Development of Novel Electrode Structures and Stabilization of Metal Components for Cost Competitive SOFCs

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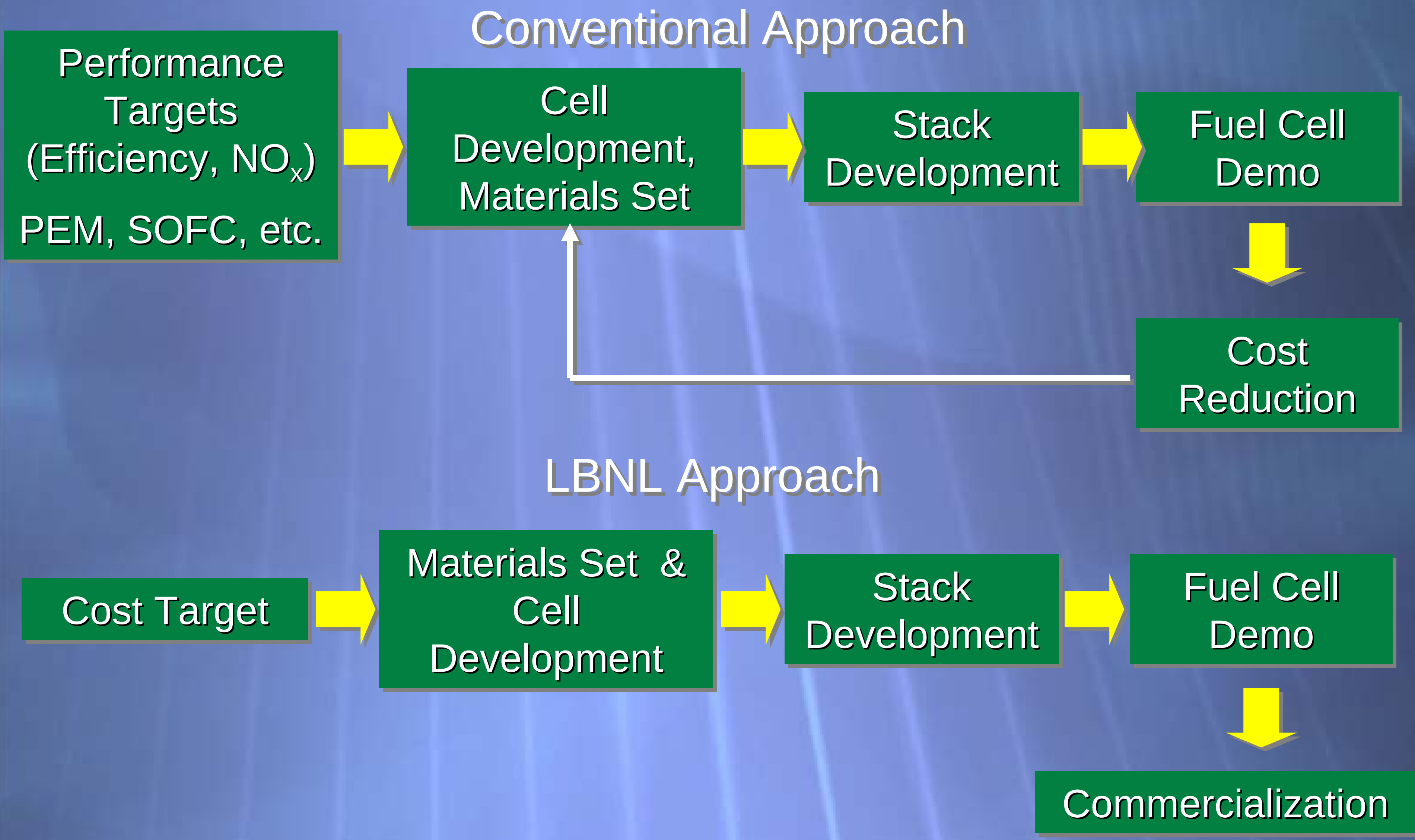
Fuel Cell Development Paths



Alternative Materials

- Replace ceramic components with low-cost, high-strength stainless steel
  - This introduces new materials issues including metal oxidation (Cr_2O_3) leading to ASR rise and Cr vaporization (cathode poisoning)
  - Might be eliminated by coatings
- Develop electrode infiltration technology to improve cell performance.
  - Enables broader choice of electrode materials due to lower processing temperature
  - Need to demonstrate long-term stability.

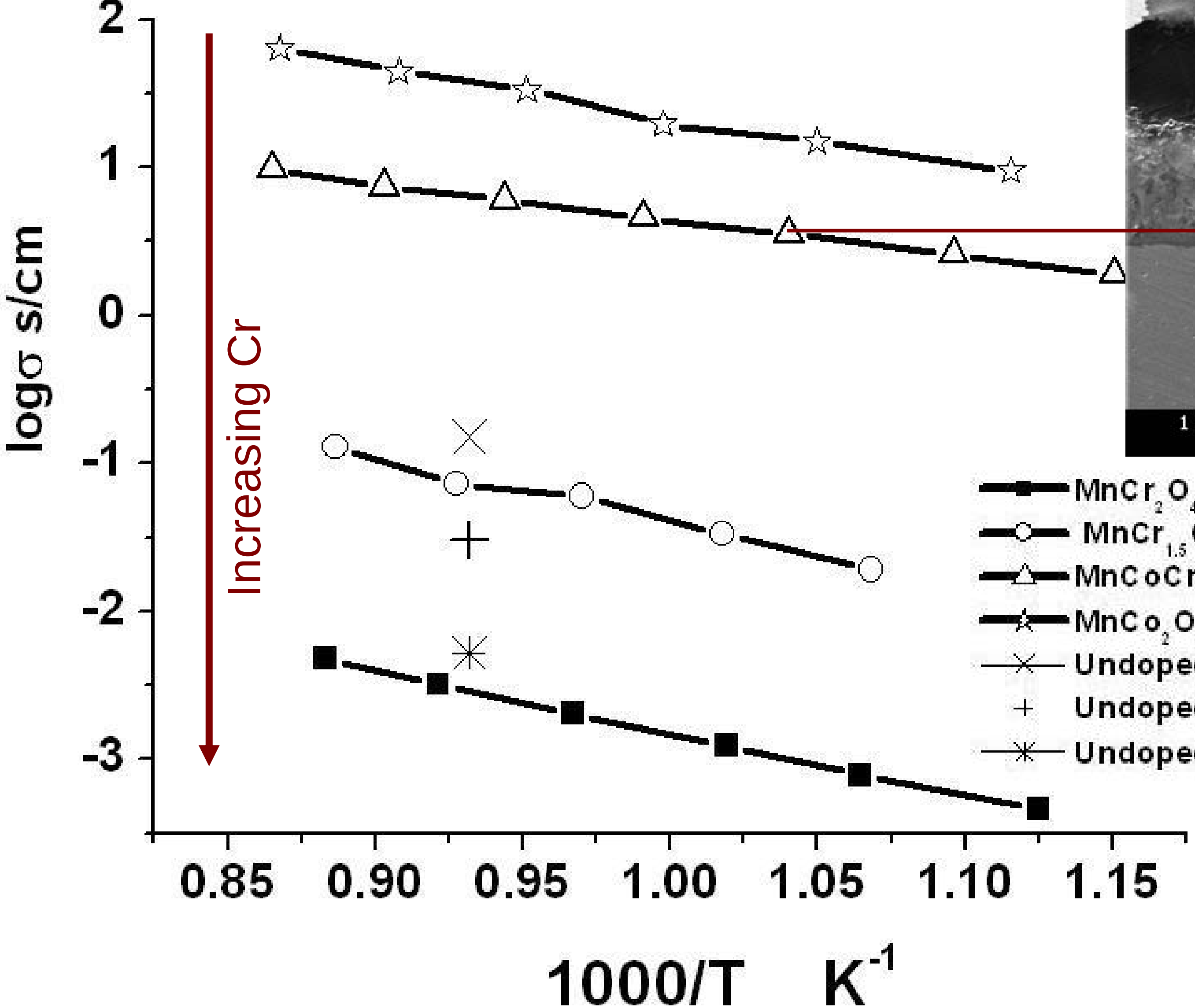
Use of High Conductivity Spinel Coatings on S.S.

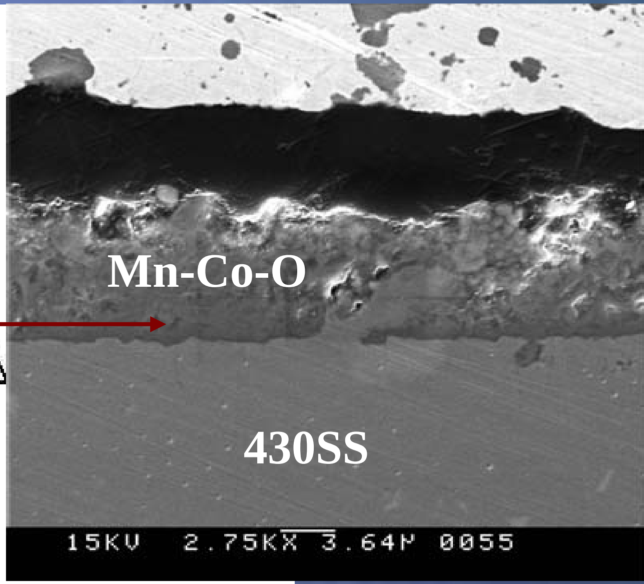
- LBNL described the use of protective $MnCo_2O_4$ spinel coatings for stainless steel at SECA core technology review in Boston, May 11-13, 2004
- A number of labs have duplicated the results
- Ceramic Fuel Cells Limited described the use of spinel coatings on steel interconnects in U.S. Patent 5,942,349 (Badwal, Foger, Zheng, Jaffrey) filed in 1996

Conductivity of Oxide Films

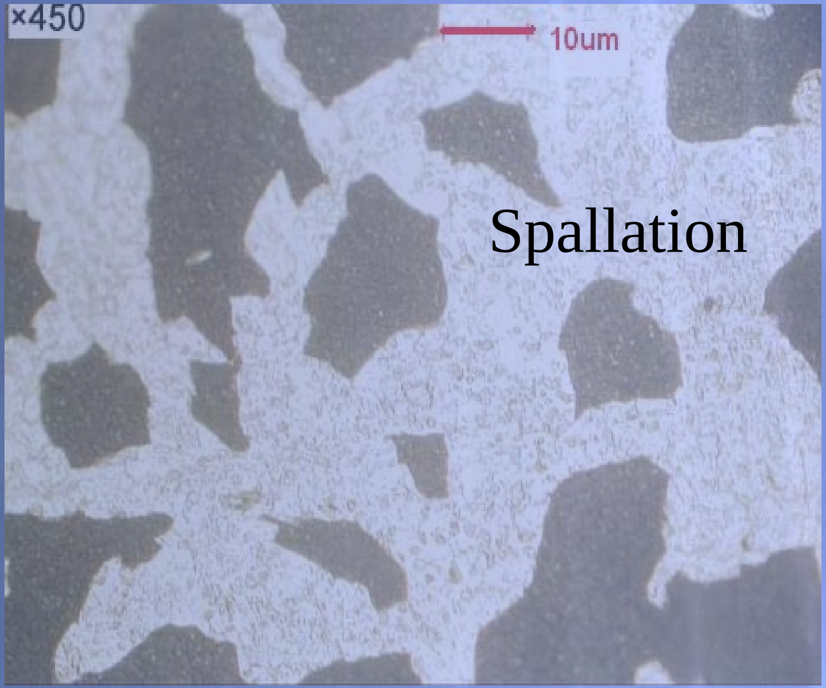
	Conductivity at about 800^oC (S/cm)
$MnCo_2O_4$, GNP, sintered at 1300^oC	31.6
$MnCrCoO_4$, GNP, sintered at 1300^oC	6.3
$Mn_{1.5}Cr_{1.5}O_4$, GNP, sintered at 1300^oC	$7.9*10^{-2}$
$MnCr_2O_4$, GNP, sintered at 1300^oC	$2.5*10^{-3}$
Undoped Cr_2O_3, Hauffe and Block (1951) [18] sintered at 1200^oC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

