Cathode-Chromia Interactions

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Technical Issues

- Recent studies at PNNL have shifted from enhancing cathode electrochemical activity to understanding the effects of Cr containing alloys on cathode degradation.

- Generally agreed that there are at least two degradation mechanisms associated with Cr poisoning.

  - Solid state reaction of cathode and alloy oxide scales (typically Cr_2O_3 and $MnCr_2O_4$) ➔ poorly conducting interfacial phases.

  - Cr volatilization ➔ predominantly CrO_3 (g) and $CrO_2(OH)_2$ (g) evaporation, and subsequent re-condensation/reaction within the cathode, and at cathode-electrolyte interface.

R&D Objectives and Approach

- Principal objective is understanding the level of Cr interaction with established cathodes such as La(Sr)FeO_3, La(Sr)MnO_3 and La(Sr)Fe(Co)O_3.

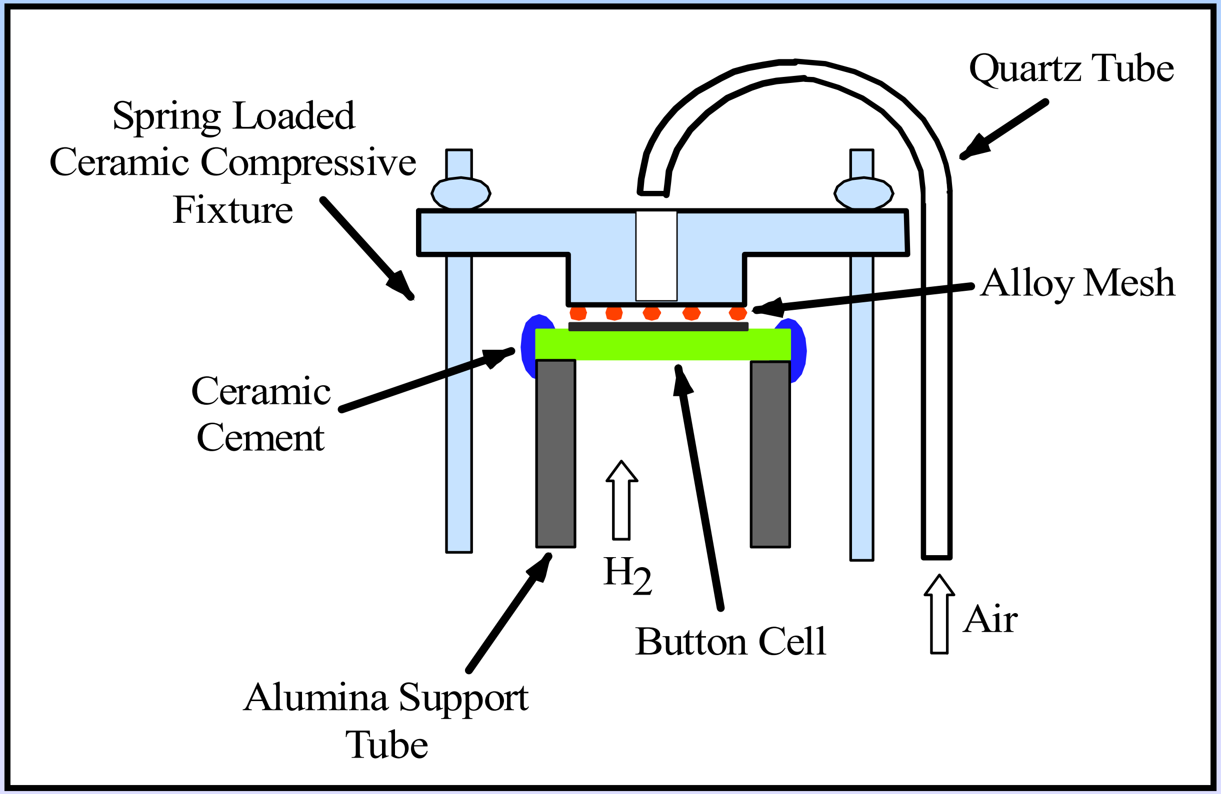
- Modified button cell testing utilizing an alloy mesh compressed directly onto cathode ➔ assessment of solid-state and vapor interactions.

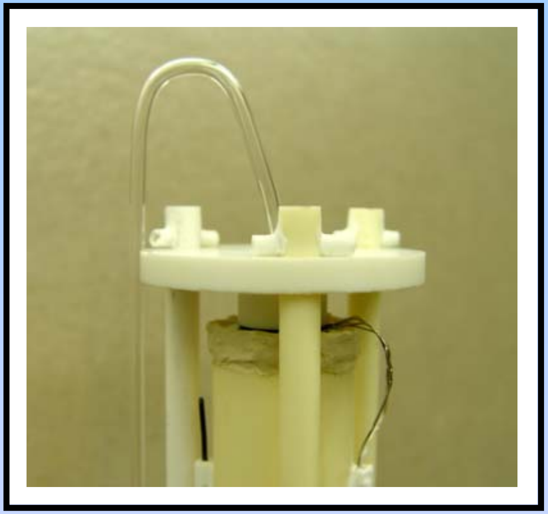
- Conventional button cell testing utilizing a sintered Pt current collector with physical separation between the cathode and various Cr containing compounds (Cr_2O_3, $LaCrO_3$ and $MnCr_2O_4$) ➔ relative vapor effects of different Cr sources.

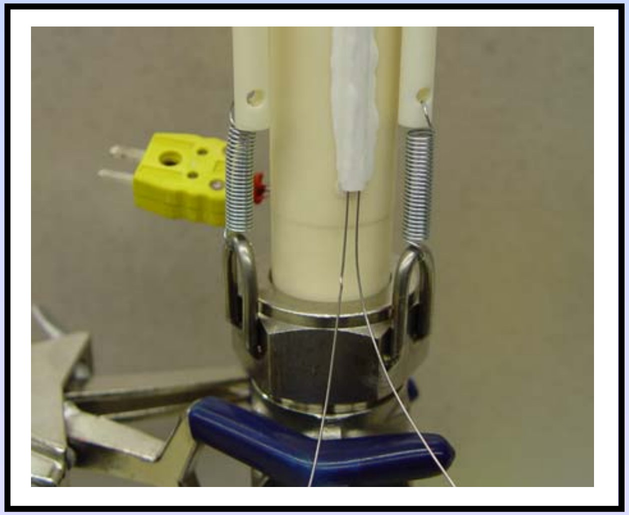
- In-situ reactivity of aforementioned cathodes on alloy foil using HTXRD ➔ technique enables direct assessment of phase formation at the cathode-alloy interface.

Compressive Button Cell Fixture

- Fixture enables compressive loading of alloy mesh onto cathode negating the need for sintered Pt/Ag contacts.







Experimental Details

- All cells consisted of anode-supported thin film YSZ configuration, and incorporated an Sm-doped ceria (SDC-20) protective interlayer.

