Improvement of SOFC Electrodes through Catalyst Infiltration & Control of Cr volatilization from FeCr components

Steven J. Visco, Craig Jacobson, Hideto Kurokawa, Tal Sholklapper, Chun Lu, and Lutgard De Jonghe

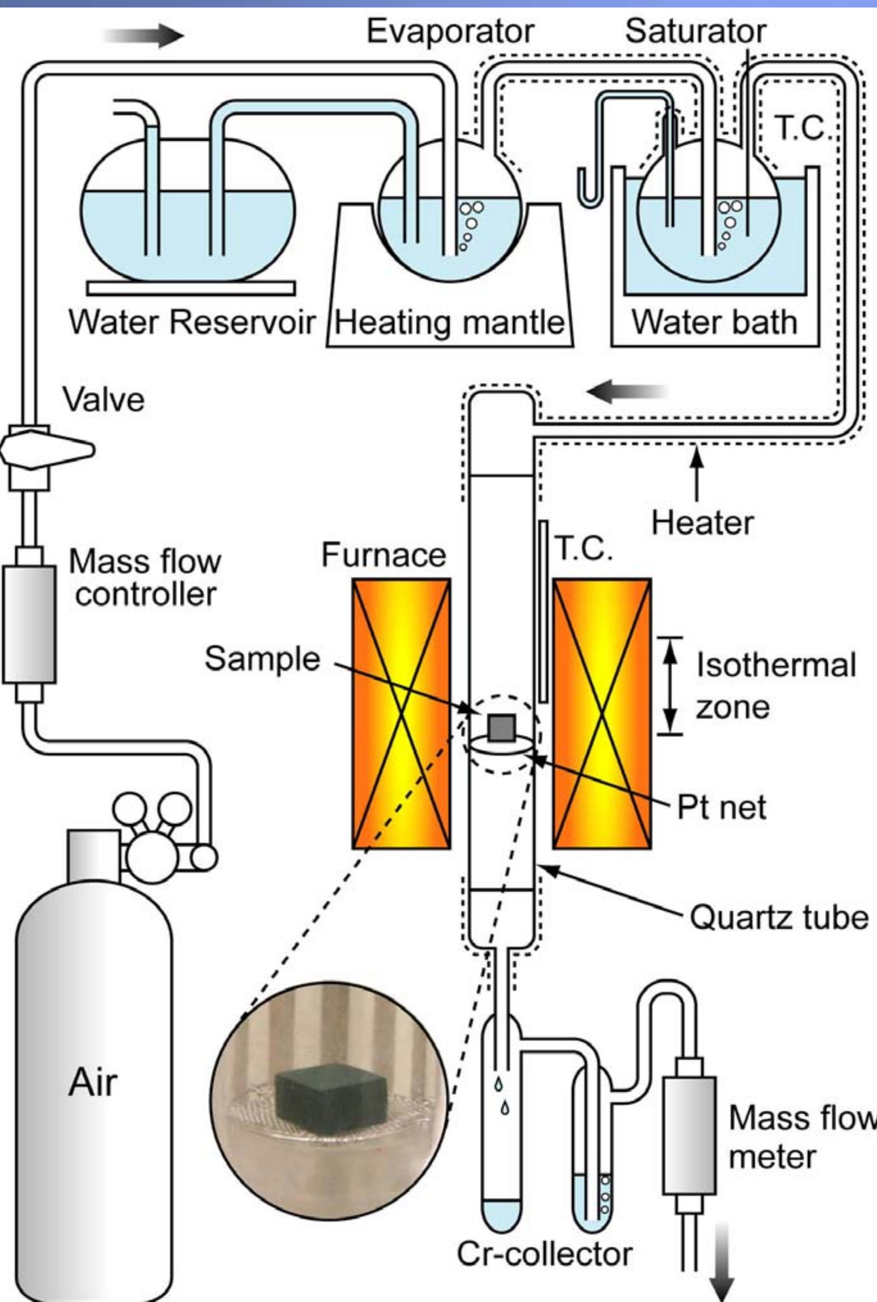
Materials Science Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

BERKELEY LAB

Motivation for LBNL Work

- Use of metal interconnects introduces problems of Cr_2O_3 scale growth and Cr volatilization on cathode side
- Lower temperature operation reduces scale growth problem
- Lower temperature operation permits the use of TEC matched braze seals under development at LBNL
- Lower temperature operation reduces electrode performance, however, performance can be significantly improved by catalyst infiltration
- Single-step electrode infiltration under development at LBNL allows novel cell manufacture

Cr Volatilization I



P_{H_2O}

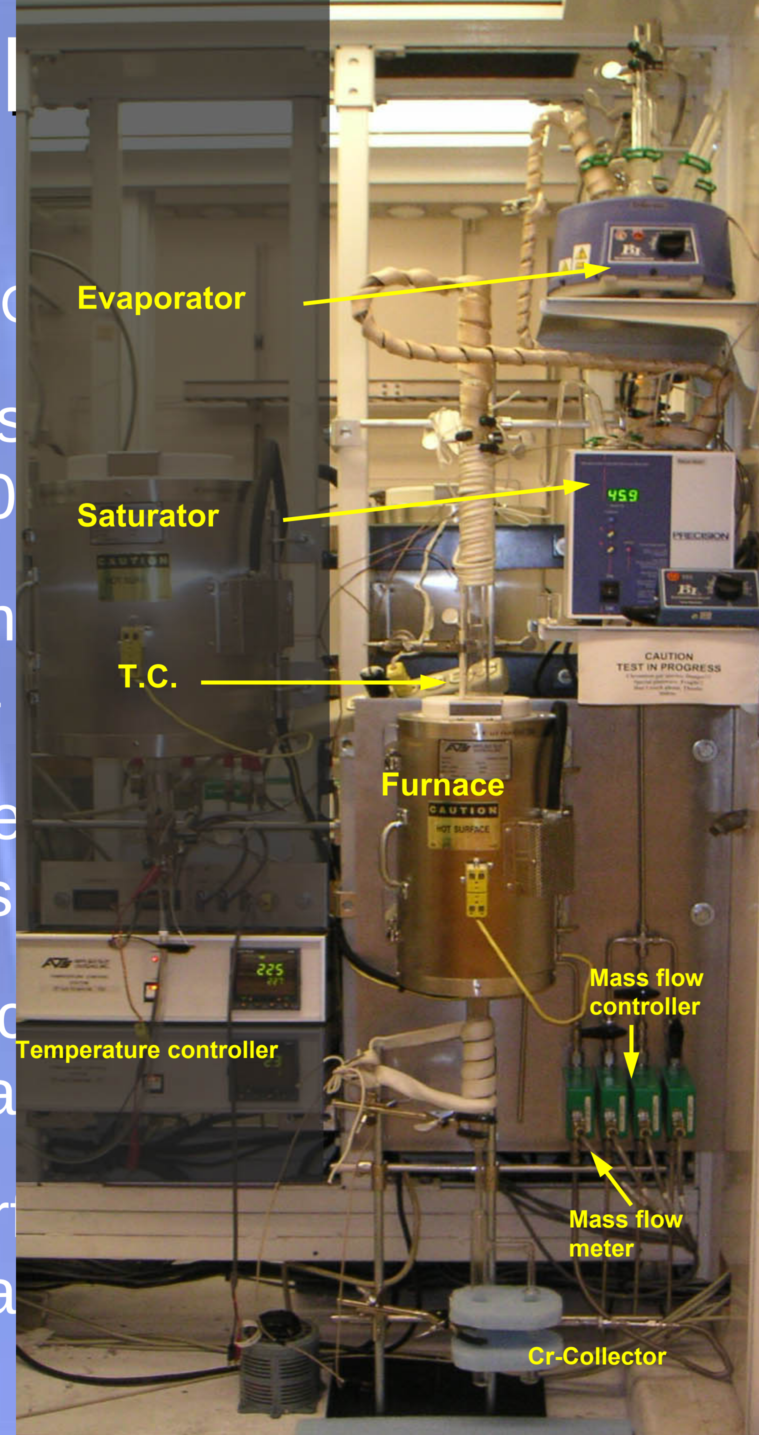
Cr s
700

Tim
(24

Afte
rins

Cr c
ana

Surf
ana



es

Sample Preparation

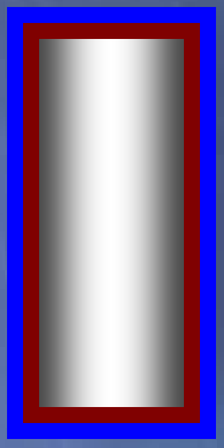
- Baseline tests done with 99.8% Cr_2O_3
- Cr_2O_3 samples 10 x 10 x 6 mm, ground and polished with 0.5 μm diamond paste
- 430 SS (Fe-16Cr) 15 x 14 x 0.6 mm ground and polished with 0.5 μm diamond
- Some SS alloys samples coated with LSM ($La_{0.65}Sr_{0.3}MnO_{3-x}$) or $MnCo_2O_4$
- Coated and uncoated alloy samples pre-oxidized at 800 ^{o}C for 50 hours

