Cost-effective Stabilization of Nanostructured Cathodes by Atomic Layer Deposition (ALD)

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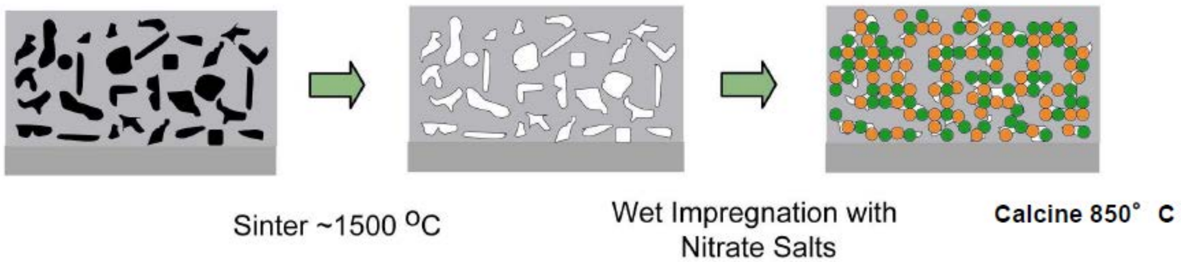
Long Term Goals:

Make Electrode Fabrication by Infiltration Practical.

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:

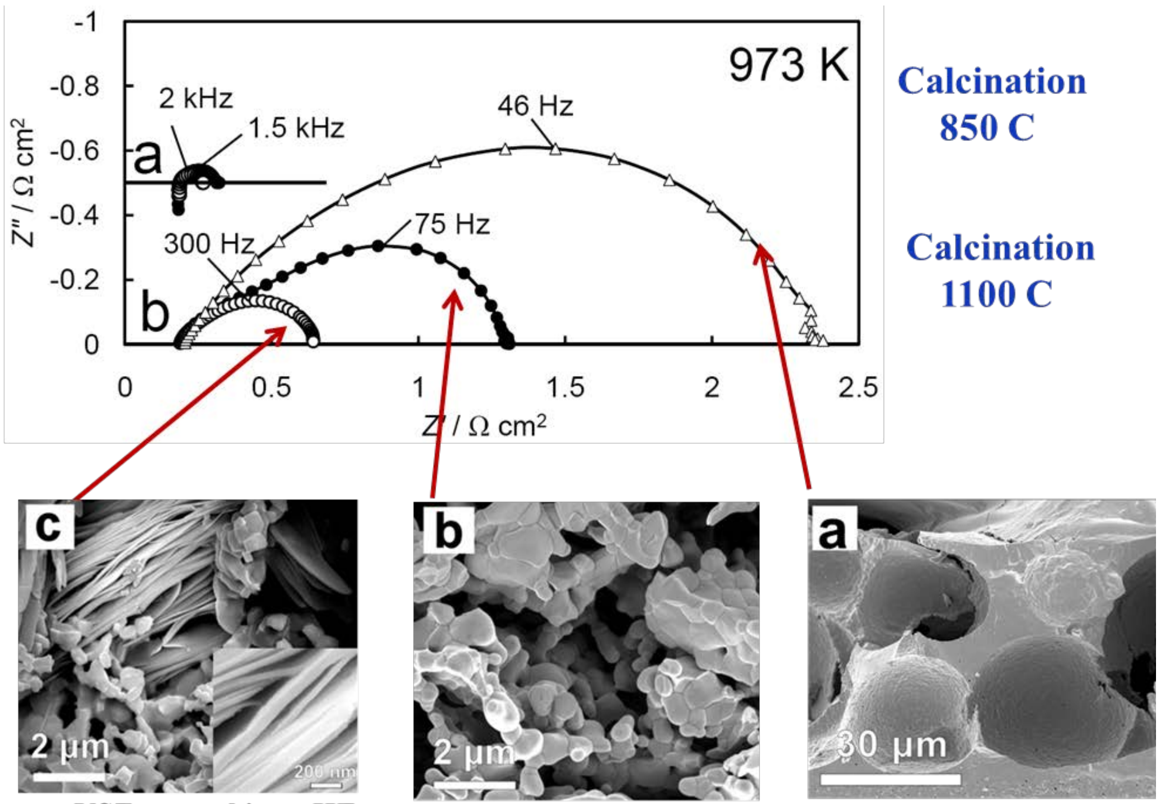
→ Need 35-wt% (20-vol%) perovskite phase for conductivity

→ To get this loading requires many steps.

