Infiltration Technology for Anode & Cathode Performance Improvement

Principal Investigator: Steven J. Visco
NETL Program Manager: Briggs White
Materials Science Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720
sjvisco@lbl.gov

LBNL-SECA Objectives

- Development of technologies enabling improvement of SOFC performance at equivalent (or lower cost) relative to existing SOFC components
- Target high risk/high benefit strategies and basic science, not incremental engineering advances that are better suited to industrial developers.
- Characterization of performance improvement
- Transfer of technology to industrial teams, national labs, and/or university teams.

Key Program Tasks

1. Infiltration of perovskites into composite cathodes
2. Determination of baseline performance and long term stability of infiltrated and non-infiltrated air cathodes, including testing in the presence of Cr vapor
3. Infiltration of ceria and other appropriate materials into Ni-YSZ anodes to improve sulfur tolerance
4. Design and fabrication of 2-cell stack for national labs and industrial teams as a standard for testing electrodes

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LBNL Team

Staff	Position
Steven J. Visco	Principal Investigator
Craig P. Jacobson	Principal Scientific Engineering Associate
Dr. Michael Tucker	Staff Research Associate
Dr. Tal Sholklapper	Postdoctoral Fellow
Dr. Peggy Hou	Staff Scientist
Grace Lau	Research Associate
UC Berkeley Engineering Students	Undergraduate staff

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Task Execution

1. Infiltration of perovskites into composite cathodes
2. Determination of baseline performance and long term stability of infiltrated and non-infiltrated air cathodes
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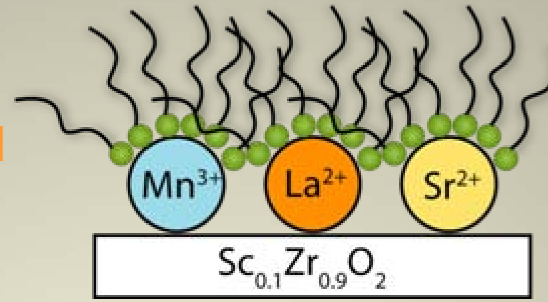
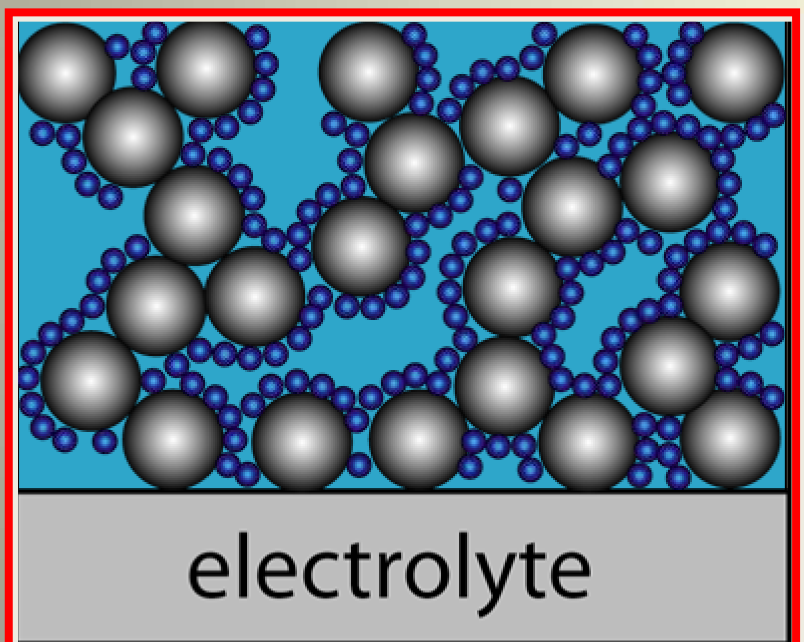
Infiltration Step

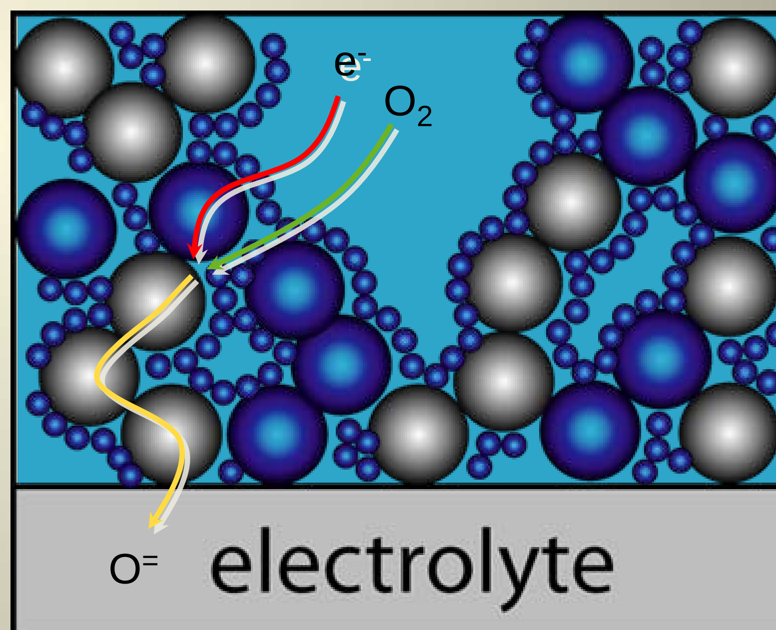
Nitrate-Surfactant Concentrated Precursor



Surfactant dispersed Electrode Precursors



Porous electrolyte matrix

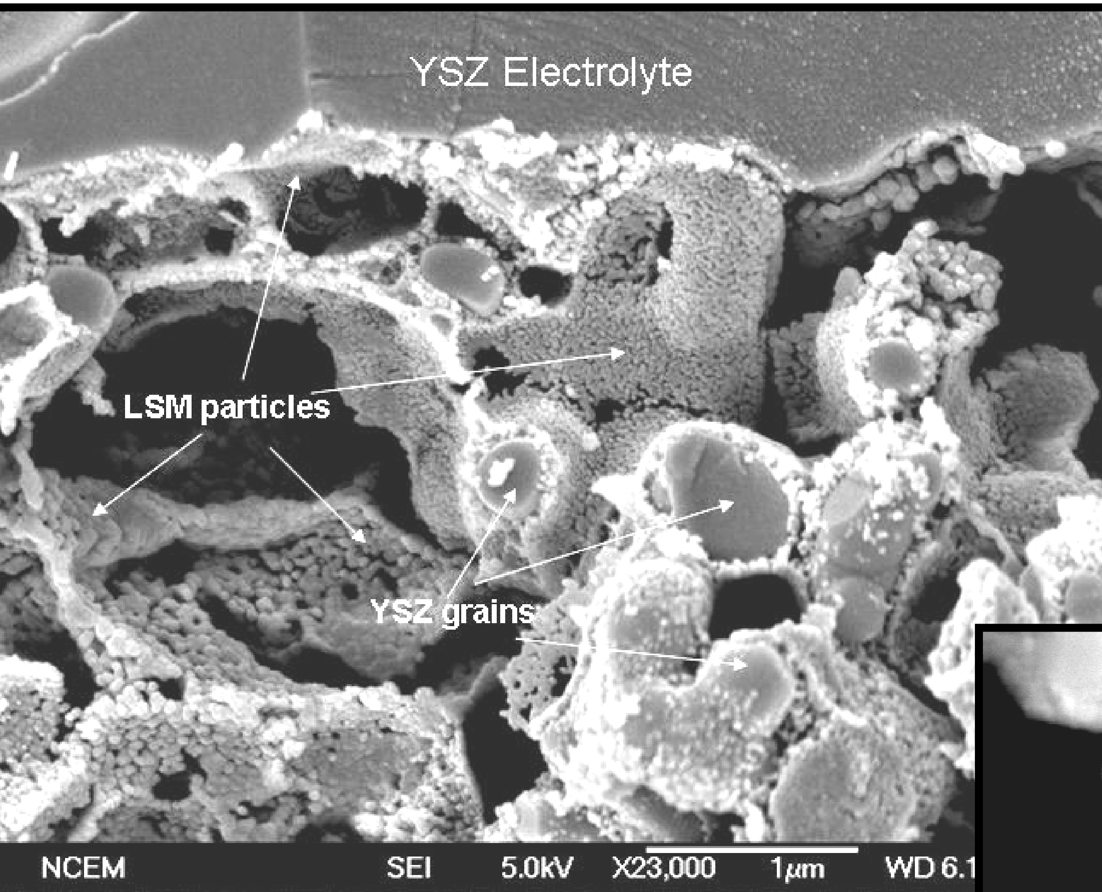


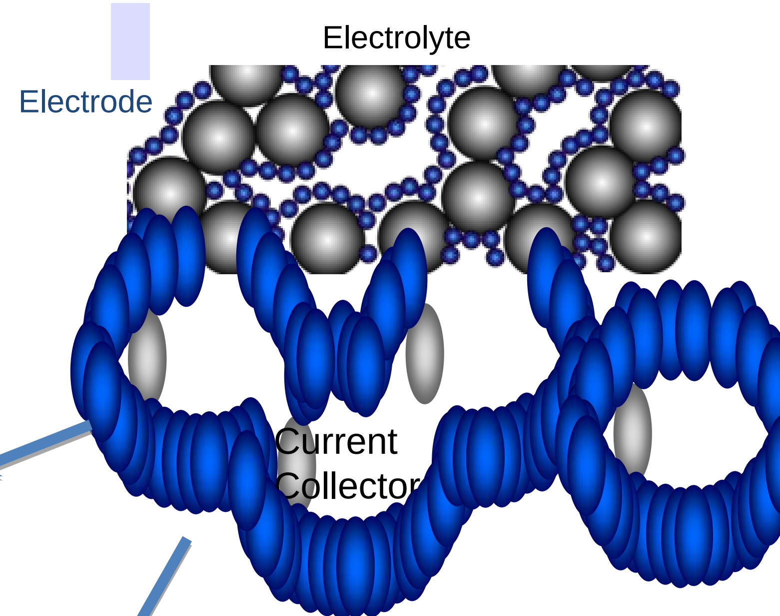
Composite Commercial electrodes (YSZ-LSM)

