PNNL Cathode Development - SECA CTP Review

Steve Simner, Mike Anderson, Gordon Xia, Gary Yang, and Jeff Stevenson

January 28th, 2005

Funded as part of the Solid-State Energy Conversion Alliance (SECA) Core Technology Program by the U.S. Department of Energy's National Energy Technology Laboratory (NETL).

Battelle

U.S. Department of Energy
Pacific Northwest National Laboratory

Current R&D Objectives

- **Protective Coatings** – feasibility of a protective $(Mn,Co)_3O_4$ spinel coating on Crofer22 APU to prevent Cr volatility, and subsequent cathode poisoning.

  ➔ long-term testing (750-800^{o}C/0.7V) La(Sr)FeO_3 and La(Sr)MnO_3 cathodes considered.

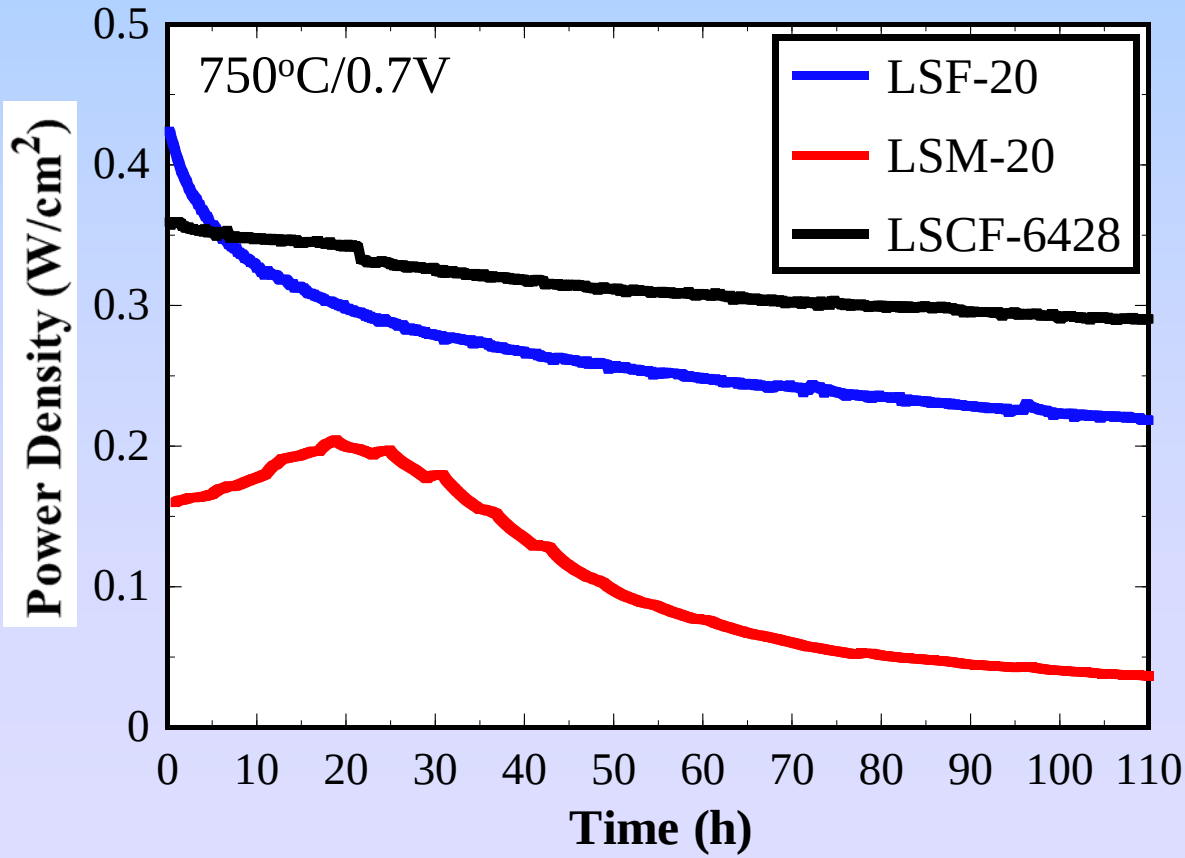
  ➔ full-cell impedance analysis (without a reference electrode).

  ➔ extensive micrstructural/chemical analysis of pre- and post-tested samples.

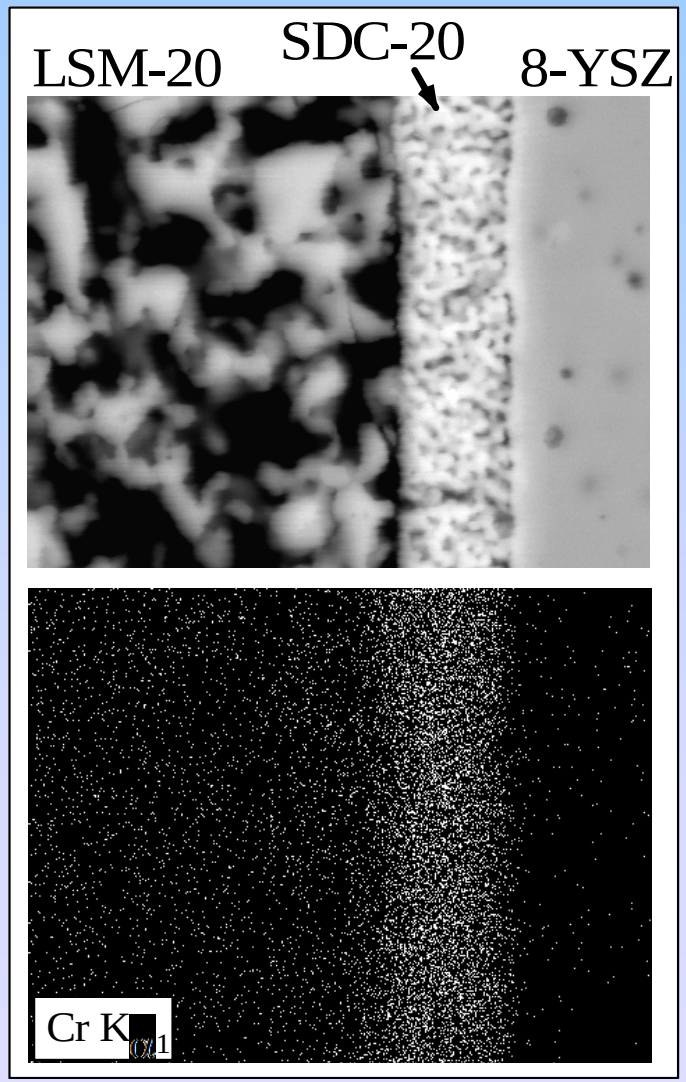
- **True Cathode Performance** – in conducting the above studies it has become apparent that the use of Pt as a current collector for lab-scale SOFC testing may artificially enhance cathode activity at the cathode-electrolyte interface.

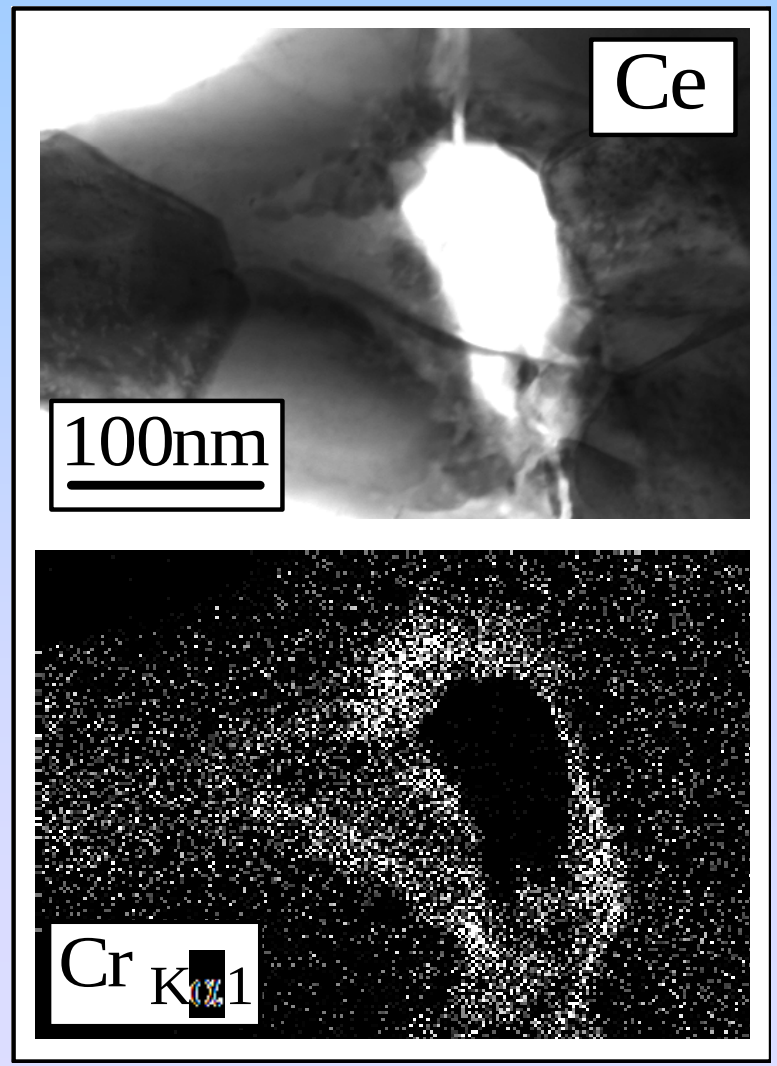
Cathode Poisoning via Cr Volatility/Reactivity

- Typical SOFC cathodes indicate rapid performance degradation when ferritic stainless steels (e.g. Crofer22 APU) are used as current collectors ➔ CrO_x volatility from oxide scale on alloy.



