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Chromium Reactivity and Transport

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THE UNIVERSITY OF CHICAGO

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Chromium Transport According to Hilpert (J. Electrochem. Soc. 143 (1996) 3642)

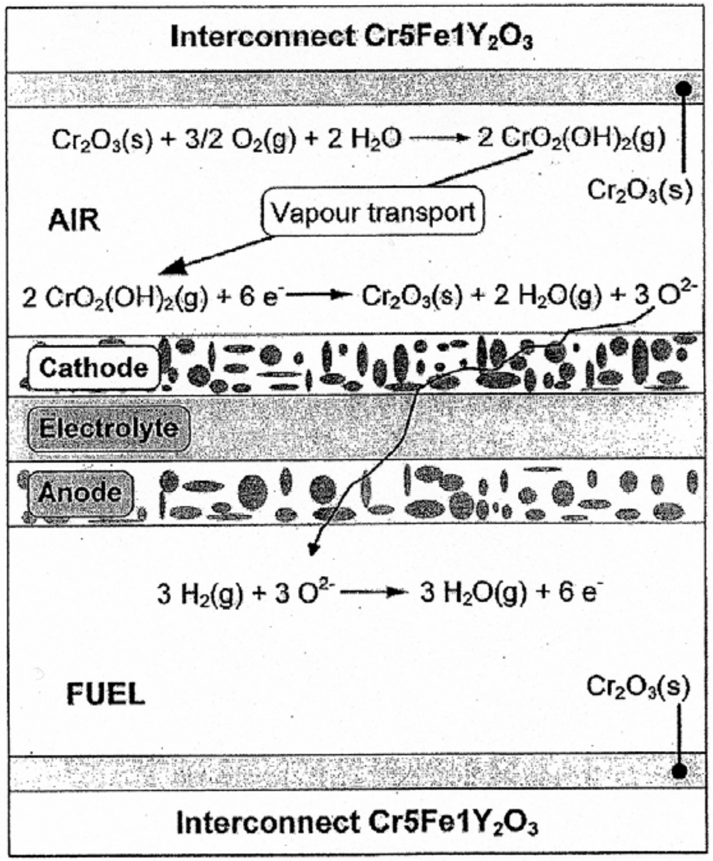


Fig. 6. Cr transport at the cathode side of a SOFC.