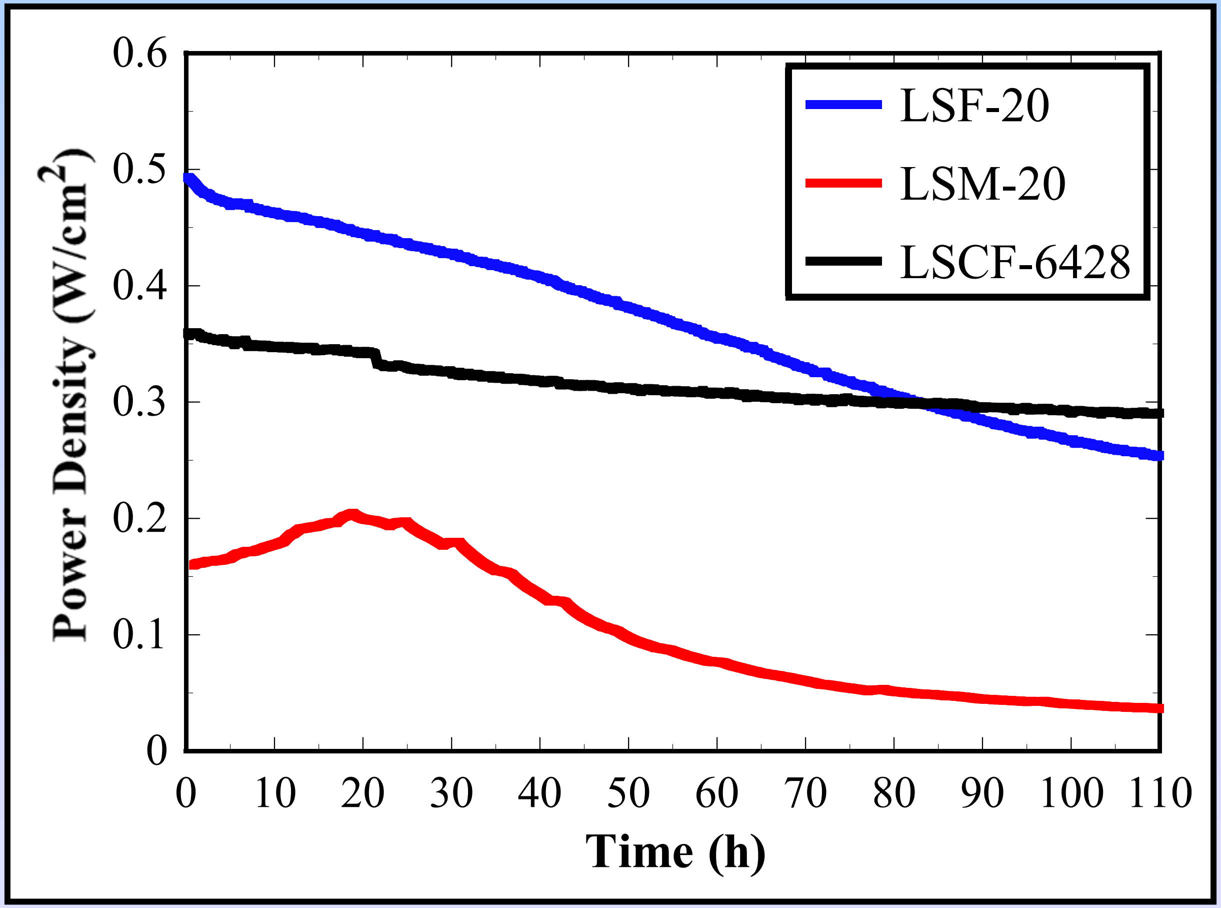
- 3 cathodes considered: LSM-20 (sintered at 1150^{o}C/2h), LSF-20 (1150^{o}C/2h), LSCF-6428 (1050^{o}C/2h).

- Preliminary data utilized a Crofer 22 APU mesh embedded in cathode contact paste and fired on cell at 800^{o}C (temperature required for sealing). Contact pastes were the same composition as the bulk cathode.

- Typical operating conditions:
  - Cell temperature – 750^{o}C
  - Cell voltage – 0.7V
  - Anode gas – 100 sccm H_2 – 100 sccm N_2 (3% H_2O)
  - Cathode gas – 300 sccm air (~25-35% relative humidity)
  - Test duration – ~100-120 hours

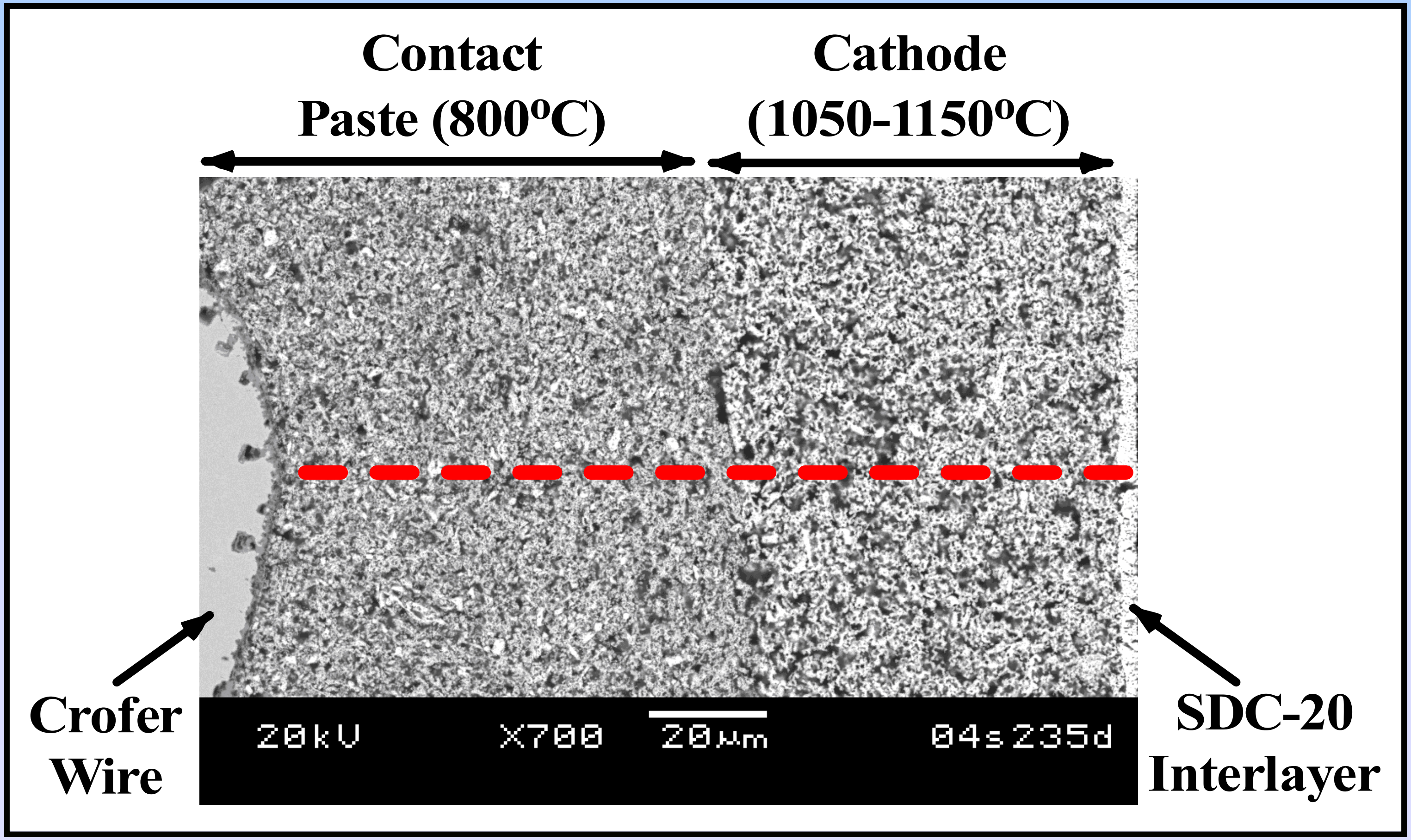
Cell Data with Compressed Crofer Mesh

- All 3 cathodes indicate significant degradation. LSM and LSF appear most susceptible to short-term Cr poisoning (50% or greater power loss in 110 hours).



