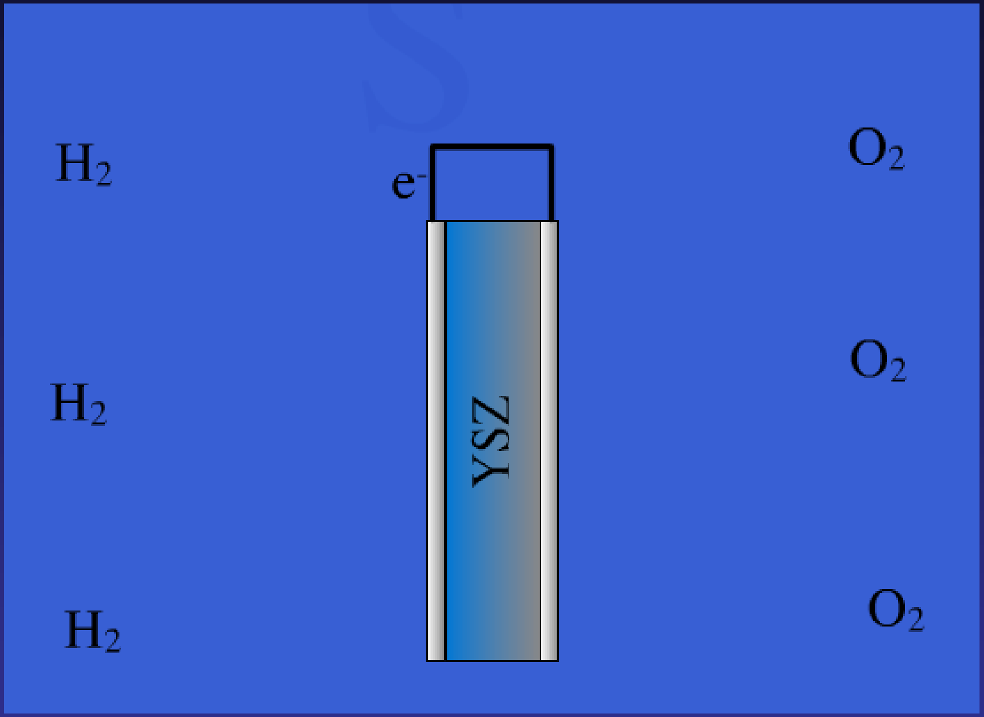
Enhancement of Electrode and Interconnect Performance



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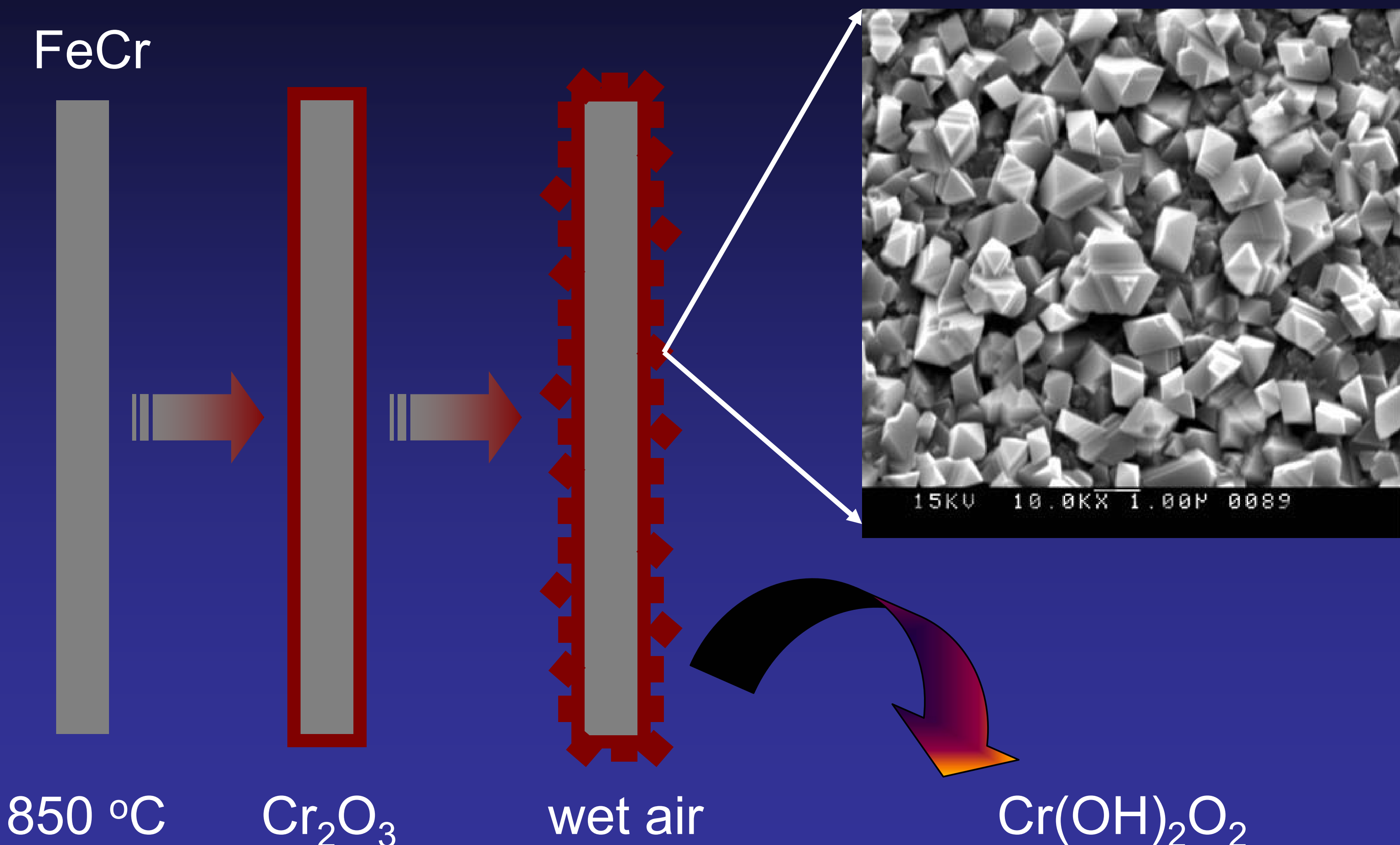
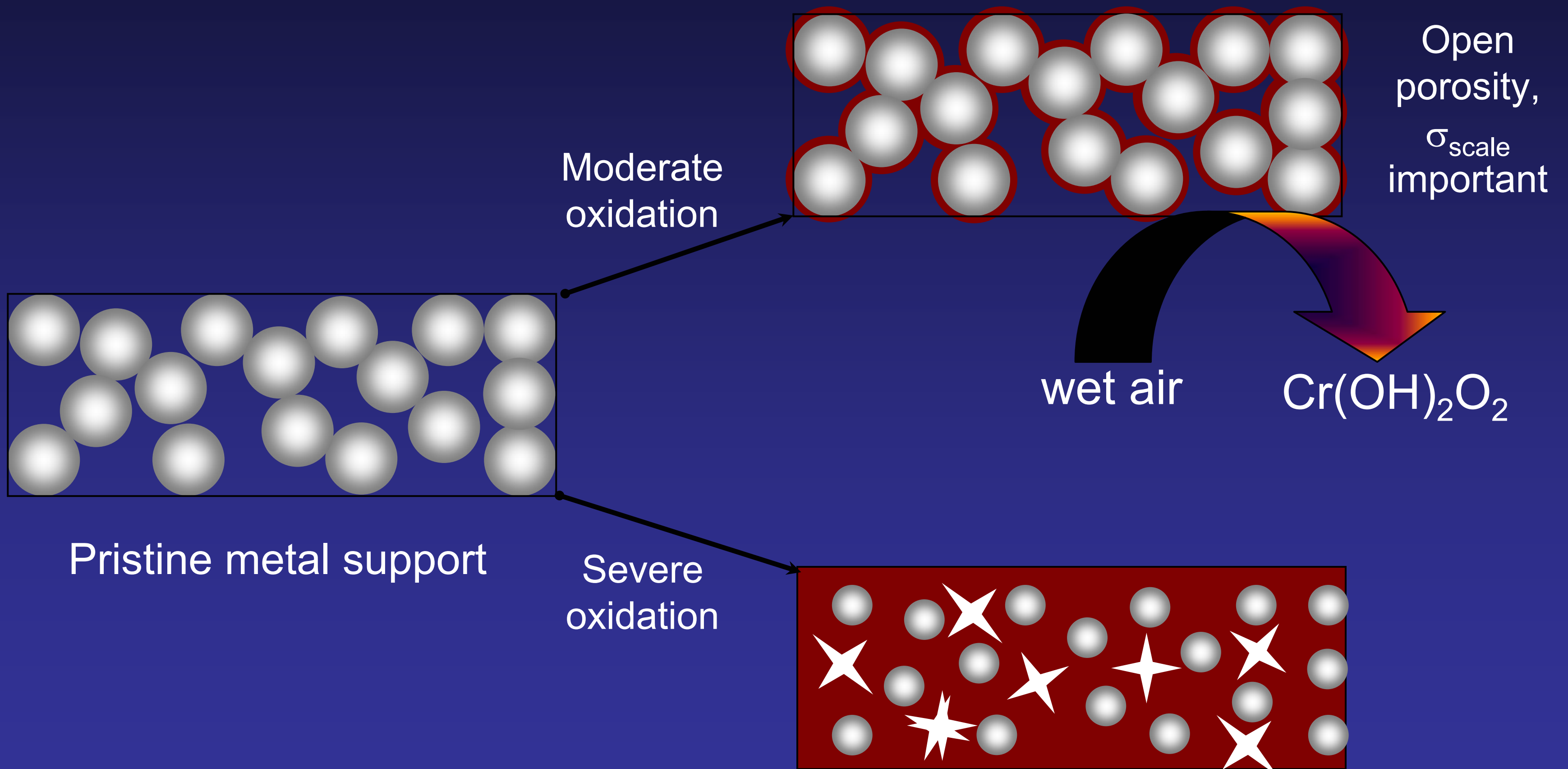
Oxidation of Ferritic Steels