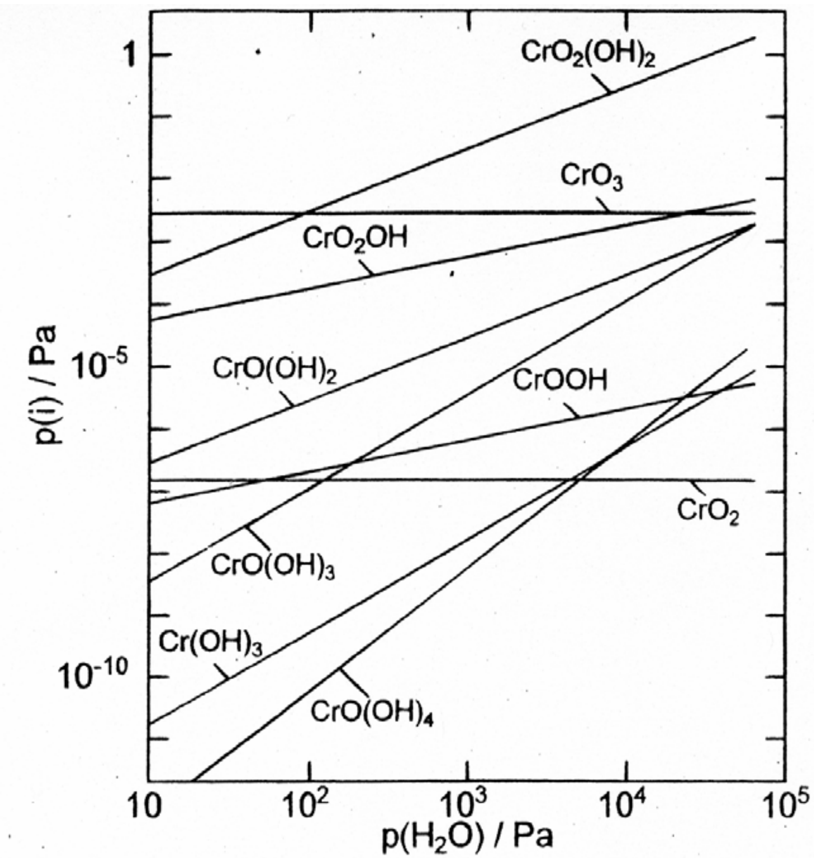
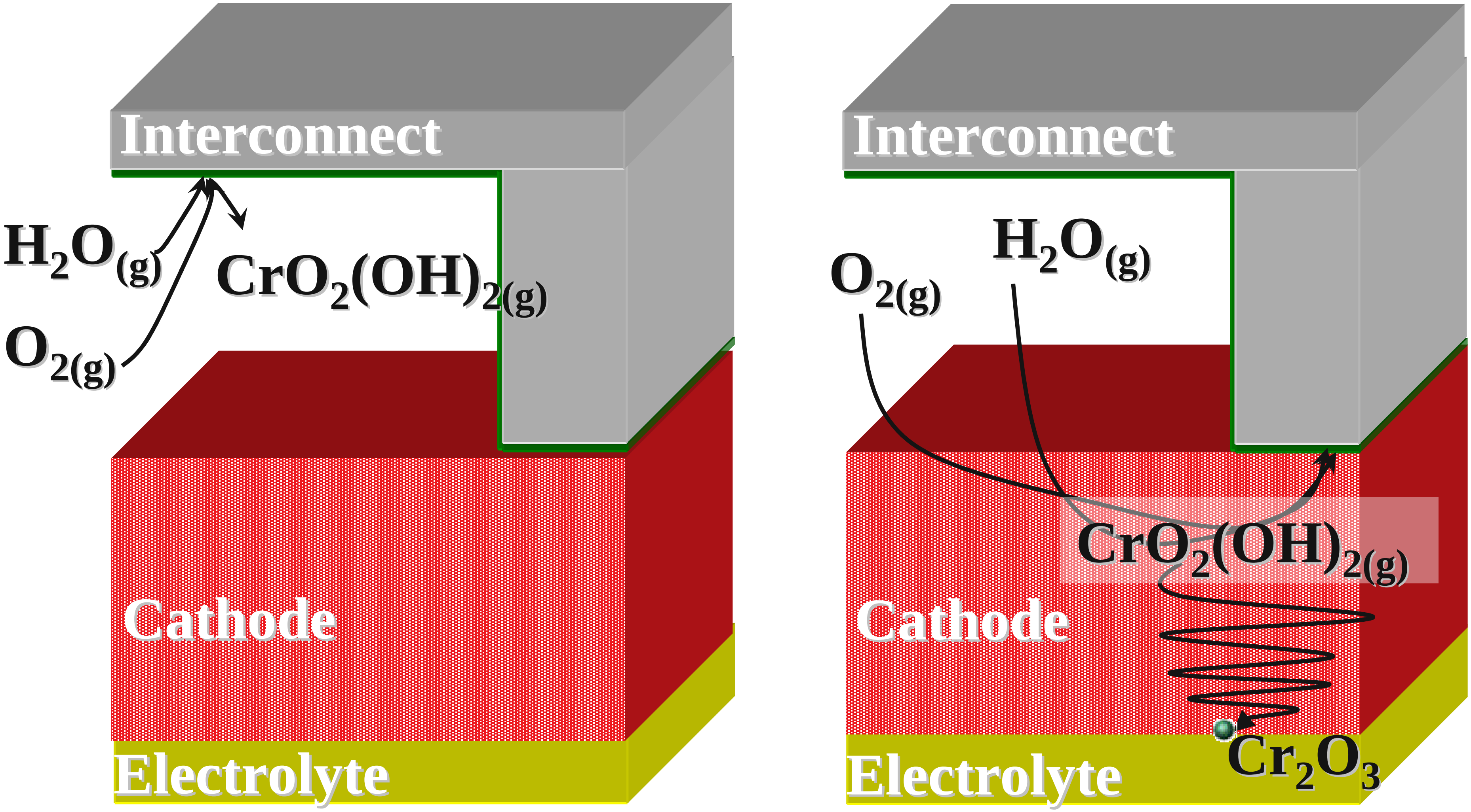
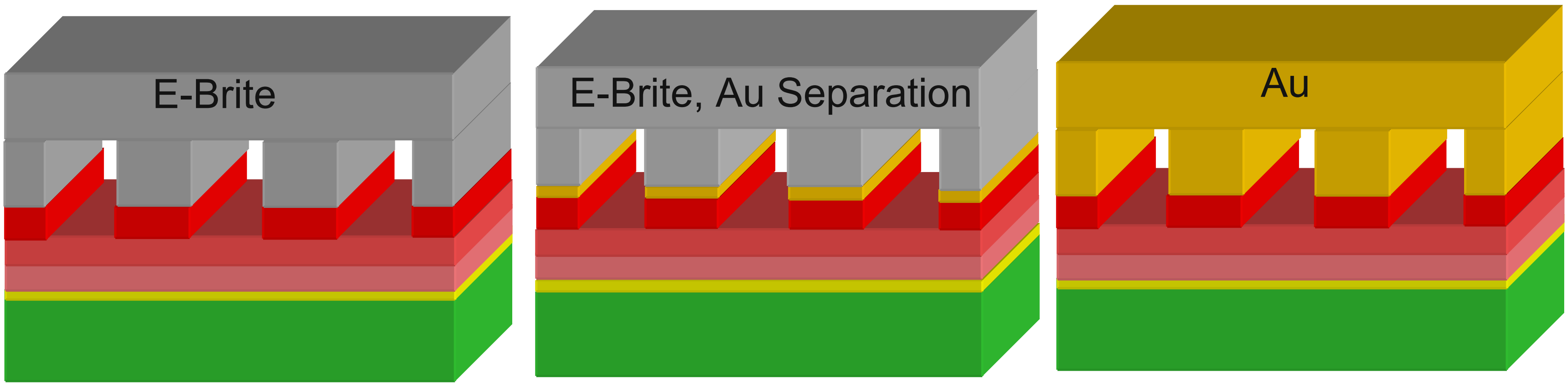


Fig. 3. Partial pressures over $Cr_2O_3(s)$ at 1223 K in humid air [$p(O_2) = 2.13 \times 10^4$ Pa] with different H_2O partial pressures.

