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

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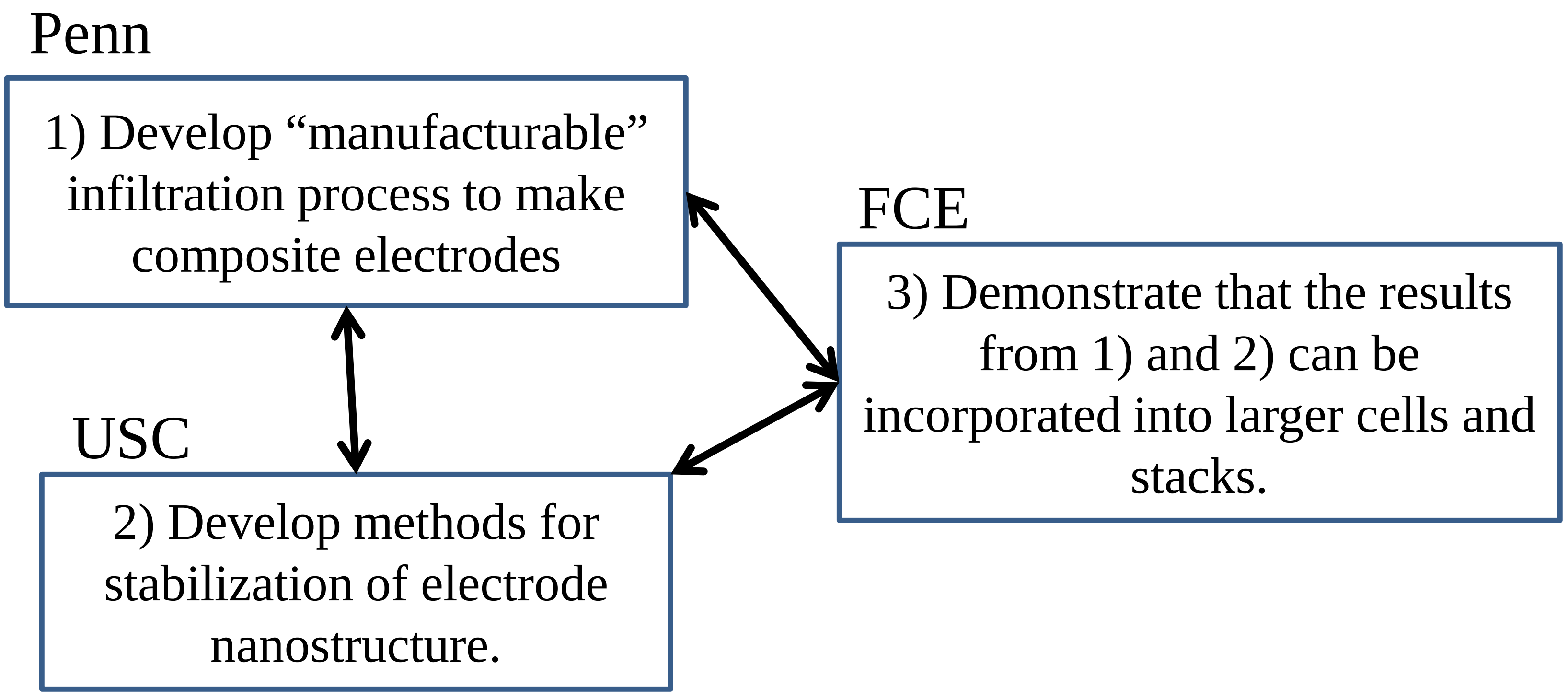
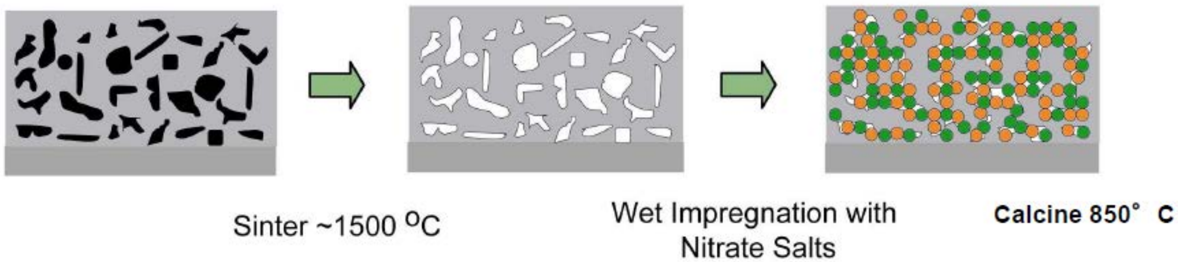
Project Organization and Structure



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.

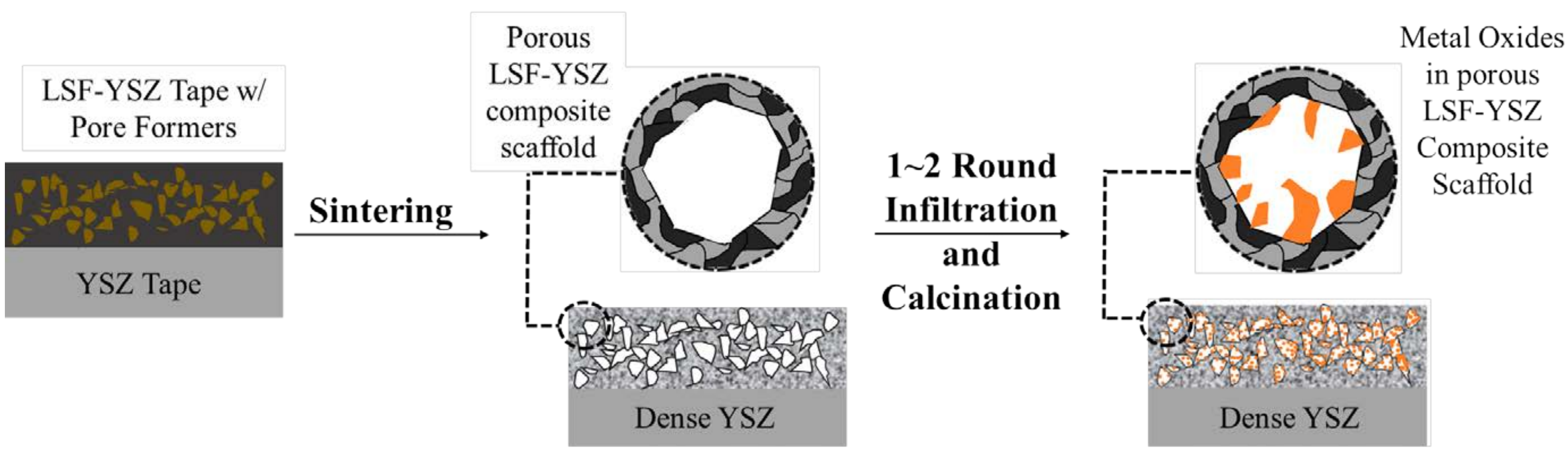
2) Long-term stability – nanoparticles coarsen.

