Cost-Effective Manufacturing and Morphological Stabilization of Nanostructured Cathodes for Commercial Solid Oxide Fuel Cells

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Just to be clear…

Recent representative papers from U. Penn.

"Nano-socketed nickel particles with remarkable coking resistance grown in situ by redox exsolution"

Tae-Sik Oh†, Dragos Neagu† et al., Nature Communications, Accepted.

"Decreasing interfacial losses with catalysts in $La_{0.9}Ca_{0.1}FeO_3$ membranes for syngas production"

Anthony S. Yu et al., Applied Catalysis A, 486 (2014) 259

"Synthesis and stability of Pd@CeO_2 core-shell catalyst films in SOFC anodes"

Lawrence Adijanto et al., ACS Catalysis, 3 (2013) 1801

Project Organization and Structure

Penn

1) Develop “manufacturable” infiltration process to make composite electrodes

FCE

3) Demonstrate that the results from 1) and 2) can be incorporated into larger cells and stacks.

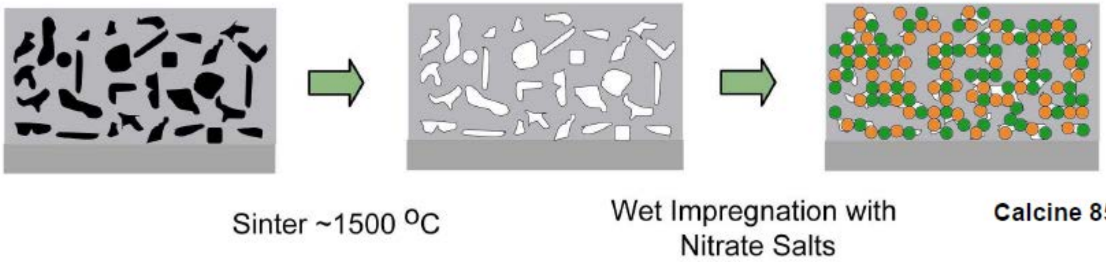
2) Develop methods for stabilization of electrode nanostructure.

USC

Project period: 10/01/14 - 09/30/17

Electrode Fabrication by Infiltration:

1) Make porous scaffold of electrolyte
2) Infiltrate catalysts and electronic conductor



Advanced Materials 21 (2009) 943-956

Advantages for cathode fabrication:

A) Separate firing temperatures for YSZ and perovskite.

B) Composite structure is not random; perovskite coats pores.

⟶ High conductivity with low perovskite loading

⟶ CTE is that of the scaffold

C) High-performance is possible.

Problems with Infiltration:

1) Difficult to Manufacture:

→ Need 35-wt% (20-vol%) perovskite phase for conductivity

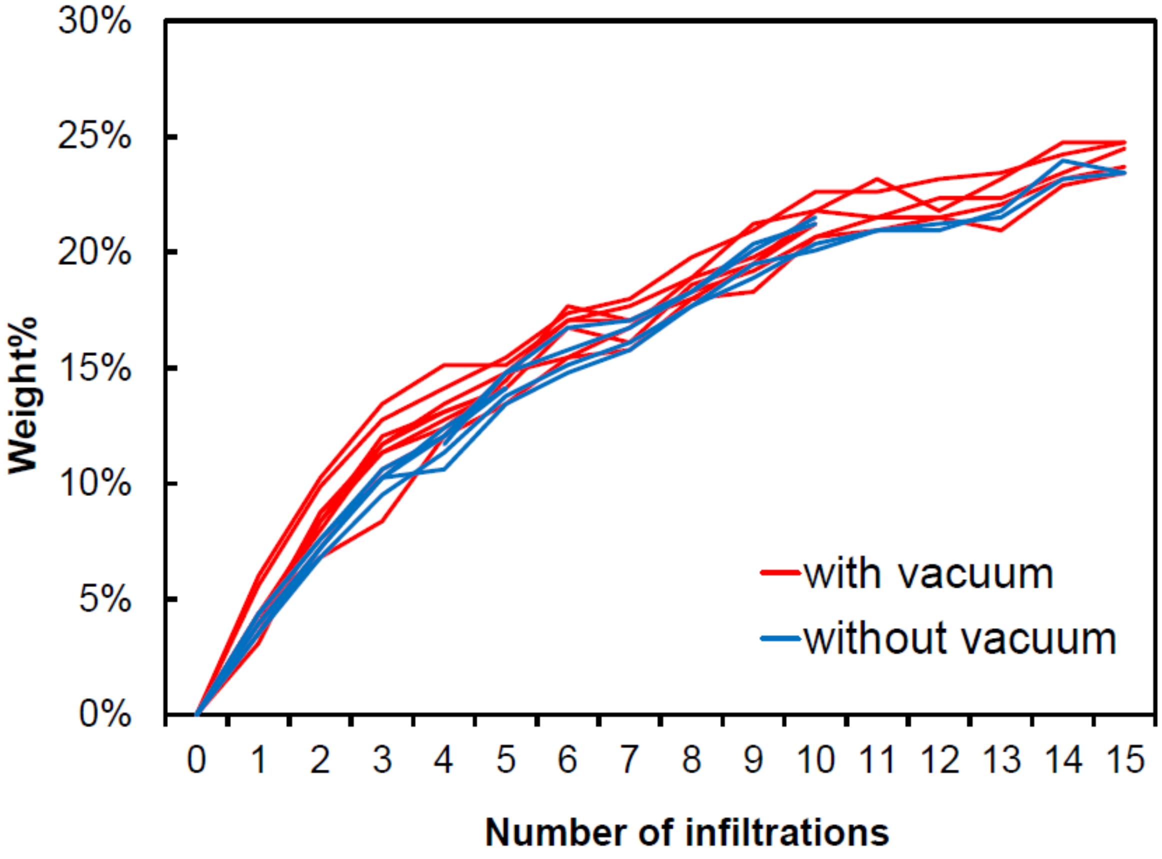
→ To get this loading requires many steps.

