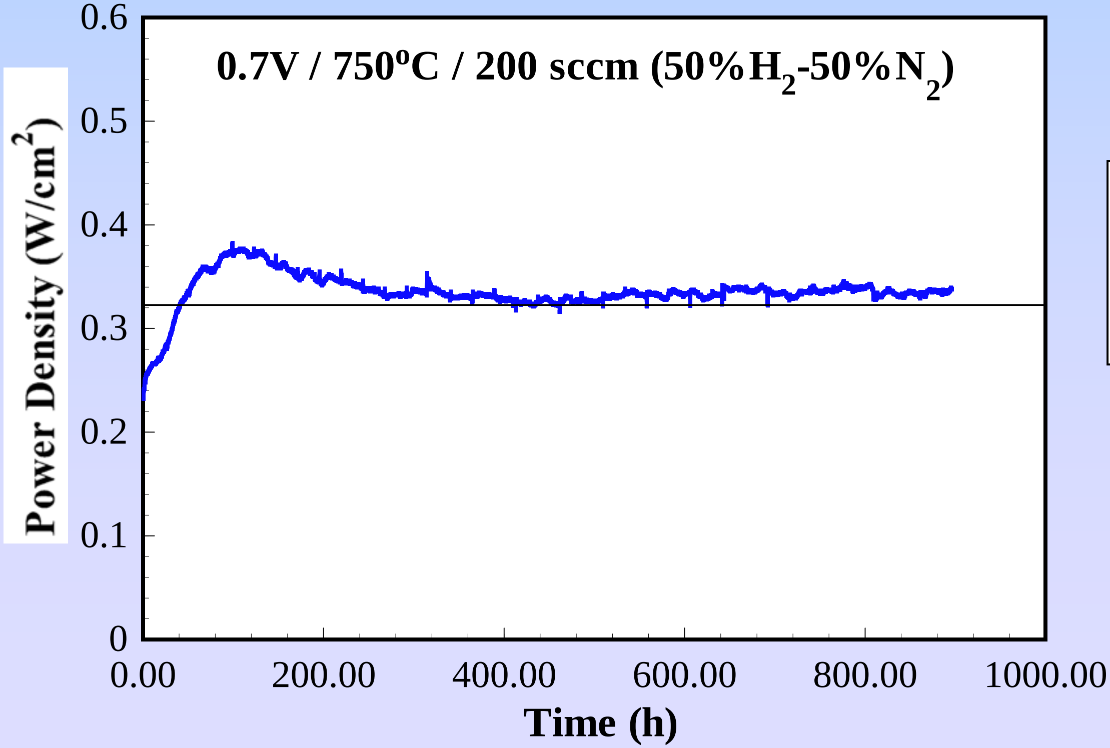




- Pt at LSF-SDC interface (for cells that show conditioning/stability) contains higher Ni levels than surrounding materials ➔ Pt may act as a Ni getter.
- Potential degradation mechanism involving Ni has not been established

LSM-20 Optimization

- Variables include:
  - A/B ratio – 0.99 and 0.95
  - Cells prepared with and without a ceria interlayer
  - Additions of ceria or YSZ to form a composite active cathode layer.
  - Microstructure: Sintering temperature, pore former addition, starting particle size.
  - B-site dopant additions.



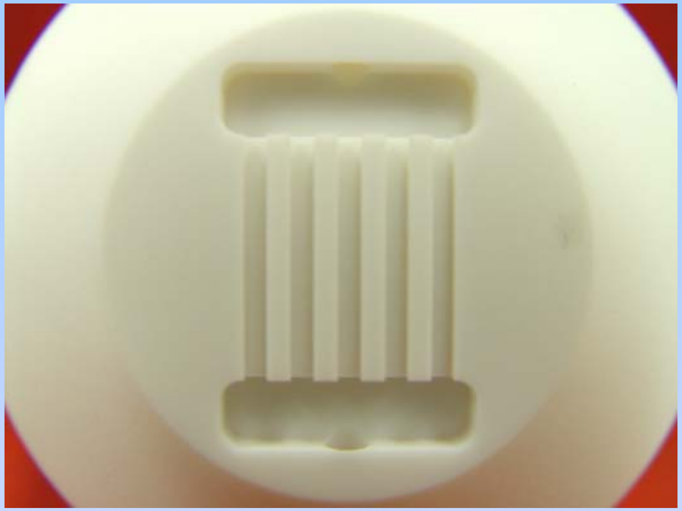
LSM-SDC mixed cathode with SDC interlayer. Au mesh/paste current collector.