Protective Coatings

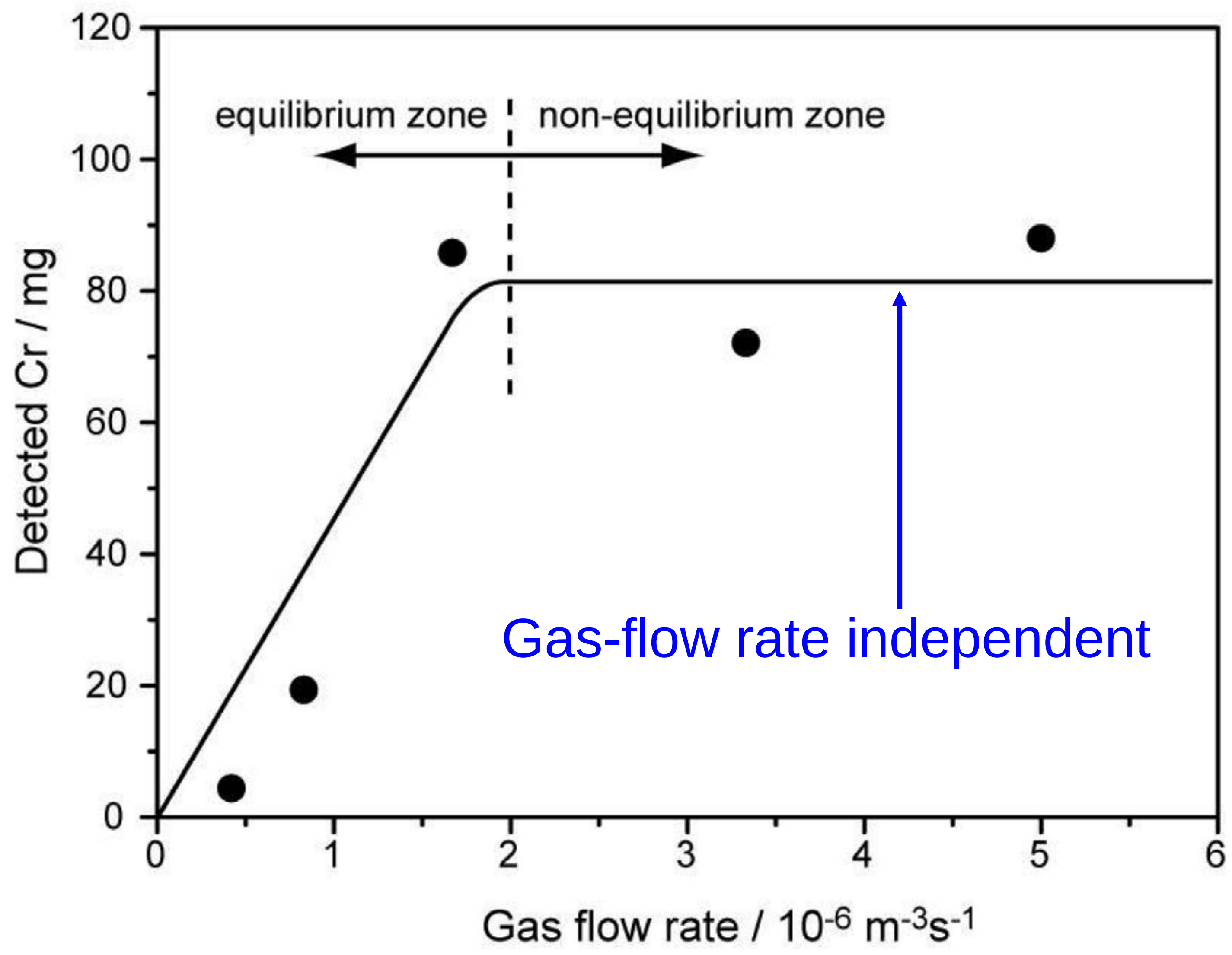
800 ^{o}C for 50 hours

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

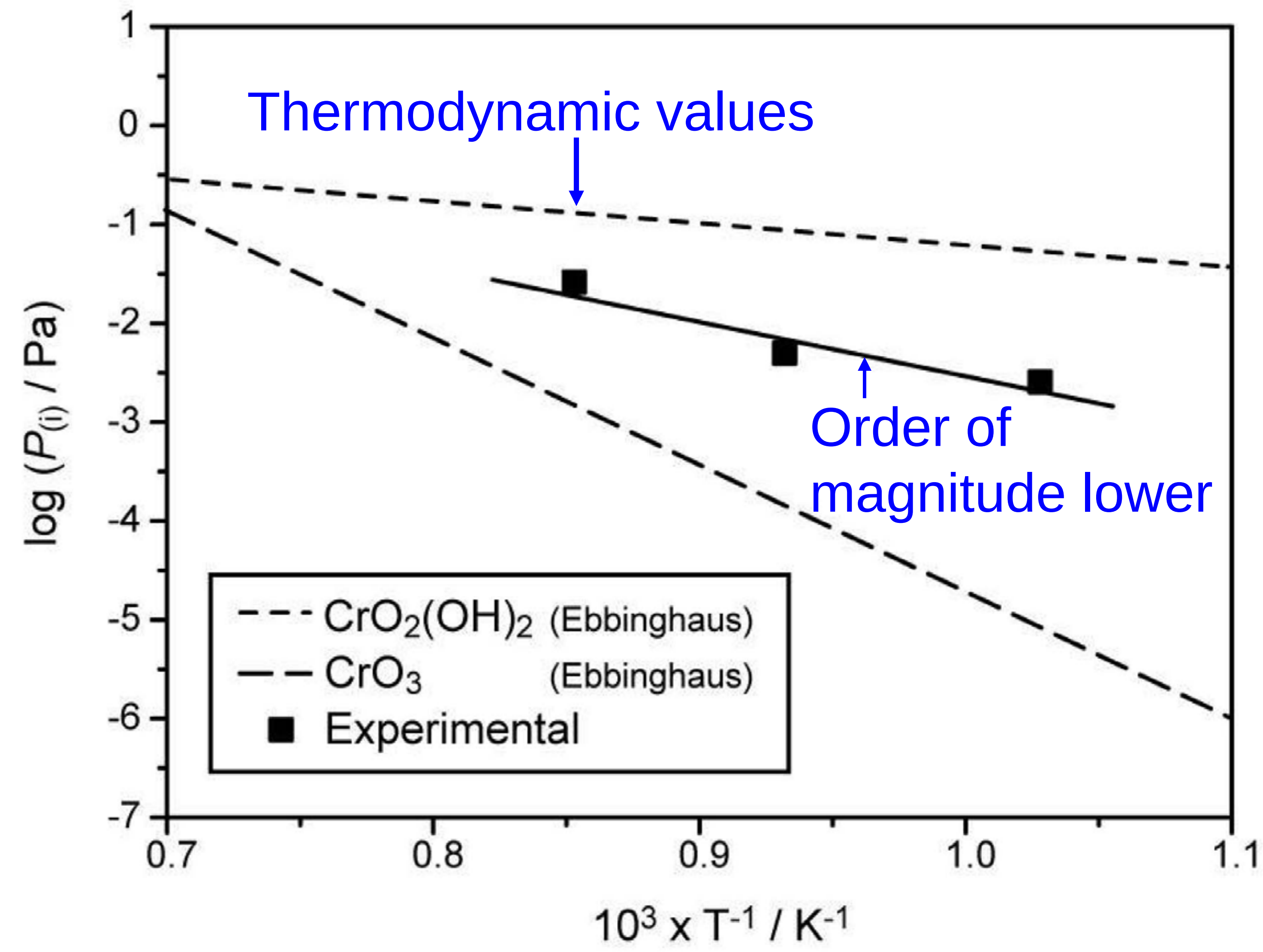
800 ^{o}C for 50 hours



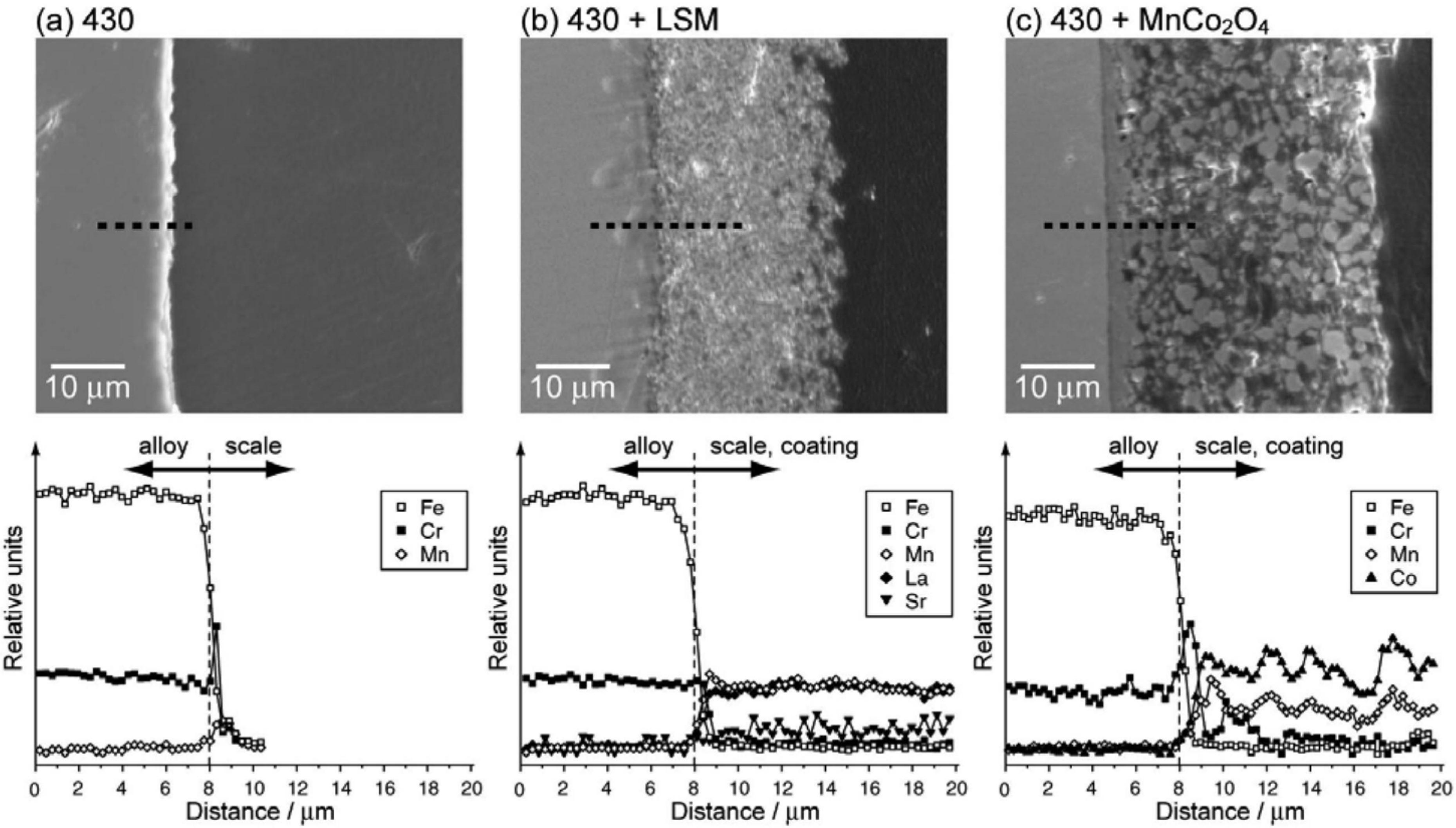
Cr transport as a function of Carrier Gas Flow Rate (Cr_2O_3)