Approach: Prepare conducting scaffold; infiltrate only "catalyst".

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

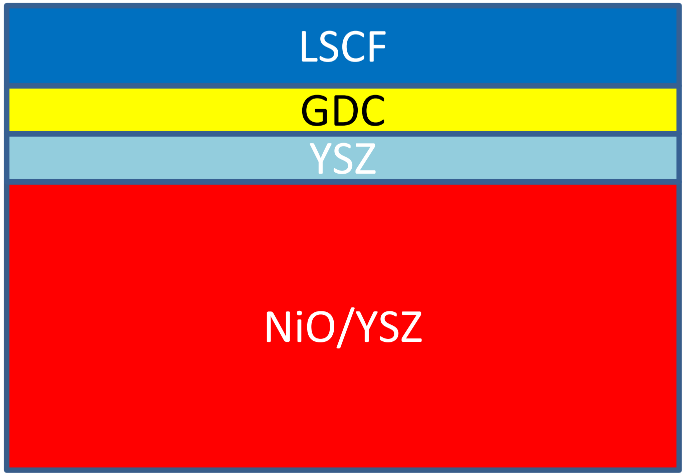
→S. P. Simner, et al, JECS 152 (2005) A1851; W.-S. Wang, et al, JECS 154 (2007) B439

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



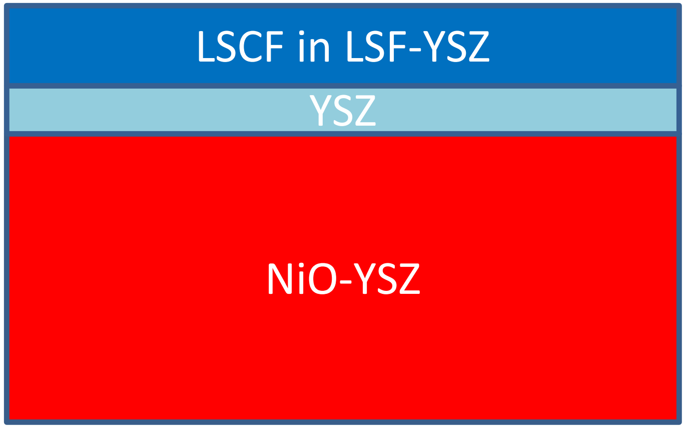
Single-step infiltration into a conducting scaffold simplifies fabrication:

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)

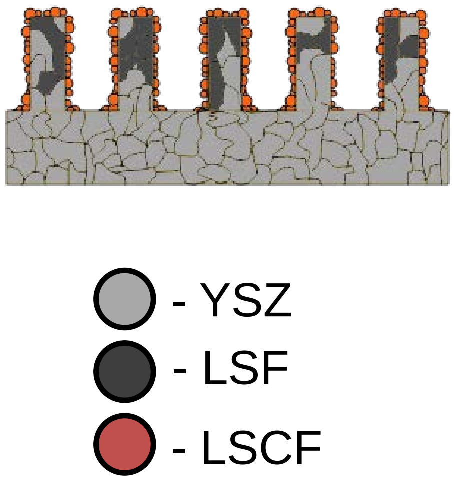
One-Step Infiltration

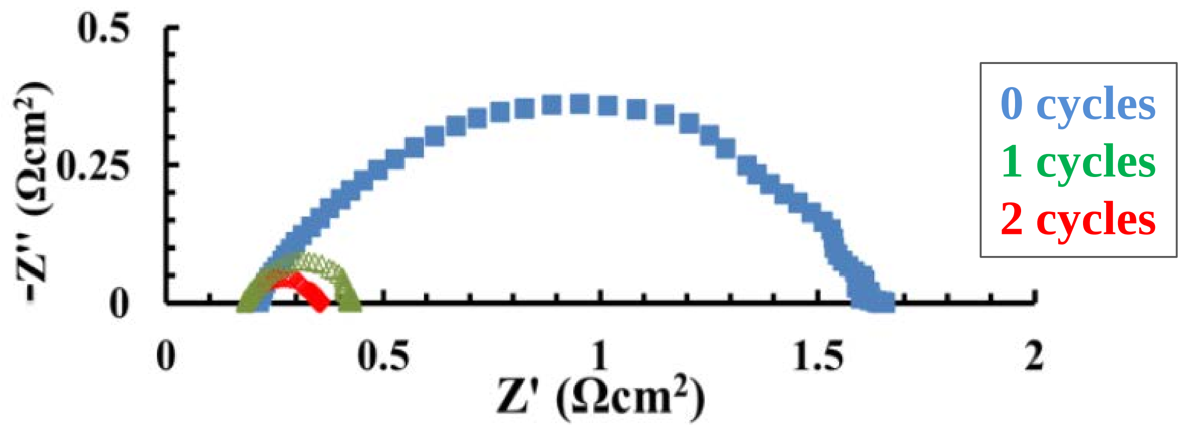


1) Co-fire NiO-YSZ/YSZ/LSF-YSZ (1350°C)
2) Infiltrate LSCF; fire to operating temperature.