Evidence of CrO_x Deposition

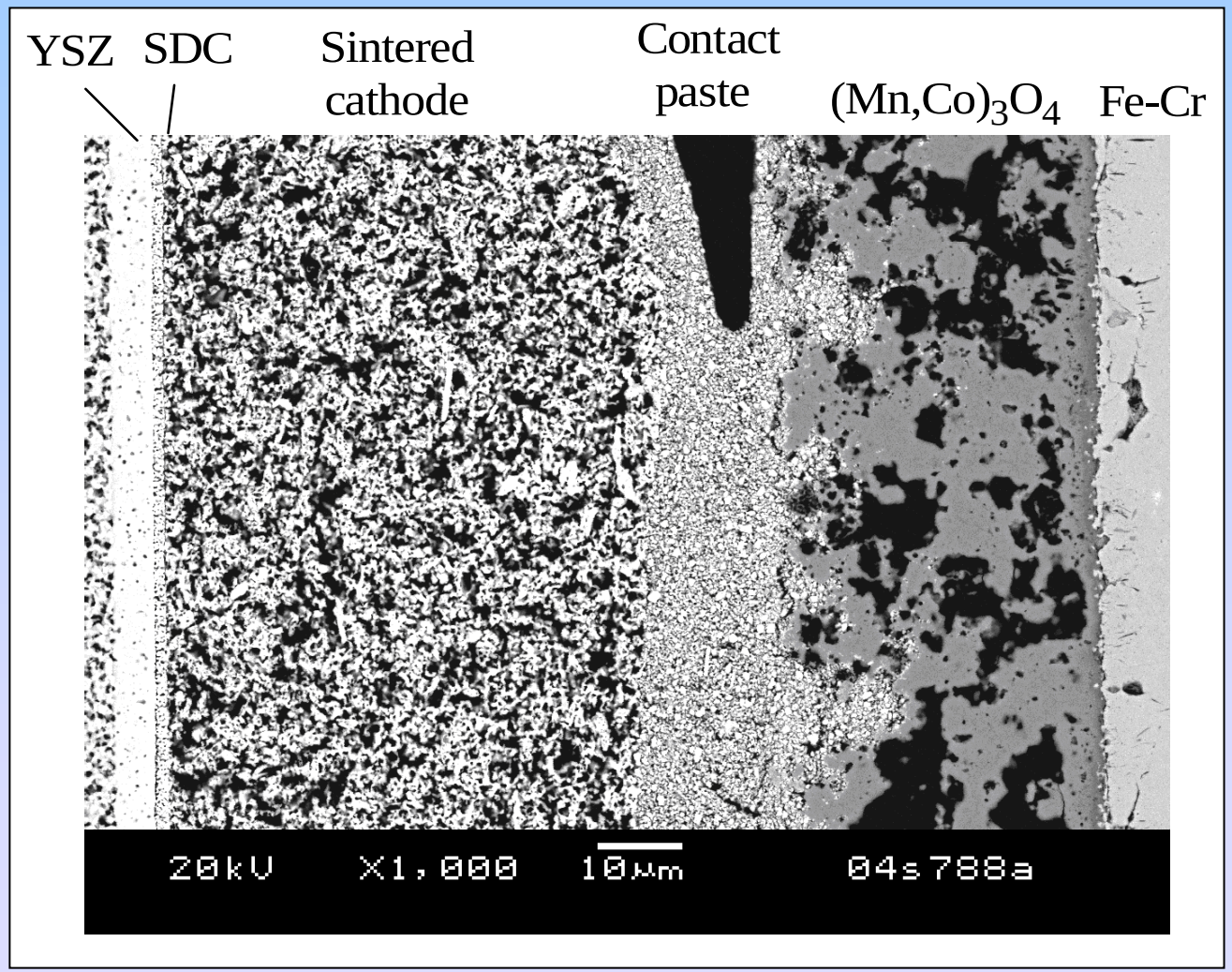




Long-Term Assessment of $(Mn,Co)_3O_4$ Coatings - *Test Details*

- Anode-supported thin film YSZ button cells (25 mm diameter).
- All cells utilized a protective Sm-doped CeO_2 interlayer between the YSZ and the cathode (LSM and LSF presented here).
- All tests conducted at 750-800^{o}C and 0.7V.
- 200-300 sccm air (30-50% relative humidity); 200 sccm 50-50% H_2/N_2 fuel ➔ low fuel utilizations (~20%).
- Coated alloy interconnects (Crofer22 APU) contacted to cathode via a combination of oxide paste (same composition as cathode) and compressive loading.

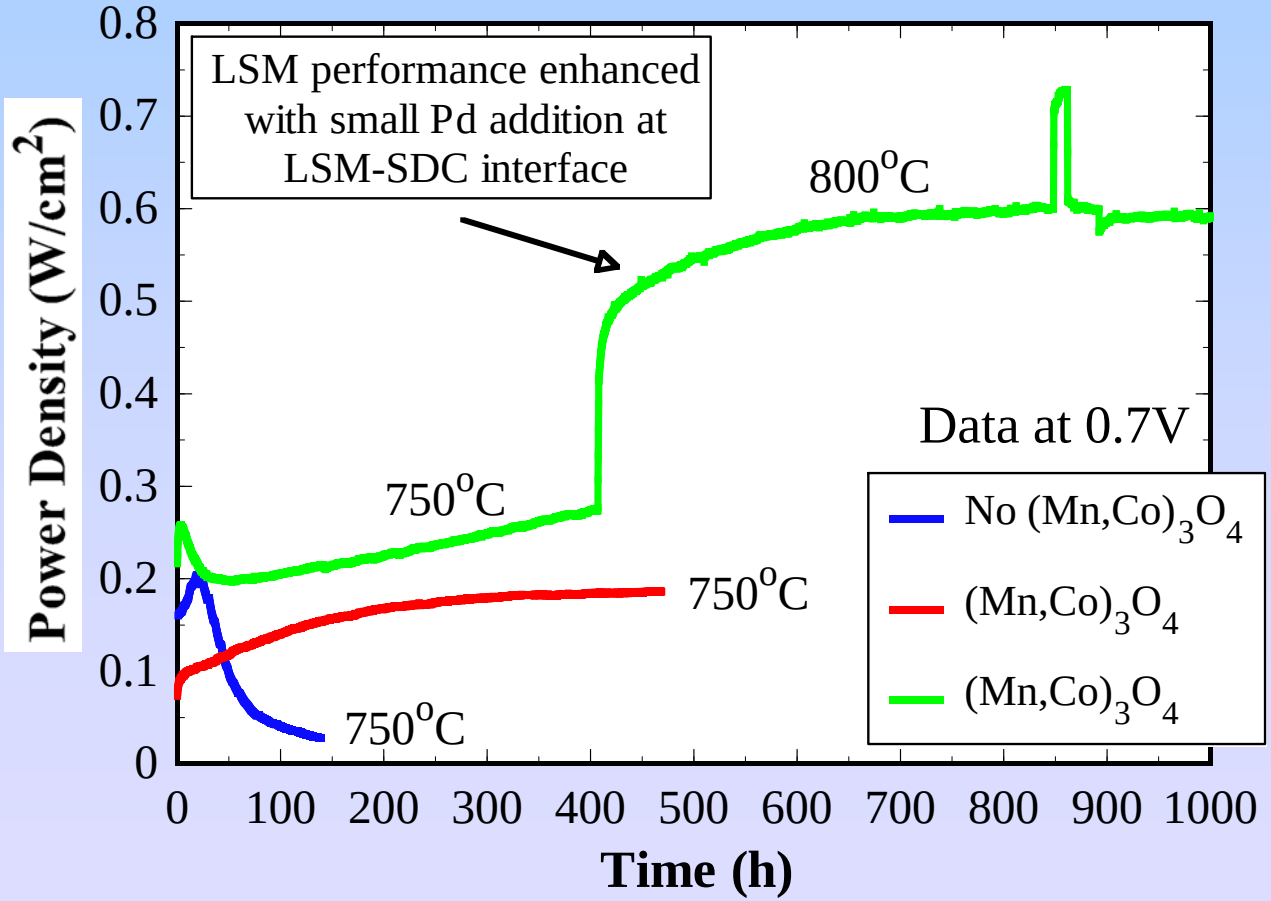
$(Mn,Co)_3O_4$ Coating to Prevent Cr Volatility