Temperature Dependence of Chromium Vaporization for Cr_2O_3 Exposed to Moist Air



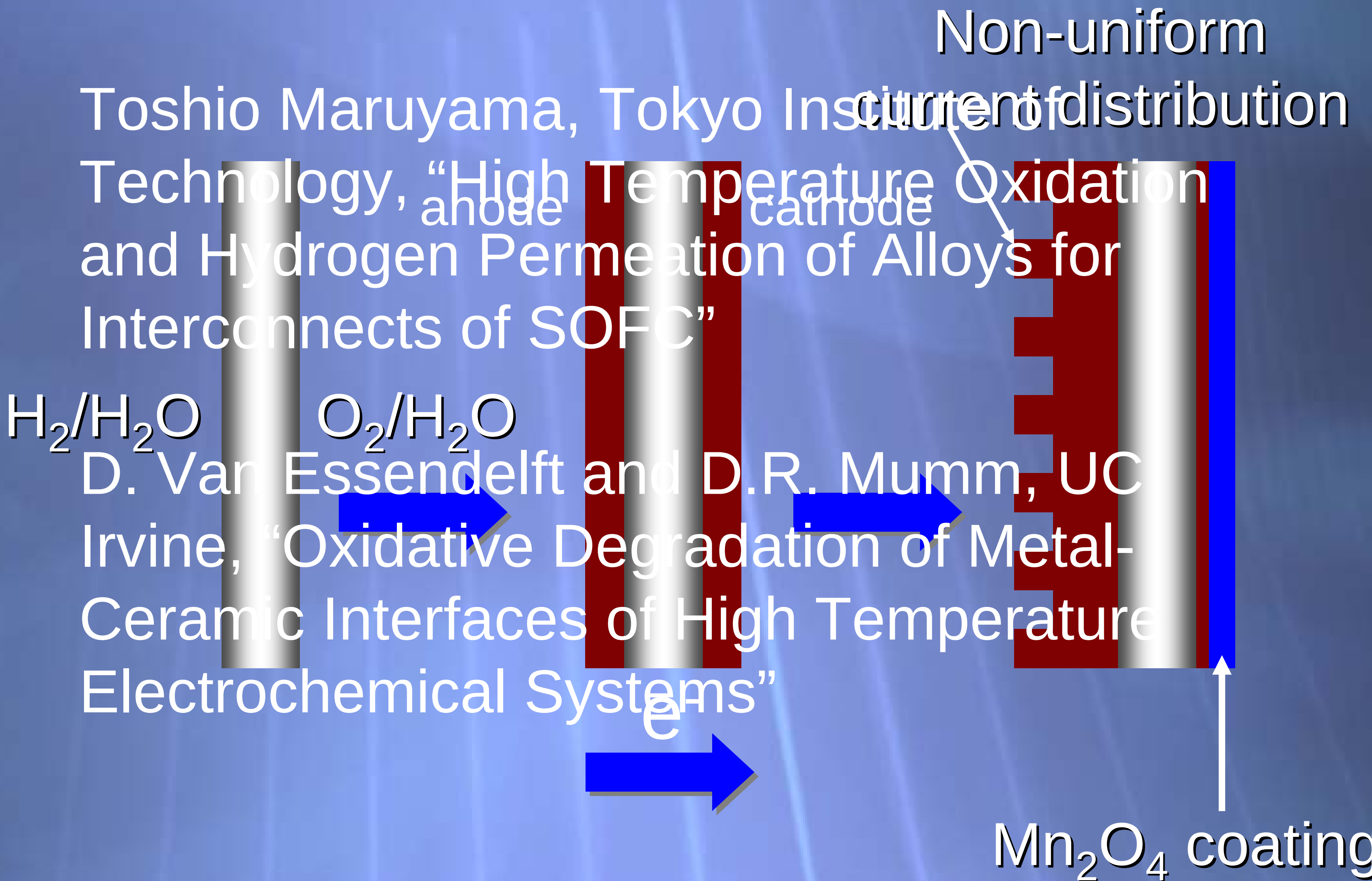
Control of Cr Vaporization



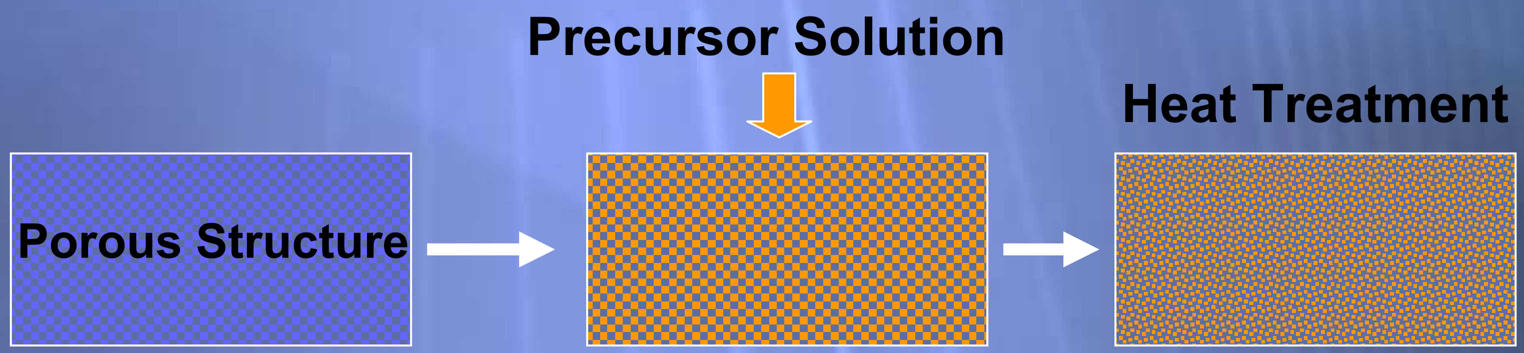
Asymmetric Scale Growth Under Current

Toshio Maruyama, Tokyo Institute of Technology, “High Temperature Oxidation and Hydrogen Permeation of Alloys for Interconnects of SOFC”

D. Van Essendelft and D.R. Mumm, UC Irvine, “Oxidative Degradation of Metal-Ceramic Interfaces of High Temperature Electrochemical Systems”



