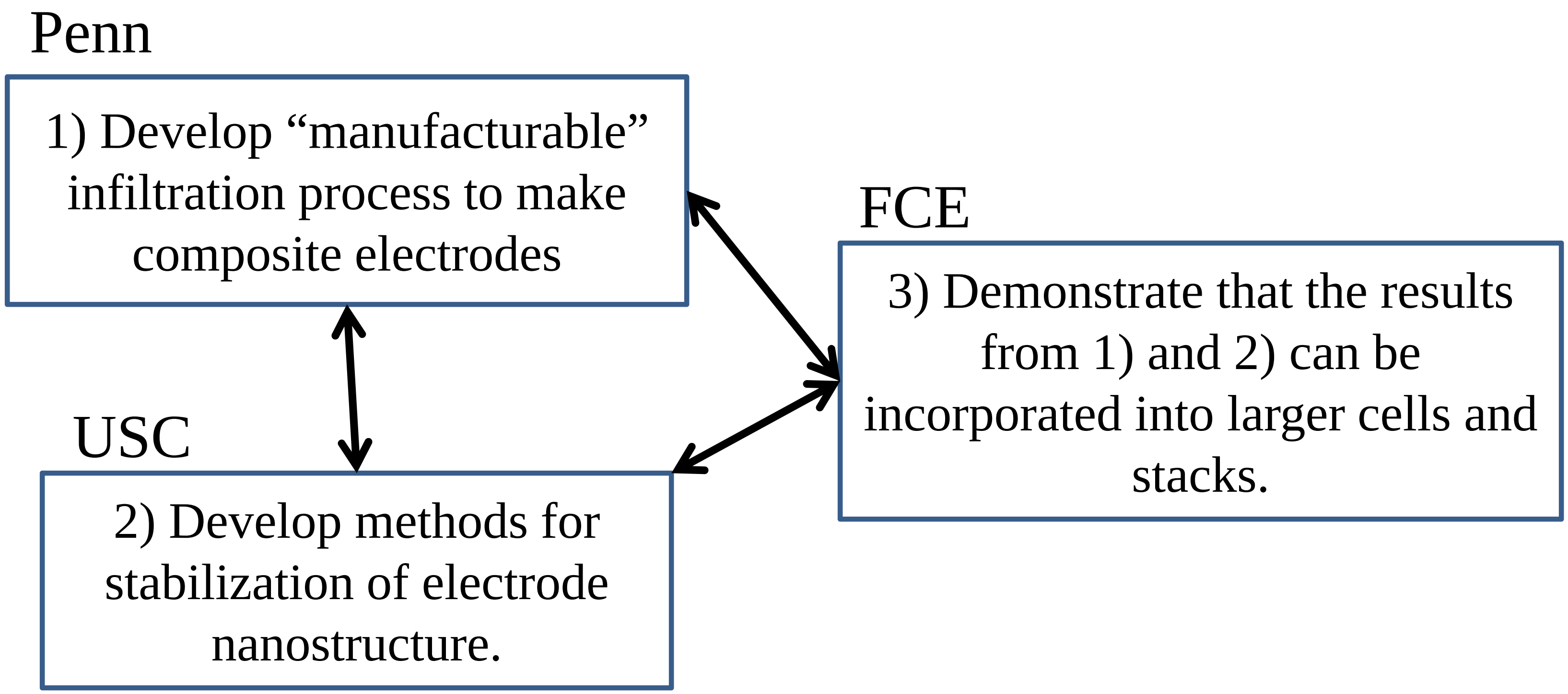
Cost-Effective Manufacturing and Morphological Stabilization of Nanostructured Cathodes for Commercial Solid Oxide Fuel Cells

Yuan Cheng
Raymond J. Gorte, John M. Vohs
University of Pennsylvania

Kevin Huang
University of South Carolina

Joseph E. Barton, Hossein Ghezel-Ayagh
FuelCell Energy

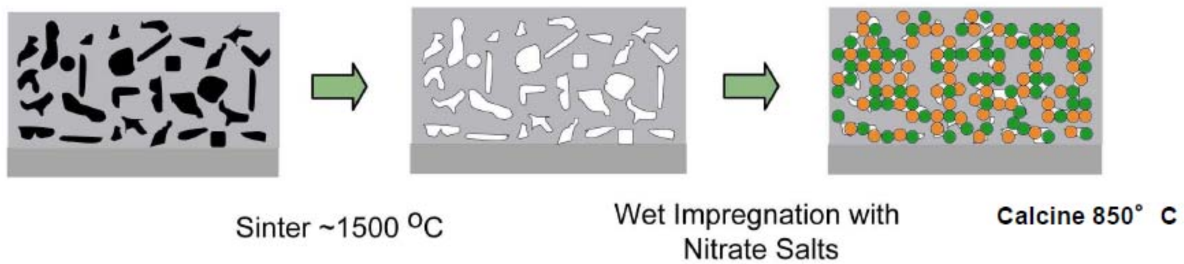
Project Organization and Structure



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

Electrode Fabrication by Infiltration:

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



J. M. Vohs and R. J. Gorte, *Adv. Mater.*, **21,** 1 (2009).

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:

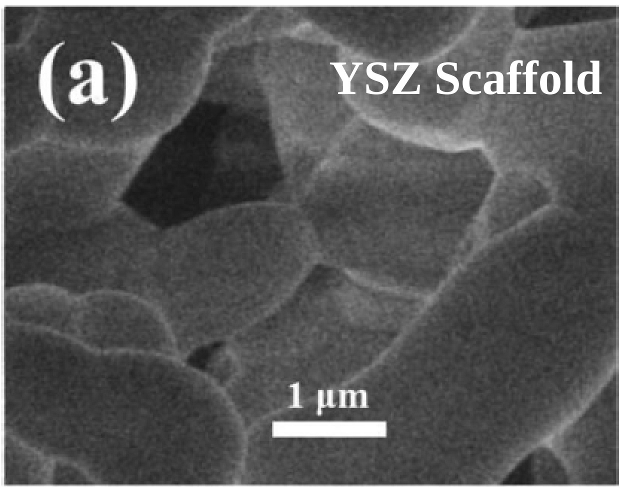
→ Need 35-wt% (20-vol%) perovskite phase for conductivity

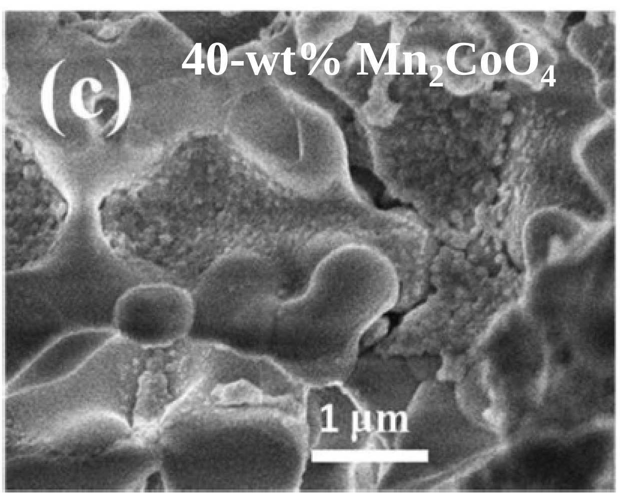
→ To get this loading requires many steps.

