Development of Low-Cost Alloy Supported SOFCs

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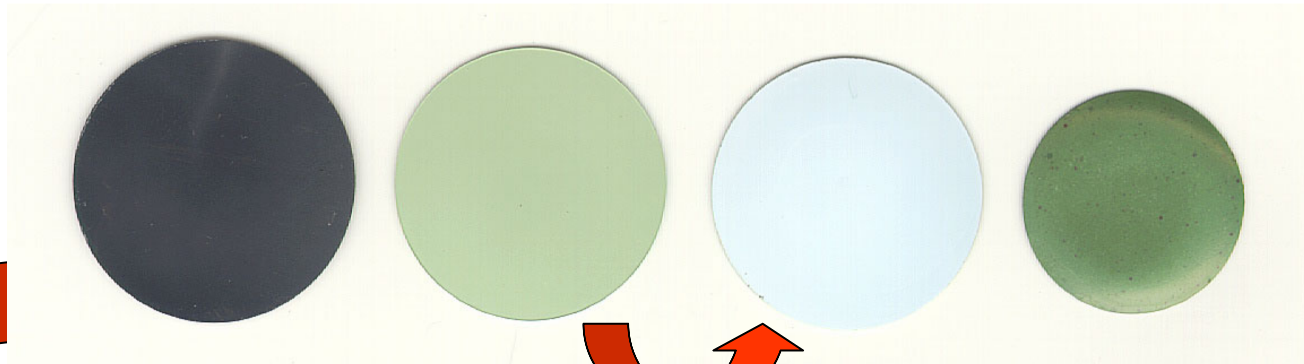
Background: Accomplishments

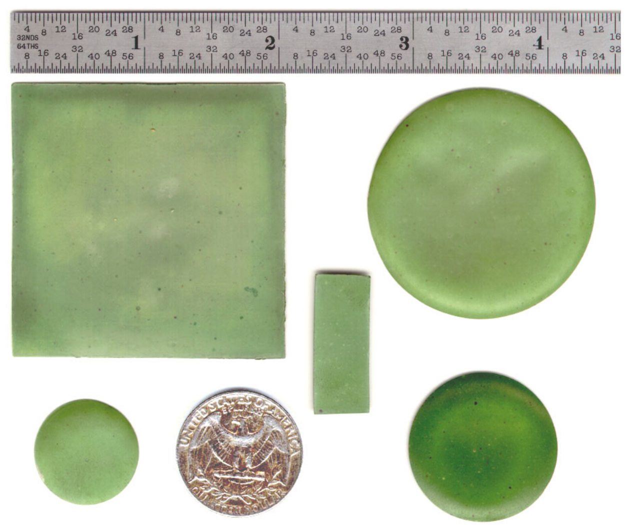
Co-fired Thin-Film Structures by Colloidal Deposition

NiO/YSZ substrate (pressed)	NiO/YSZ fired at 950 °C	NiO/YSZ substrate with green YSZ film	NiO/YSZ-YSZ bilayer fired at 1400 °C



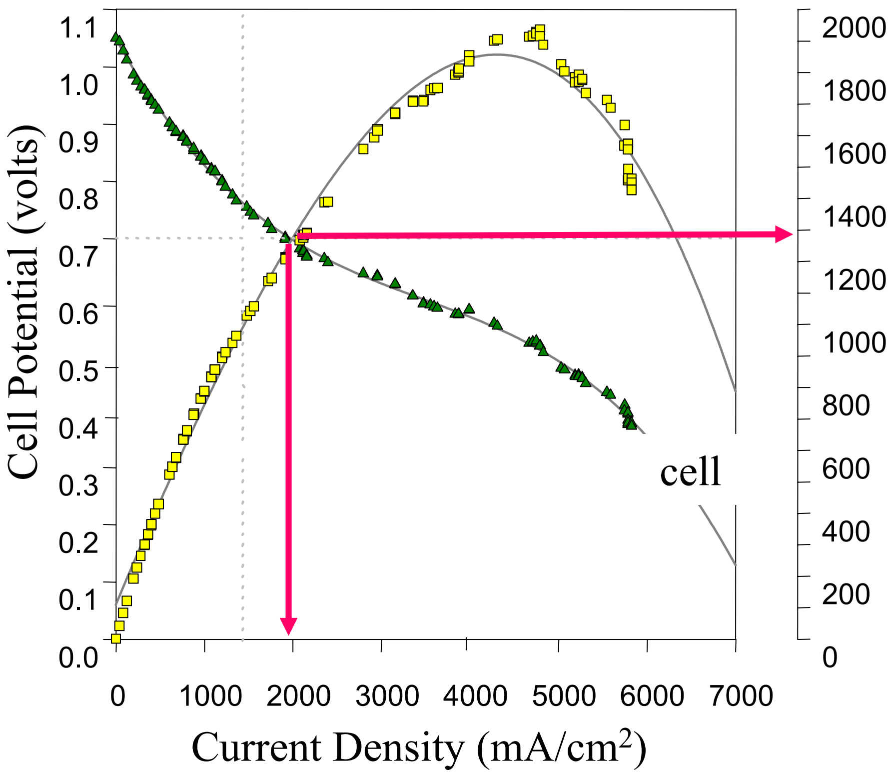
Dip-coat, aerosol spray, EPD...

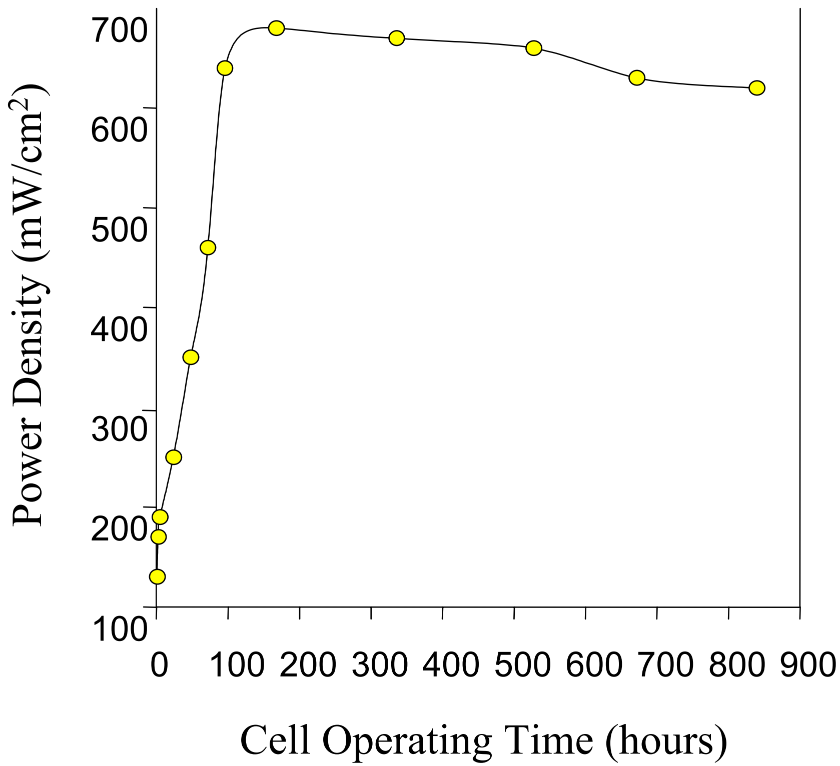
- Geometry Independent
- Low Cost
- Scaleable



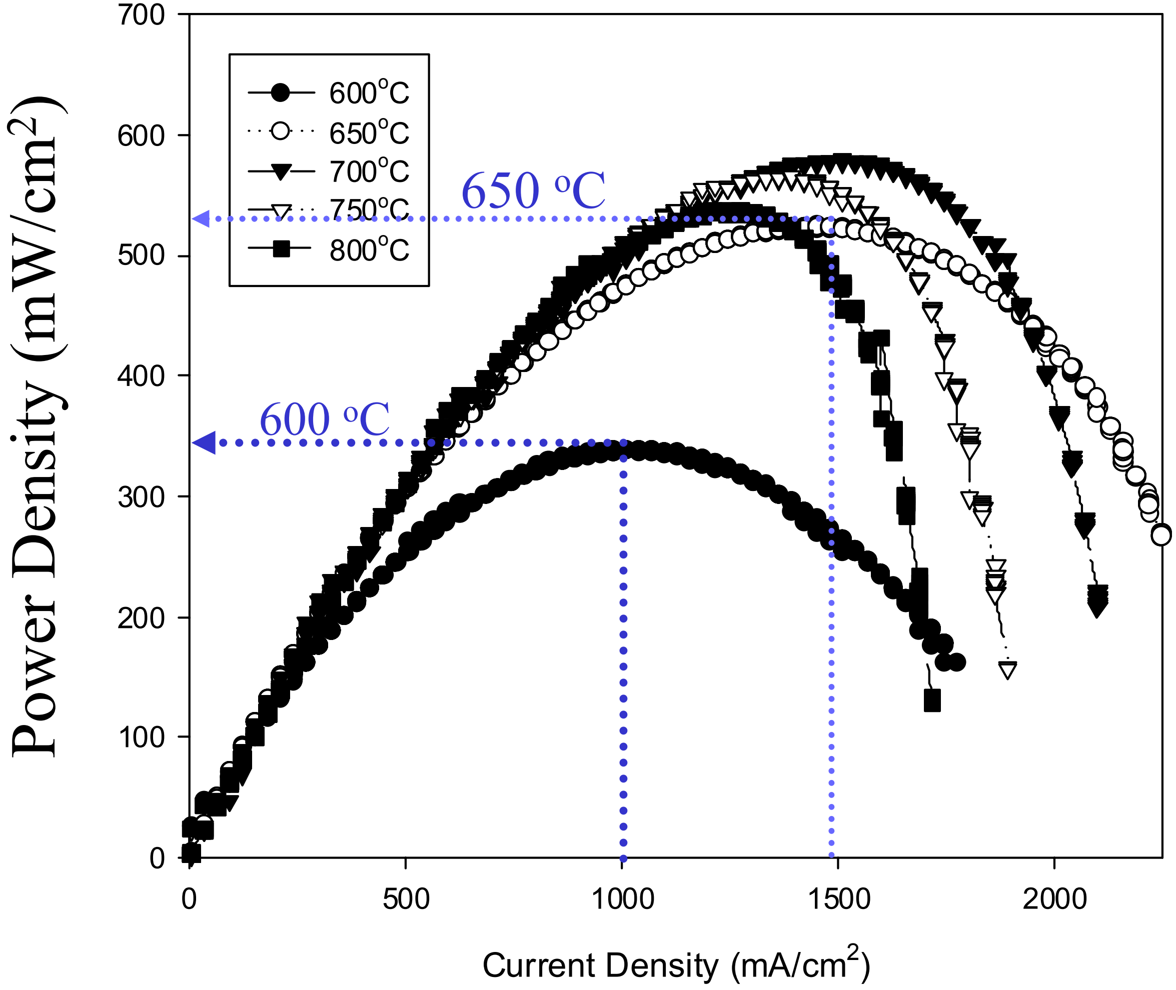
Intermediate Temp: 750 to 850 ^oC; PLANAR