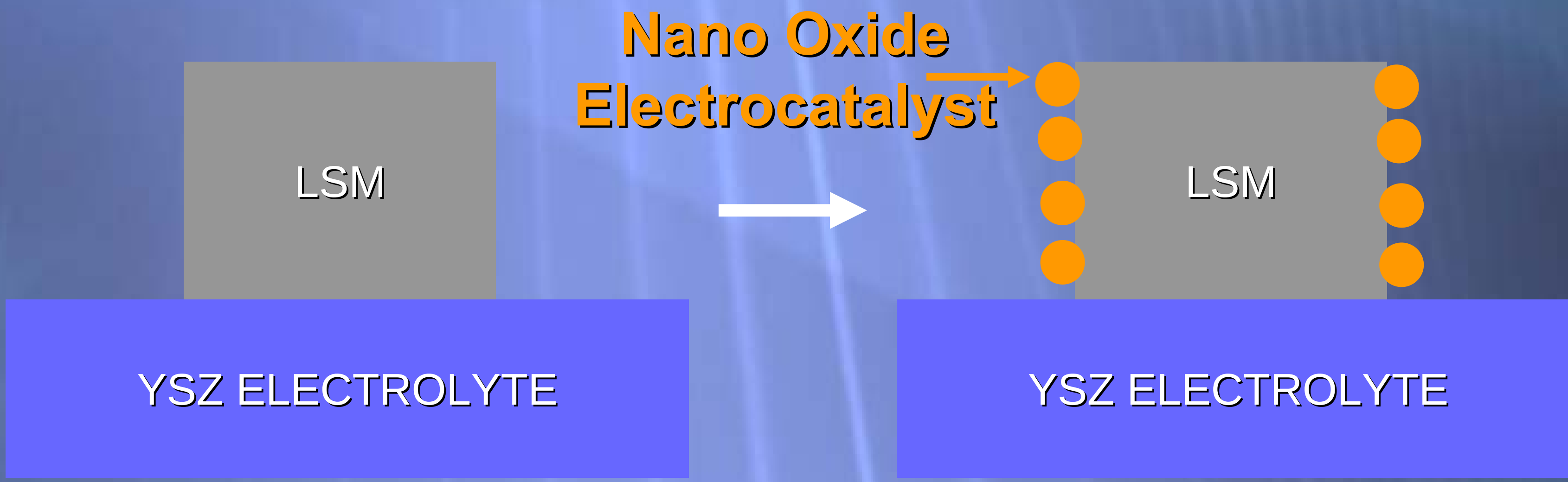
Infiltration Approach



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

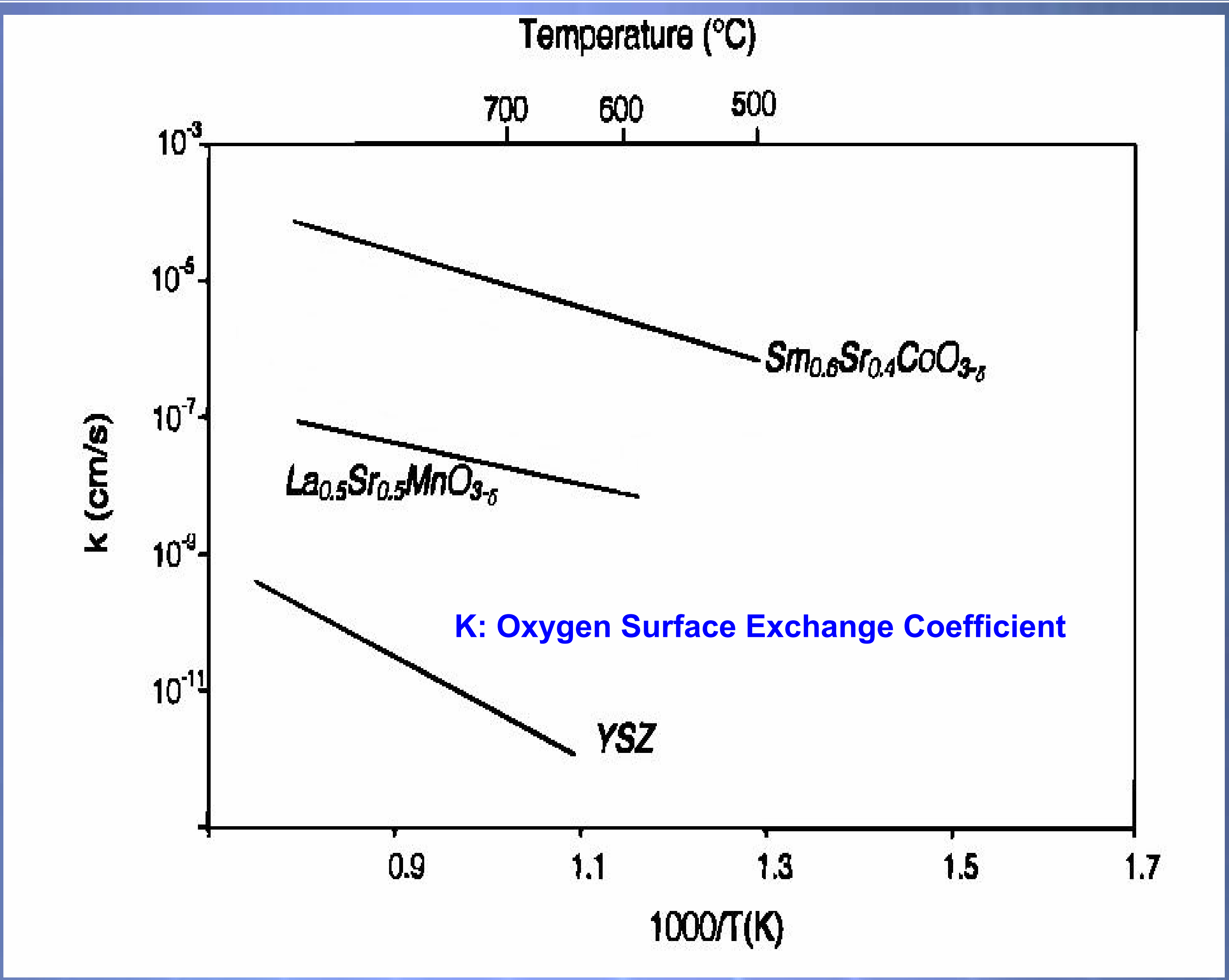
I. Improving LSM-YSZ Cathode Performance With Nano $Sm_{0.6}Sr_{0.4}CoO_{3-\delta}$ (SSC) Particles

Objective



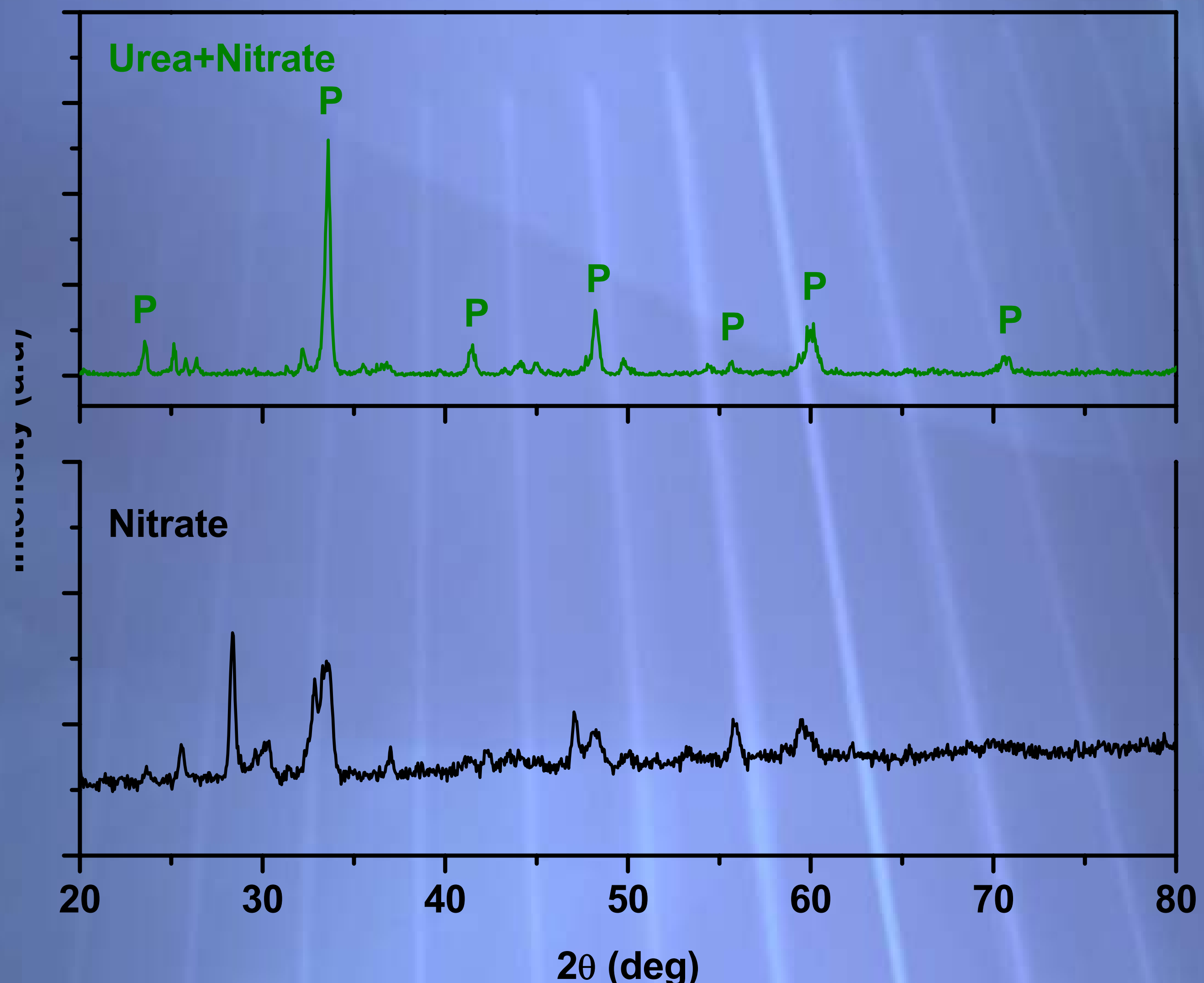
Introducing nano oxide electrocatalyst into LSM-YSZ cathodes enhances the oxygen reduction reaction and reduces cathode polarization at low temperatures

Materials Selection
$Sm_{0.6}Sr_{0.4}CoO_{3-\delta}$ – Superior Electrocatalyst



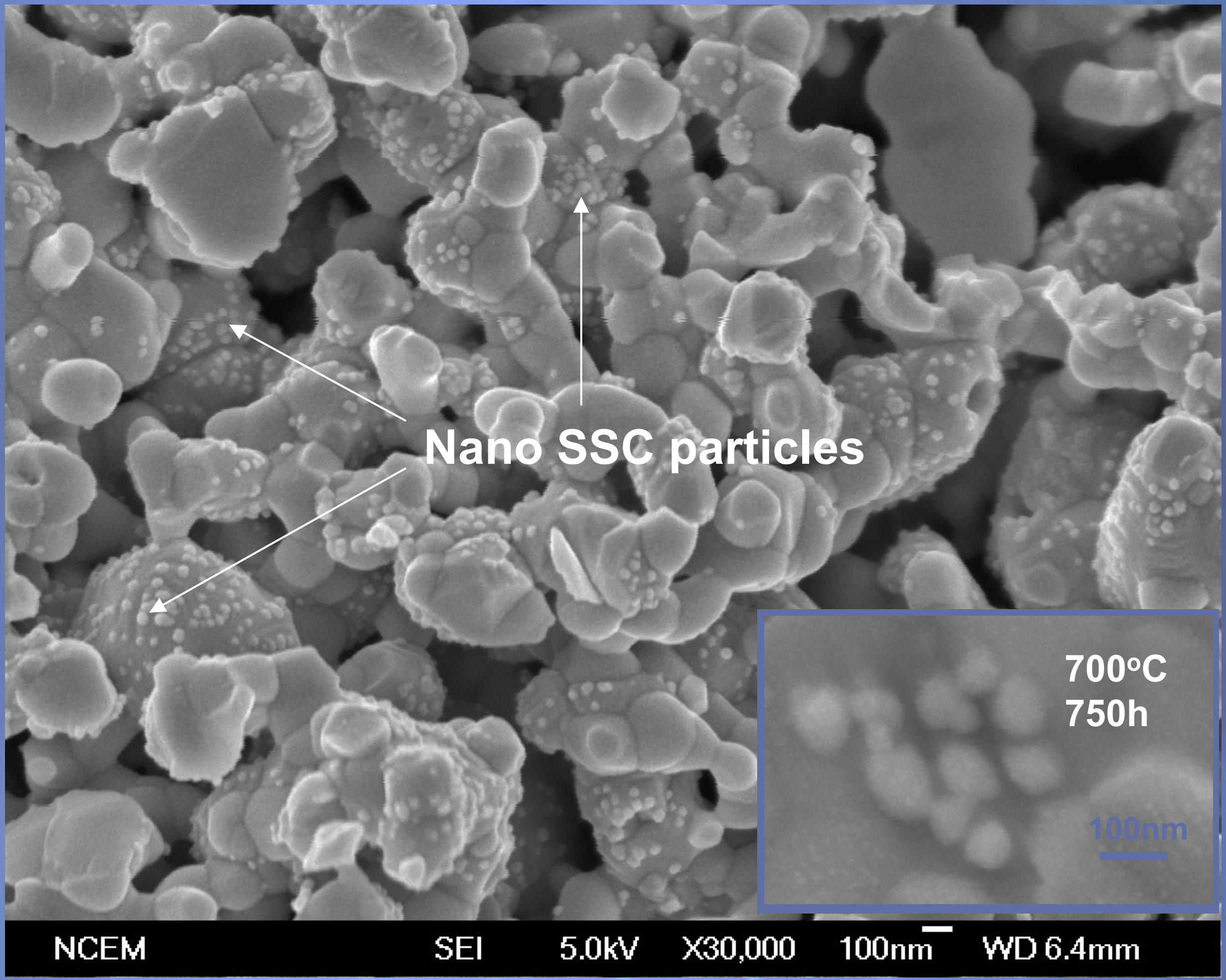
R. Doshi, V. Richards, J. D. Carter, X. Wang, and M. Krumpelt, *J. Electrochem. Soc.*, 146 (4), 1273 (1999).