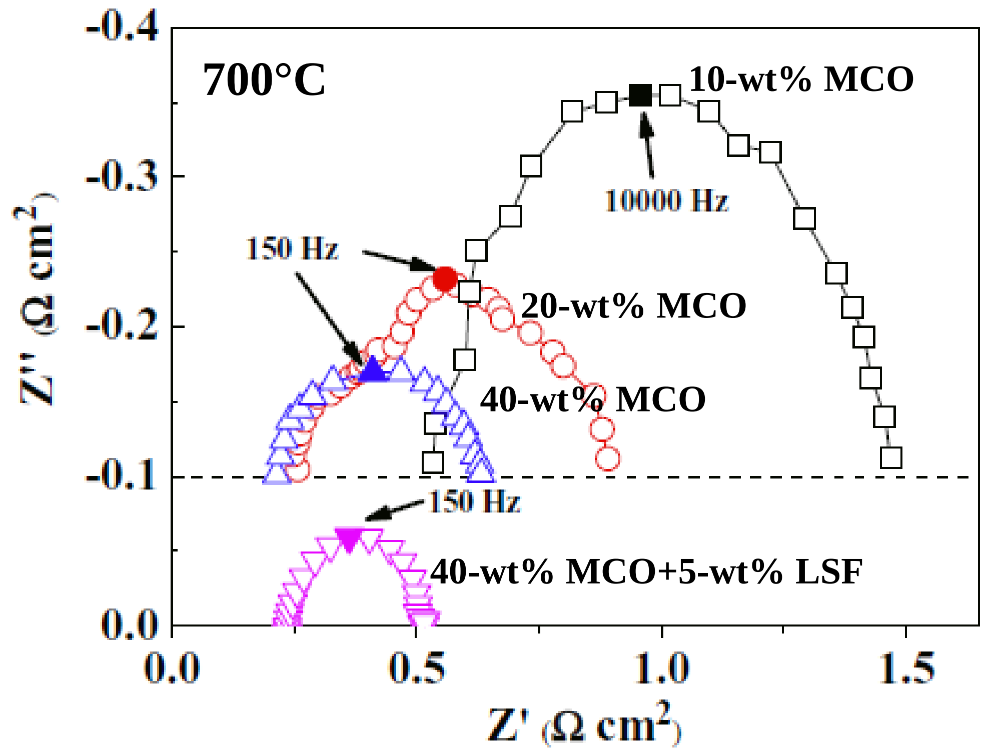
2) Long-term stability – nanoparticles coarsen.

Approach 1: Electrodeposit Cathode:

Step 1: Make scaffold conductive: Coat pores with carbon (pyrolysis of butane).
Step 2: Electrodeposit Mn & Co; then heat in air to 800°C to form $MnCo_2O_4$:







σ(40-wt% MCO) = 11 S/cm @ 700°C

J. Electrochem. Soc., **163,** F863-F866 (2016)

Issues:

1) **Electrodeposition is single-step but slow:**

   → **Need to deposit slowly to prepare uniform coverages**

2) **Very difficult to electrodeposit Rare Earths:**

   → **J. Electrochem. Soc., 153, A1539-A1543 2006**

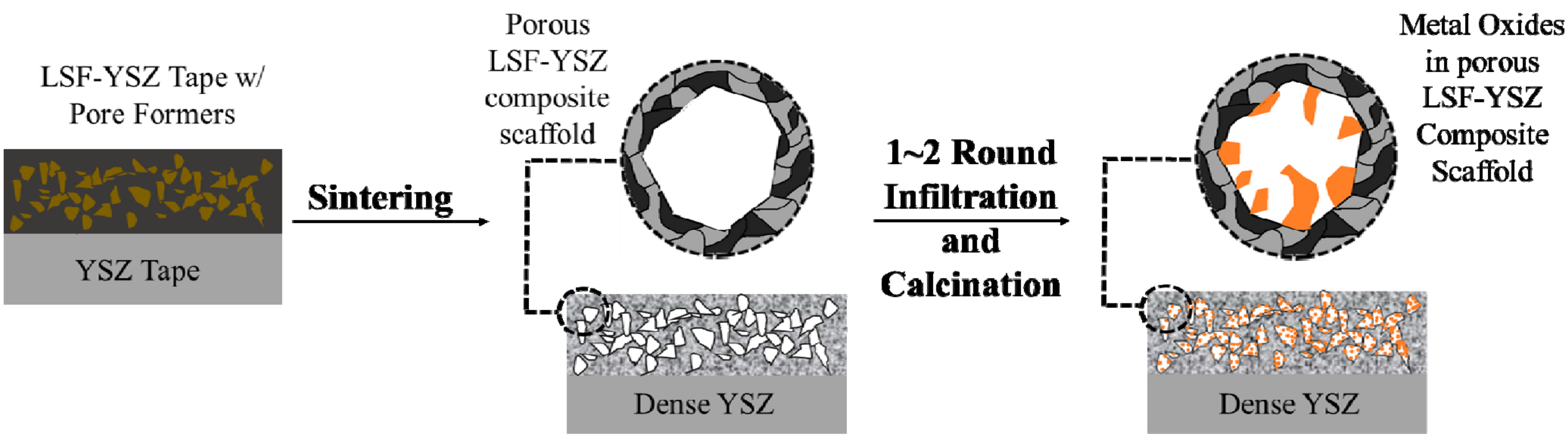
3) **Performance is just okay:**

Approach 2: Prepare a Conducting Scaffold

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

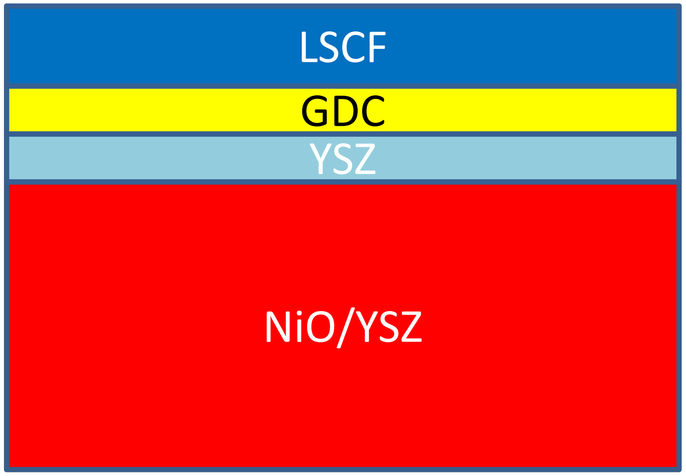
→S. P. Simner, et al, JECS 152 (2005) A1851; W.-S. Wang, et al, JECS 154 (2007) B439