Ni-YSZ/YSZ/LSM-YSZ Thin-film Cell at 800 ^oC



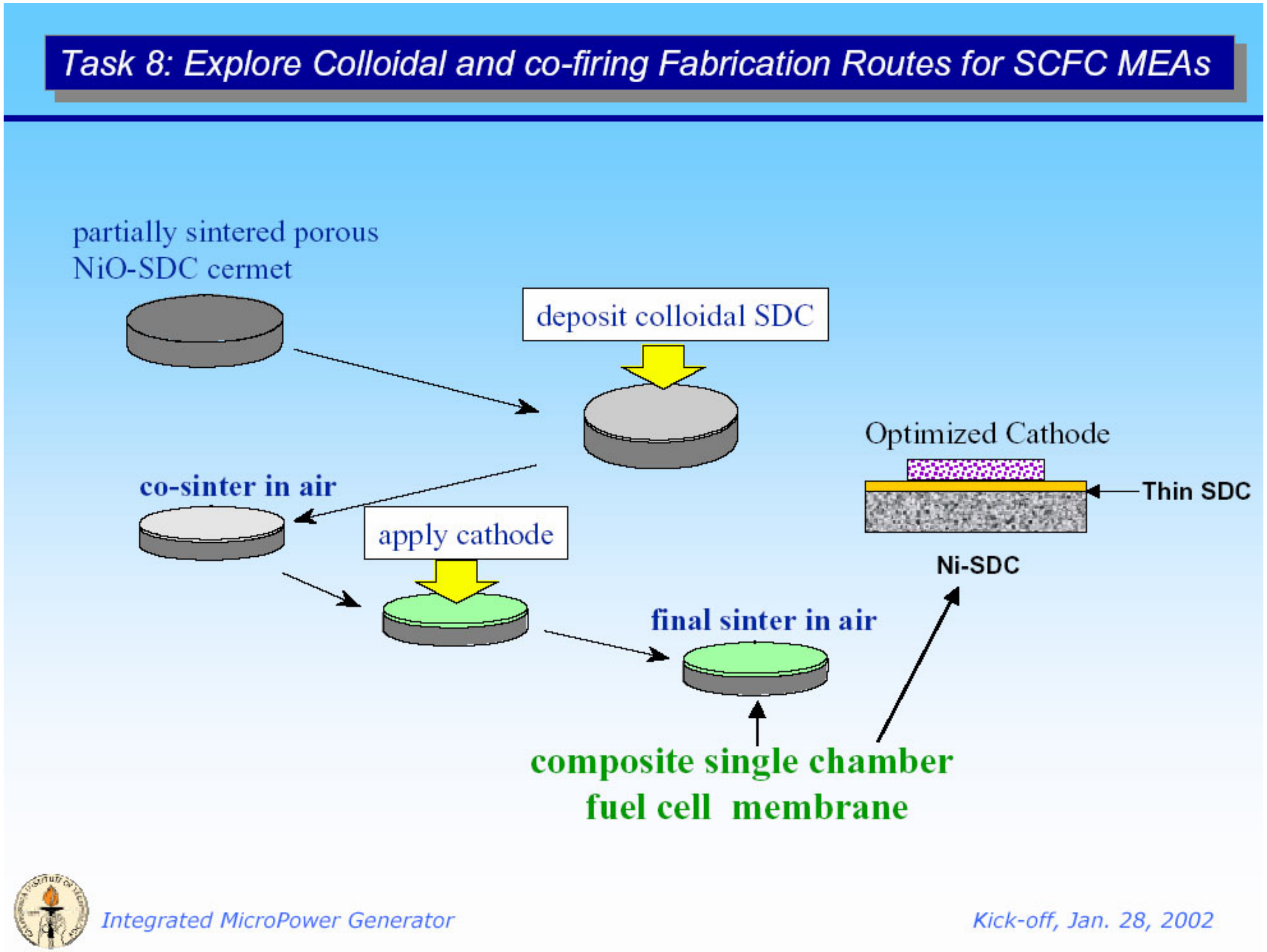


Thin-film Ceria Cell Performance: 650 - 800 °C



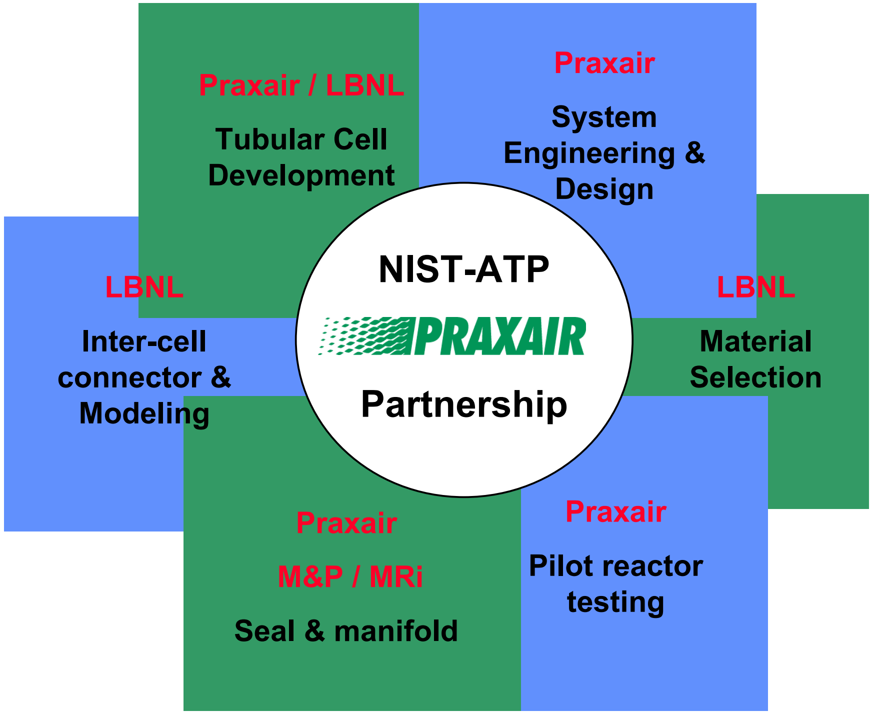
Integrated Program Overview

DARPA: Integrated MicroPower Generator



Praxair NIST-ATP

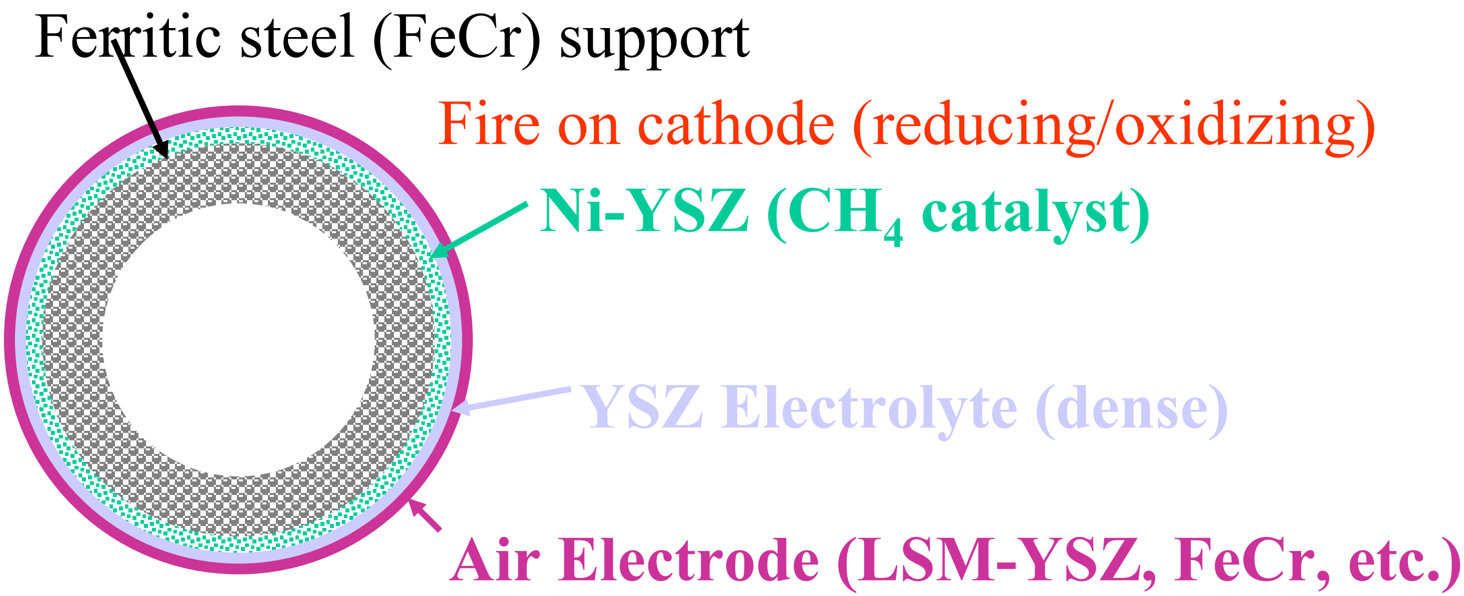
Advanced Electrolytic System for Combined Oxygen Separation and Compression



Project Objectives

The principal project objective is to develop the technology for a new, point-of-use, oxygen generator and electrochemical compressor that will economically and efficiently replace the practice of supplying oxygen by cylinders and liquid. The end goal of the project is to demonstrate the technology in a pre-commercial, pilot-scale integrated system.

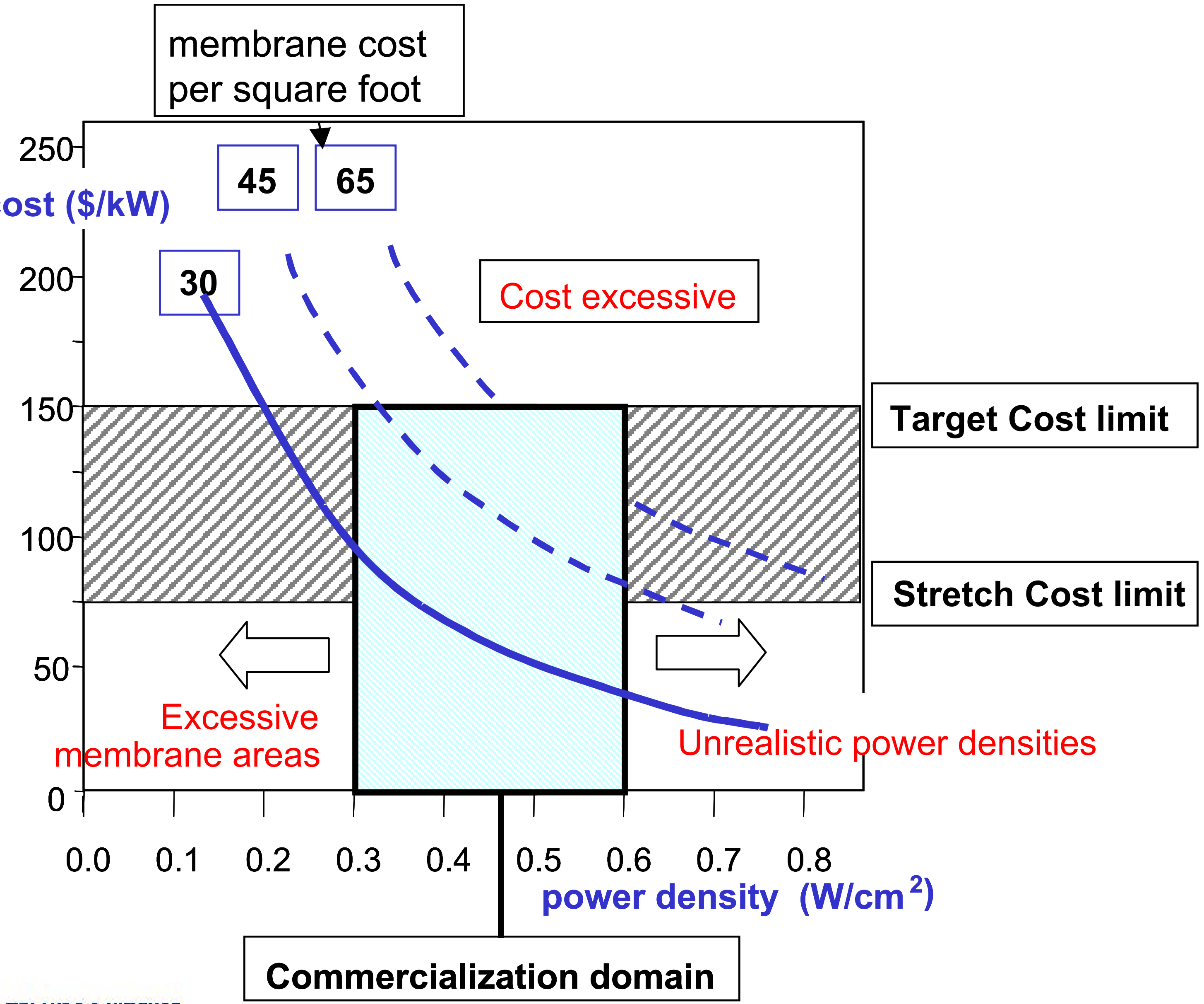
Ikerlan: Residential Fuel Cell System



Sinter tube in <u>reducing furnace</u> at 1200 to 1400 ^{o}C

NETL Program

BASIC STACK COST/PERFORMANCE RELATIONSHIP



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NETL Project: Development of Inexpensive Metal Alloy Supports for Cost-Competitive Solid Oxide Fuel Cells

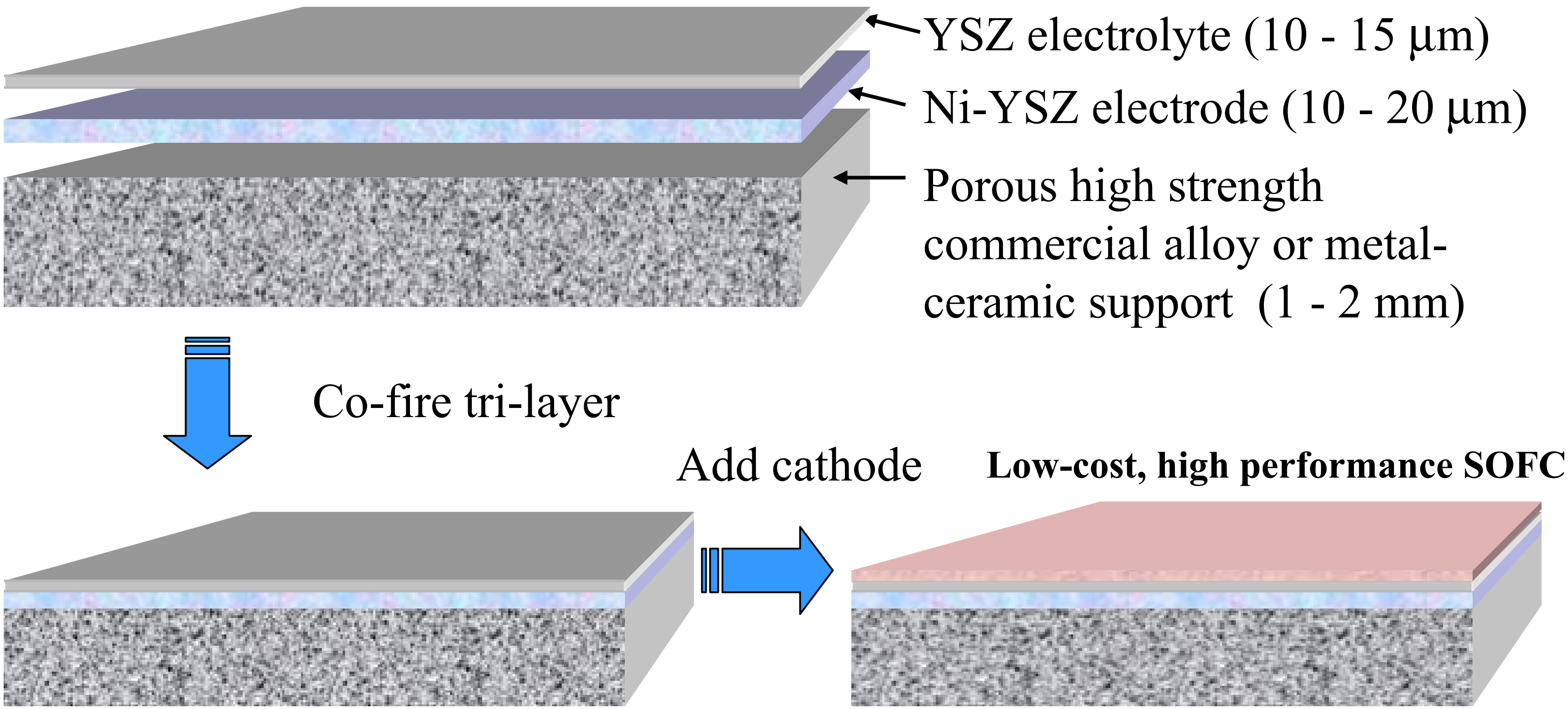
•The LBNL group has recently developed a novel approach to SOFC fabrication where mechanically robust and inexpensive metal alloy electrode supports are used in the construction of the SOFC stack.

•Use of porous alloy support should increase the strength and toughness of the stack as well as greatly increase the electronic and thermal conductivity, decreasing losses due to current collection and improving thermal management of the stack.

•Alloy support structures should allow novel sealing technology including welding, brazing, and even crimp seals. Seals have been one of the biggest barriers to planar SOFC technology and innovative designs are needed.