Synthesis of SSC at Low Temperatures

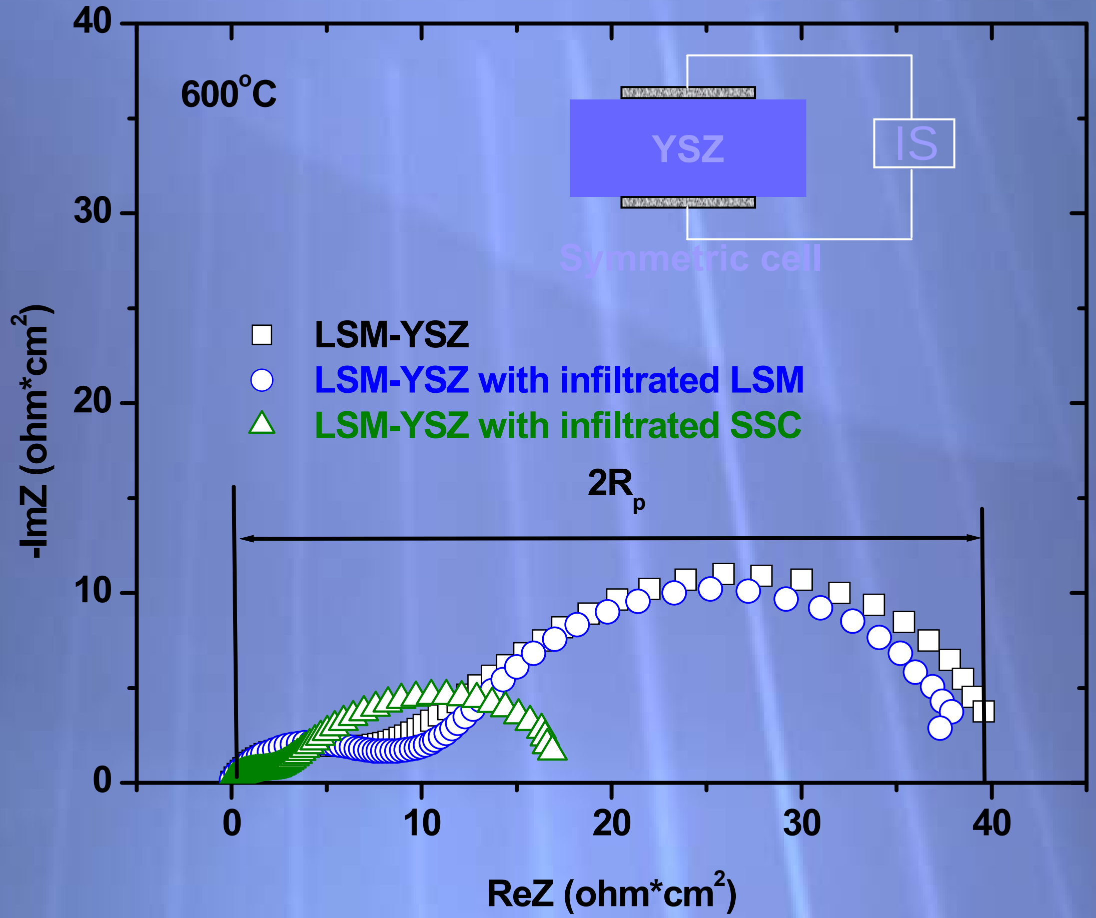


800°C; 2h

SEM Images of Fractured LSM-YSZ-SSC Cathodes

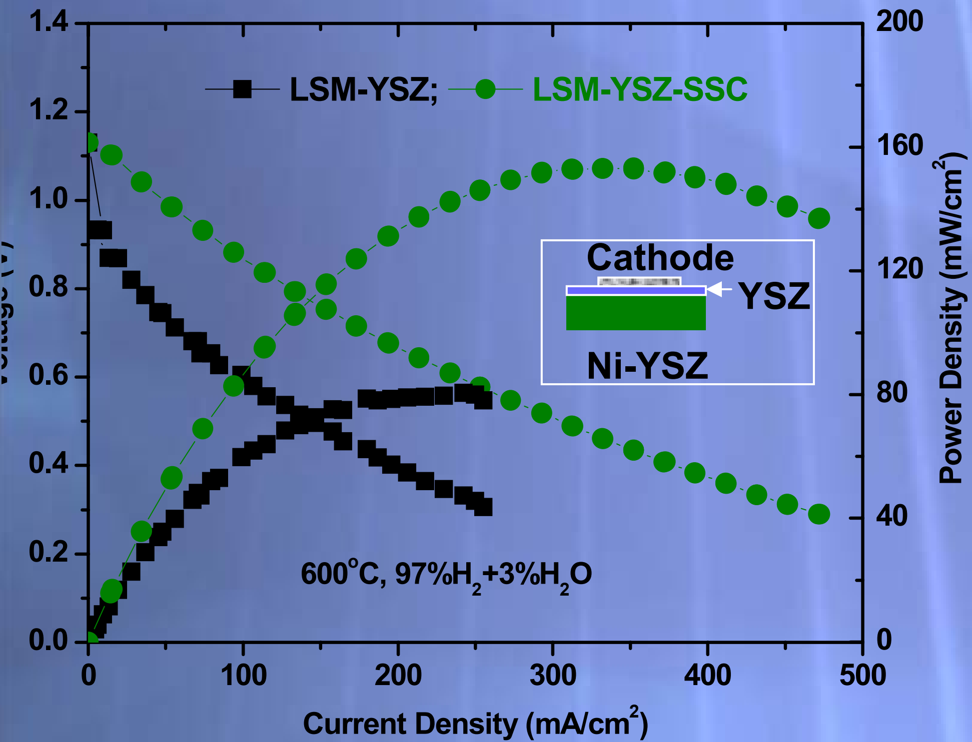


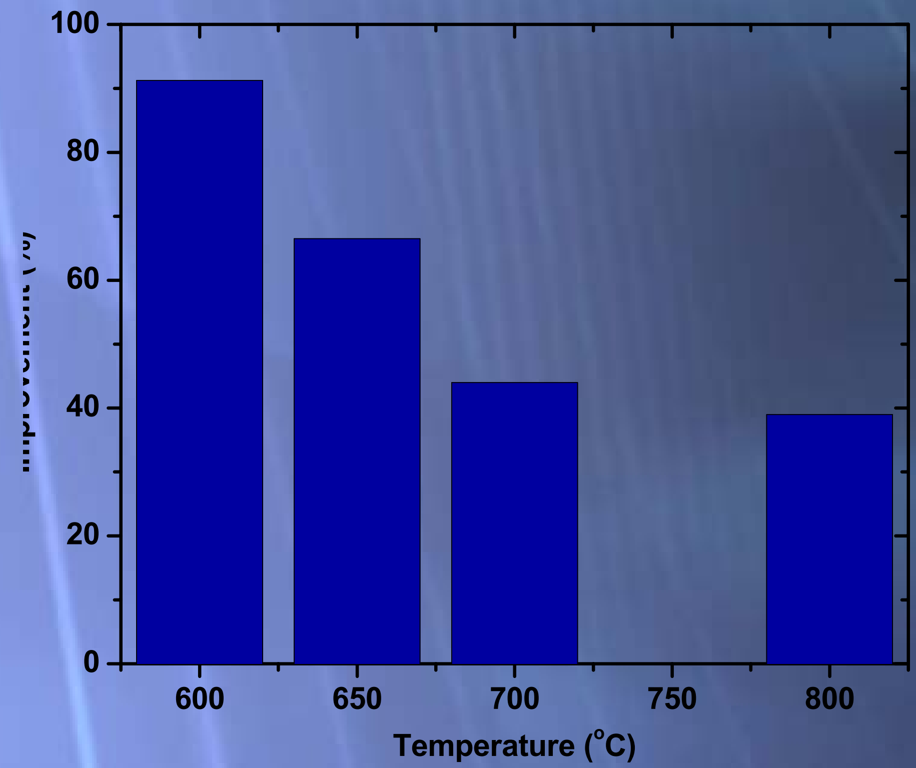
SSC Reduces Cathode Polarization Resistance