electronic conductor   ionic conductor

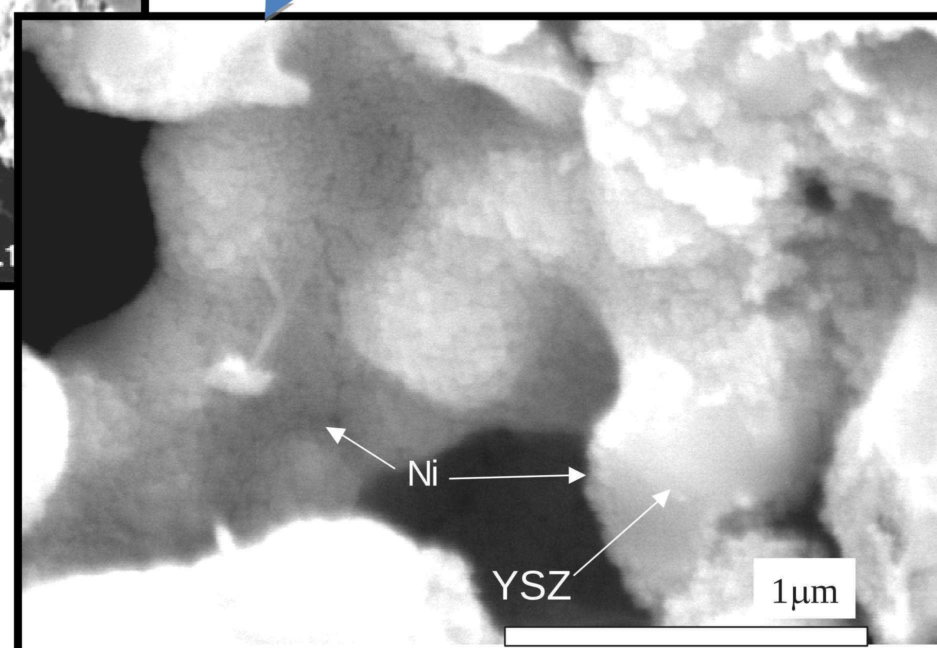
Infiltrated Catalysts

LSM-YSZ Cathode

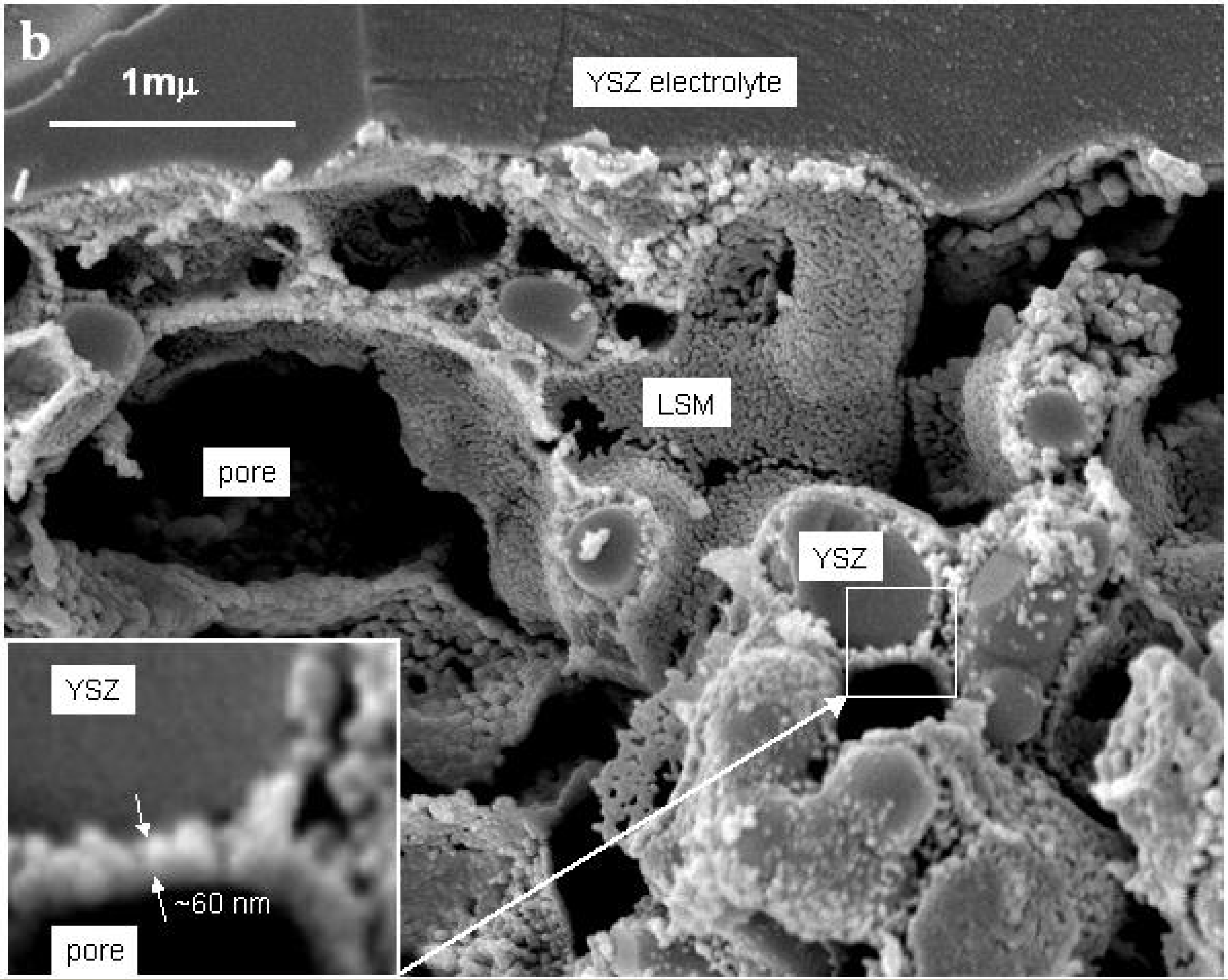




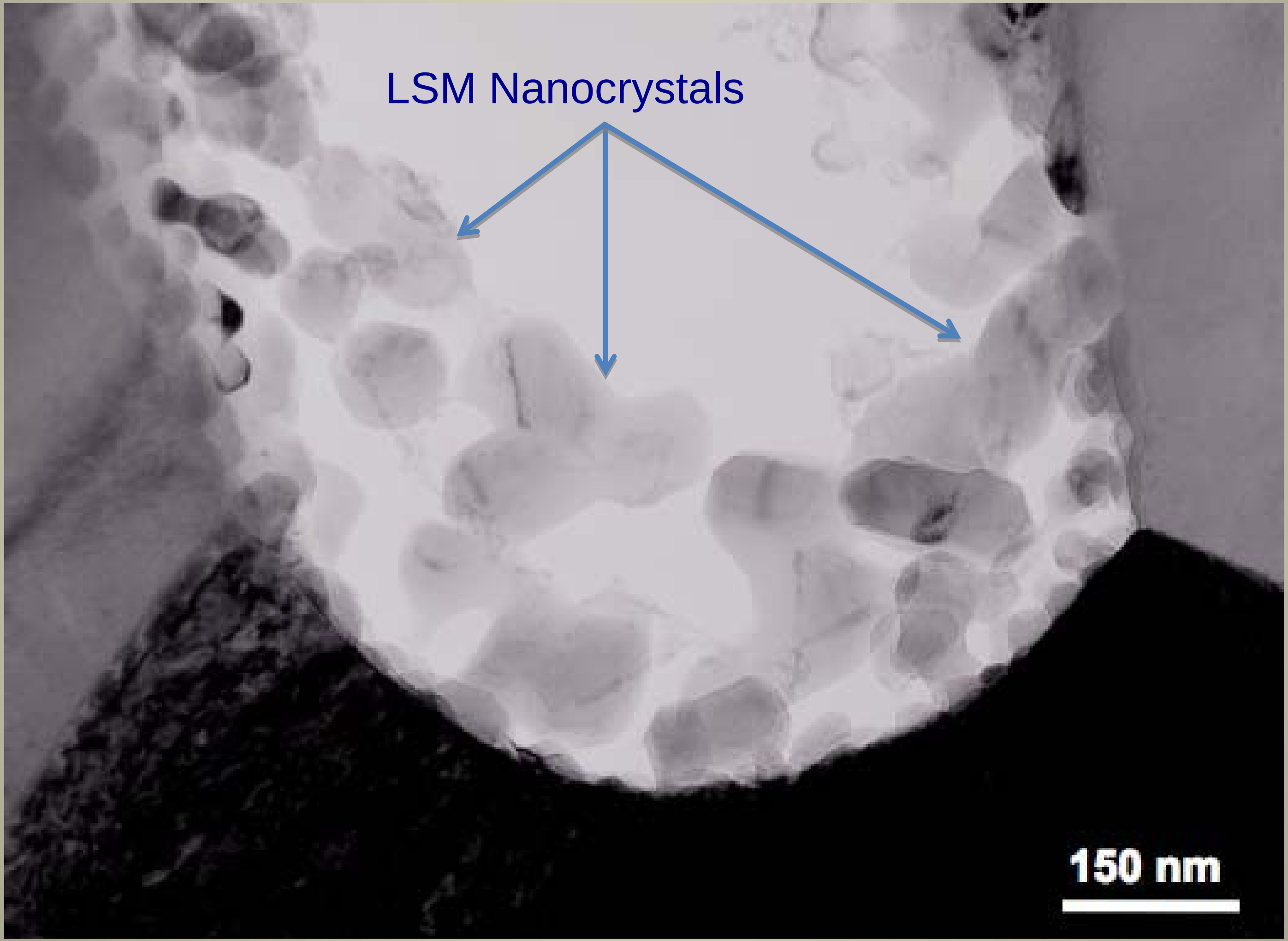
Ni-YSZ Anode



Infiltration of LSM Into Porous YSZ Structure



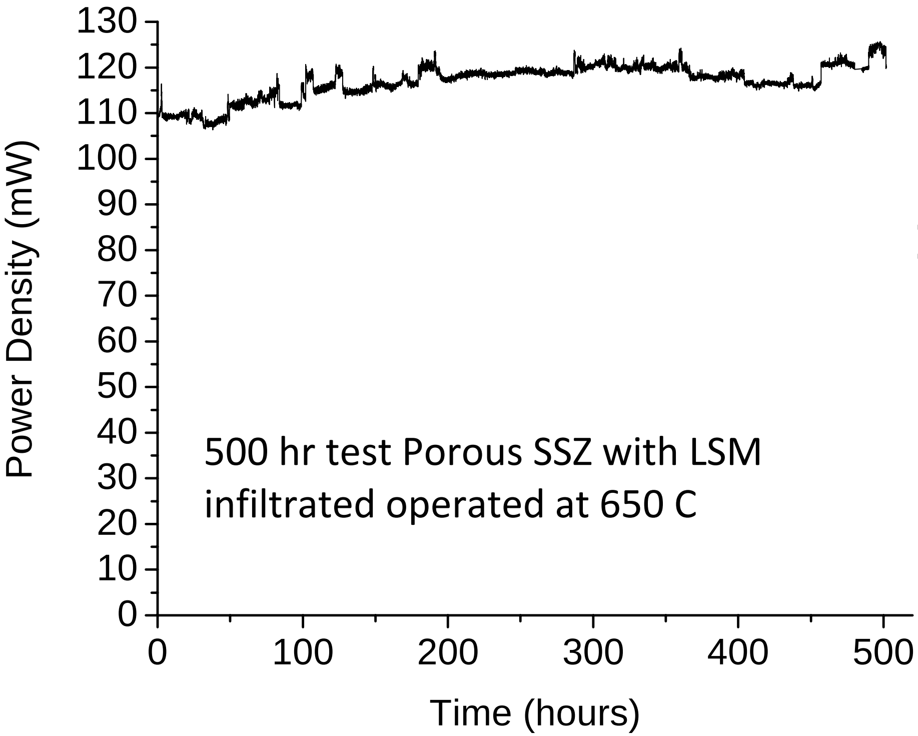
TEM Shows Good Coverage

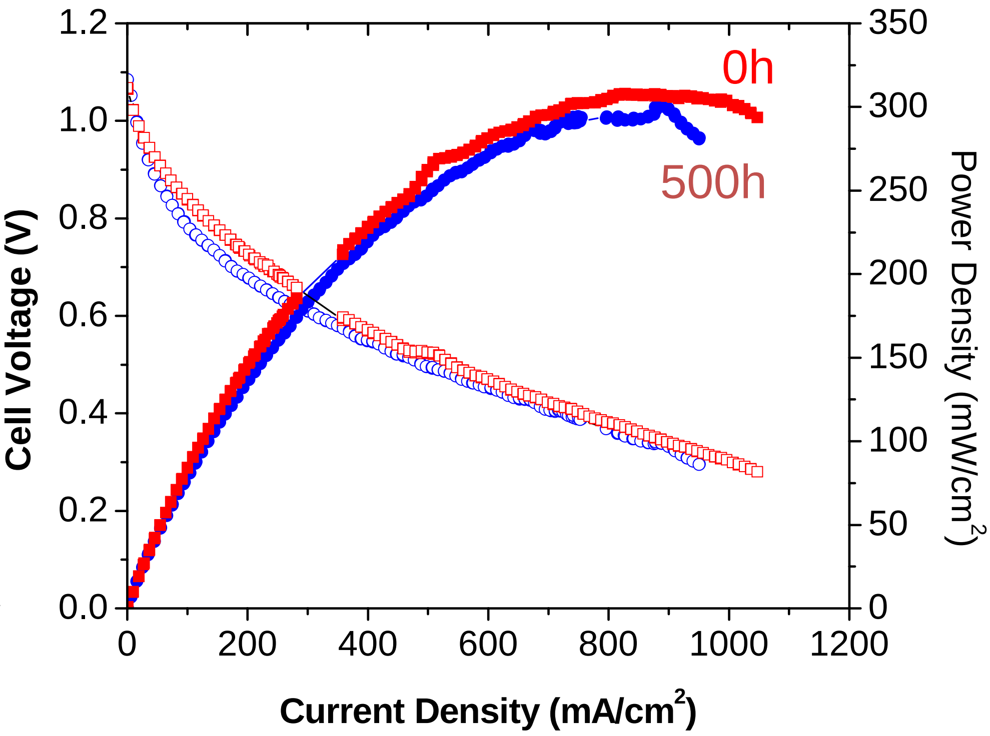


LSM on porous YSZ

Long-term Stability of Infiltrated LSM Cathode

LSM infiltrated 1x (nanoparticulate coating)
Achieved high power density at 650°C for 500+ hours

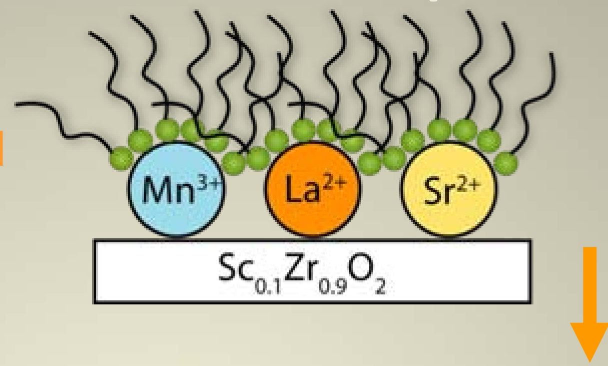




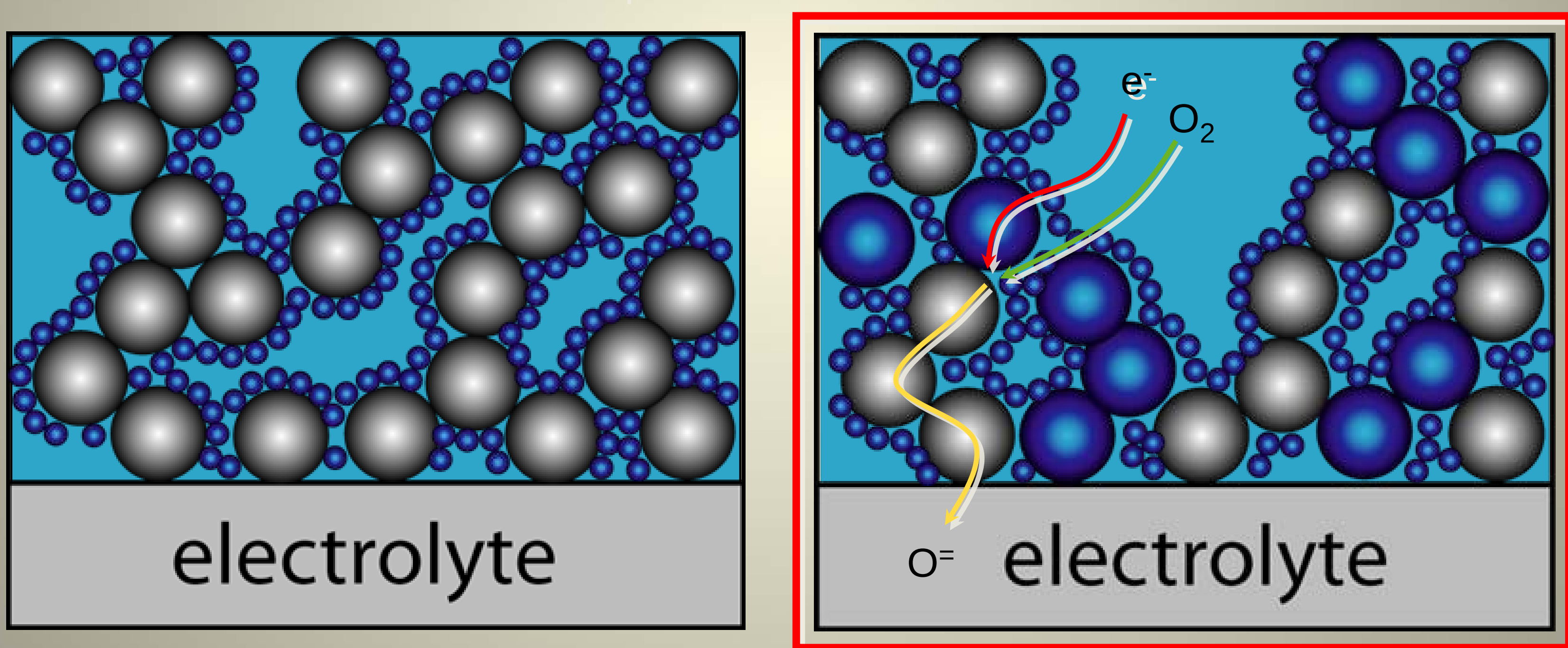
Infiltrated oxide catalysts provide the desired stability, minimal infiltration steps