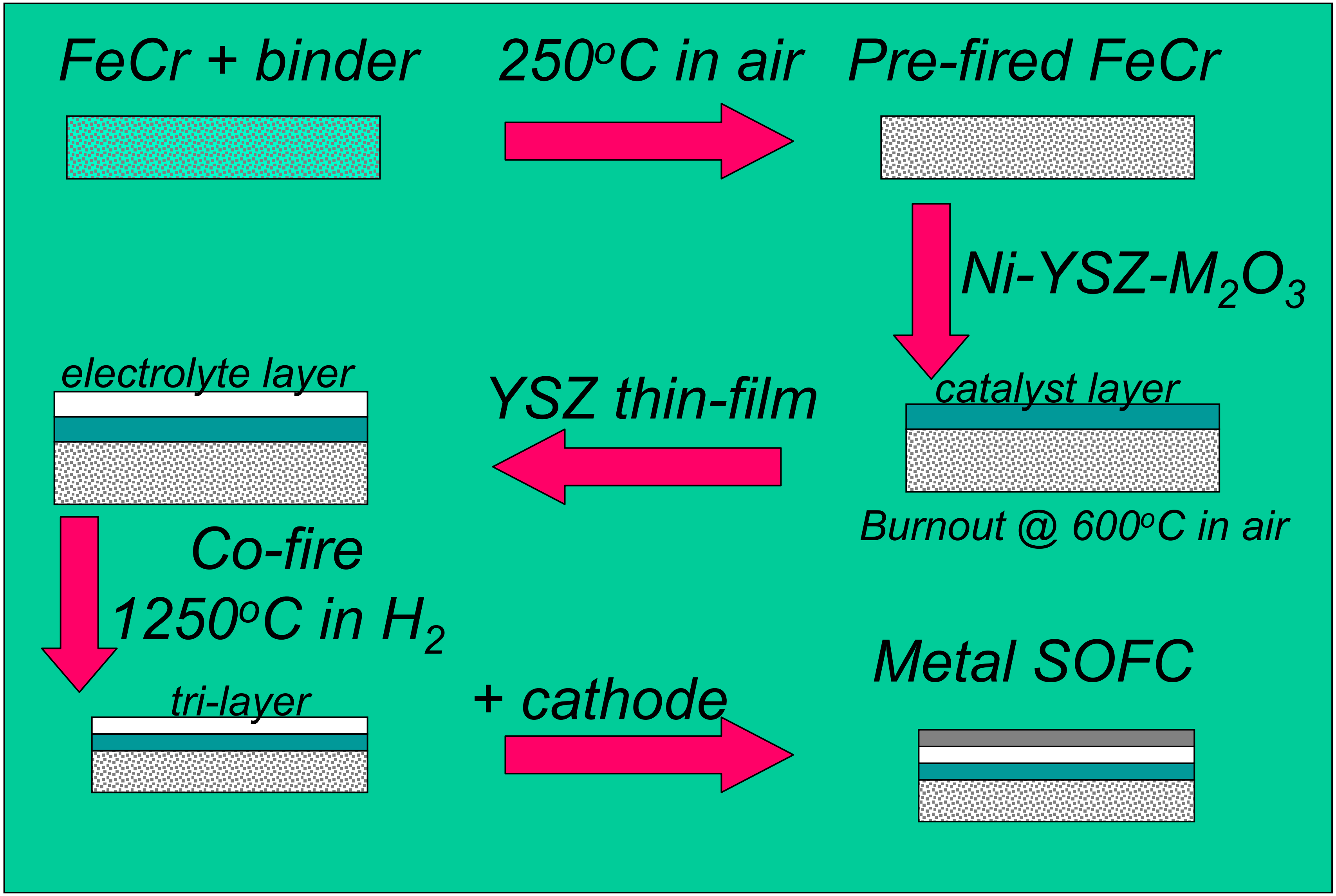
•The purpose of the initial work was to demonstrate proof of the principle and identify needed research.

Fabrication of Low-Cost Planar SOFC

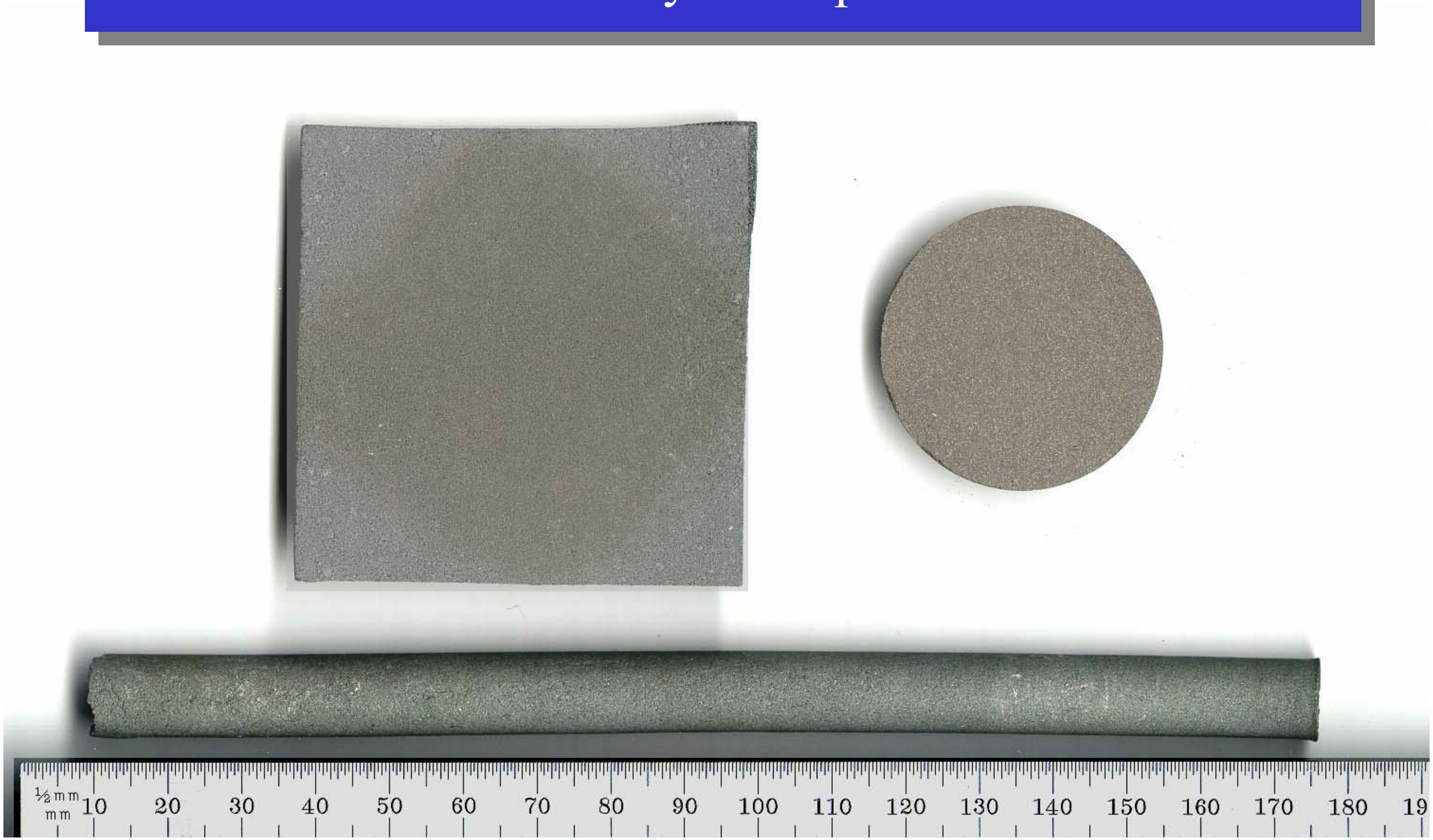


The anode in Ni-YSZ supported thin-film cells must be maintained in reducing environments; whereas alloy support is oxidation resistant allowing cool-down and thermal cycling in the presence of air

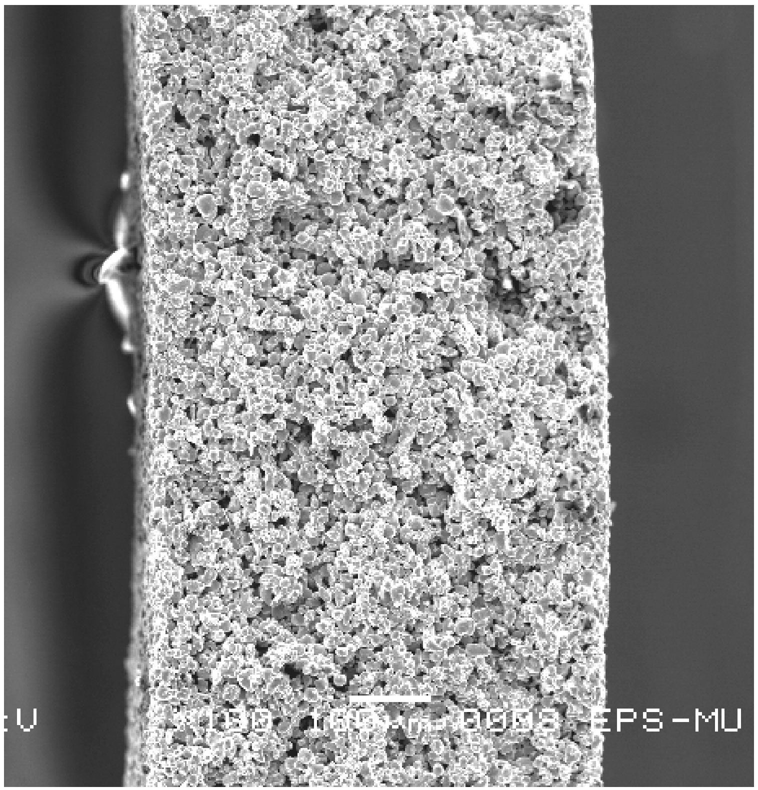
Fabrication of Thin-film Metal SOFC

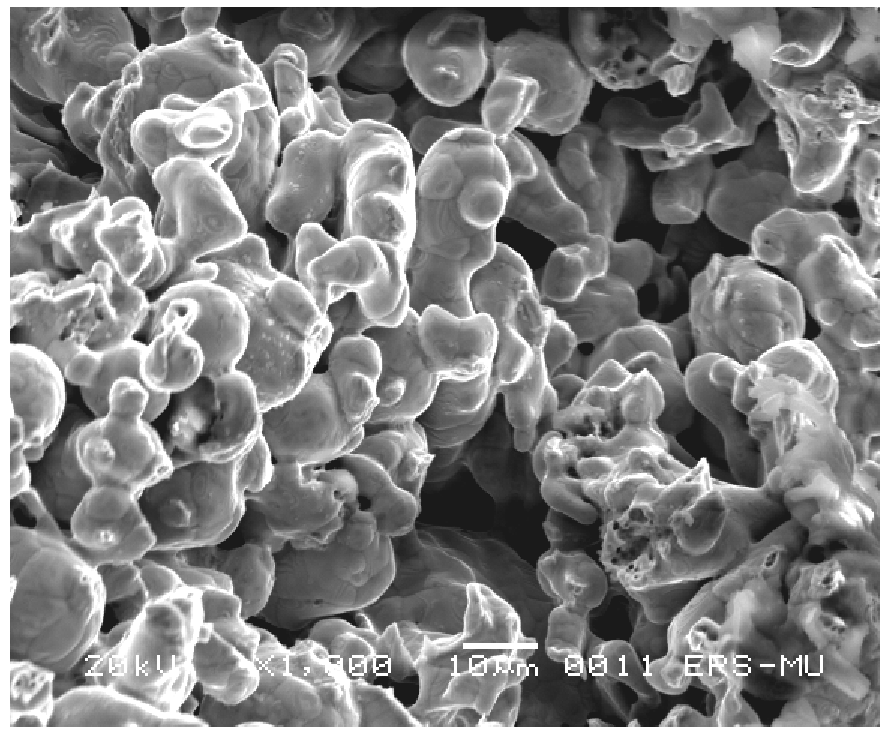


LBNL Group has fabricated porous alloy supports in a variety of shapes

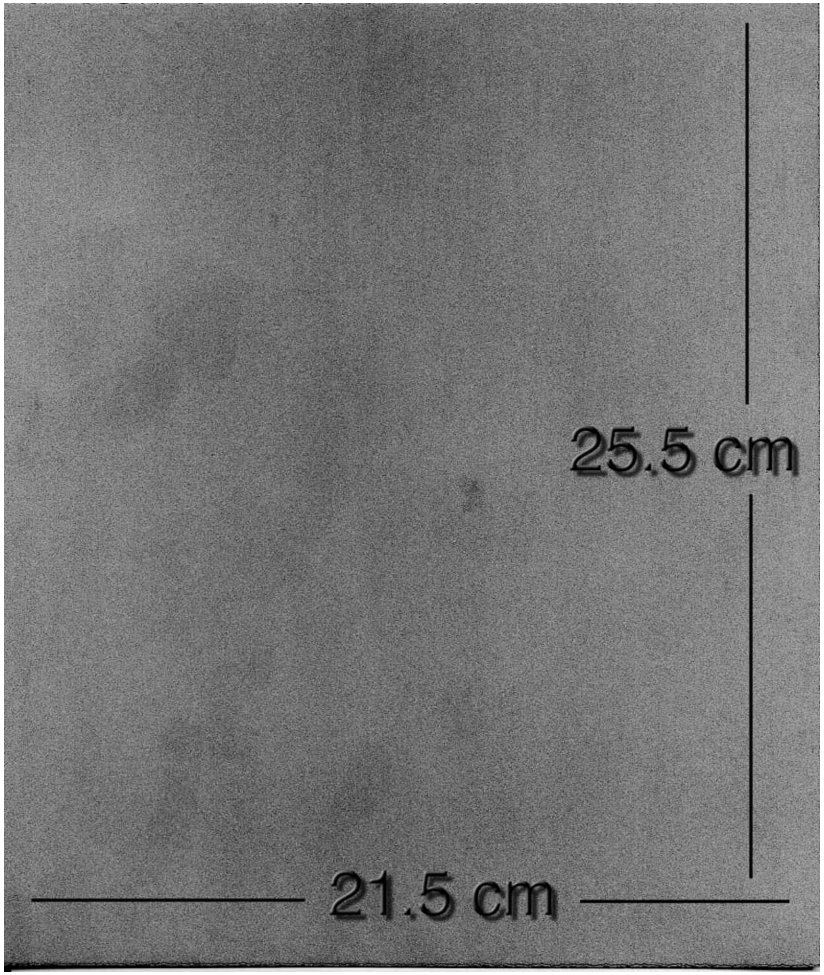


Commercial “Pall” Tube Microstructure



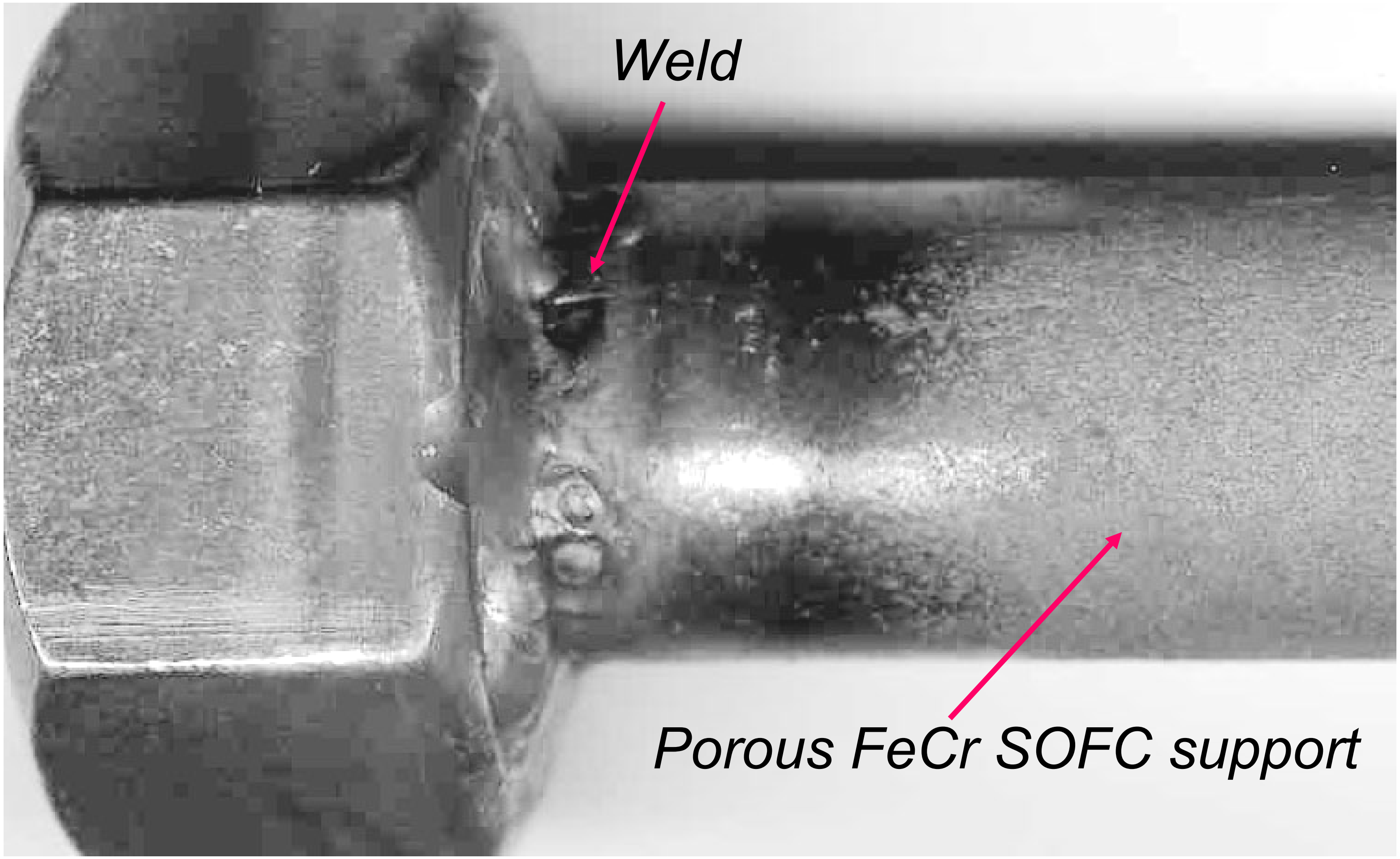


Porous Metal Filters Available Commercially



- Area = 550 cm^2
- 0.5 cm seal
- 500 cm^2 active
- 0.3 to 0.5 W/cm^2 =
- 150 to 250 W/plate
- 4 to 7 plates/kW