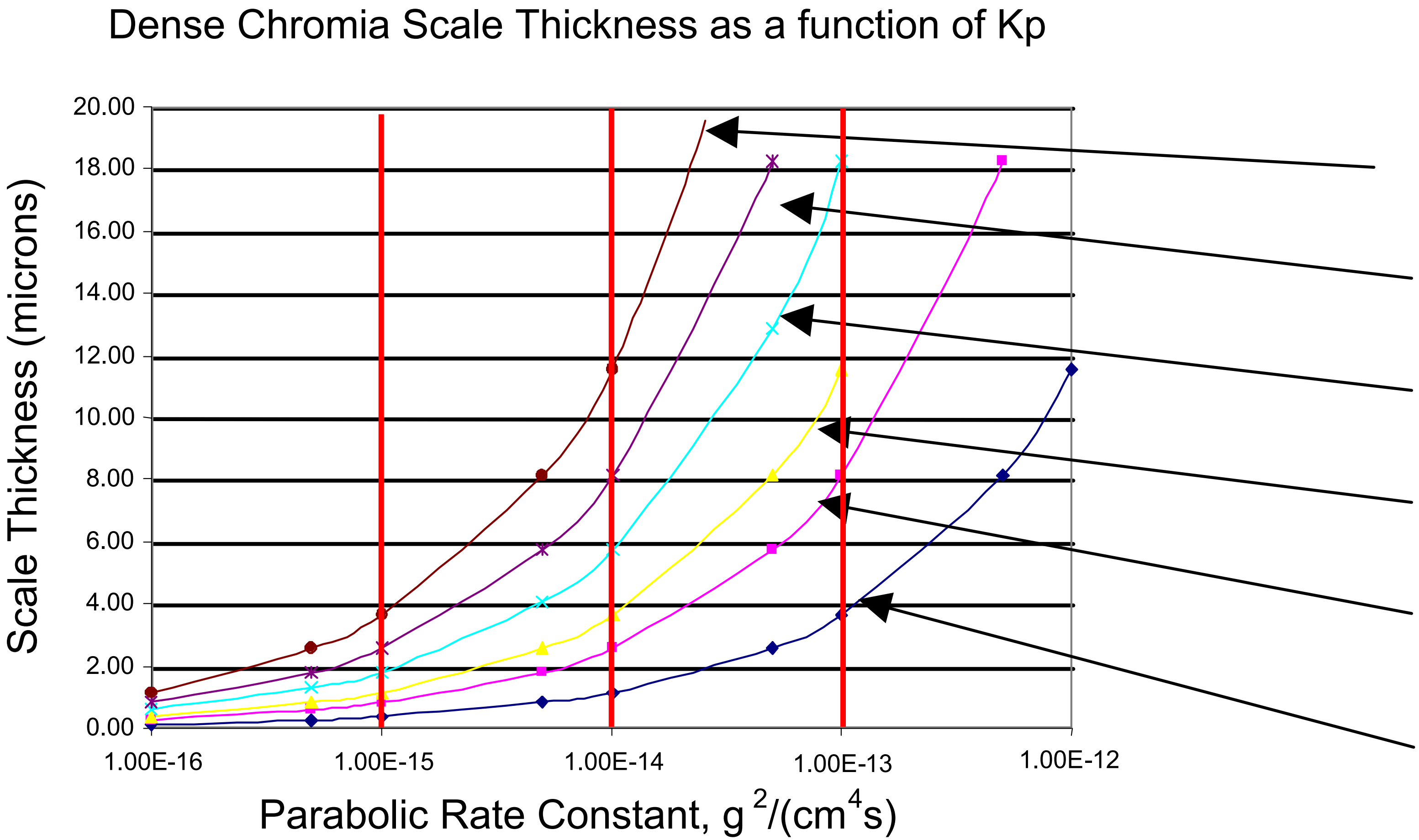


(original target operating temperature was 750 to 850 °C)

Metal Supported SOFCs



Chromia scale thickness as a function of parabolic growth rate constant and operational lifetime of the device



Ferritic Steel Oxidation Rate Studies

- Oxidation studies in air and in wet H_2 for a variety of ferritic steels (Cr content 12-30 wt%) have been performed for fuel cell and related applications. At 800°C the growth rates for these alloys, with or without a surface treatment of a reactive element such as yttria, **is grouped around ~10^{-13} g^2/cm^4s**.

- Ferritic steels have scale growth rates that are acceptable for SOFC application ($<10^{-14}$ g^2/cm^4s) at temperatures ≤700°C.

- However, to minimize resistive losses the conductivity of the chromia scale should be >0.005 S/cm at 650°C in so that the contribution to cell resistance is <0.1 Ω cm^2 after 50,000 hours.

Target Parameters for Ferritic Steel

- Scale thickness limit at <10μm for the life of the device.

- Growth rate constant, K_p=(weight gain $g/cm^2)^2/sec$, should be $<10^{-14} g^2/cm^4 s$ and preferably $\sim 10^{-15} g^2/cm^4 s$.

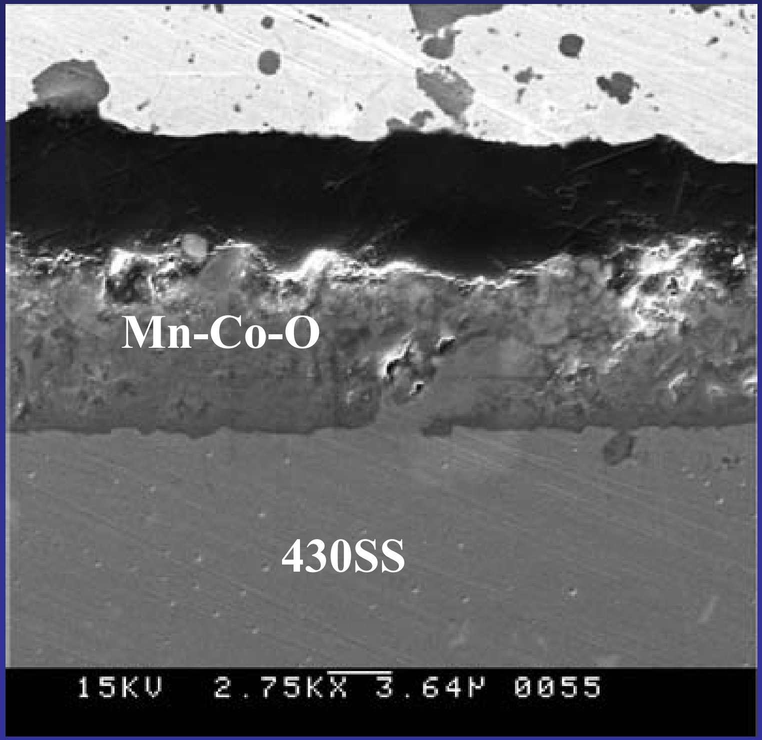
- Conductivity of the chromia scale should be >0.005 S/cm at 650°C

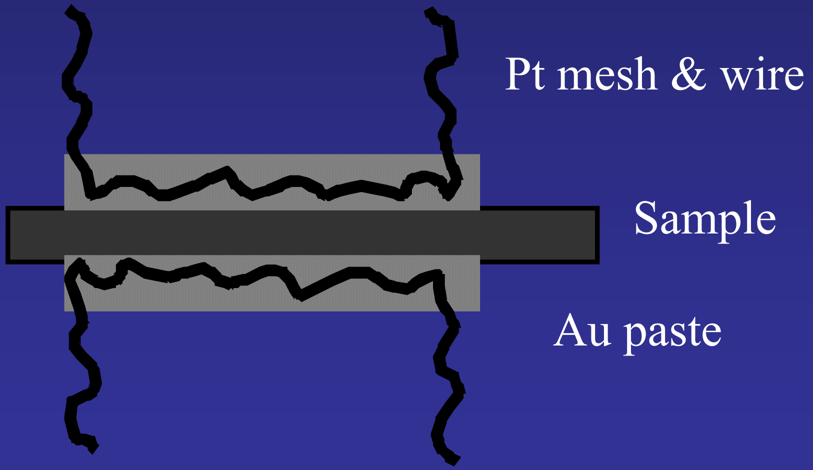
- Cr volatilization should be below threshold for cathode poisoning and below EPA limits (0.015 mg/m^3)

Oxidation Studies

430 SS composition

Element	Cr	C	Ni	Mn	Si	Fe
wt%	16.3	0.04	0.2	0.45	0.40	balance

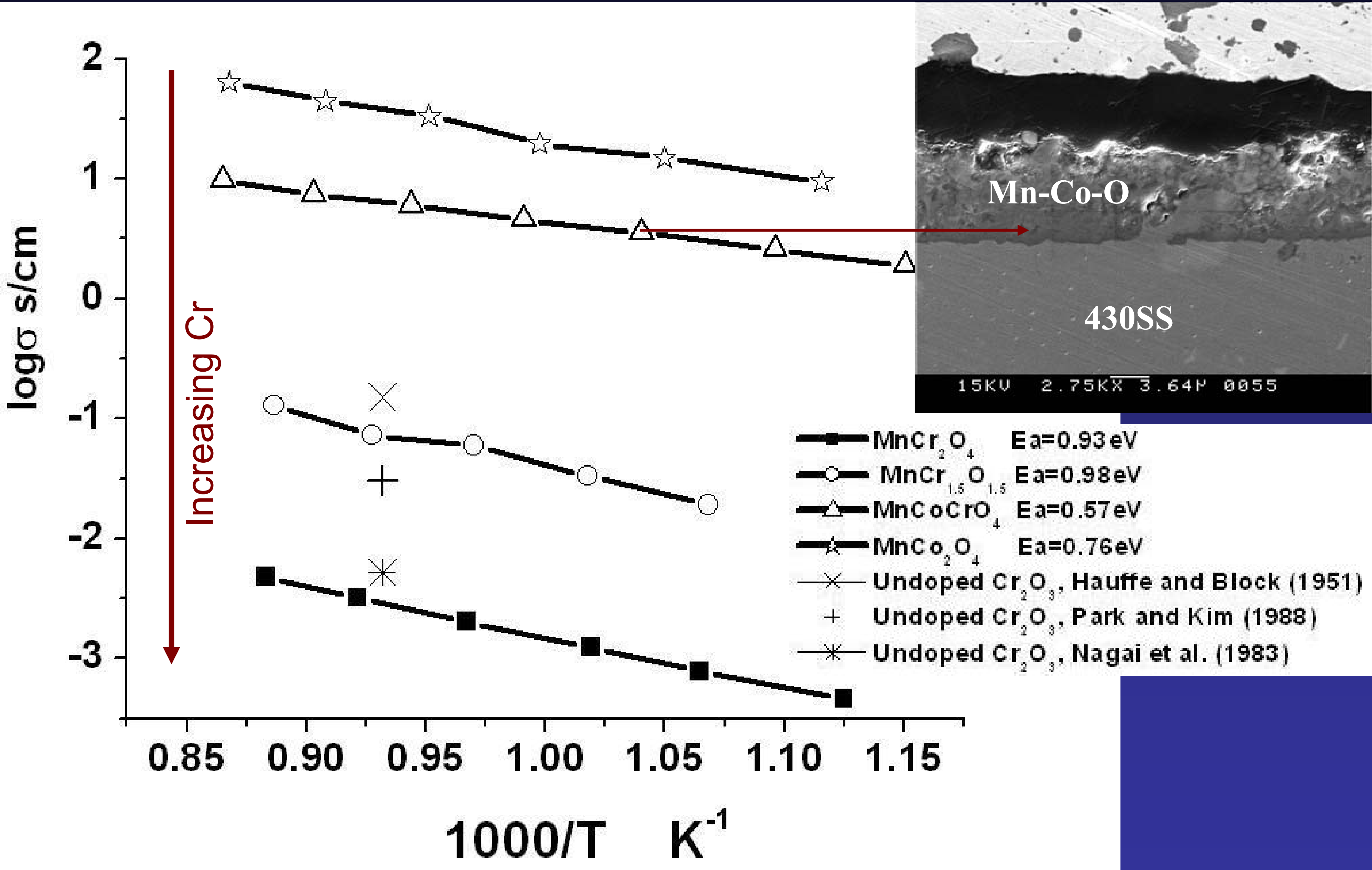




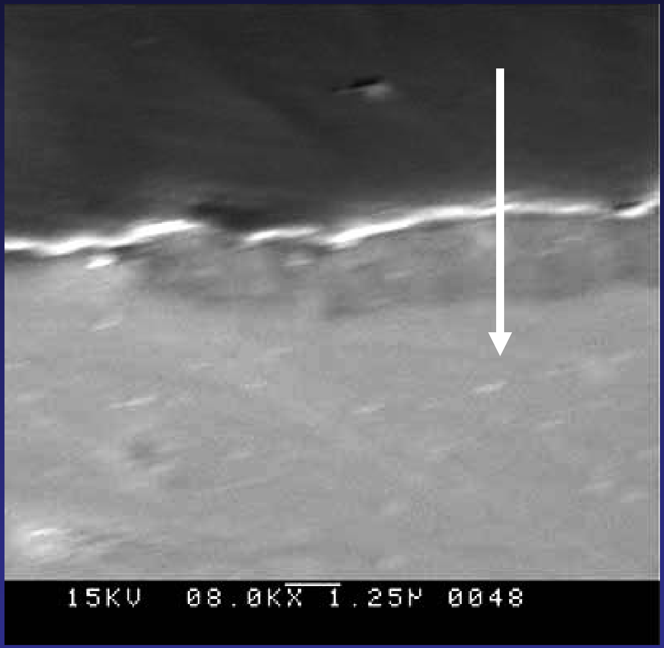
Conductivity of Oxide Films

	Conductivity at about 800^{o}C (S/cm)
$MnCo_2O_4$, GNP, sintered at 1300^{o}C	31.6
$MnCrCoO_4$, GNP, sintered at 1300^{o}C	6.3
$Mn_{1.5}Cr_{1.5}O_4$, GNP, sintered at 1300^{o}C	$7.9*10^{-2}$
$MnCr_2O_4$, GNP, sintered at 1300^{o}C	$2.5*10^{-3}$
Undoped Cr_2O_3, Hauffe and Block (1951) [18] sintered at 1200^{o}C	0.15
Undoped Cr_2O_3, Park and Kim (1988) [19] 99.9% sintered at 1400^{o}C	$3.02*10^{-2}$
Undoped Cr_2O_3, Nagai et al. (1983) [20] 99.9% sintered at 1200^{o}C	$5.2*10^{-3}$