Symmetric Cell - 700°C in air

LSF/YSZ composite scaffold with infiltrated LSCF



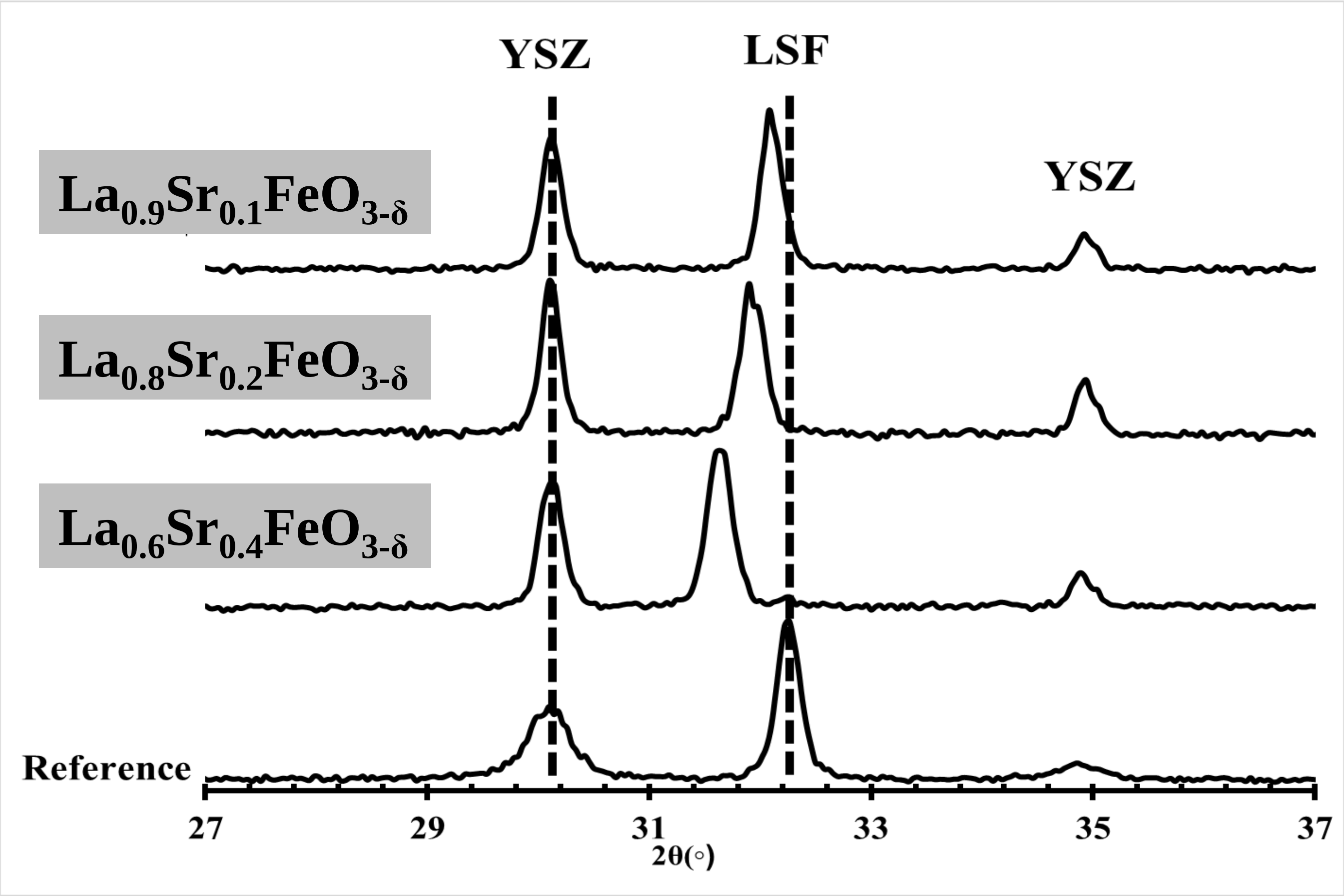


Scaffold provides conductivity.
Infiltration decreases non-ohmic losses.

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

Co-firing LSF-YSZ leads to Zr doping of LSF:

XRD of 50:50 wt% LSF-YSZ calcined at 1623 K

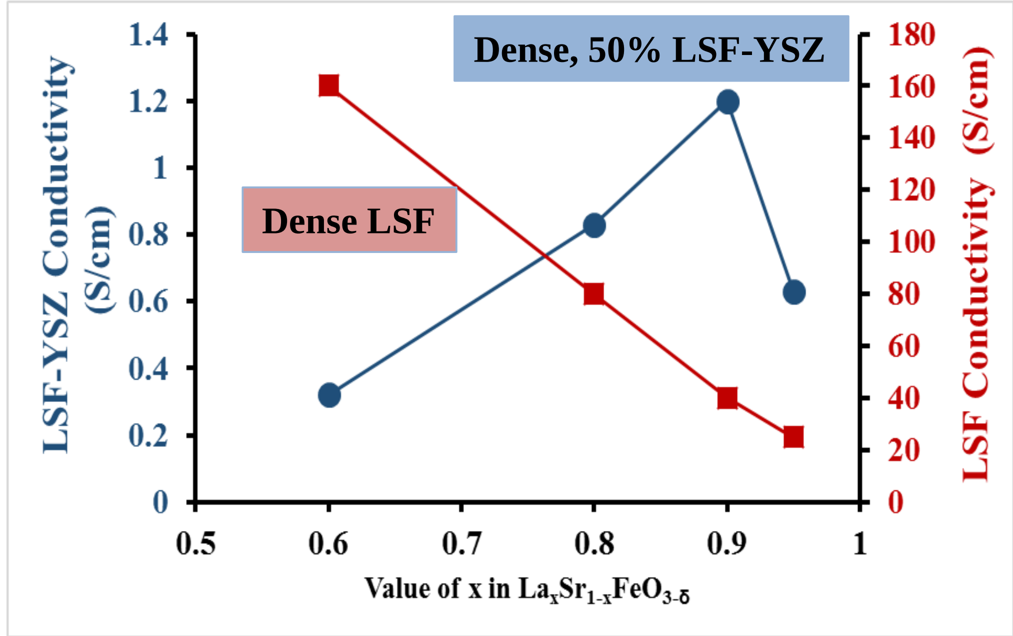


1) LSF peak shifts upon calcination.
2) Shift is due to Zr doping of LSF phase.
3) Zr doping increases with Sr:La ratio

J. Electrochem. Soc., **164,** F525-29 (2017)

Loss of LSF conductivity due to Zr; $La_{0.9}Sr_{0.1}FeO_3$ is optimal.