LBNL Welded Porous FeCr SOFC Support Tube



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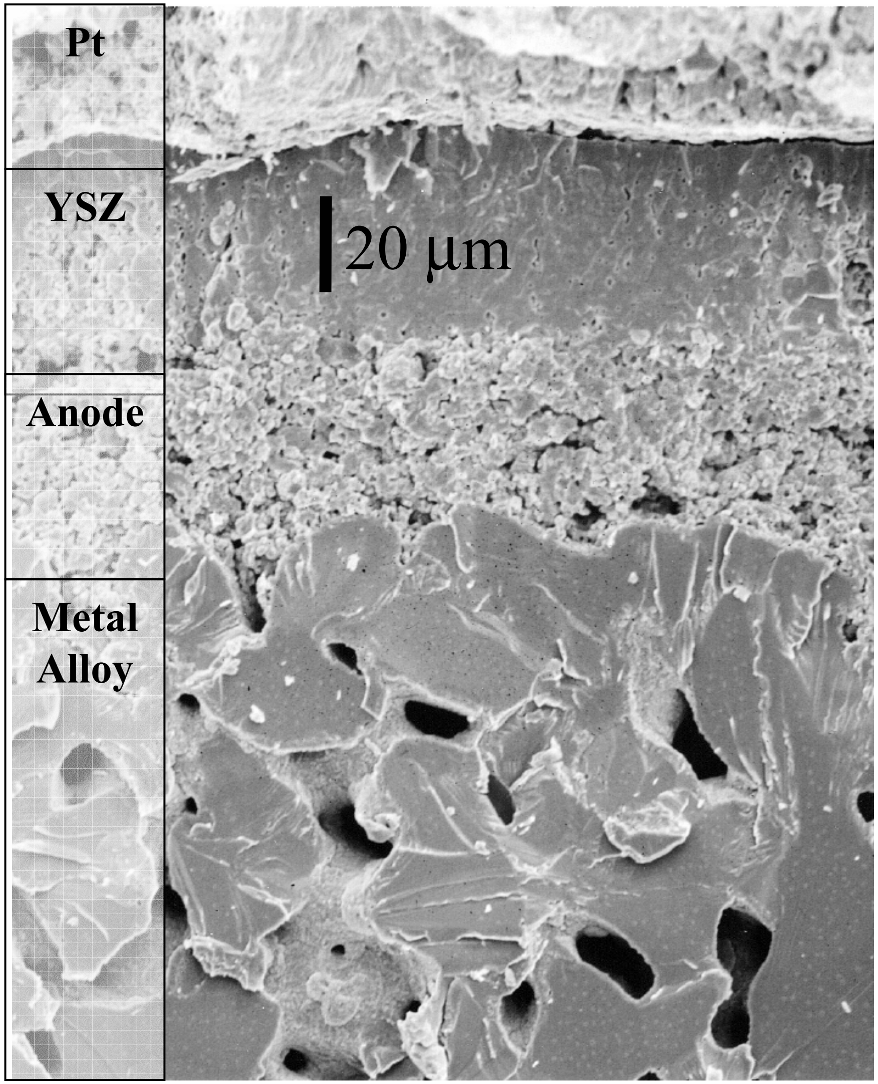
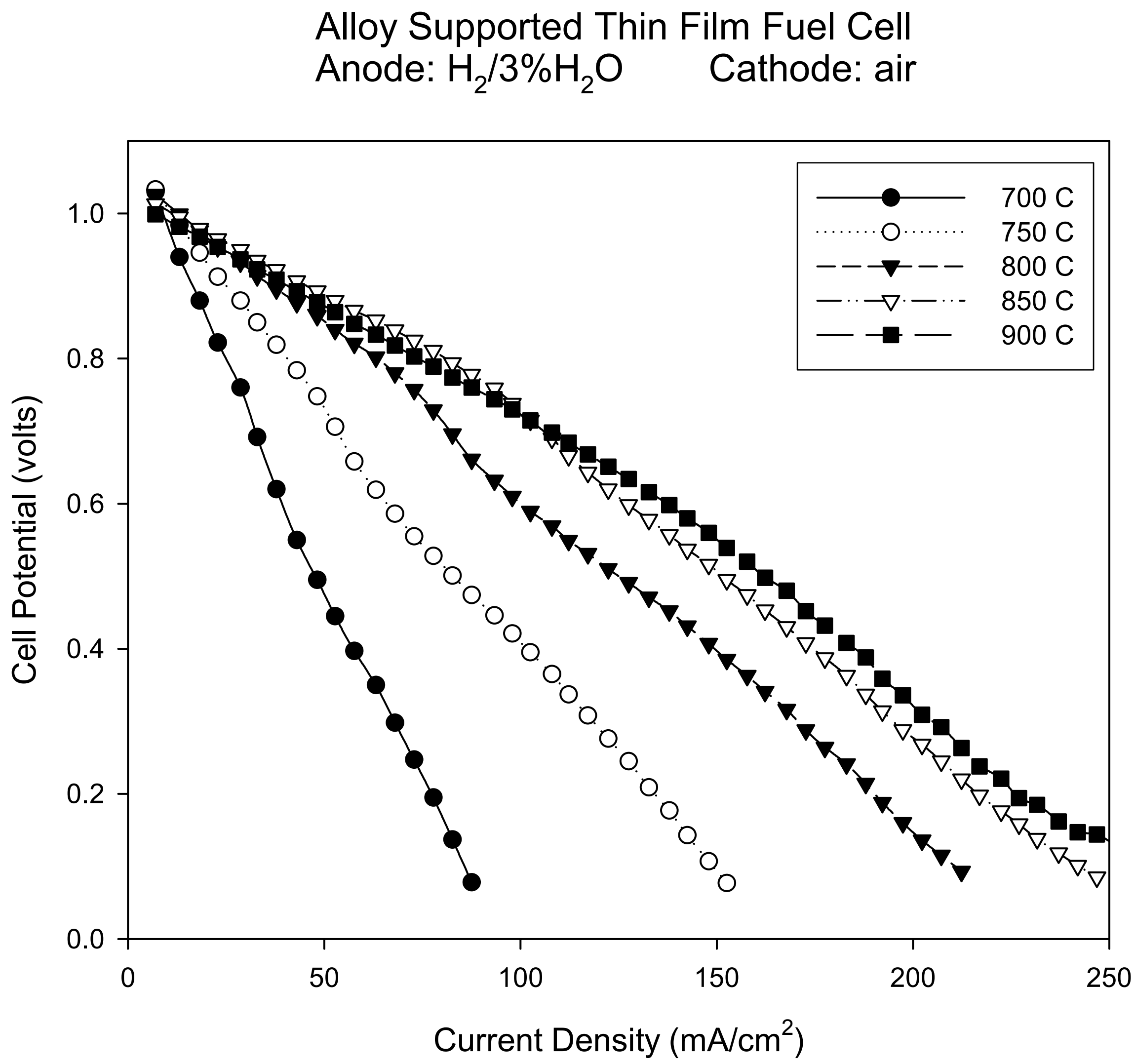
Issues Under Investigation

- Processing of alloy/electrode/electrolyte structure
- Electrical, mechanical, and corrosion properties of porous alloy support
- Porous alloy/electrode interface stability
- Constrained sintering of dense electrolytes and porous electrodes
- Adhesion strength of porous alloy/metal and ceramic interfaces
- Stable, well bonded, high performance cathodes operating at 650-750°C
- Cathode current collector protective coating (prevent chromium evaporation)
- Sealing alloy supported cells using welding, brazing, crimping, etc.

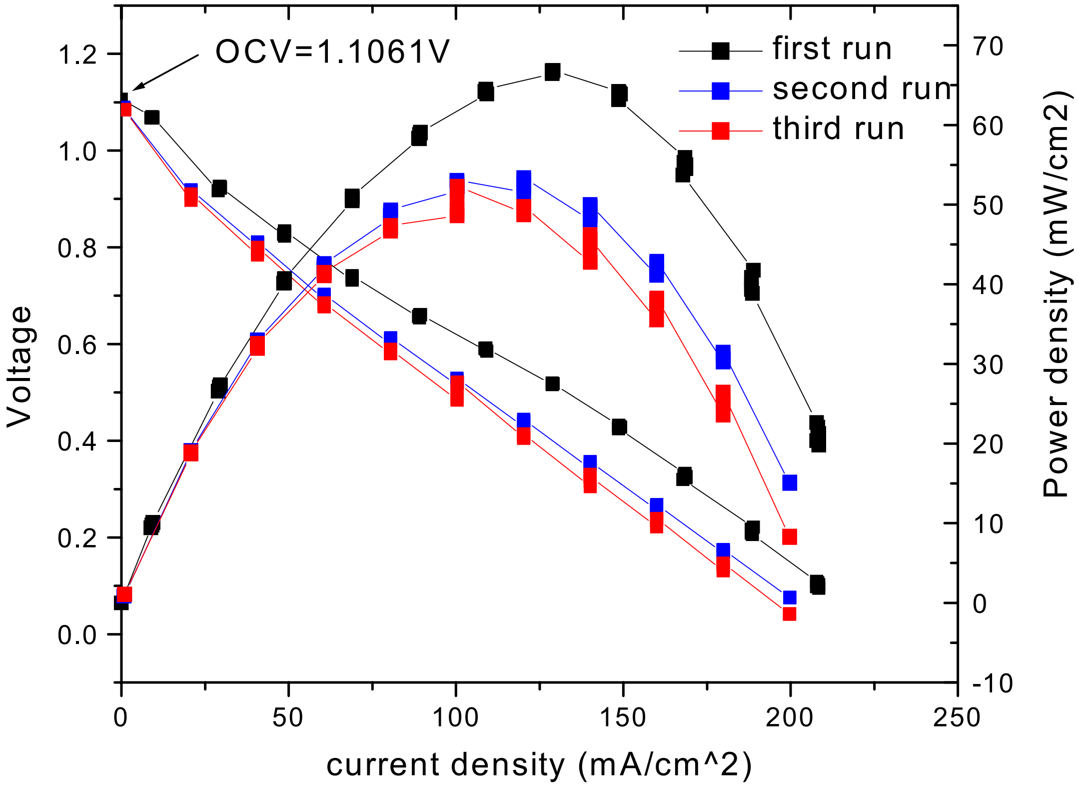
Proof of principle has been demonstrated