a) Using 1 M solution of La, Mn salts in 65% porous scaffold, 1 infiltration cycle gives 2.3-vol% $LaMnO_3$.

b) Even with infiltration of molten $La(NO_3)_3$, $Mn(NO_3)_3$, maximum loading <10-wt% per cycle.

Note: These numbers are theoretical; Vacuum infiltration will not help!

Problems with Infiltration: (La, Sr)FeO_3



Courtesy of Dr. Küngas (Haldor Topsøe)

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2) Long-term stability – nanoparticles coarsen.

Approach 1: Use Composite Scaffold

1) LSF ($La_{(1-x)}Sr_xFeO_3$) is relatively unreactive with YSZ:

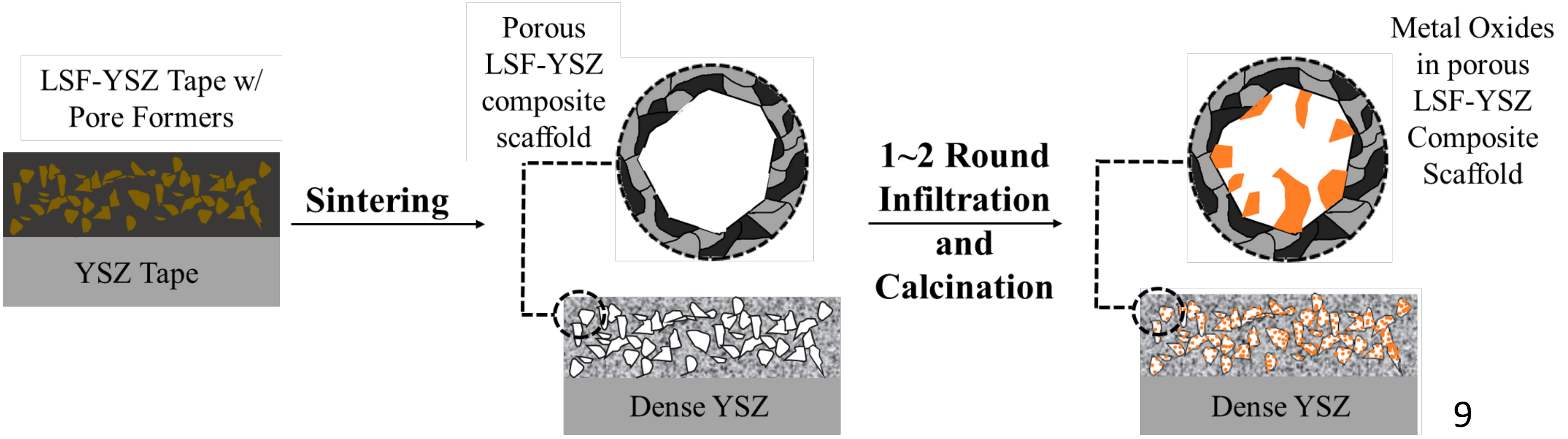
→S. P. Simner, et al, JECS 152 (2005) A1851; W.-S. Wang, et al, JECS 154 (2007) B439

2) Doped $LaFeO_3$ has higher ionic conductivity than YSZ.