2) Long-term stability – nanoparticles coarsen.

Performance of LSF-YSZ depends on YSZ structure:

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



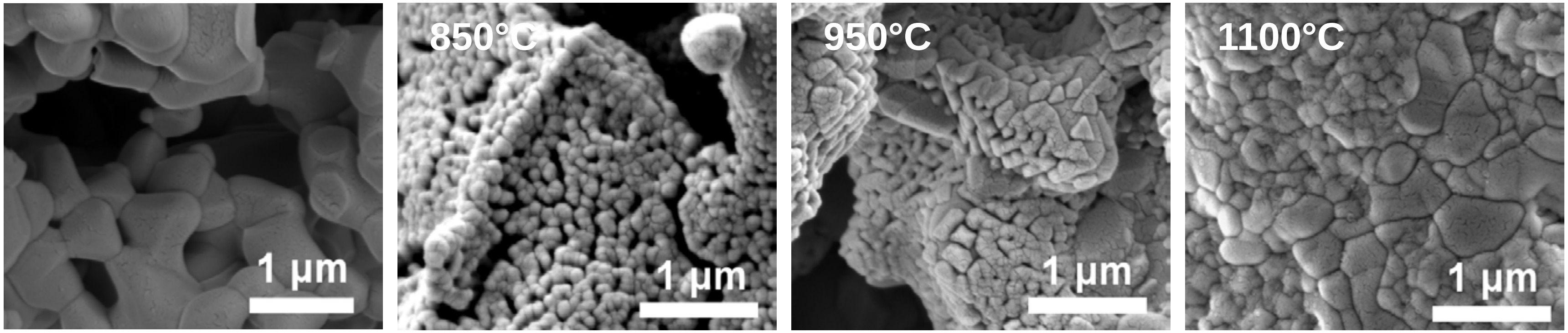
YSZ + graphite + HF	YSZ + graphite	YSZ + PMMA
S_{BET} = 3 m^2/g	S_{BET} = 0.48 m^2/g	S_{BET} = 0.04 m^2/g

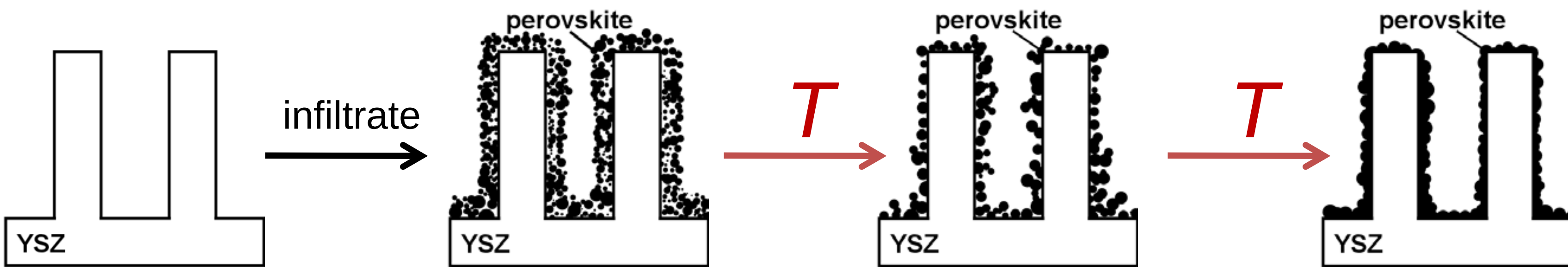
J. Am. Ceram. Soc. 94 (2011) 2220.