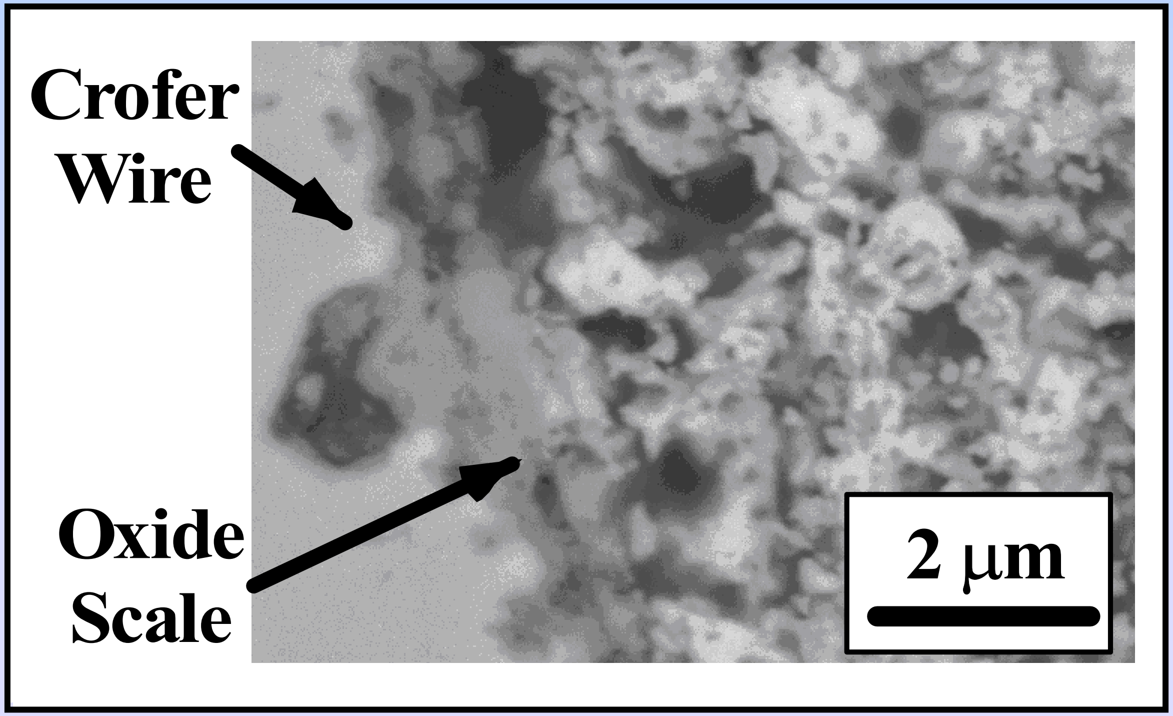
SEM/EDX Analysis of Post-Tested Cathode-Crofer Samples

- EDX area and spot analysis conducted at 2-20 µm intervals from SDC interlayer to Crofer wire to establish Cr distribution.



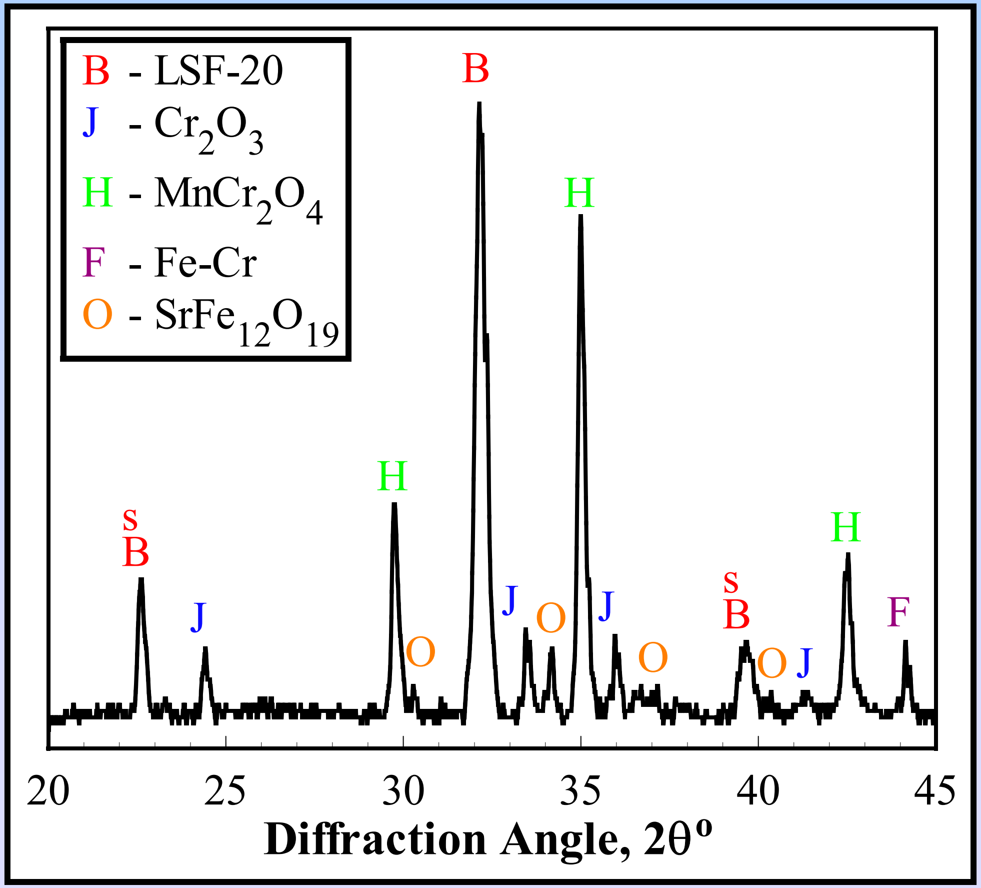
LSF-Crofer (SEM/EDX Analysis)

- SDC interlayer and LSF cathode (fired at 1150^{o}C) contain ~1 at.% Cr.
- LSF contact paste (fired at 800^{o}C) contains ~3 at.% Cr – very defined boundary between the high and low Cr content regions – finer particles in contact paste presumably getter more Cr.
- LSF close to Crofer wire ~4-5 at.% Cr.
- A separate Cr rich phase is not readily discernible ➔ Cr probably forms a solid solution with the LSF perovskite.



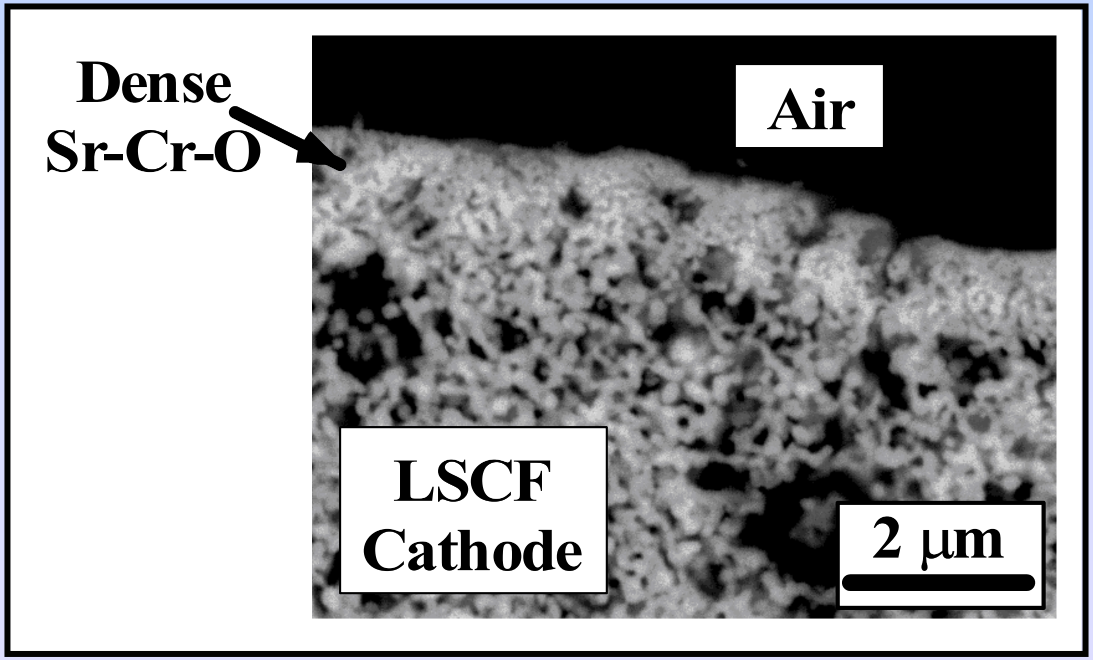
HTXRD – LSF-20 on Crofer Foil – 800°C/72h

- No discernible $SrCrO_4$ ➔ in agreement with SEM/EDX data. A high Fe/Sr ratio compound is formed again possibly implying that Cr is occupying Fe cation sites in the LSF perovskite.