Conductivity of Potential Coatings

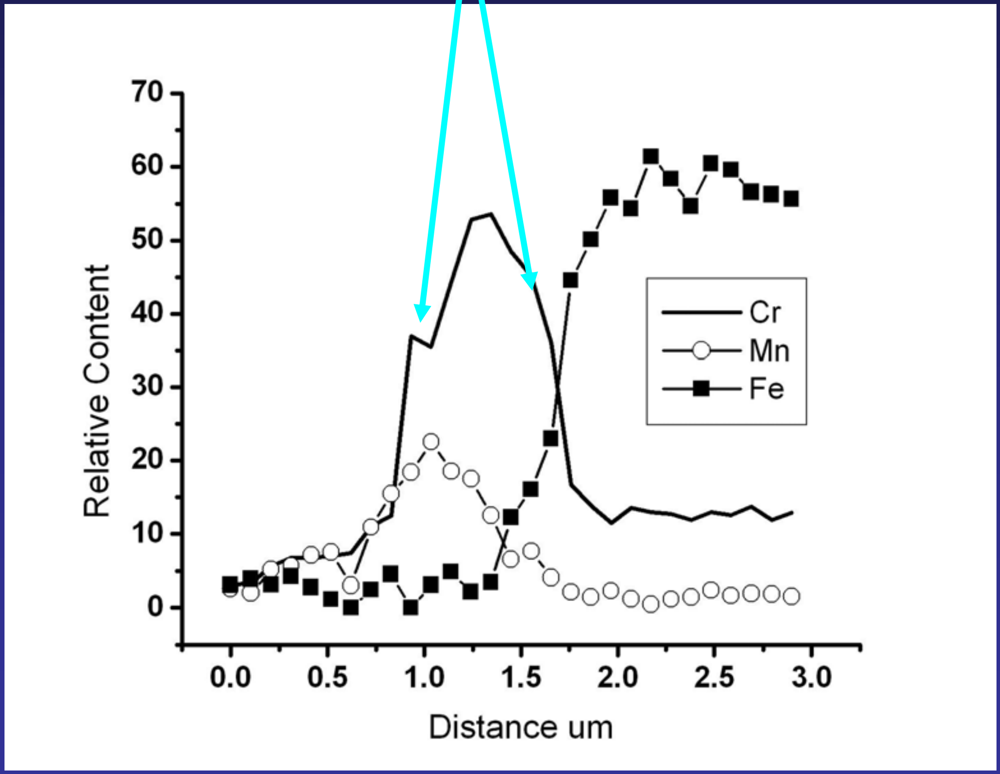


$MnCr_2O_4$ film is grown from alloy (low σ)

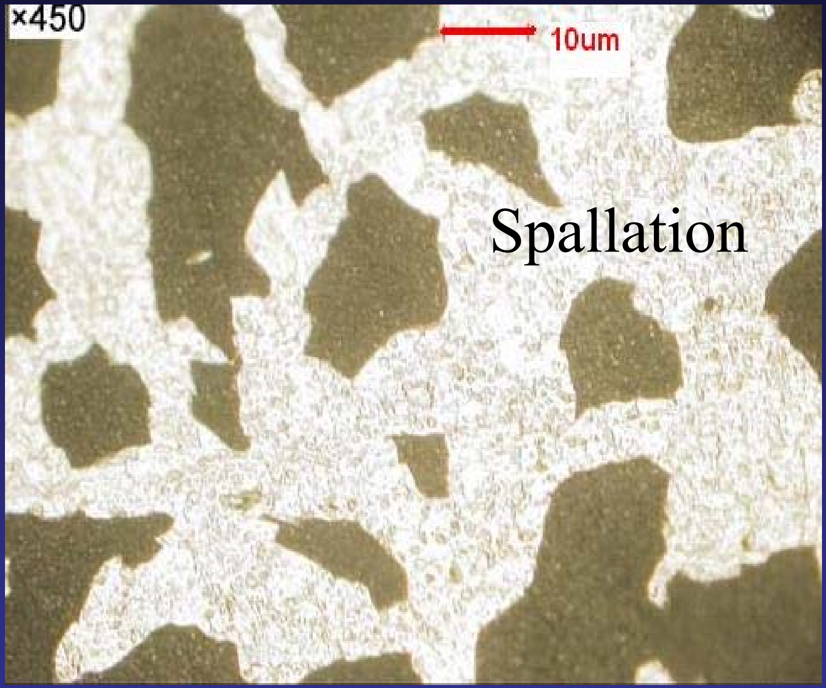


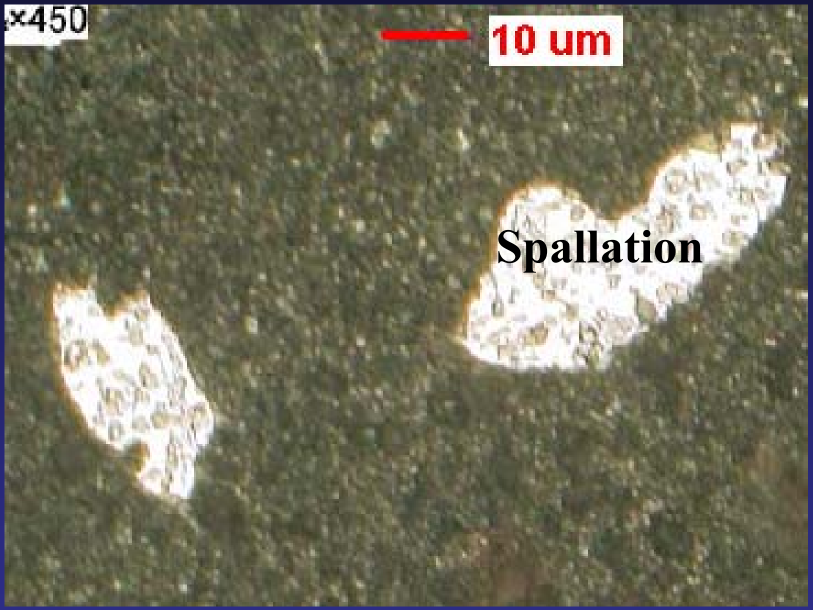
Mn already present in alloy forms spinel, but low conductivity will be an issue for applications

$MnCr_2O_4$ (1.5 µm)



Spallation of Uncoated 430 Oxide film

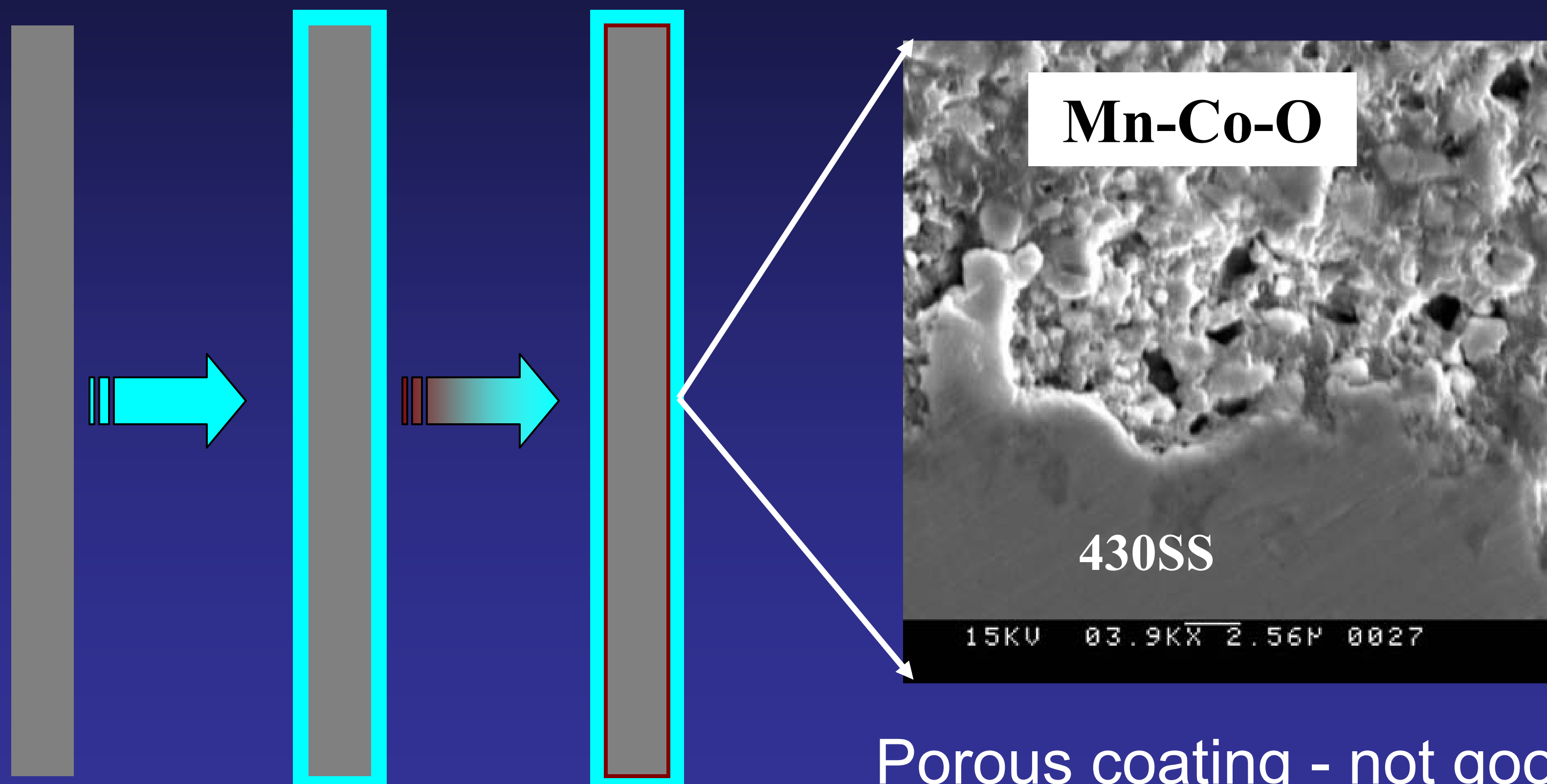




After thermal cycling from 850 oC to RT (~50 oC/min cooling)