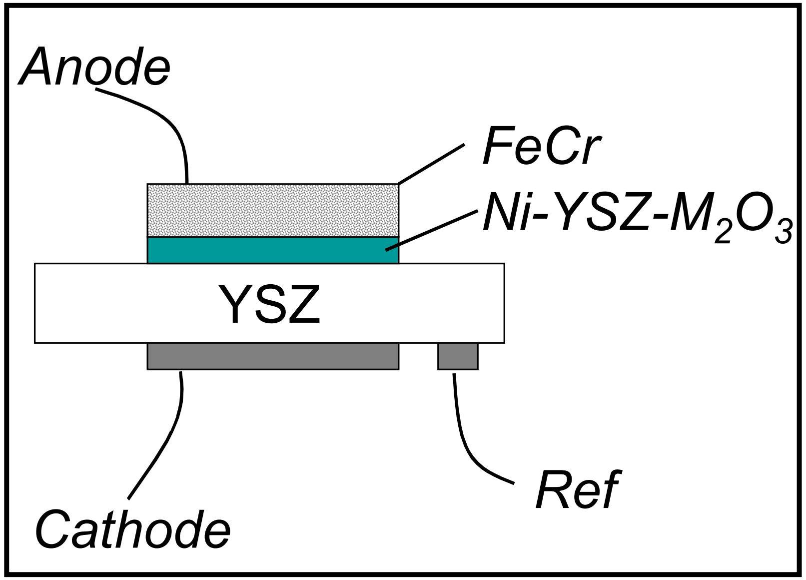


Proof of principle has been demonstrated

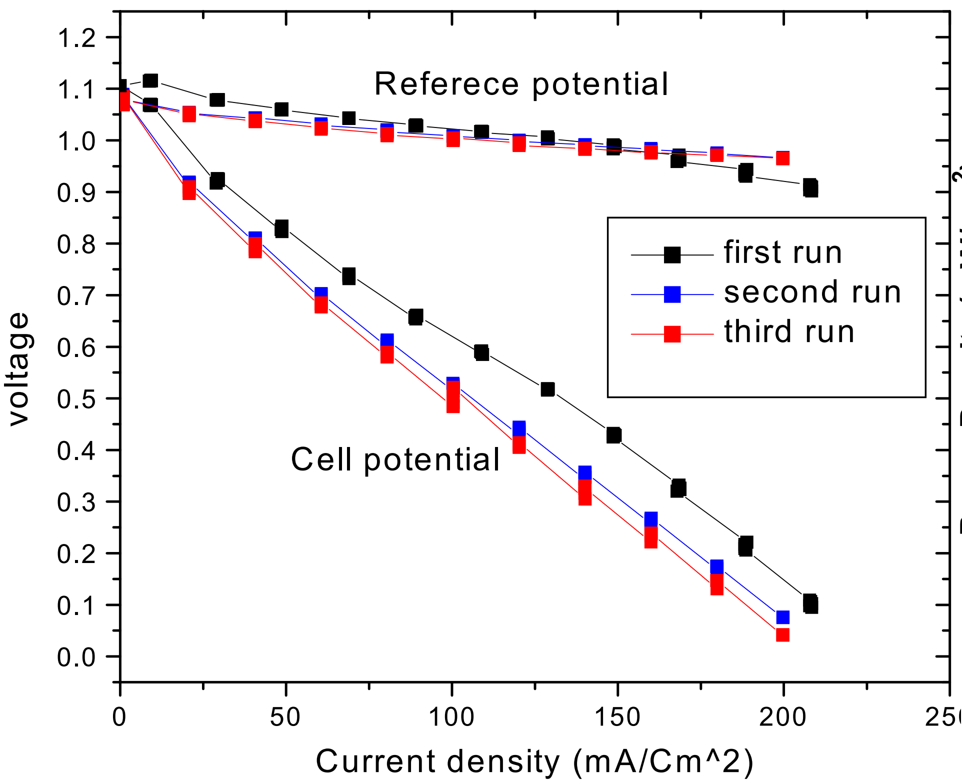


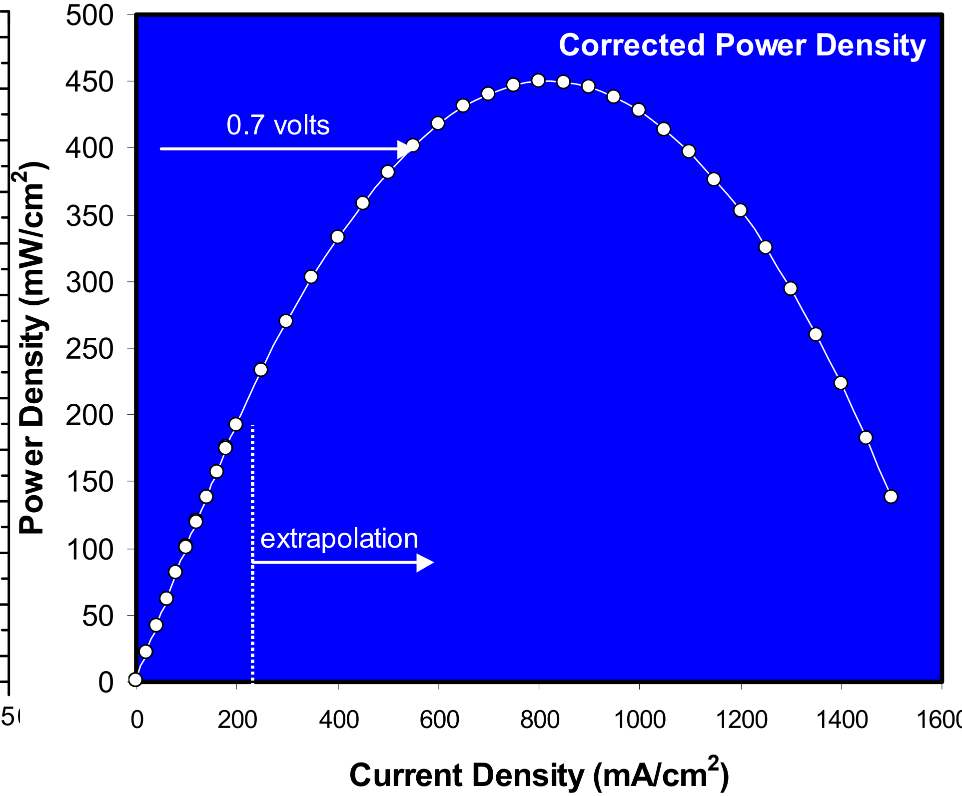
Electrochemical Characterization of Metal-based YSZ Cells





Power Density of Metal-Based SOFCs





Majority of Polarization from Pt Cathode

(due to sintering in reducing environment)

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related work elsewhere

The Use of Plasma-Spray to Fabricate Metal Electrode Supported SOFCs

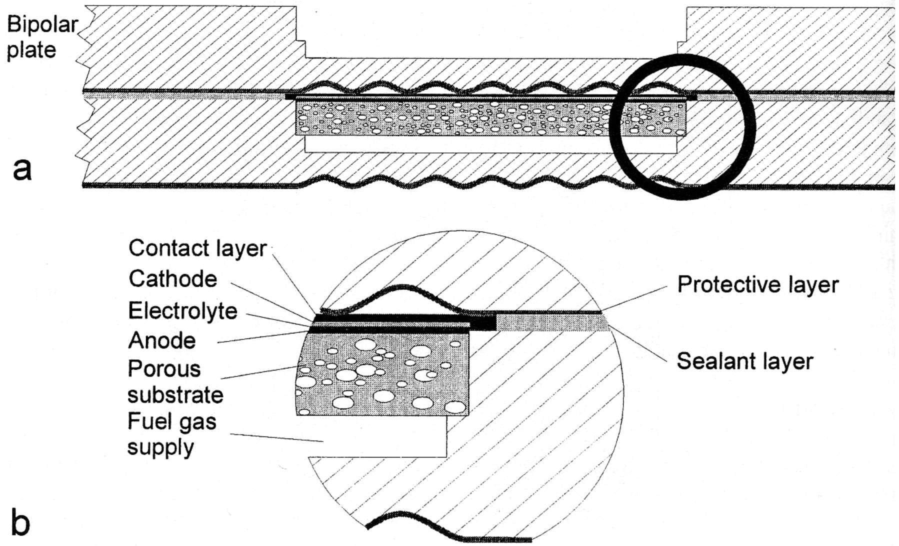


Figure 1. Principle of the SOFC design according to the DLR spray concept: overview (a) and detailed view (b)

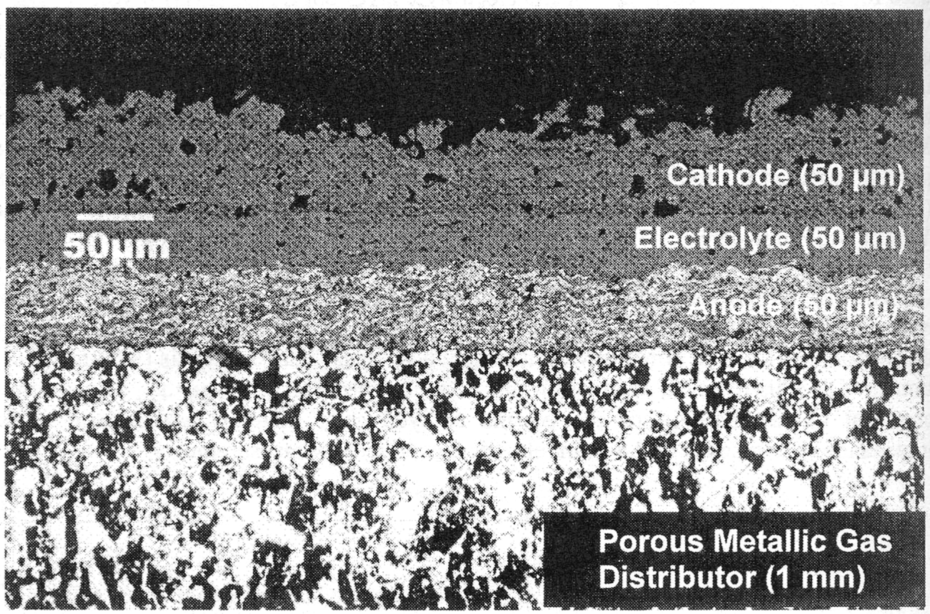


Figure 2. Optical micrograph of a metallographic cross-section of an entirely plasma sprayed thin-film cell

Plasma-spray is too expensive to meet SECA cost targets

G. Schiller, R. Henne, M. Lang, S. Schager
Deutsches Zentrum fur Luft-und Raumfahrt (DLR)
Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany
SOFC VI pg 893

Performance of Planar Metal Supported SOFC

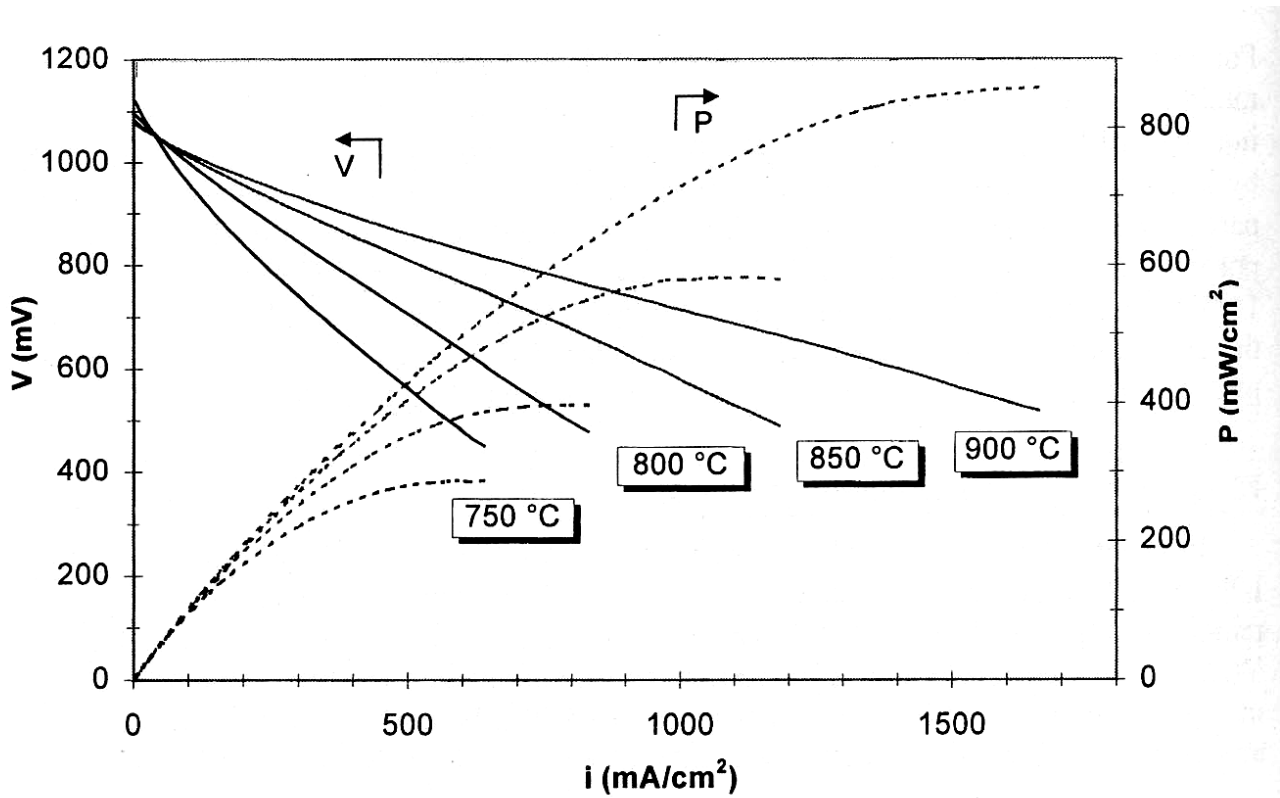


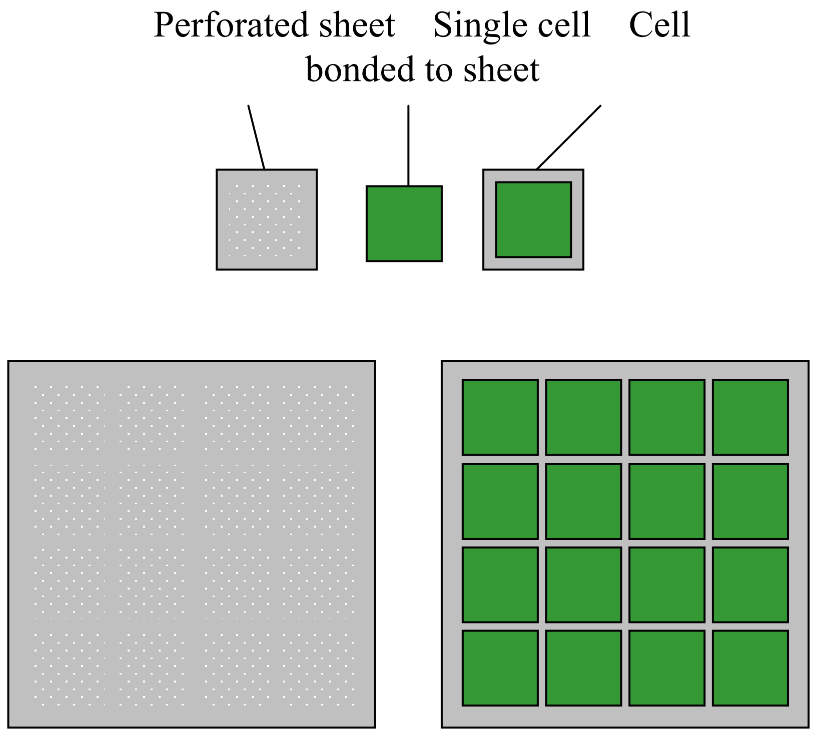
Figure 4. Performance of a VPS thin-film cell (YSZ/Ni anode, YSZ electrolyte, YSZ/LSM cathode) with H_2/air as the operating gases in dependence of temperature