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



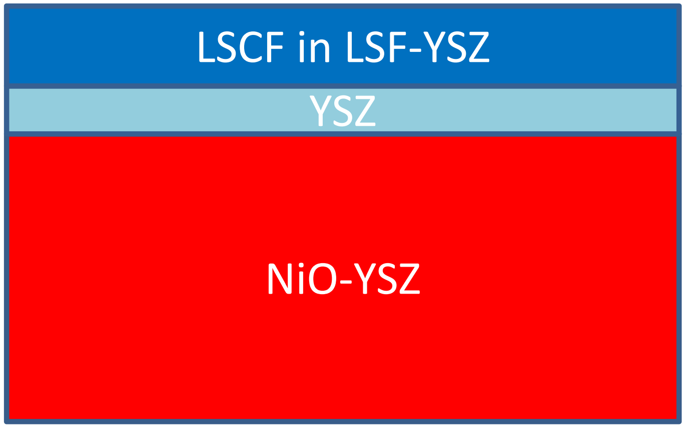
Single-step infiltration into a conducting scaffold could simplify fabrication:

Conventional Cell Fabrication



1) Co-fire NiO-YSZ/YSZ (1350°C)
2) Deposit GDC interlayer; fire (1150°C)
3) Screen-print cathode; fire (1150°C)

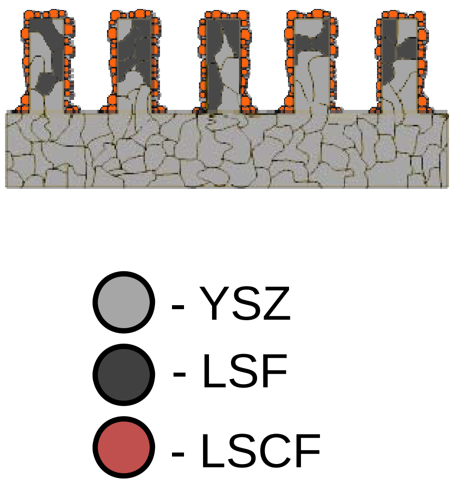
One-Step Infiltration

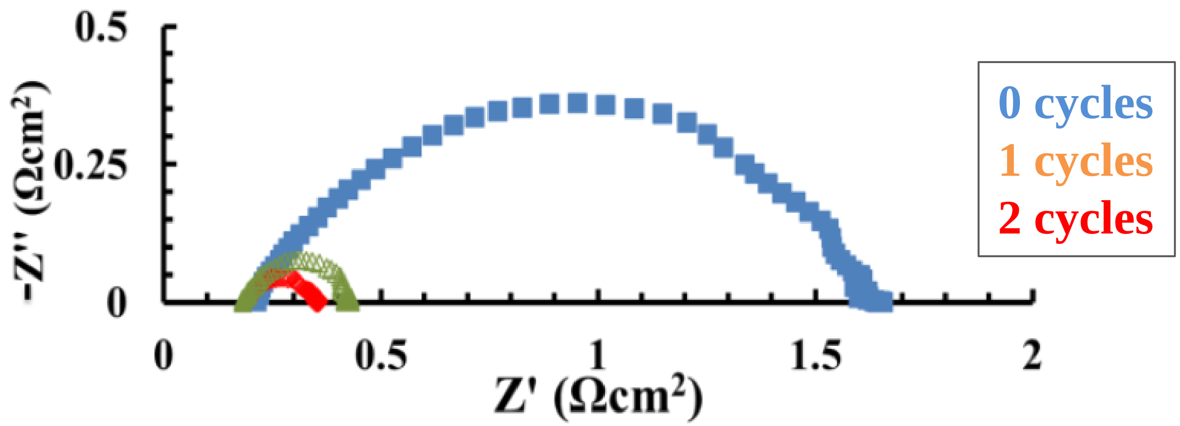


1) Co-fire NiO-YSZ/YSZ/LSF-YSZ (1350°C)
2) Infiltrate LSCF; fire to operating temperature.

Symmetric Cell - 700°C in air

LSF/YSZ composite scaffold with infiltrated LSCF

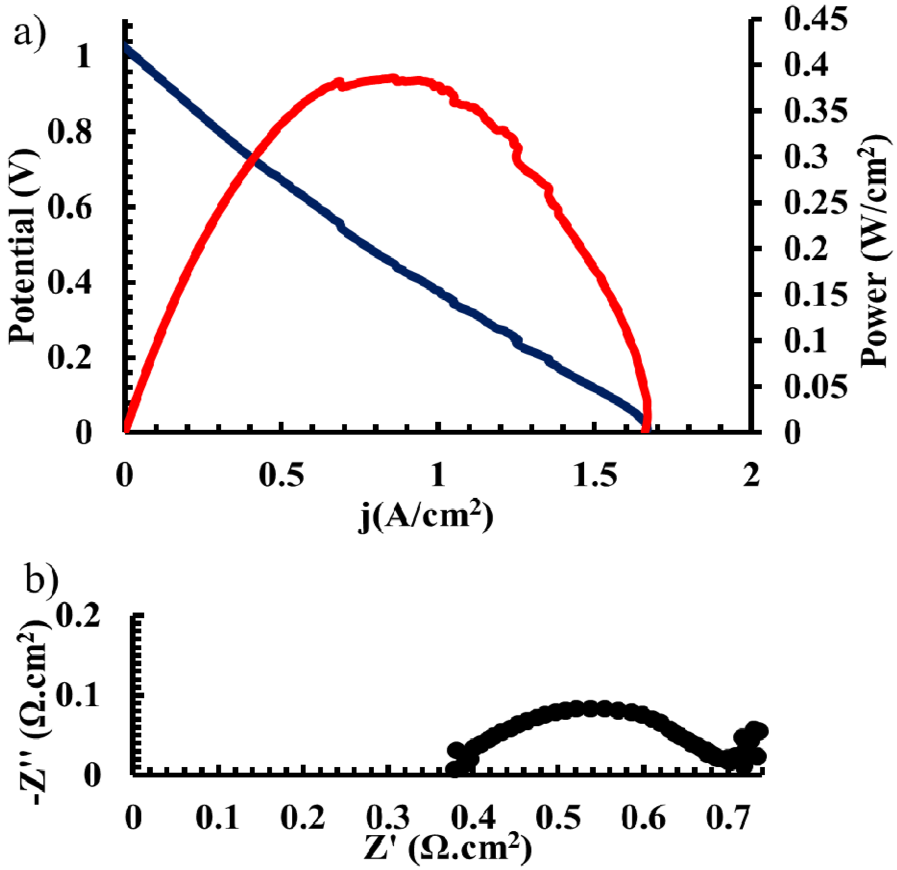




Scaffold provides conductivity.
Infiltration decreases non-ohmic losses.