Cr Degradation Study

- Collaboration between GE, PNNL, & ANL
- <u>Objectives</u>
  - Determine under what conditions, if any, chromium transport has a detrimental effect on LSM-based cathodes
  - Determine if the observed Cr transport is predominantly vapor phase, solid state or both
  - Determine Cr compounds formed at cathode/electrolyte interface and cathode/interconnect interface regions
  - Correlate Cr observed at interfaces vs. observed performance degradation (if any)

- Test Conditions
  - InDEC cells w/ LSM-YSZ cathodes; 700, 800ºC; 1000 hours
  - Cr sources evaluated:
    - E-brite flow field (ANL, GE)
    - Vapor phase from outside fixture (PNNL)
    - Transpiration experiments (PNNL)

Fixture for Cr Degradation Tests

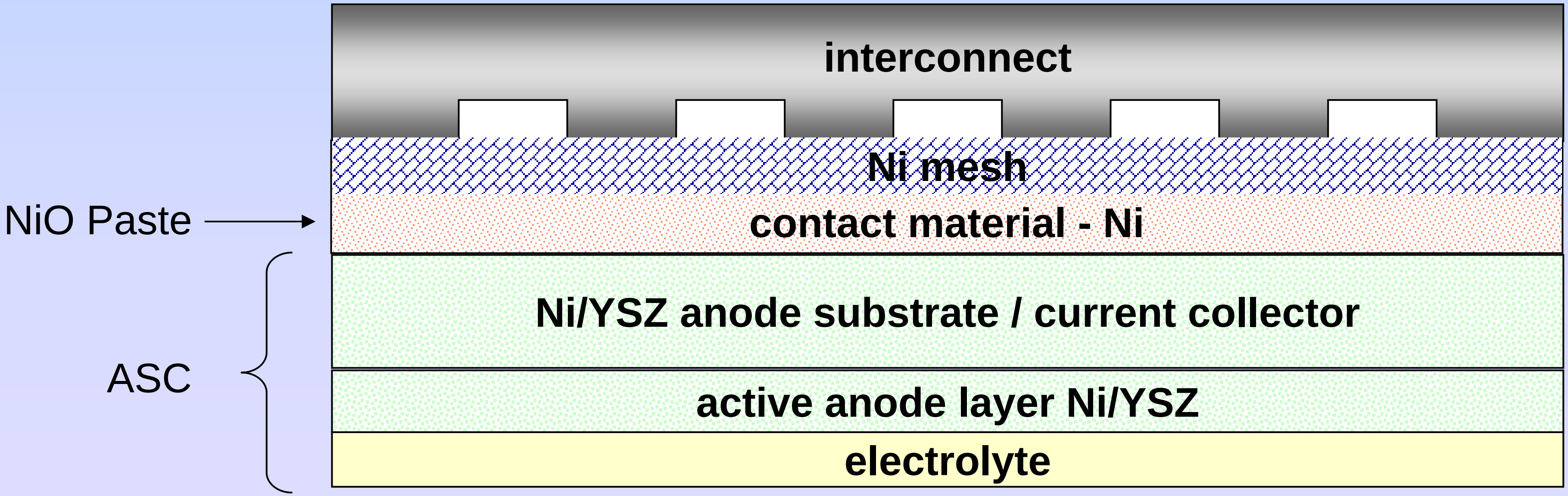


Anode Development - Introduction

- Ni-based anodes offer excellent performance in clean hydrogen or reformed hydrocarbon fuels
  - Challenges include redox stability, hydrocarbon tolerance (coking, thermal gradients), sulfur tolerance
- Ceramic anodes (doped $SrTiO_3/CeO_2$ mixtures) combine high electrocatalytic activity for fuel oxidation with redox stability, tolerance of hydrocarbons, and tolerance of sulfur
  - Electronic conductivity, redox stability provided by titanate, activity for fuel oxidation provided by ceria
  - Challenges include relatively low electronic conductivity (compared to Ni-based anodes), processing temperature limitations (reactivity and microstructure coarsening at high processing temps).
  - Need to develop current collector / contact materials for ceramic anode / alloy interconnect interfaces