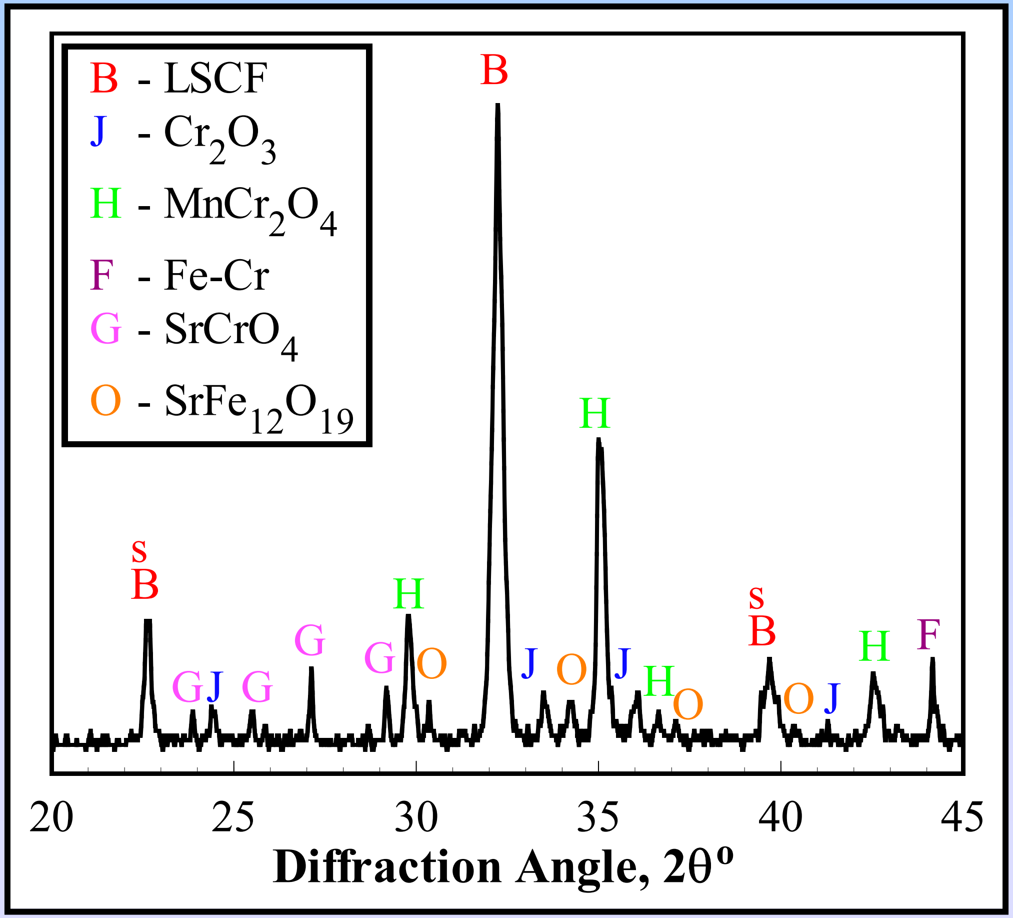
LSCF-Crofer (SEM/EDX Analysis)

- No Cr detected in SDC layer or LSCF cathode layer.
- Contact paste (particularly close to Crofer wire) contains as much as 5 at.% Cr. Distinct high Sr-Cr phases detected ➔ $SrCrO_4$.
- At cathode-air interface a dense layer of $SrCrO_4$ appears to form.



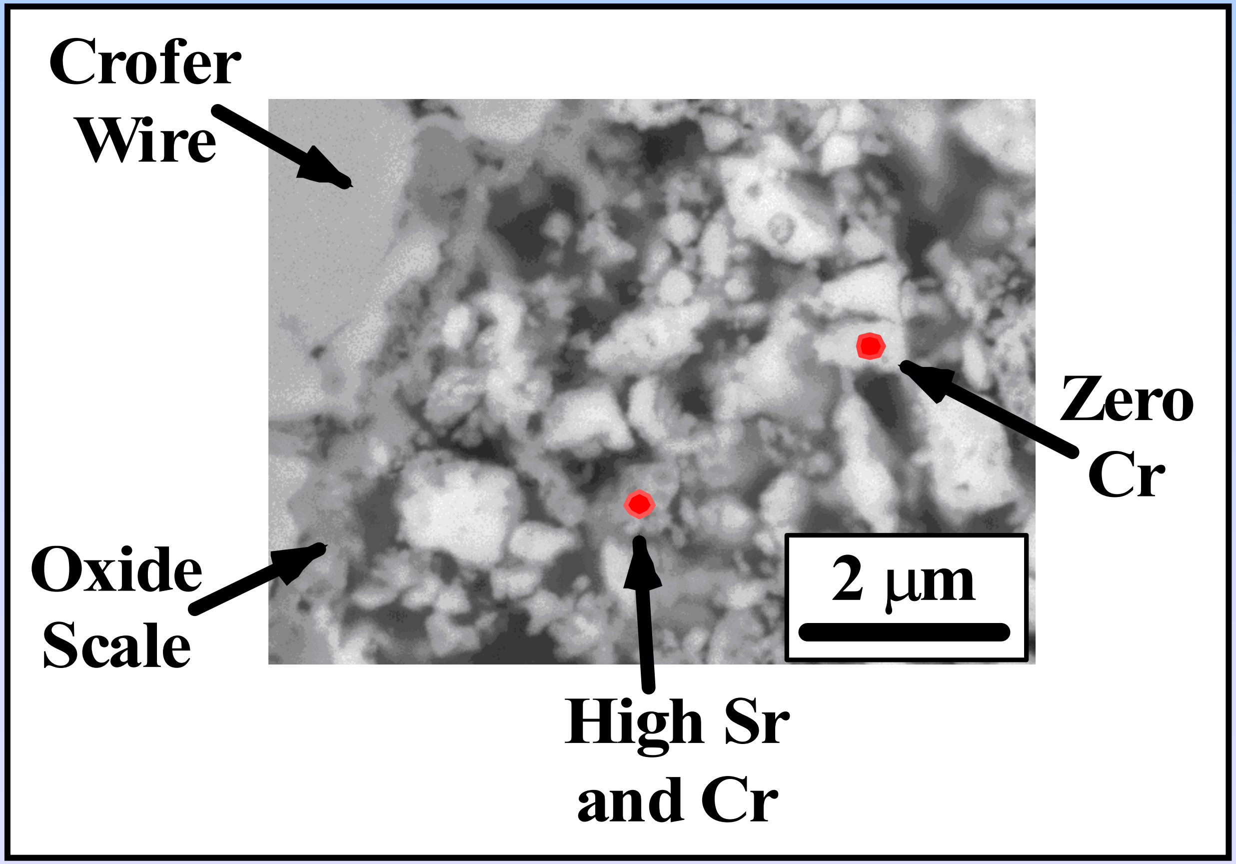
HTXRD – LSCF-6428 on Crofer Foil – 800°C/72h

- LSCF-6428 indicates substantial $SrCrO_4$ formation at 800°C (due to higher Sr content). A high Fe/Sr ratio compound is also observed.