R_p: Cathode Polarization Resistance

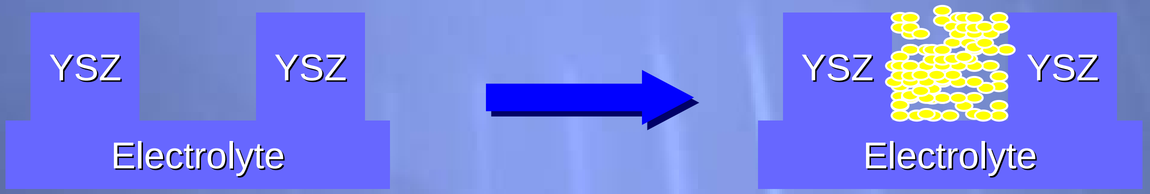
SSC Particles Enhance Cell Performance



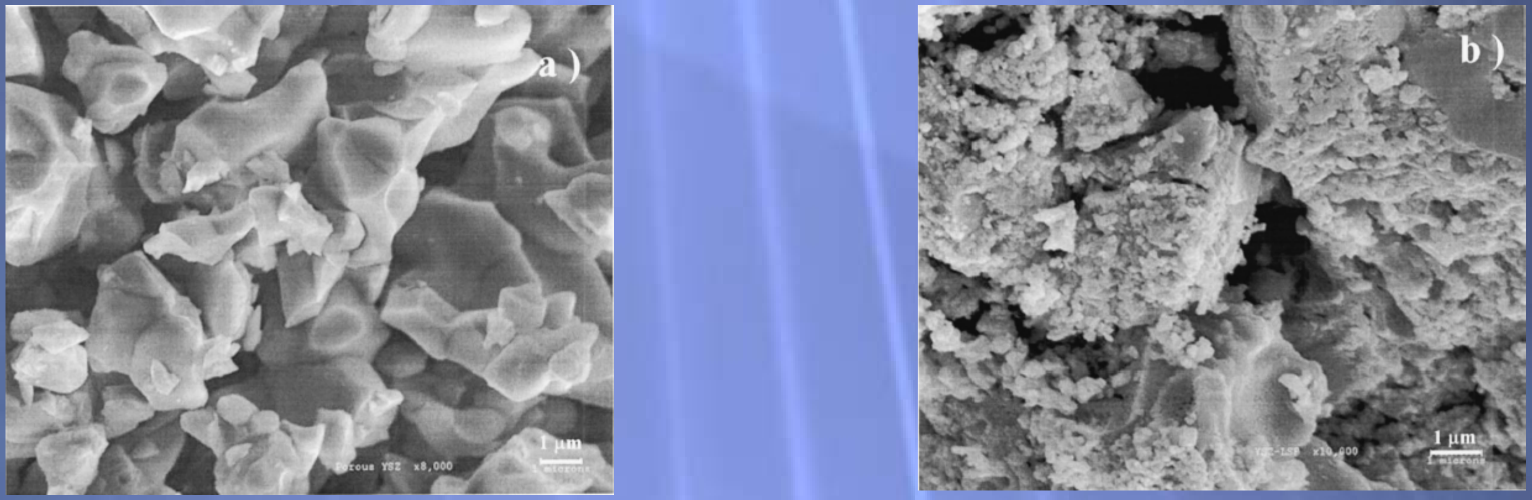


II. Complete Infiltration of SOFC Cathodes into Porous YSZ in a Single-Step

Background



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



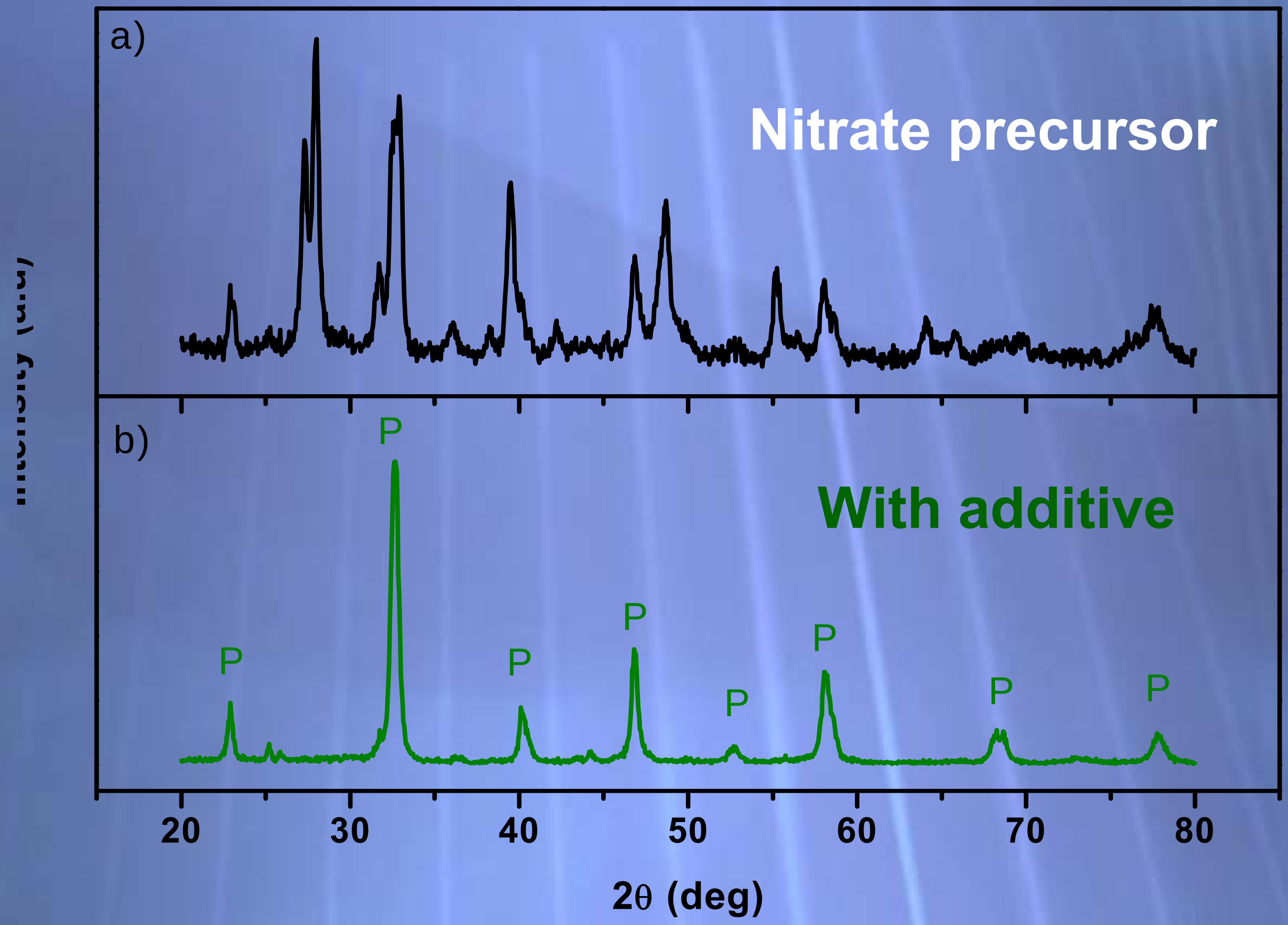
Y. Huang, J. M. Vohs, and R. J. Gorte, *J. of Electrochem. Soc.*, 151, A646 (2004).

- 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

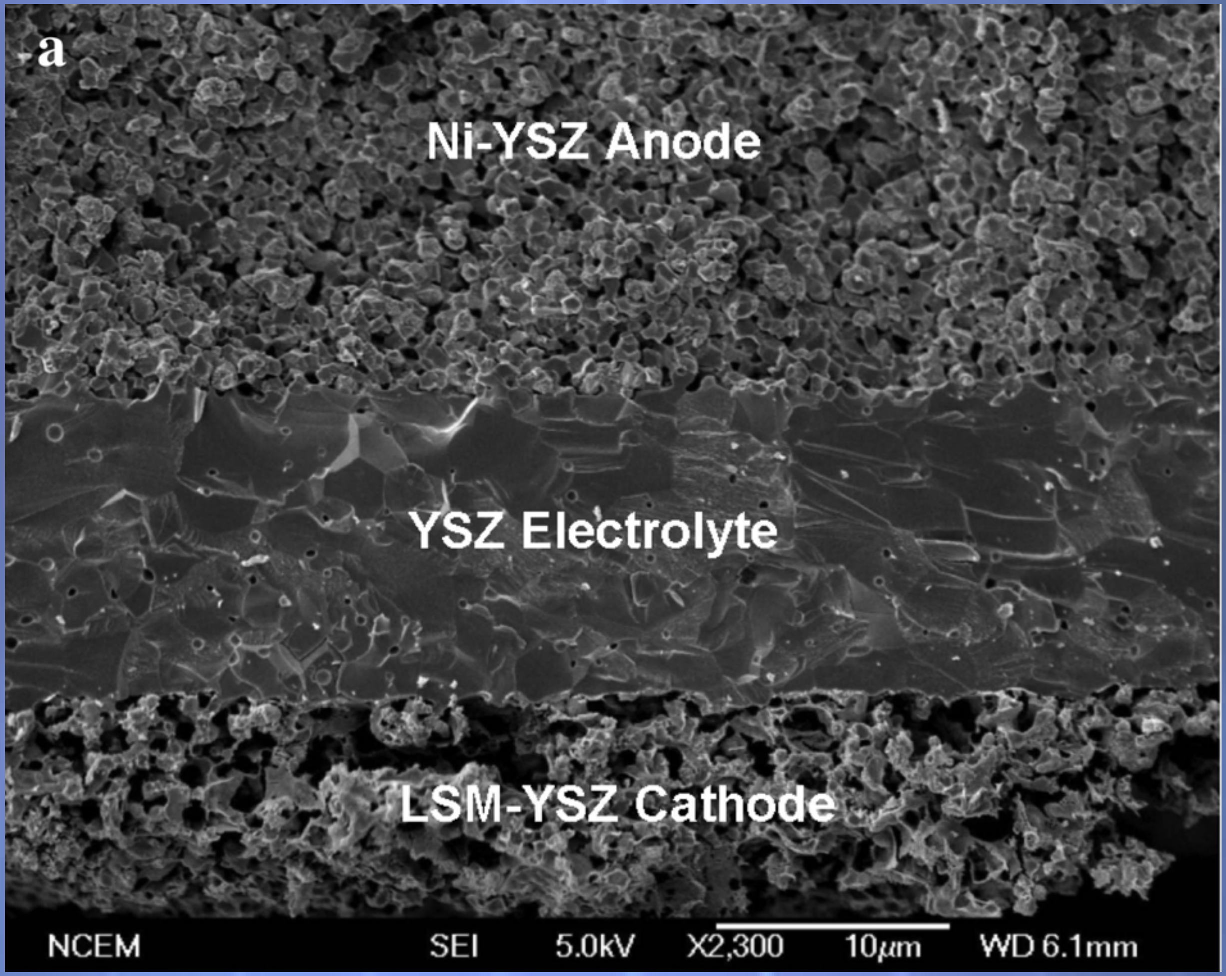
- One-step infiltration to form cost-effective electrodes
- Nano-sized materials distributed in a mono-layer fashion