J. Electrochem. Soc., **163,** F54-F58 (2016)

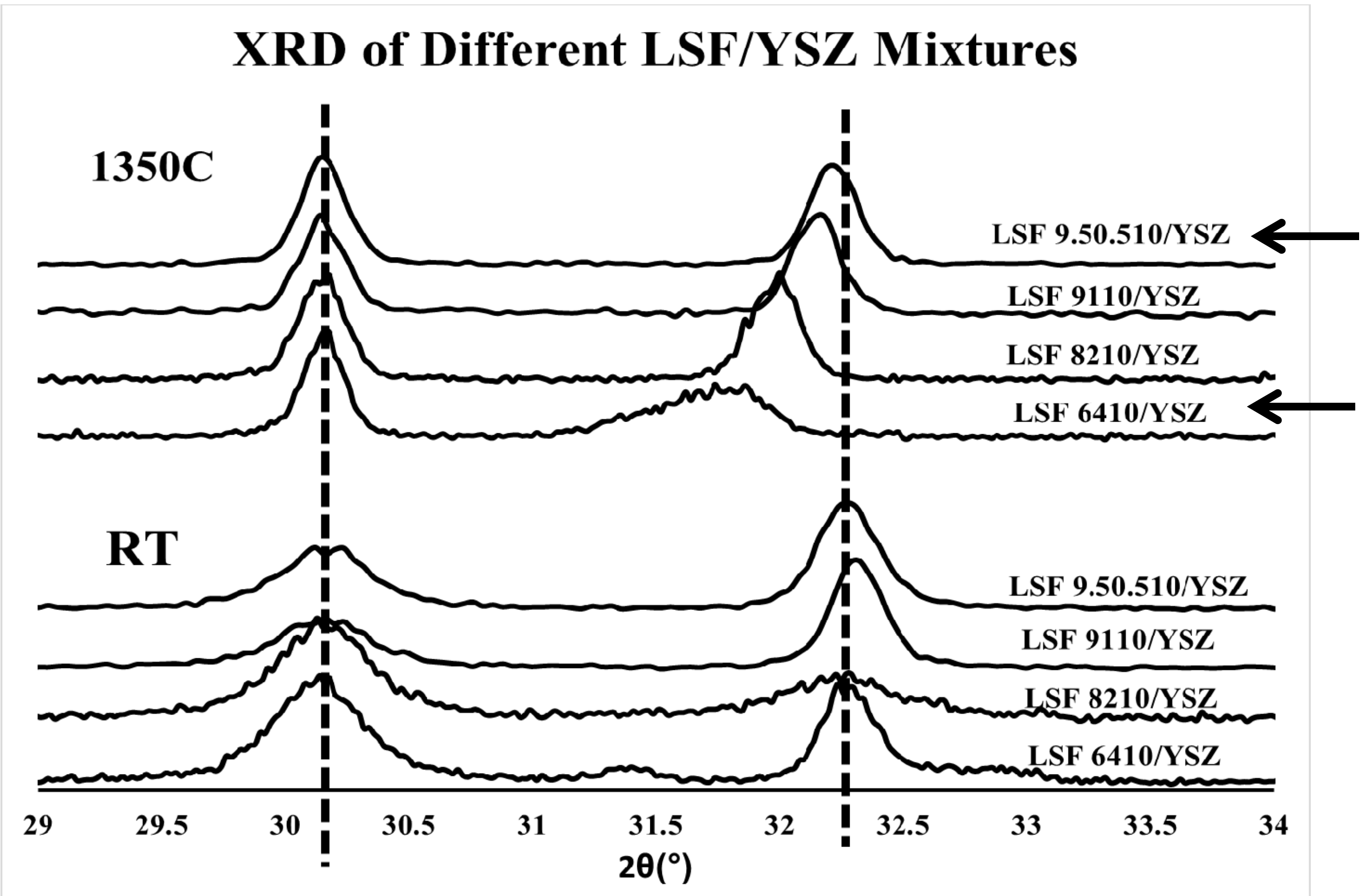
Fuel-cell performance consistent with cathode ASR:



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

Need improved conductivity of LSF-YSZ composites:

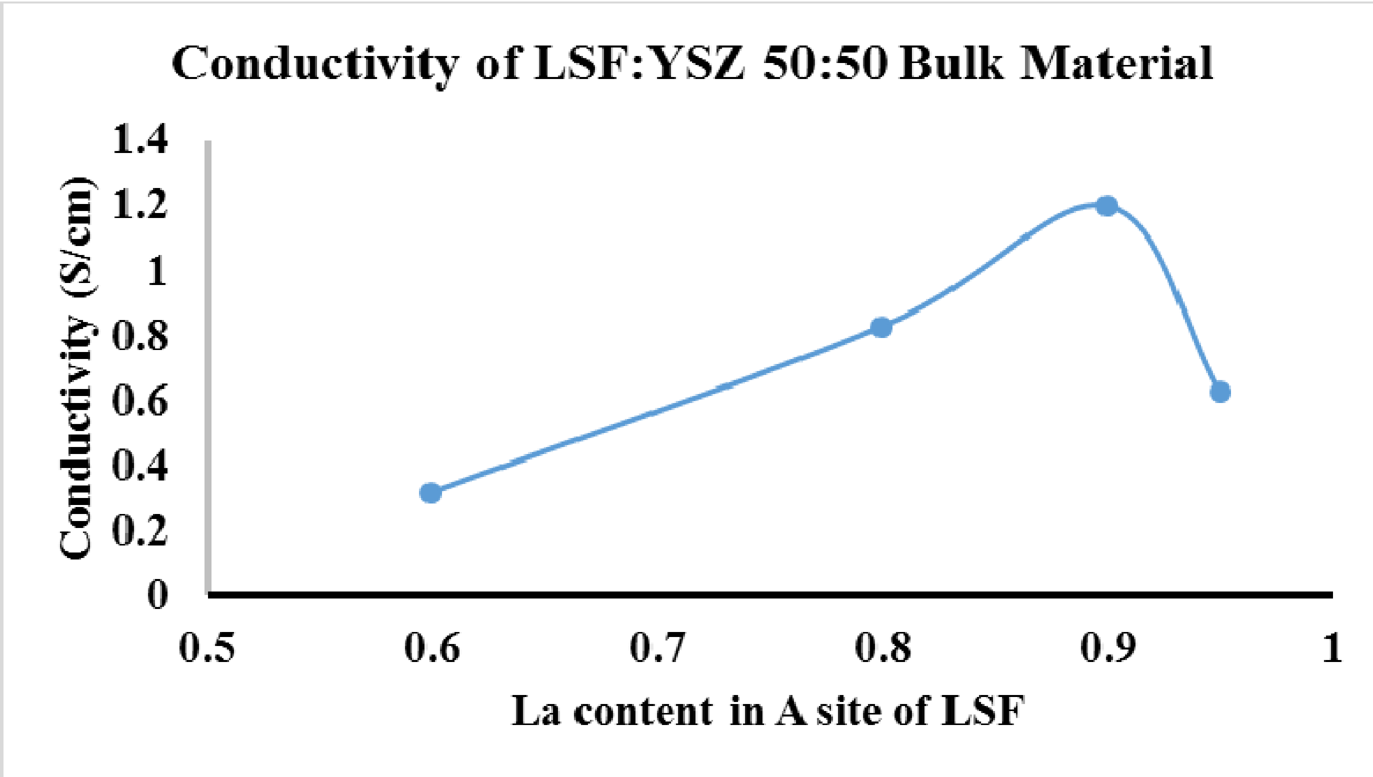
1) Upon calcination, there is Zr doping of LSF phase.
2) Zr-doped LSF has a lower conductivity.
3) Level of doping depends on Sr content.



$La_{0.95}Sr_{0.05}FeO_3$

$La_{0.6}Sr_{0.4}FeO_3$

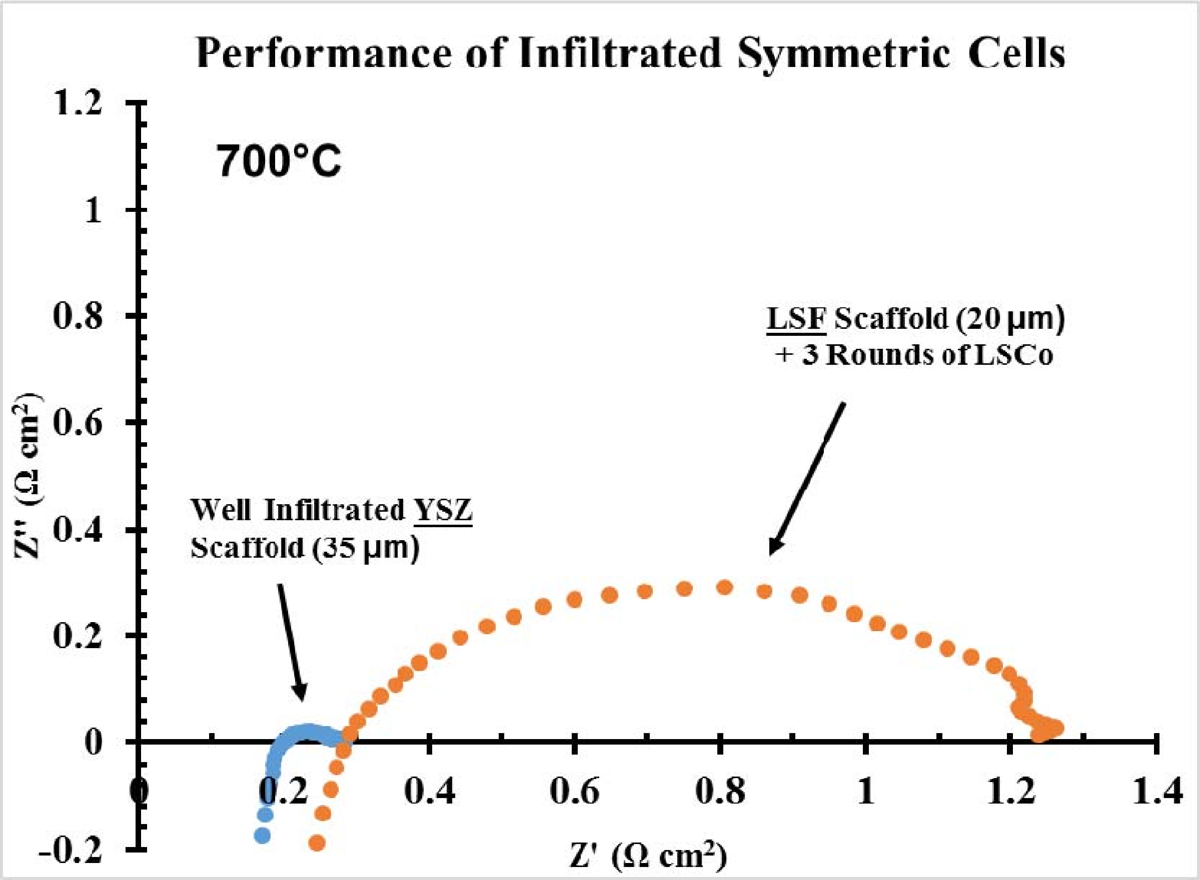
Conductivity of dense, 50% LSF-YSZ mixtures:



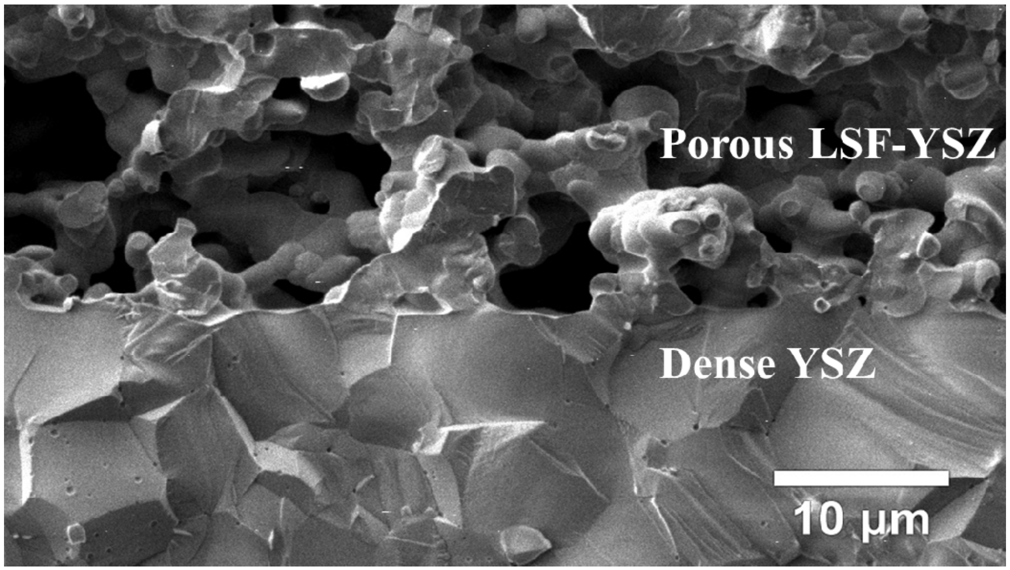
1) Conductivity of LSF increases with Sr:La ratio.
2) Loss of conductivity depends on level of Zr doping.
3) Optimum Sr:La ratio minimizes reaction, maximizes conductivity.