Preparation of Protective Coatings

400 series $MnCo_2O_4$ 850 ^oC

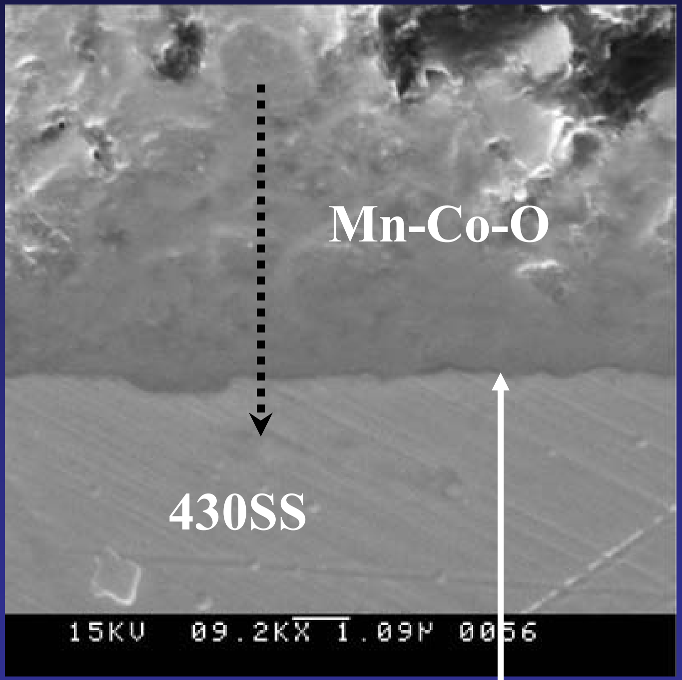


Porous coating - not good

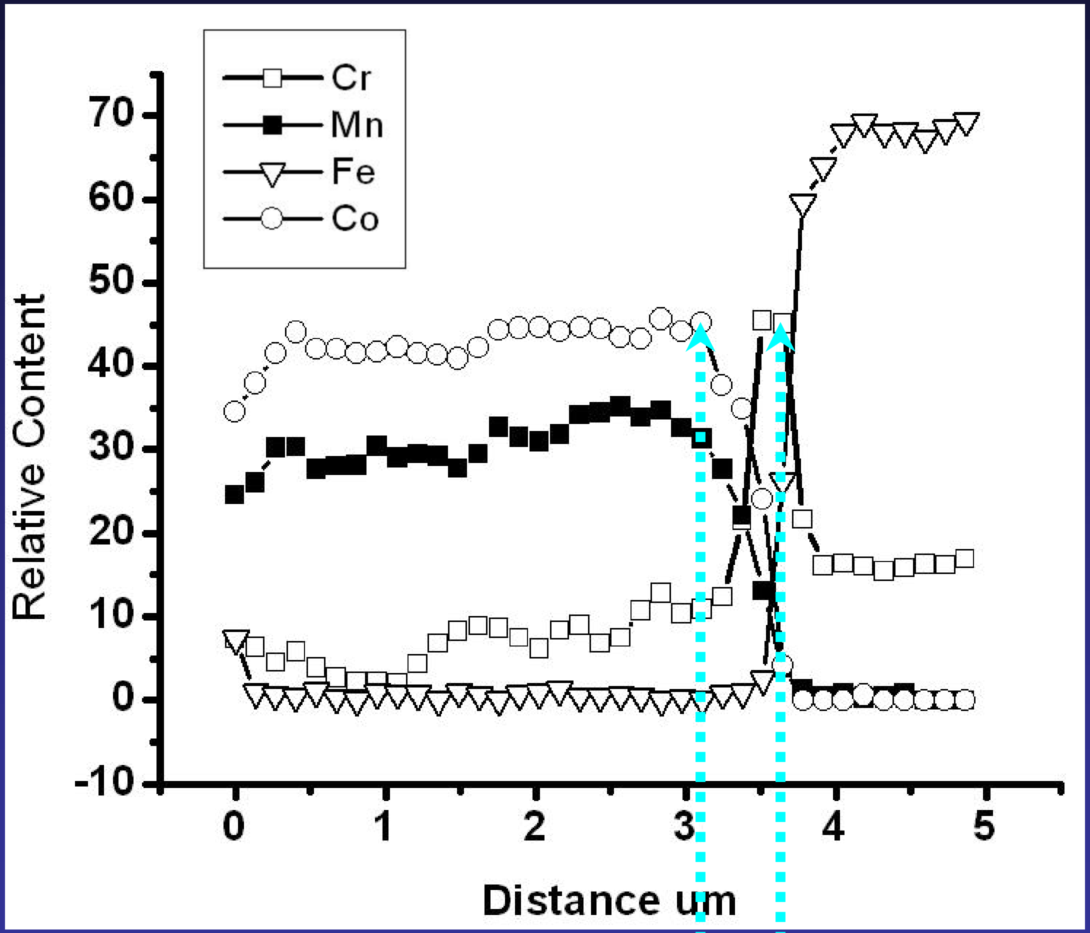
Colloidal spray coating (~10 μm)

High quality LBNL coating

EDAX

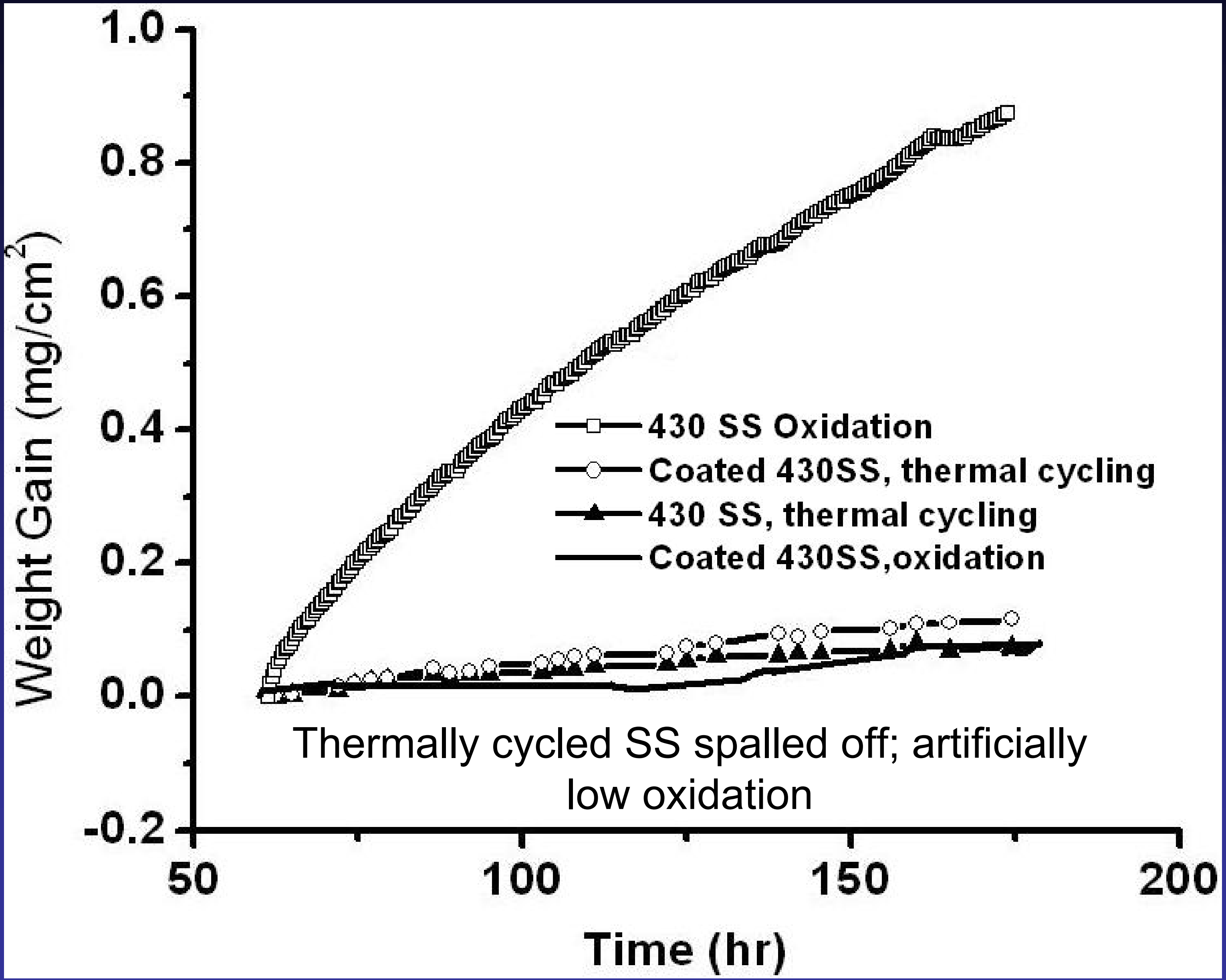


Cr_2O_3

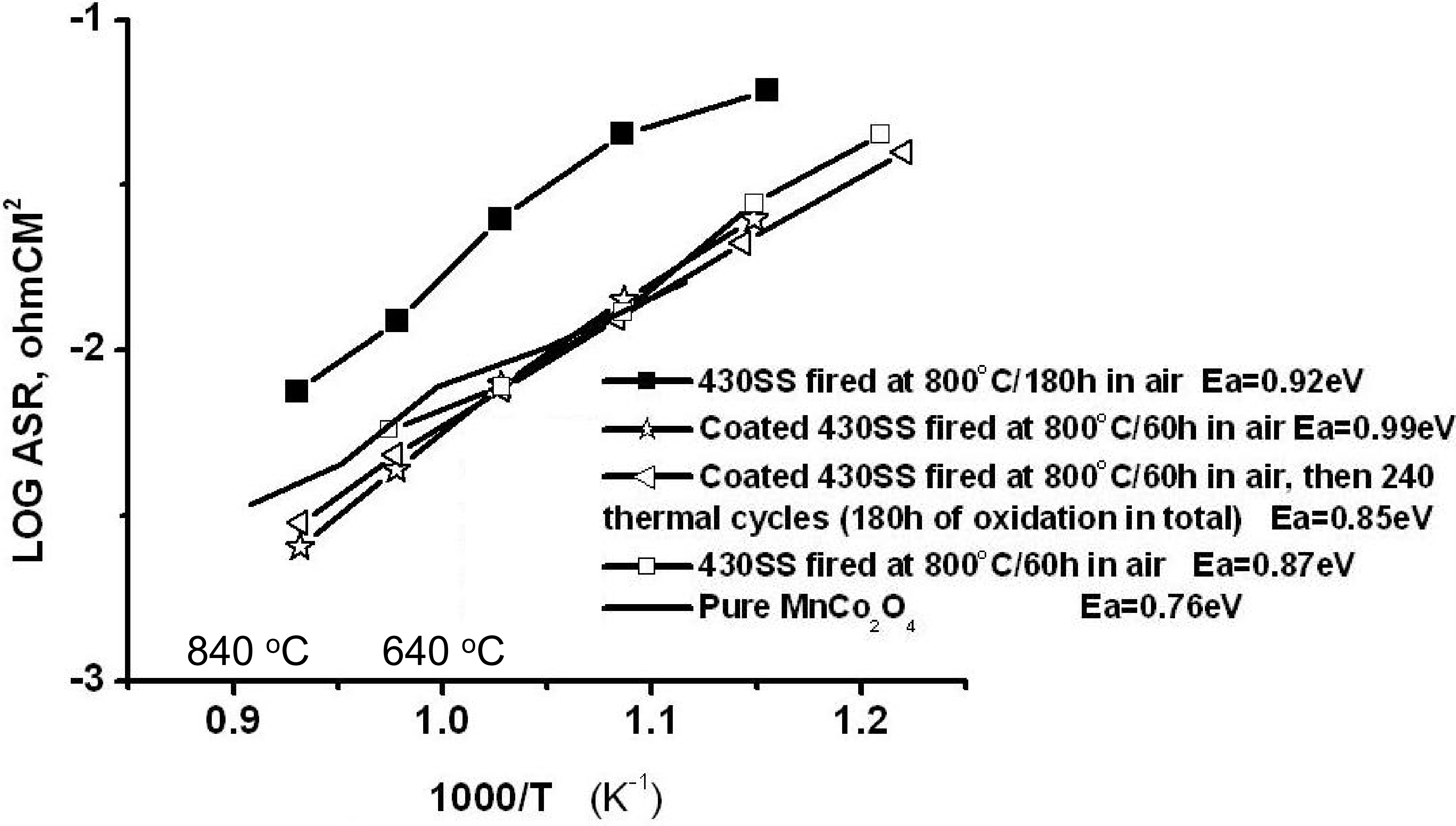


Mn-Cr-Co-O (0.3 μm)