"Traditional" Anode / Interconnect Interface

- Need to establish stable, conductive interface between anode and alloy interconnect
- Ni-based anodes allow establishment of metallurgical bond between anode and interconnect
- Typical approach: Bond Ni Mesh to alloy interconnect; Apply NiO contact paste between cell and mesh/interconnect during stack fabrication (850-950ºC)



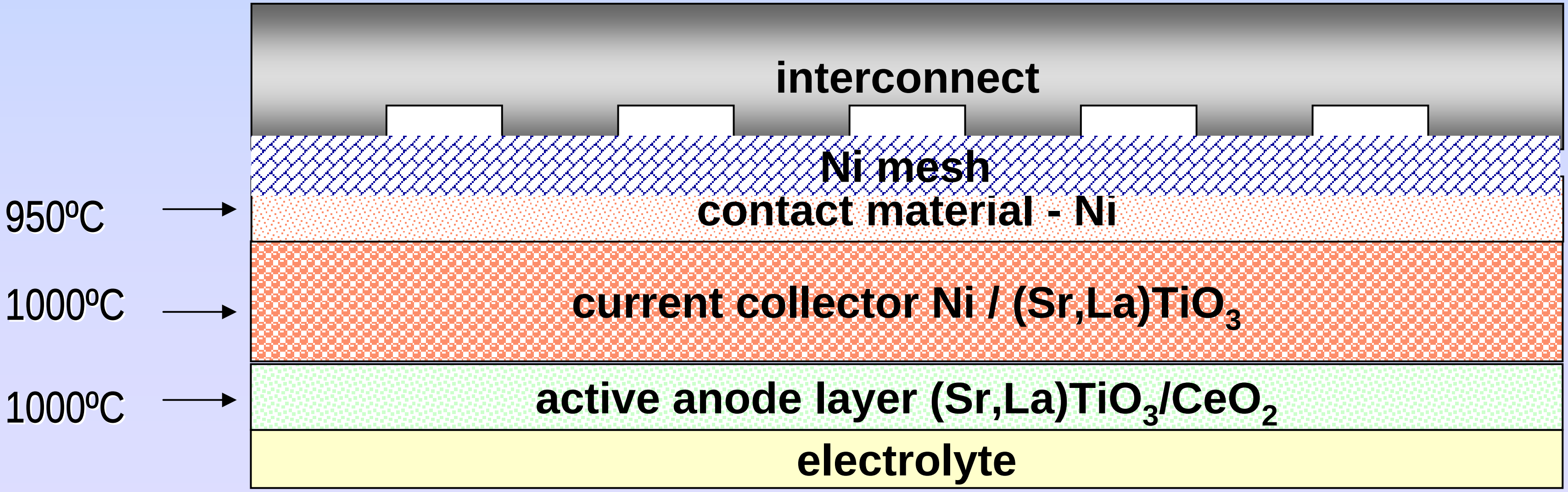
Ceramic Anode / Interconnect Interface

•Need to establish stable, conductive interface between thin active ceramic anode and alloy interconnect