Scaffold cannot be pure LSF:

1) Ohmic losses cannot be completely removed by infiltration of pure LSF scaffold.
2) Likely due to poor interfacial contact.



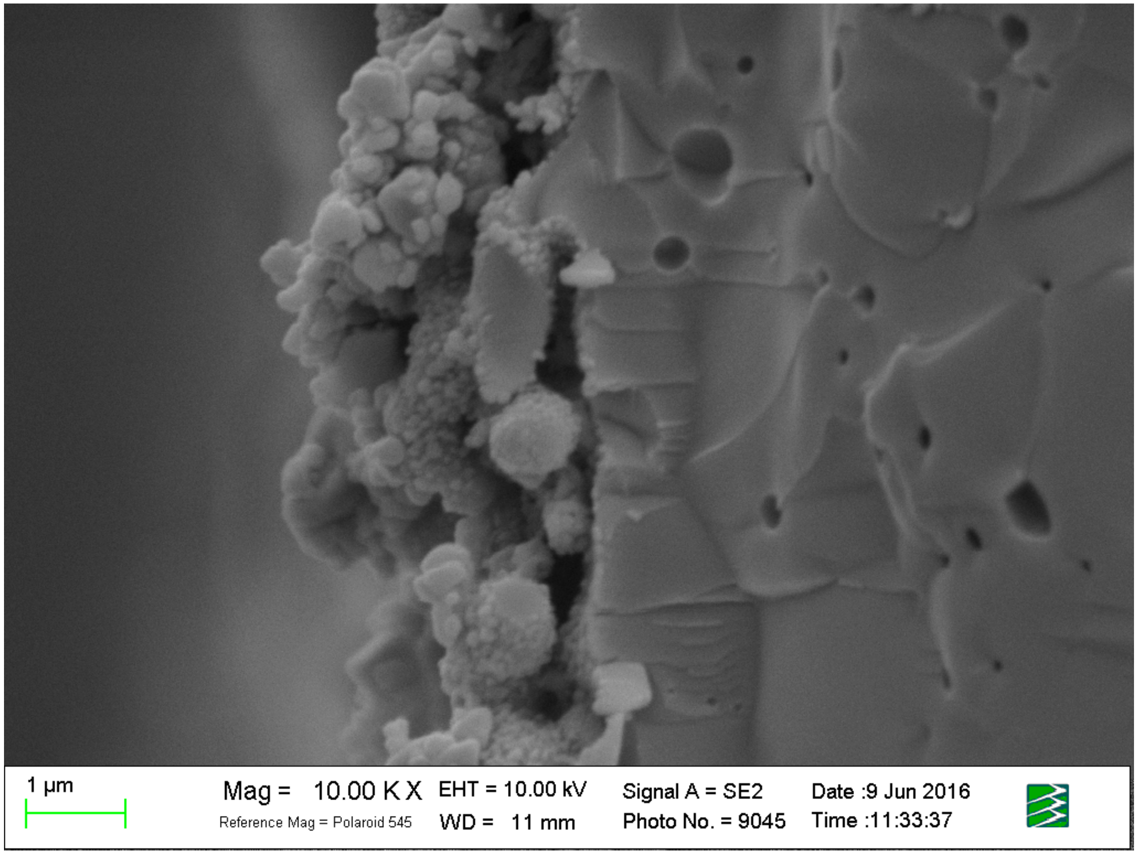
Good YSZ/LSF-YSZ Interface Is Essential:



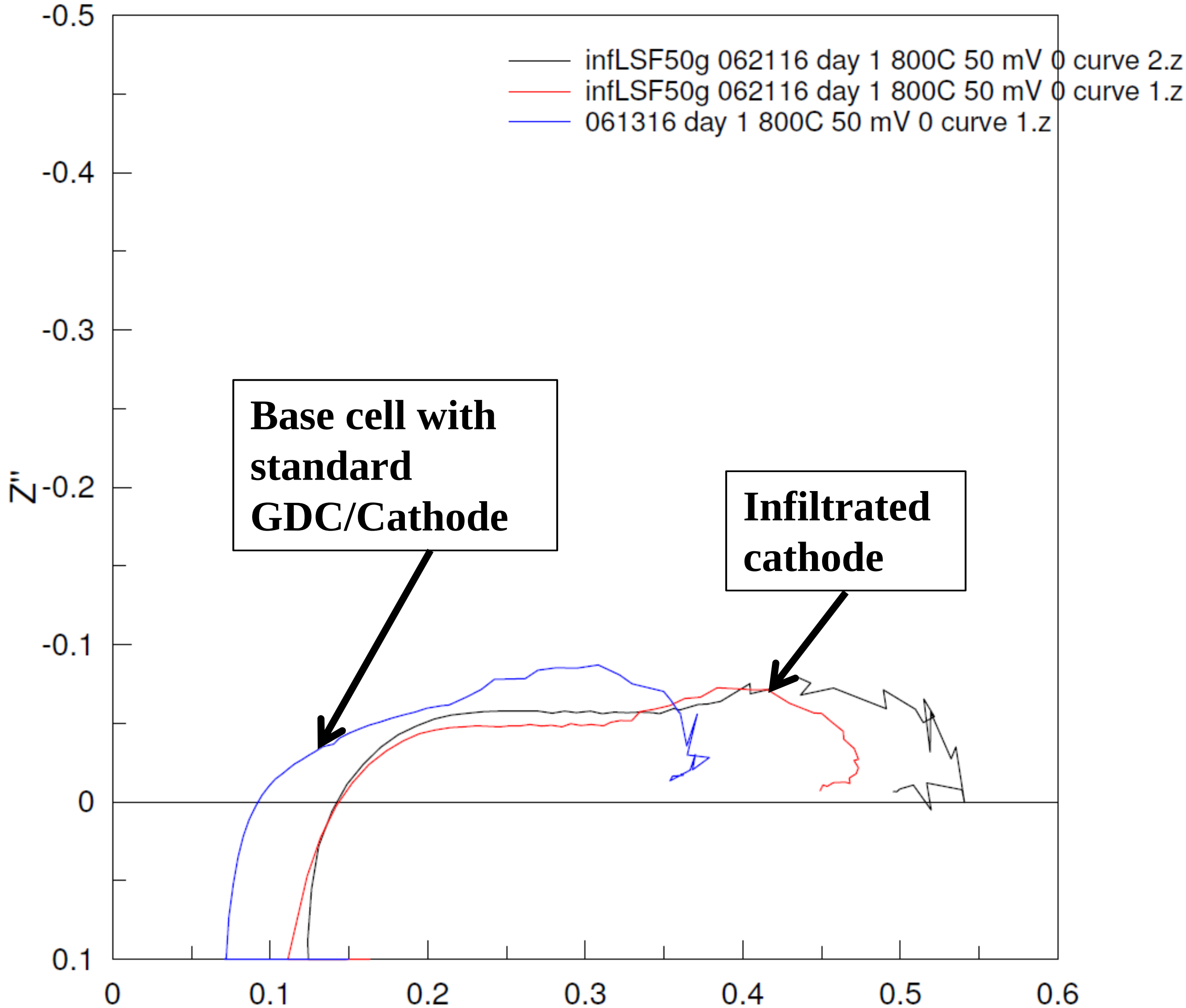
1) Need to optimize porosity.
2) Improve pore size distribution.