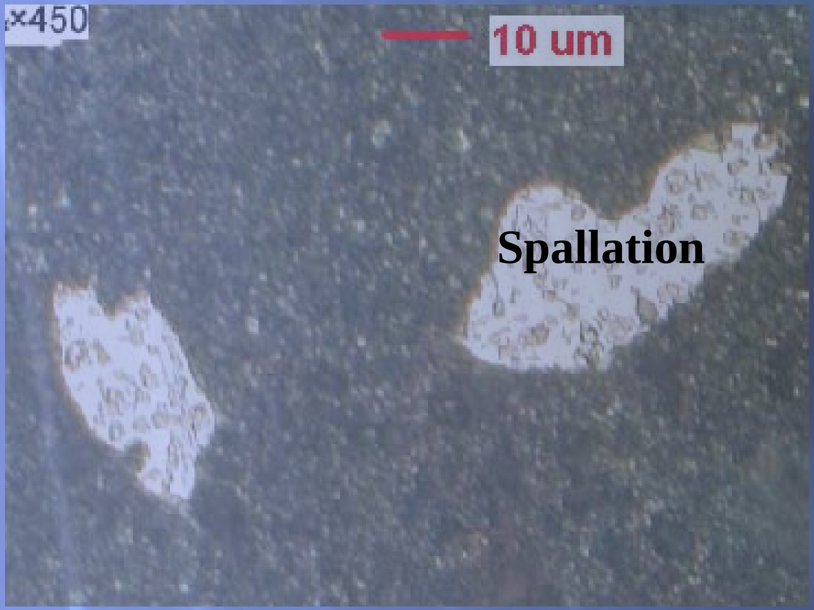
Conductivity of Potential Coatings





Spallation of Uncoated 430 Oxide film





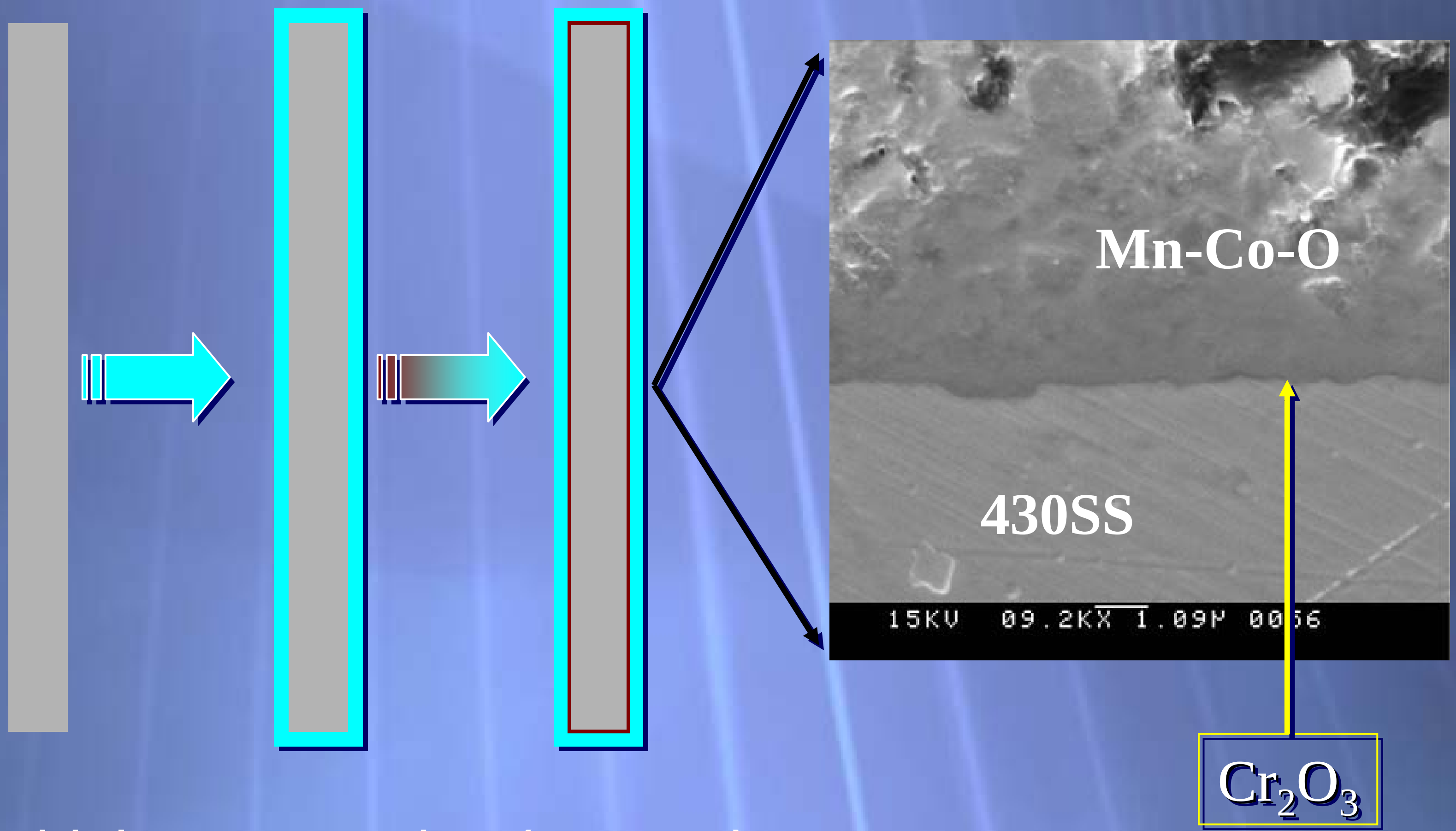
240 rapid thermal cycles:

850 ^{o}C to RT at 50 ^{o}C/min cooling

APUs probably need 100 ^{o}C/min. startup

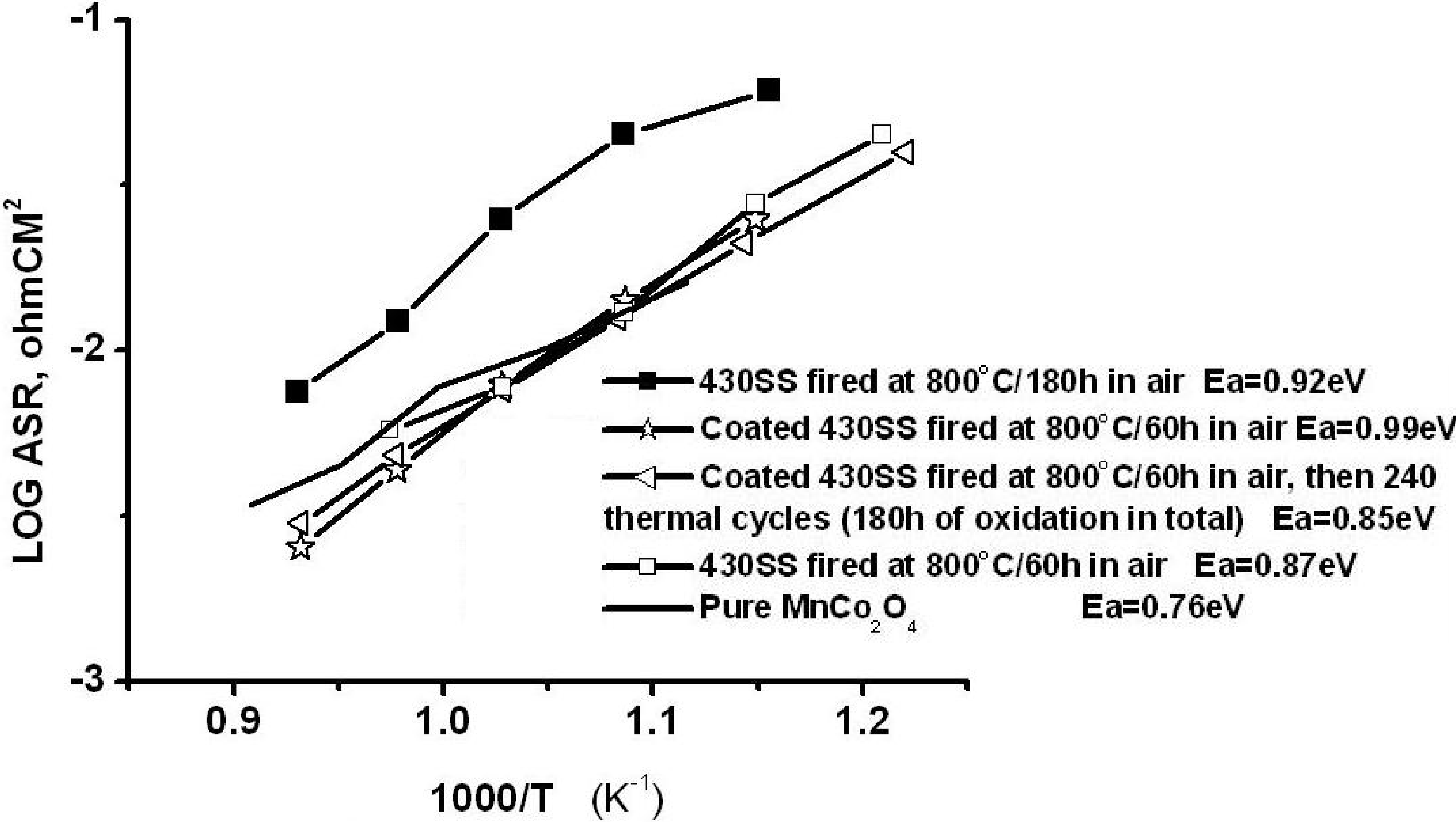
Preparation of Protective Coatings

400 series $MnCo_2O_4$ 850 °C



Colloidal spray coating (~10 µm)

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

Cr Volatilization Studies

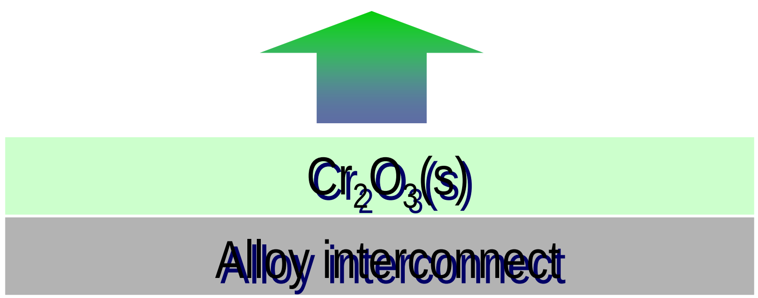
Oxidation of 430 SS

Oxidation of coated SS

Volatilization of Cr must be determined by transpiration measurements

Chromium gas species

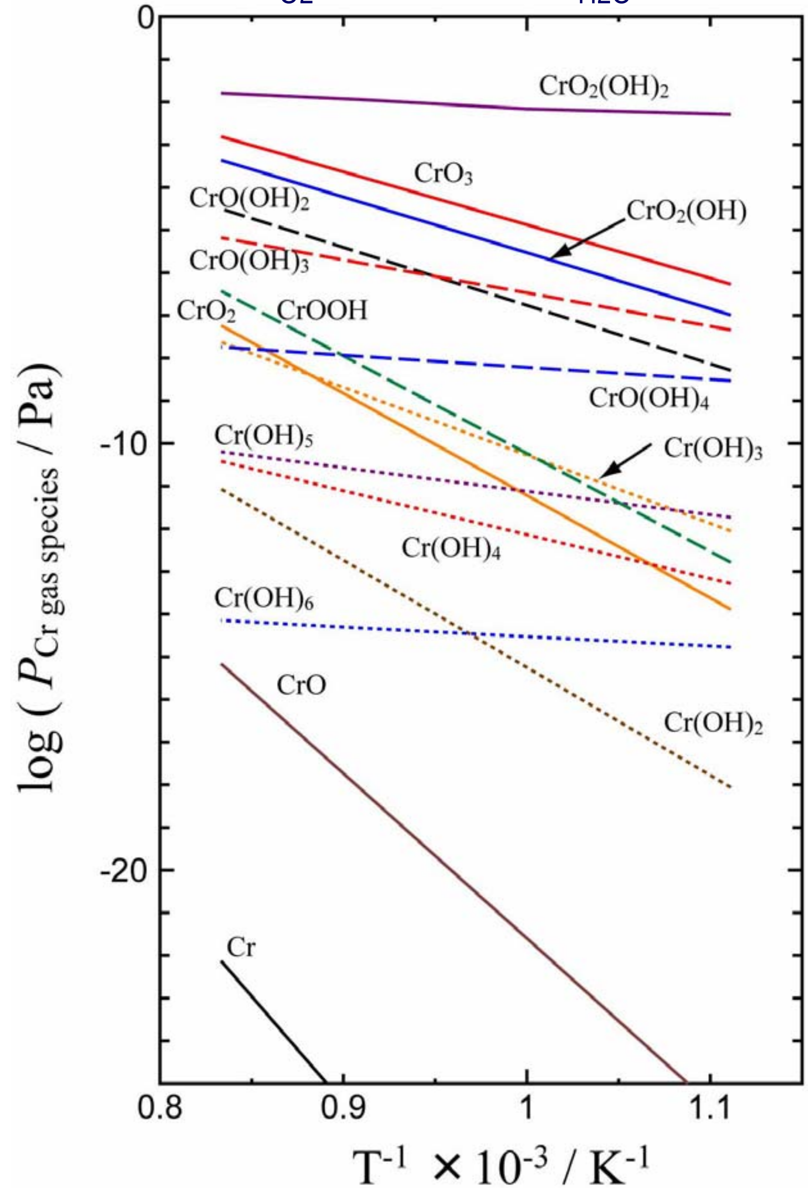
Cr	CrOH	CrOOH
CrO	$Cr(OH)_2$	$CrO(OH)_2$
CrO_2	$Cr(OH)_3$	$CrO(OH)_3$
CrO_3	$Cr(OH)_4$	$CrO(OH)_4$
	$Cr(OH)_5$	$CrO_2(OH)$
	$Cr(OH)_6$	$CrO_2(OH)_2$



B.B. Ebbinghaus, *Combus. Flame.*, **93** (1993) 119

- Equilibrium partial pressures

Air side: $P_{O2} = 2 \times 10^4$ Pa, $P_{H2O} = 2 \times 10^3$ Pa



Cr vaporization - mechanism & effect -

- Mechanism

Alloy interconnect

$Cr_2O_3(s)$

$Cr_2O_3(s) + 3/2\ O_2(g) + 2\ H_2O(g)$ $2\ CrO_2(OH)_2(g)$

AIR

Vapor transport

$2\ CrO_2(OH)_2(g) + 6\ e^-$ $Cr_2O_3(s) + 2\ H_2O(g) + 3\ O^{2-}$

Cathode

Electrolyte

Anode

FUEL

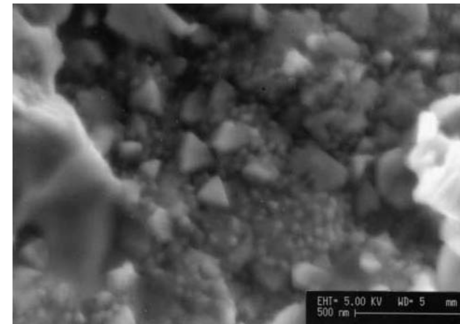
$3\ H_2(g) + 3\ O^{2-}$ $3\ H_2O(g) + 6\ e^-$