Infiltration Step

Nitrate-Surfactant Concentrated Precursor



Surfactant dispersed Electrode Precursors

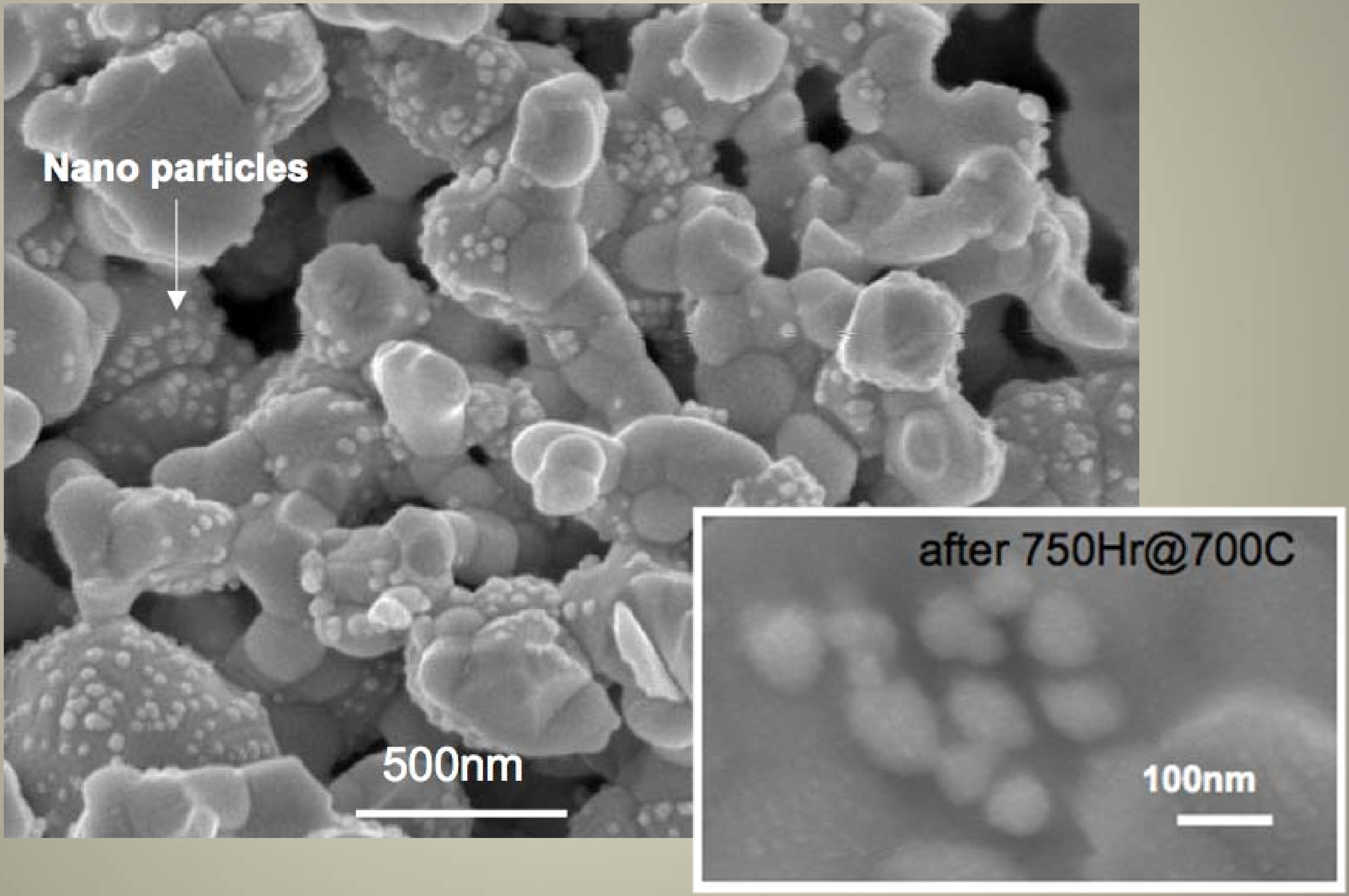


Porous electrolyte matrix

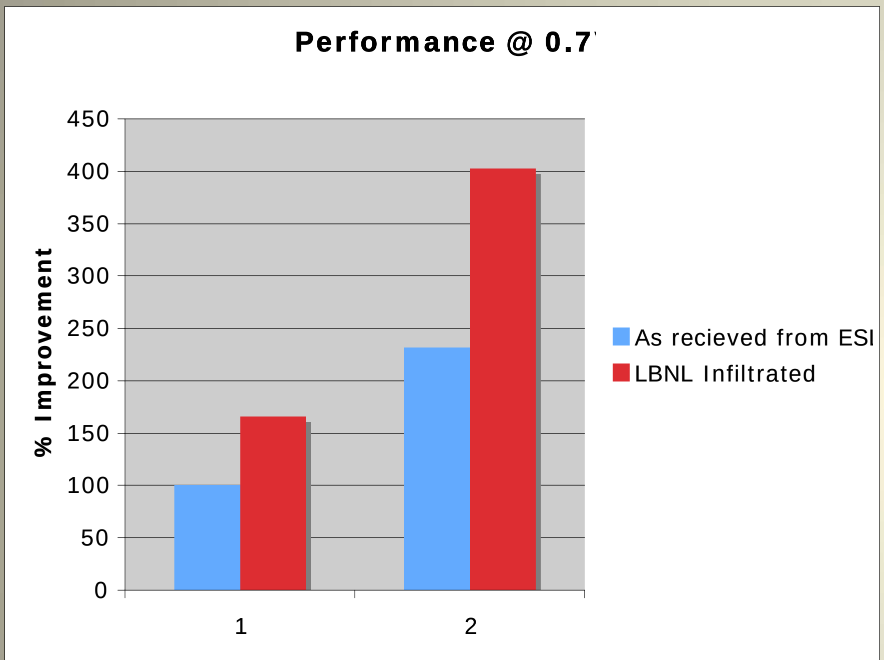
Composite Commercial electrodes (YSZ-LSM)

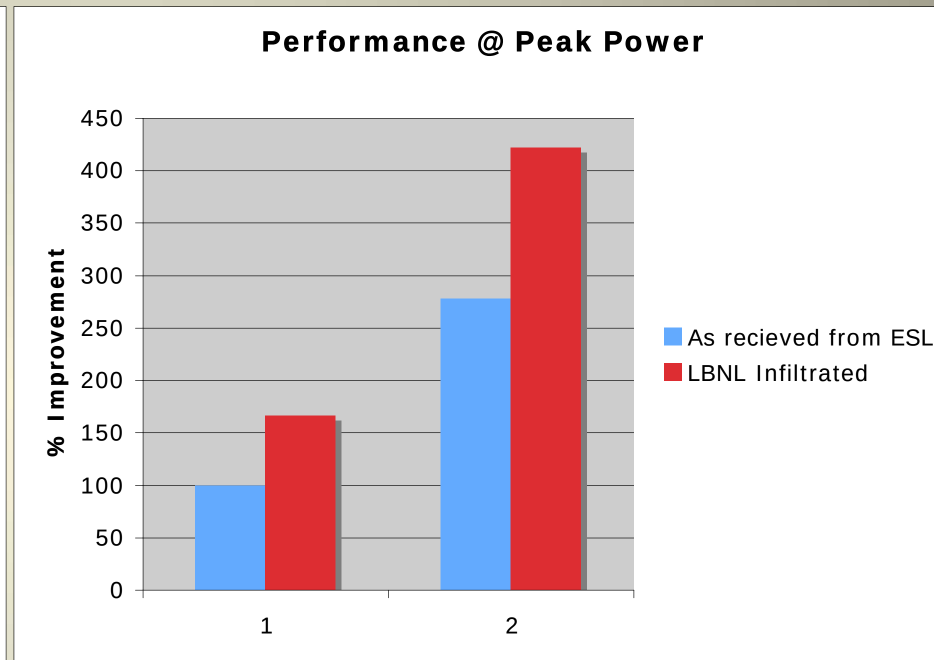
electronic conductor ionic conductor

LSM NanoParticles Infiltrated into LSM/YSZ cathode



LBNL Collaboration with Electro Sciences Lab to Accelerate Development of Anode Supported SOFC Components and Performance Improvement through Infiltration





Initial performance = 41 mW/cm^2 @ 0.7 and 45 mW/cm^2 PPD, with infiltration increasing to 68 mW/cm^2 and 75 mW/cm^2 respectively; recent results at 425 mW/cm^2 @ 0.7 V and 570 mW/cm^2 PPD with infiltration increasing to [redacted]

Working on standard cell for **700 ^{o}C** operation - available to industrial teams, Universities, and National Labs - US supplier

Task Execution

1. Infiltration of perovskites into composite cathodes
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Baseline performance and long term stability of infiltrated and non-infiltrated air cathodes

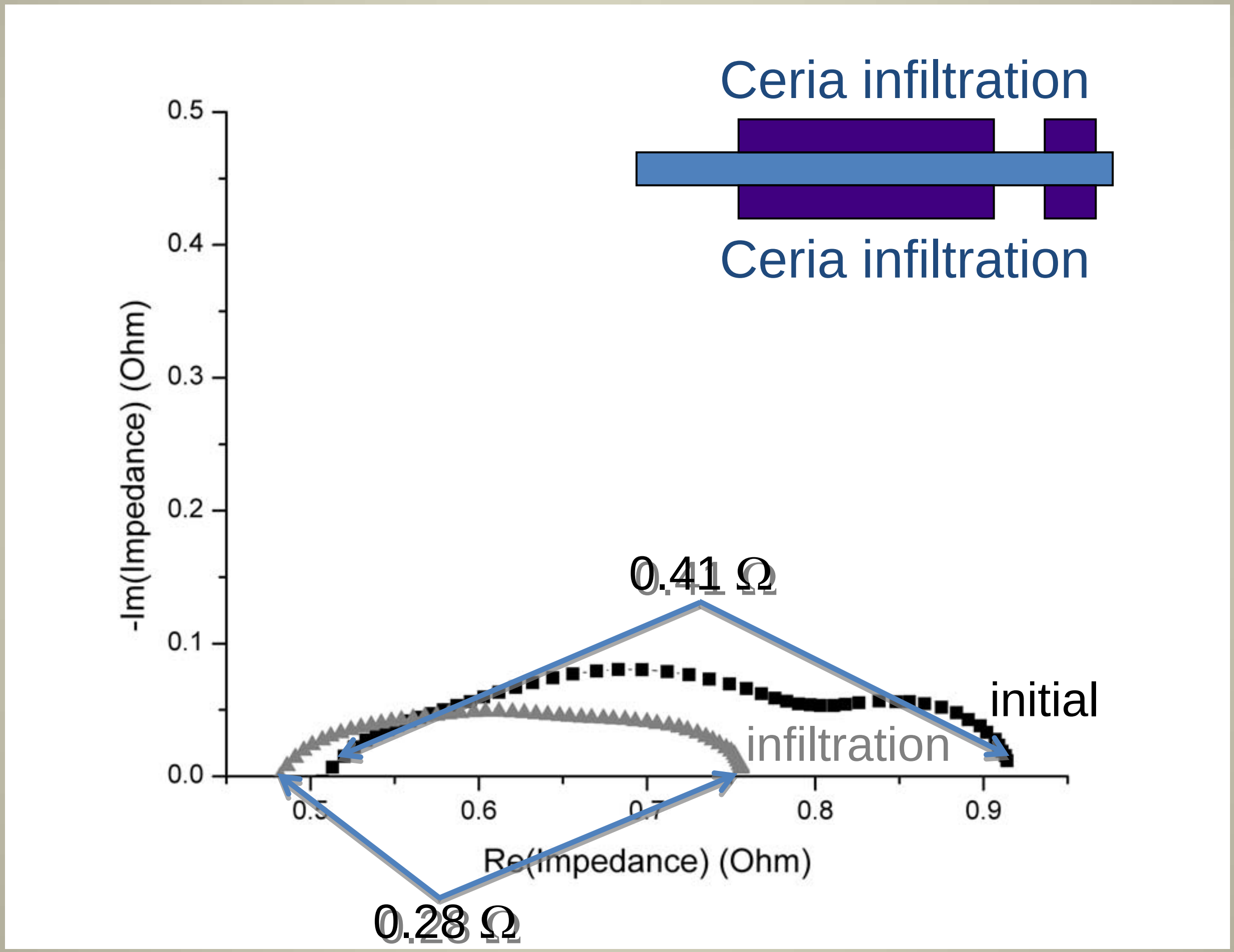
H.C. Starck HCST Engineered Material Solutions

InDEC B.V.