Flow-channel Hydrodynamics

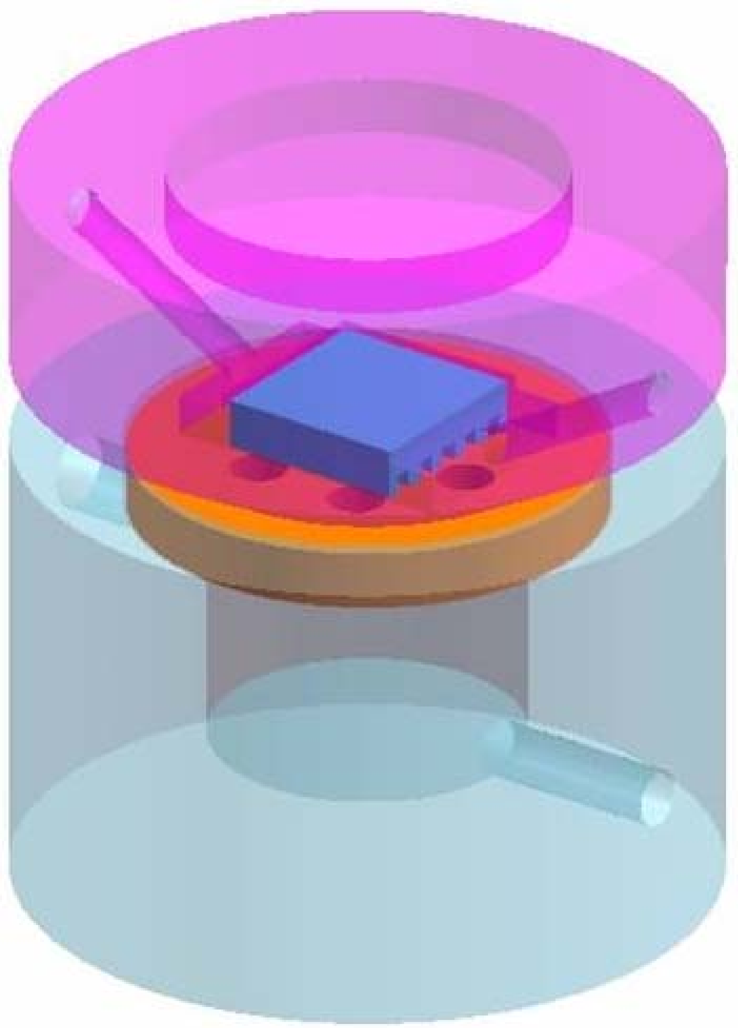


Three Cell Configurations Were Tested



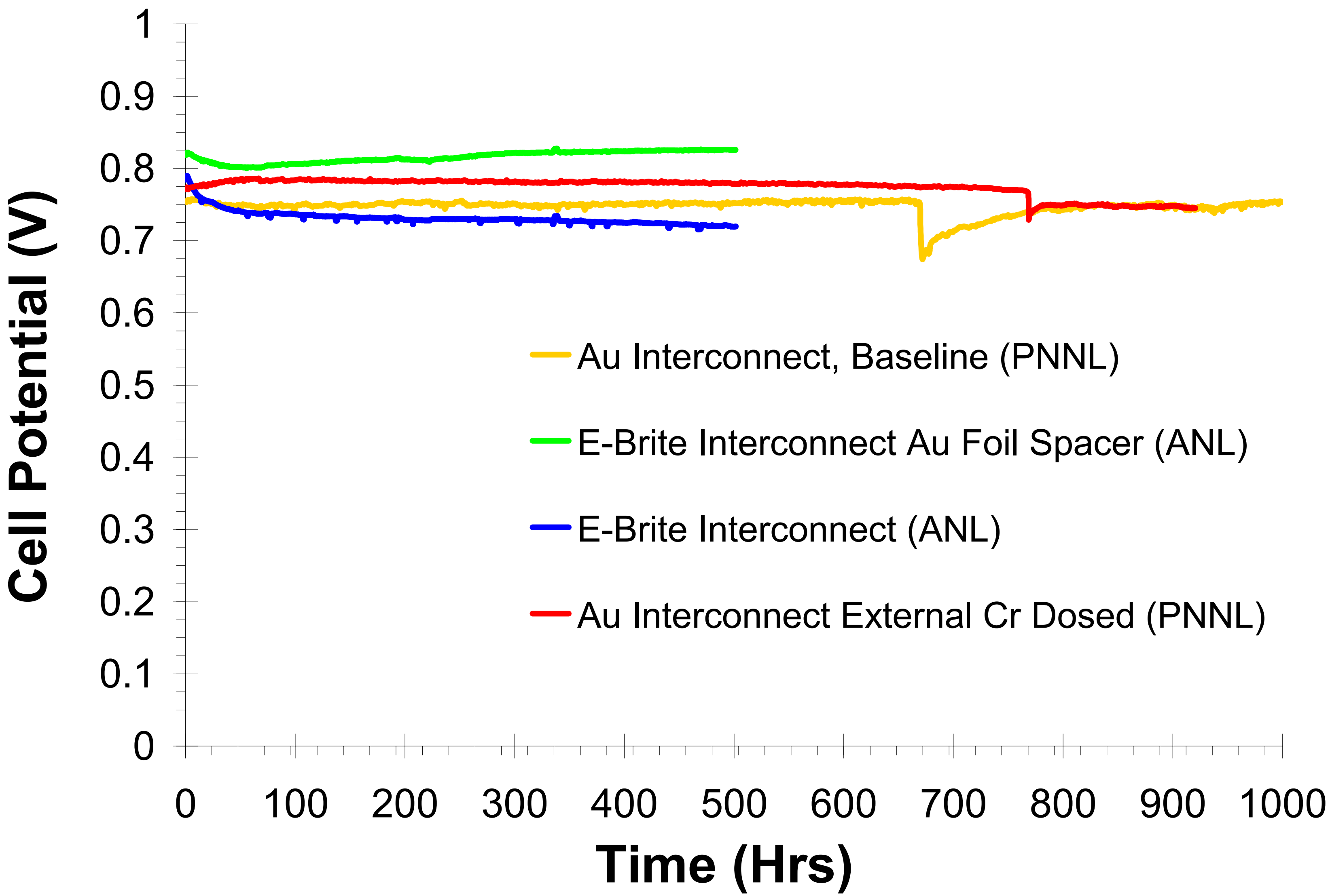
With and without external dosing

Schematic of a Fixture with ribbed Flow-field

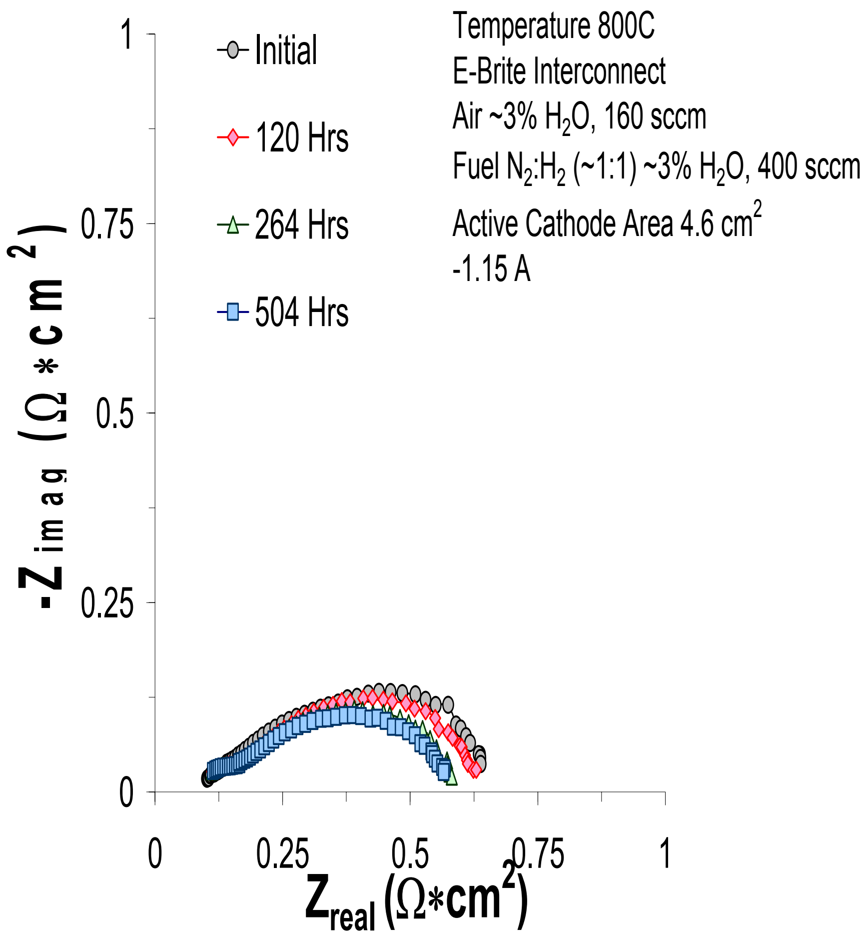


- Metallic Interconnect
  - ANL
    - *E-Brite*
    - *Au Barrier Between E-Brite and Cathode*
    - *Au*
  - PNNL
    - *Au*
    - *Au with External Cr Dosing*
- LSM Contact Paste
- LSM Cathode
- LSM/8YSZ Active Cathode
- 8YZS Electrolyte
- Ni/8YSZ Anode