G. Schiller, R. Henne, M. Lang, S. Schager
Deutsches Zentrum fur Luft-und Raumfahrt (**DLR**)

NETL

Metallic Supported Tile Design

Use existing thin-film cells bonded to perforated sheet

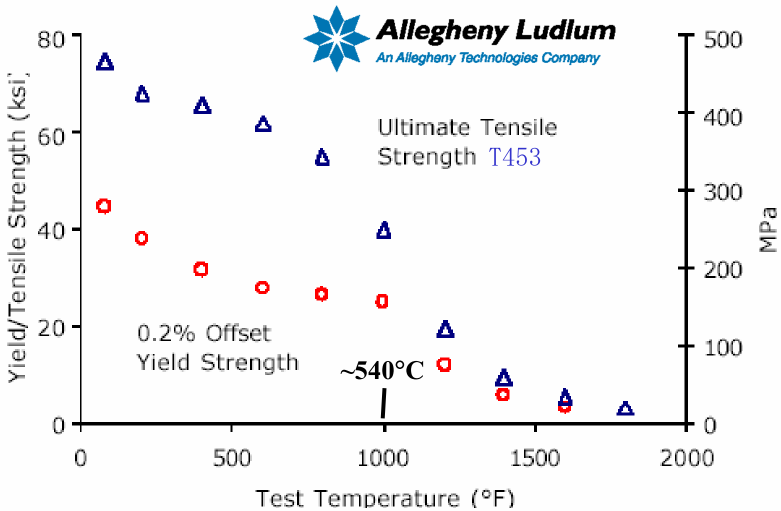


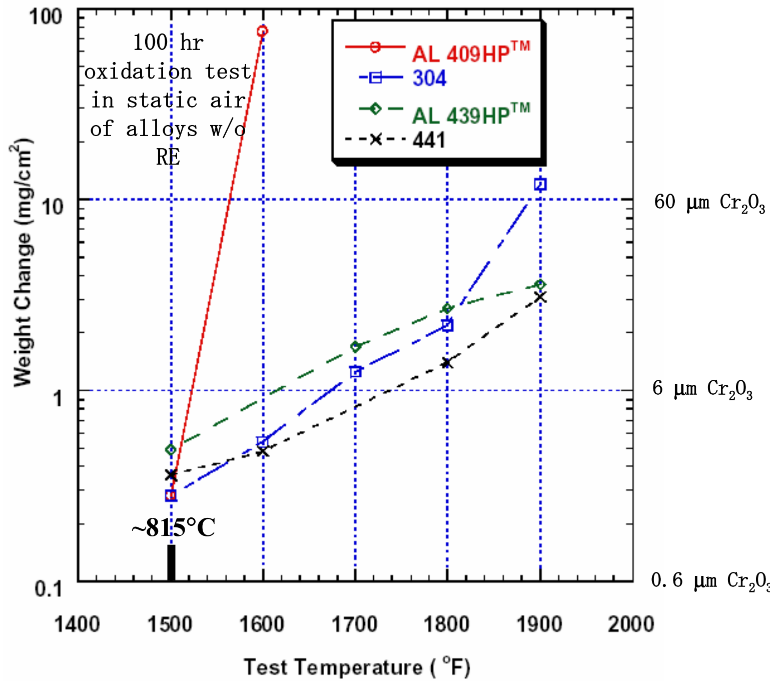
Advantages of Tile Design

- Sealing
- Manufacturing small pieces
- Existing thin-film technology
- Lower tolerances required
- Lower stress per tile
- Flexible sheet formed
- Non-catastrophic failure (parallel design)
- Tailored catalyst over cell area

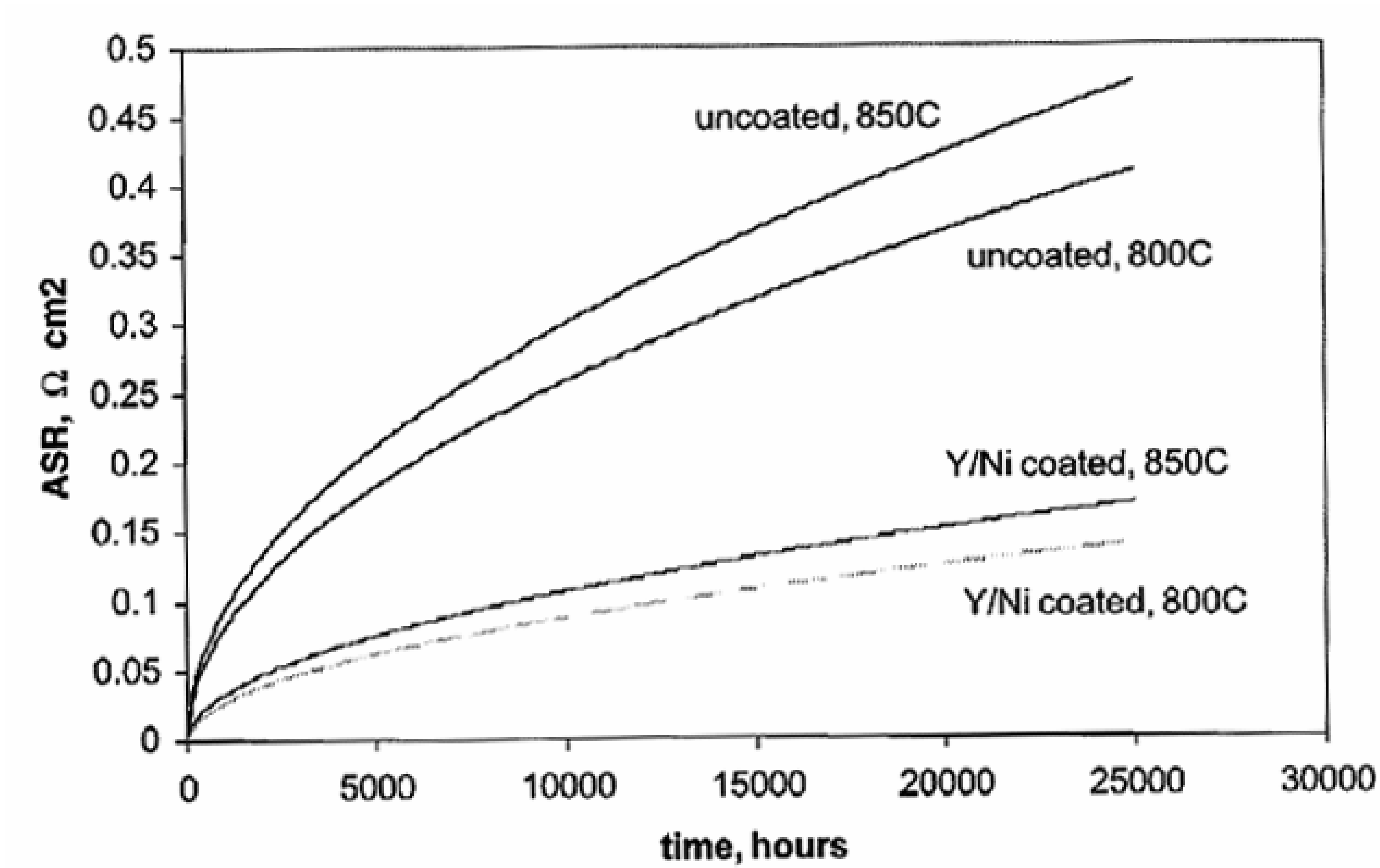
Alloys for porous support and/or interconnect

- Ferritic steels with 16-26 wt% Cr are starting point.
- 430 Stainless Steel (Fe18Cr) is base alloy being investigated (steel powders with 16-30 wt% Cr of various particle sizes and type 430 and 444 sheet in hand)
- Alloys such as type 439, 441, 444, 446, 453, etc are modified with various stabilizers, reactive elements, Cr up to 26%, etc.
- Typical alloy applications: automotive exhaust manifold, heat exchanger tubing, hot water tanks, etc.
- Typical alloy properties
  - TEC ~12 ppm/°C to 800°C
  - 7.6-7.8 g/cc
  - Thermal conductivity ~20 W/m•K
  - Electronic conductivity ~12,500 S/cm at RT and ~ 9,000 S/cm at 800°C
- Strength drops above 600°C, but this is not a high strength application (<1 ksi!)
- Oxidation limits uncoated alloys ≤ 800°C



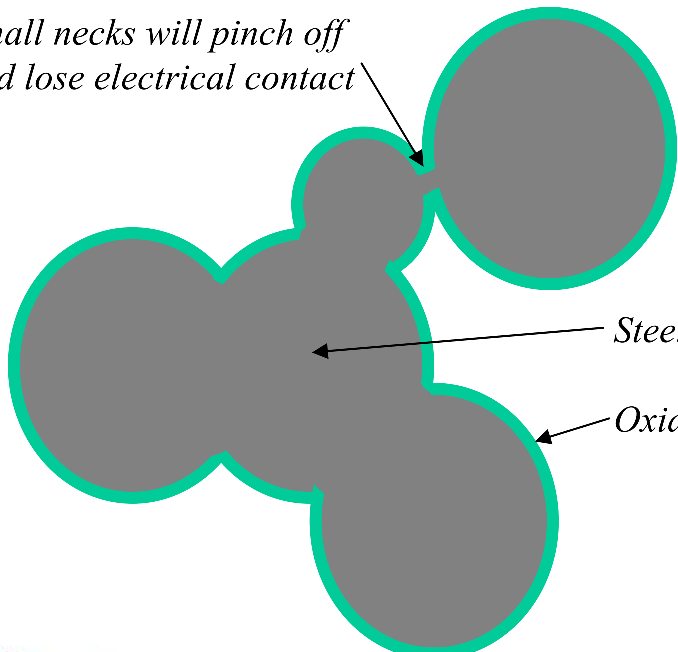


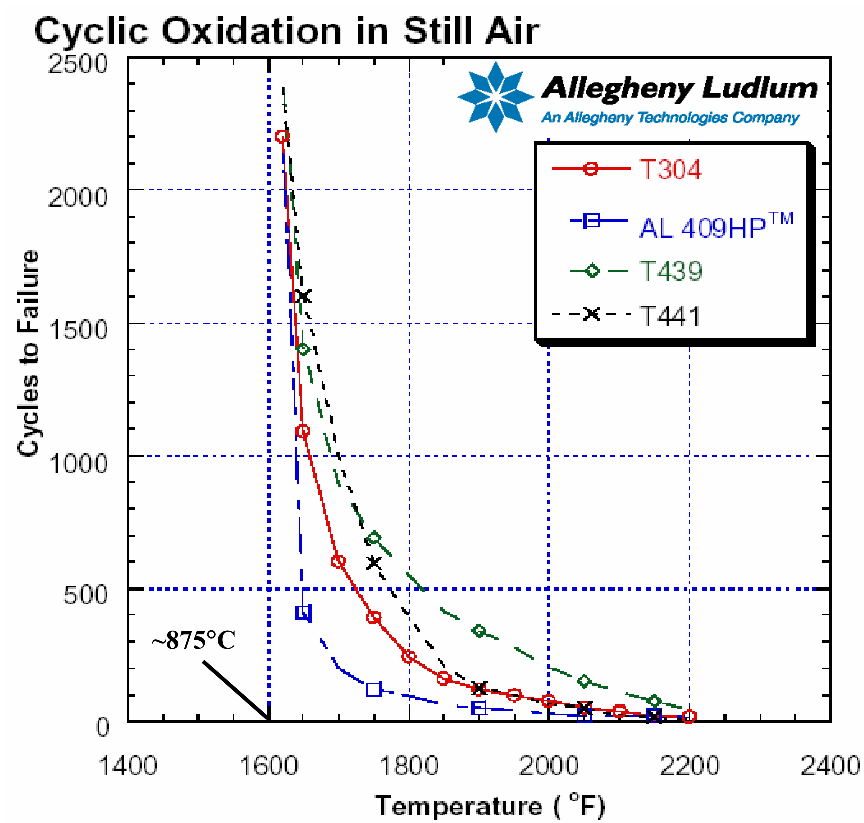
ASR of uncoated and Y/Ni coated Ebrite



Oxidation and possible neck failure

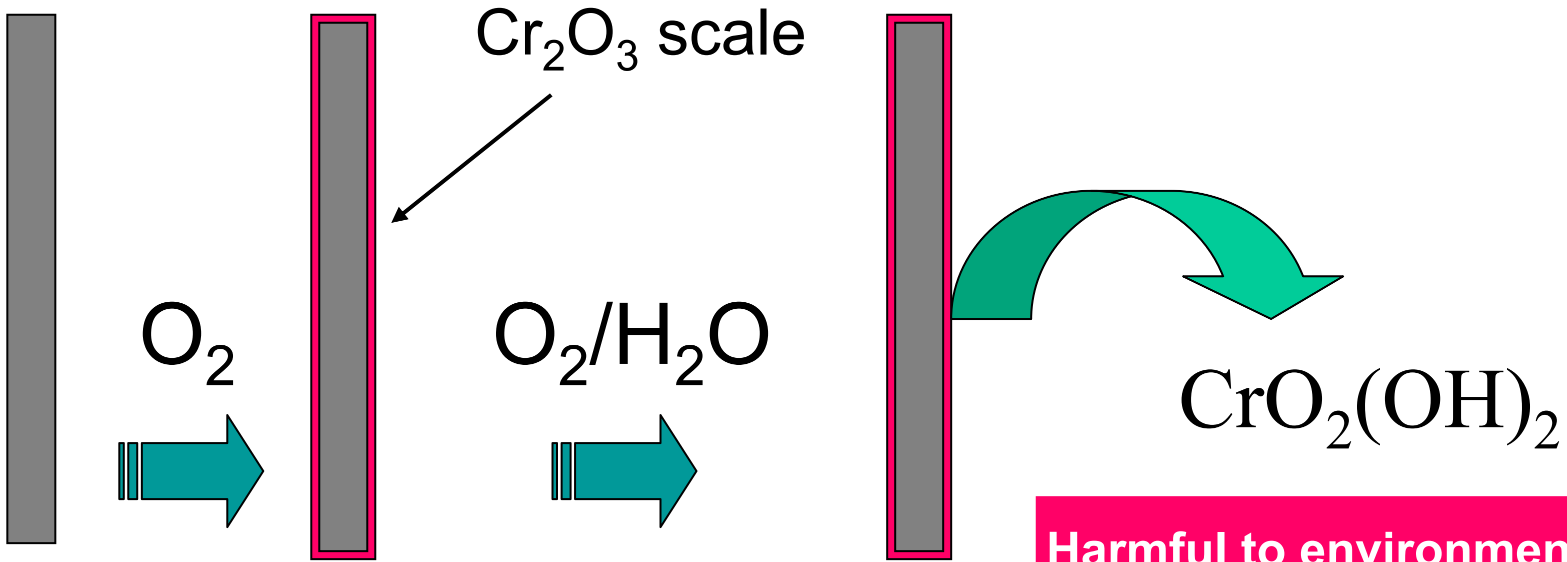
One concern is the failure of the porous alloy due to oxidation of the sintered necks. Is data available to guide us? Yes….





50 µm foil is cycled between RT and test temperature in air.
Failure occurs when oxidizes through and foil breaks.
This type of oxidation test previously developed gives an indication
Of the maximum operating temperature for a given neck size.
In this case a 50 µm neck should be stable up to ~875°C for
thousands of thermal cycles.