→at 700C, σ(YSZ) = 0.02 S/cm; σ(LCF) = 0.03 S/cm

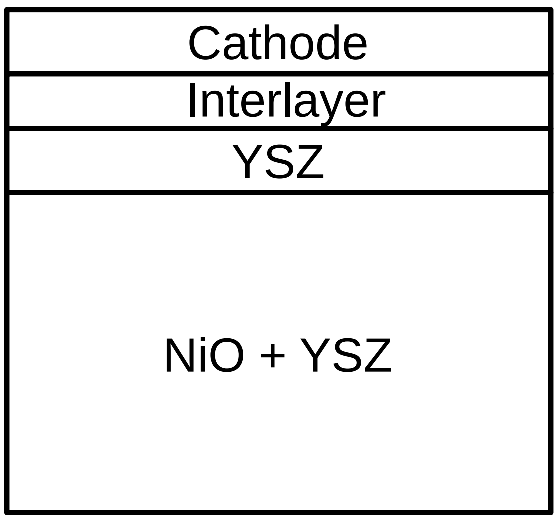
(A.S. Yu, et al, Appl. Catal. A, 486 (2014) 259.)

3) Make LSF-YSZ Scaffold for Conductivity; add LSCF for Catalytic Activity

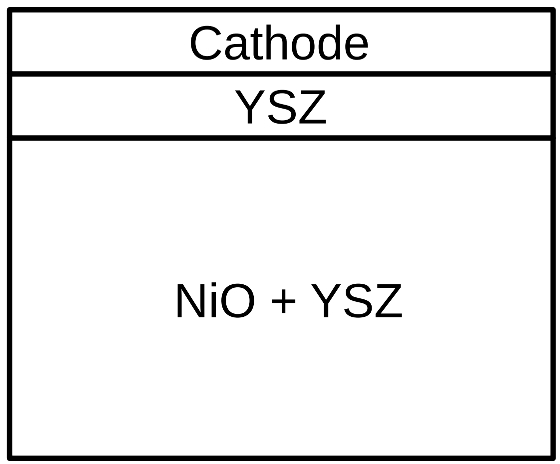


Single step infiltration is simpler than fabrication by conventional processes:

1) Anode, electrolyte, and scaffold can all be co-fired.
2) One, room-temperature infiltration step.