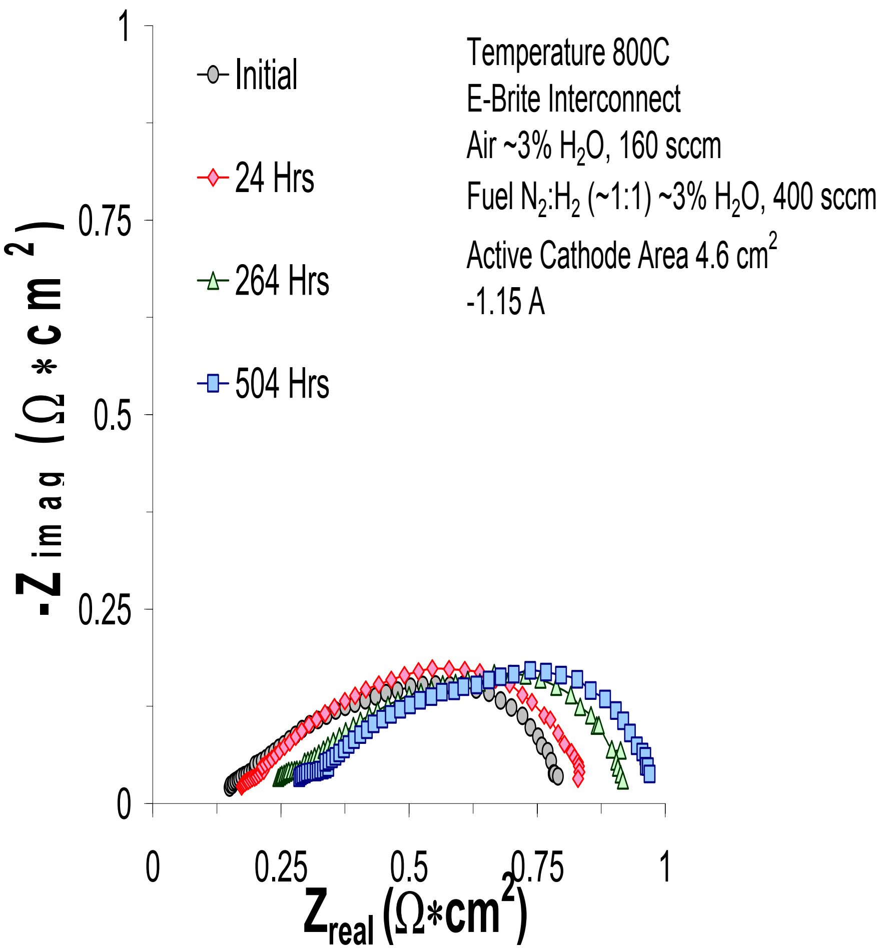
Cell Potentials versus Time



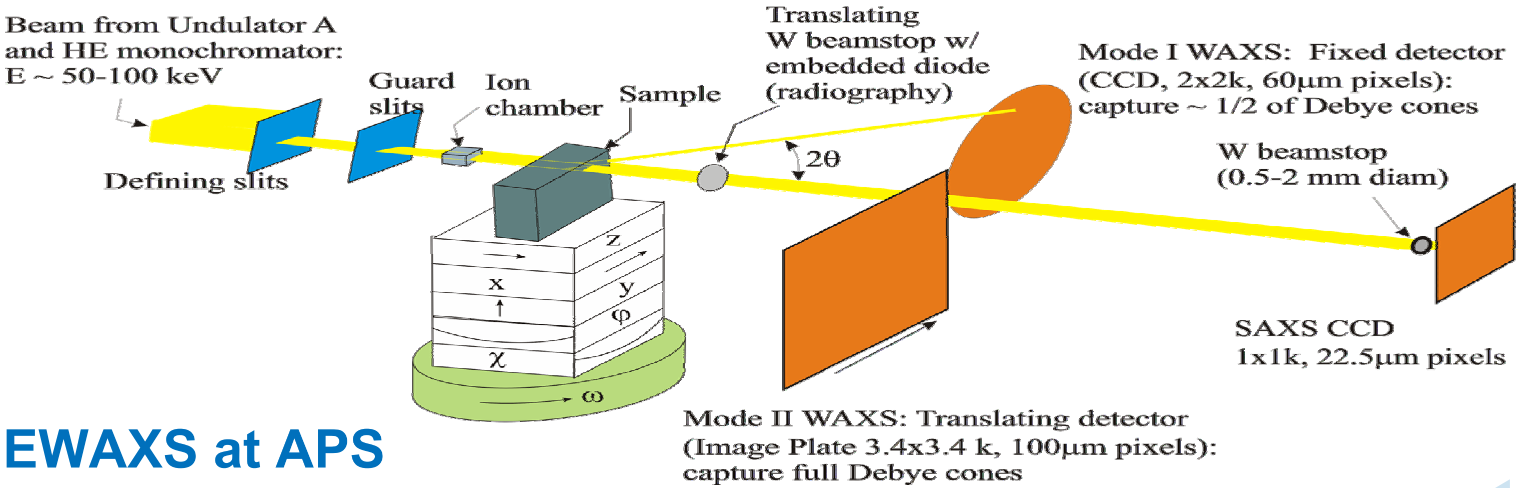
Au Between E-Brite and Cathode



Direct Contact

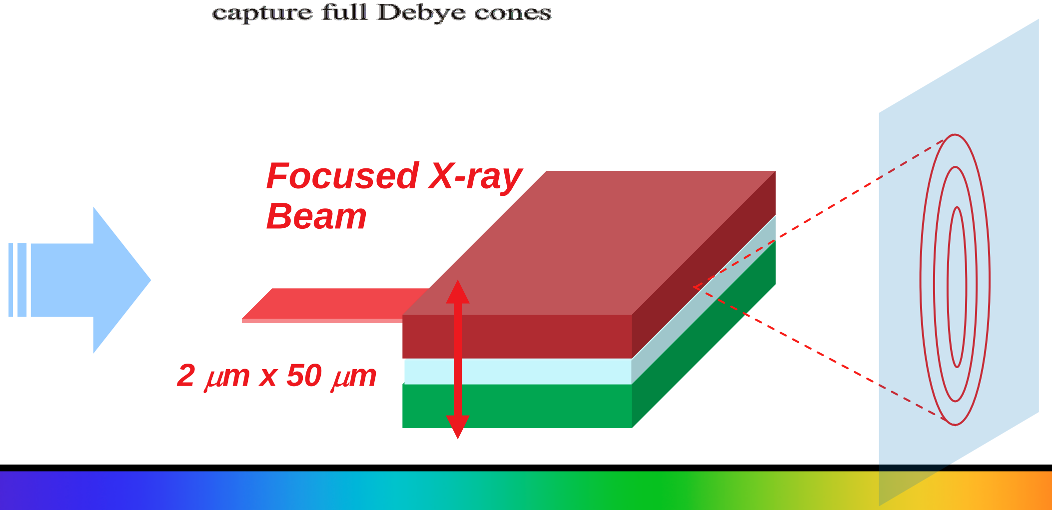