$Cr_2O_3(s)$

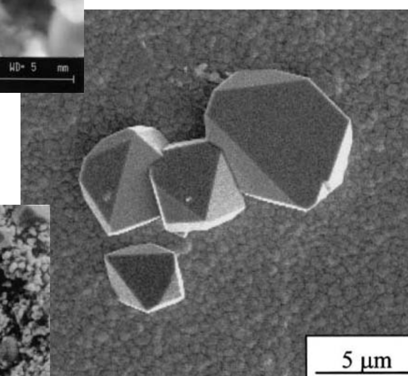
Alloy interconnect

Hilpert et al., *J. Electrochem. Soc.*, **143** (1996) 3642

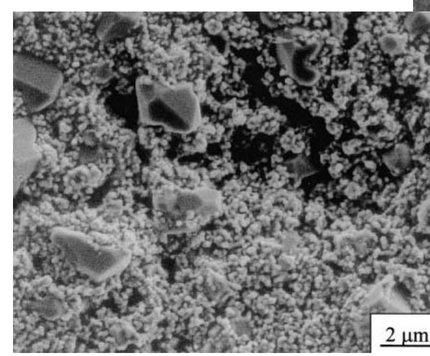
- Effect – deposition on electrolyte and electrode



Cr_2O_3 on YSZ



Cr_2O_3 on LSM

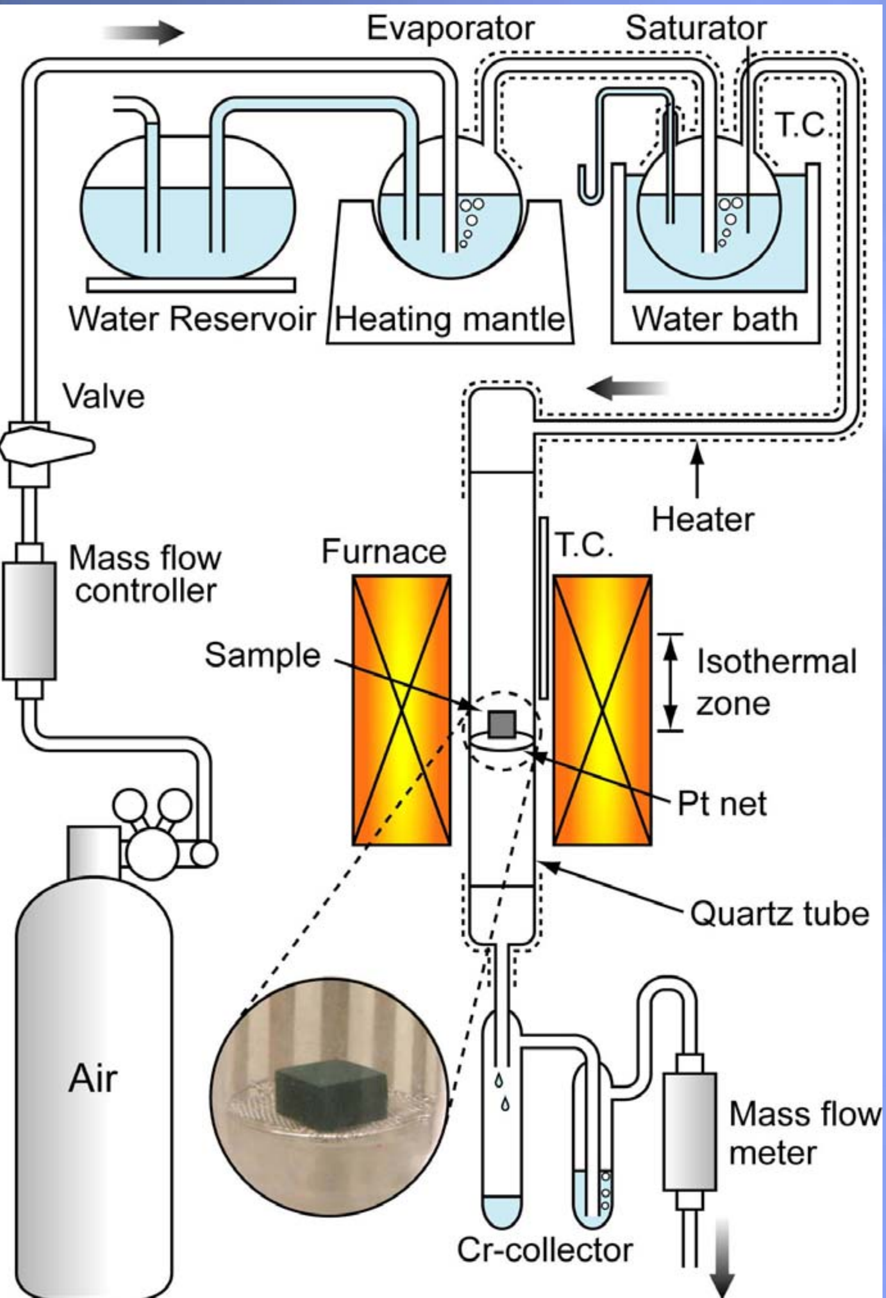


Cr_2O_3 on LSCF

Jiang et al., *J. Europ. Ceram. Soc.*, **22** (2002) 3610

Decreases Three-phase boundary

Cr Volatilization I s



P_{H_2O}

Cr s
700

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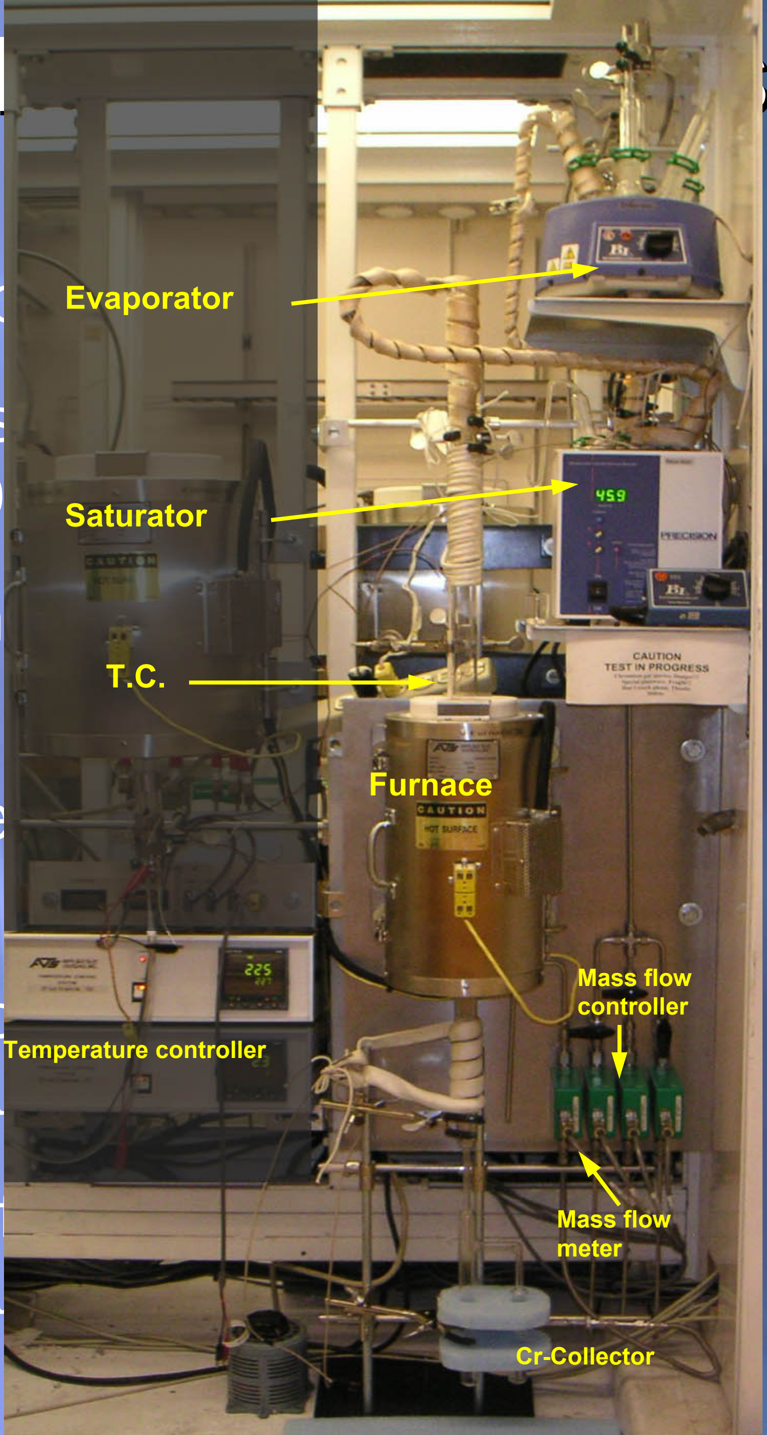
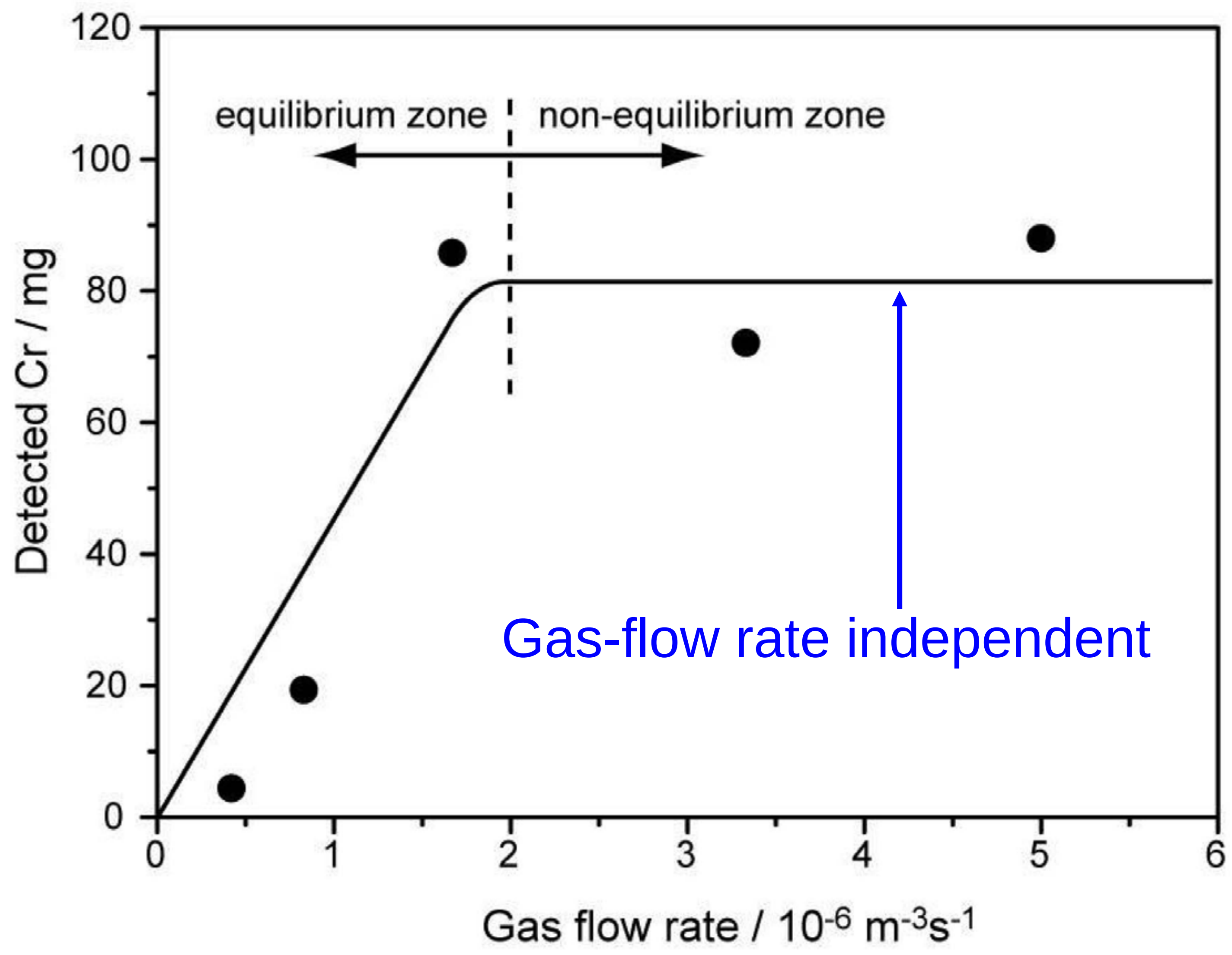
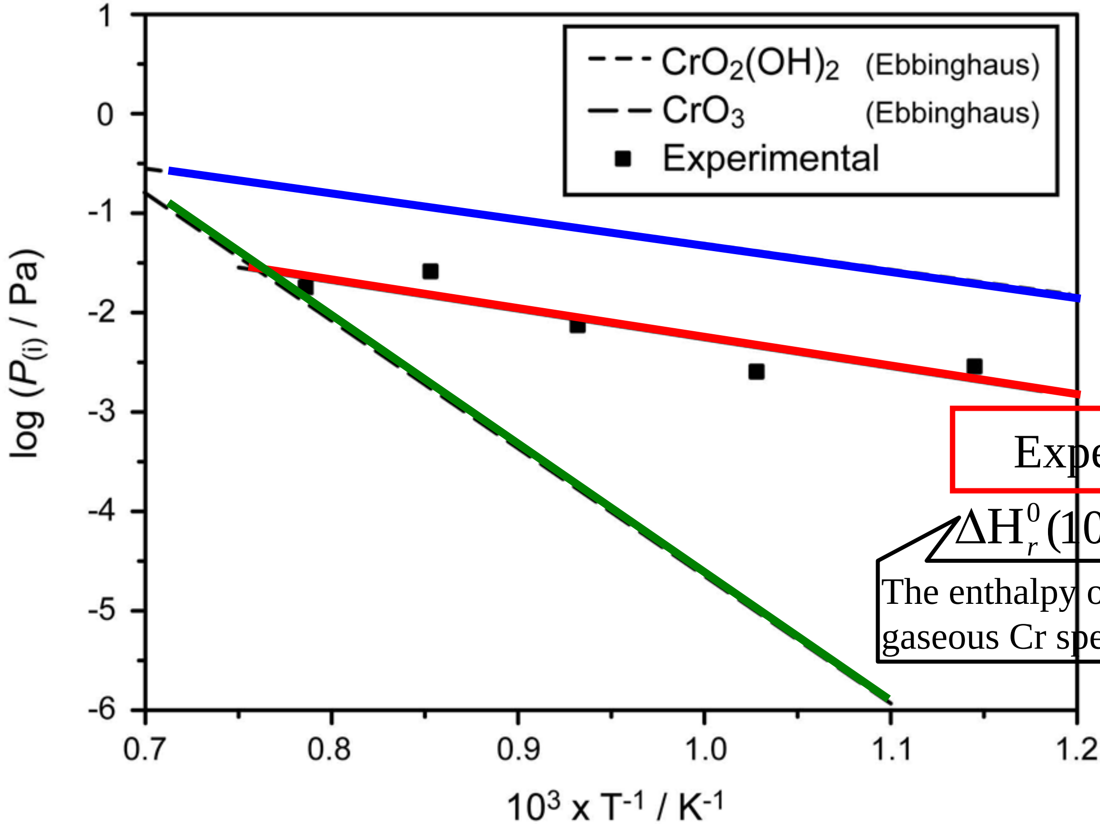