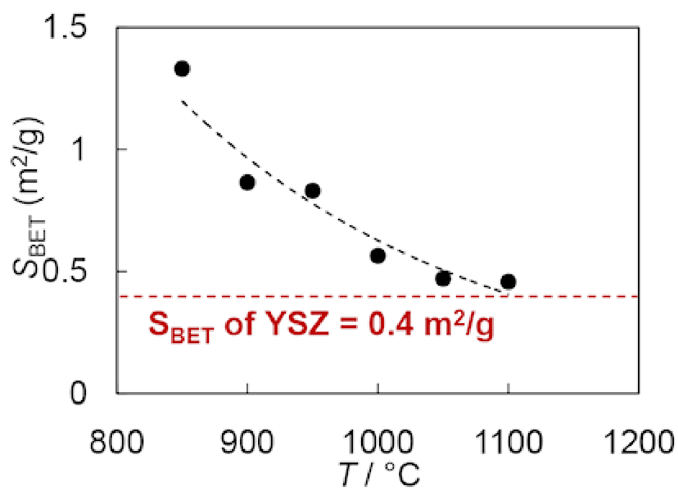
Also Depends on Perovskite (Infiltrant) Structure:

Blank YSZ

YSZ + perovskite ($La_{0.8}Sr_{0.2}CoO_{3-\delta}$)

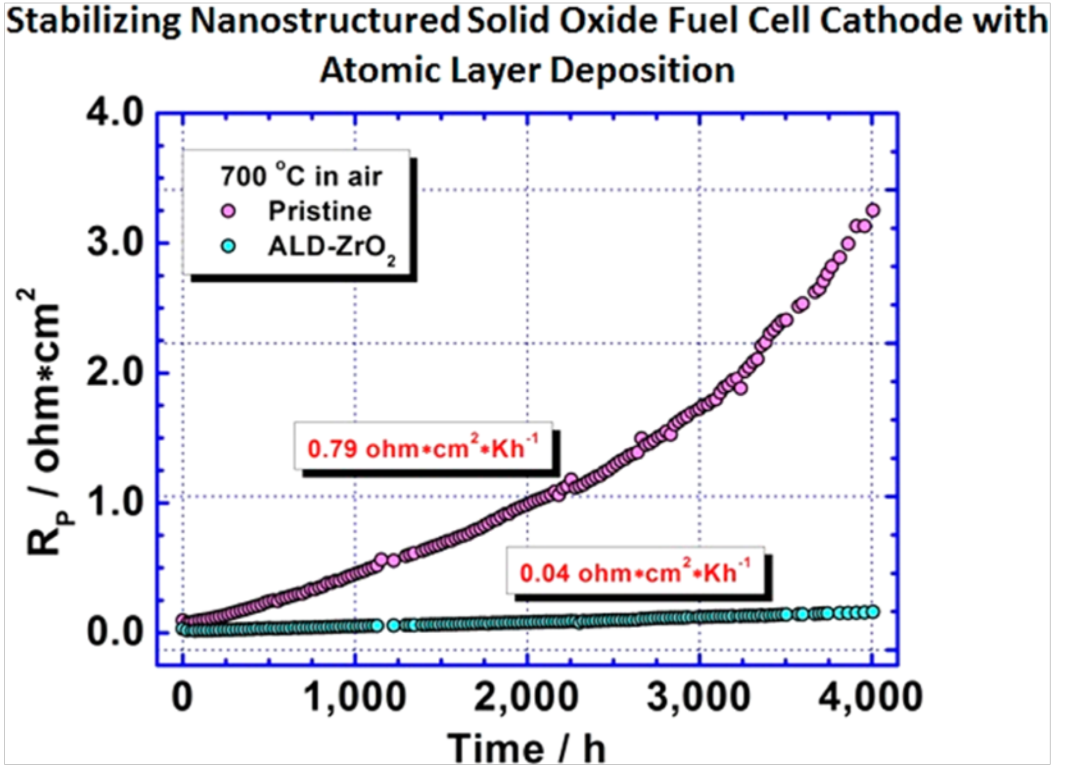






Film formation after 1373 K.
Loss of surface area.

Intriguing Results from South Carolina:



K. Huang and coworkers, Nanoletters, 2013

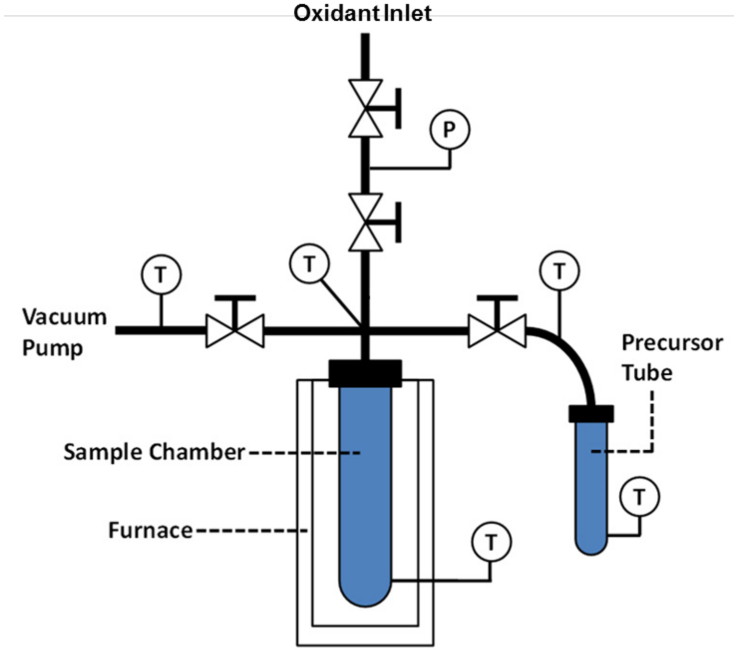
Issues With ALD Modification of Electrodes:

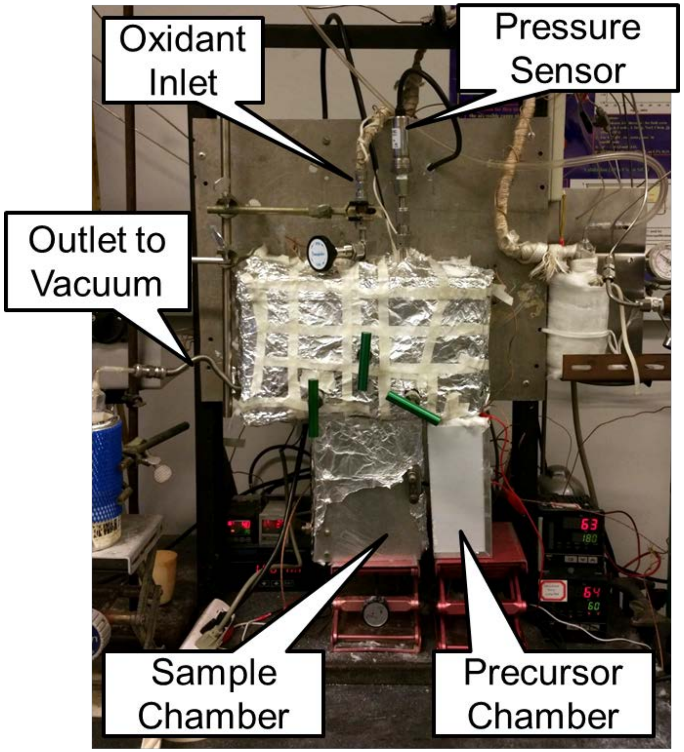
a) The ZrO_2 growth rates in the Huang, et al. work were 0.6 nm/cycle. That is not ALD. Max growth rate in ALD is < 0.1 nm per cycle.
b) ALD equipment is expensive!
c) Cost of precursors with ALD in flow systems is prohibitive.
d) Scale-up to cells and stacks is prohibitive (i.e. There would be no way to deposit onto tubular cells.).

However….:

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

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

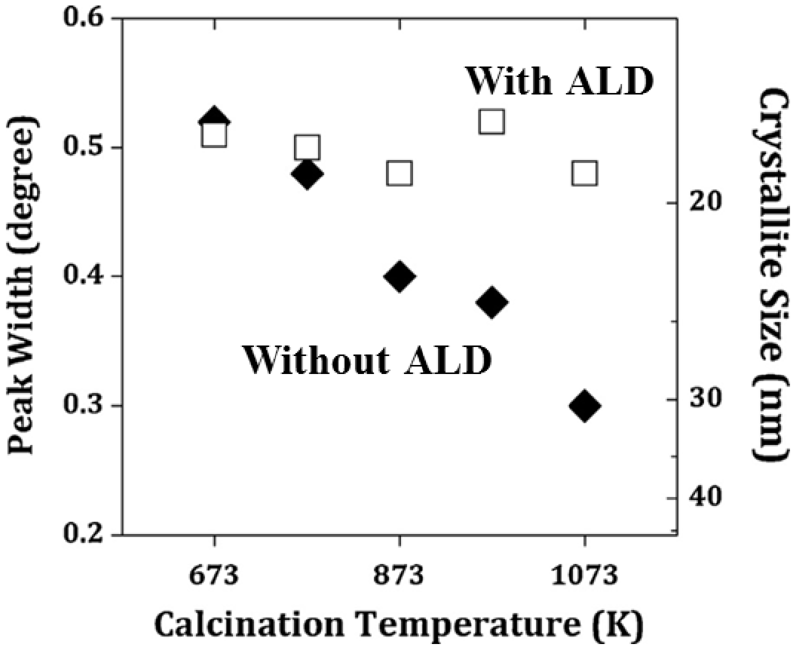




I. ALD can stabilize surface area.

0.5-nm ZrO_2 on CeO_2:

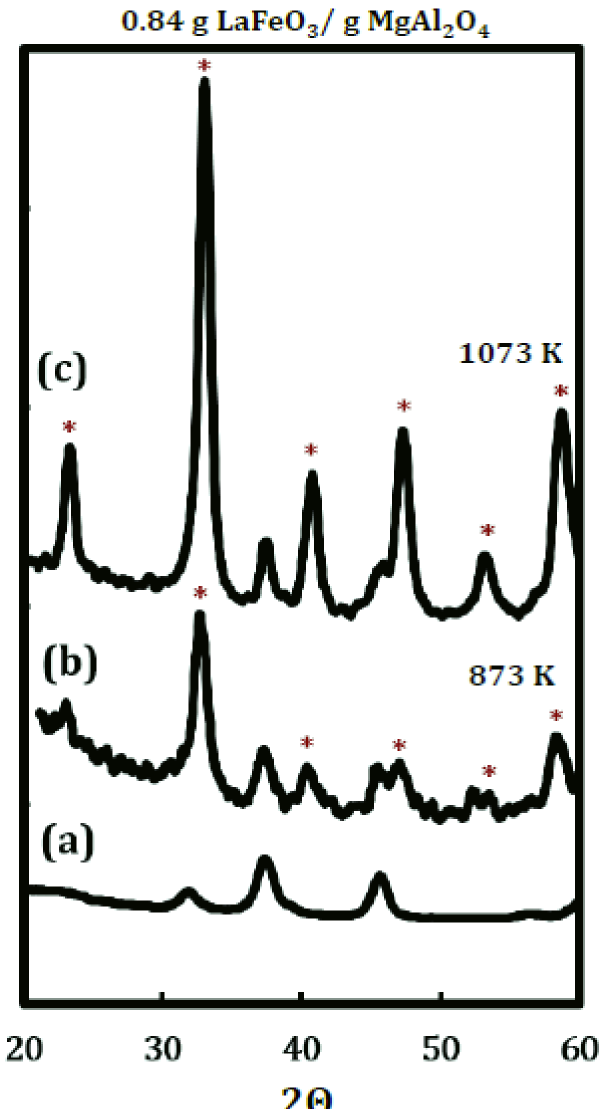
Crystallite size of CeO_2 powder as a function of calcination temperature