Corrosion of FeCr in Moist Air



FeCr Interconnect plate

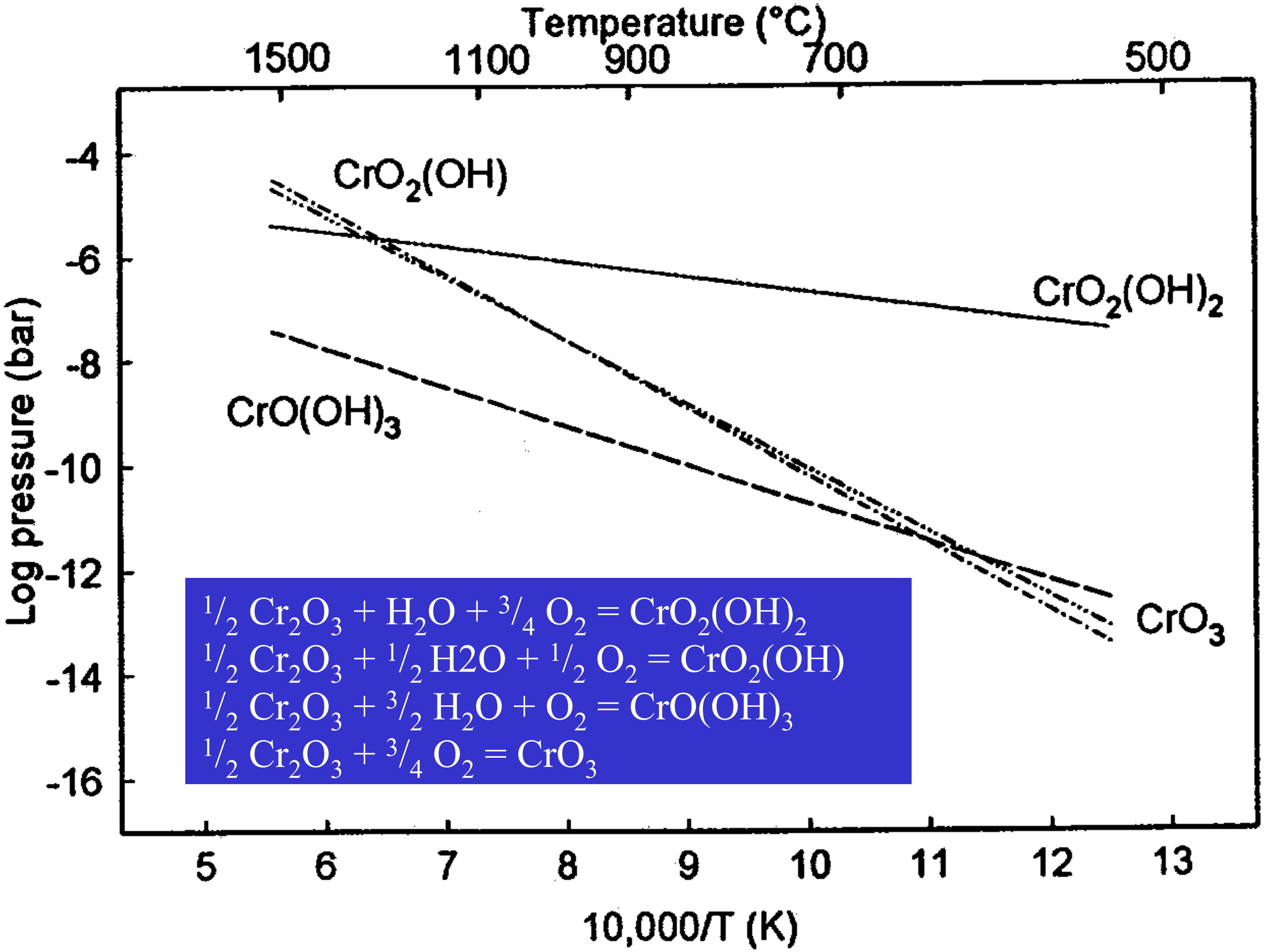
Harmful to environment
Can poison cathode

Need inexpensive coating technology

LBNL is monitoring weight loss of Cr_2O_3 in moist air at 800 ^{o}C

Berkeley Lab
Ernest Orlando Lawrence Berkeley National Laboratory

Vapor species in equilibrium with Cr_2O_3 in 0.1 bar H_2O, 0.1 bar O_2 at 1 bar total pressure



$\frac{1}{2}\, Cr_2O_3 + H_2O + \frac{3}{4}\, O_2 = CrO_2(OH)_2$

$\frac{1}{2}\, Cr_2O_3 + \frac{1}{2}\, H2O + \frac{1}{2}\, O_2 = CrO_2(OH)$

$\frac{1}{2}\, Cr_2O_3 + \frac{3}{2}\, H_2O + O_2 = CrO(OH)_3$

$\frac{1}{2}\, Cr_2O_3 + \frac{3}{4}\, O_2 = CrO_3$

Protective Coatings for Cathode Current Collectors

- We want to use FeCr stainless steel as current collector in SOFC with LSM cathode.
- The disadvantage is Cr_2O_3 evaporation during SOFC operation.
- A dense coating with proper electrical conductivity and thermal expansion is needed to prevent Cr_2O_3 evaporation.
- Possible candidates are doped chromite or Cr-based spinels

NETL

Spinel coatings at the interface of LSM cathode and FeCr current collector

Mn-Cr-O, Mn-Co-Cr-O, Co-Cr-O, Mn-Co-O spinel are promising coating materials for FeCr current collector. Two goals should be reached.

1) A dense layer of spinel should be formed between FeCr and LSM to block the evaporated Cr oxide to diffuse into LSM.

2) The spinel layer should have enough conductivity at least bigger than usual coating materials such as La-Cr-O.

LSM green power sintered on dense FeCr stainless steel at 1200°C/4h in air results in porous MnCr spinel layer. Chromium oxyhydroxide evaporation is not prevented.

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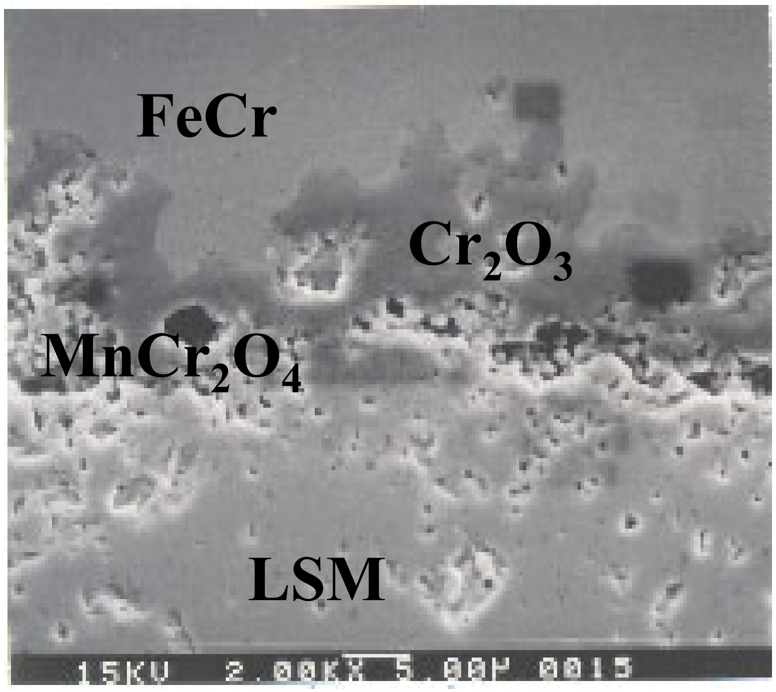
LSM Cathode and FeCr Interfacial Reactions

LSM reacts with the alloy to produce a *porous* spinel coating



LSM green power with fully dense FeCr stainless steel sintered at 1200°C/4h in air

EDS shows a porous layer of $MnCr_2O_4$ spinel formed at the interface, this is insufficient for preventing chromium evaporation…

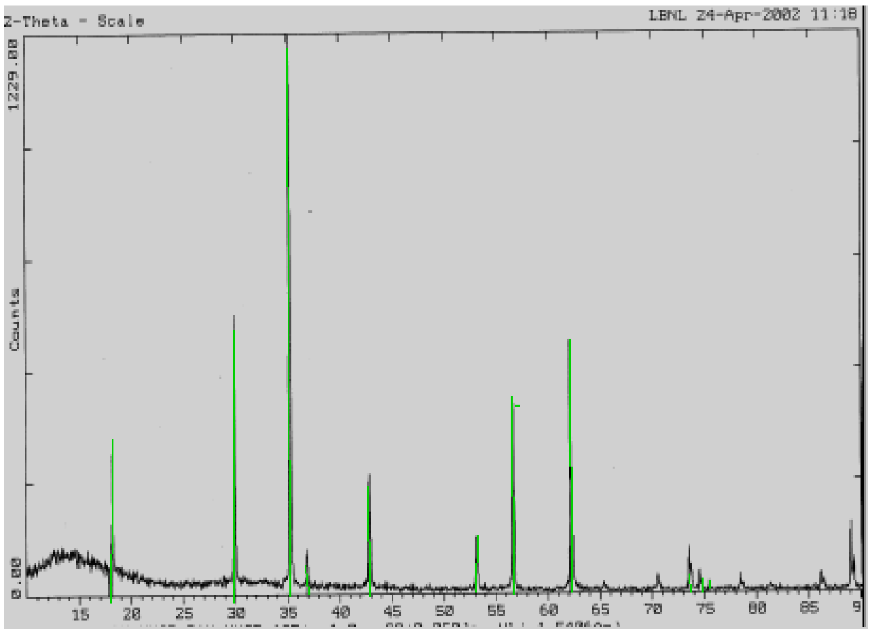
Can this spinel be made dense to prevent Cr_2O_3 from evaporating?

Does the spinel have enough electronic conductivity?

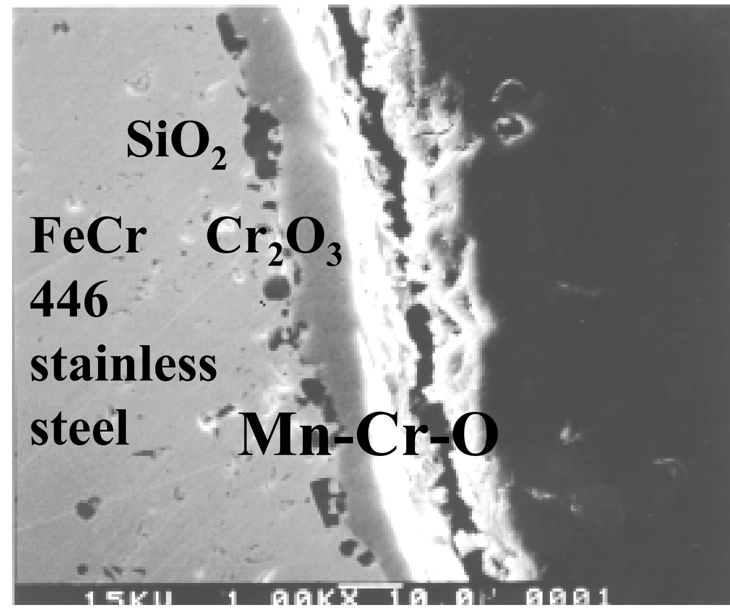
Does the thermal expansion of the spinel match that of the cathode?

This works will determine the suitability of various spinels for this application and then seek means of creating dense layers on FeCr alloys

One approach is to obtain a dense coating of the desired spinel

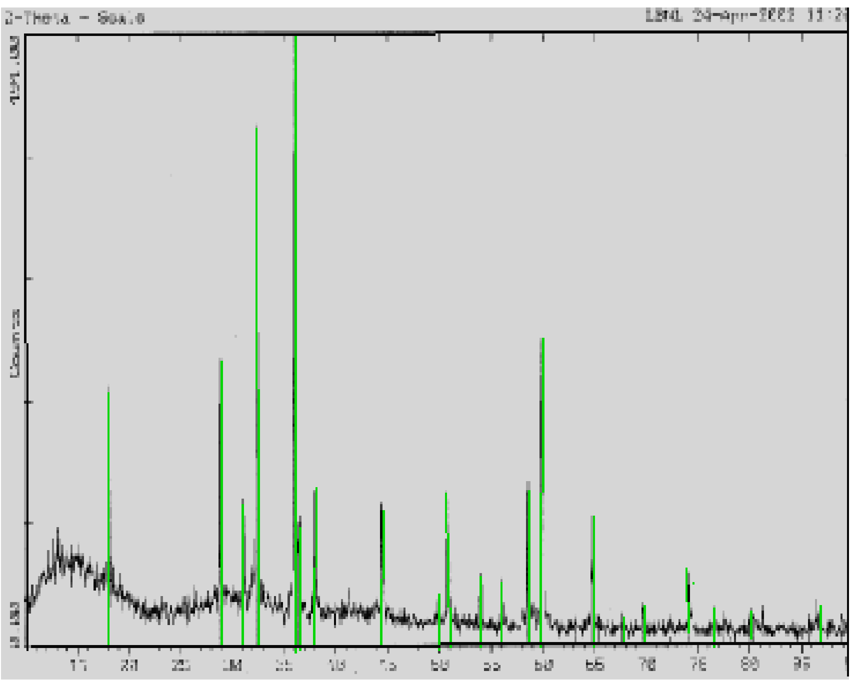


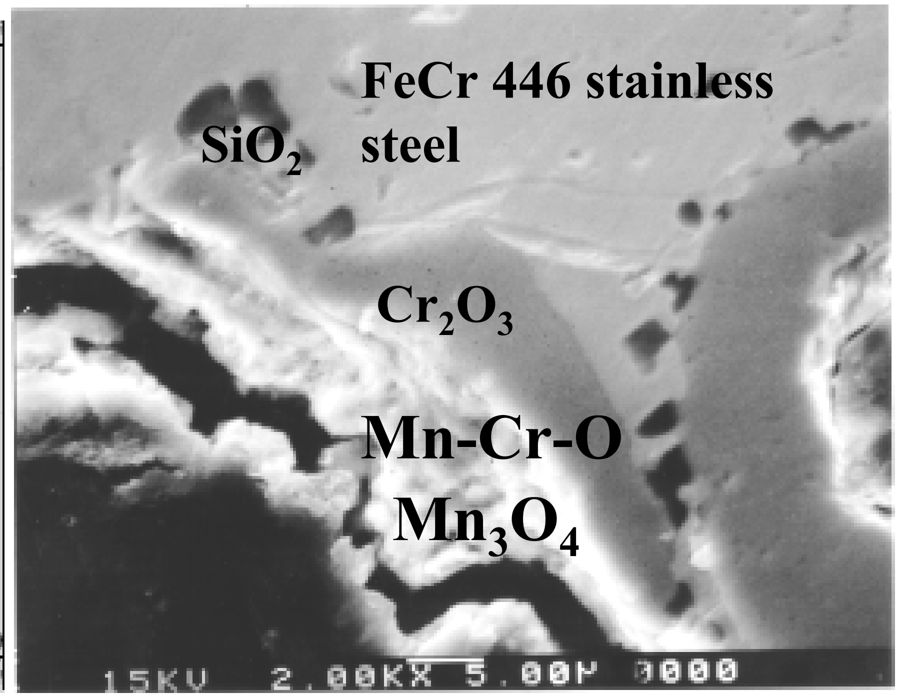
X-ray of $MnCr_2O_4$ spinel made by GNP synthesis. This powder is then applied to the alloys surface and sintered.



SEM of $MnCr_2O_4$ and FeCr interface sintered at $1200^oC/4h$ in air

A second approach is to deposit a continuous Mn-oxide layer and grow a continuous layer of the desired spinel.