Cr transport as a function of Carrier Gas Flow Rate (Cr_2O_3)



Results - Cr vaporization from Cr_2O_3 -

- 873 ~ 1273 K, $P_{H2O} = 1.0 \times 10^4$ Pa



Experimental value

$$\Delta H_r^0(1073) = 110.1 \text{ kJmol}^{-1}$$

The enthalpy of the vaporization reaction of gaseous Cr species over Cr_2O_3(s) at 1073 K

Calculation with thermodynamic values

$$Cr_2O_3(s) + \frac{3}{2}O_2(g) + 2\ H_2O(g) \rightarrow 2\ CrO_2(OH)_2(g)$$

$$\Delta H_r^0(1073) = 124.3 \text{ kJmol}^{-1}$$

$$Cr_2O_3(s) + \frac{3}{2}O_2(g) \rightarrow 2\ CrO_3(g)$$

$$\Delta H_r^0(1073) = 469.2 \text{ kJmol}^{-1}$$

M. W. Chase et al., *JANAF Thermochemical Tables 3rd Edition* (1986).
B.B. Ebbinghaus, *Combus. Flame.*, **93** (1993) 119

Criterion measures for Cr exposure limit

- OSHA PEL (Permissible exposure limit)

  0.001 mg Cr(VI)/m^3 (TWA)
  0.5 mg Cr/m^3 (TWA) for Cr(II) and Cr(III) compounds
  1.0 mg Cr/m^3 (TWA) for chromium metal and insoluble salts.

- NIOSH REL (Recommended exposure limit)

  0.001 mg Cr(VI)/m^3 (TWA)
  0.5 mg Cr/m^3 (TWA) for chromium metal and Cr(II) and Cr(III) compounds

- NIOSH IDLH (Documentation for Immediately Dangerous to Life or Health Concentrations)

  15 mg Cr(VI)/m^3 25 mg Cr(III)/m^3

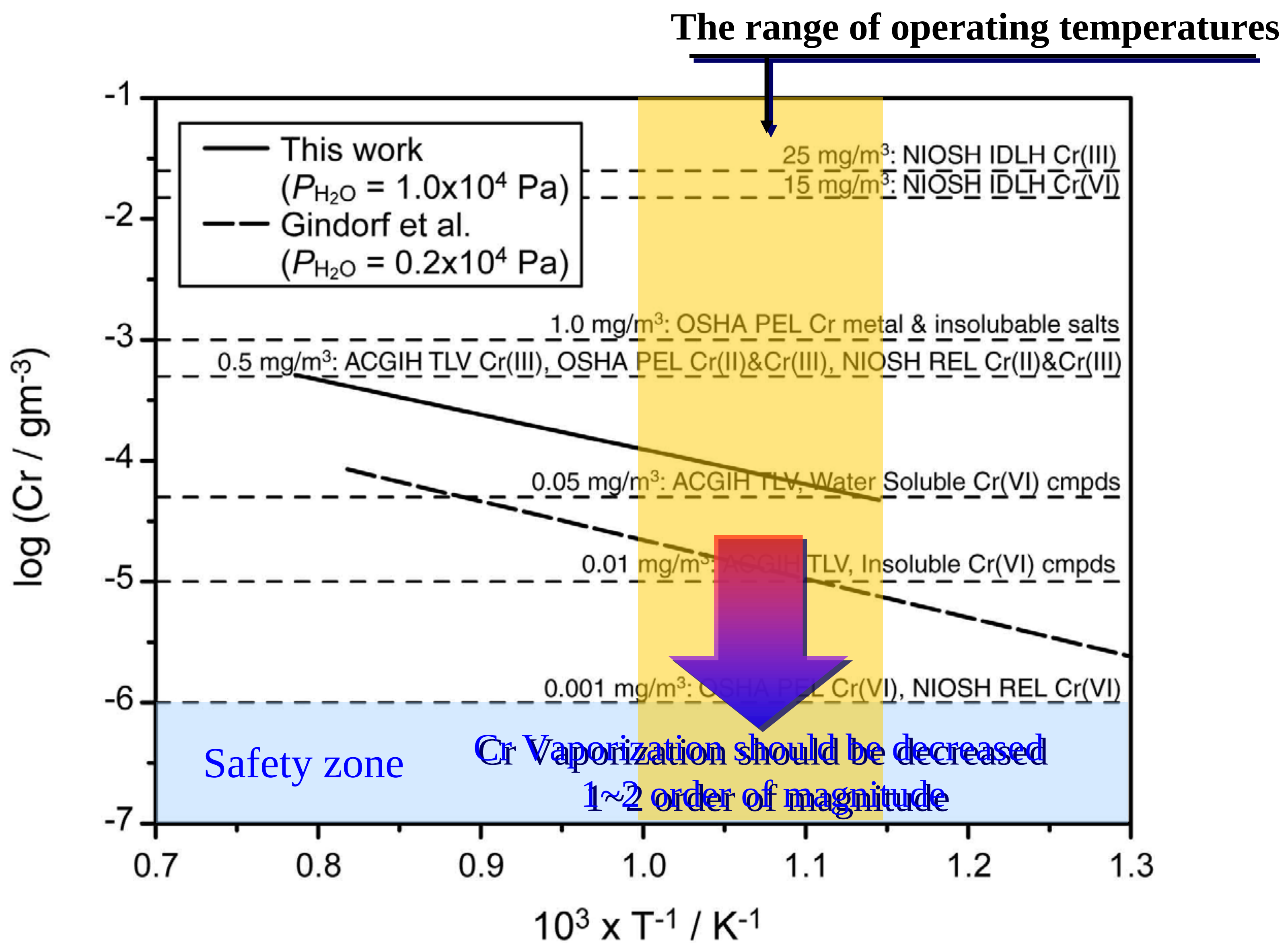
ACGIH: American Conference of Governmental Industrial Hygienists

- ACGIH TLV (Threshold Limit Value)

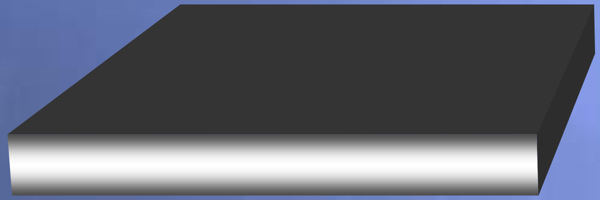
  0.5 mg Cr(III)/m^3 (TWA)
  0.05 mg Cr(VI)/m^3 (TWA) for Water Soluble Cr(VI) compounds
  0.01 mg Cr(VI)/m^3 (TWA) for Insoluble Cr(VI) compounds

TWA: the time-weighted average concentration for a conventional 8-hour workday and 40-hour workweek. This is the concentration to which it is believed nearly all workers may be repeatedly exposed, day after day, without adverse health effects.

Experimental values and exposure limits



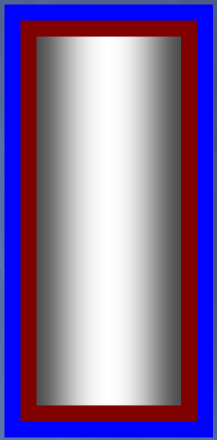
Protective Coatings



800 ^{o}C for 50 hours

LSM (Praxair) or
$MnCo_2O_4$ (glycine nitrate)
Attritor milled, dispersed with polymer binders, samples dip-coated

800 ^{o}C for 50 hours



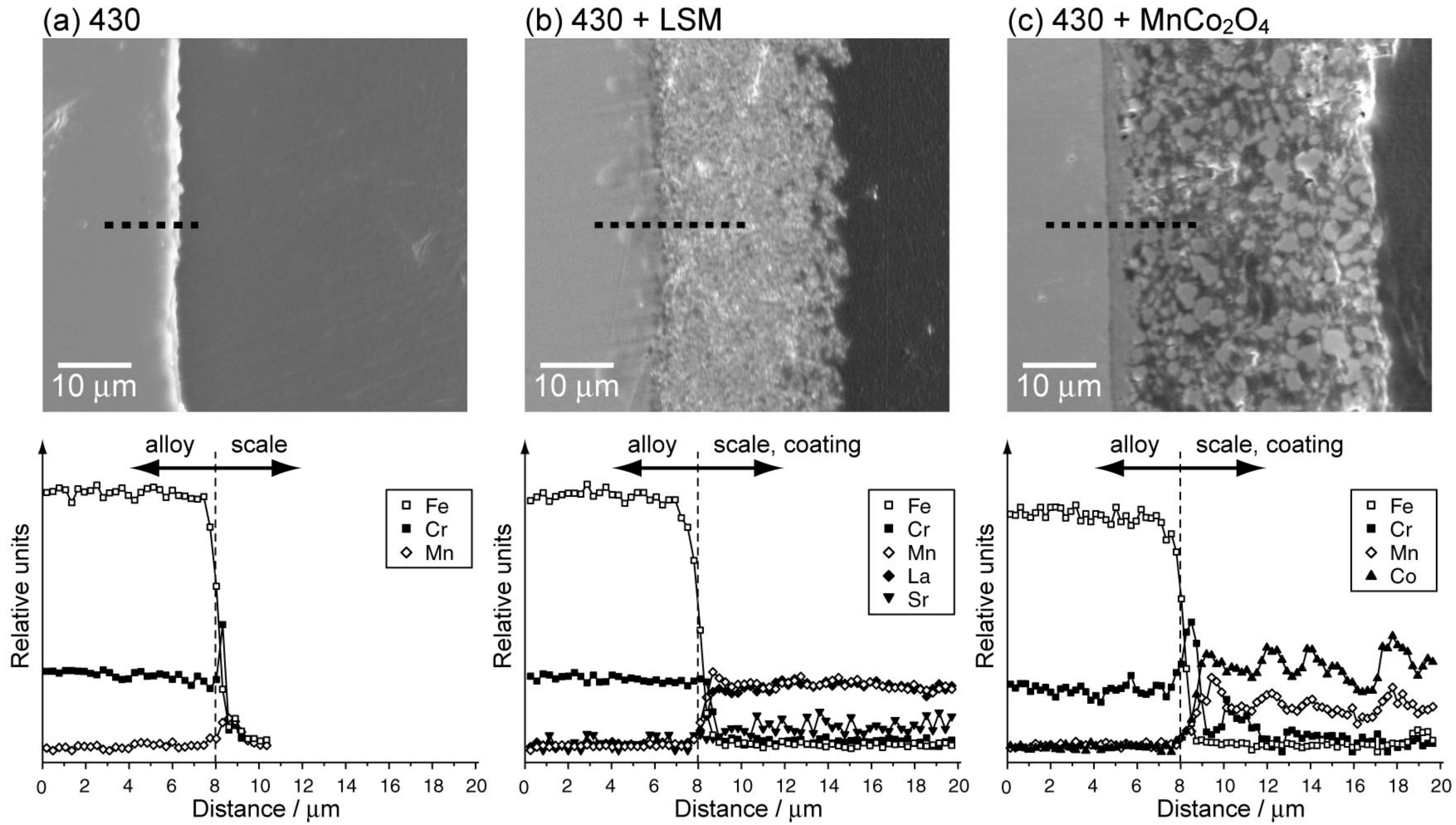
Results – Uncoated and coated 430 -

- 1073 K, 86.4 ks (24 hrs), P_{H2O} = 1.0×10^4 Pa, 3.33×10^{-6} m^3s^{-1} (200ml/min)

Sample	Cr transport rate / $ngm^{-2}s^{-1}$	Comparative reduction factor
Uncoated 430	968	-
430 + LSM (dip)	32	~30
430 + $MnCo_2O_4$ (dip)	337	~3

Results – Uncoated and coated 430 -

- 1073 K, 86.4 ks (24 hrs), P_{H2O} = 1.0x10^4 Pa, 3.33x10^{-6} m^{3}s^{-1} (200ml/s)