HEWAXS at Argonne APS is a Powerful Tool for Microscopic XRD Investigation

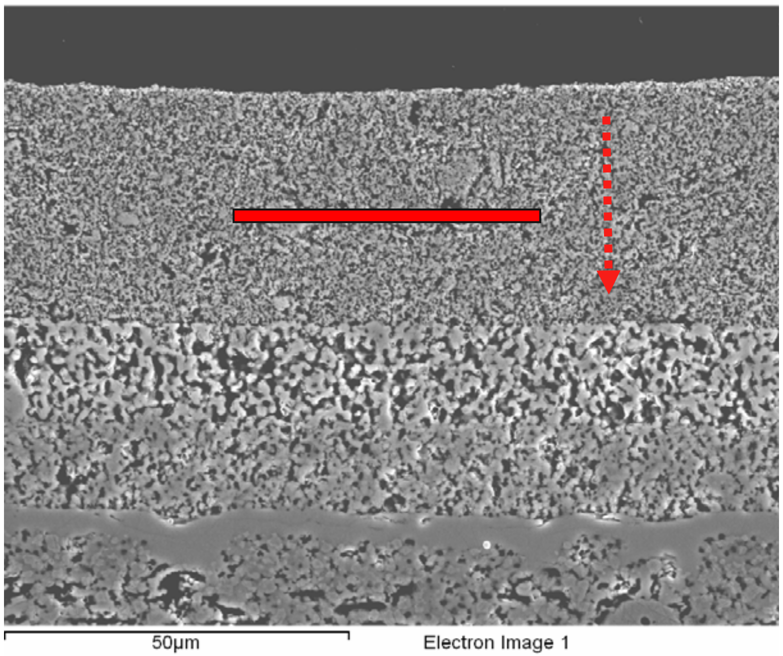


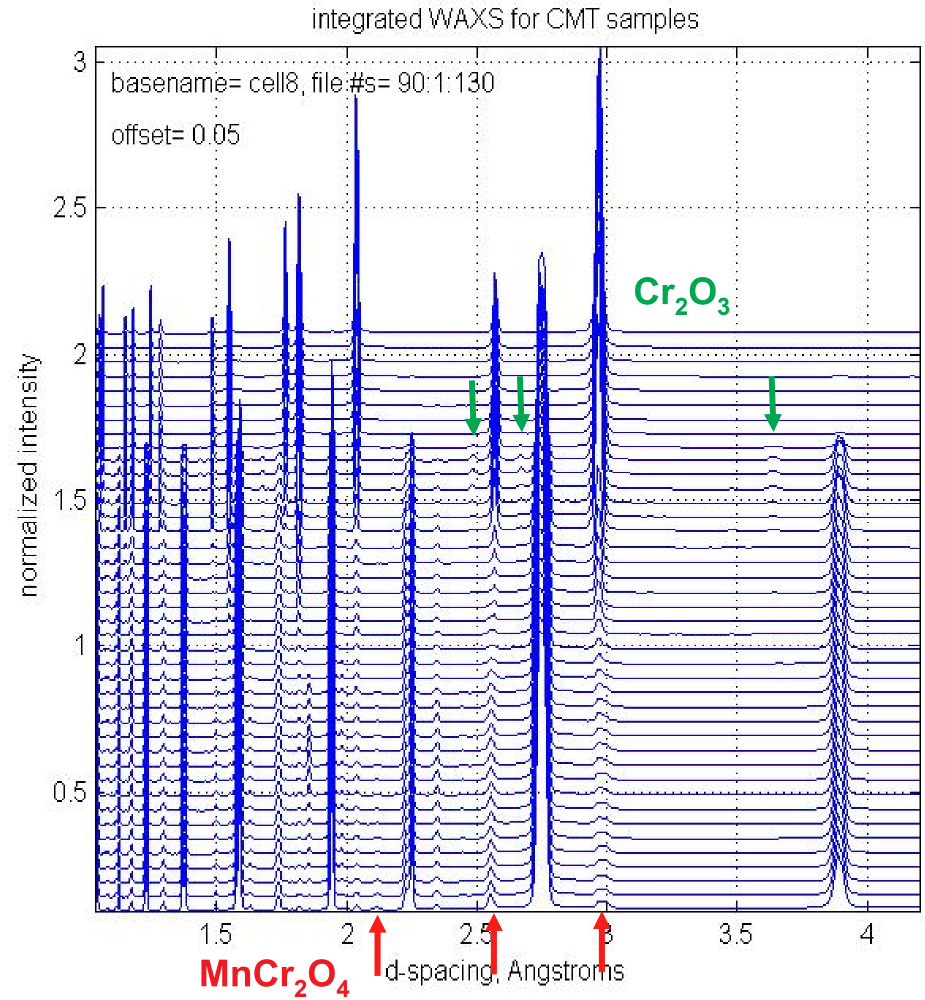
HEWAXS at APS

Investigation for Cr poisoned SOFC