Commercial Symmetric Electrolyte Supported LSCF Cell from INDEC
LSCF-YDC/TZ3Y/YDC-LSCF

HC Starck LSCF/LSCF Cell

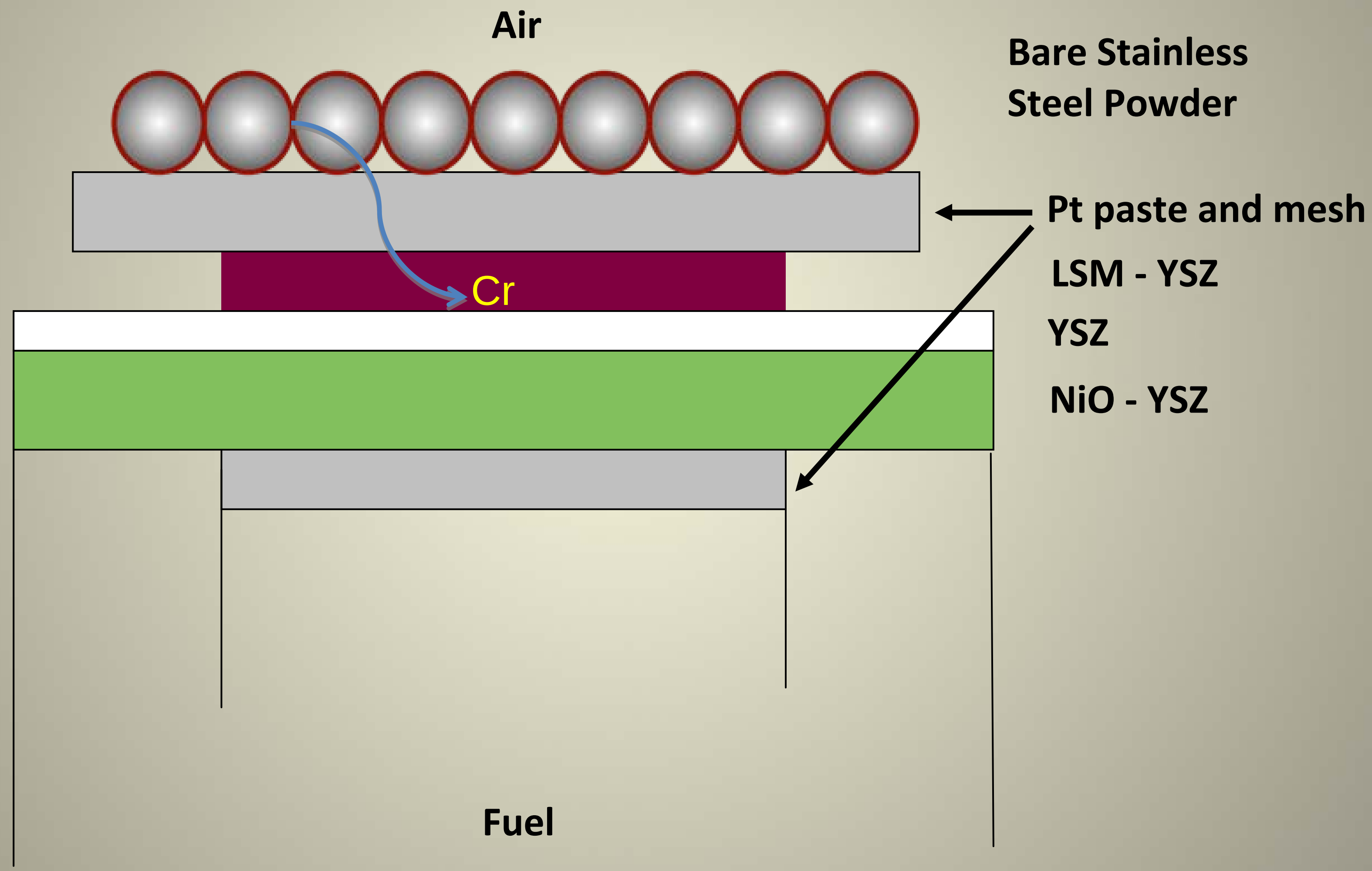
Electrolyte supported cell: electrode Impedance before and after infiltration 700 ºC



=>45% improvement in cell resistance

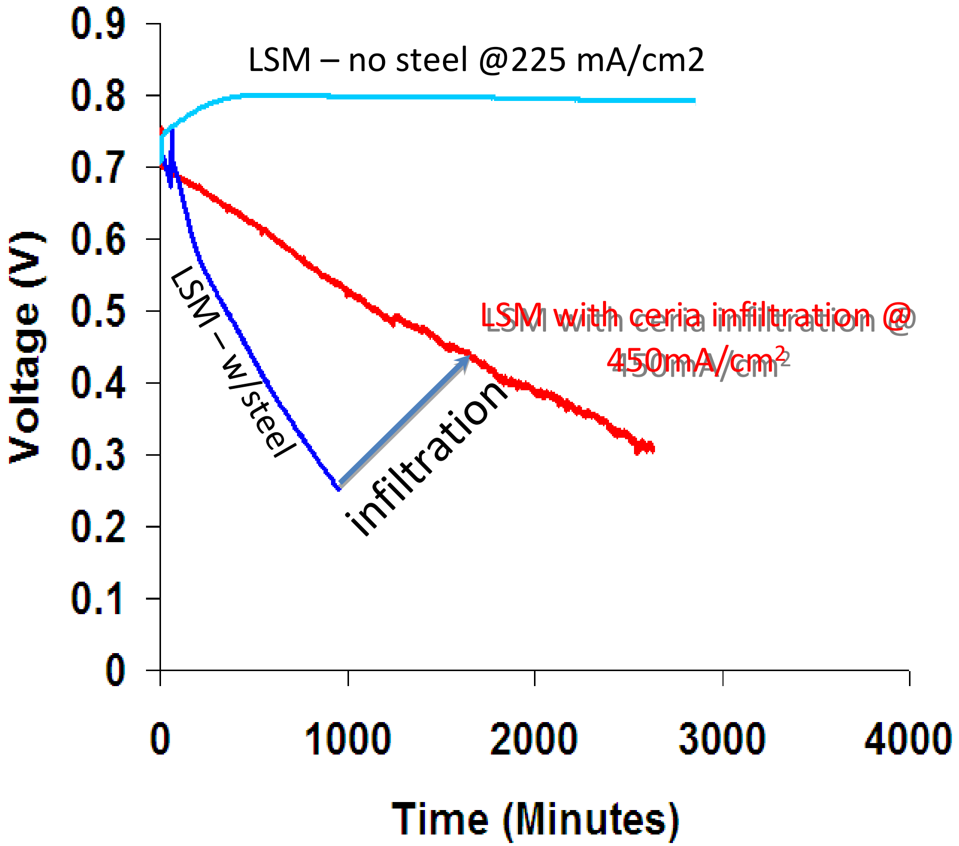
Secondary Degradation Study:

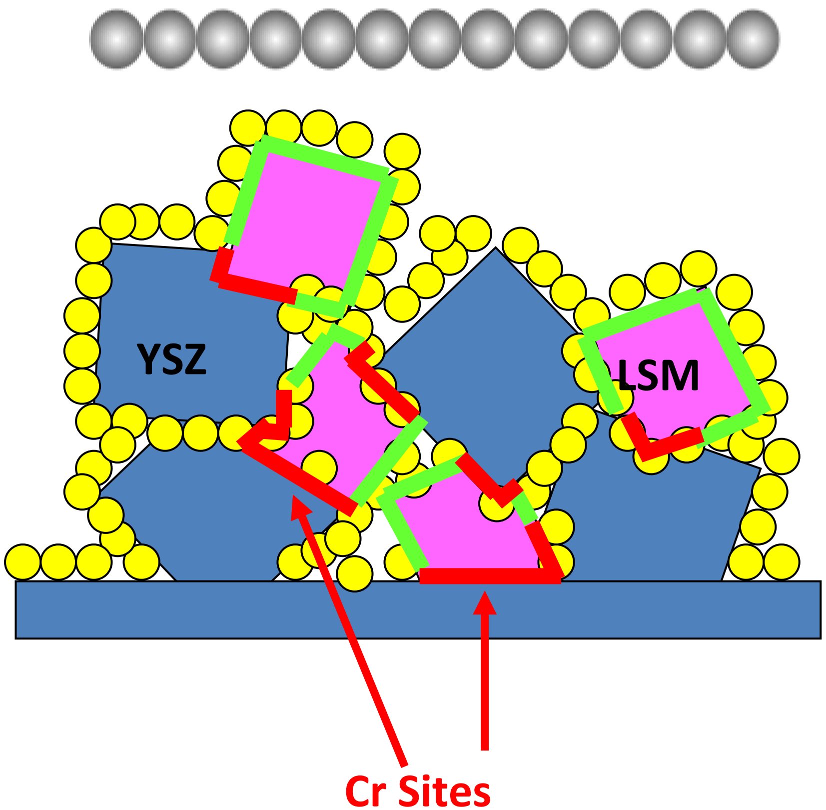
Effect of Cr on Infiltrated & Non-infiltrates Cathodes



Effect of Ceria Infiltration on Cathode Tolerance to Cr

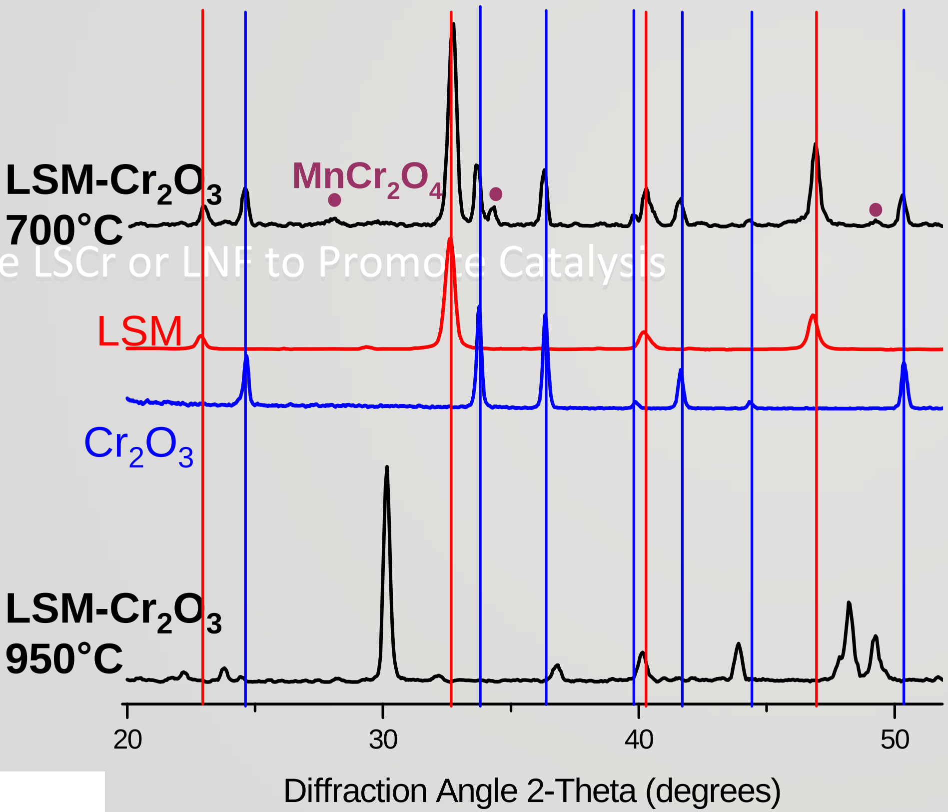
Rate of Degradation vs Time





Investigating Alternative Cr Tolerant Cathodes

Pellets of LSM and Cr_2O_3 powder mixtures reacted for 150h at 700°C and 950°C



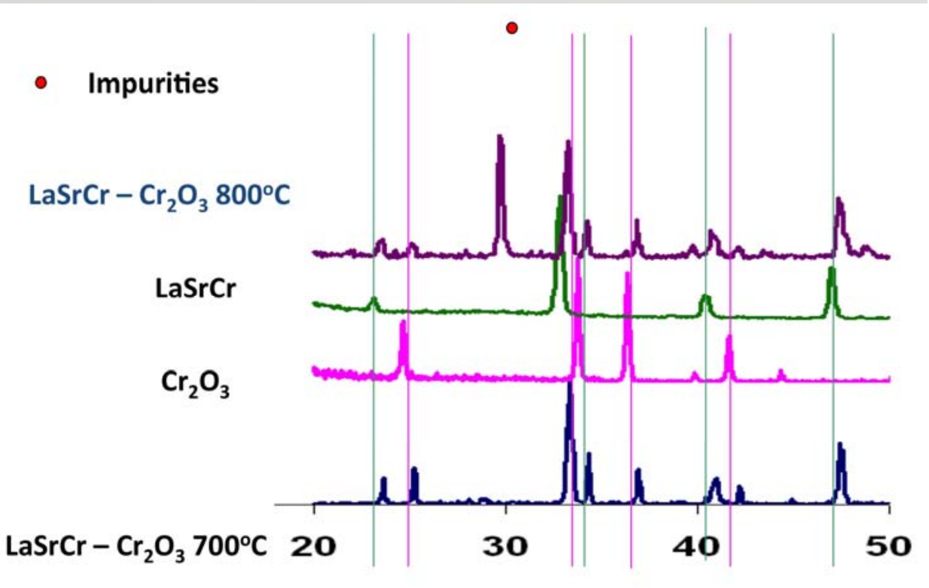
700°C
Minimal reaction
- trace $MnCr_2O_4$ formed

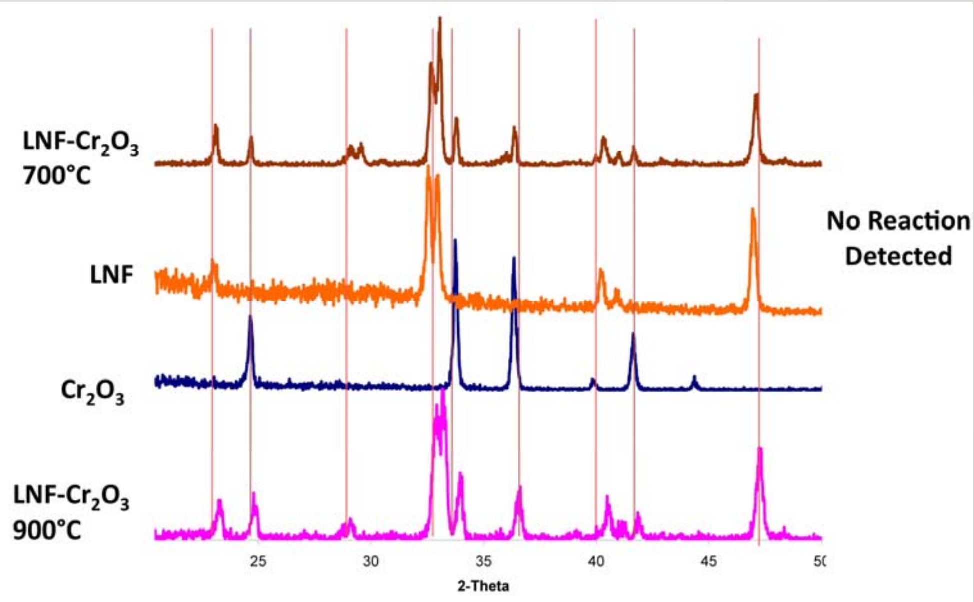
950°C
Complete reaction to mixed oxides
- Sr_2CrO_4, Mn_5O_8, $La_4Mn_4O_{11}$, etc
- no $MnCr_2O_4$ detected