Compressive Load

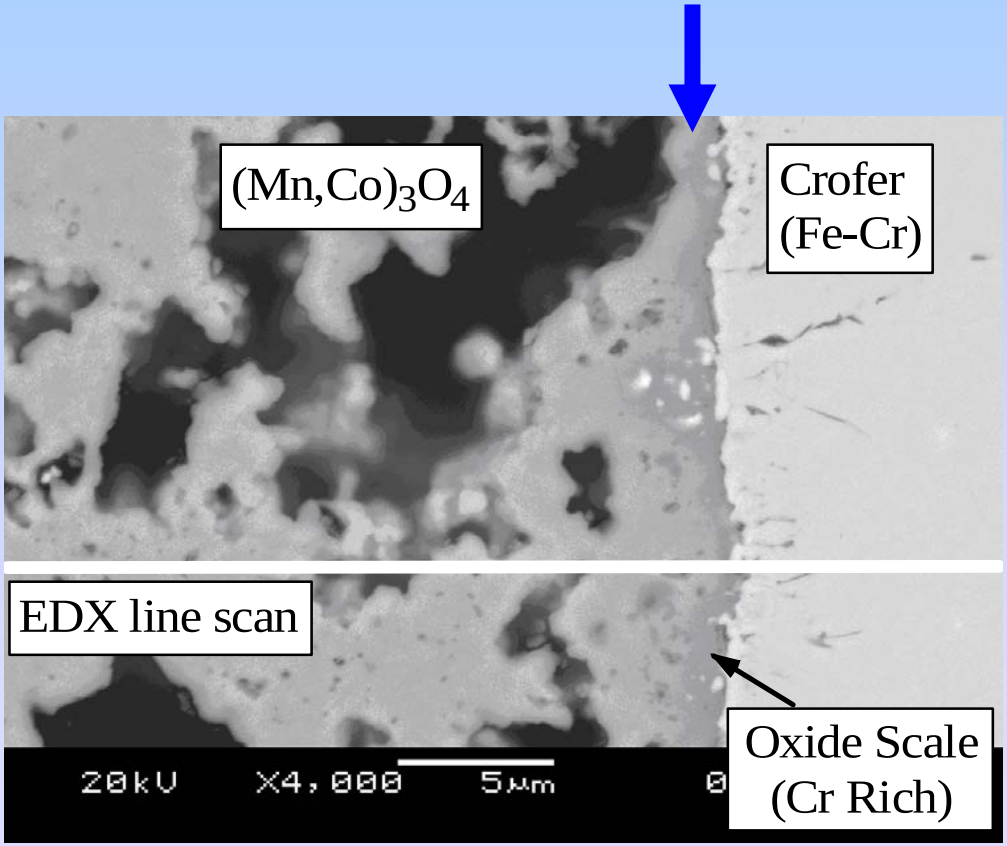
$(Mn,Co)_3O_4$ Coated Crofer – *LSM Cathode*

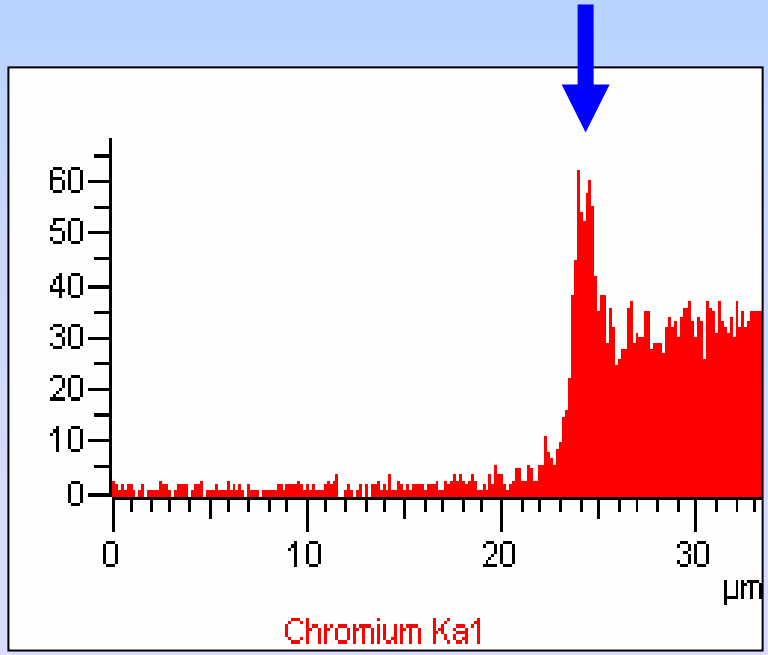
- LSM-based cell (LSM cathode + LSM contact paste) indicated stable performance even at 800°C when utilized with a coated Crofer interconnect.



LSM-Based Cell – *SEM/EDX*

- No Cr detected in LSM or SDC interlayer (despite obvious porosity in spinel layer) – indeed Cr barely penetrates (<5 μm) into the $(Mn,Co)_3O_4$ coating.

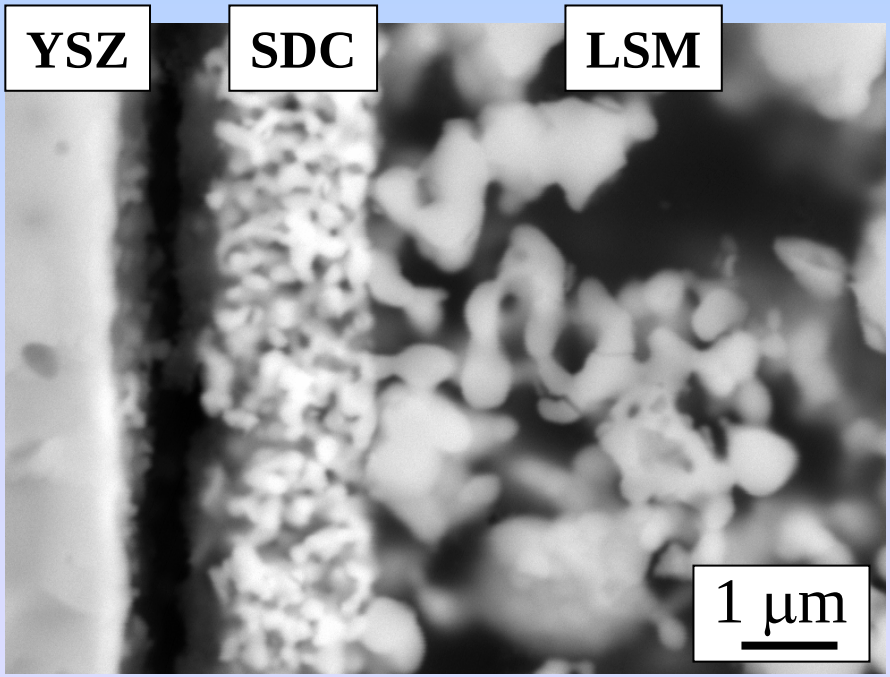




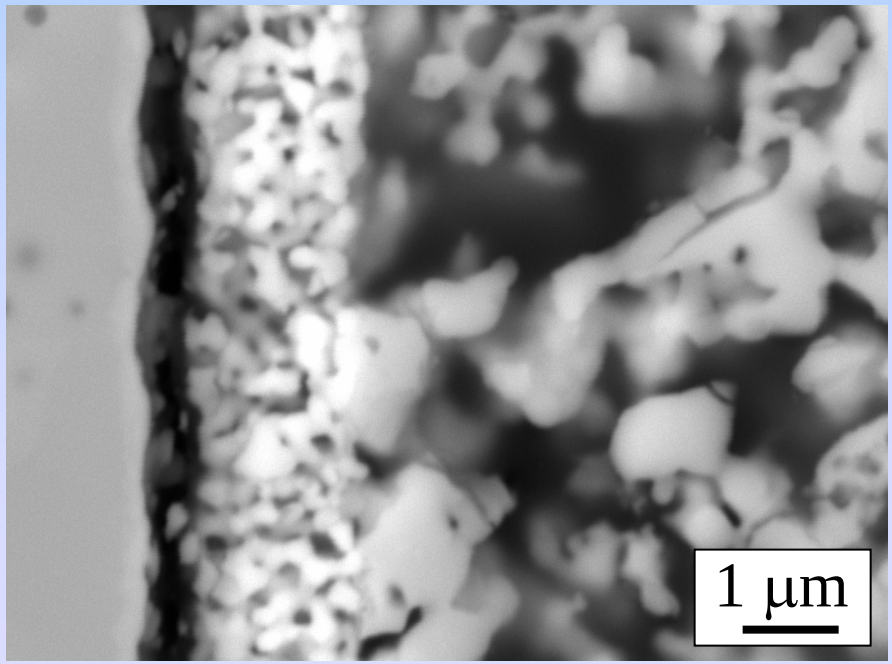
LSM-Based Cell – *SEM*

- No discernible differences in microstructures of pre- and post-tested LSM samples.