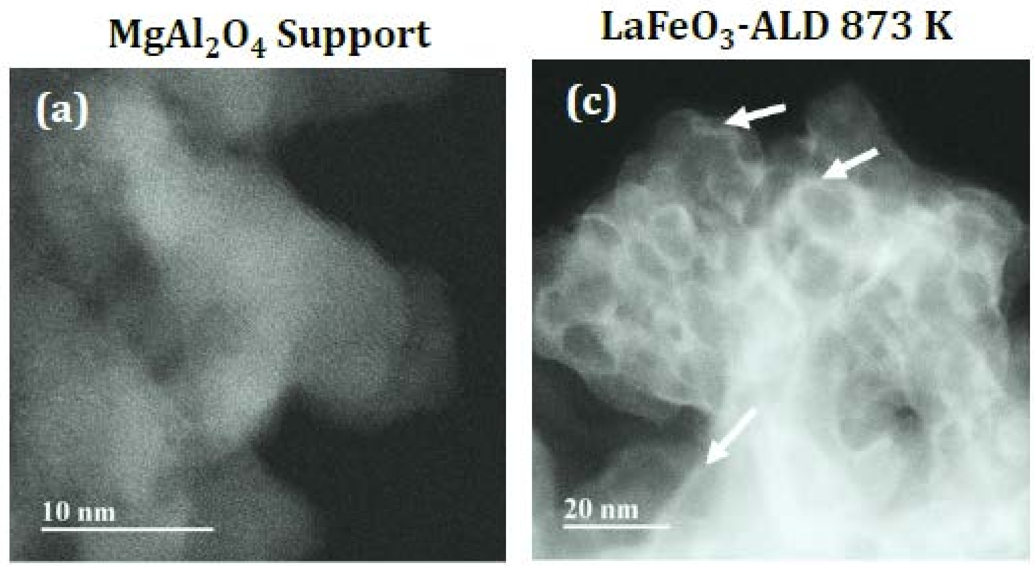


	BET Surface Area (m^2/g)	
Calcination Temp (K)	CeO_2	ALD ZrO_2 on CeO_2
673	51	38
773	42	41
873	36	42
973	30	40
1073	18	39