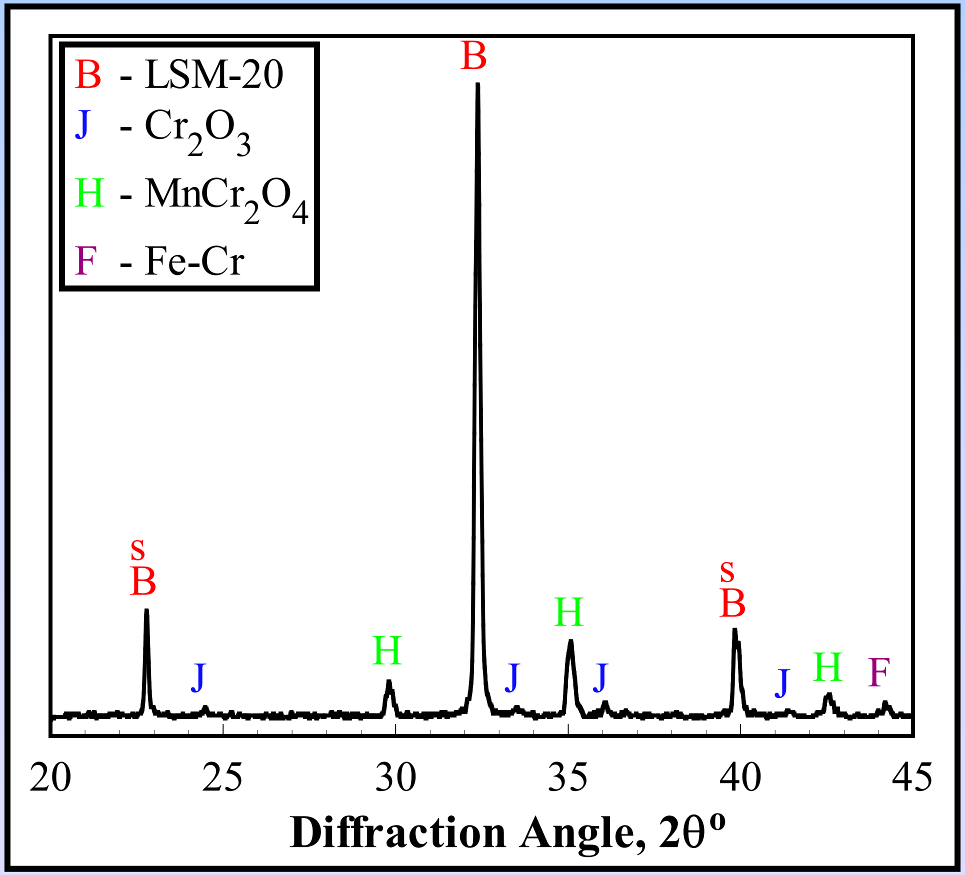
LSM-Crofer (SEM/EDX Analysis)

- SDC interlayer contains ~4-5 at.% Cr. No Cr detected in the LSM cathode (fired at 1150°C) – even adjacent to SDC layer. No Cr detected in bulk of 800°C fired LSM contact paste layer.
- LSM close (10-20 μm) to Crofer wire ~1-2 at.% Cr.
- 2 distinct phases discernible – one with zero Cr (likely pure LSM) and one with elevated Sr and Cr contents (possibly indicating $SrCrO_4$).



HTXRD – LSM-20 on Crofer Foil – 800^{o}C/72h

- LSM-20/Crofer interaction does not indicate $SrCrO_4$ formation – possibly amount formed below XRD detection limit. However, HTXRD analysis of an LSM/Cr_2O_3 powder mixture does suggest trace $SrCrO_4$ formation.



Summary of Crofer-Cathode Cell and XRD Data

- Solid state reactivity of cathodes with Crofer.

  ➔LSCF > LSF > LSM

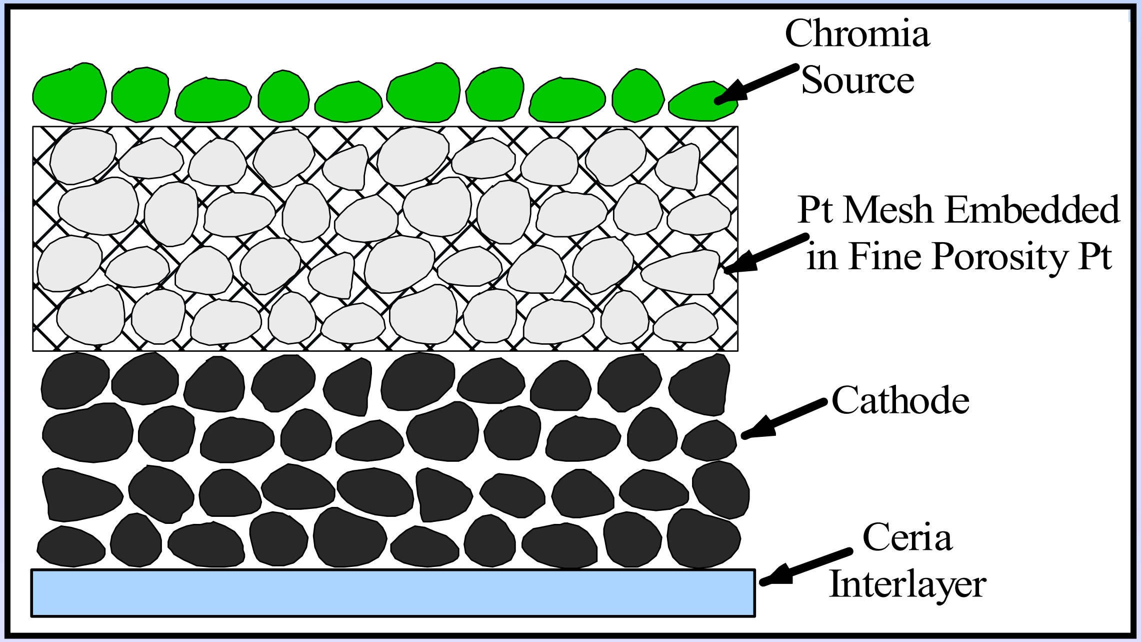
- Short term (110 hours) cell degradation.

  ➔LSM > LSF > LSCF

- In the short term LSCF and LSF may getter more Cr and prevent Cr vapor migration to the cathode-electrolyte interface.
- LSM more susceptible to Cr evaporation due to low solid state reactivity.
- Implication is perhaps that Cr volatility and re-condensation adjacent to the electrolyte is more detrimental than cathode-Cr solid state reactivity.

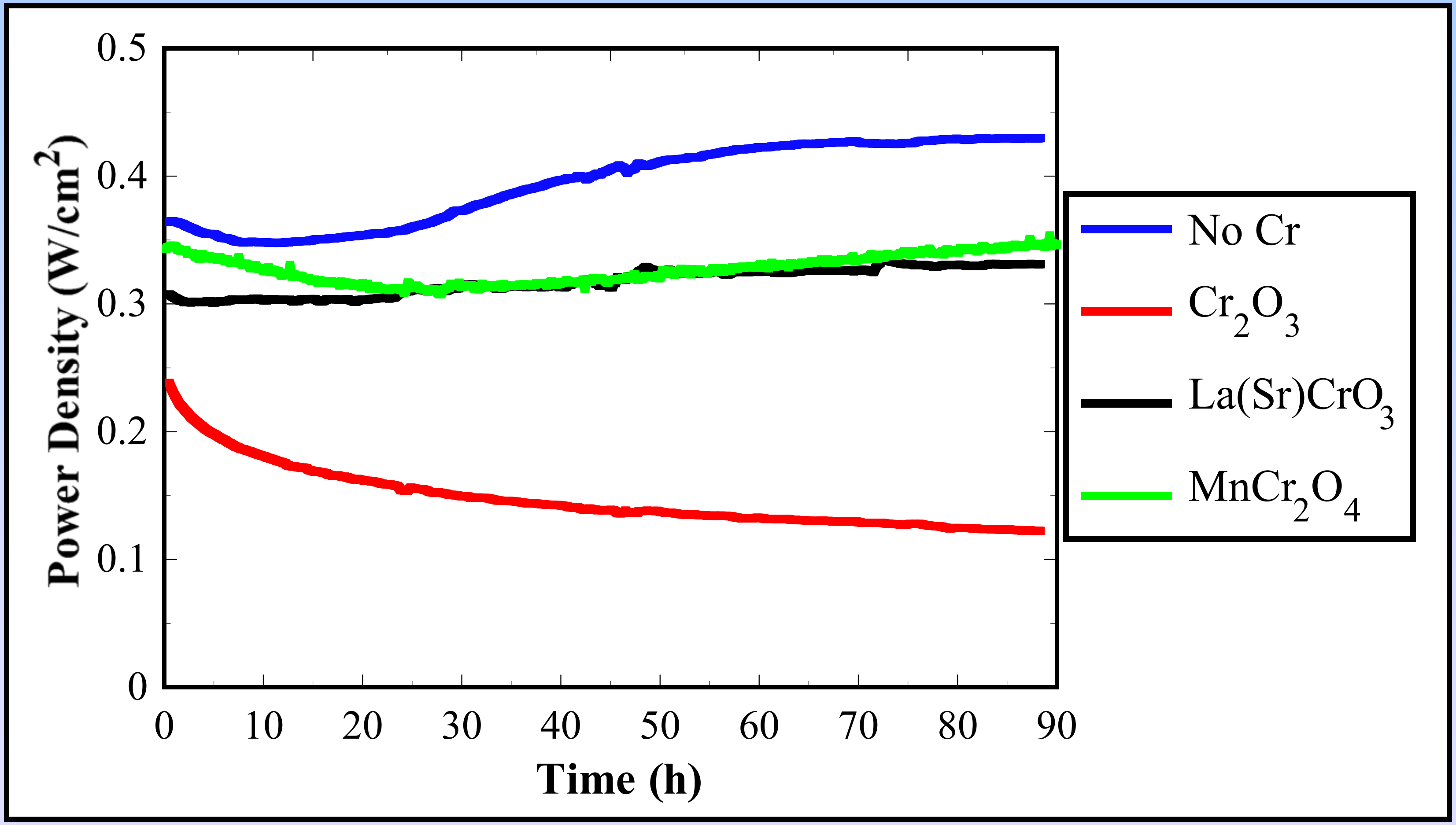
Effect of Variable Chromia Sources on Cell Performance (750°C/0.7V)