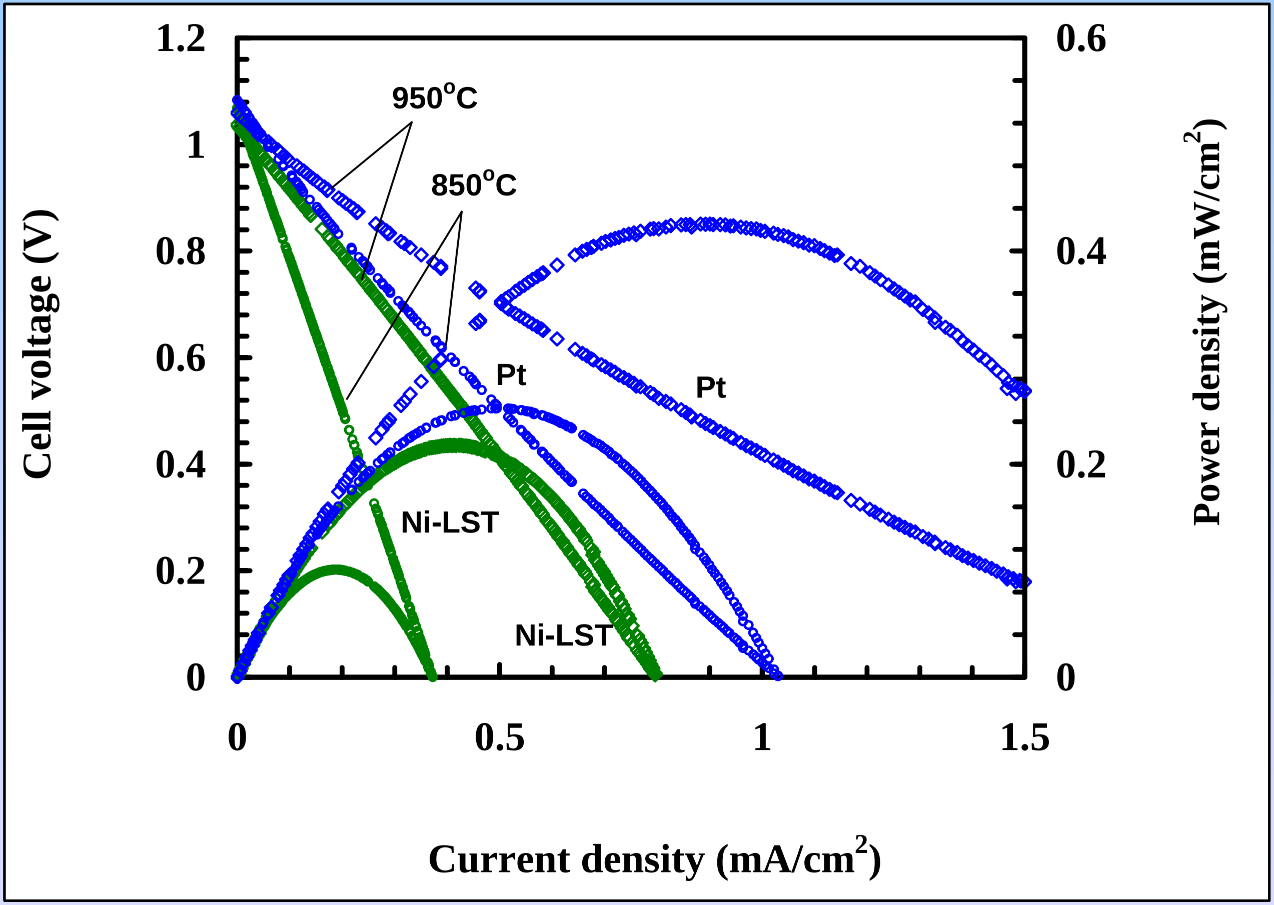
•Pt too expensive

•One option: Ni based contact material - high conductivity - may retain S tolerance (not concerned with S poisoning away from active anode) - probably lose redox, hydrocarbon tolerance

•Graduated approach to improve bonding between Ni and anode



Electrolyte-supported cell operation with Pt/Pt and Ni-LST/Ni current collector/contact paste