Electronic conductivity:

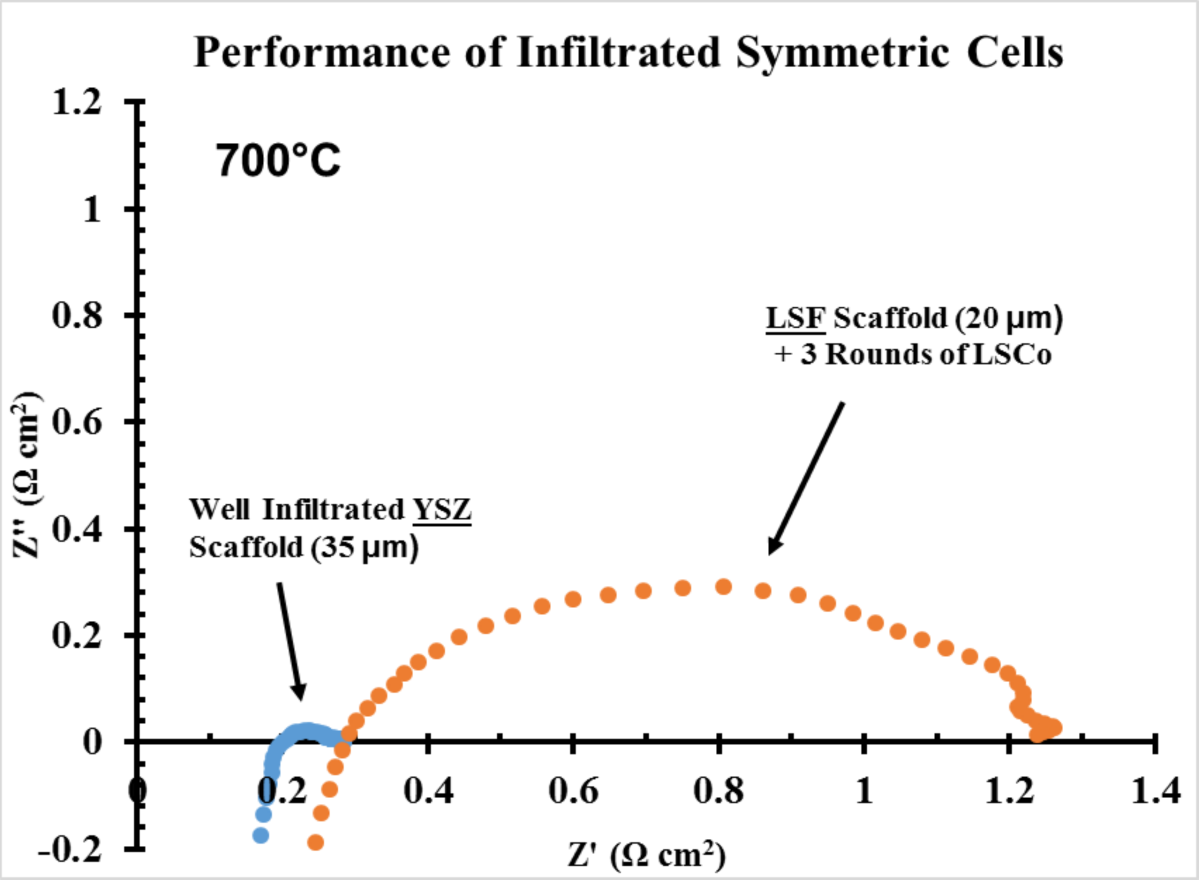


Ionic conductivity:

Temp (K)	40-wt% LSF82-YSZ (S/cm)	LSF82 (S/cm)	YSZ8 (S/cm)
973	0.006	0.072	0.019
1073	0.017	0.089	0.042

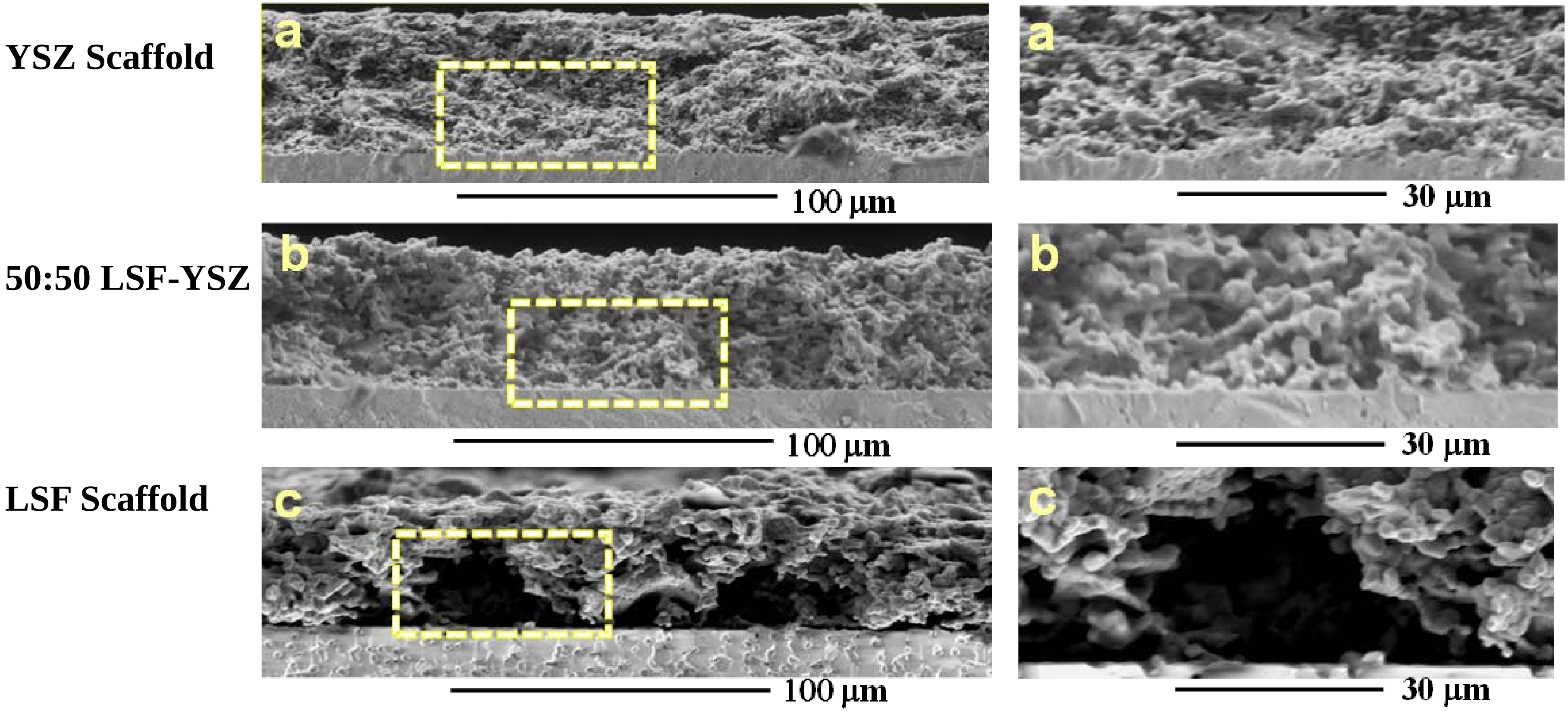
Scaffold cannot be pure LSF:

1) Ohmic losses cannot be completely removed by infiltration of pure LSF scaffold.
2) Problem is poor interface.