Pre-test

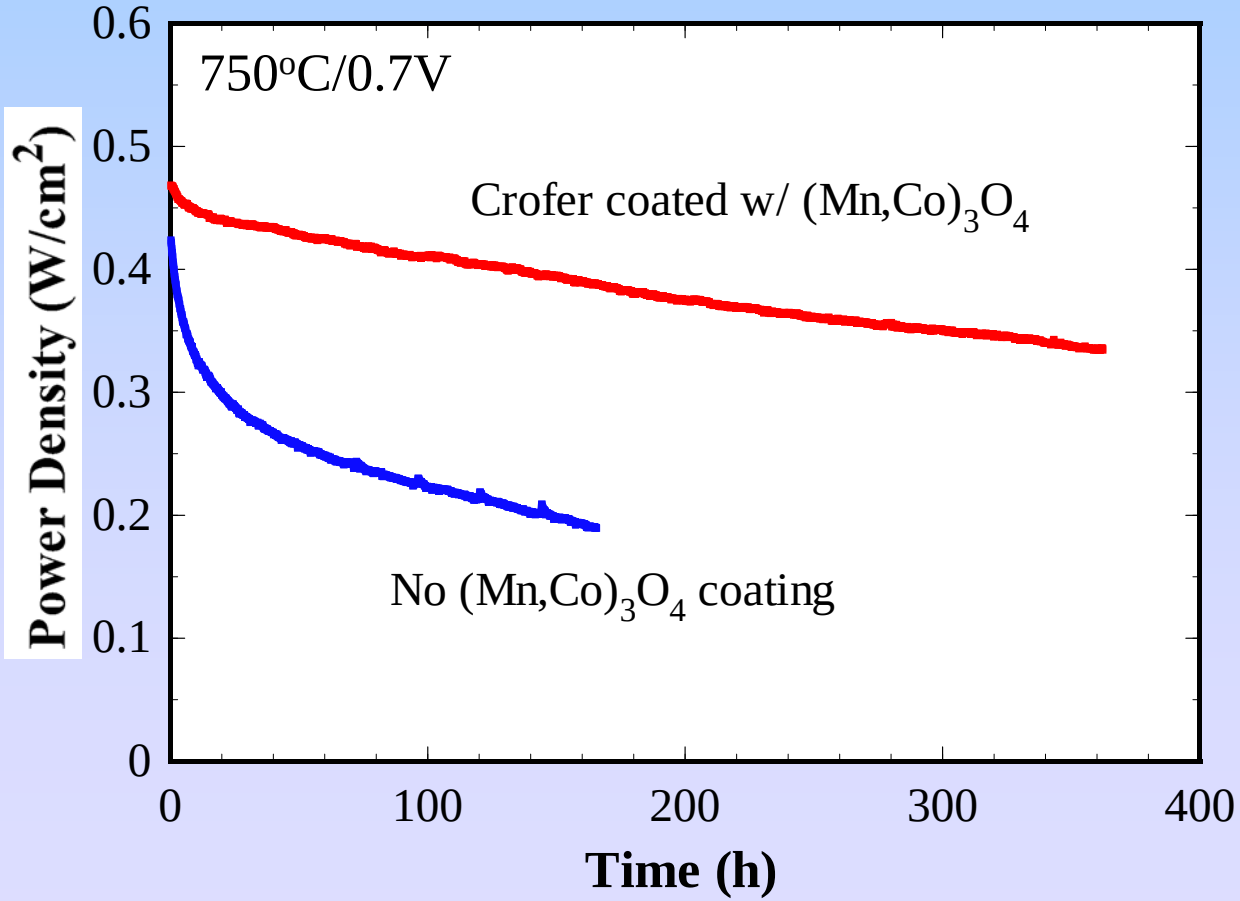


Tested at 800°C for 1000h



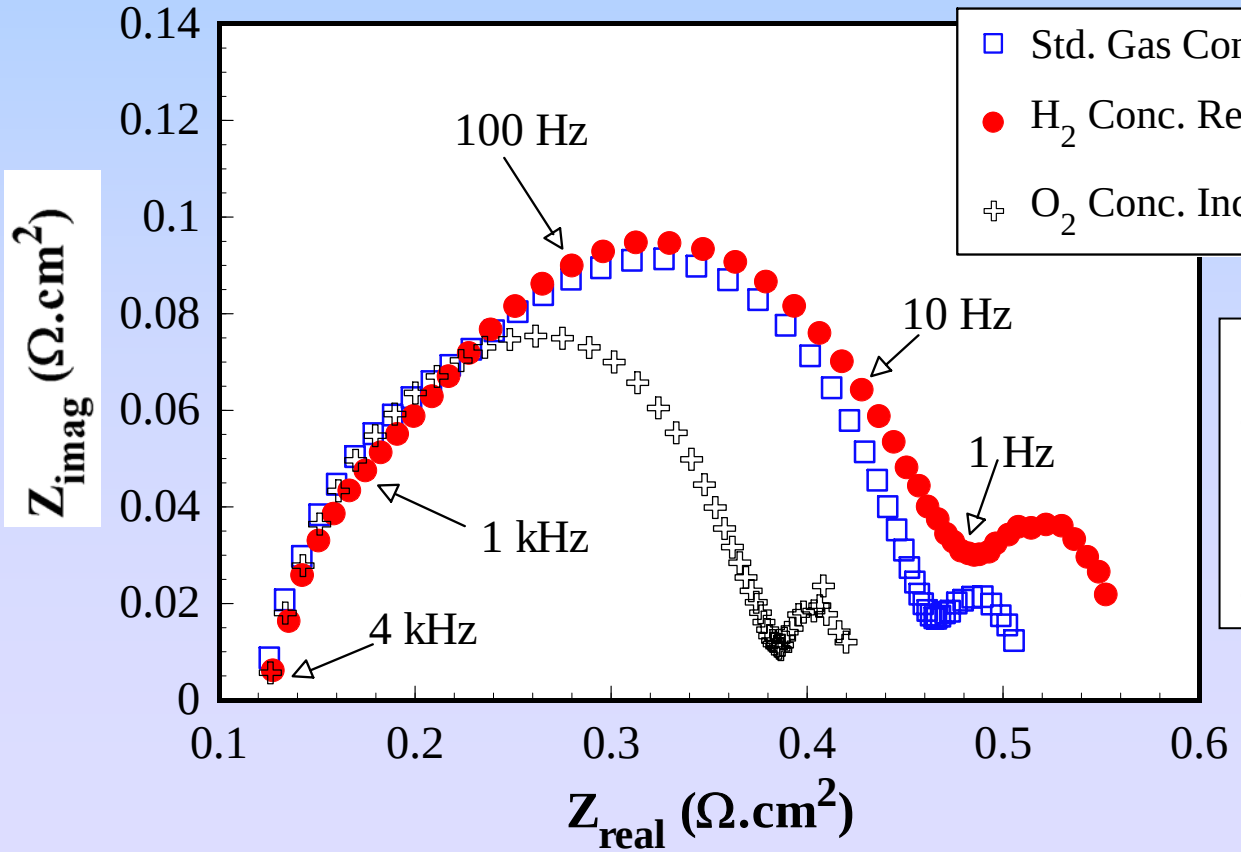
$(Mn,Co)_3O_4$ Coated Crofer – *LSF Cathode*

- LSF-based cells (LSF cathode + LSF contact paste) indicated severe degradation with or without the protective spinel coating on the Crofer current collector.



AC Impedance of Full Cell (no reference electrode)

- Aware of limitations of impedance without a reference electrode, but confident that the analysis can at least differentiate between ohmic and polarization resistances, and at best may indicate that performance changes are cathode or anode related.