Improved $MnCo_2O_4$ Coatings

(a) GNP (b) AHC co-precipitation

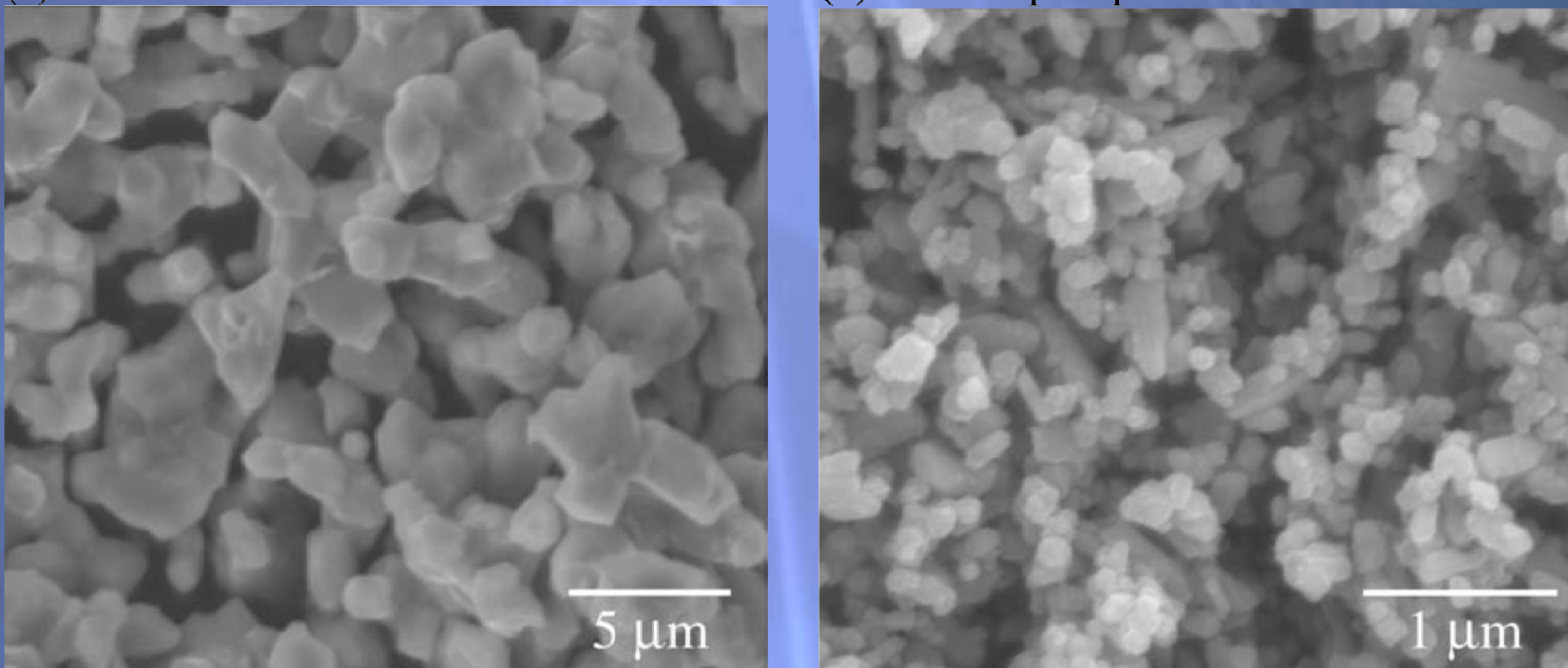
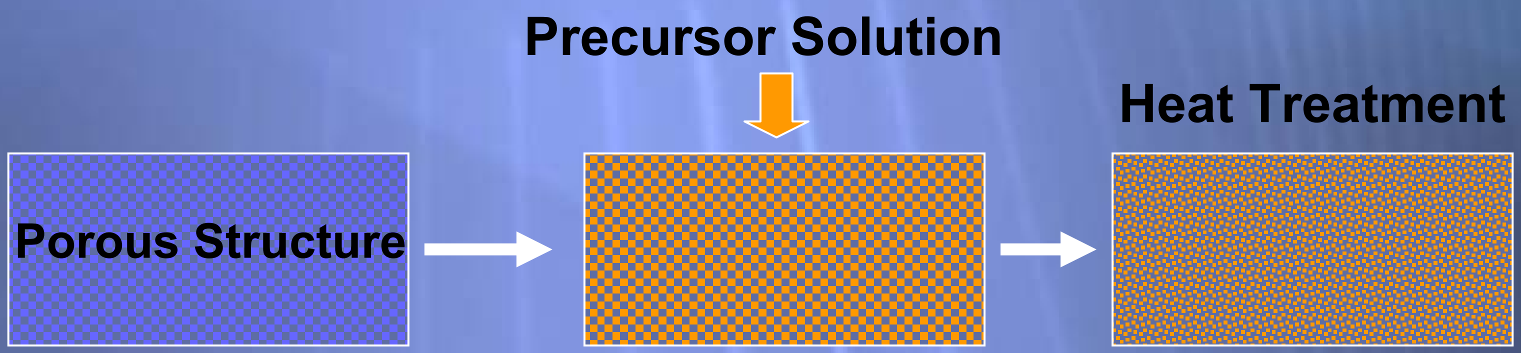


Fig. 4 Secondary electron micrographs of $MnCo_2O_4$ powder synthesized via GNP (glycine nitrate combustion synthesis) and AHC co-precipitation methods.

Cr Vaporization: Next Steps

- Measure Cr vaporization from S.S. with improved $MnCo_2O_4$ coatings
- Novel coatings - LBNL and industry teams
- Arcomac has provided coated samples
  - 1) Crofer 22 APU (uncoated)
  - 2) Crofer 22 APU (2 hrs CrCoAlY/Al/O + 30min CoMnO)
  - 3) Crofer 22 APU (CoMnO only)
- Cr vaporization measurements are complete (waiting for ICP-MS results)

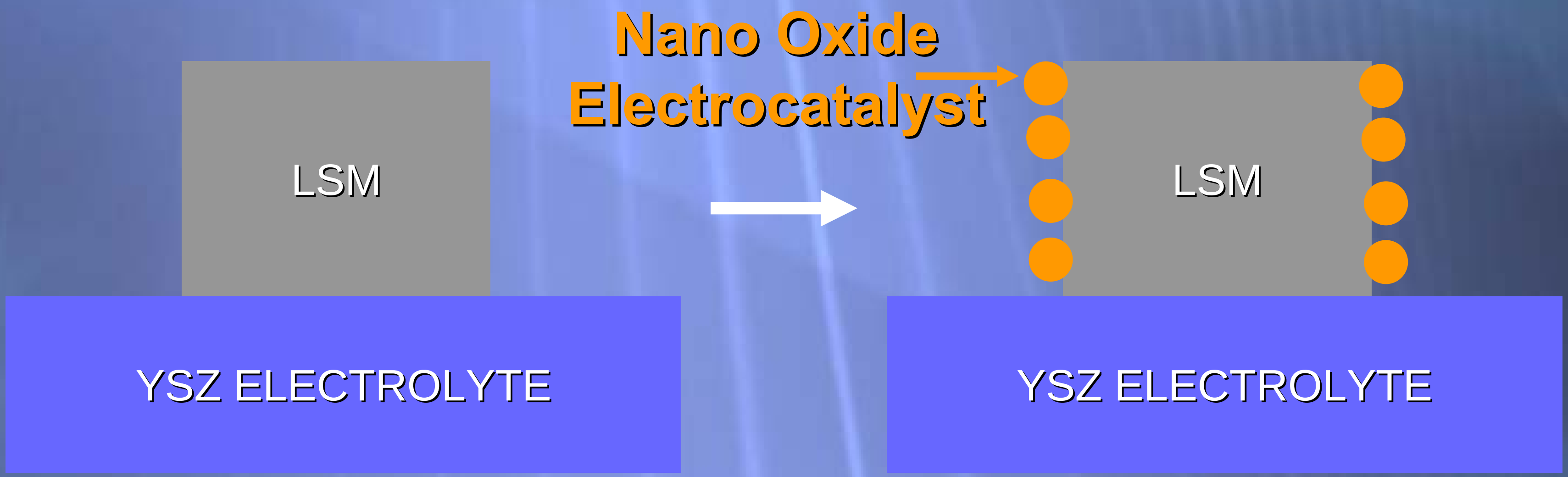
Infiltration Approach



- A low-temperature processing technique
  - Allows use of electrode materials unsuitable for high-temp fabrication
  - Create nano-structured features

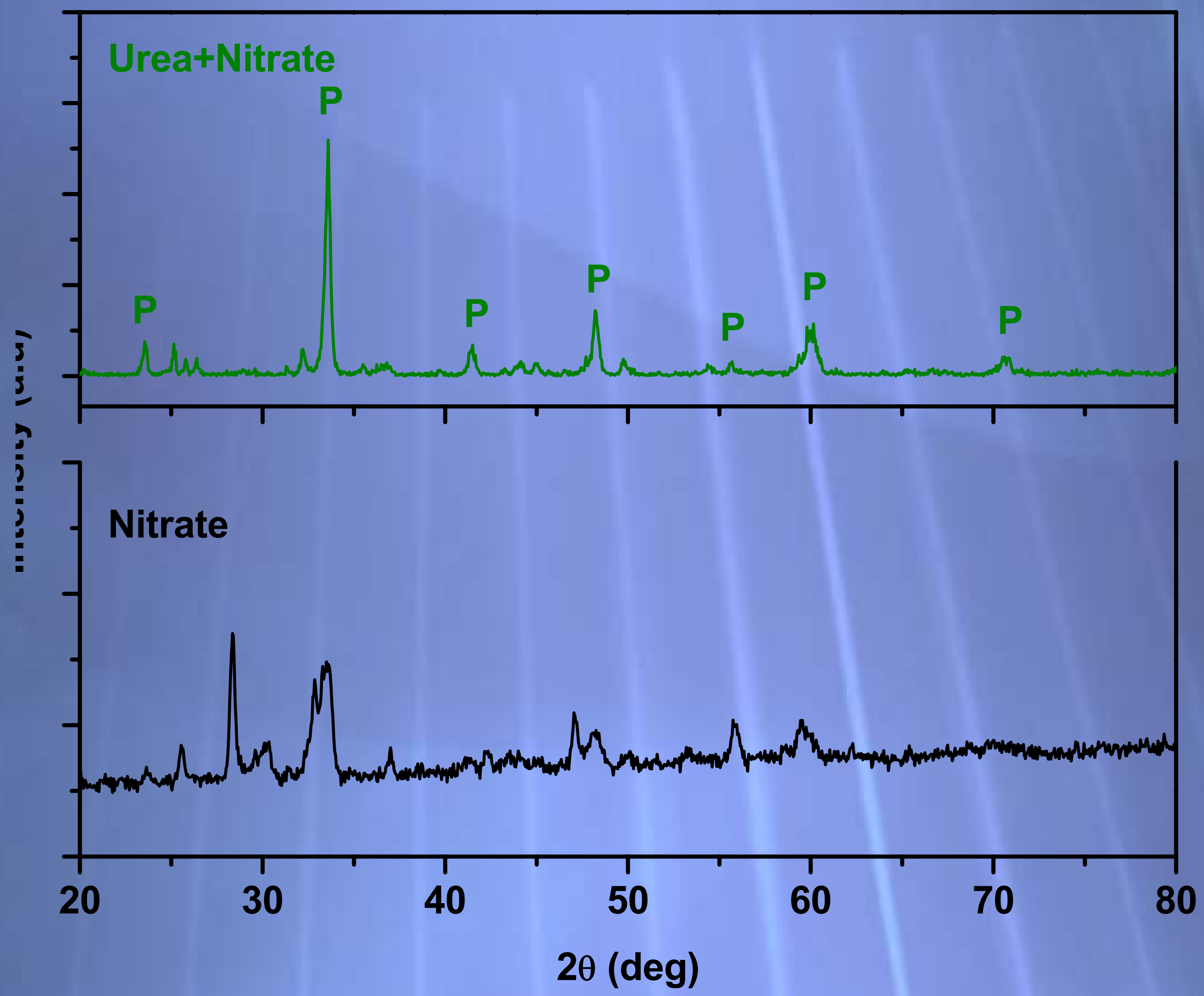
I. Improving LSM-YSZ Cathode Performance With Nano $Sm_{0.6}Sr_{0.4}CoO_{3-\delta}$ (SSC) Particles

Objective



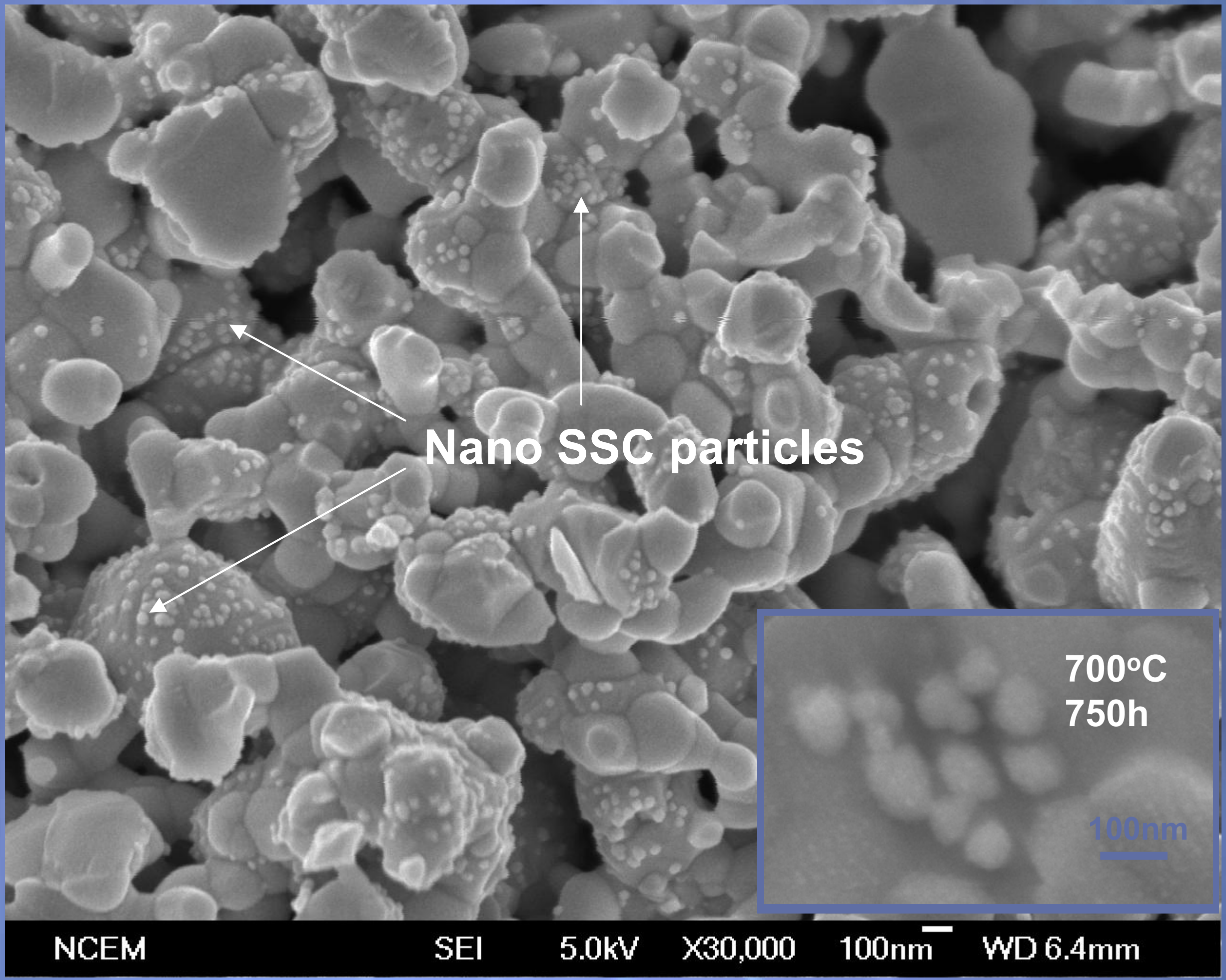
Introducing nano oxide electrocatalyst into LSM-YSZ cathodes enhances the oxygen reduction reaction and reduces cathode polarization at low temperatures