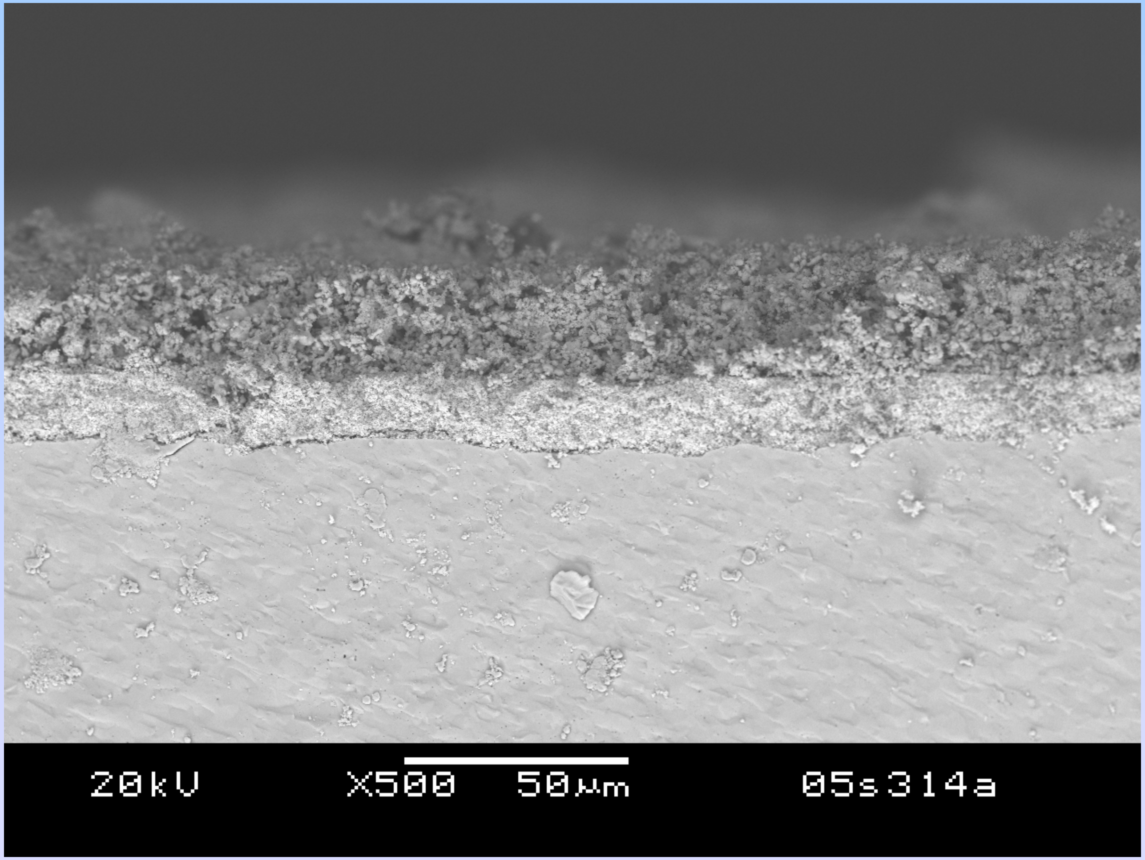


160 µm YSZ electrolyte-supported cell
(La,Sr)TiO_3- Ce(La)O_2 anode and LSF20 cathode with SDC interlayer;
Fuel: H_2/H_2O=97/3; Oxidant=air

SEM image of a tested titanate/ceria ceramic anode w/ Ni-titanate (60/40 v%) current collecting layer

CC layer

Anode



Bonding between Ni/titanate cc layer and Ni contact paste requires improvement

Summary

- LSF-based cathodes
  - Considerable performance disparity depending on the type of noble metal current collector used.
  - The LSF-Au configuration is most representative of true LSF performance, and reveals LSF instability.
  - Impact of Ni migration (from the anode into YSZ, SDC and LSF layers) on cathode degradation is being examined.
- LSM-based cathodes
  - Encouraging long-term stability data but modest power densities.
  - Cr Degradation study in progress – GE, PNNL, ANL
- Ceramic anodes
  - Optimization of Ni-based current collection / contact layers in progress

Future work

- Cathode:
  - Evaluate LSF degradation mechanisms, including role of Ni
  - Optimize LSM-based cathodes
  - Joint GE-PNNL-ANL Cr poisoning study
- Anode:
  - Develop/optimize current collector/contact materials for the ceramic anode
    - Improve bonding, performance of Ni based current collection
    - Develop alternative current collectors/contact materials to maintain HC, redox tolerance
  - Evaluate anode performance in reformates

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