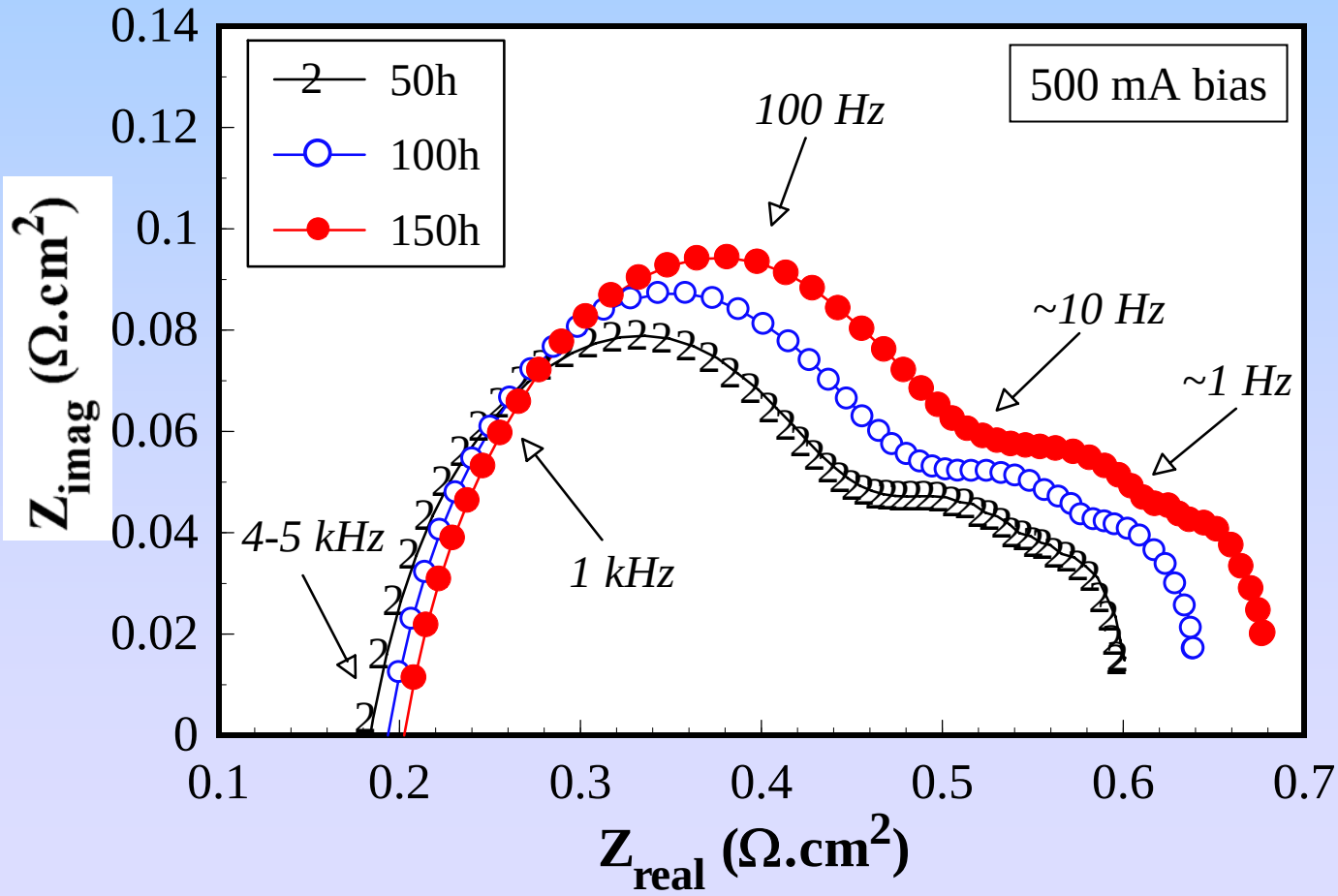


<1 Hz influenced by H_2 concentration in anode gas.

>10 Hz influenced by O_2 concentration in cathode gas.

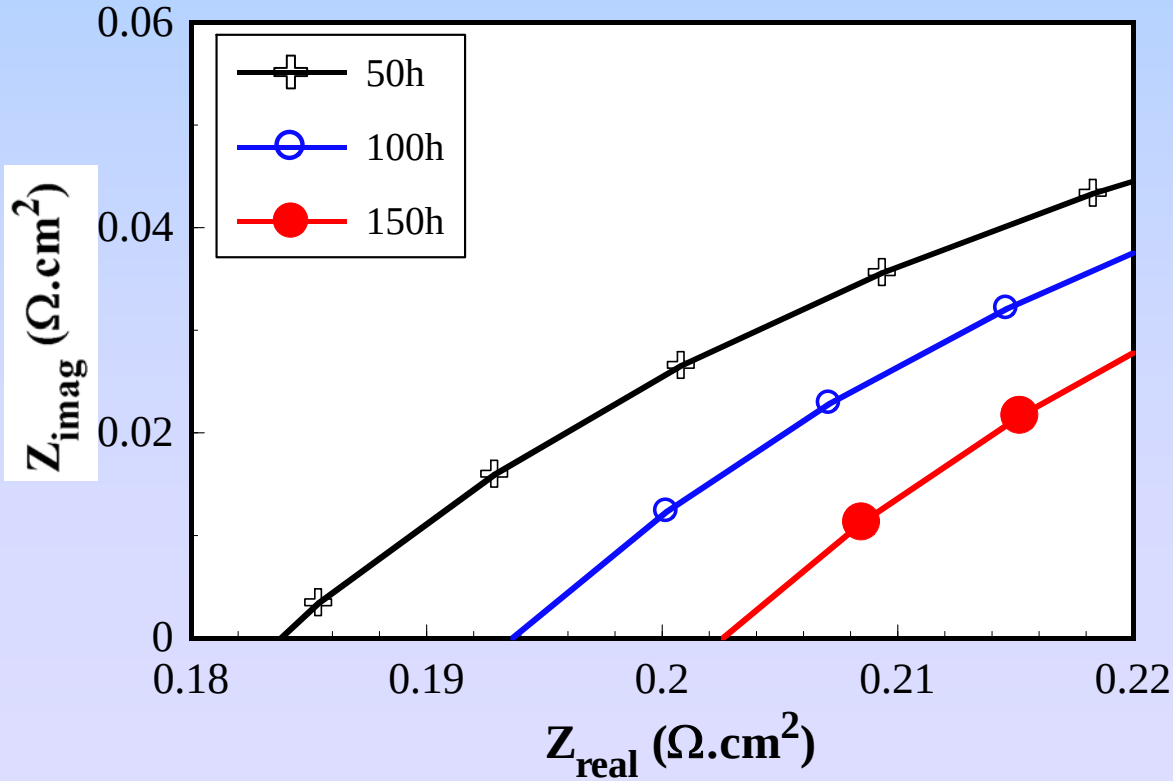
Impedance of LSF Cell with Coated Crofer

- Cell indicates increase in ohmic resistance (high frequency intercept) and non-ohmic polarization (>10 Hz ➔ likely cathode related).



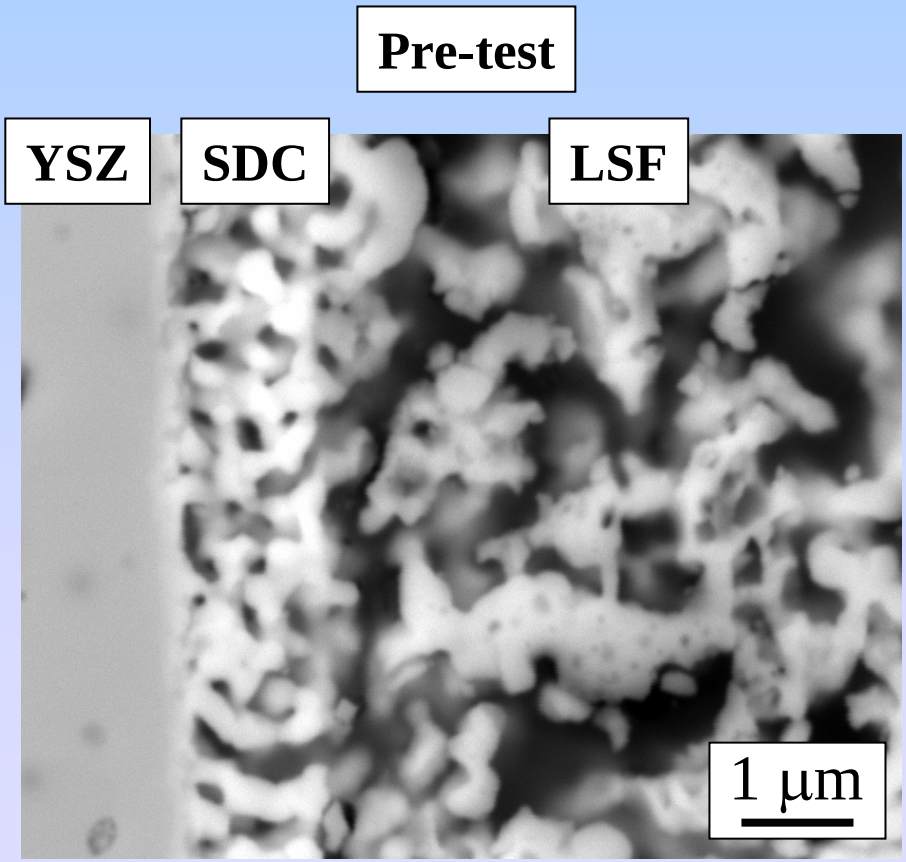
High Frequency Intercept – *Ohmic Resistance*