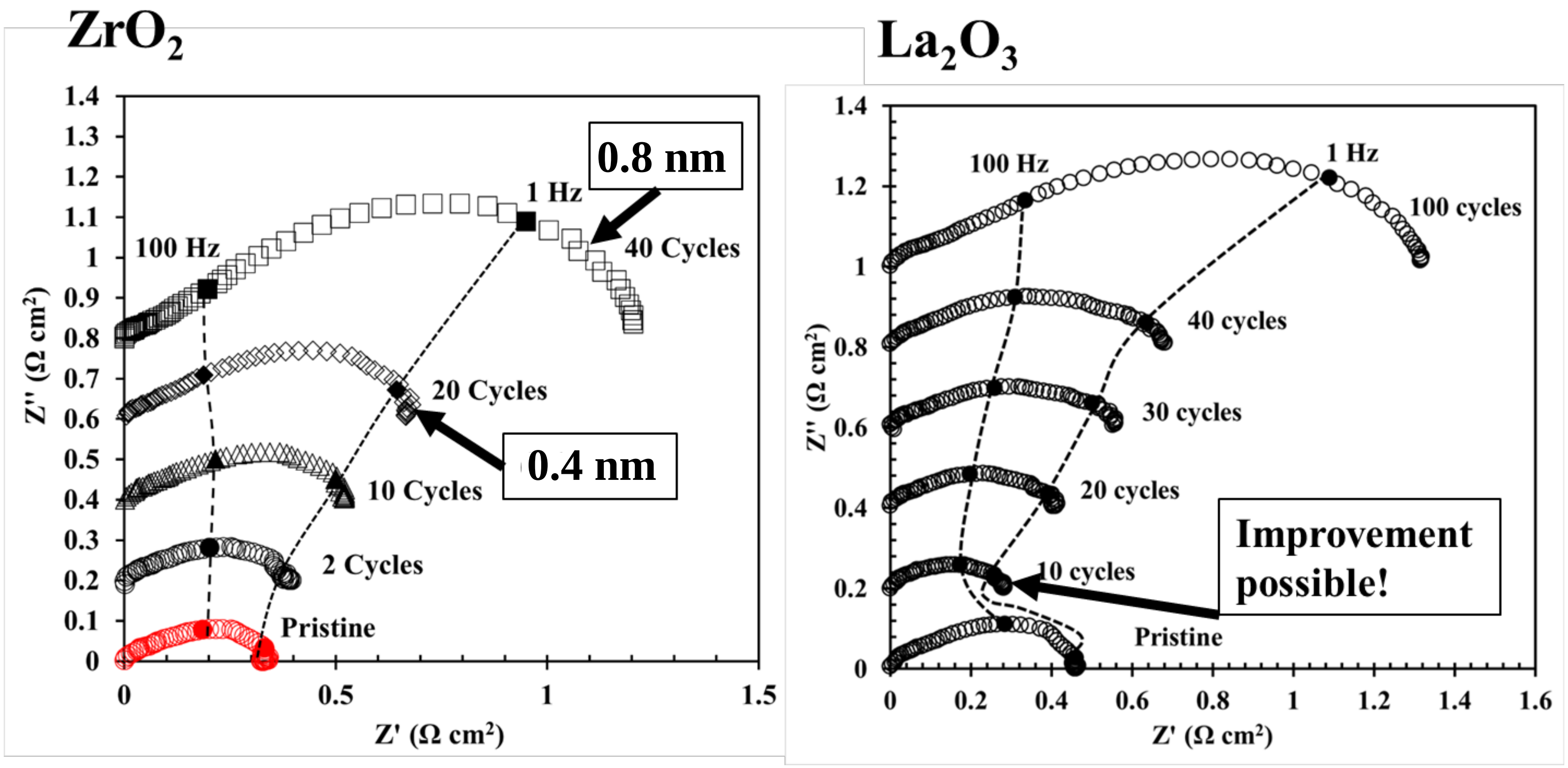
Applied Catalysis B, 197 (2016) 280–285

II. ALD can be used to add catalysts:





Preliminary results for ALD on LSF-YSZ cathodes (600 ^oC):



1) ZrO_2 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., **164**, F879 (2017)

Project Objectives:

- **To determine how SOFC cathode performance is altered via the Atomic Layer Deposition of thin films of oxide promoter.**
- **To determine the best oxide film compositions and thicknesses for optimal cathode performance.**
- **To demonstrate that enhancement of cathode performance through ALD addition of structural and electrochemical promoters can be scaled-up to commercial size cells.**
- **To transfer this capability to a fuel-cell developer for implementation on larger cells and stacks.**

Project Structure:

- **Task 2.1: Set up and cell fabrication.**
  - We need to build a dedicated ALD system capable of handling larger cells.
  - Prepare large batches of button cells with LSCF cathodes to test.
  - Develop ALD protocols (e.g. Oxidation of some precursors at the deposition temperature is difficult.).

- **Task 2.2: Examine the effect of various single component oxides.**
  - Deposit CeO_2, La_2O_3, Fe_2O_3, NiO, and Co_2O_3.
  - Determine effect of oxide thickness on performance.
  - Determine effect of pretreatment (e.g. temperature treatments on performance.

- **Task 2.3: Deposit Mixed Oxides and Perovskites.**
  - Prepare $LaFeO_3$, $LaNiO_3$, $LaCoO_3$ overlayers.
  - Determine effect of pretreatment on performance.

Project Structure (continued):

- **Task 2.4: Deposit Layered Structures.**
  - Prepare cells with 1-nm films of ZrO_2.
  - Deposit $LaFeO_3$, $LaNiO_3$, $LaCoO_3$ overlayers.
  - Determine the effect on performance.

- **Task 2.5: Characterization of ALD films.**
  - BET
  - XRD
  - SEM.

- **Task 3: ALD on Atrex Cells.**
  - Demonstrate ALD onto Atrex Cells.
  - Modify Atrex Cells using the most promising ALD formulations.

Project Timeline:

Task	Task Description	1	2	3	4	5	6	7	8
1	Task 1.0: Project management Task 1.1 Communicating with Atrex Task 1.2 Communicating with NETL project managers Task 1.3 Technical reports, conference presentations, journal articles, patents								
2	Task 2.0: ALD modification of button cells Task 2.1 Set up and cell fabrication Task 2.2 Single component oxides Task 2.3 Mixed oxides and perovksites Task 2.4 Layered structures Task 2.5 Characterization of ALD films								
3	Task 3.0: ALD modification of Atrex cells Task 3.1 Modification of ALD setup Task 3.2 ALD on cells supplied by Atrex Task 3.3 Cell testing at Atrex Task 3.4 Reporting								
	Progress Milestone								

Project Management:

- The experimental work at Penn will be carried out by students, under the direction of Profs Gorte and Vohs.
- Gorte will be primarily responsible for report writing and communicating with NETL and with Atrex.
- Dr. Cheekatamarla will direct efforts at Atrex Energy.

Risk Management:

- Performance may not be enhanced by ALD of anything

  We already have evidence that this is not true.
- ALD Films may not be stable at SOFC operating temperatures.
- ALD Films may not improve performance of Atrex cells.

Project Budget:

Penn: Total $375,000.

Senior personnel (salary):	12,992.00
Graduate Student salary (2):	127,000.00
Travel:	2,000.00
Materials and Supplies	3,982.00
Subcontract (to Atrex)	28,254.00
Tuition:	93,088.00
Indirect Costs:	103,684.00