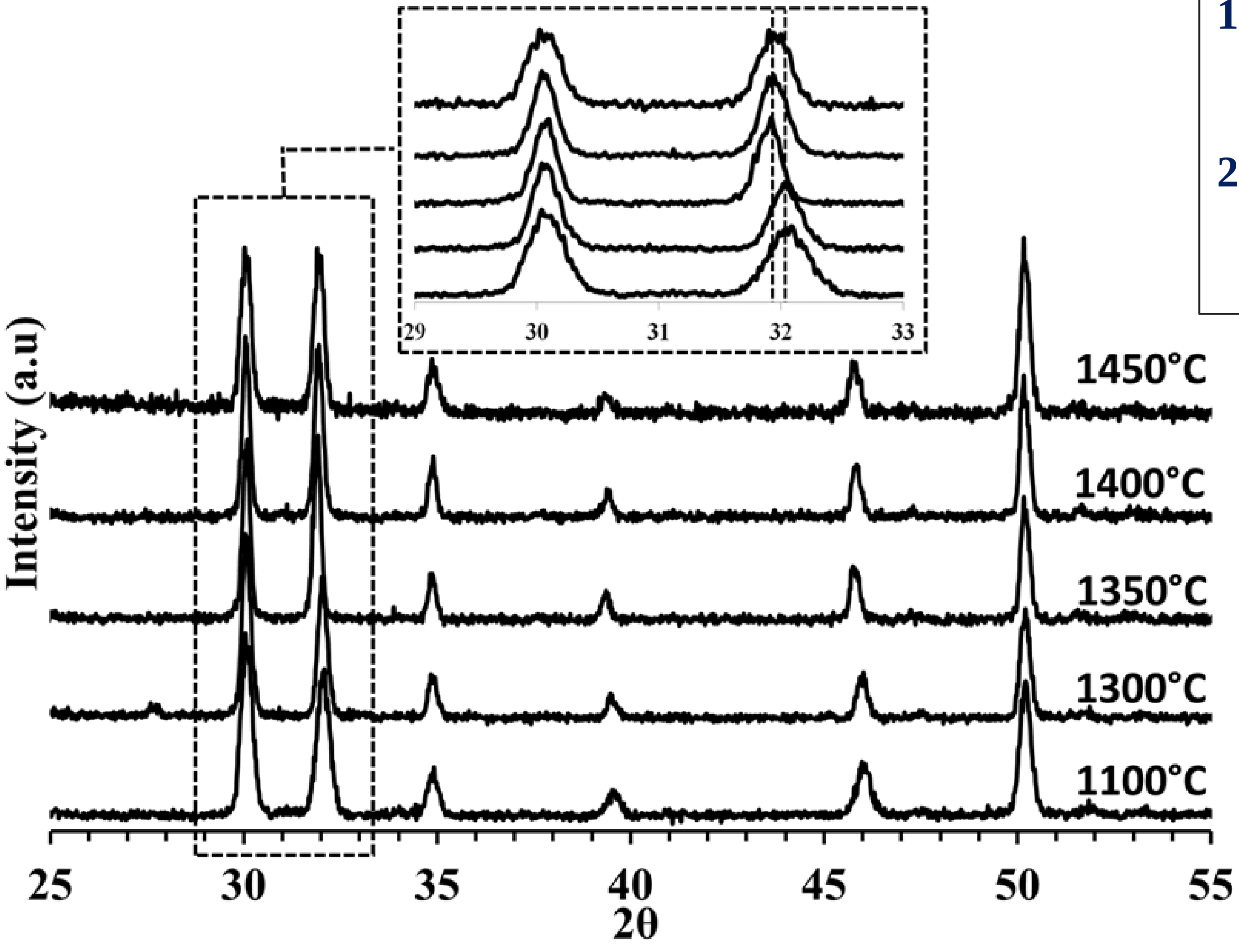


3 firing steps



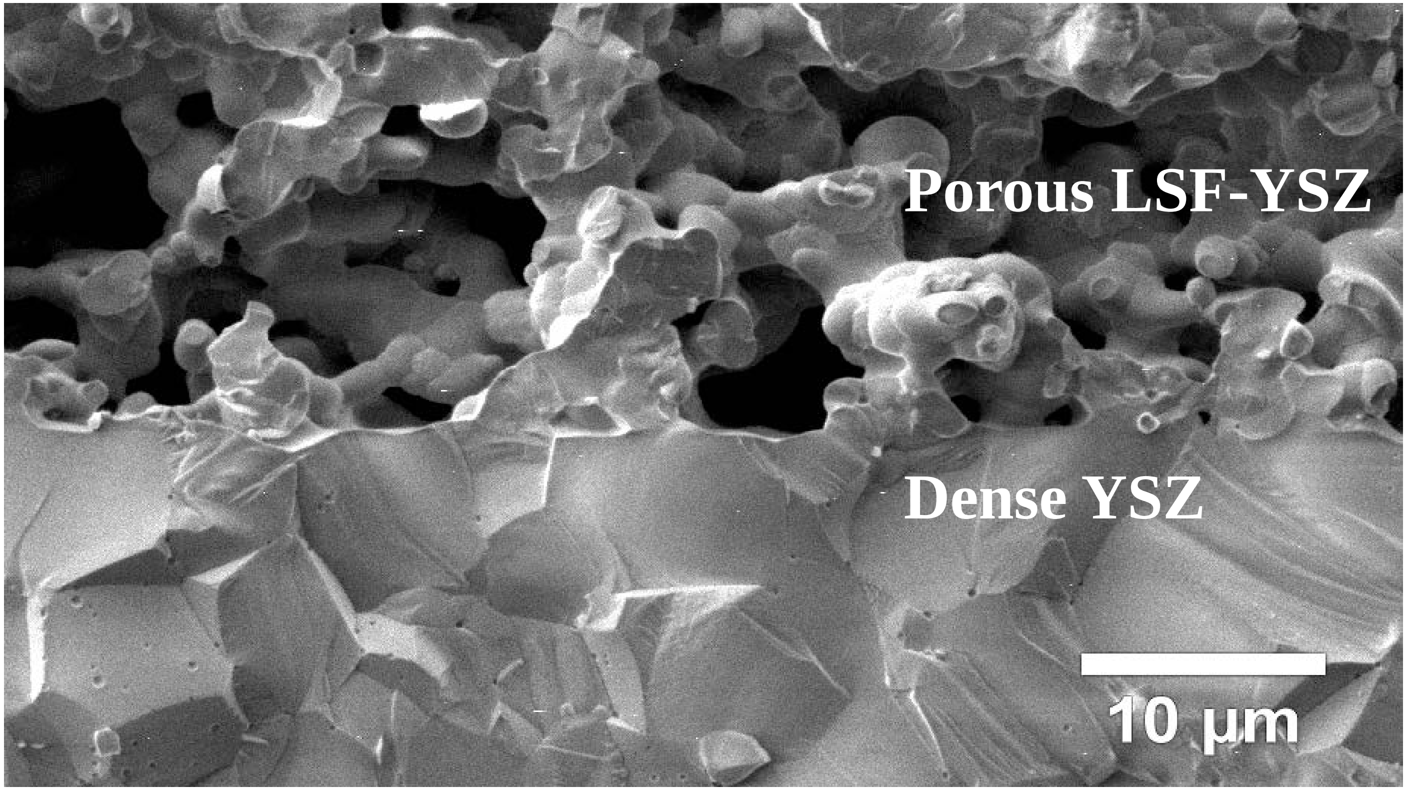
2 firing steps

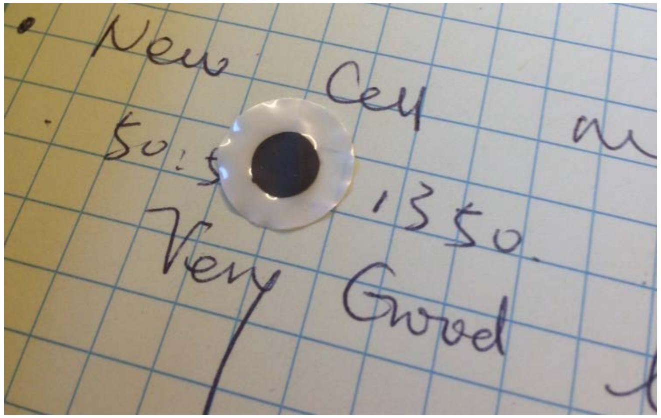
XRD of LSF-YSZ mixtures:



1) No new phases – only perovskite and fluorite.
2) Zr-doping on perovskite observed.

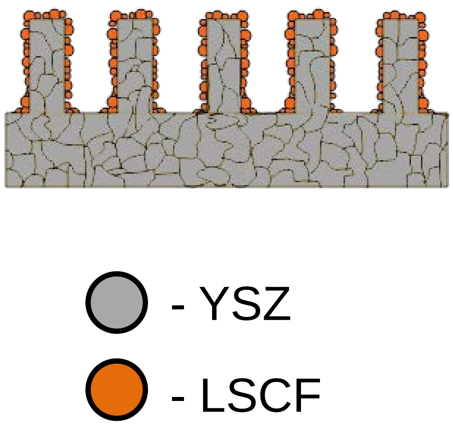
Good YSZ/LSF-YSZ Interface:

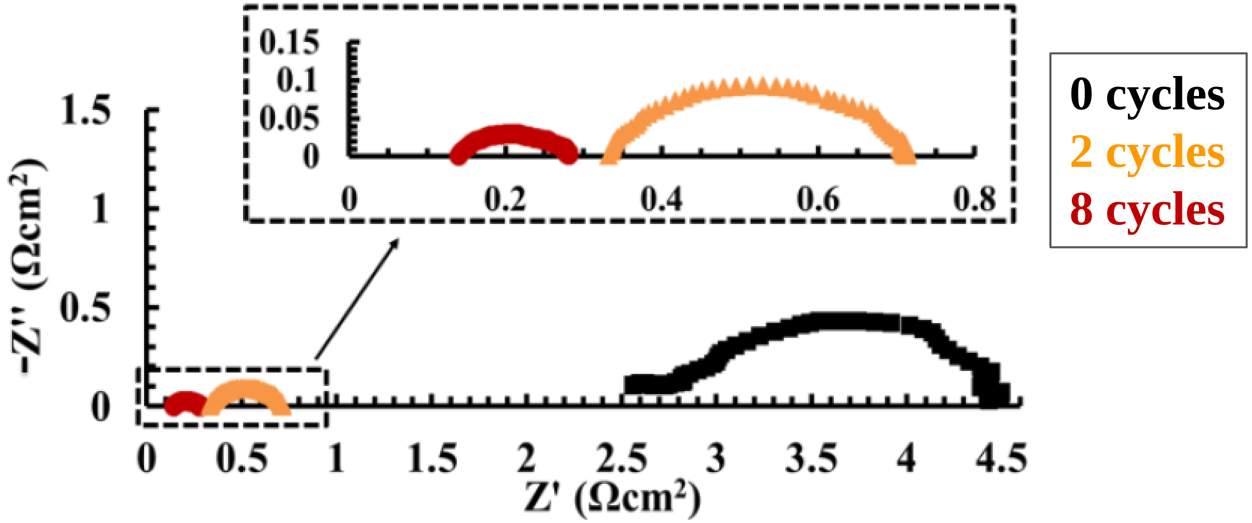




Symmetric Cell (I) - 700°C in air

YSZ Scaffold with infiltrated LSCF

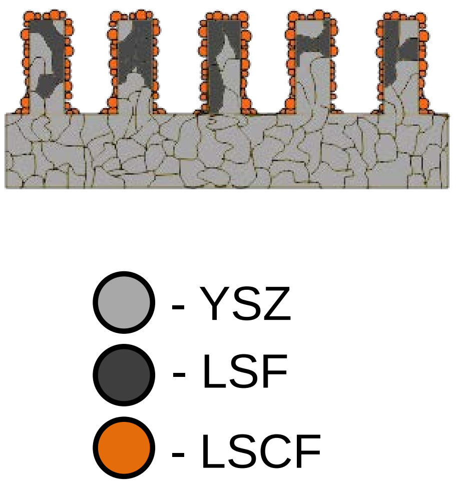


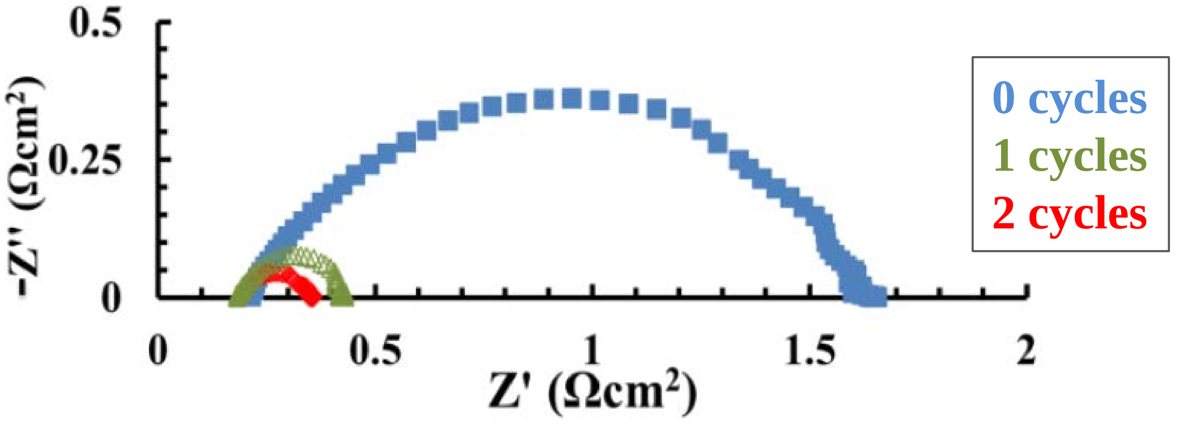


Large number of cycles required for achieving conductivity.
Both Ohmic and Non-Ohmic losses are initially large.

Symmetric Cell (II) - 700°C in air

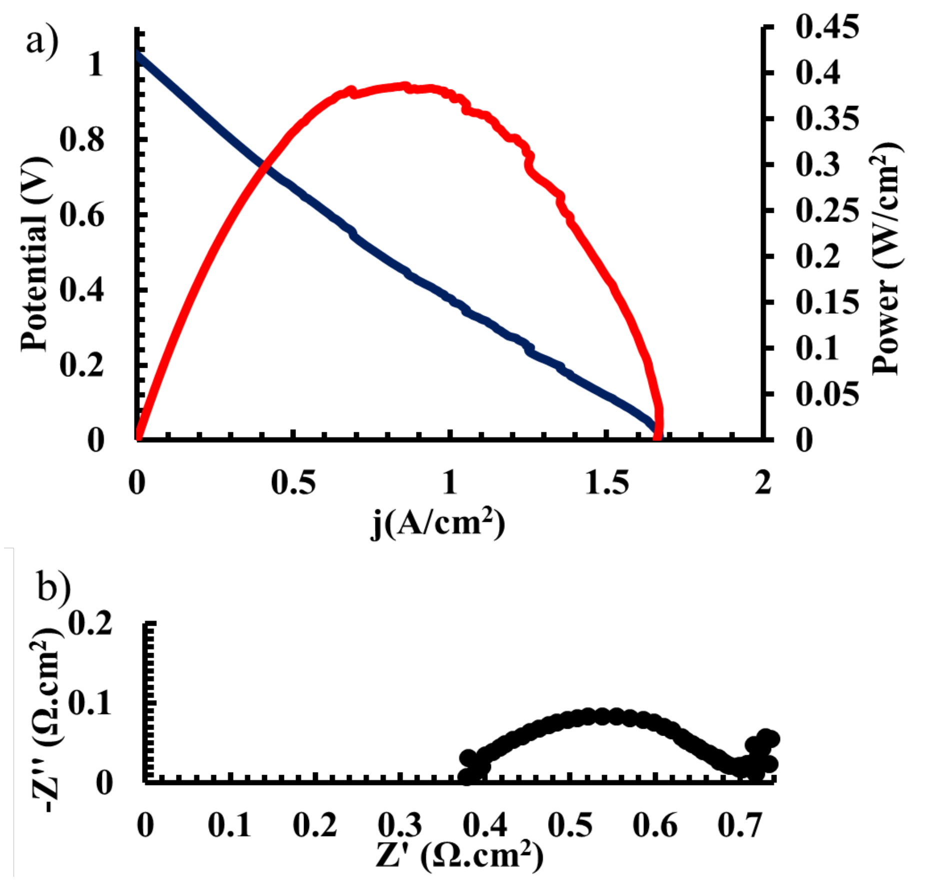
LSF/YSZ composite scaffold with infiltrated LSCF