Synthesis of SSC at Low Temperatures

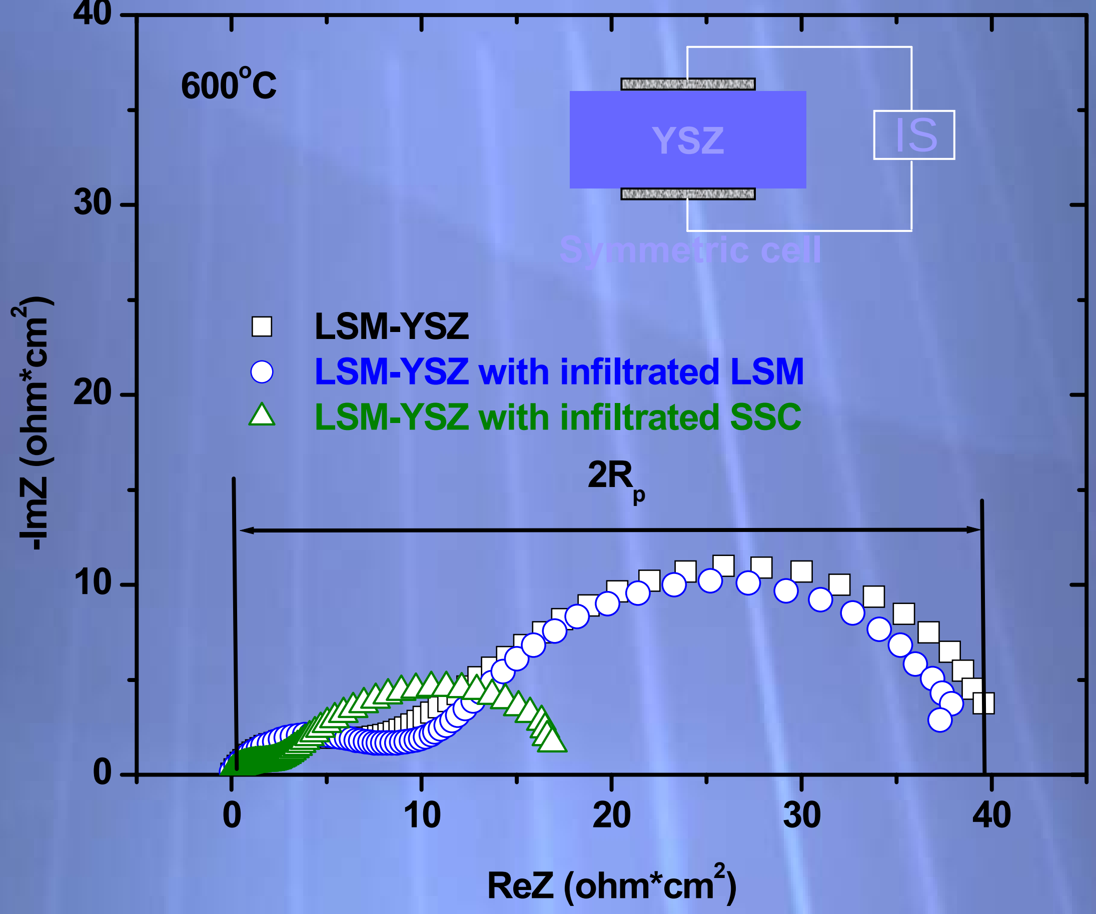


800°C; 2h

SEM Images of Fractured LSM-YSZ-SSC Cathodes

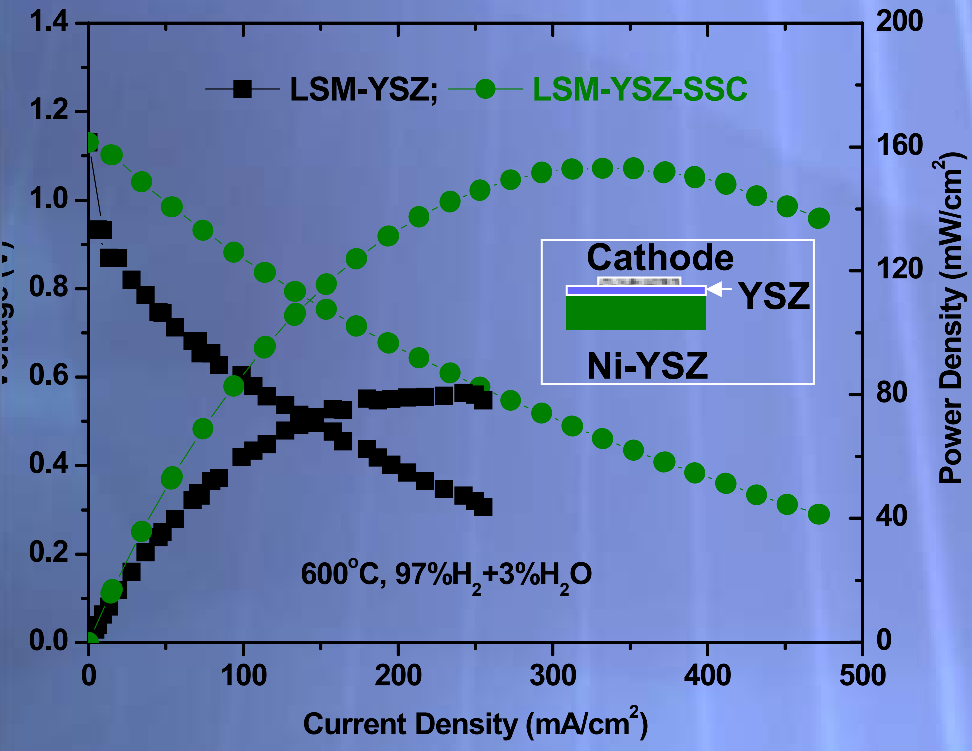


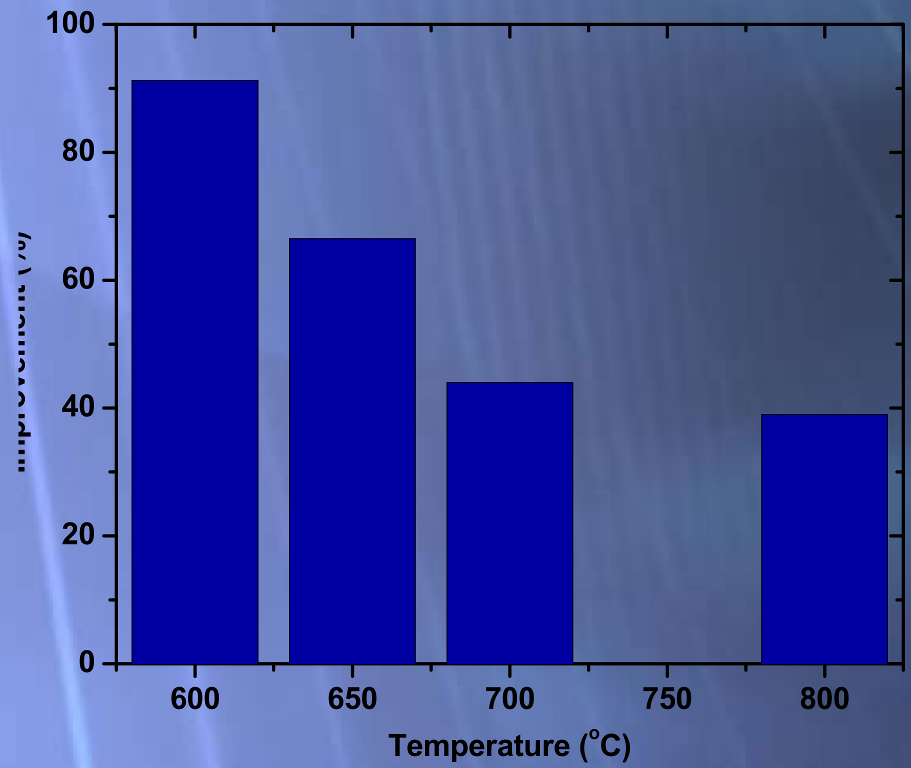
SSC Reduces Cathode Polarization Resistance