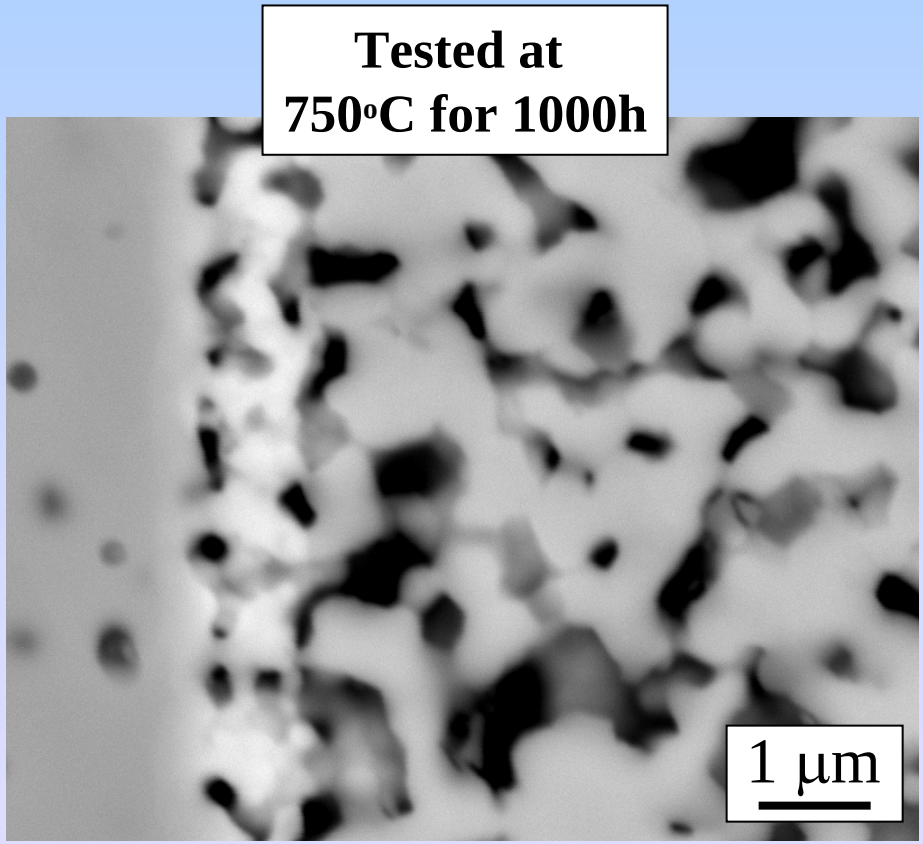
- Fairly linear increase in ohmic resistance with time ➔ possibly associated with increased contact resistance between layers (interfacial reaction layers, delamination etc.), Ni sintering in the anode, changes in electronic/ionic conductivities of materials etc.



LSF-Based Cell – *SEM*

- Unlike LSM, the LSF-based cells indicate significant microstructural change after testing ➔ densification of both LSF and SDC layers.





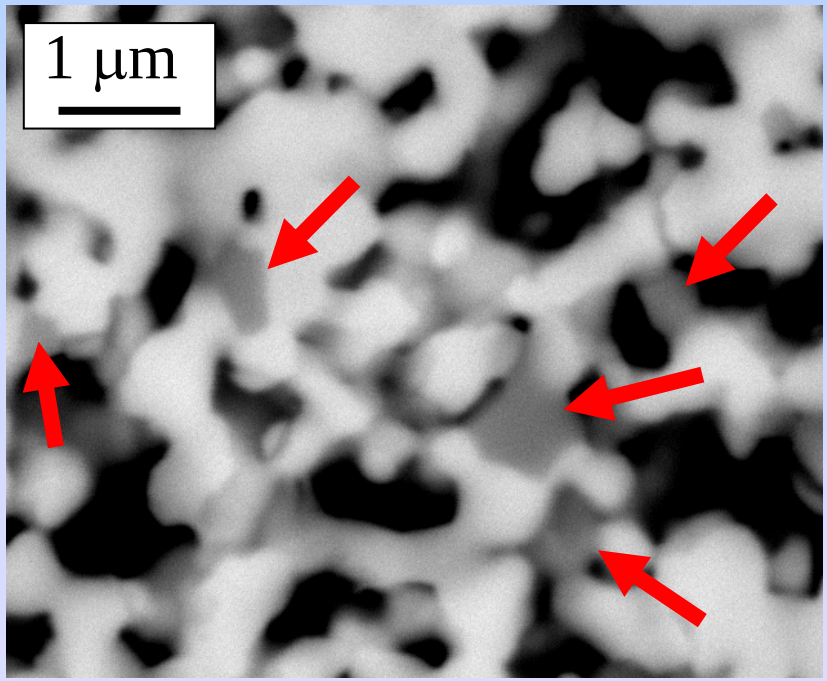
Tested LSF Samples - *EDX*

- Extensive elemental analysis conducted *but* EDX has its limitations – beam spreading and with 9 + elements in our samples there is potential for significant energy peak overlap ➔ interfaces are particularly problematic.

- Confident that:

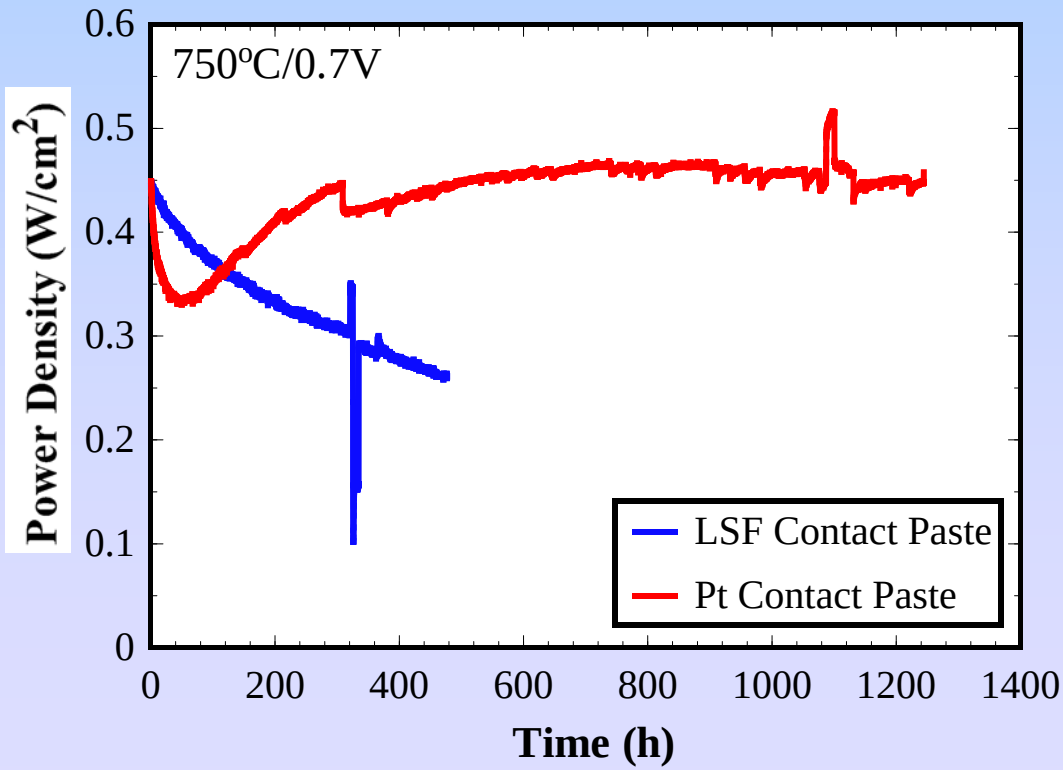
- No Cr in LSF or SDC layers.

- High Fe-phase precipitated in cathode.