- The chromia sources were physically separated from the cathodes via a fine porosity Pt layer ➔ study the relative effects of Cr vapor species.
  - Cr_2O_3 – initially the majority oxide scale component on Cr-containing alloys
  - $MnCr_2O_4$ – can form a continuous layer above Cr_2O_3 scale on certain alloys
  - $La(Sr)CrO_3$ – potential coating for alloy interconnects to reduce Cr volatility

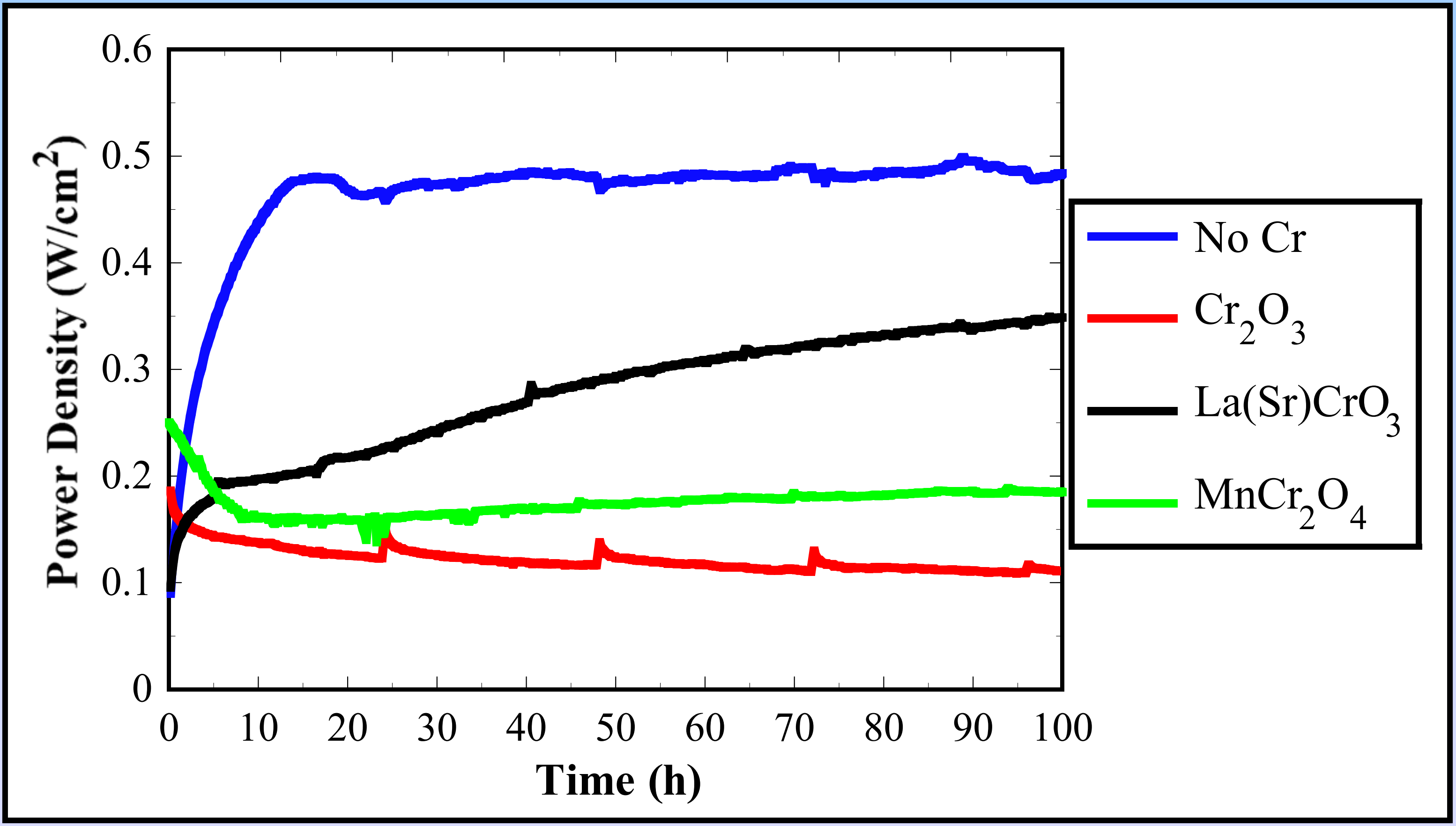


LSF Cells with Variable Chromia Sources

- Only the presence of Cr_2O_3 initiates rapid degradation.