Oxidation Behavior of LBNL Coated SS



Coated SS's 10x lower ASR - even with 240 thermal cycles



LBNL Coated Samples Exhibit 10x Lower Oxidation Rate & 10x Higher σ

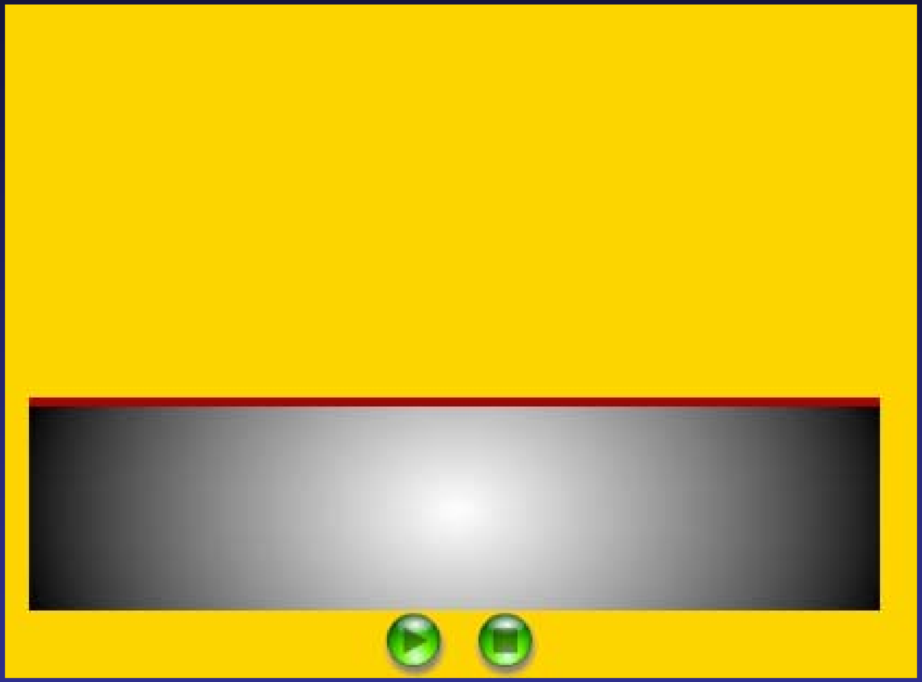
	Oxidation Temp. (^{o}C)	kg ($g^2cm^{-4}s^{-1}$)	kp (cm^2s^{-1})
Sample 3 (430)	850	$3.6*10^{-12}$	$1.3*10^{-13}$
Sample 2 (coated)	850	$1.1*10^{-13}$	$4.1*10^{-15}$

*the density of Cr2O3 is 5.21 g/cm3

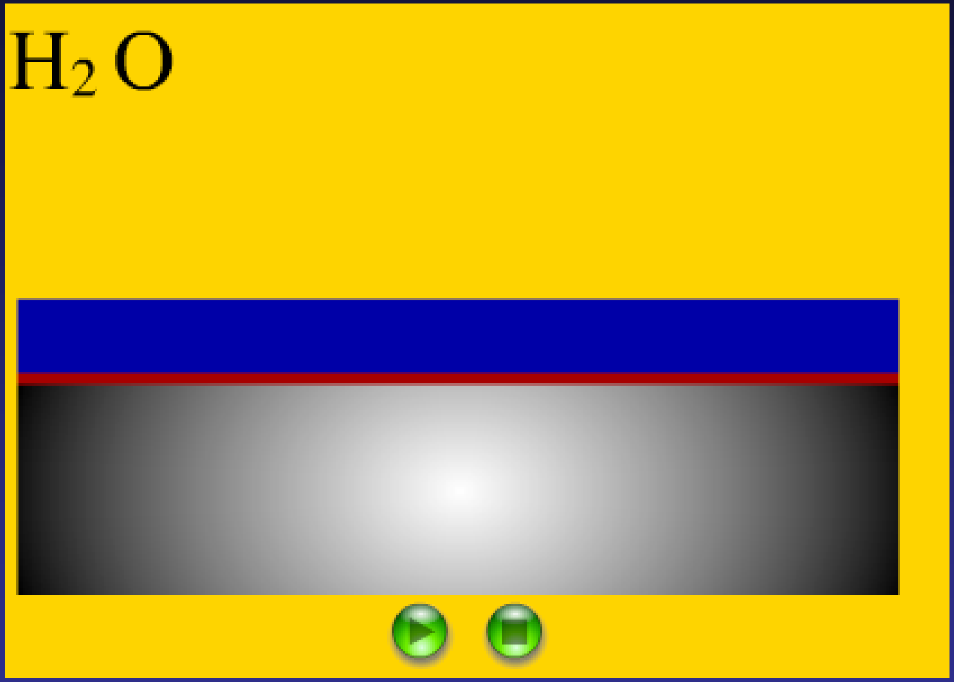
Summary of FeCr corrosion studies

- At 850 ^oC, untreated 430 stainless steel exhibited spallation of scale after repeated thermal cycles
- At 850 ^oC, $MnCo_2O_4$ coated 430 SS exhibited 10x lower oxidation rate & 10x higher σ
  - Scale growth rate constant, K_p=(weight gain g/cm^2)^2/sec, should be $<10^{-14} g^2/cm^4 s$ and preferably $\sim 10^{-15} g^2/cm^4 s$ - *Ferritic steels have scale growth rates that are acceptable for SOFC application ($<10^{-14}$ $g^2/cm^4 s$) at temperatures ≤700 °C*
- Cr volatilization rate has not yet been determined, but should be kept below threshold for cathode poisoning and below EPA limits (0.015 mg/m^3)

Cr Volatilization Studies



Oxidation of 430 SS



Oxidation of coated SS

Volatilization of Cr must be determined by transpiration measurements

Long Term Performance of Co-infiltrated Thin-Film SOFCs

<u>Cell Configuration</u>

Cathode

$La_{0.85}Sr_{0.15}MnO_3$

$(Sc_2O_3)_{0.1}(Y_2O_3)_{0.01}(ZrO_2)_{0.89}$

(10Sc1YSZ)

Post doped with 2mg/cm^2 Co-nitrate

Electrolyte

10Sc1YSZ

Anode

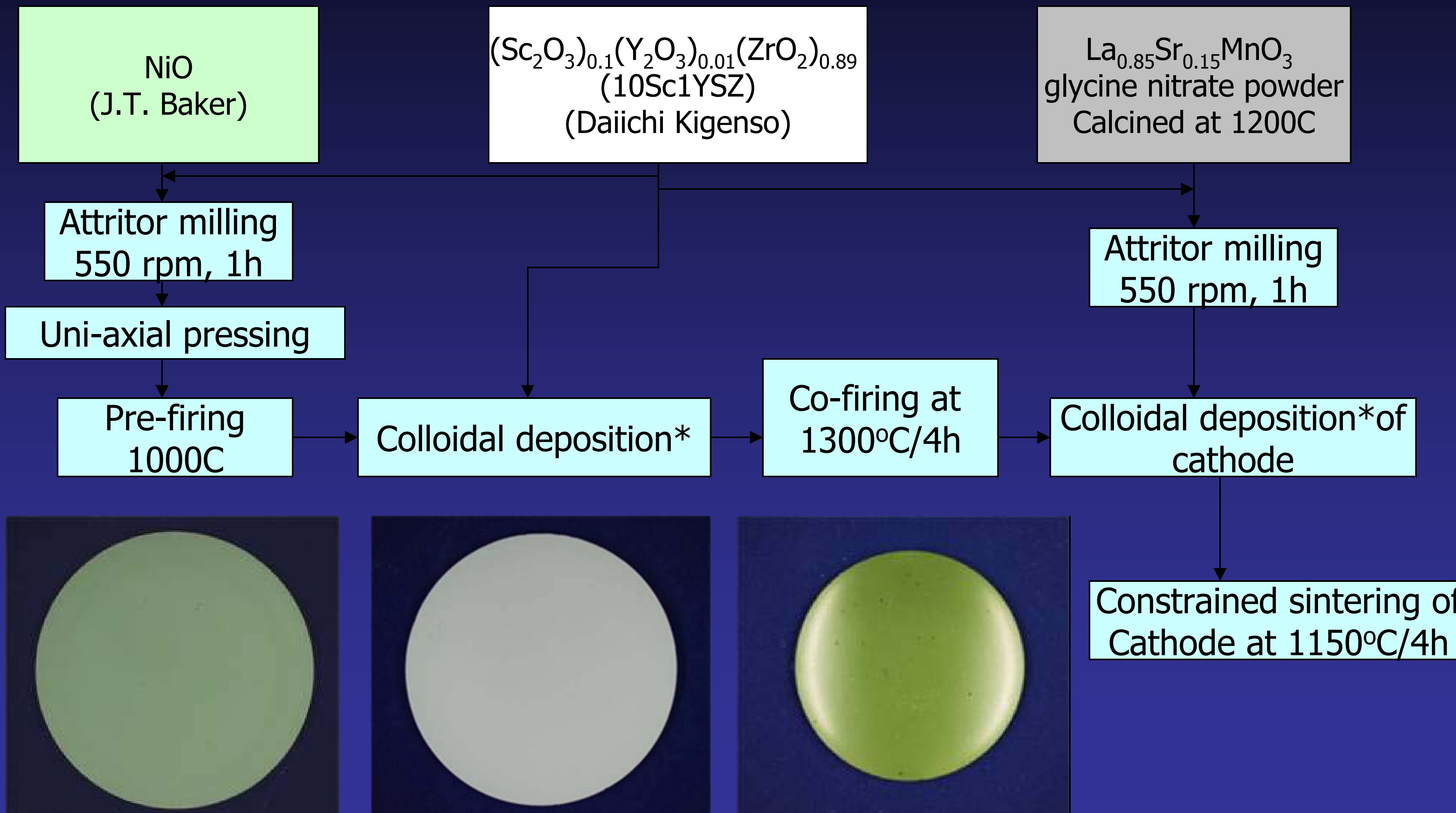
NiO

10Sc1YSZ

Motivation for Co Infiltration

- Longterm operation of SOFCs having stainless steel components will likely be operated at < 700 ^{o}C
- Performance of standard LSM electrode is poor below 700 ^{o}C
- Infiltration of appropriate catalysts (Co) into the air electrode can significantly boost performance
- Longterm stability of infiltrated electrodes is not yet known

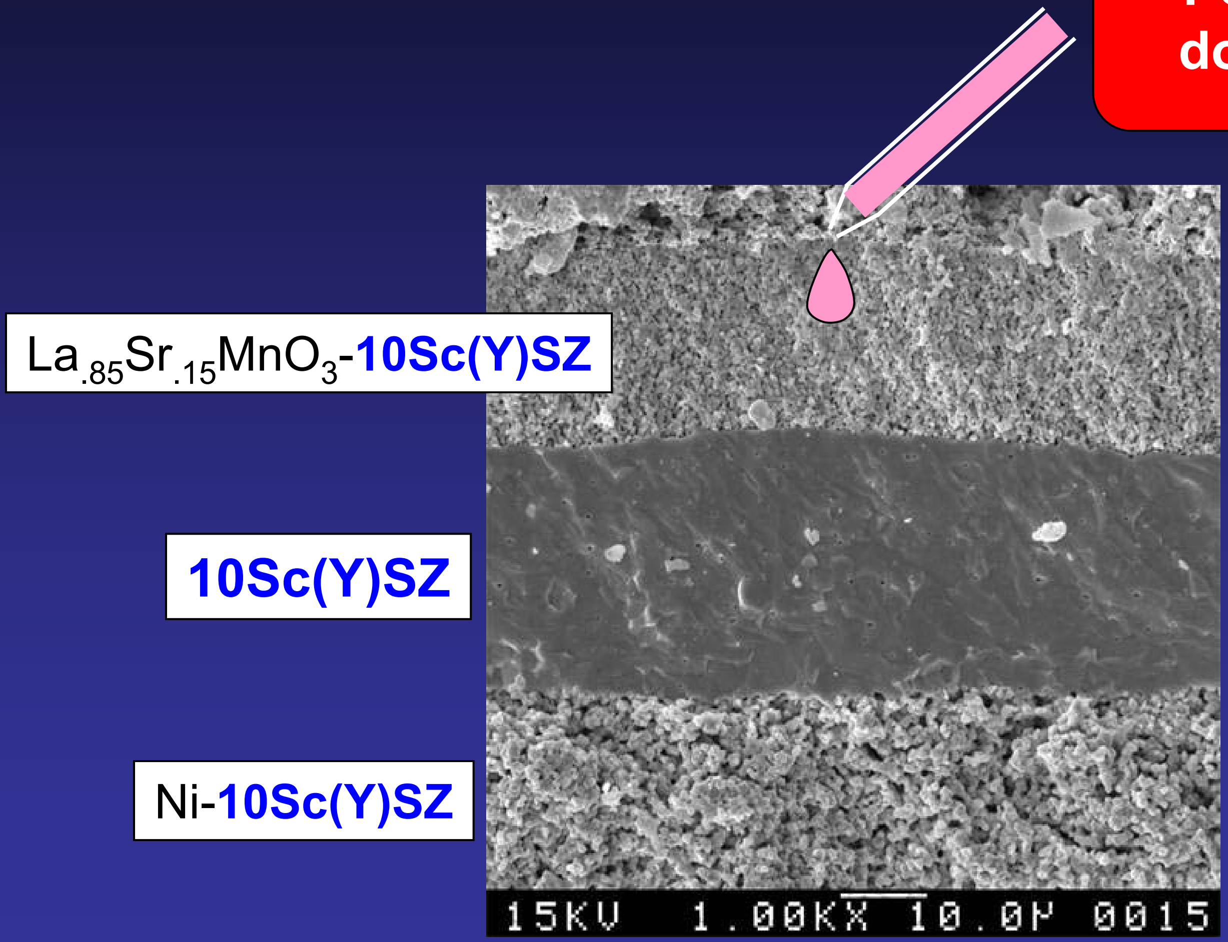
Cell Fabrication



*S.J. Visco, C.P. Jacobson and L.C. De Jonghe, U.S. Pat. No. 6458170, October 1 (2002)