Technology Transfer to FuelCell Energy:

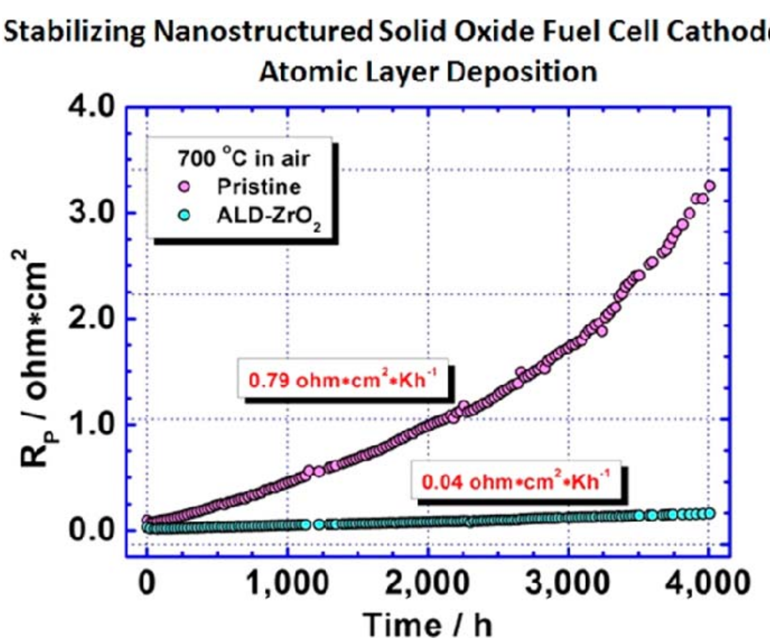
50:50 LSF-YSZ composite (co-fired at 1350°C)
Infiltrated with LSCo.