Development of Cr Tolerant Cathodes

$La_{0.9}Sr_{0.1}CrO_3$ does not react with Cr_2O_3

$La_{0.98}Ni_{0.6}Fe_{0.4}$ does not react with Cr_2O_3





Infiltrate LSCr or LNF to Promote Catalysis

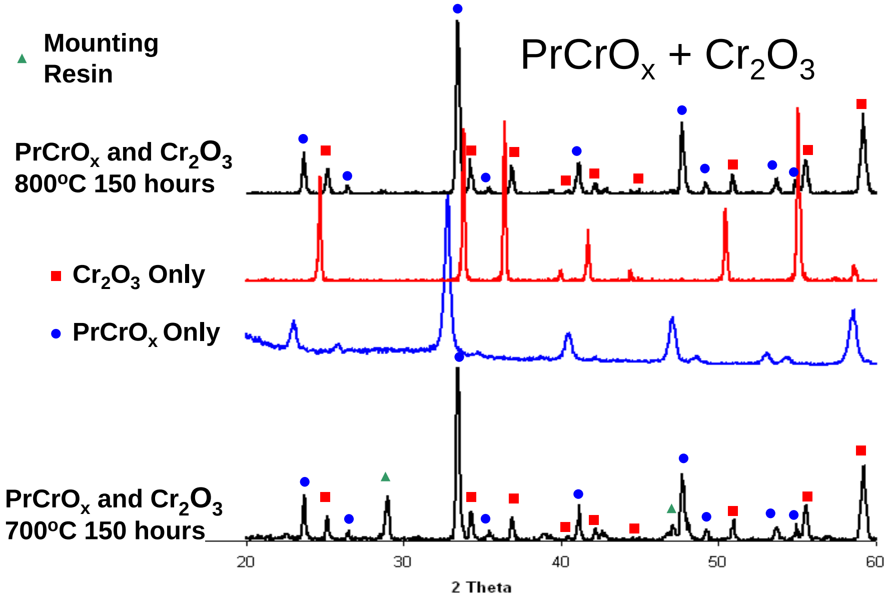
Cr-Tolerant Compositions

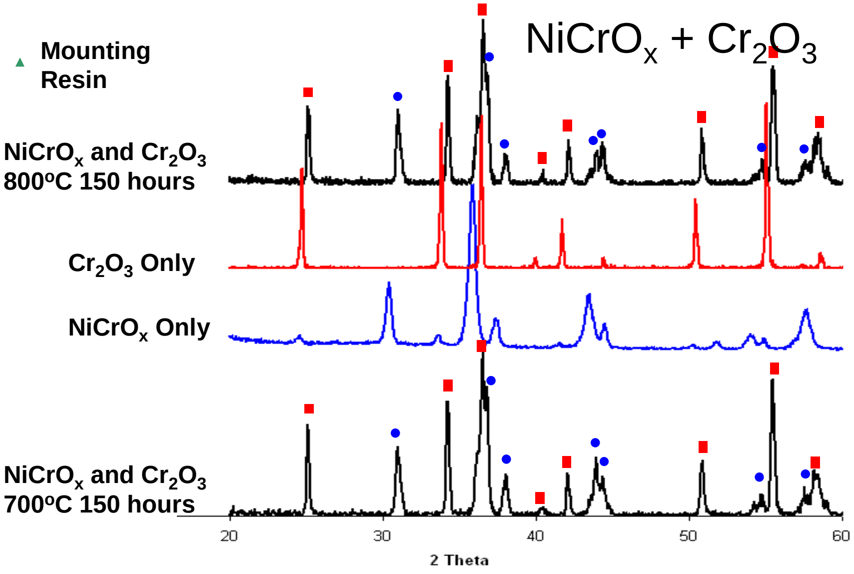
Alternative to LSM

Decomposition to stable species

$Pr_2NiO_4 + Cr_2O_3 \rightarrow PrCrO_x + NiCrO_x$

Are these stable in contact with Cr_2O_3?

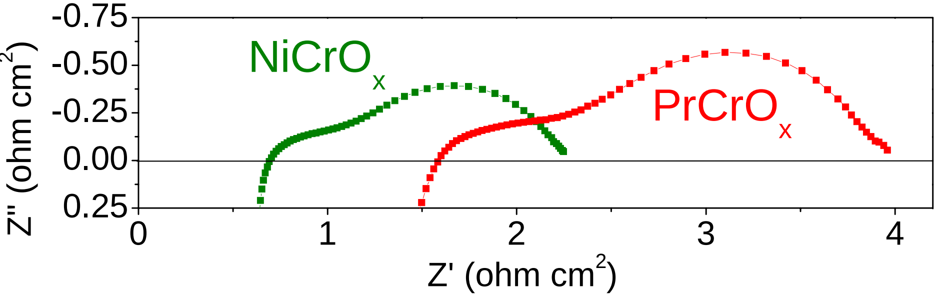




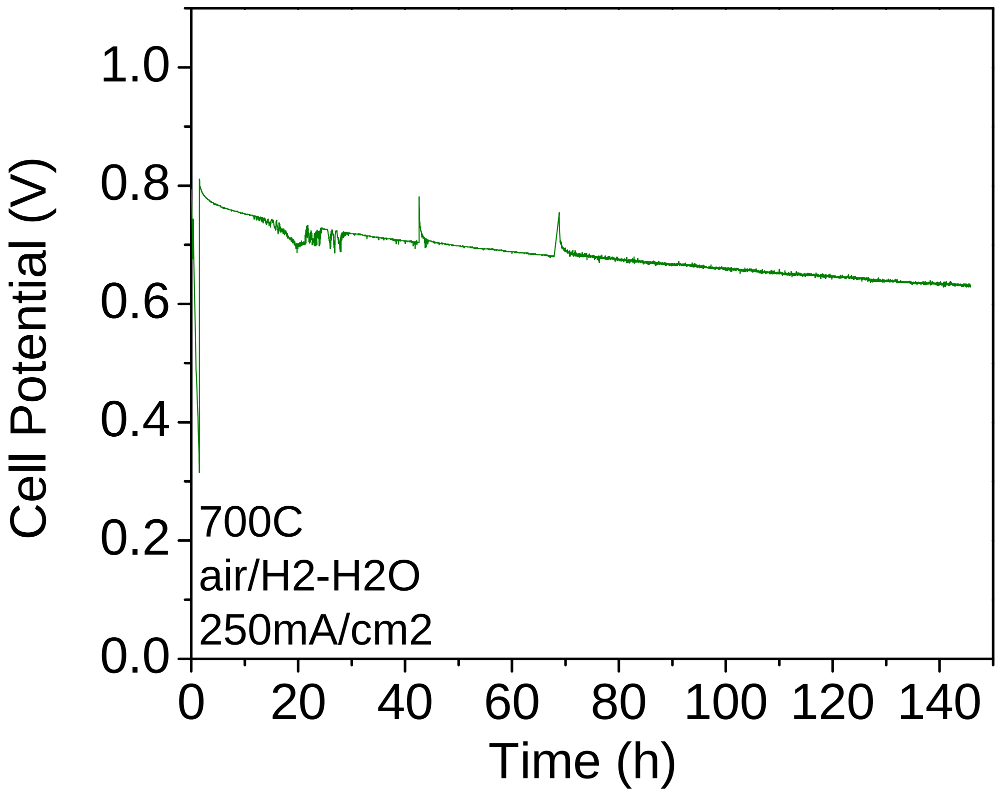
$PrCrO_x$ and $NiCrO_x$ are stable with Cr_2O_3

→ Active as cathode?

Electrochemical Testing of NiCrOx and PrCrOx



NiCrOx + SDC cathode
Anode-supported cell



Promising initial performance in anode supported cell
Promising stability in Cr-free configuration
→ move on to long-term testing with Cr-NiCrOx contact

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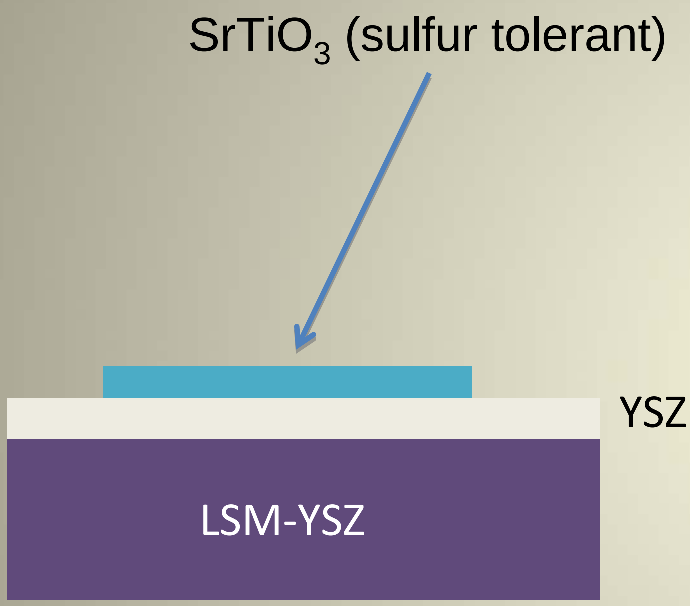
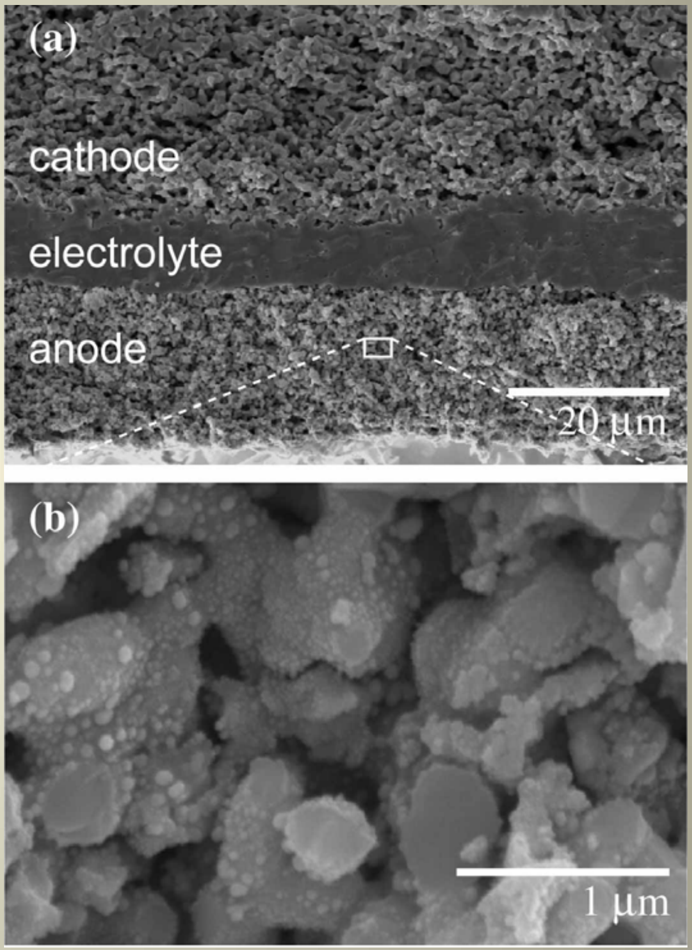
Infiltration of Ceria & Ru into $SrTiO_3$ anodes

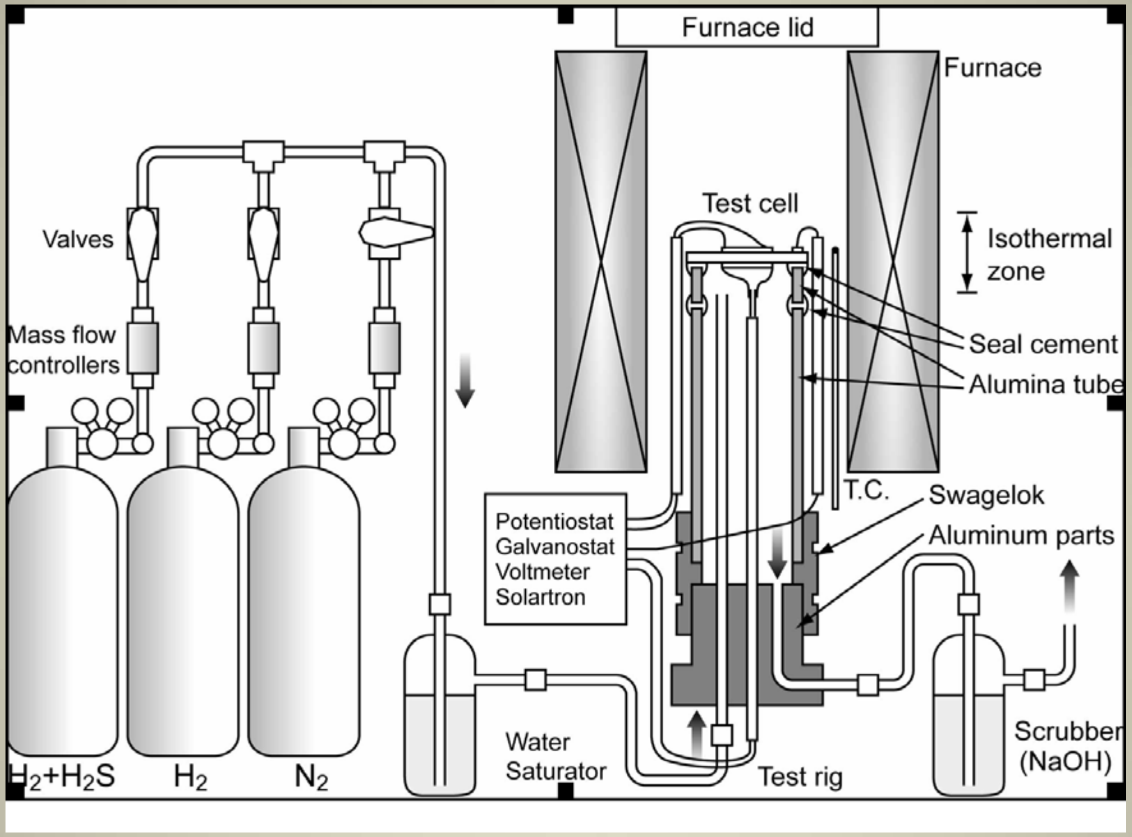


Cathode supported cells with ceria and Ru infiltrated SYTO-YSZ anode were prepared to investigate sulfur tolerance of the anode.