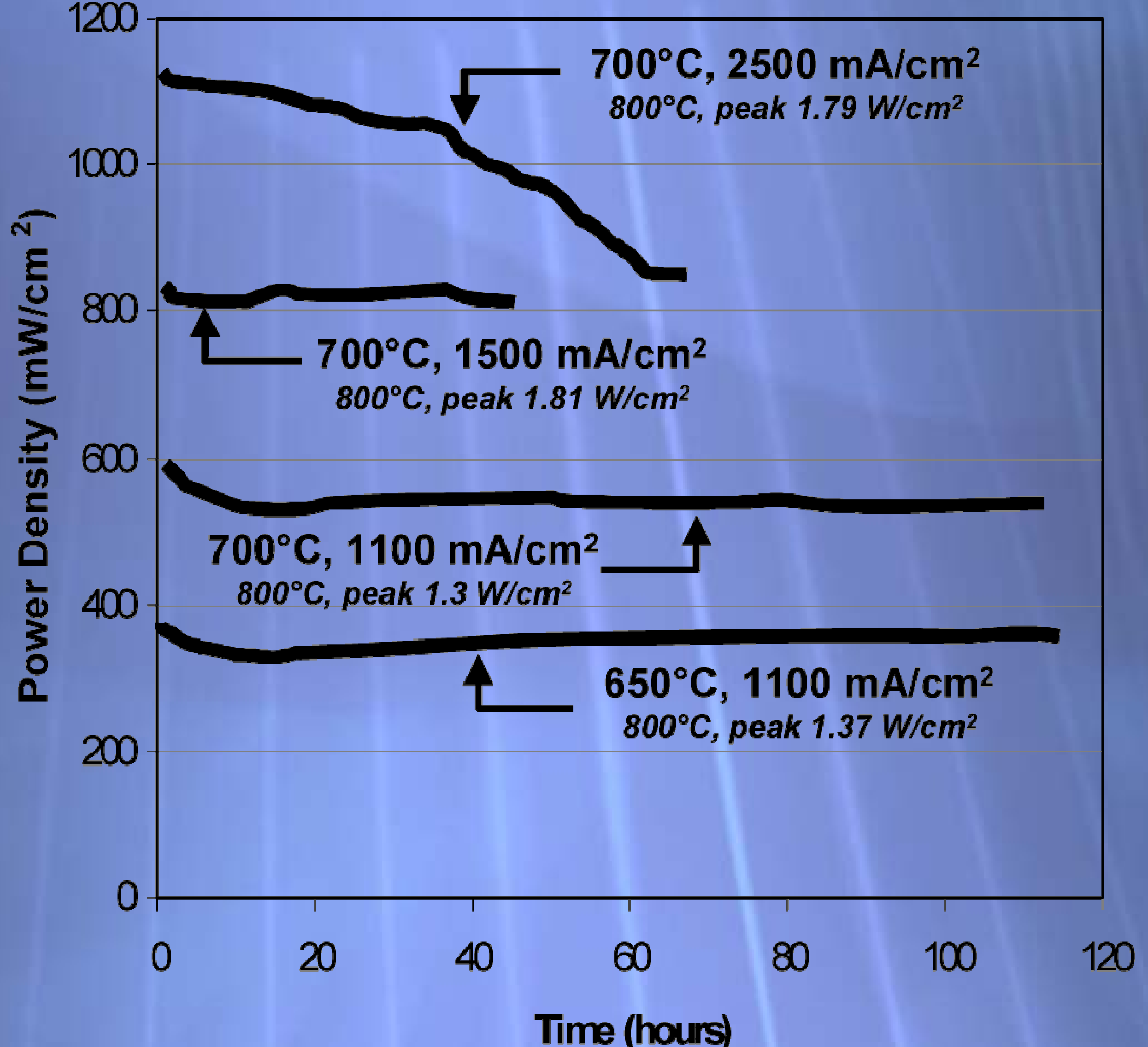
R_p: Cathode Polarization Resistance

SSC Particles Enhance Cell Performance



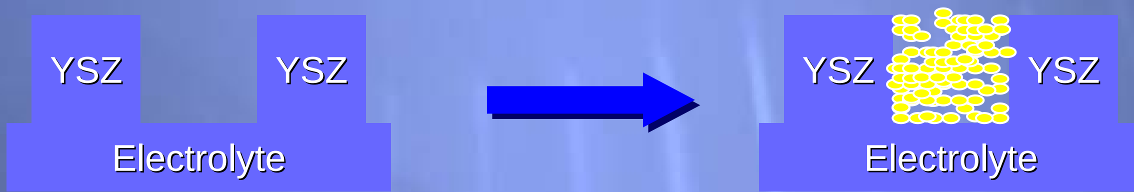


Stability of Co-Infiltrated LSM

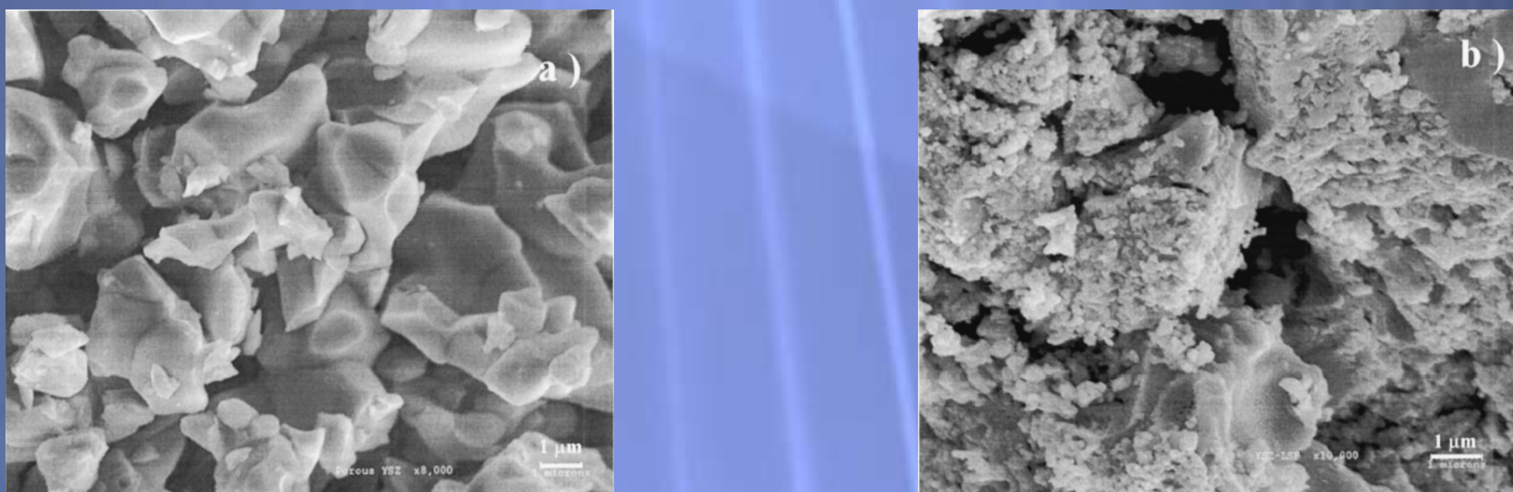


II. Complete Infiltration of SOFC Cathodes into Porous YSZ in a Single-Step

Background



Perovskite
$La_{1-x}Sr_xFeO_3$ etc.



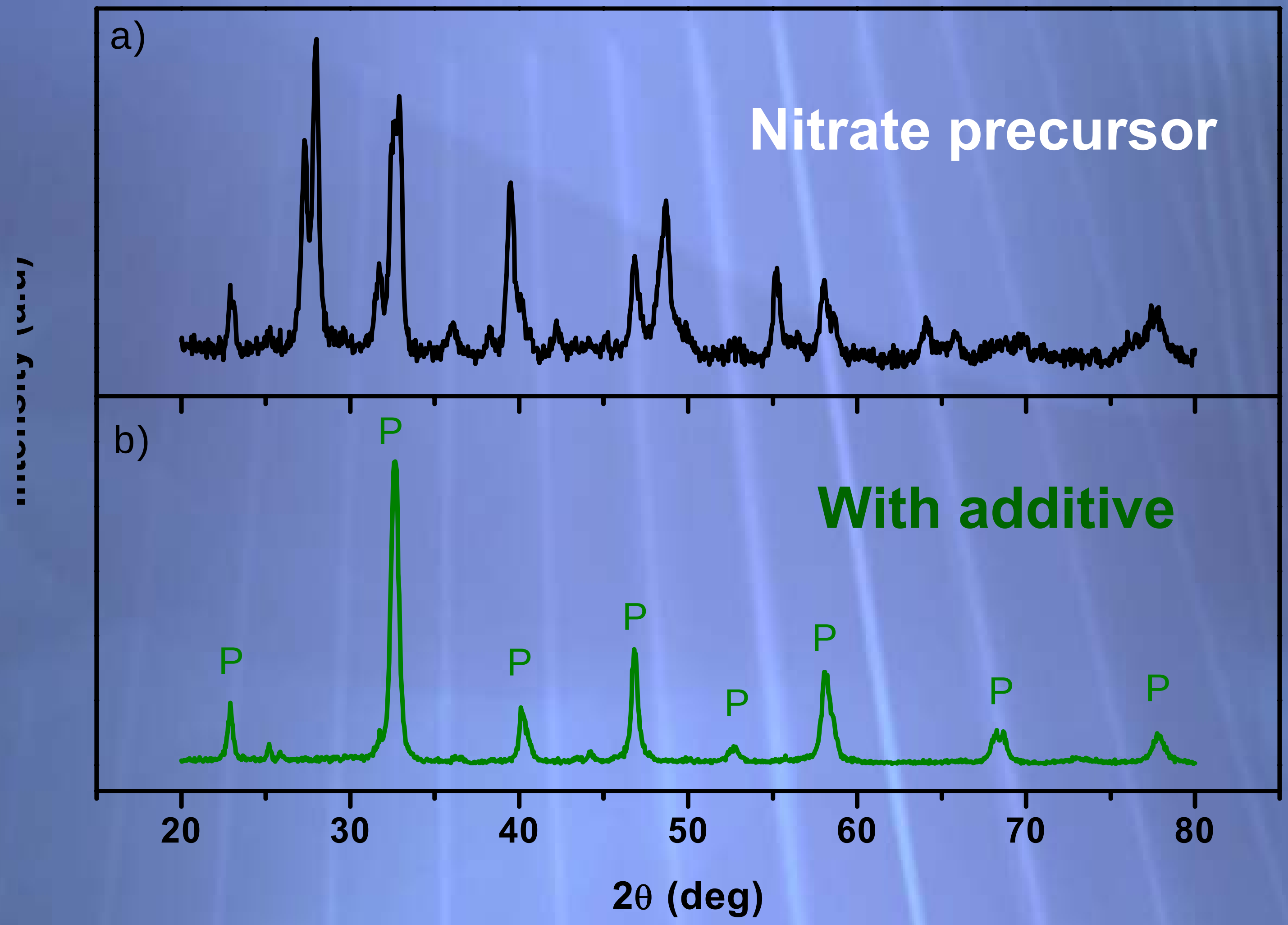
Y. Huang, J. M. Vohs, and R. J. Gorte, *J. of Electrochem. Soc.*, 151, A646 (2004).

- Require multiple infiltration steps to add sufficient material for percolation through porous YSZ networks
- Randomly-distributed material decreases porosity and may impede gas-phase diffusion

Goals

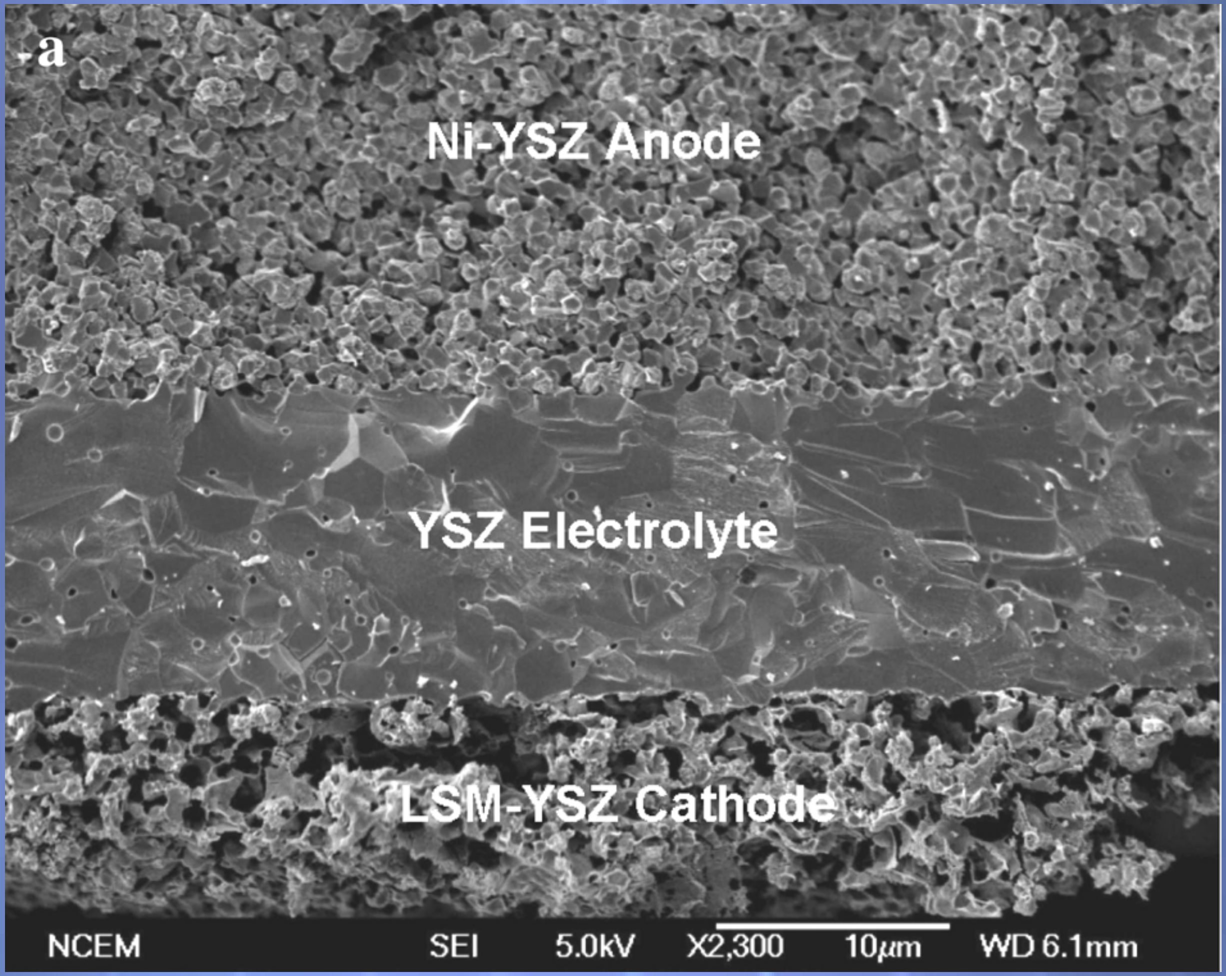
- One-step infiltration to form cost-effective electrodes
- Nano-sized materials distributed in a mono-layer fashion