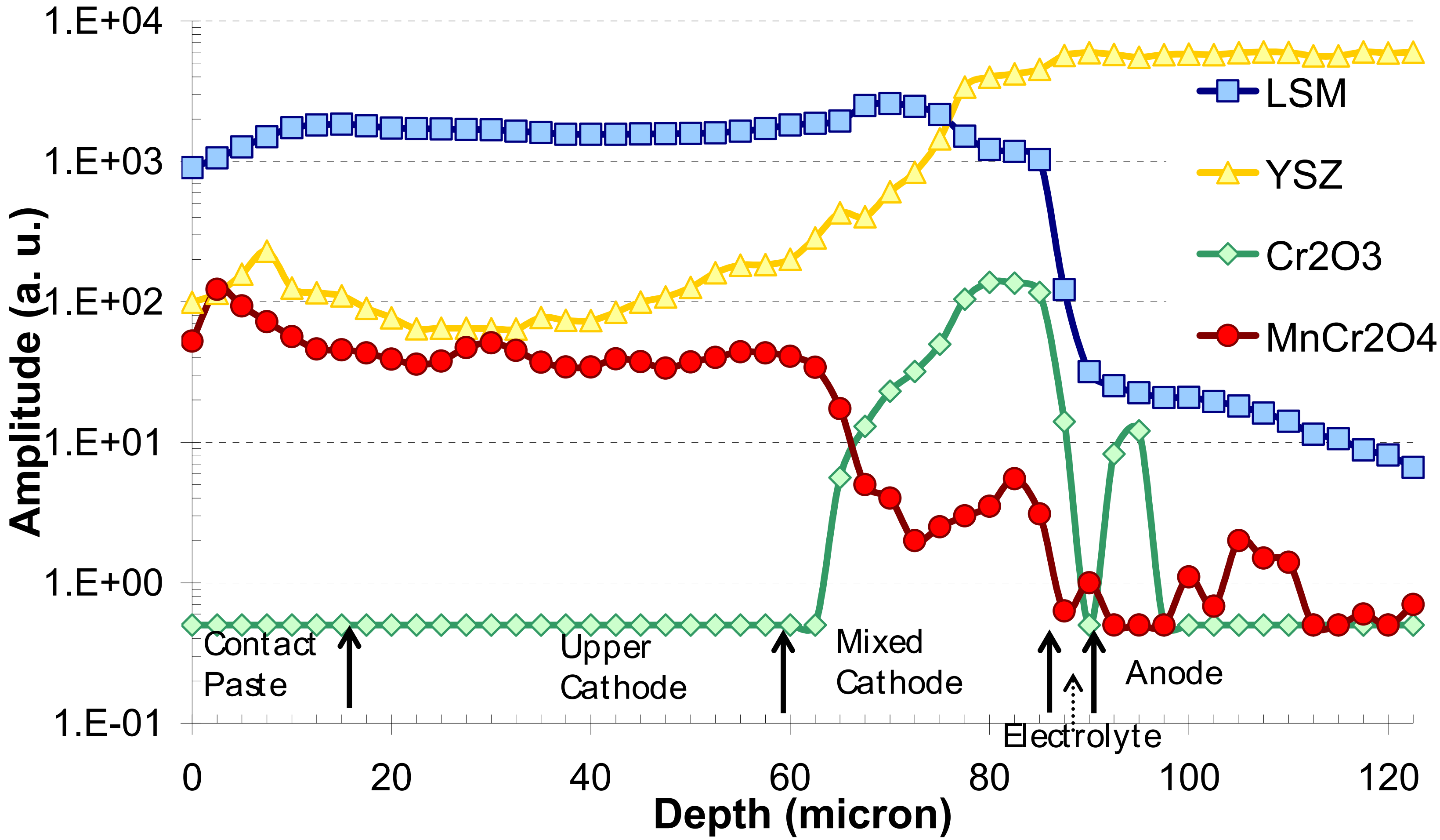


Cr2O3 and MnCr2O4 were unambiguously identified





Profiles across Cathode



Formation and Transport of Chromium Compounds

- Cr_2O_3:

  $Cr_2O_3 + O_2 + 2H_2O \longrightarrow 2CrO_2(OH)_2$ $\Delta G = +84KJ$

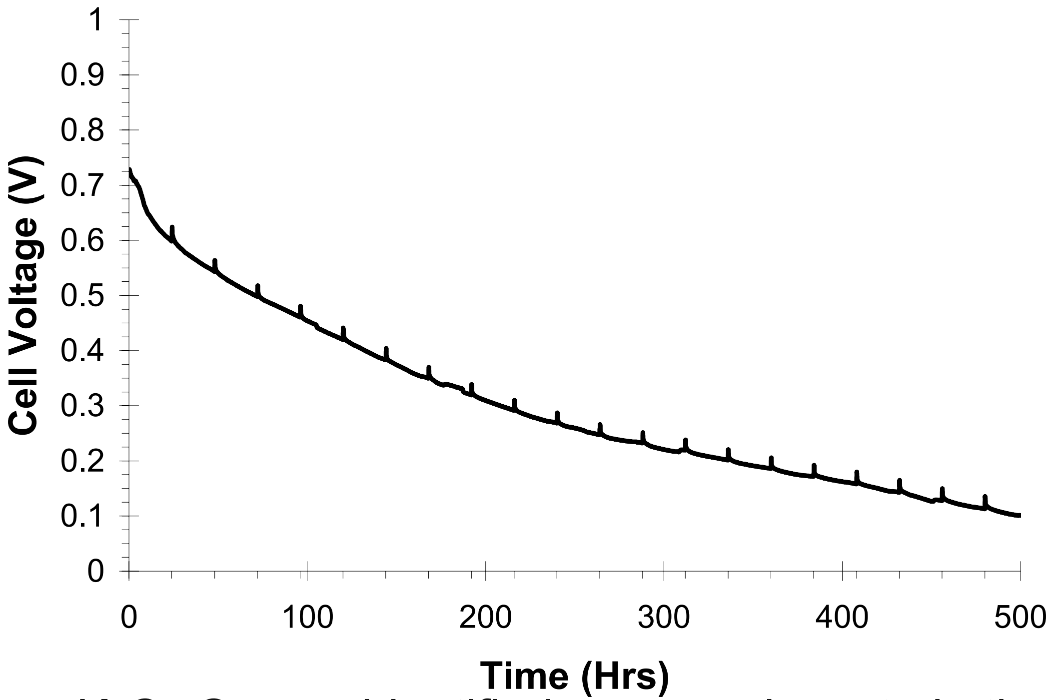
  $2CrO_2(OH) + 6\bar{e} + 3V\ddot{o} \longrightarrow Cr_2O_3 + 3O^{2-}$

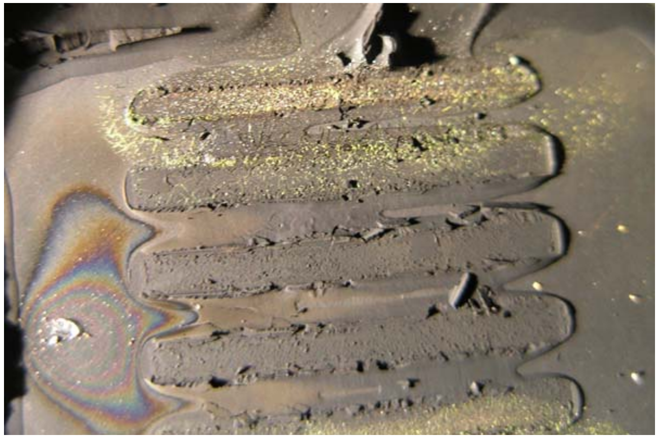
- $MnCr_2O_4$:

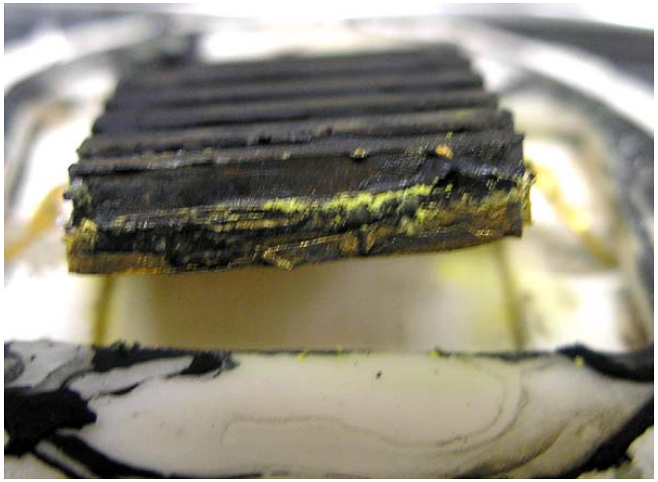
  1. $7.5\ Cr_2O_3 + 5\ La_{.8}Sr_{.2}MnO_3 \longrightarrow 4\ LaCrO_4 + 5\ MnCr_2O_4 + SrCrO_4 + \frac{3}{4}\ O_2$ $\Delta G = -297KJ$

  2. $2CrO_2(OH)_2 + MnO \longrightarrow MnCr_2O_4 + 2H_2O + 1/2O_2$

Incremental Chromium Transport in MACOR fixture







- $K_2Cr_2O_7$ was identified as a condensate in the exhaust tube

Chromium Mass Balances

Oxyhydroxide formation:

- theoretical: 15 mg
- measured: 0.22 mg

Cr_2O_3 deposits:

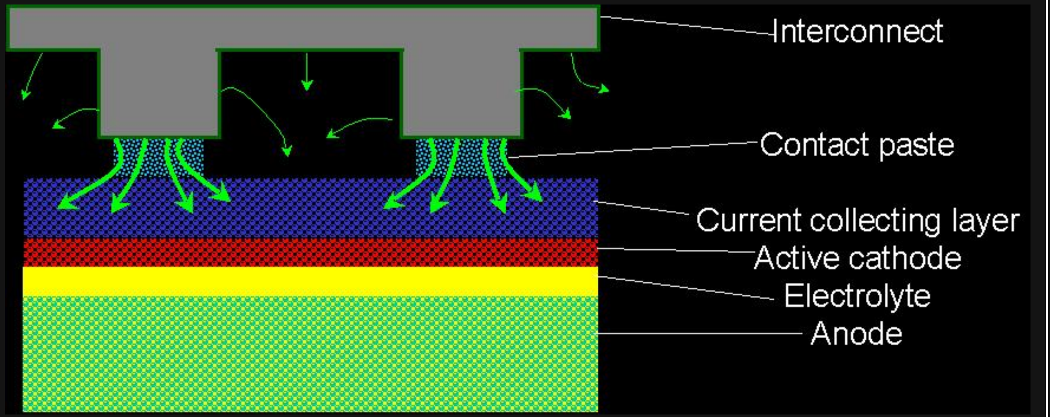
- E-Brite with gold foil: not detectable
- E-Brite: 0.12 mg
- E-Brite in Macor: 1.5 mg

Summary

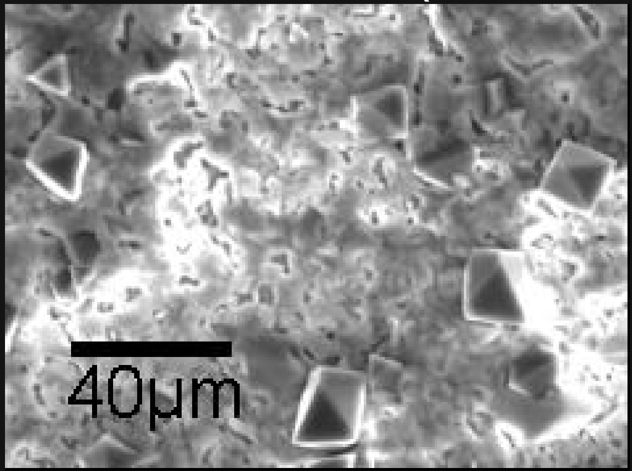
- Hilpert's oxyhydroxide mechanism can account for a cell potential degradation of 5% with E-Brite current collectors
- Spinel forming alloys or spinel coatings will largely prevent the chromium transport
- Alkali and perhaps alkaline earth oxides can dramatically increase it

2 transport mechanisms for Cr:
vapor ***and*** solid state diffusion

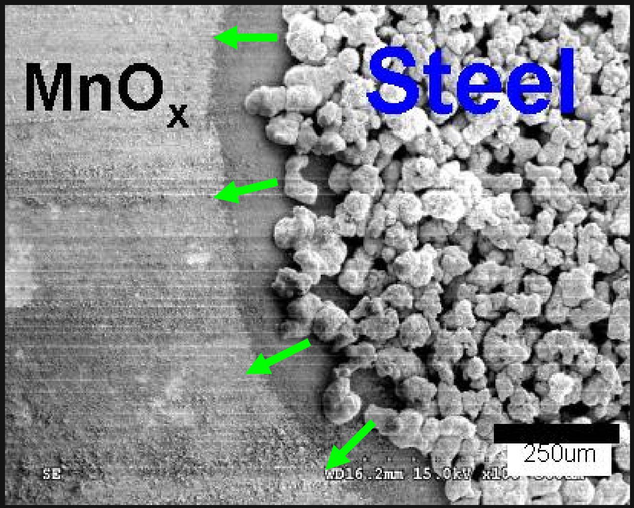
Both mechanisms are material and temperature dependent.
Cr transport into the cathode is greatly reduced by lowering the operating temperature to a range suitable for metallic components (650-750°C).
However it does not stop solid state transport through the contact paste. Barrier layers or coatings solve this problem.



Cr deposited from ***vapor*** on LSM surface (1000°C)



Cr diffusion across ***surface*** of oxide (800°C)

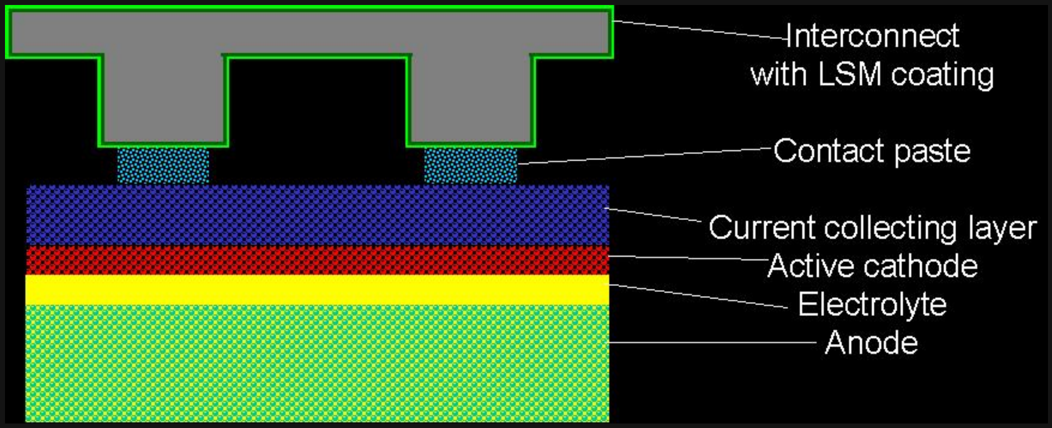


Solutions for Coated Interconnect

Coating decreases Cr vaporization rate by ~100x.

Contact paste can be Ag, LSM, LNF, etc.

Contact paste and/or current collection layer can include Cr getters such as Co to further protect the cathode.



Solutions for Uncoated Interconnect

Choose a contact paste that does not have significant solid state diffusion or vapor deposition (Ag), or a contact paste that reacts with the chromia scale to form an effective barrier.

Accept degradation rate or develop Cr tolerant cathodes.