Need Additive

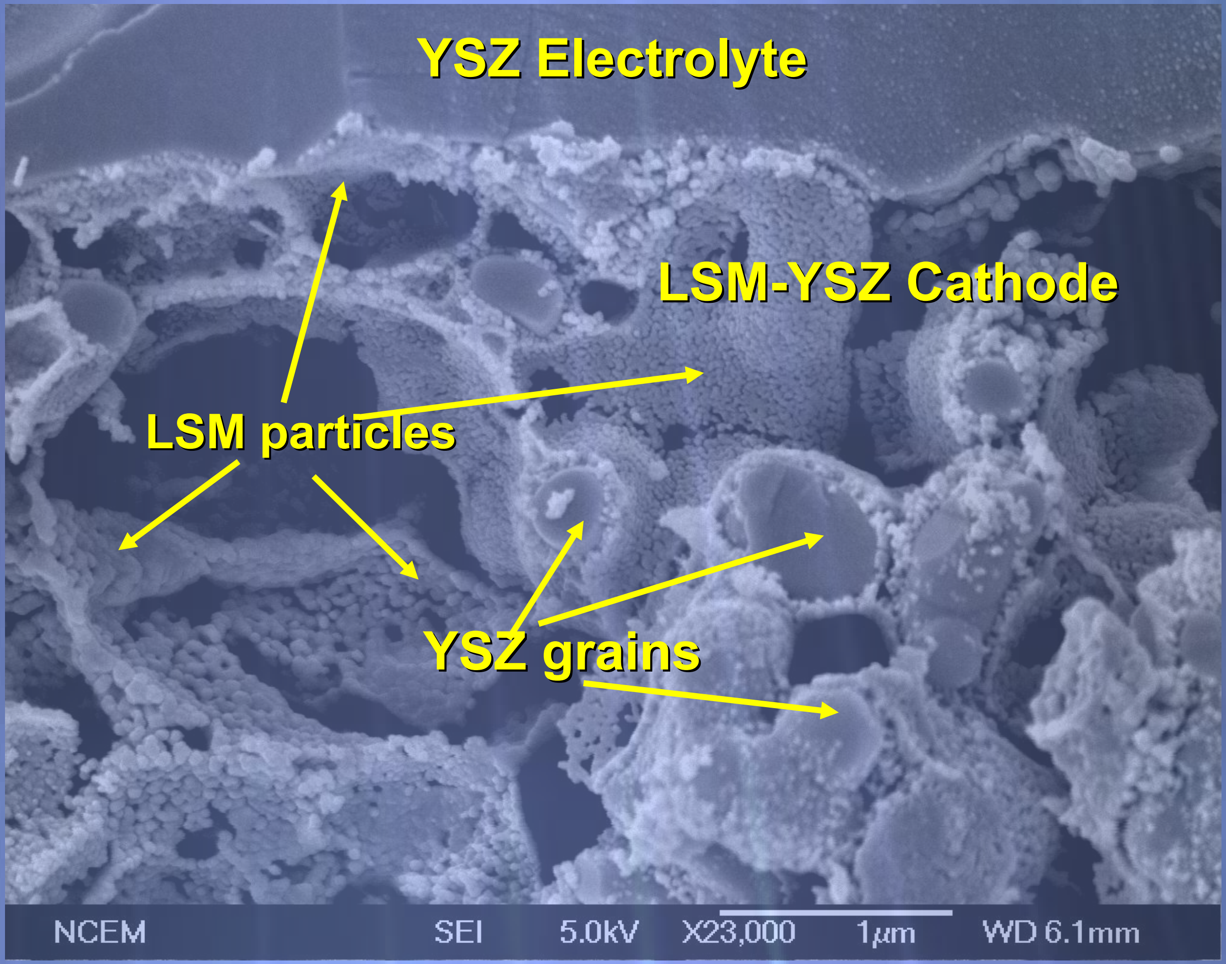


800°C, 2h

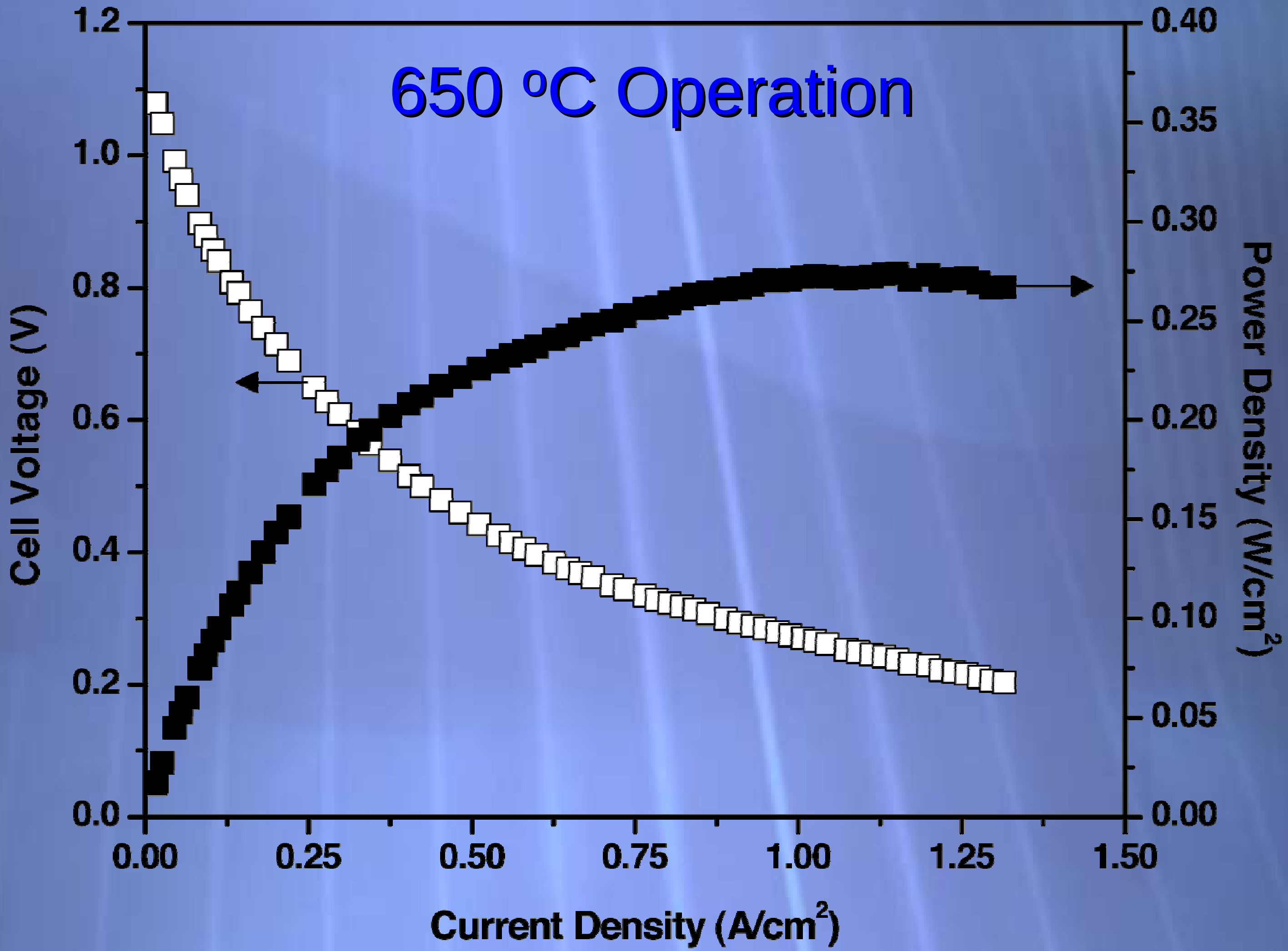
SEM Image of a Single-Step Infiltrated LSM-YSZ Cathode