Reduction of Electrode Overpotential

Post-firing cobalt doping of cathode

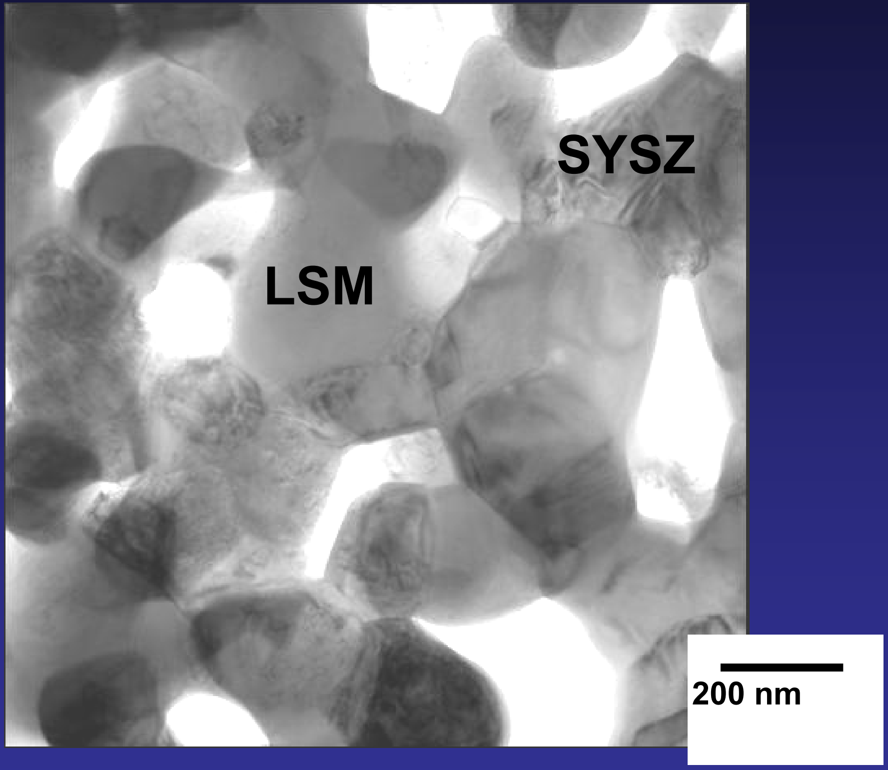


$2mg/cm^2$ cobalt nitrate

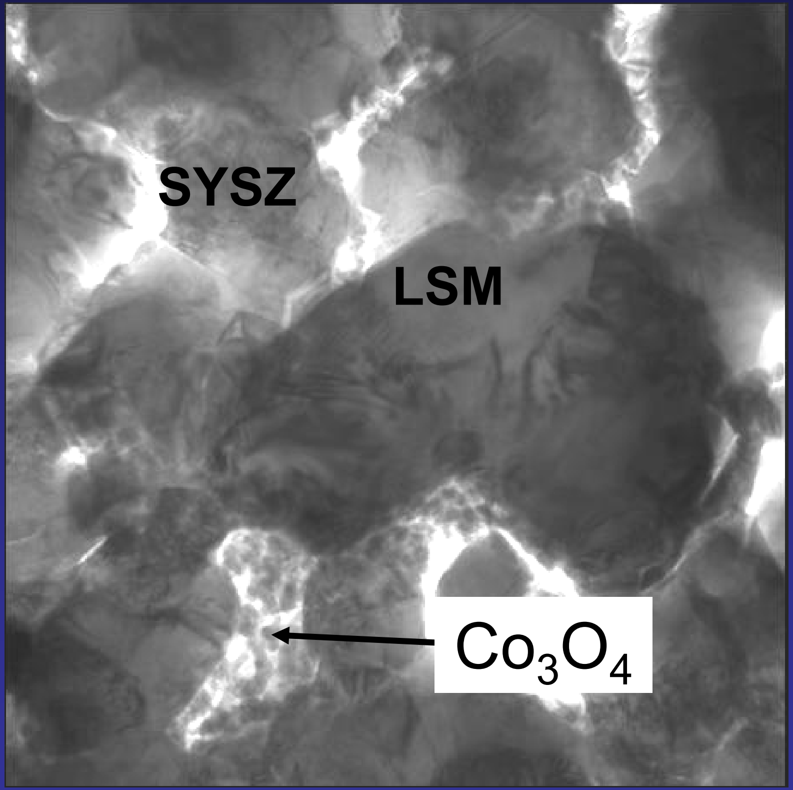
Cross-section micrograph of an anode supported 10Sc1YSZ cell