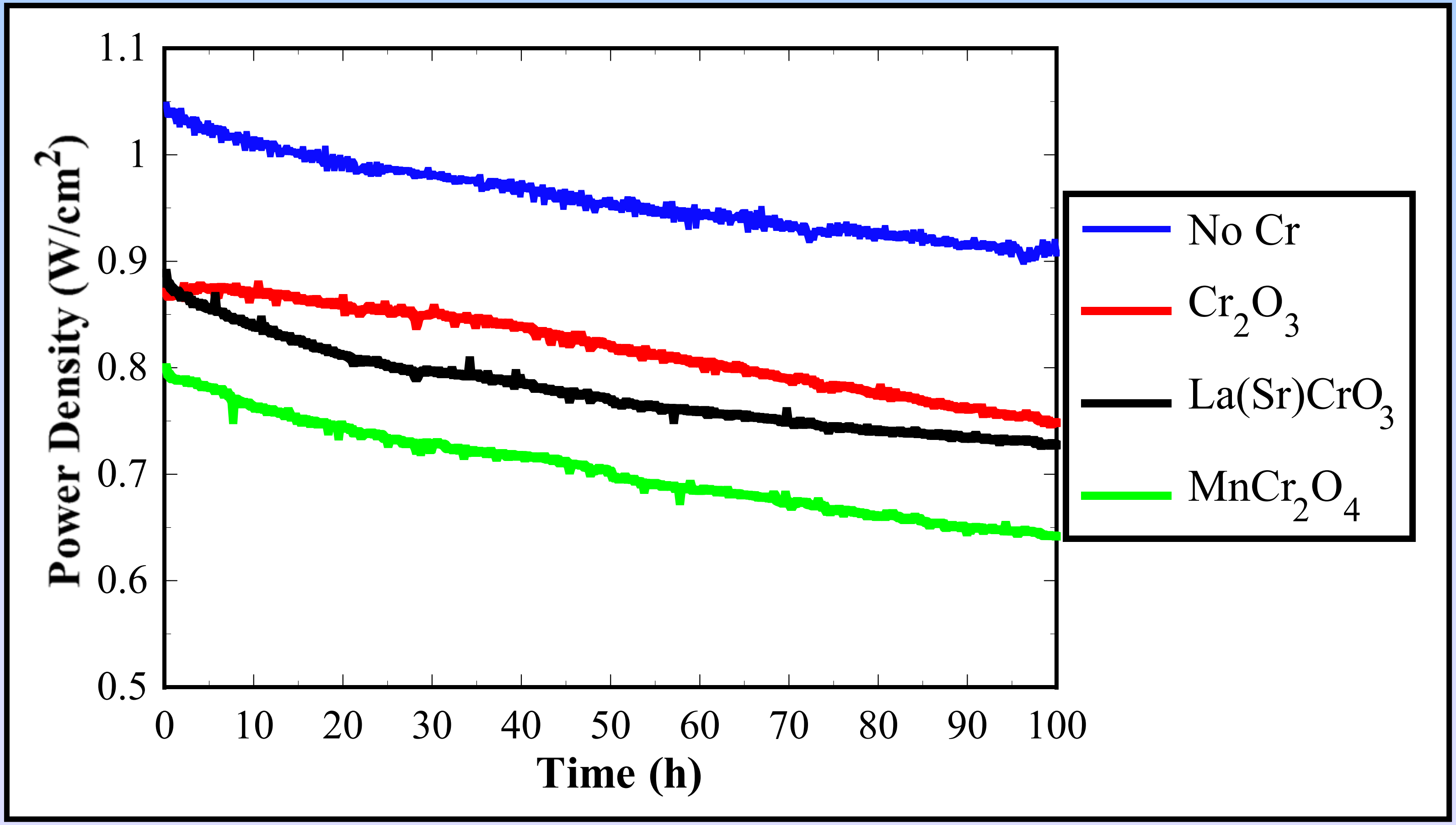
LSM Cells with Variable Chromia Sources



- SEM/EDX indicates significant Cr deposition at the LSM-electrolyte interface when Cr_2O_3 used as Cr source – other samples not yet analyzed.

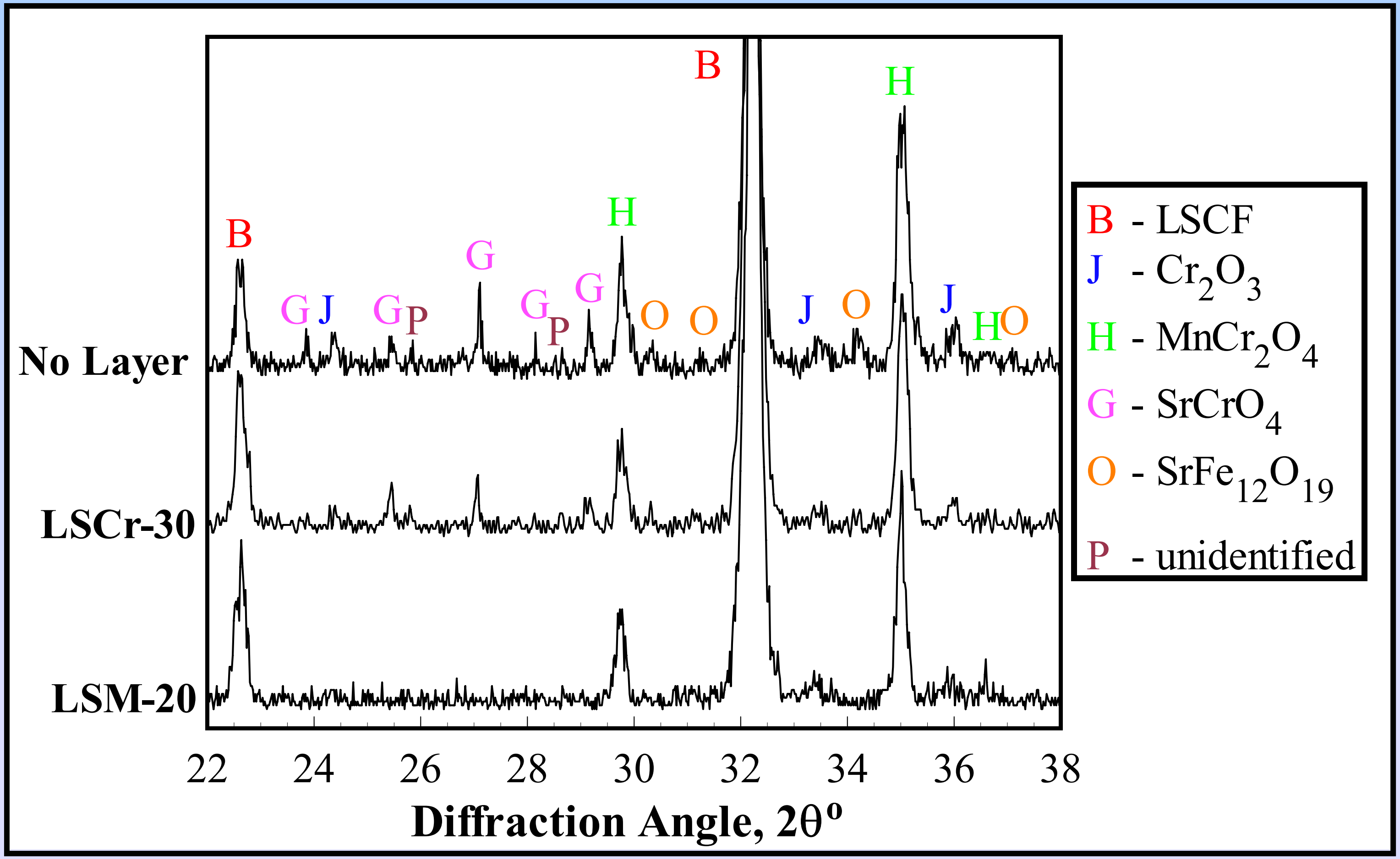
LSCF Cells with Variable Chromia Sources

- LSCF cells indicate their own intrinsic degradation ➔ difficult to discern increased degradation rates with any of the Cr sources.



Protective Coatings for Crofer – LSCF

- Approximately 0.3 μm LSCr-30 and LSM-20 sputtered onto Crofer foil prior to LSCF application.