Need Additive

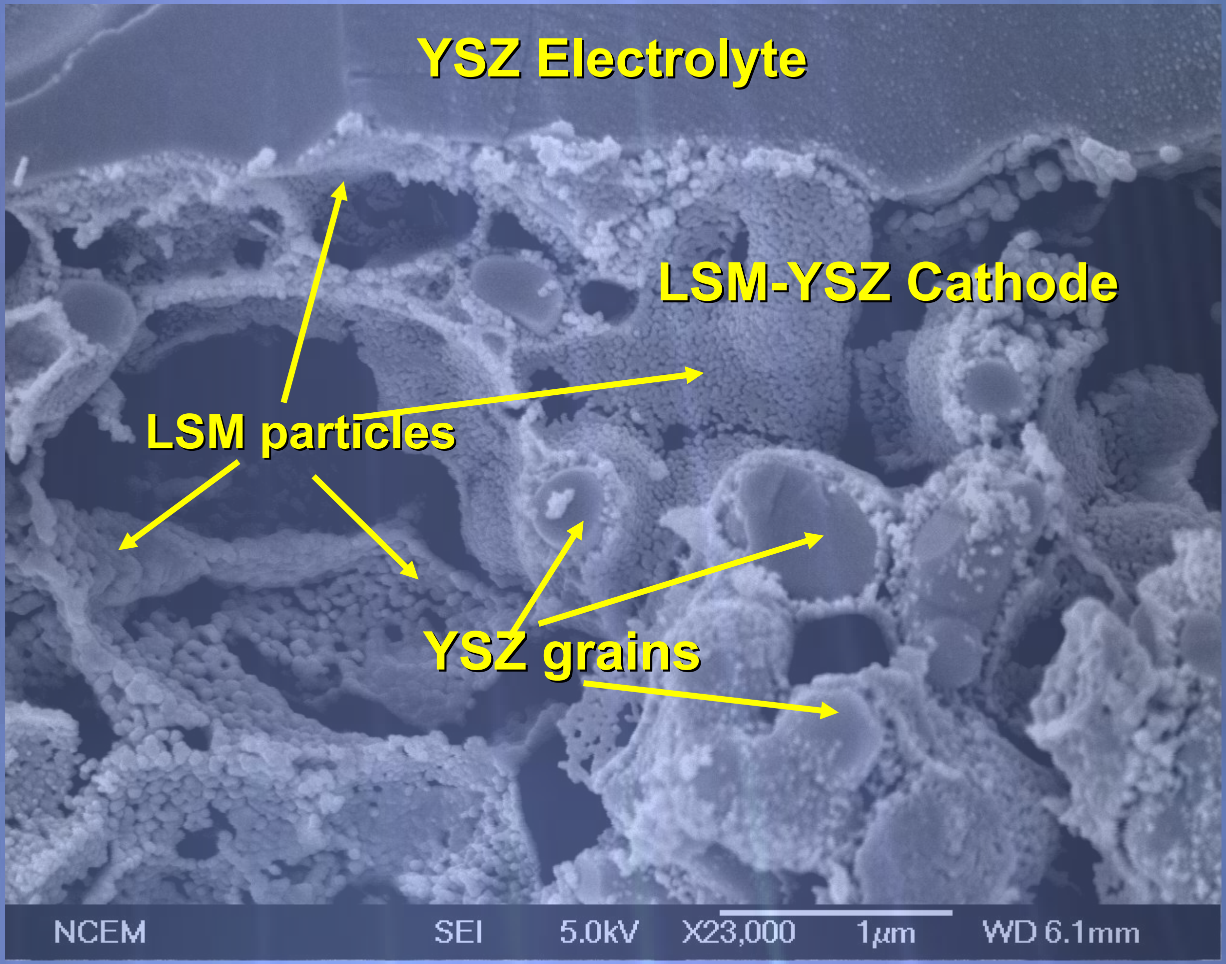


800°C, 2h

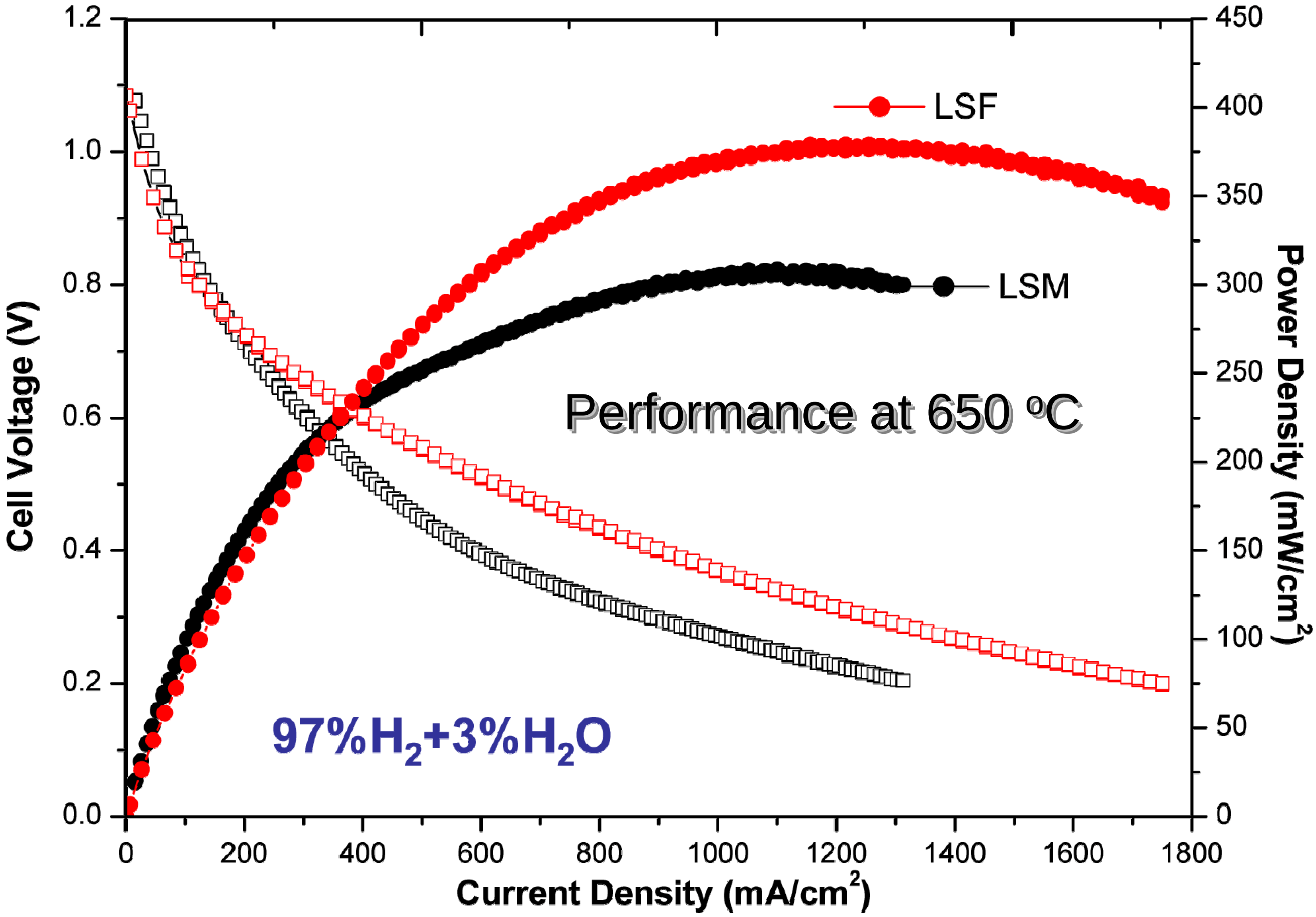
SEM Image of a Single-Step Infiltrated LSM-YSZ Cathode



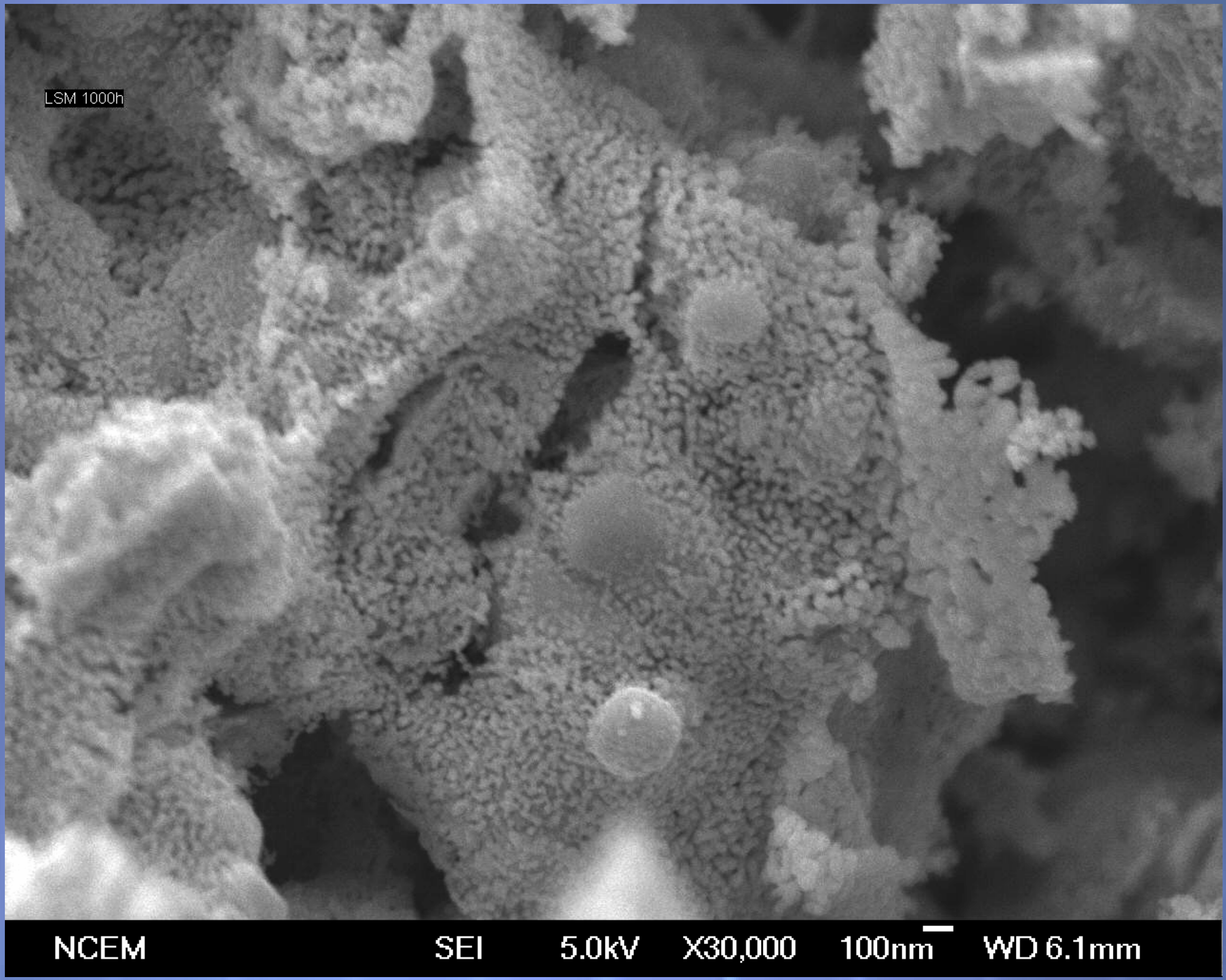
HRSEM Image of an LSM-YSZ Cathode



Performance of SOFC with Single-step Infiltrated LSM-YSZ and LSF-YSZ Cathodes

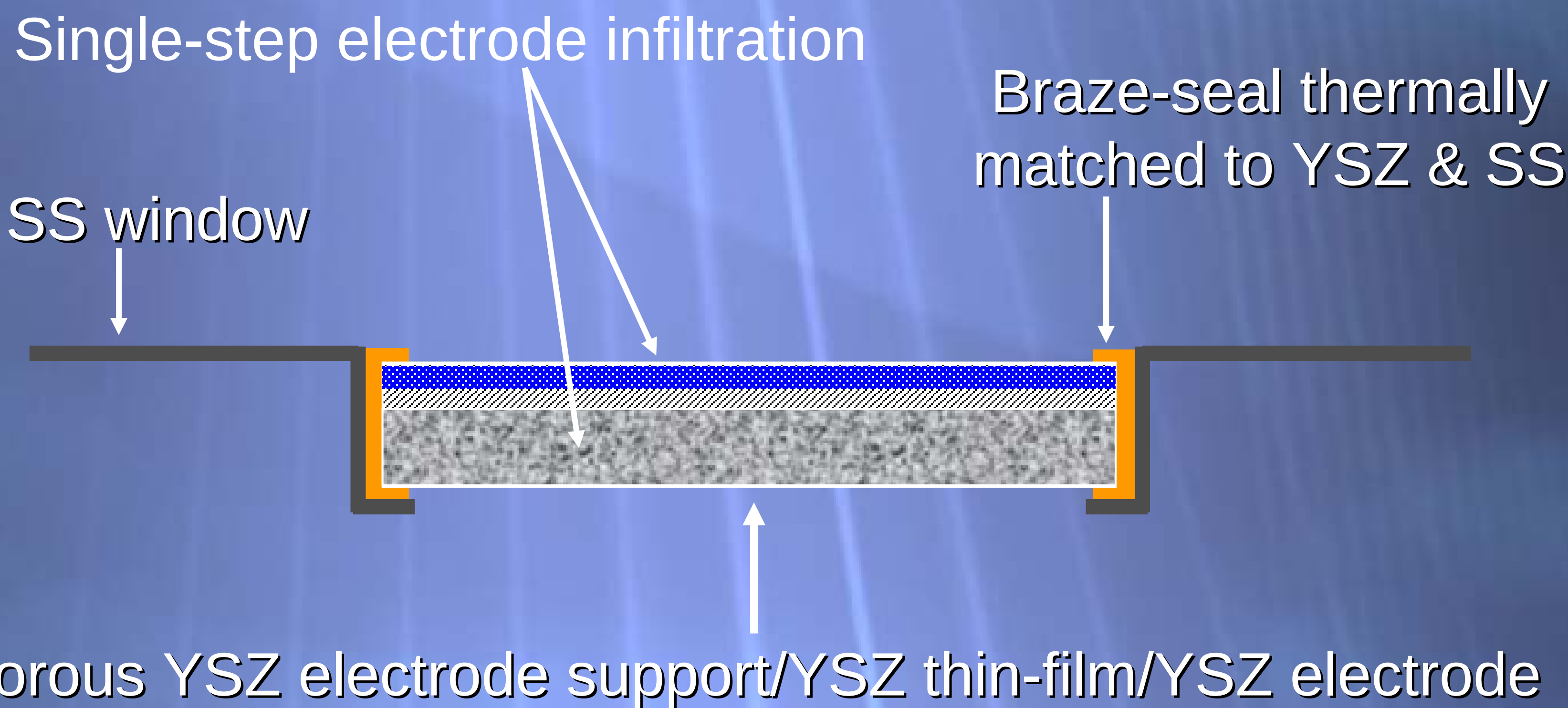


Stability of the LSM-YSZ Cathode



After 1000h @ 700°C

Simplified SOFC Manufacture



Summary

- Chromium volatilization from Cr_2O_3 exposed to moist air at 700 to 900 ^oC is an order of magnitude lower than expected from thermodynamic calculations.
- Coatings are effective physical barriers to Cr vaporization from metal interconnects exposed to moist air (factors of 3 to 30 reduction observed for porous coatings)
- Incorporating nano-sized $Sm_{0.6}Sr_{0.4}CoO_{3-\delta}$ particles into LSM-YSZ cathodes dramatically improves cathode and cell performance at low temperatures.
- Due to the unique distribution of SSC particles in the cathode, they appears very resistant to coarsening at 700^{o}C.
- SOFC cathodes (e.g. LSM-YSZ) can be effectively fabricated using an single-step infiltration approach.
- Single-step infiltration led to nano-sized LSM covering the surface of porous YSZ networks in a monolayer distribution; performance at low temperature was quite good.
- Single-step infiltration and braze seals may lead to low-cost SOFCs.