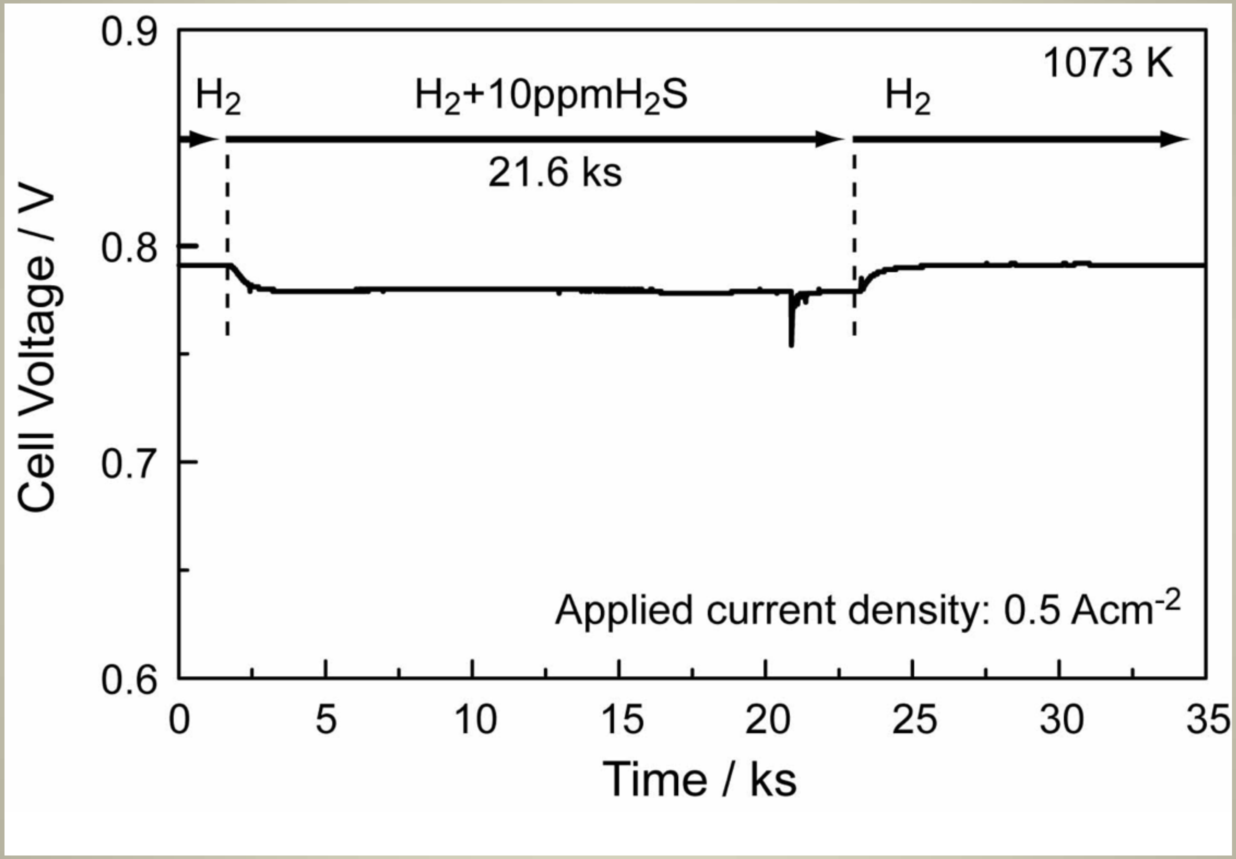
Secondary electron micrographs of cathode support cell tested in H_2S conditions for 500 hours.

Experimental Setup for H_2S Testing



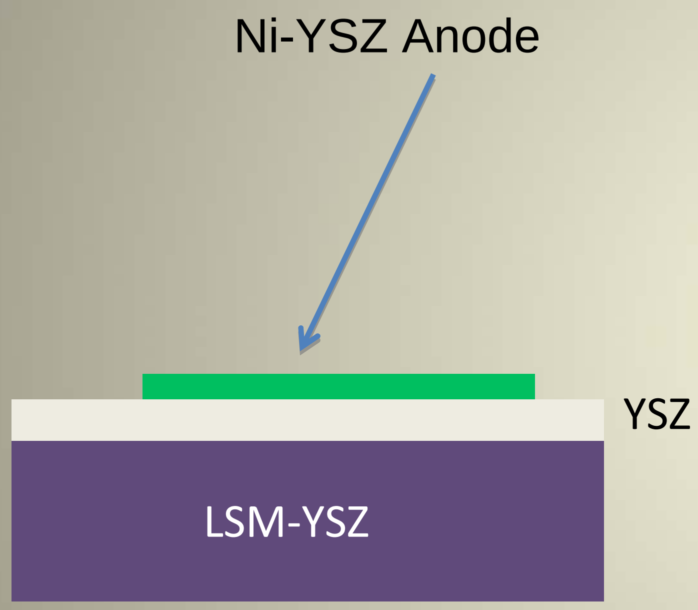
The experimental setup for the sulfur tolerance test was constructed as shown in Fig. 2. The gas flow system consists of stainless steel tubes, flow controllers, valves and glass parts: a water vapor saturator and scrubber. About 3 % of water vapor was added to the fuel gas by flowing the H_2 gas through the water vapor saturator at 298 K. Nitrogen was used to purge the system before H_2 and H_2S was introduced. 10~40 ppm H_2S gas was generated by mixing a pure H_2 flow with a controlled flow of 50 ppm H_2S premixed H_2 gas.

$SrTiO_3$ Anode Sulfur tolerance



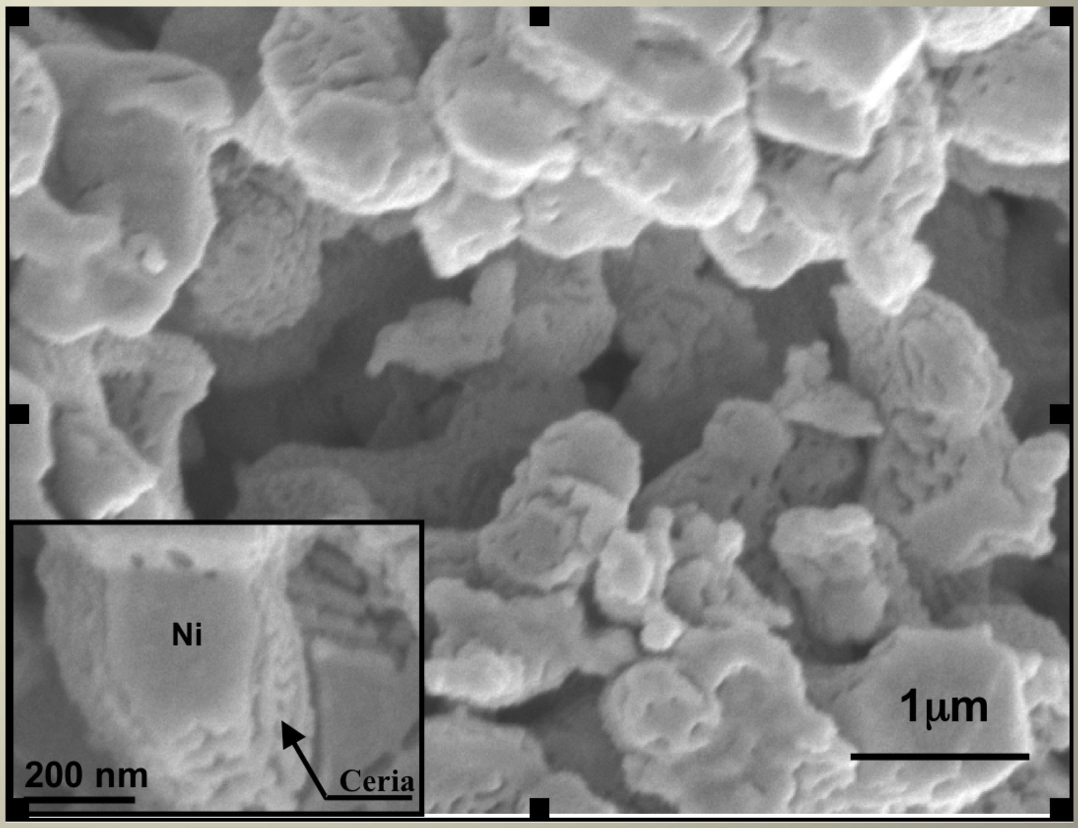
Cell voltage as a function of time for a cell exposed to 10 ppm H_2S at 1073 K.