X-ray of Mn_3O_4 powder

SEM of Mn_3O_4 and FeCr interface sintered at 1200°C/4h in air

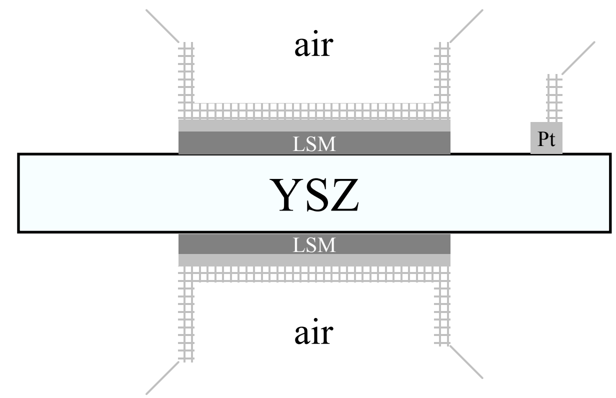
Protective CoatingFuture Work

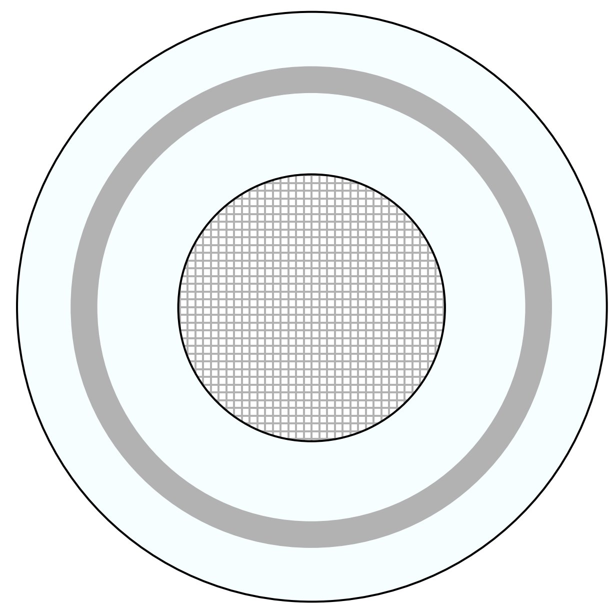
- Measure the electrical conductivity and thermal expansion of $MnCr_2O_4$ spinel
- Test whether this $MnCr_2O_4$ spinel layer is effective in preventing Cr evaporation
- Develop a low-cost, effective method of creating the $MnCr_2O_4$ on FeCr current collectors

NETL Cathode Studies

Purpose: Stable, high performance cathodes for operation between 650-750°C
Basic Problem: High performance cathodes involve unstable microstructures and/or chemical and thermal expansion incompatibility with YSZ

- Preparation of YSZ thick electrolyte discs with controlled surface
- Basic electrochemical studies using Ag, Pt, Pd-Ag, and Au as electrodes
- Study the effect of bulk and surface additives on the electrochemical performance of LSM and LSM + YSZ on YSZ symmetric cell
- Preparation of LSM + YSZ electrodes with and without bulk additives such as: LSCF, CGO, and Co_2O_3
- Preparation of LSM electrodes with and without surface additives such as CoO/Co_2O_3





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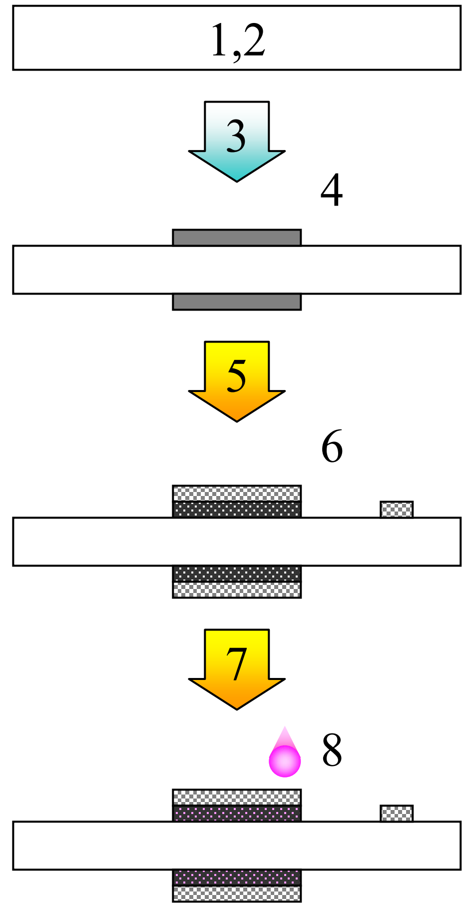
Surface Doped Electrode Fabrication

1) Die press YSZ disk
2) Sinter disk at 1500°C
3) Polish disk (30 µm)
4) Spray cathodes
5) Sinter cathodes at 1200°C
6) Attach platinum current collectors and reference
7) Fire at 950°C
8) Dope cathodes with cobalt solution
9) Fire at 600°C

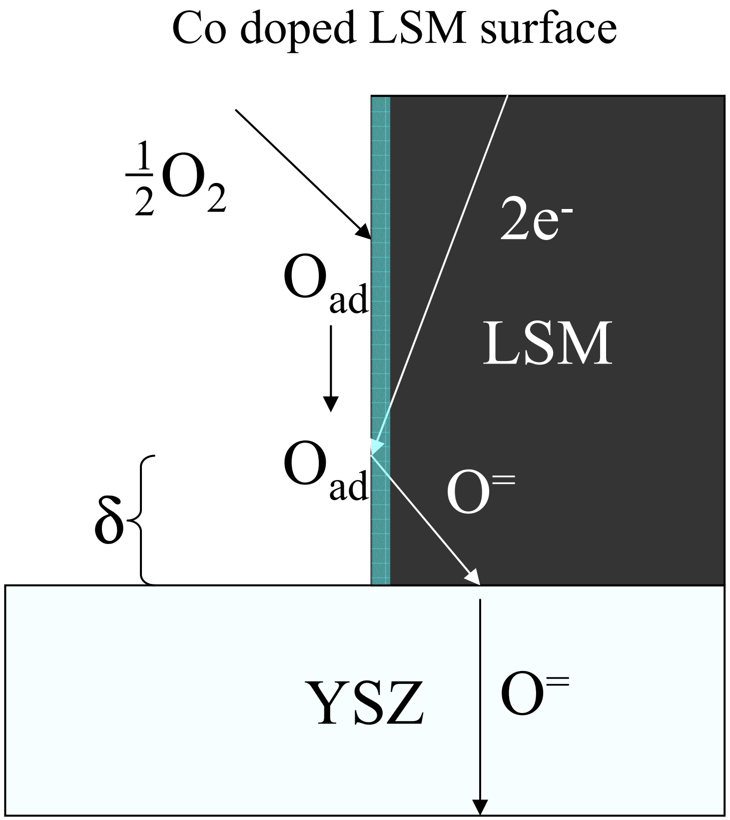


Related prior art:

ELECTRODE STRUCTURE FOR SOLID STATE ELECTROCHEMICAL DEVICES, U.S. Pat. No. 5,670,270. Dow Chemical Company

Proposed O_2 Reaction Mechanism

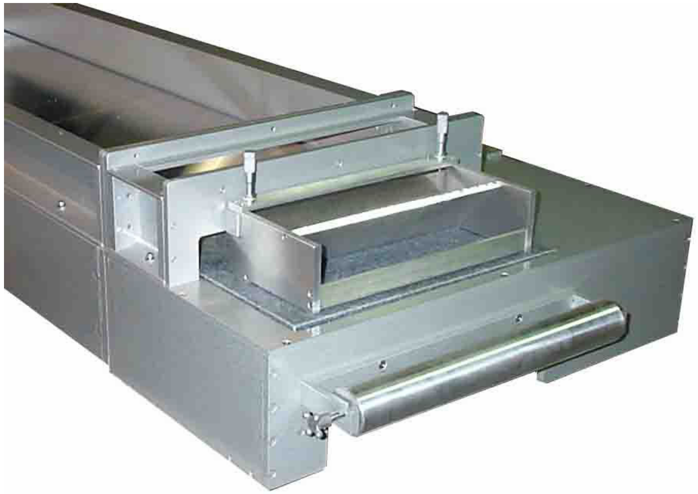
- Highlights
  - O_2 surface diffusion to active site
  - Charge transfer
  - $O^{=}$ diffusion through LSM to YSZ
- Cobalt increases ionic conductivity and δ
- Critical question: *Is this strictly a surface effect or does the Co diffuse into the bulk and alter the LSM composition?* This has implication for long-term stability of these doped electrodes.

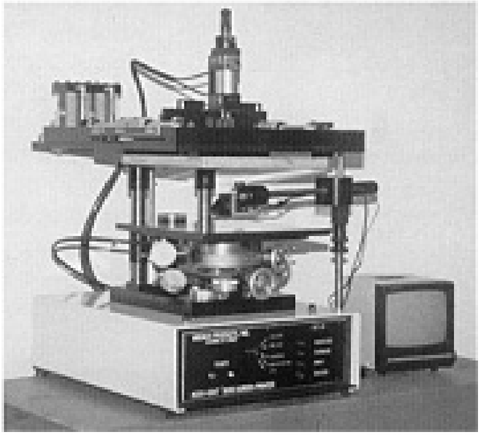


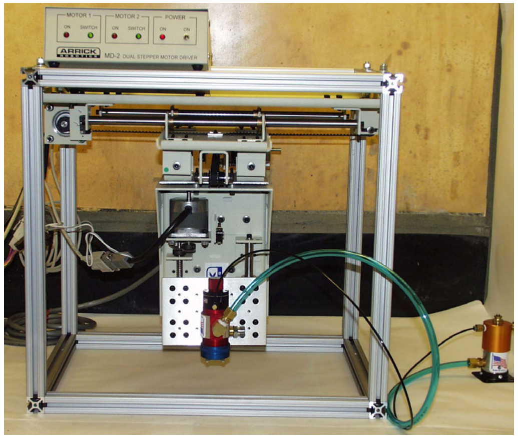
NETL Projects April-June 2002

Scale-up and automate process

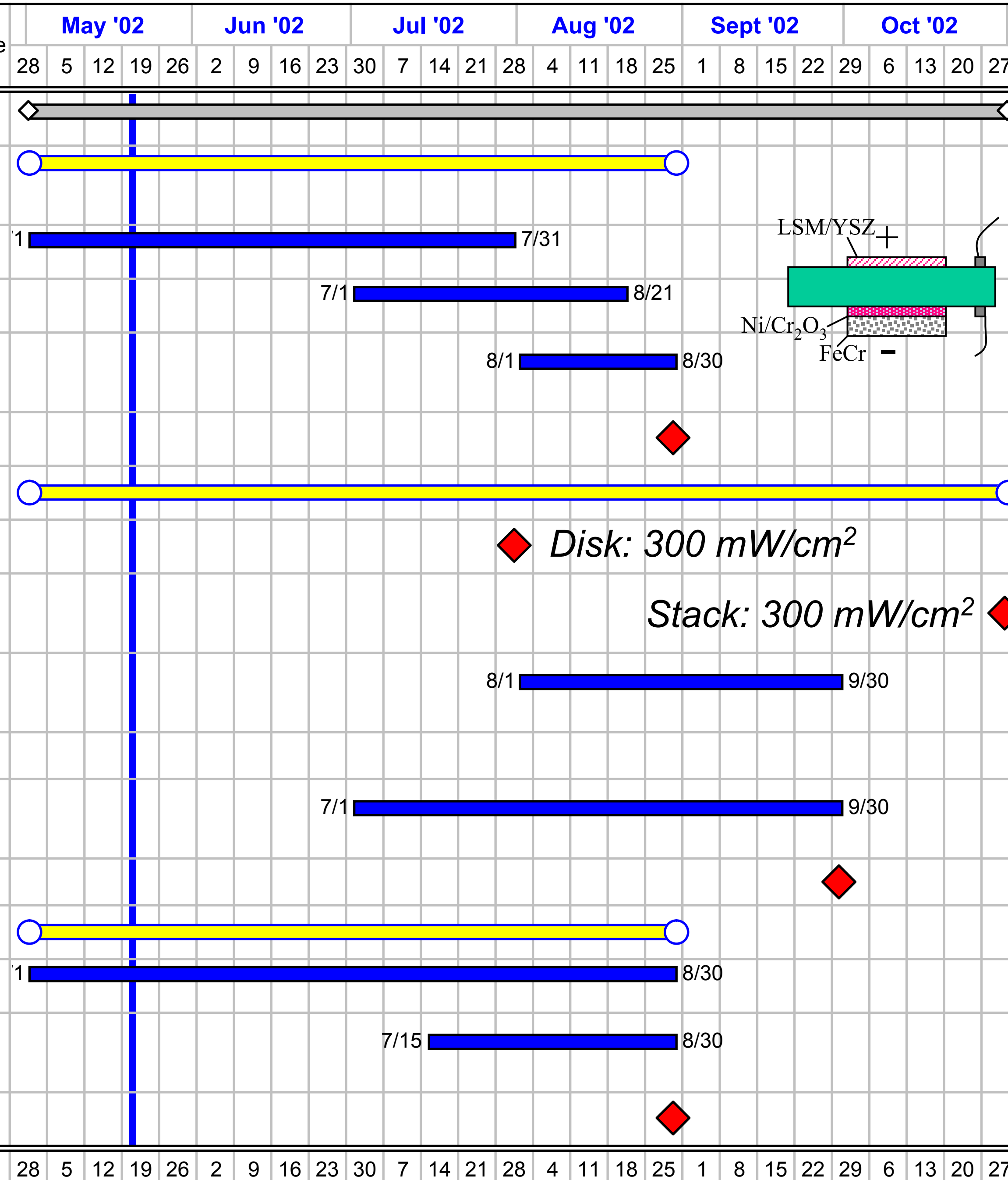
1. Tape casting of metal supports
2. Automated screen printing of electrodes
3. Automated spray deposition or electrodes and electrolytes







Activity Name	Start Date	Finish Date
Development of Planar Metal supported SOFC	5/1/02	10/31/02
Fundamental electrochemical studies (AC impedance, I-V)	5/1/02	8/30/02
Refinement of anode composition	5/1/02	7/31/02
Refinement of cathode composition	7/1/02	8/21/02
Development of low-Temp cathode (500 to 650C)	8/1/02	8/30/02
Electrode composition defined	8/30/02	
Metal-Ceramic SOFC Development	5/1/02	10/31/02
Single metal supported cells @ 300 mW/cm2	7/31/02	
2-cell planar metal supported SOFC stack @ 300 mW/cm2	10/31/02	
Real-time GC mass spec analysis of fuel exhaust stream	8/1/02	9/30/02
Seal Development		
Development of insulating metal gasket/seal	7/1/02	9/30/02
Seal defined	9/30/02	
Interconnect Development	5/1/02	8/30/02
Development of coating for metal interconnect	5/1/02	8/30/02
Microbalance measurements of Cr evaporation	7/15/02	8/30/02
Interconnect coating defined	8/30/02	



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Summary

- Proof of principle: low-cost alloy support architecture effective
- Support-plate concept: Ni-YSZ , LSM, and alloy bonding demonstrated
- Evaluation of cathode-interconnect interface initiated: conductive spinel interlayer expected to be effective
- Development of stable, high performance cathode for 650-750°C operation
- Invention disclosure:
  - IB-1790: Support for planar fuel cells

Future work

- Improve low-cost alloy support architecture
- Support-plate concept: integrate in functioning fuel cell
- Continued development of cathode-interconnect interface
- Continued development of intermediate temperature cathodes
- Constrained sintering of electrolyte film on metallic support electrode structure