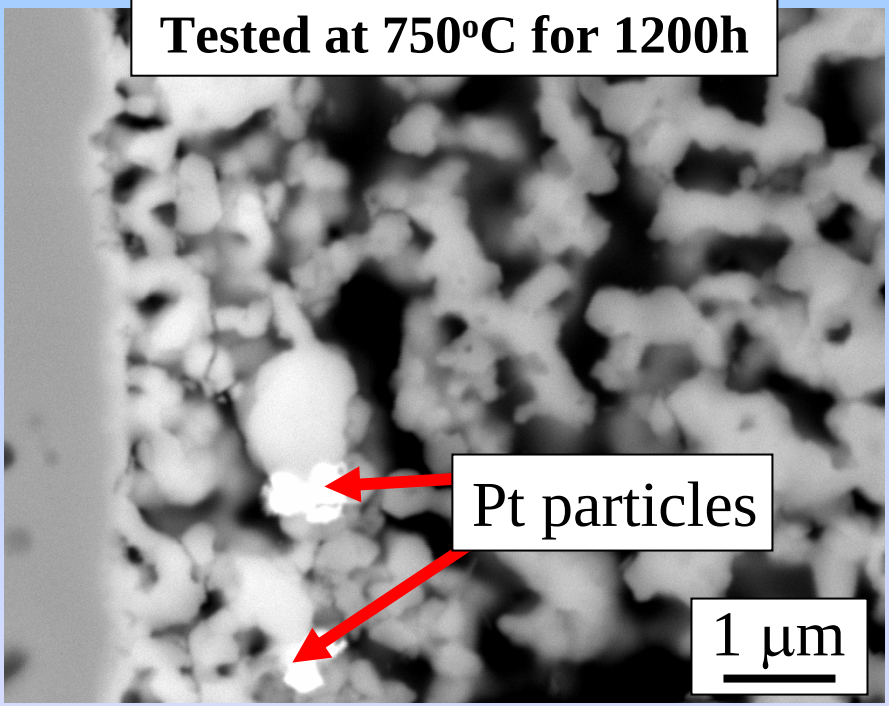


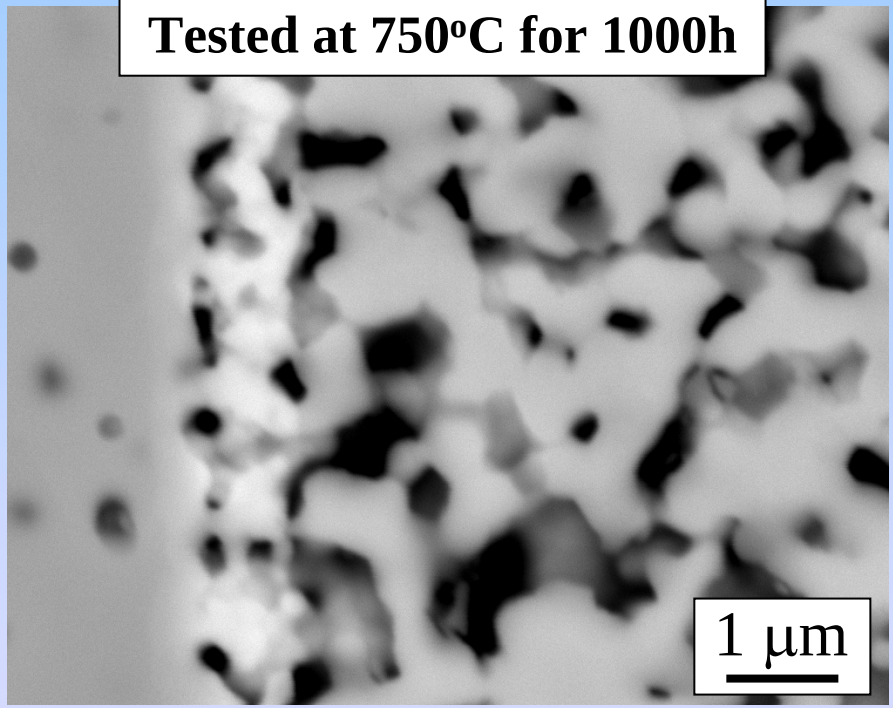
Effect of Pt on LSF Performance

- Why don't we see these morphological changes/degradation in standard button cell tests utilizing Pt mesh/Pt paste current collectors?
- What happens if the coated Crofer is contacted to the LSF cathode using Pt paste rather than LSF paste?



Tested Cells - *SEM*

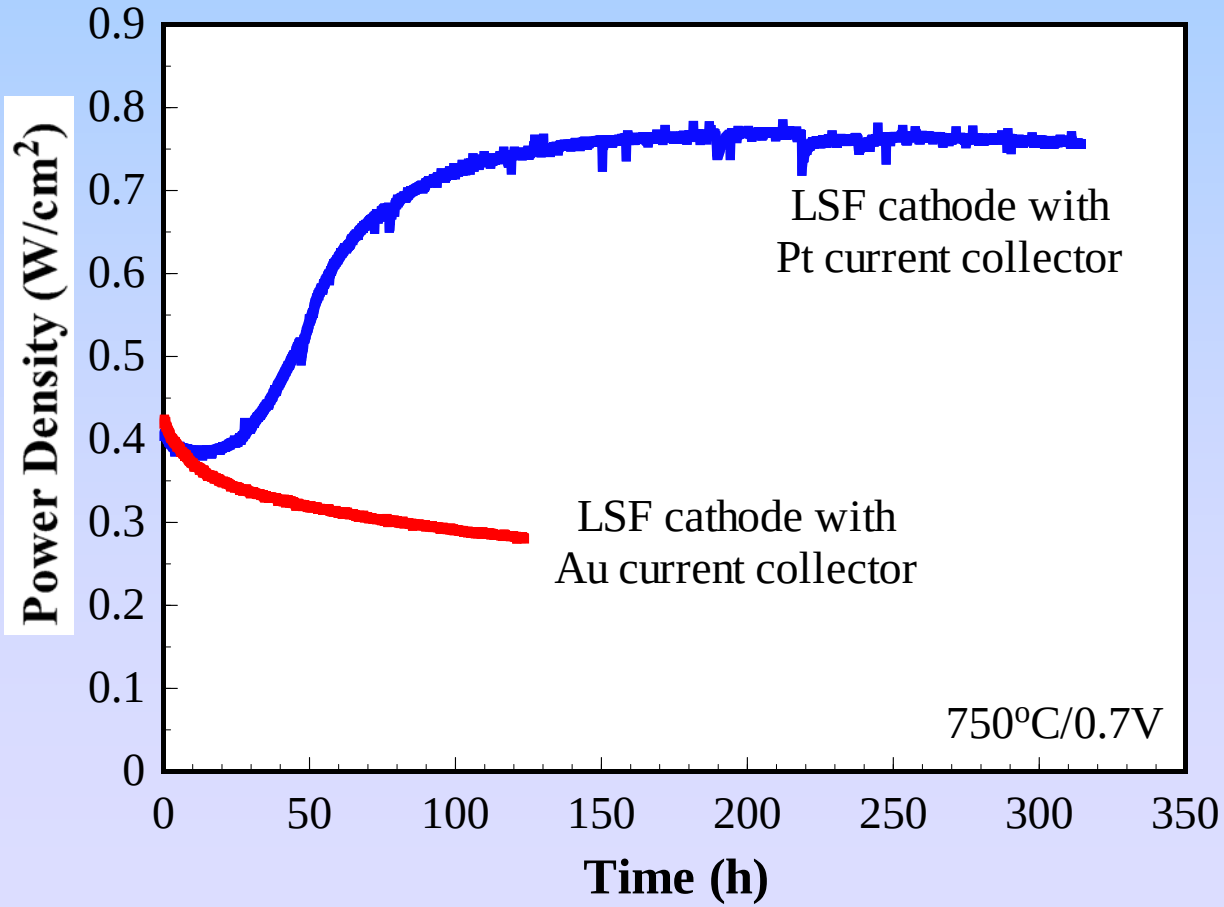




- Regularly observe migration of Pt to the SDC-LSF interface – believed to be evaporation of Pt-oxides and deposition/reduction at SDC-LSF.
- Not presently understood how the presence of Pt inhibits the observed microstructural changes.

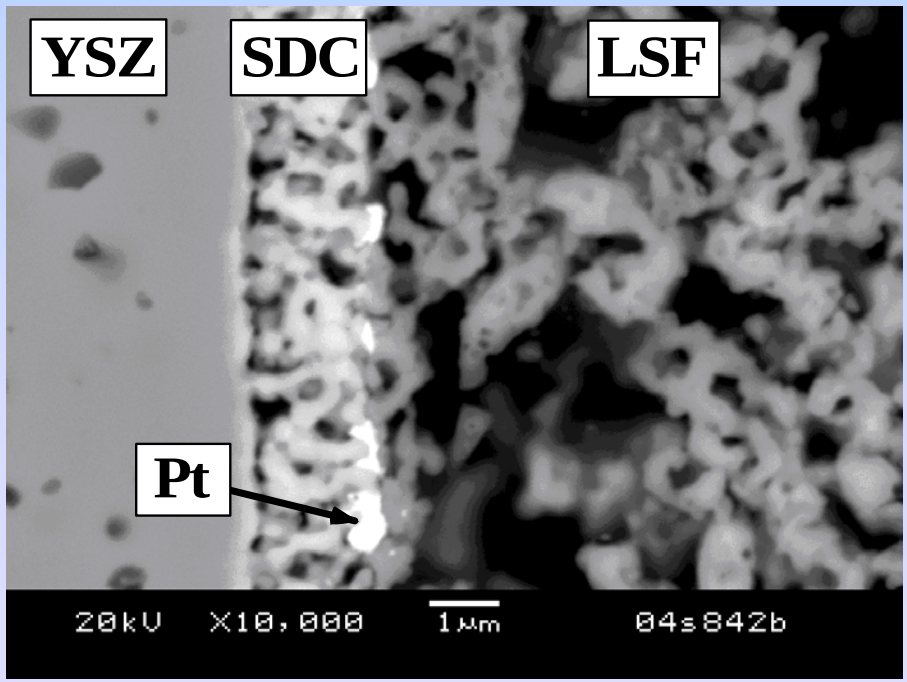
Influence of Pt on LSF Performance

- Pt and Au current collectors on LSF were assessed – Pt (or Au) mesh contacted to the cathode with Pt (or Au) paste (data verified with 3+ tests).