Nano Cobalt Oxide

Co-nitrate infiltration into LSM-SYSZ

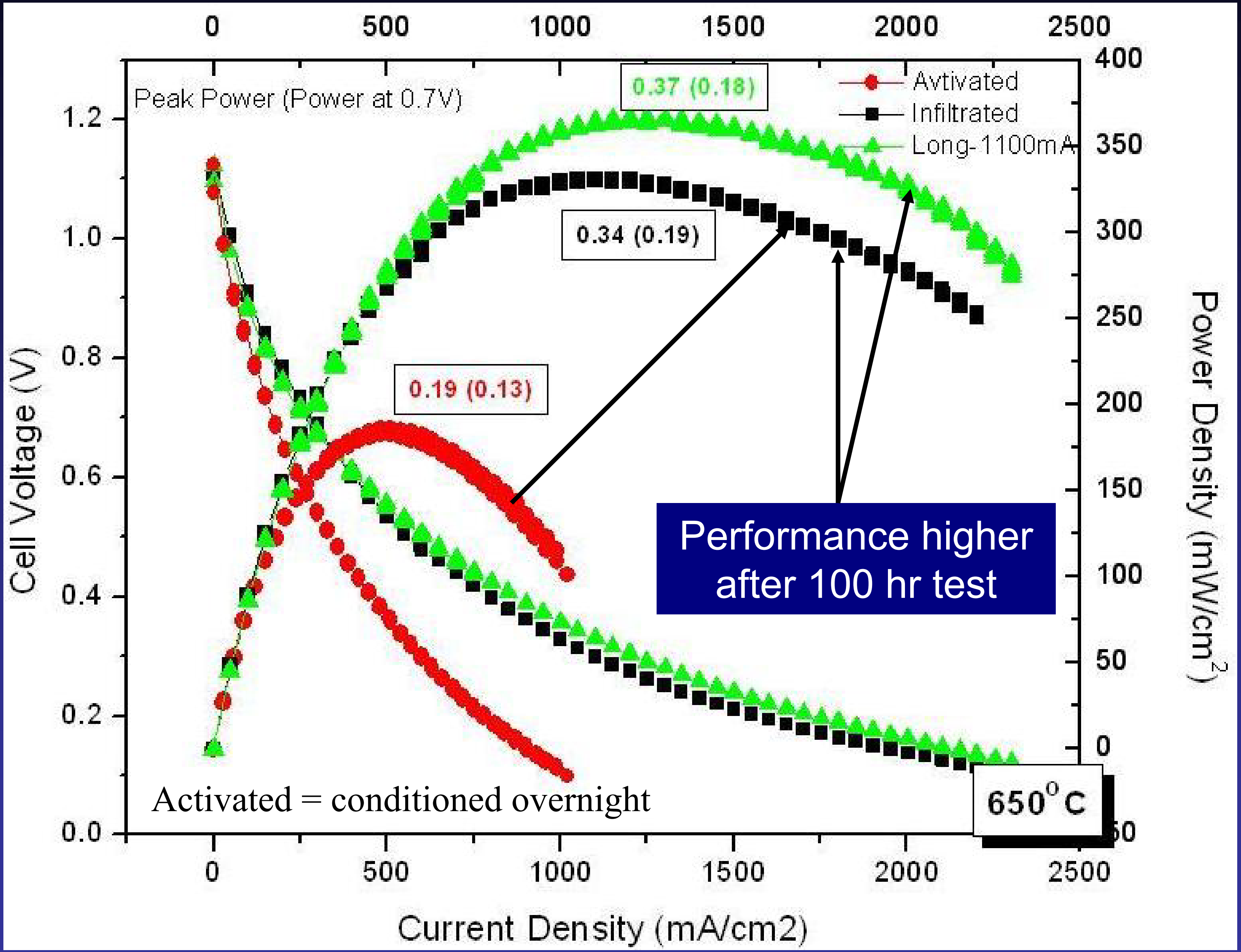


TEM image

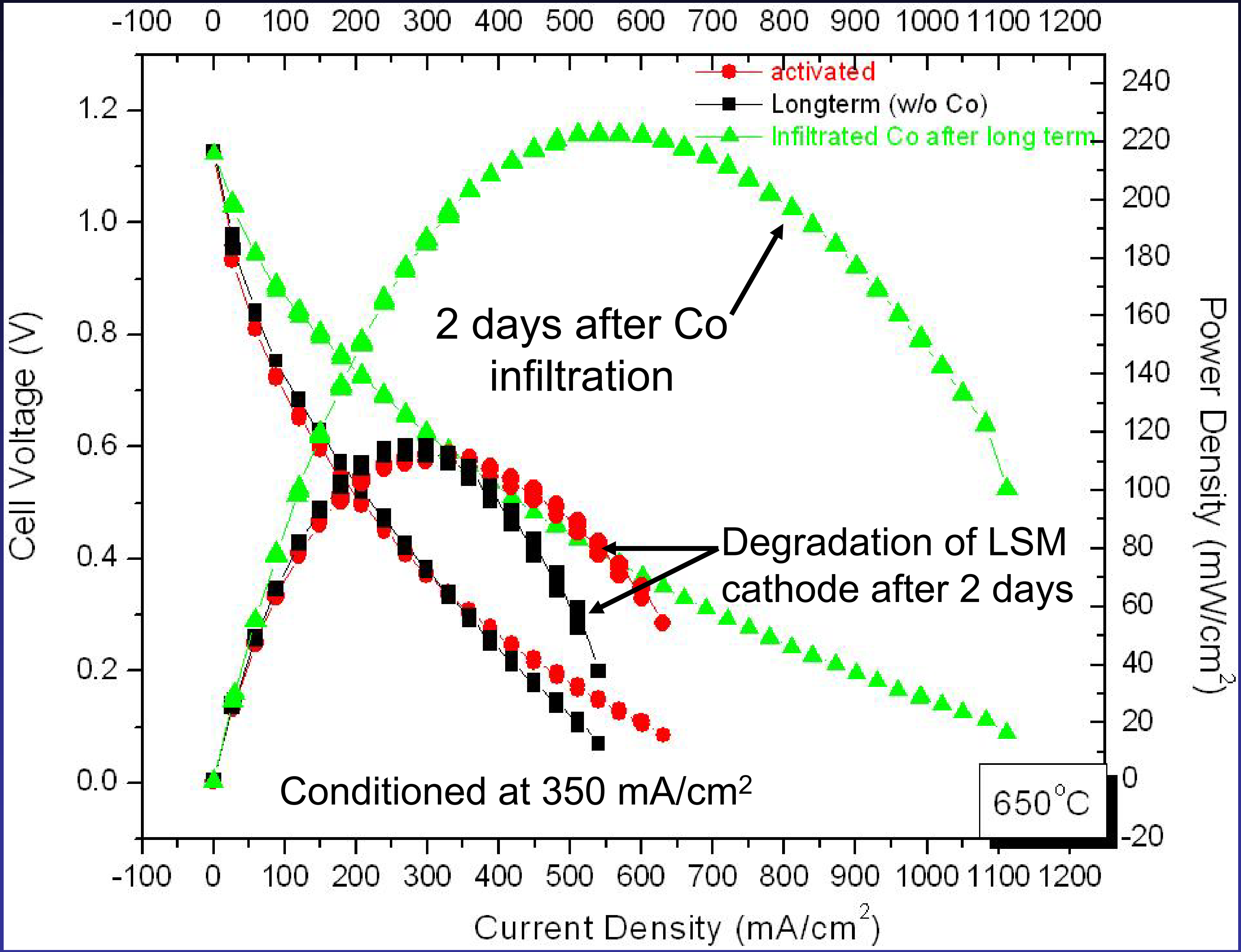


TEM image

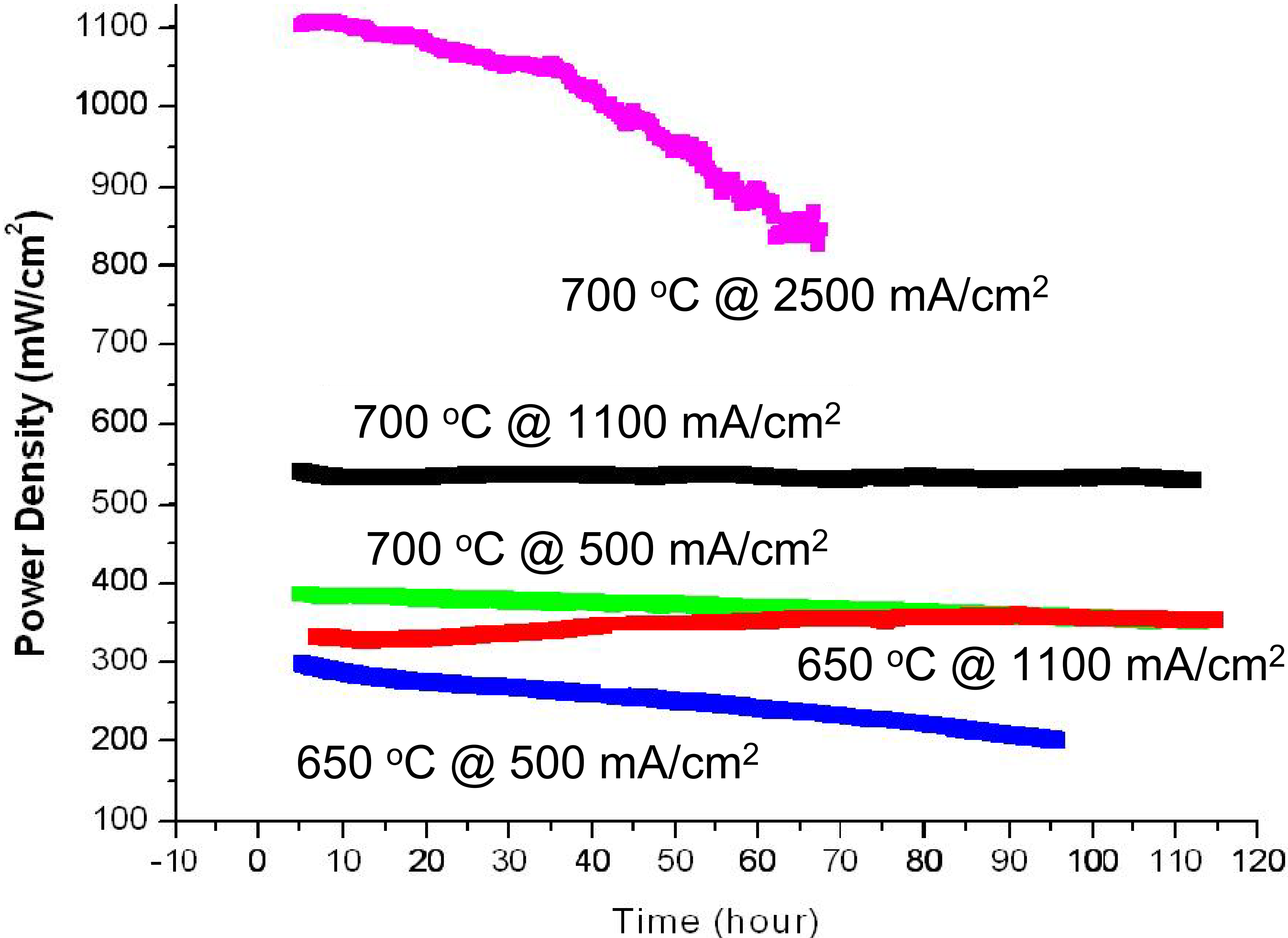
Cobalt infiltration boosts performance



Repair of Cathode After Degradation



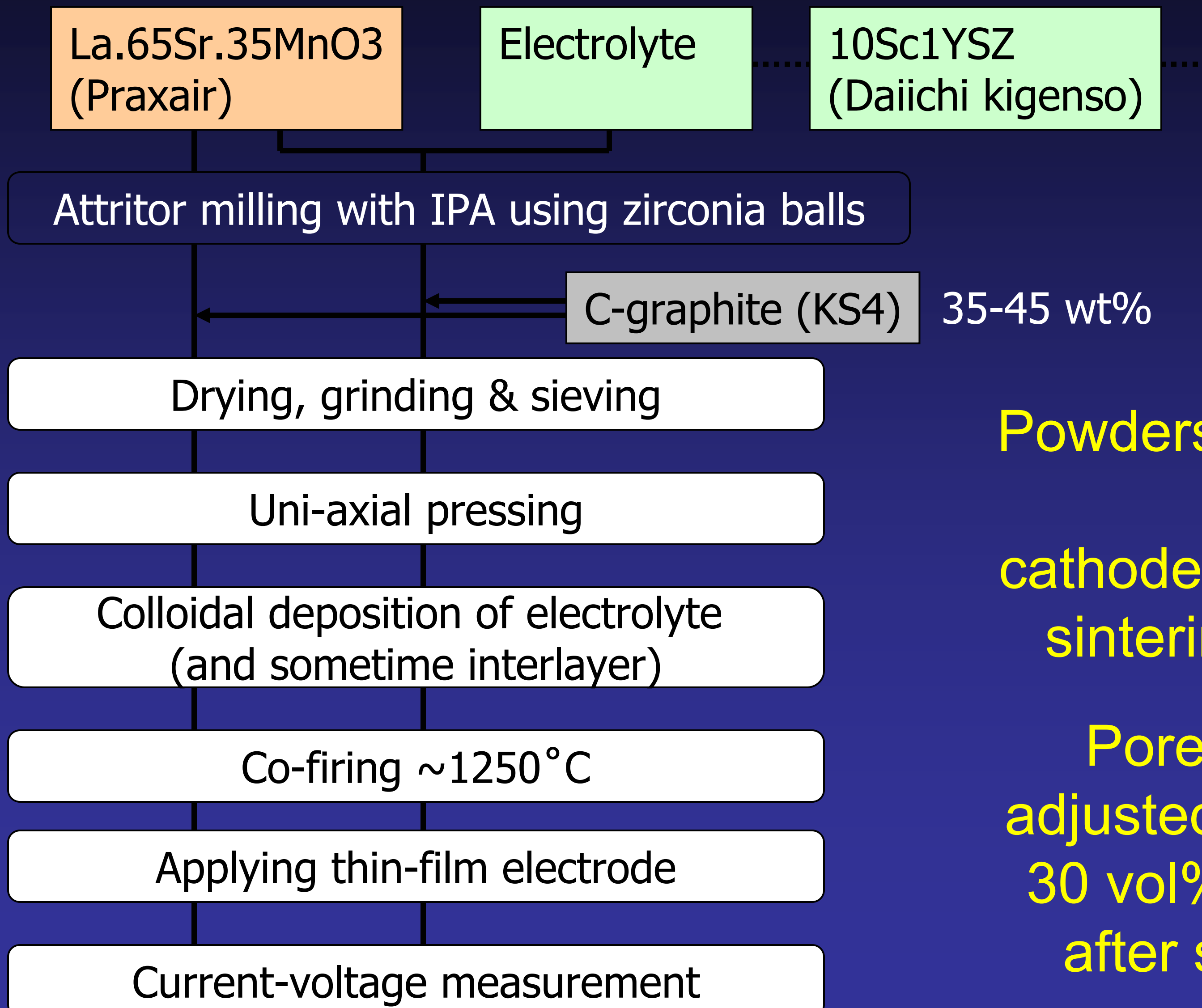
Stability of Co Infiltrated Cathodes as a fcn of i and Temp.



Motivation/Issues for Cathode Supported Cell

- Alternative anodes, such as $SrTiO_3$, Cu-CeO_2, $LaCrO_3$, etc., can react or incompatible with firing conditions for anode supported cells
- Control of porosity in cathode supported cells is more difficult than anode supported cells
- There is a potential for reaction of cathode with electrolyte if firing temperature is too high
- Cobalt infiltration into cathode dramatically improves cell performance