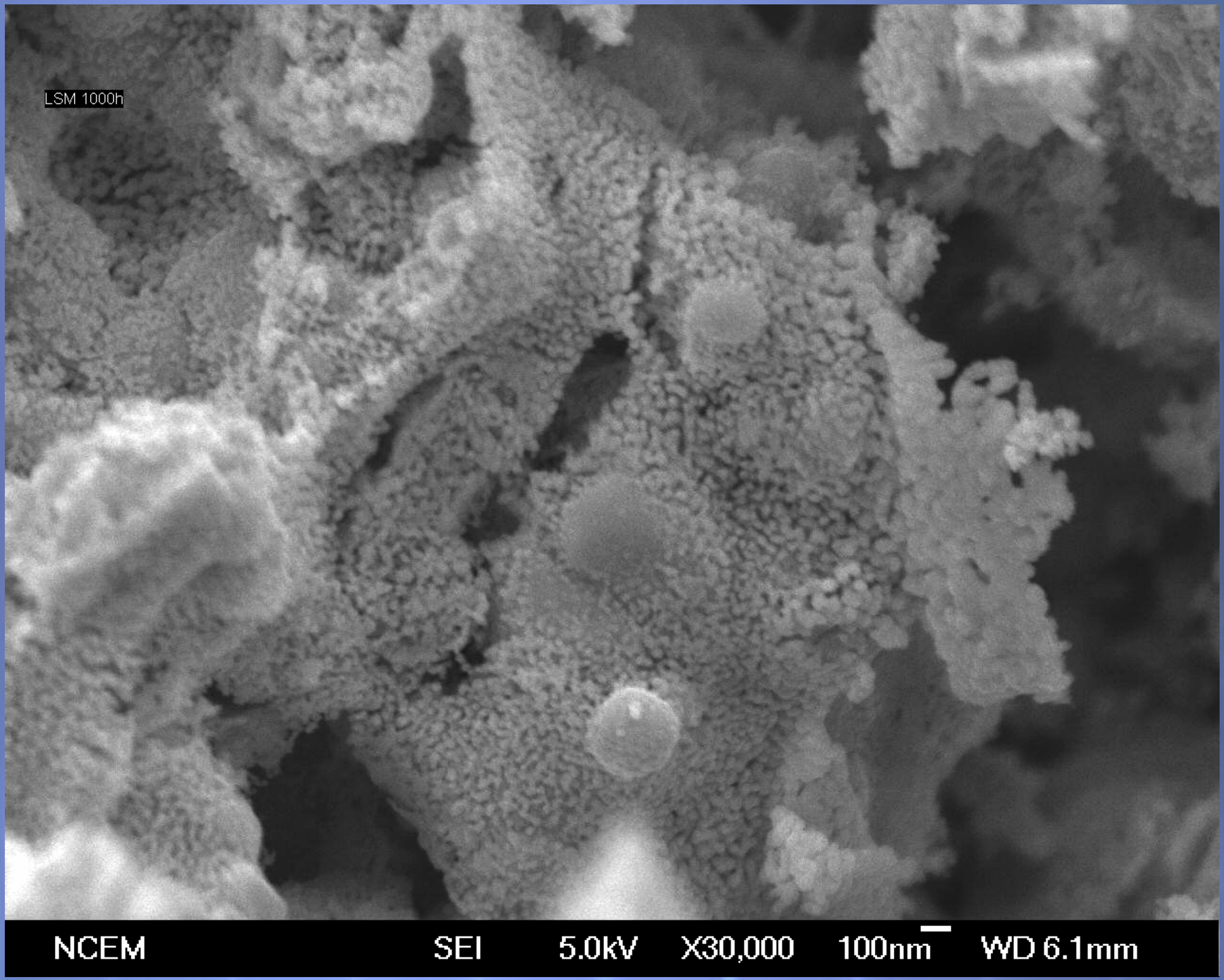
HRSEM Image of an LSM-YSZ Cathode



Performance of SOFC with Single-step Infiltrated LSM-YSZ Cathode

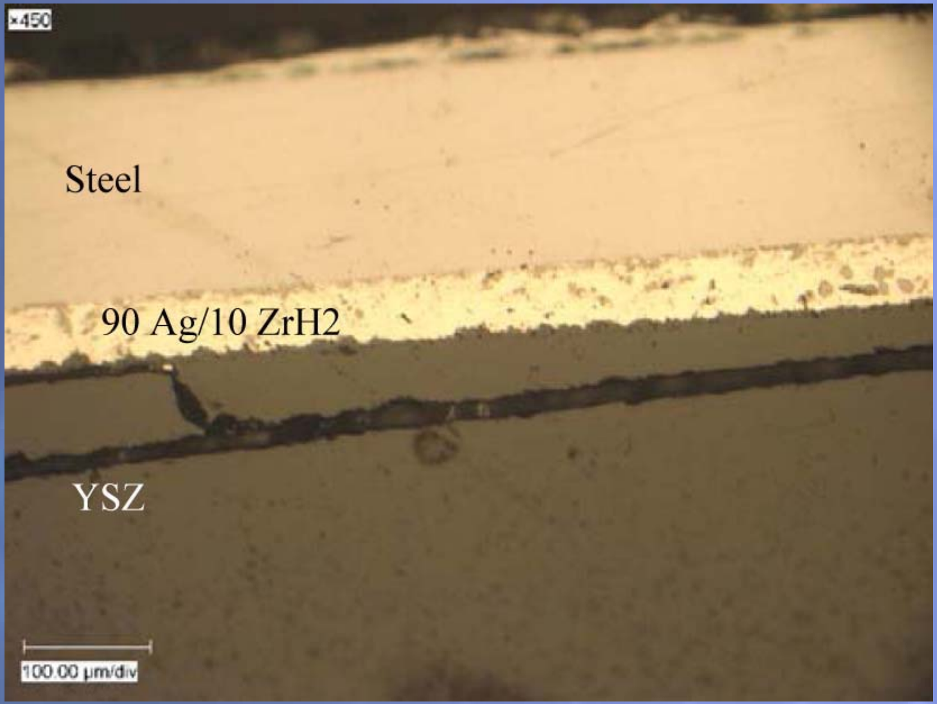


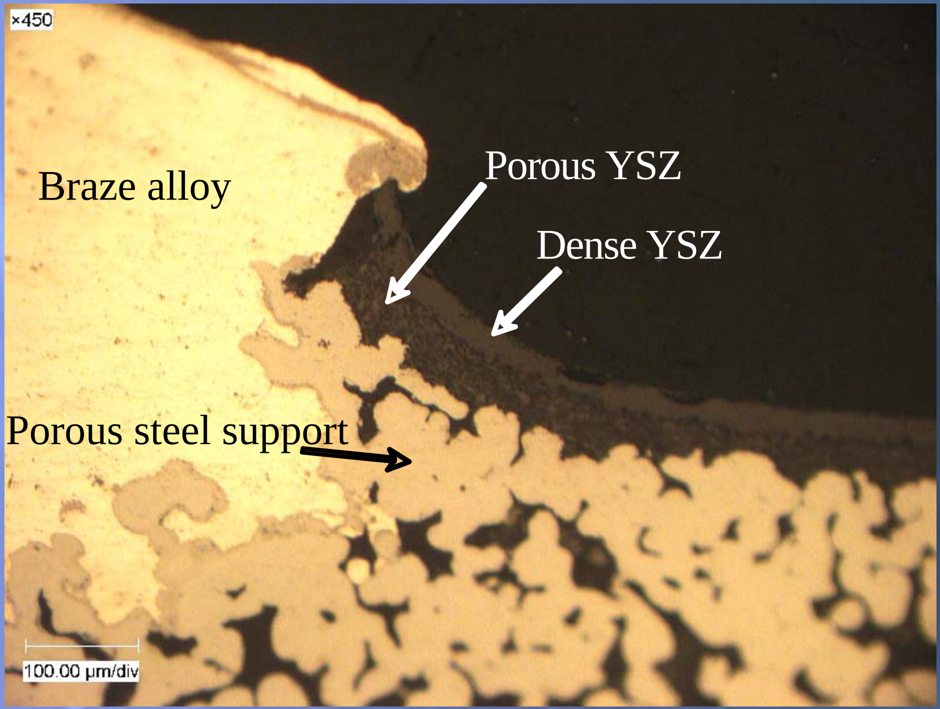
Stability of the LSM-YSZ Cathode



After 1000h @ 700°C

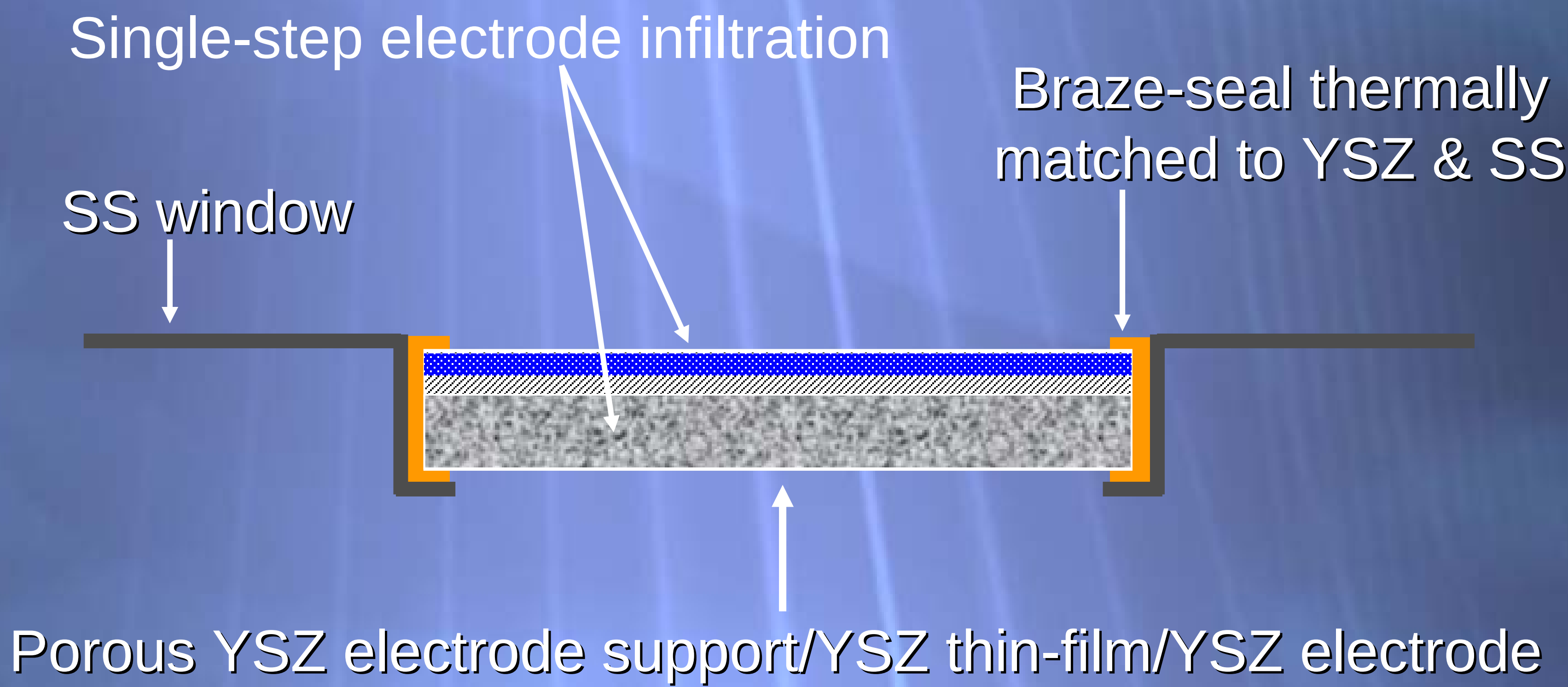
Braze Seal Development at LBNL





- Ag braze seals are not thermally matched to YSZ; thermal cycling leads to cracking
- New braze seal is well matched to YSZ and stainless steel support, no evidence of cracking after 100s of thermal cycles
- Braze seal exhibits exceptional strength and is stable to oxidation.

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.
- The development of braze seals at LBNL that are thermally matched with YSZ and stainless steel look promising.
- Single-step infiltration and braze seals may lead to low-cost SOFCs.