Initial Cell Test



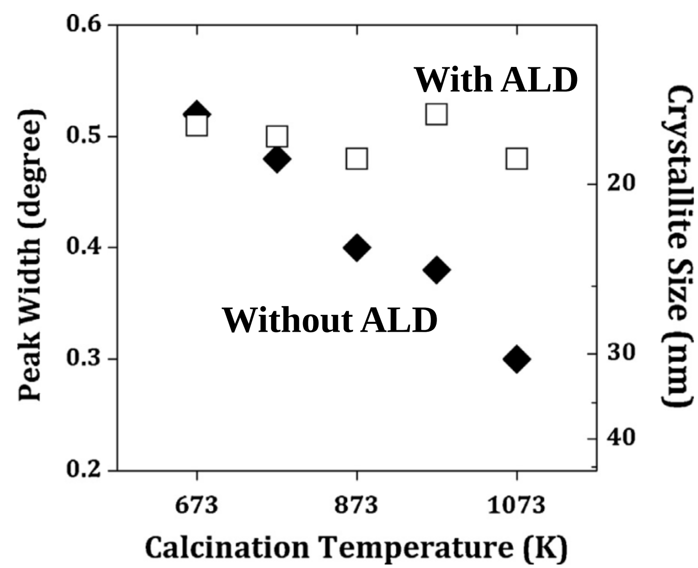
Stabilization of Nanostructure



K. Huang and coworkers, Nanoletters, 2013

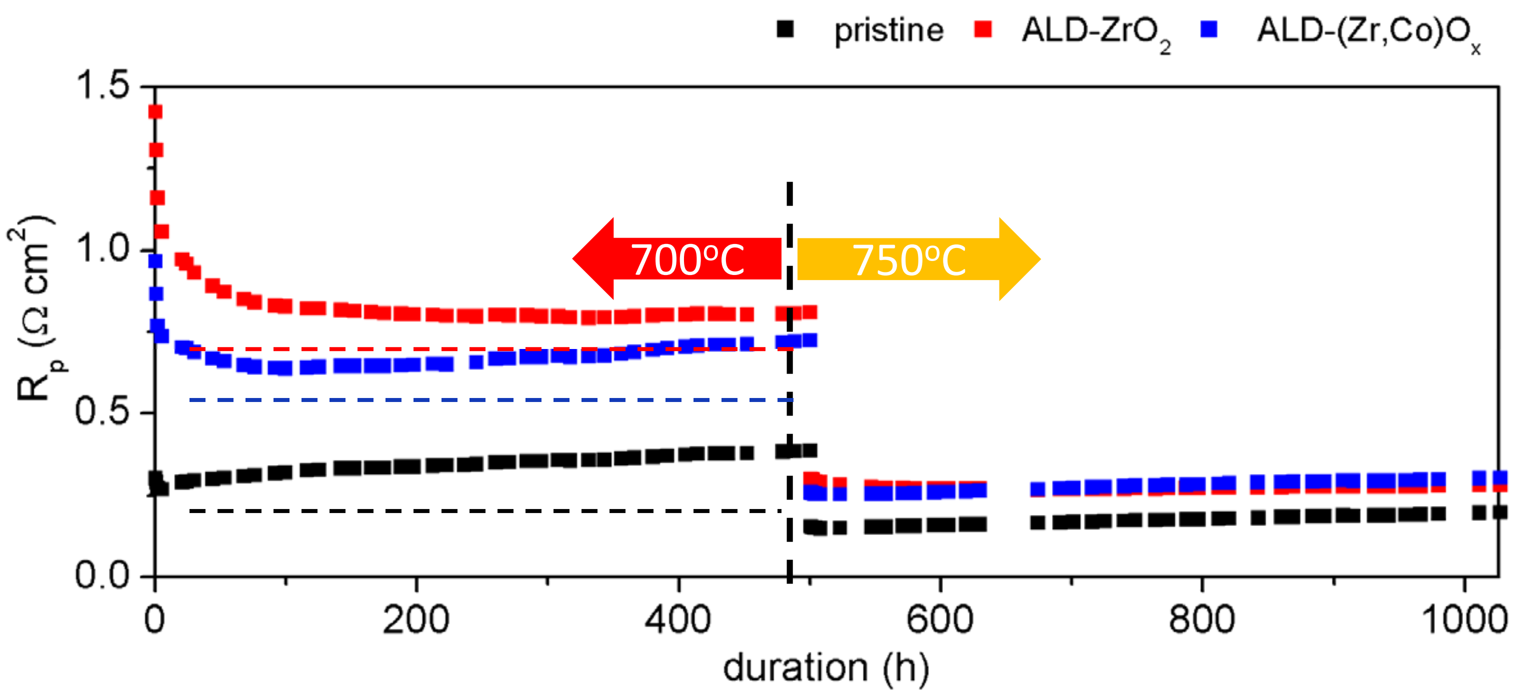
Possible reason for stabilization:

Crystallite size of CeO_2 powder as a function of calcination temperature, with and without 0.5-nm film of ZrO_2



Applied Catalysis B, 197 (2016) 280–285

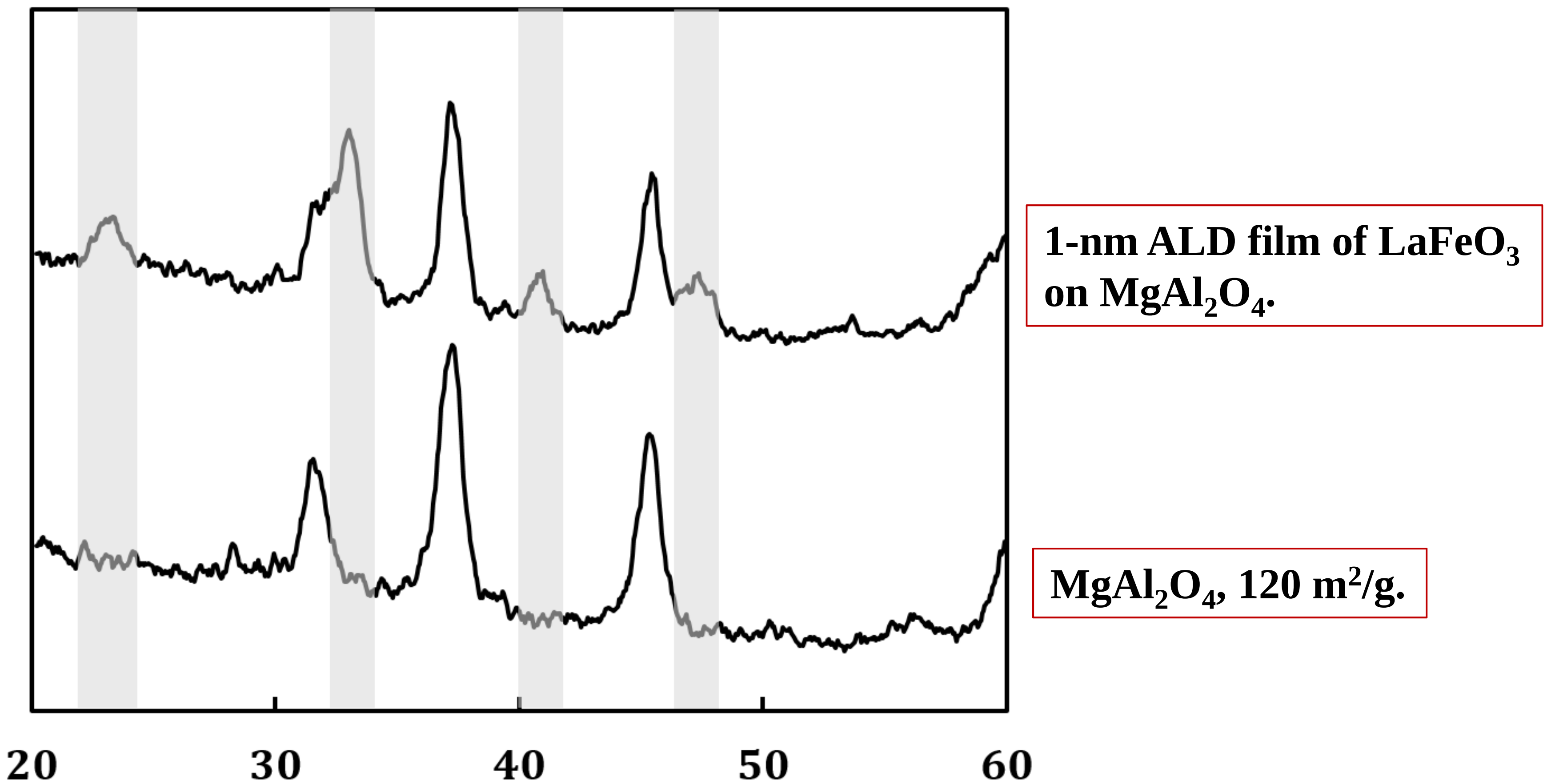
LSCF Electrode with 5-nm ZrO_2 ALD:



- ALD with ZrO_2 lowers performance, but slows degradation
- Incorporating Co helps mitigate the negative effect of the ZrO_2, but compromises stability

Possible Solution:

Make ALD film of catalytically active materials



Perovskite peaks are shown in gray.

Future Research

1. **Investigate ways to improve conductivity and performance with the LSF-YSZ scaffolds (modify porosity, composition, and fabrication conditions).**
2. **Study Coating of the cells with a conformal layer of the selected oxides using ALD process.**
3. **Continue validation of the materials set and one-step fabrication process in button cells.**
4. **Validate the down-selected materials sets and process parameters in 100 cm^2 active area cells.**
5. **Investigate scale up the one-step fabrication process to commercially-relevant sizes.**