Sulfur Tolerance in Ni-YSZ

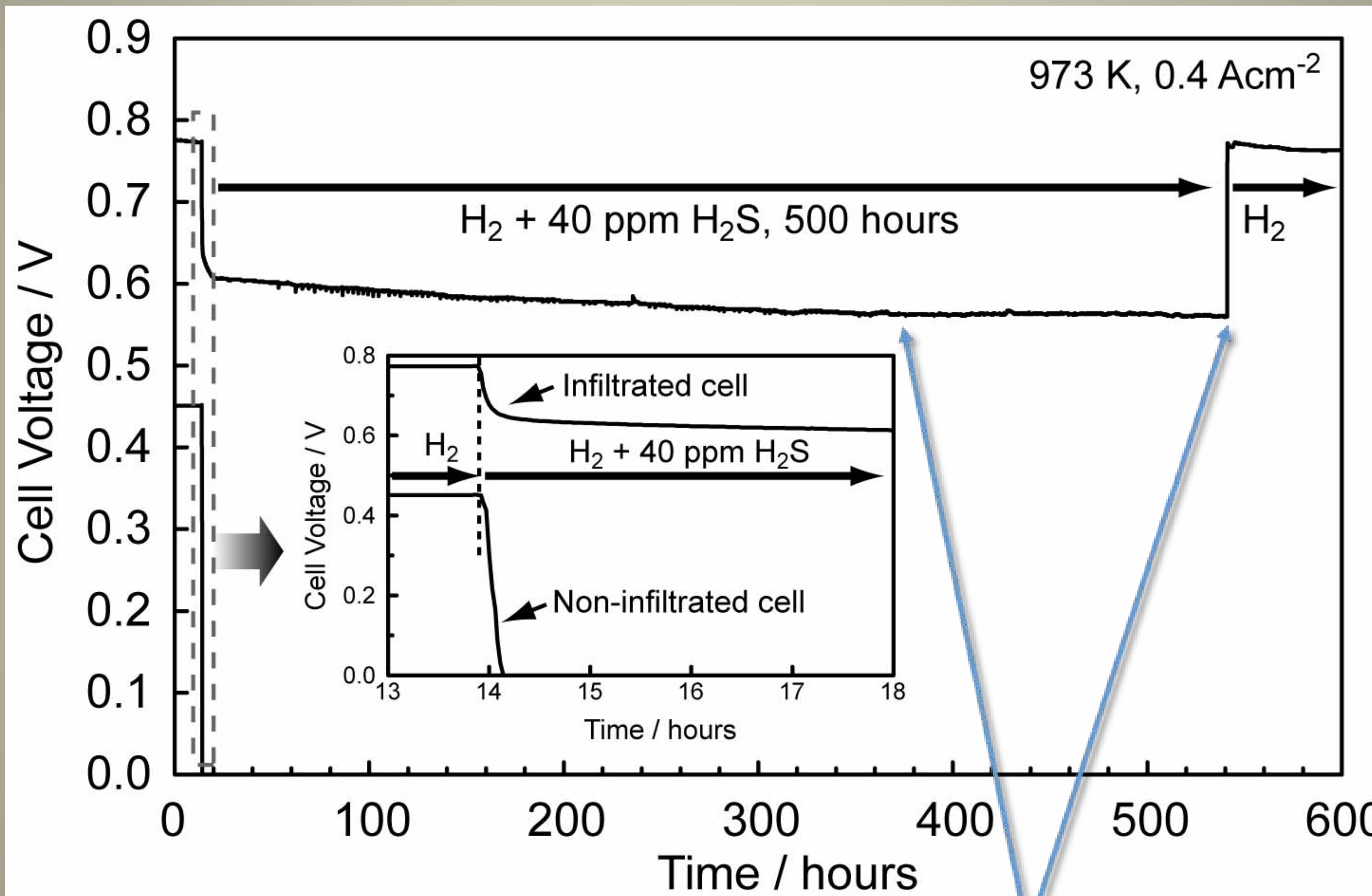


Cathode supported cell with
ceria infiltrated Ni-YSZ

Ceria nano coating after 500 hours exposure to 40 ppm H_2S 700 ^oC

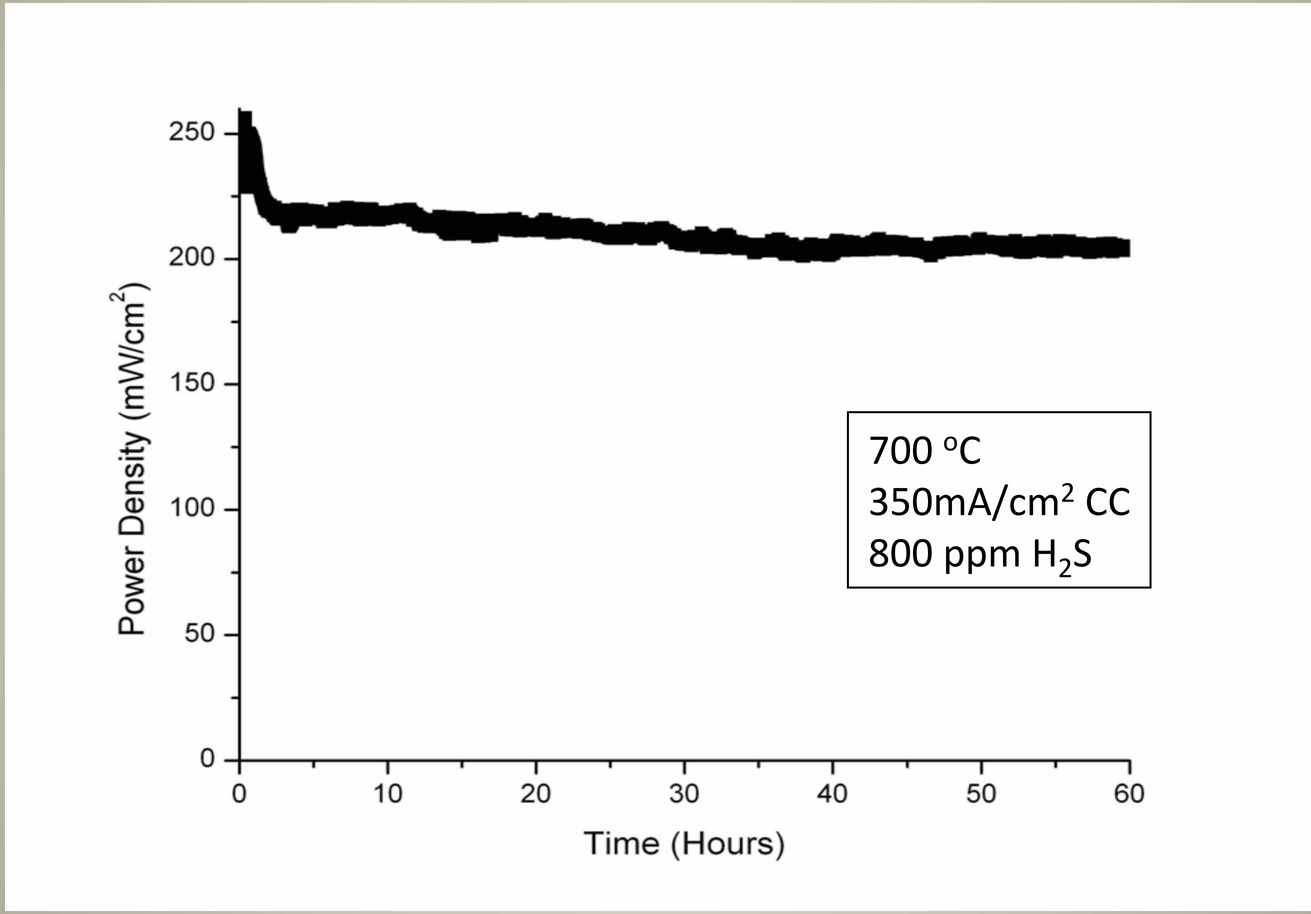


Sulfur Tolerant Ni-YSZ



0% degradation over 180 hrs

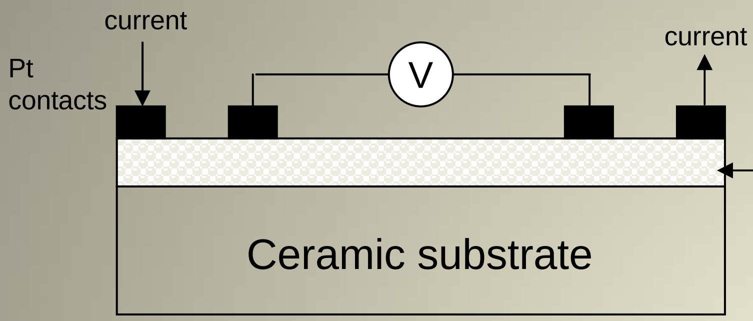
Anode Supported Cell Ni-SSZ w/ doped ceria infiltration at 800ppm H_2S



Preliminary tests under sufficiently high sulfur levels so as to accommodate any commercial or military fuel , suggests that with further optimization of the anode microstructure and infiltration composition, stable sulfur tolerant anodes can be achieved using the conventional composite Ni-YSZ material set.

Improving Conductivity of Infiltrated Catalyst

Screening conductivity of infiltrated structure of known SOFC anode oxide compositions



Porous YSZ
Infiltrated materials

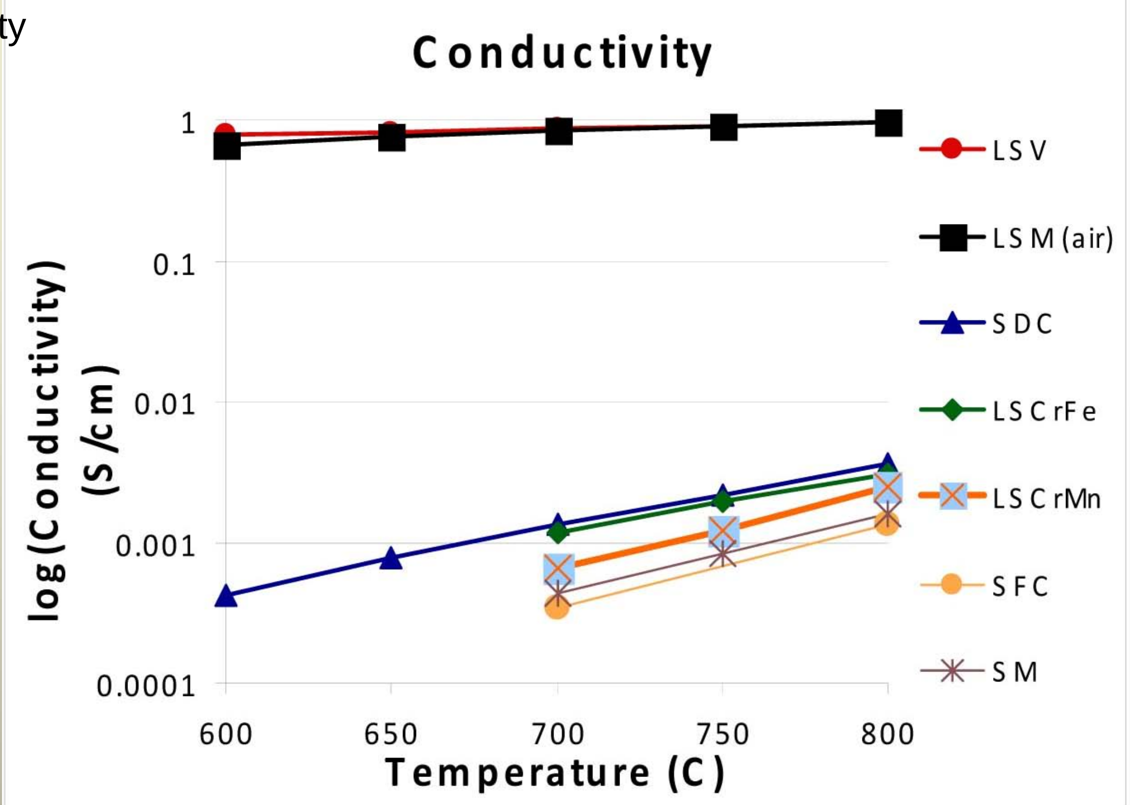
<u>$LaCrO_3$-based perovskite anodes</u>
Substitution for La and Cr improves conductivity
$La_{0.8}Sr_{0.2}Cr_{1-x}M_xO_3$

M= Fe, Mn, V, Mg

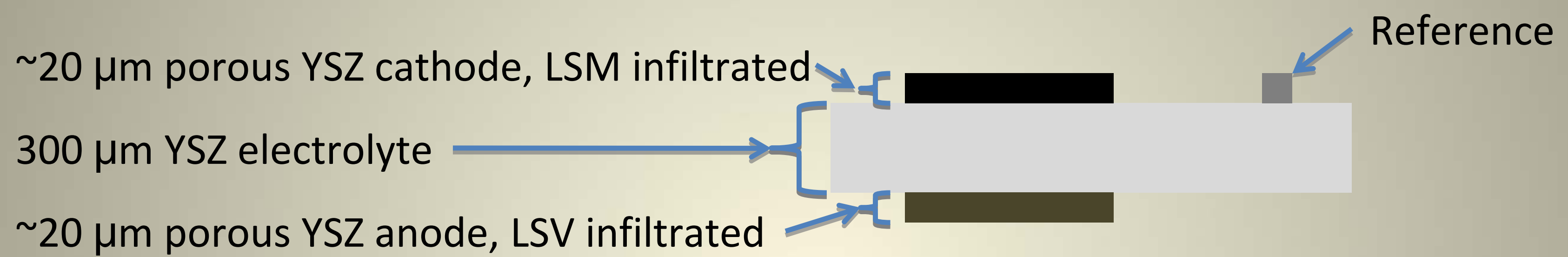
Expected redox stability

<u>$La_{0.7}Sr_{0.3}VO_3$</u>

Known for sulfur tolerance
(Meilin Liu's work)

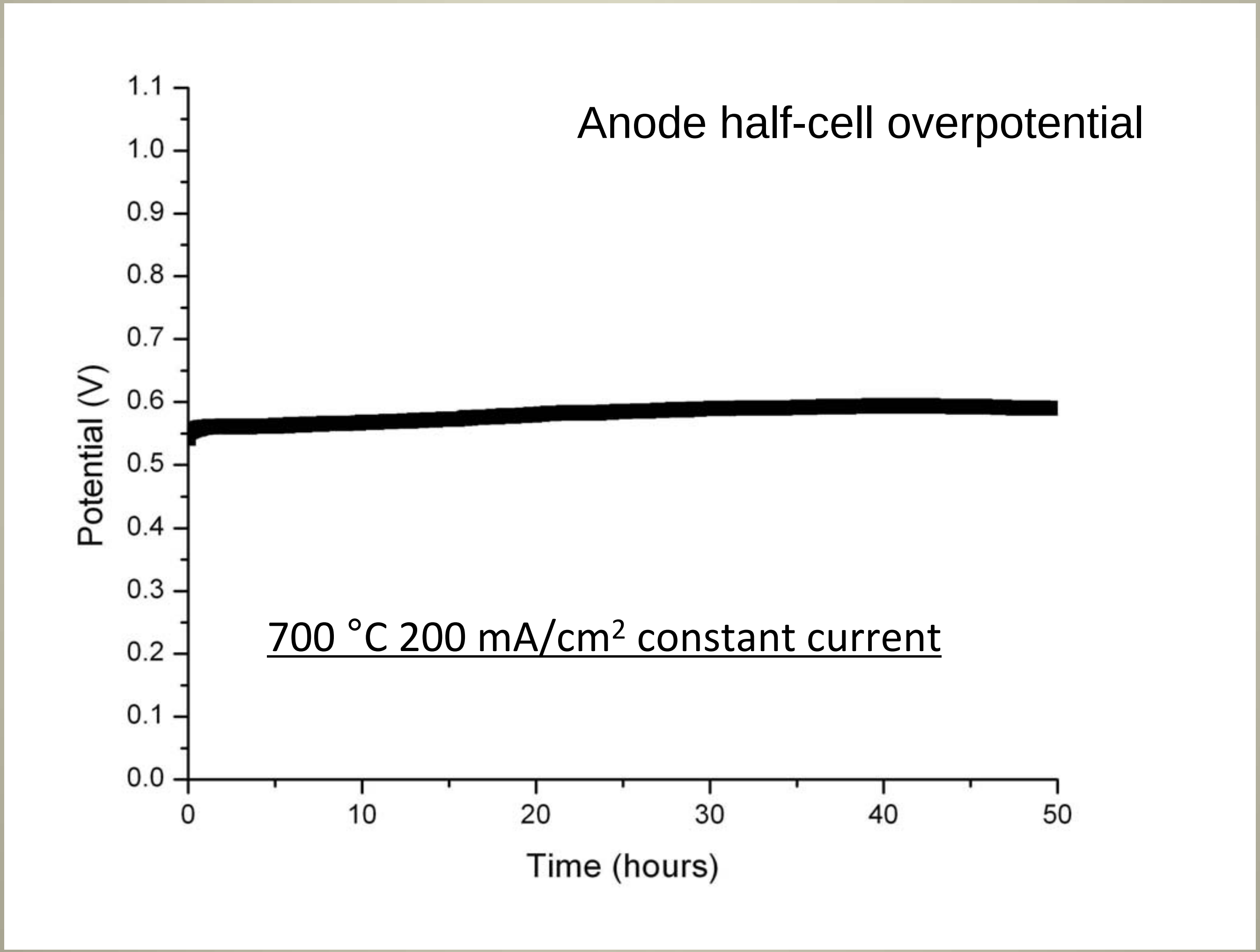


Electrolyte Supported Cell Test with $La_{0.7}S_{0.3}VO_3$ Infiltrated Anode



The cell was heated to 800 °C for 1 hour, and then brought to 700 °C for testing. Initially a 50 mA/cm² constant current was applied for 50 hours, to stabilize the cell. Following is the results under 200 mA/cm² constant current.

Electrolyte Supported Cell Test with $La_{0.7}Sr_{0.3}VO_3$ Infiltrated Anode



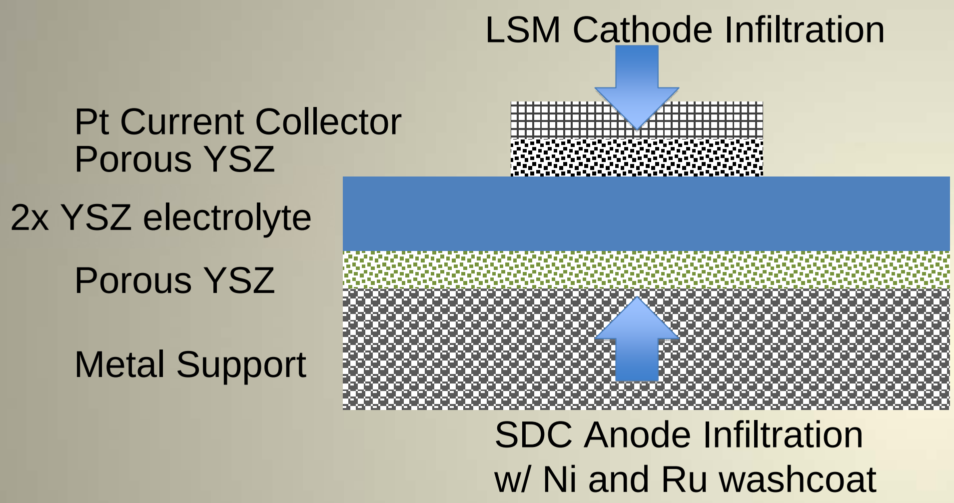
Industrial Collaboration & Tech Transfer