Summary

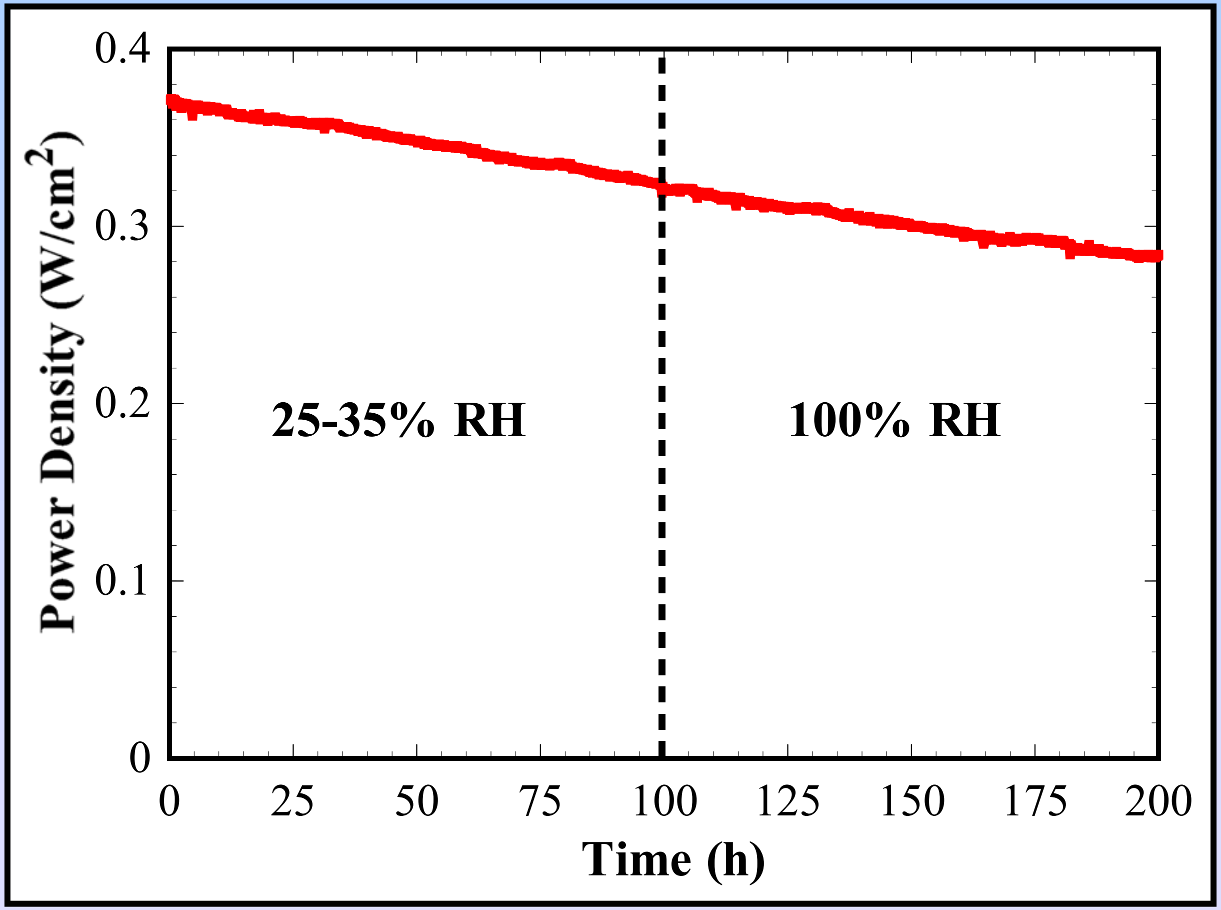
- Different Cr related degradation mechanisms may predominate for each cathode.
  - **LSM** – indicates little solid state reaction but significant Cr deposition at cathode-electrolyte interface ➔ Cr vapor phase transport probably predominates.
  - **LSF** – Cr observed throughout cathode and at electrolyte interface ➔ possibly indicates degradation due to solid state and vapor phase interactions.
  - **LSCF** – highly reactive due to high Sr content ➔ LSCF very effective Cr getter – in the short term reduces effects of Cr volatility.
- As expected using Cr_2O_3 as a Cr vapor source causes severe degradation. $La(Sr)CrO_3$ and $MnCr_2O_4$ sources do not result in significant short-term poisoning.

Future Work

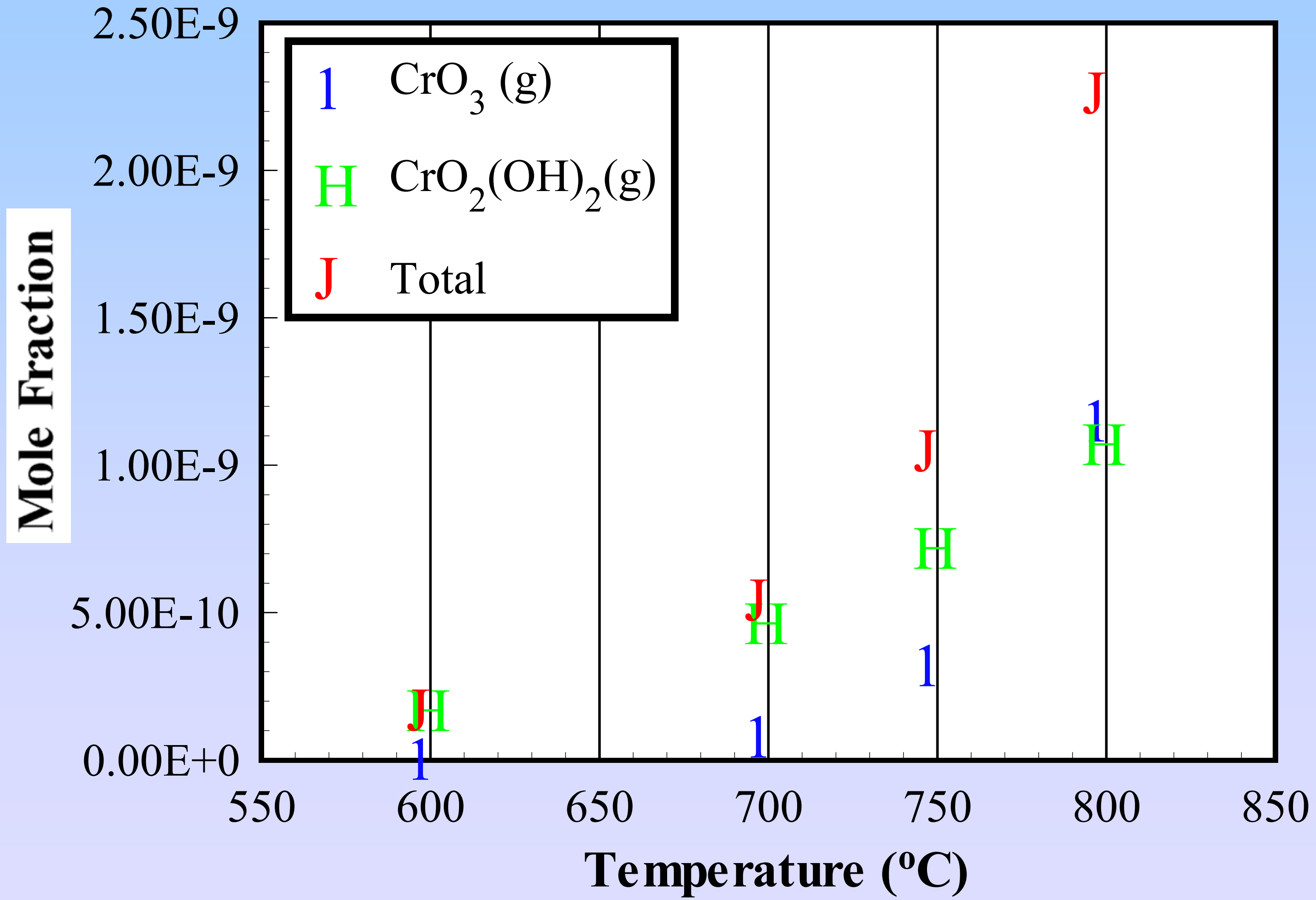
- All cell data presented is preliminary ➔ needs repeat sample verification.
- Longer-term testing (1000+ hours) of cells incorporating Crofer (and alternative alloy interconnects) ➔ Do the cells ever stabilize within this time-frame?
- Assess the effects of pre-oxidizing the Crofer ➔ after several hundred hours at 750-800^{o}C Crofer should form a continuous $MnCr_2O_4$ layer – does this scale really suppress Cr volatilization?
- Establish effectiveness of various coatings (LSCr, LSM, LSCo, Ag) on Crofer foils with respect to solid state reaction and Cr evaporation suppression ➔ cell testing and HTXRD.
- May be possible to modify cathode chemistry or utilize graded cathodes incorporating different compositions to tolerate Cr interactions (with minimal degradation) until a protective spinel scale is formed.

Humidity Effects on Cathode Degradation

- After 100 hours of testing with ambient air, the air source was humidified to 100% RH ➔ no discernible change in degradation rate.



Cr Volatility (50% RH)



LSM Cells with Cr_2O_3 Source at Various Operating Temperatures