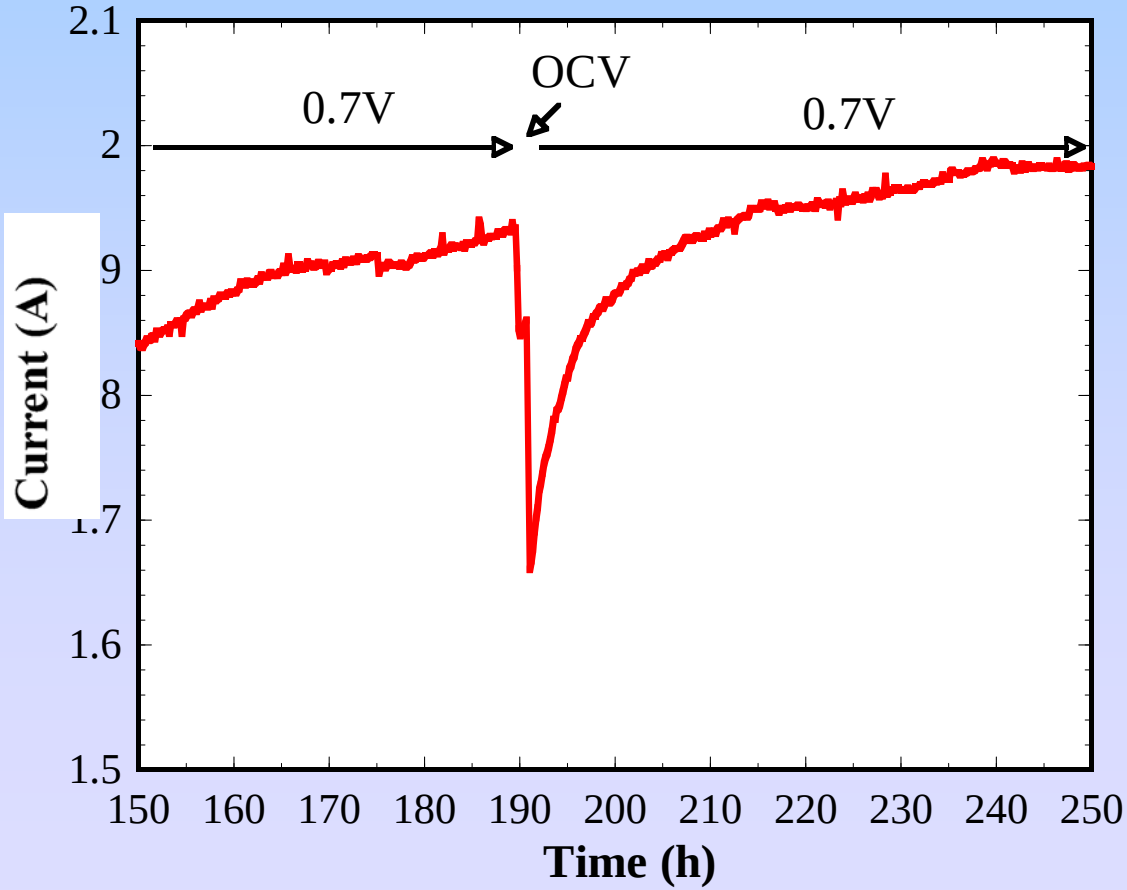
Role of Pt - *LSF Enhancement*

- PtO_x evaporates and is deposited/reduced at the LSF-SDC interface. Au oxides not stable at 750°C ➔ no migration of Au to LSF-SDC interface.
- Pt at the LSF-SDC interface may have a dual effect.
  - catalyzes O_2 reduction reaction.
  - in some way inhibits aforementioned microstructural changes in LSF and SDC.



Transient Cathode Behavior – *Additional Indicator for Pt Catalysis*

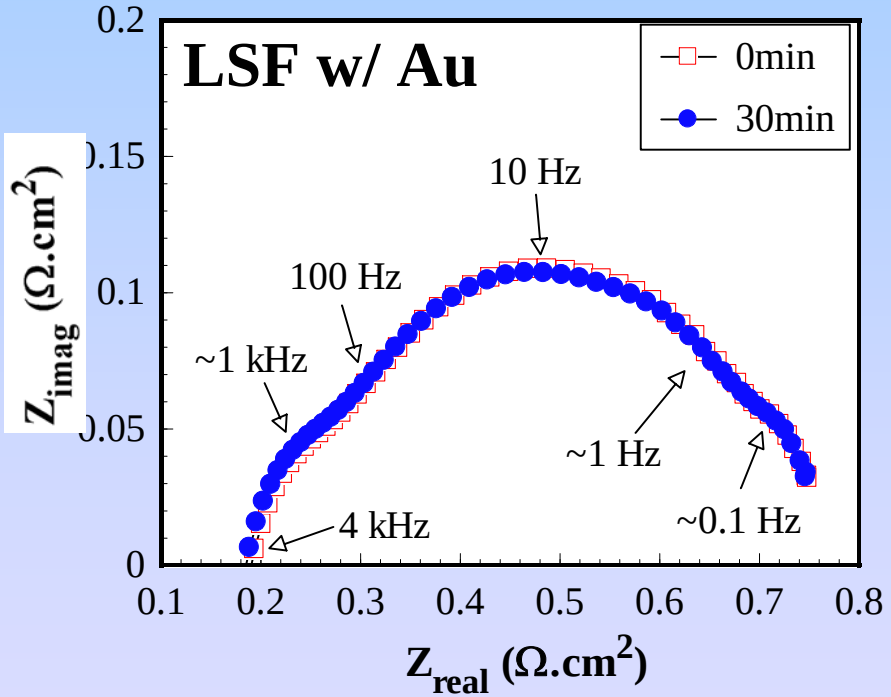
- Transient behavior is typically associated with the activation of the cathode when current is passing, and deactivation at zero current (OCV).

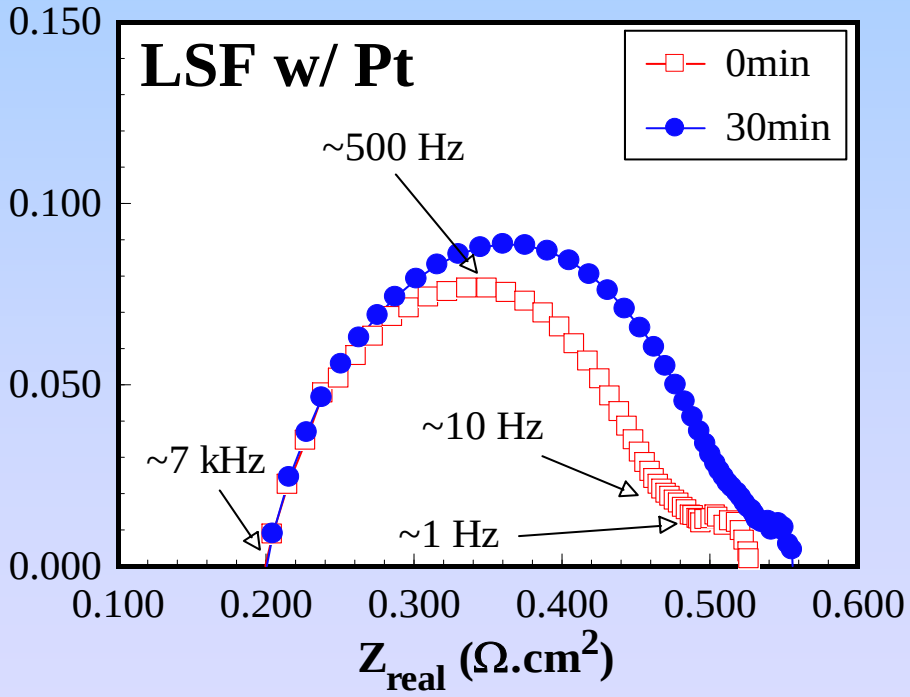


LSF with Pt current collector

Transient Behavior – *Impedance Analysis*

- Impedance analysis performed immediately after going to zero current and after 30 minute hold at OCV.





- Only LSF with the Pt current collector indicates cathode deactivation at OCV. Phenomenon well-documented for Pt cathodes on YSZ – many different theories.

Summary

- Coating Crofer22 APU with a $(Mn,Co)_3O_4$ spinel appears to alleviate Cr volatization, and subsequent cathode contamination ➔ this is in spite of the spinel layer being porous.

- LSM-based cathodes indicate long-term stability even at 800^{o}C, though power density is relatively low.

- In contrast LSF cathodes indicate rapid degradation, and significant changes in microstructure ➔ mechanisms responsible have not yet been established, but not due to Cr poisoning.

- It appears that the presence of Pt (as a current collector) enhances LSF performance. The exact role that Pt plays is not fully understood.

Future Studies

- Continued assessment of protective $(Mn,Co)_3O_4$ coatings – recently processed films much improved ➔ thinner and lower porosity.

- At present only LSM shows stable long-term performance with the coated Crofer interconnect but the power density is low ➔ need to improve performance at 750-800^{o}C.

  - Processing/microstructure optimization (already seen that very low Pd content at LSM-SDC interface improves power density).

  - Improved cathode-interconnect contact.

- Determine why Pt alleviates LSF degradation? If we can work out why it may be possible to adjust materials and/or processing to overcome the degradation.