Scaffold cannot be pure LSF:

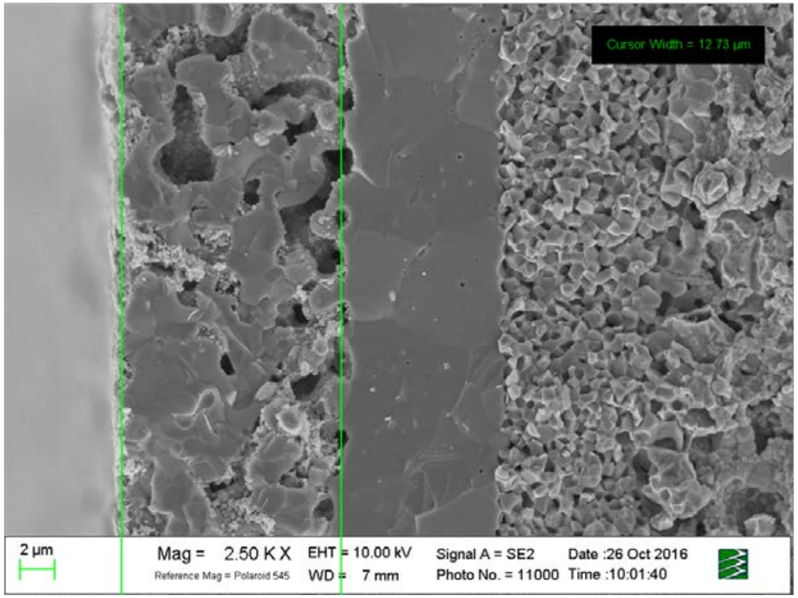
- Different sintering rates for YSZ and LSF cause interface problems.
- 50% LSF-YSZ composites seem to show the best performance.



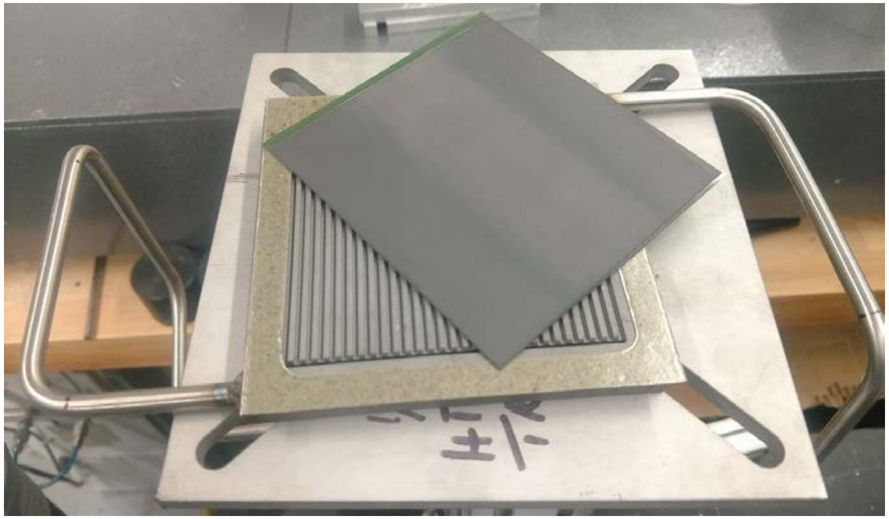
J. Electrochem. Soc., **164,** F525-29 (2017)

Technology Transfer to FuelCell Energy:

TSC3 Screen Printed Cell
Sintered @ 1370 °C, 2 hours
Single Infiltration of LSCF

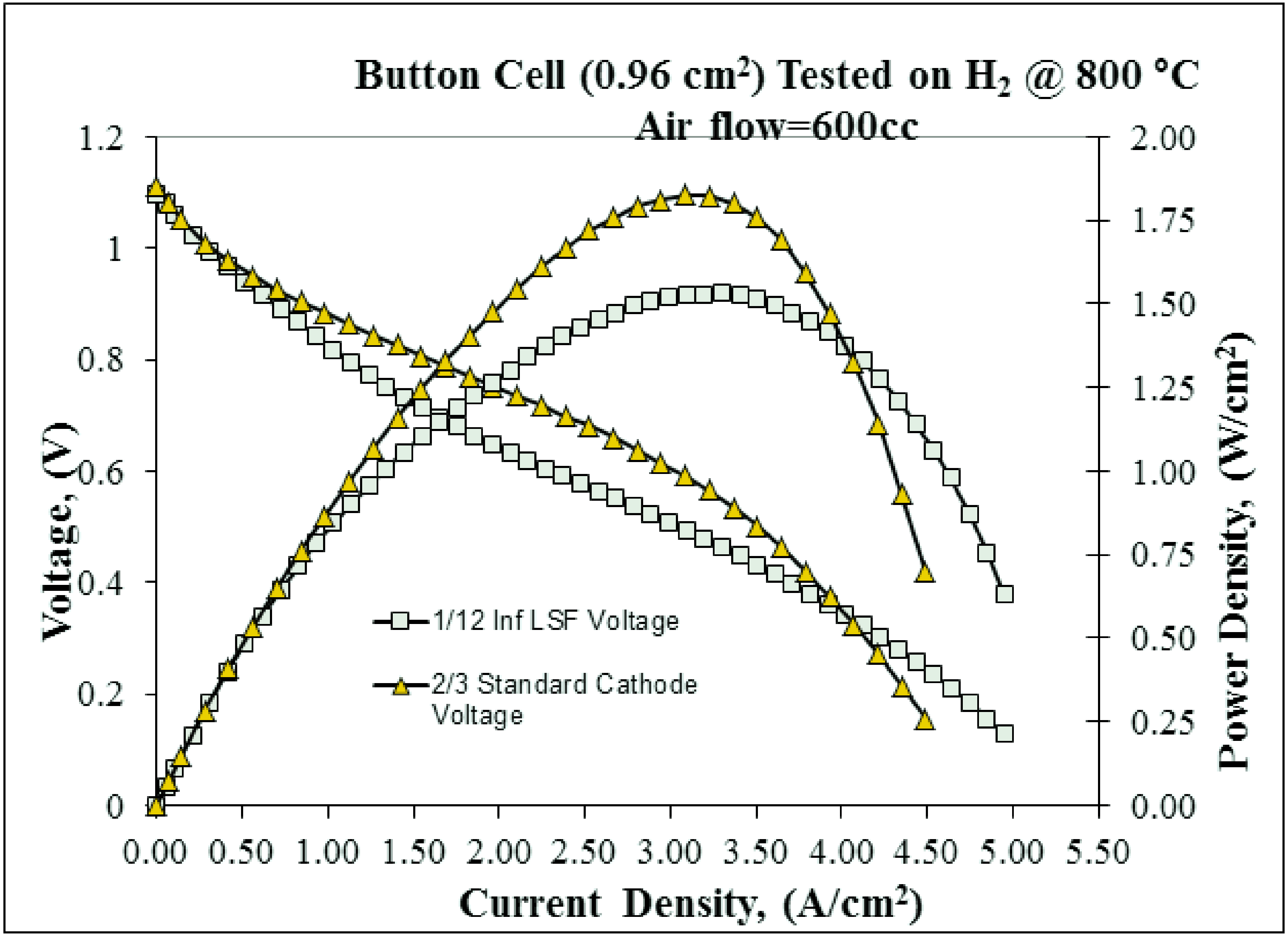


10x10 Cell



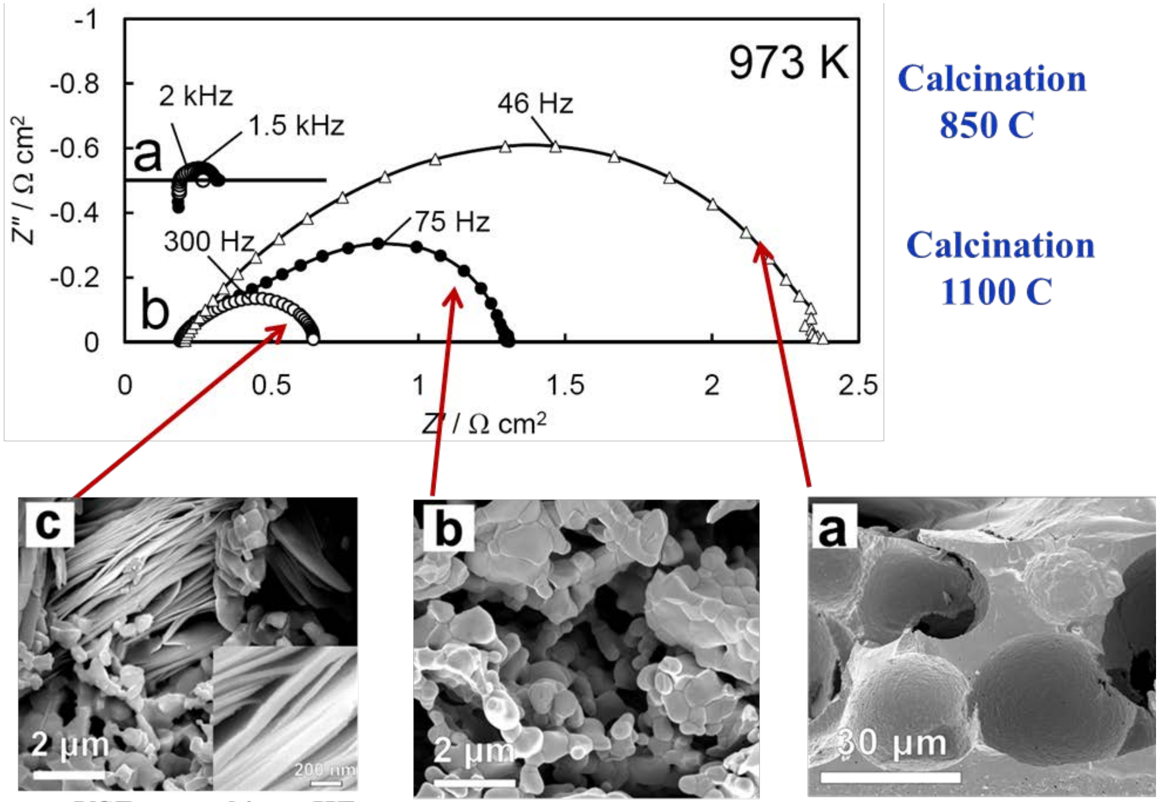
Note: Scaffold structure is not optimized.

Initial indications suggest performance is reasonable:



Performance of LSF-YSZ depends on structure:

1) **YSZ scaffold should have "fine" structure.**
2) **Infiltrated LSF should have high surface area (effect of calcination T).**



YSZ + graphite + HF

S_{BET} = 3 m²/g

YSZ + graphite

S_{BET} = 0.48 m²/g

YSZ + PMMA

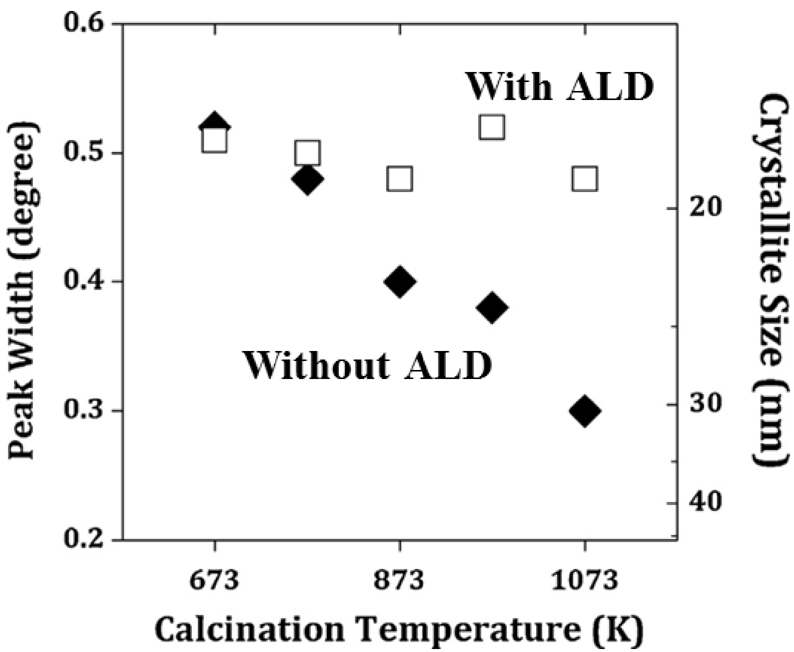
S_{BET} = 0.04 m²/g

J. Am. Ceram. Soc. 94 (2011) 2220.

Use ALD to:

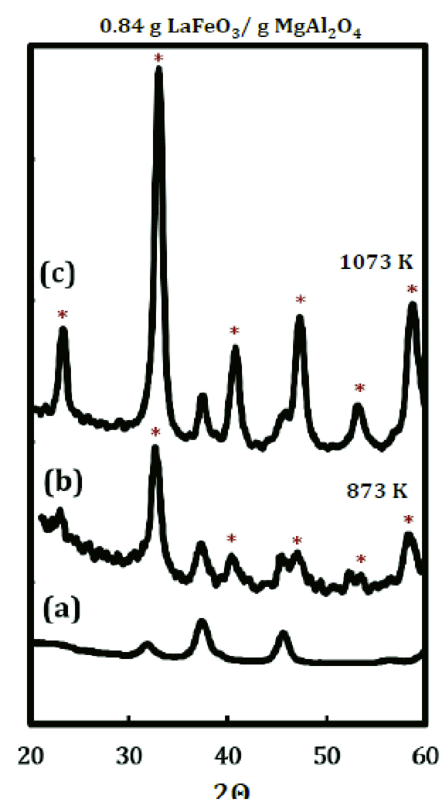
1) Stabilize nanostructure.

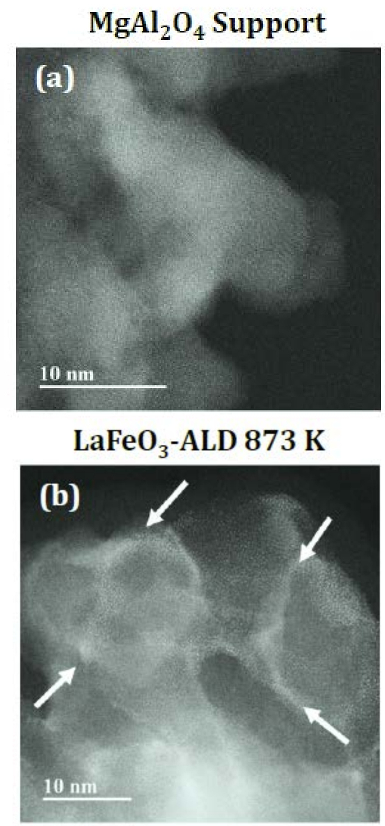
Crystallite size of CeO_2 powder as a function of calcination temperature:
- ◆ without ALD.
- □ after 0.5-nm ZrO_2 on CeO_2.



2) Add "catalyst".

1.5-nm $LaFeO_3$ on $MgAl_2O_4$ (46-wt%)



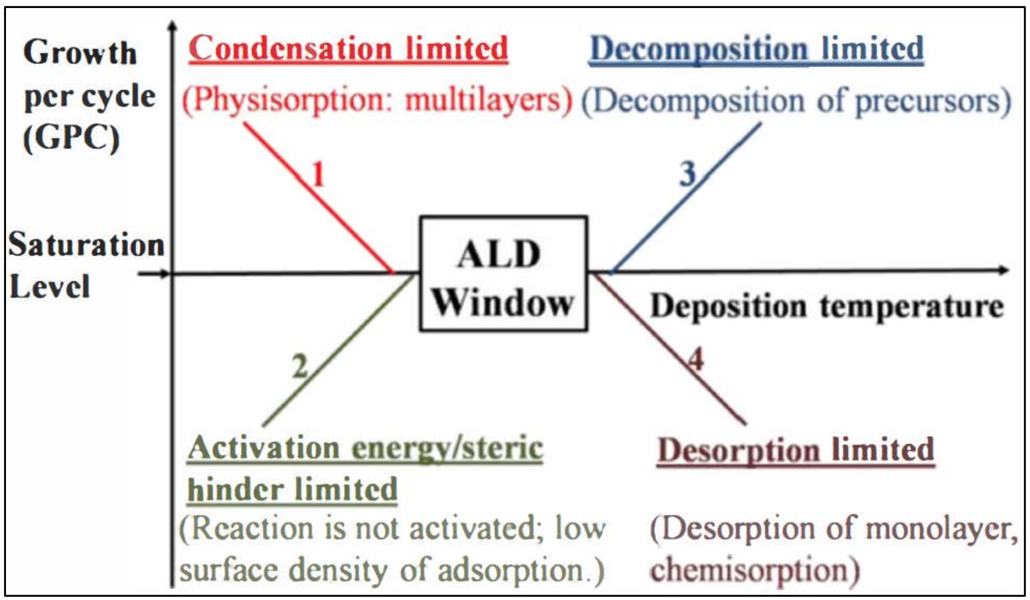


Applied Catalysis B, 197 (2016) 280–285

ALD Modification of Electrodes can be practical:

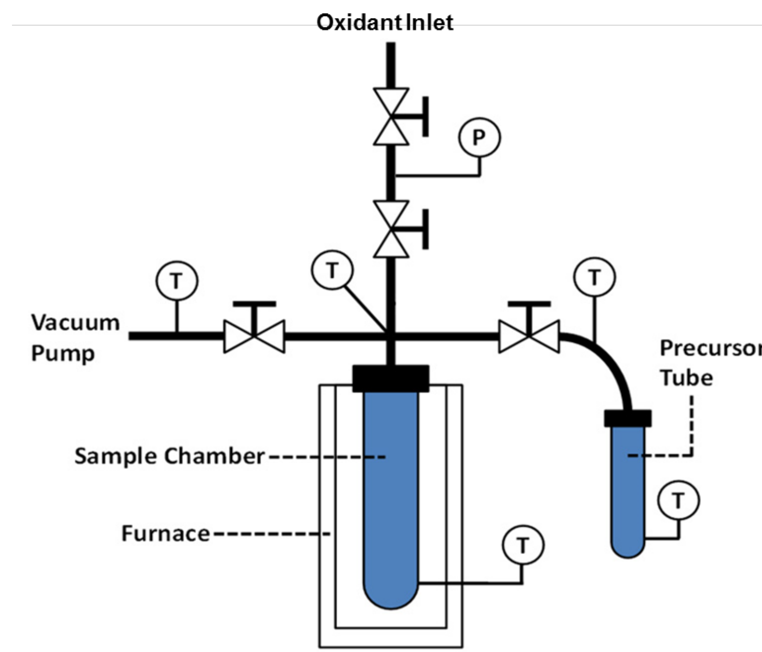
1) Commercial equipment not designed for porous materials.
2) Equipment can be very simple and cheap.

a) Condensation in pores is a problem when there is a carrier gas!
b) Max growth rate < 0.1 nm per cycle.