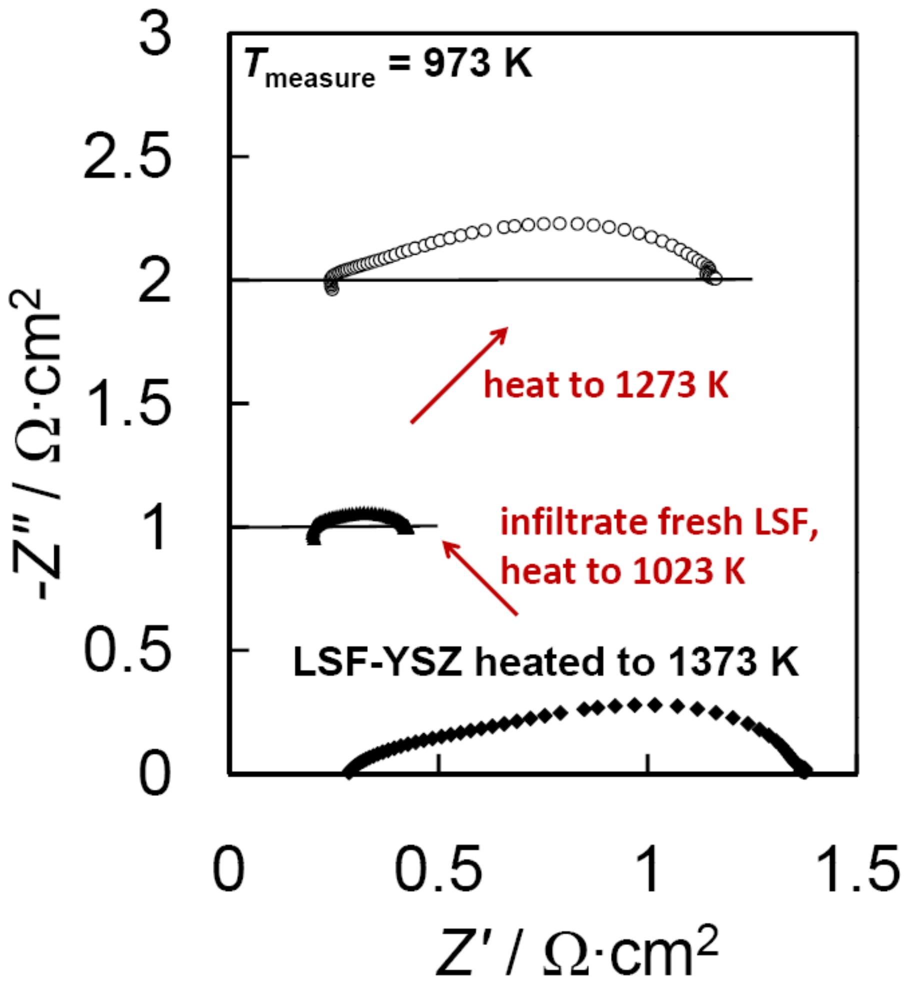
Scaffold provides good ohmic resistance.
Infiltration decreases non-ohmic losses.

Good Fuel-Cell Performance:



Temperature: 973 K
Fuel: 97% H_2- 3% H_2O
Electrolyte: 80 µm YSZ
Cathode:
LSCF (2 cycles) in LSF-YSZ scaffold
Anode: Sr-doped $LaVO_3$/Pd/CeO_2

Nano-structure of infiltrated LSCF is critical:

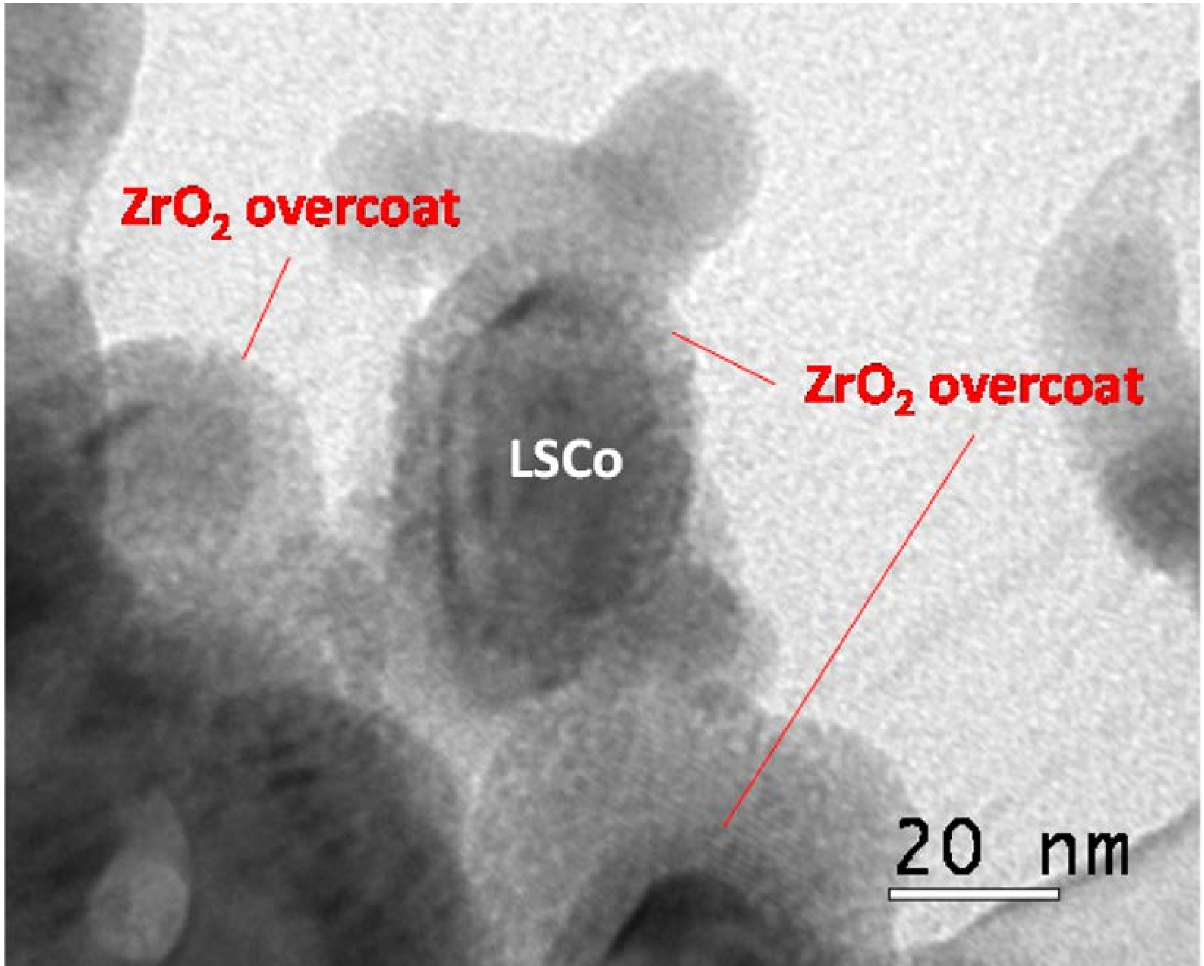


From previous work:

1) **Coarsening of perovskite (by heating to 1373 K) increases non-ohmic losses.**
2) **Adding additional nano-LSF restores performance.**

Solid State Ionics 225 (2012) 146-150

Our Team is Working to Stabilize the Nano-Structure Using ALD



$La_{0.6}Sr_{0.4}CoO_{3-\delta}$ / ZrO_2

infiltration ALD

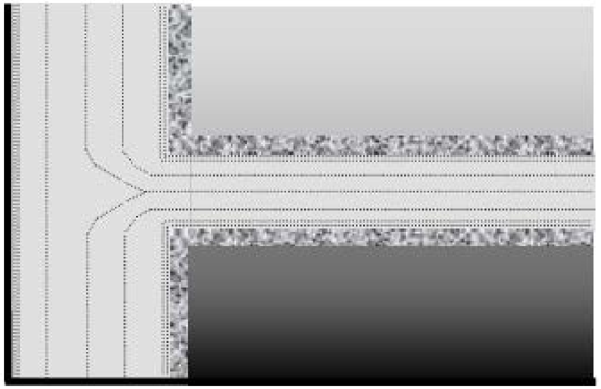
USC

Nano Letters 13 (2013) 4340-4345

Approach 2: Electrodeposit Perovskite:

Electrodeposit La, Fe, etc: With this approach, one is "driving" ions from the bulk solution into the pores using electric fields.

- Start by coating pores with carbon to make conductive.



JES 153 (2006) A1539-A1543

- Deposition must be slower than diffusion of ions.
- Need to choose solvent (water, DMSO, ionic liquid)
- Still need to calcine the deposits to prepare perovskite phase.

This approach is still at a very early stage.

Summary

We are:

1. Developing a simple, cost-effective process to manufacture nanostructured cathodes.

2. Developing unique surface functionalization process to stabilize nanostructured cathodes under SOFC operating conditions.

3. Validating the developed cathode formulations and manufacturing processes by an industrial SOFC manufacturer.

Thank you for your kind attention!

See you again in SOFC-XIV (Glasgow)!

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