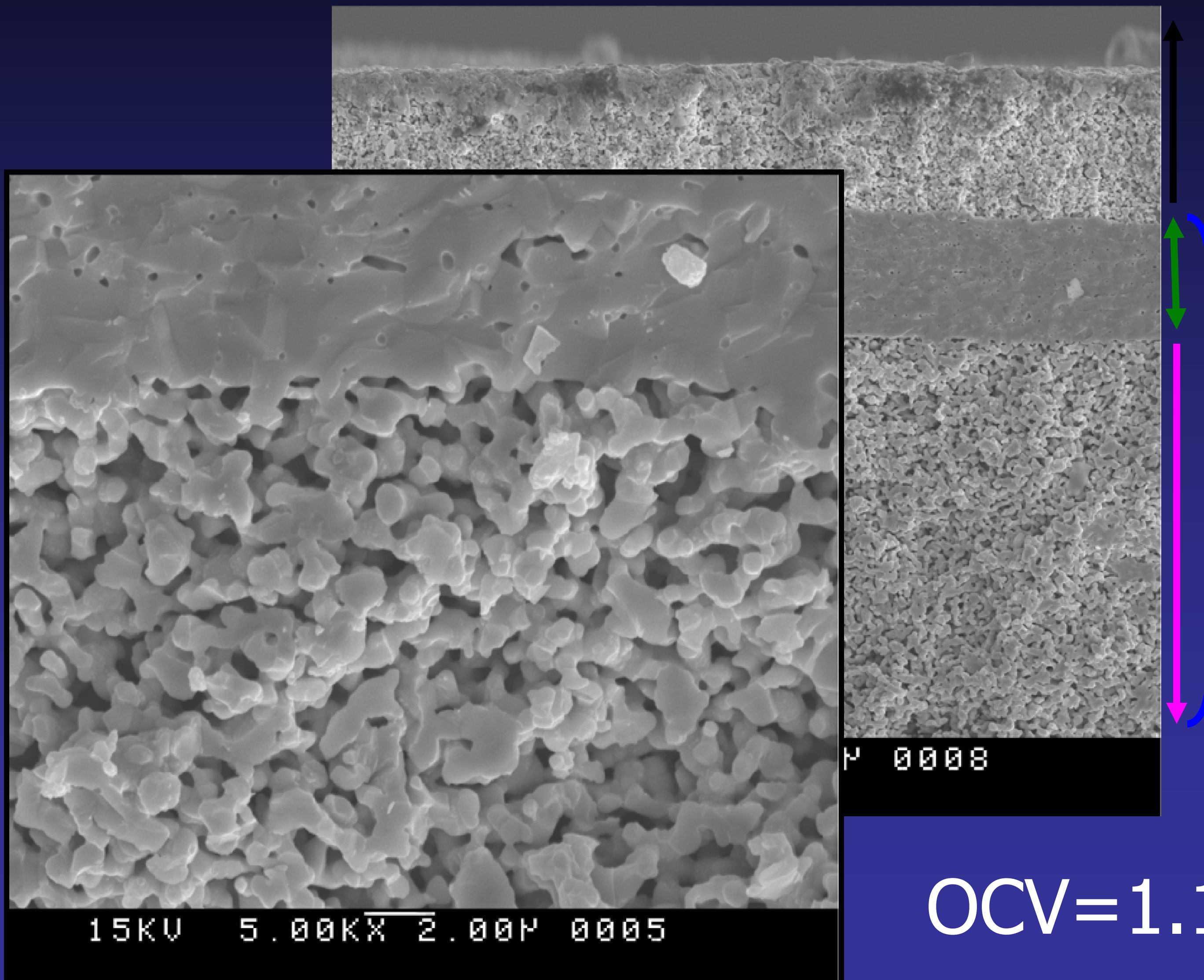
Fabrication of Cathode Supported Cells



Powders optimized for cathode/electrolyte sintering match

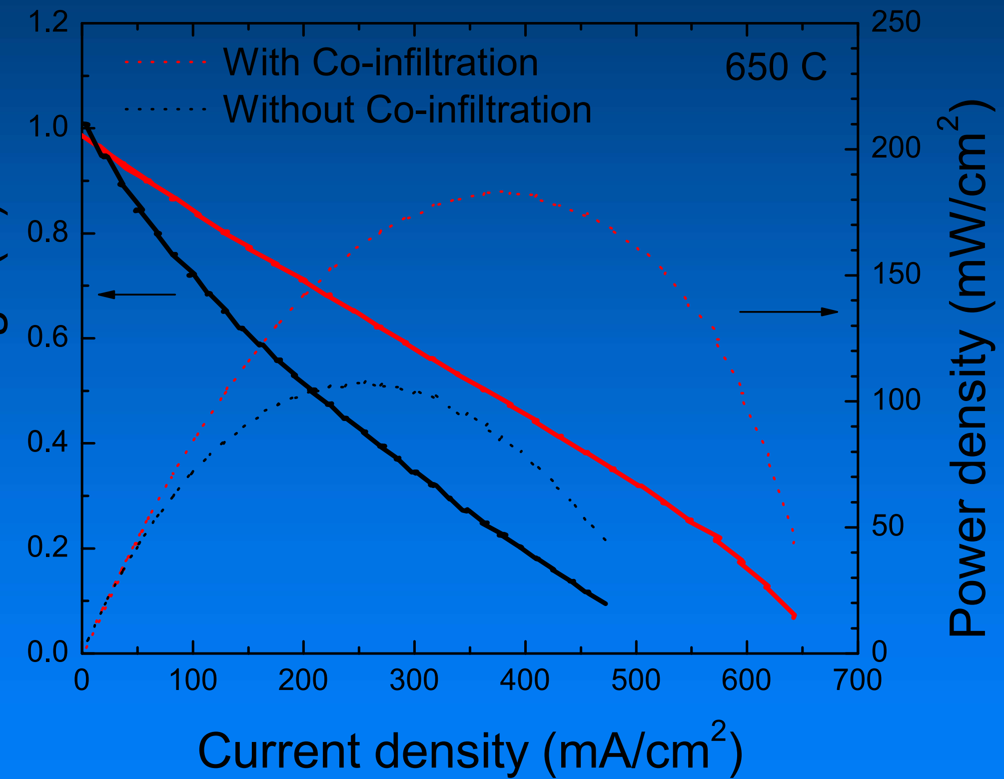
Pore former adjusted to yield > 30 vol% porosity after sintering

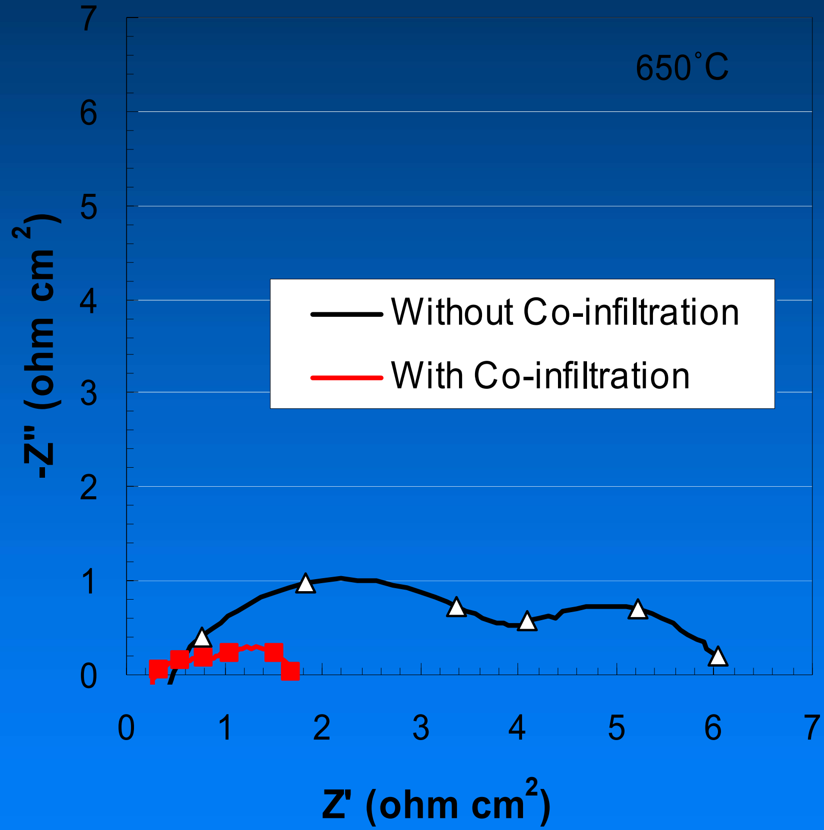
Co-Firing Bi-Layers at 1250˚C



OCV=1.1V at 800˚C

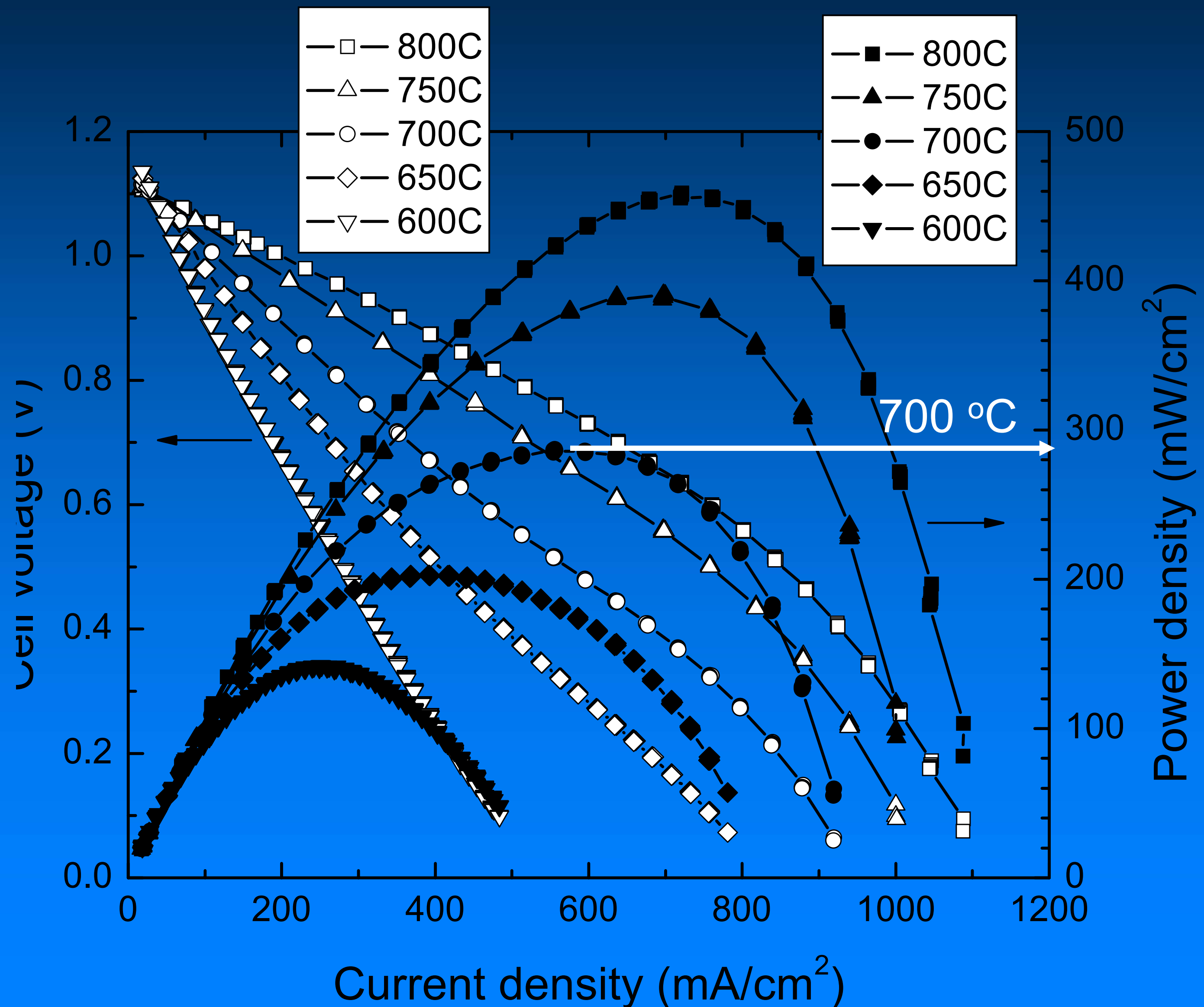
Effects of Cobalt Infiltration into the LSM-SYSZ Cathode



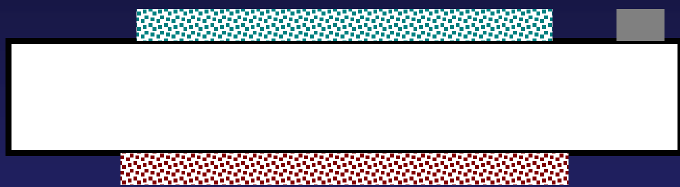


Dramatic improvement due to a reduction in non-ohmic resistance

Performance of Co Infiltrated Cathode Supported Cells



Alternative Anode Evaluation

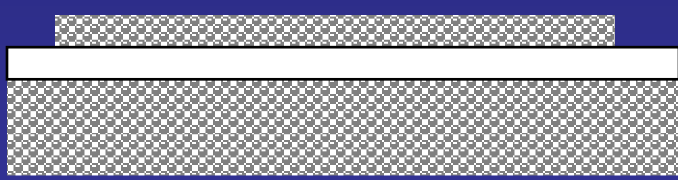


Electrolyte supported cell w/ref

Define optimum firing conditions for alternative anode; determine anode overpotential

Cathode supported cell tests follow

Infiltrate anode & cathode



Metal supported SOFC

Summary

- Durability and performance of steel components should be excellent at temperatures below 700 ^{o}C
  - Growth rate constant, K_p=(weight gain g/cm^2)^2/sec, should be <10^{-14}g^2/cm^{4}s and preferably ~10^{-15}g^2/cm^{4}s
- Protective coatings increase SS durability and improve resistivity
  - Cr volatilization may be reduced - to be determined
- Cathode performance at temperatures below 700 oC is an issue - cobalt infiltration dramatically improves performance
  - Results of 100 hr tests are promising

Summary

- LBNL has successfully developed cathode supported cells with reasonable low temperature performance
  - May enable use of alternative (C,O,S tolerant) anodes
- Alloy coating technology, low temperature cathodes, and alternative anodes can be utilized with innovative metal supported SOFCs

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