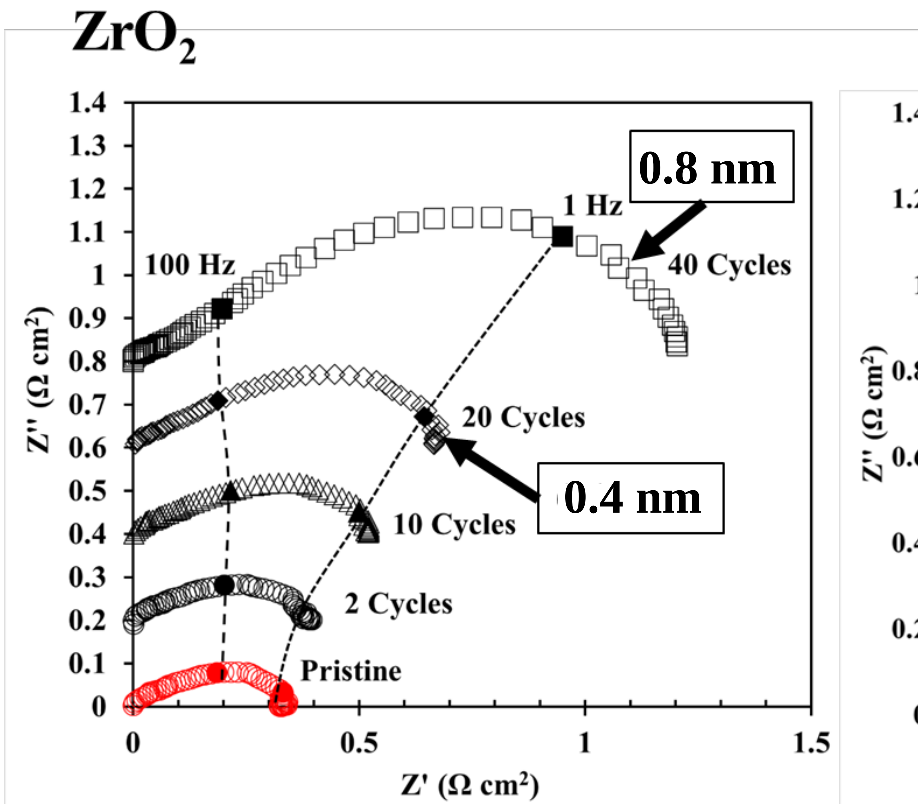


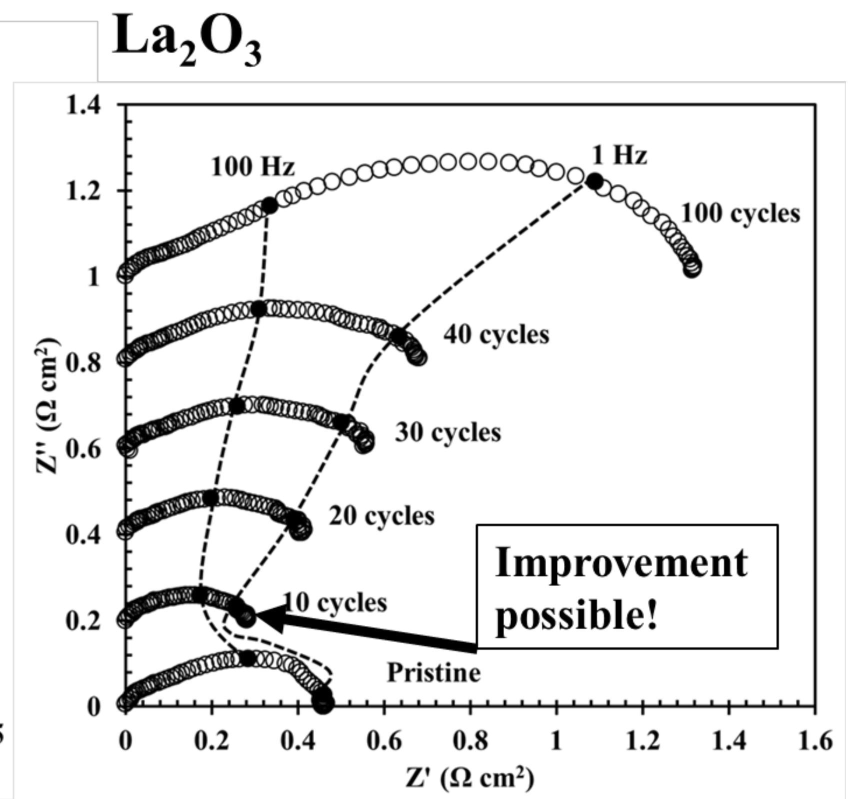
G. Yuan, et al, 2016, 17th Int. Con. Elec. Pack. Techn.

a) Fast pulsing not required! No need for many cycles.
b) Vacuum (millitorr) more effective than carrier gas.
c) Easily applied to large cells.



Effect of ALD on LSF-YSZ cathodes (600 C):





1) ZrO_2 (Fe_2O_3) very effectively blocks surface! 0.8 nm ~ 1.5 unit cell.
2) Small amounts of La_2O_3 promotes performance.
3) Performance maintained w/ thick $LaFeO_3$ films.

J. Electrochem. Soc., **in press** (2017)

Accomplishments

1. **Demonstrated utility of LSF-YSZ composite scaffolds**

    a) Enable single-step infiltration.

    b) Optimize La:Sr ratio to maximize conductivity.

2. **Demonstrated LSF-YSZ scaffolds can be applied to large cells.**
3. **Showed LSCF nano-particle infiltration improves cathode performance and stability (not discussed here).**
4. **Laid framework for modification of cathodes by ALD.**

    Catalytic properties of the film matter!

Acknowledgments:

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Rin Burke