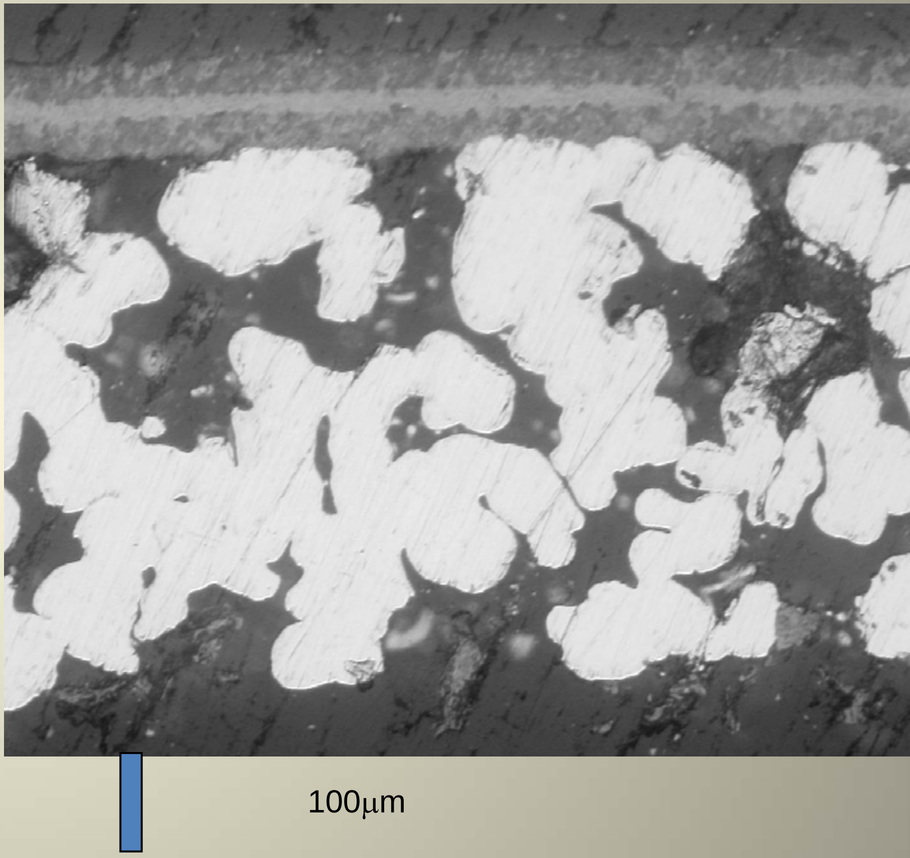
Tape-Casting Company in California

Tape-cast structures, scaleable, and optimized for infiltration

Tape Cast SOFCs Built to LBNL Specifications

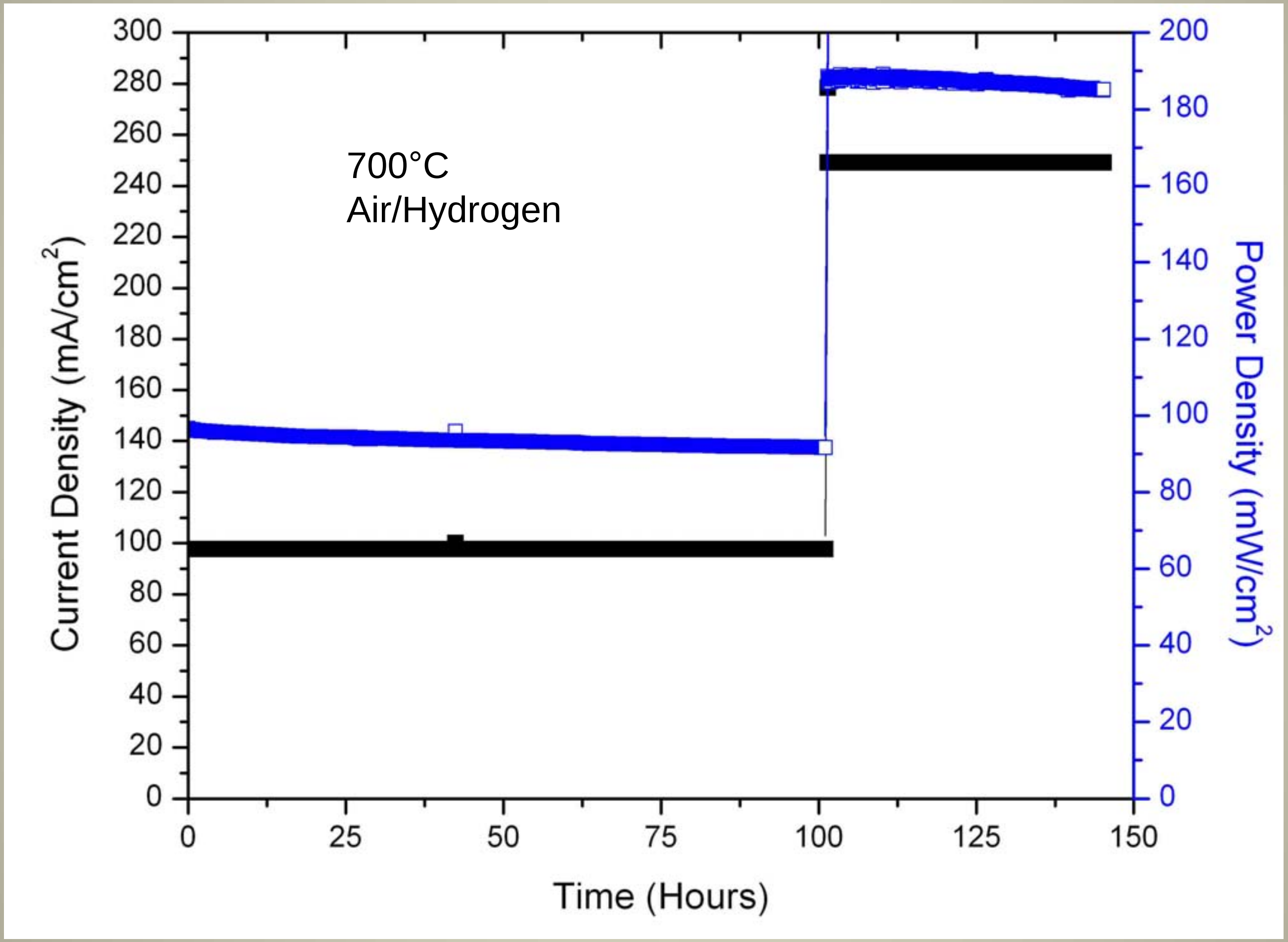
California Tape-Casting Co.
- Manufacturer of tape-cast planar ceramic structures





Rapid progress – 6 months from initial contact to planar cell fabrication

Stability of Commercial Produced SOFC Tape: Completely Infiltrated Anode & Cathode



Provides a platform for seal and electrode testing
- Cathode, anode, seal development on planar cells

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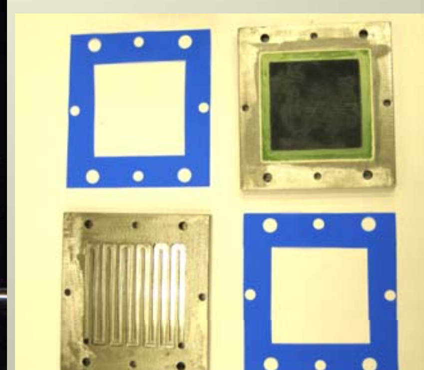
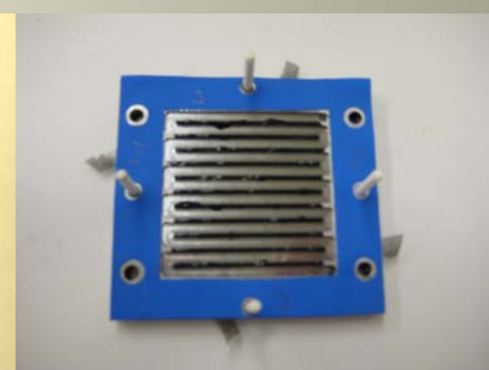
McAllister Build of 2-cell 5 x 5 cm SOFC Plate Stack

- Standardized test platform
- Allows testing of electrodes, seals, contact pastes, in a uniform manner
- Allows comparison of results between labs, universities, and industry
- Fits in inexpensive furnaces
- Is not intended as a precursor to commercial device
- ~ $2600/ea. after initial build





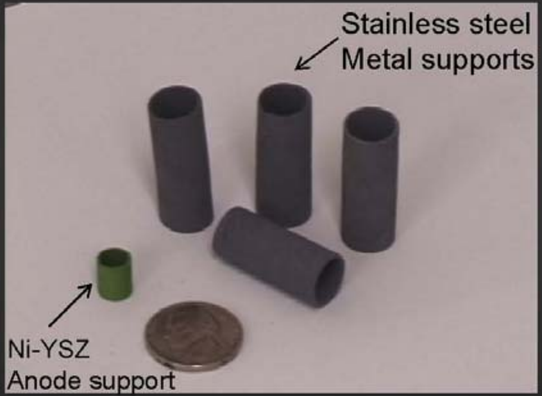
Use of Low-Cost Raw Materials to Fabricate Inexpensive SOFCs

Materials Cost Advantage

Material	$/kg (2007)
Ni	35-55
YSZ	100
430 SS	5

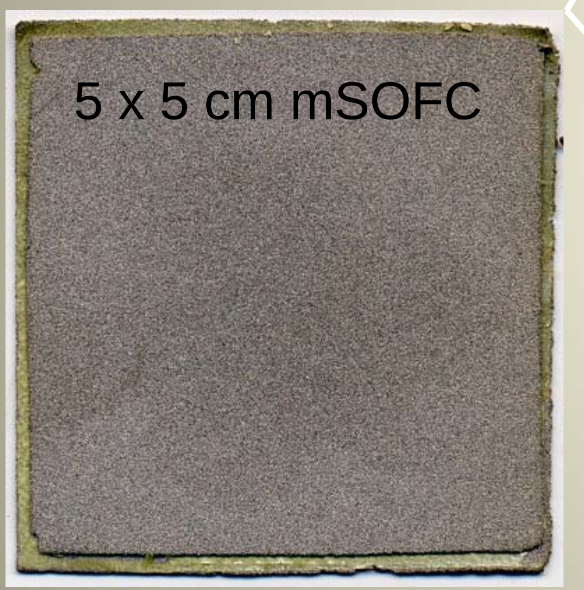
Ferritic stainless steels chosen for:
- Low cost
- CTE match with YSZ
- Good oxidation resistance

$0.05 of raw material



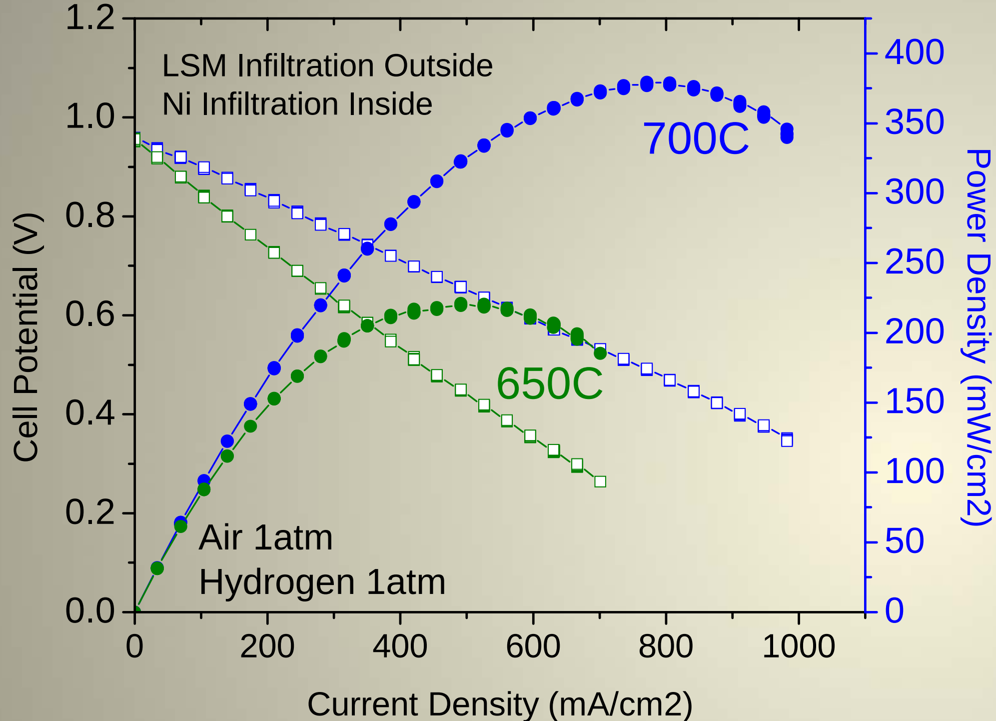
High Volume Porous Metal Media

Coal: kW to MW?

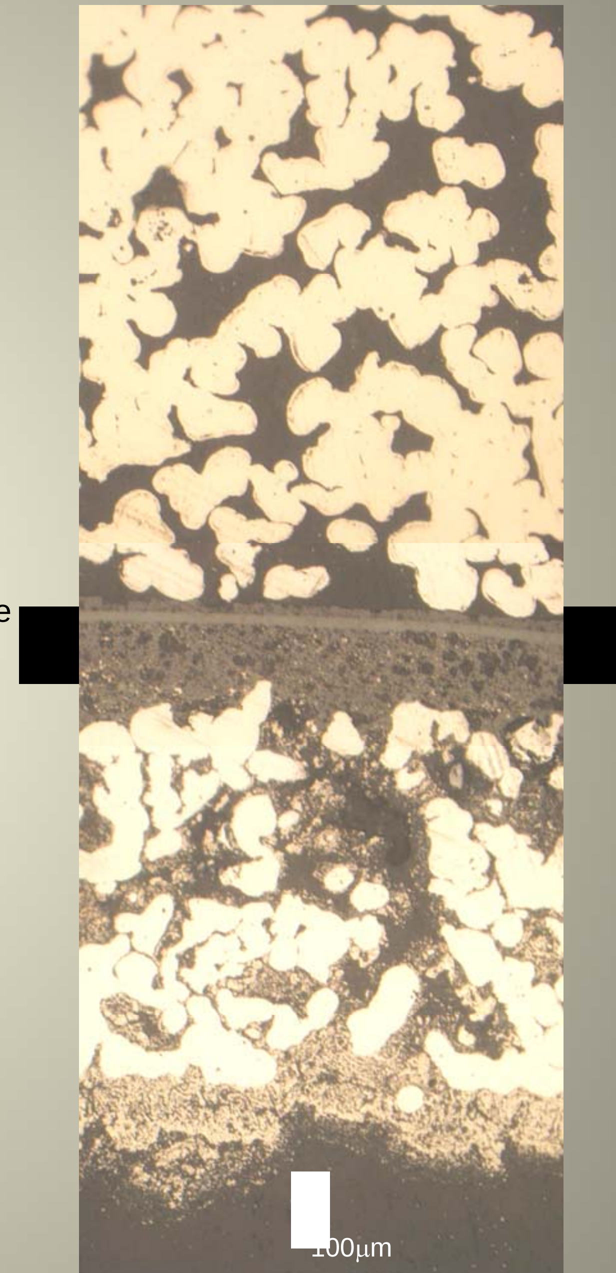


Tubular Metal Supported SOFC

Anode-Inside



No mass transport limitation
Almost 400mW/cm² at 700°C



Summary

- Cathode infiltration is working well and shows good stability to 500 hours
- Infiltration of ceria into Ni based anodes improves S tolerance; complete infiltration of anode is still in the works
- Stack design is essentially done
- Technology transfer has been successful