Modification of SOFC Anodes and Cathodes by ALD

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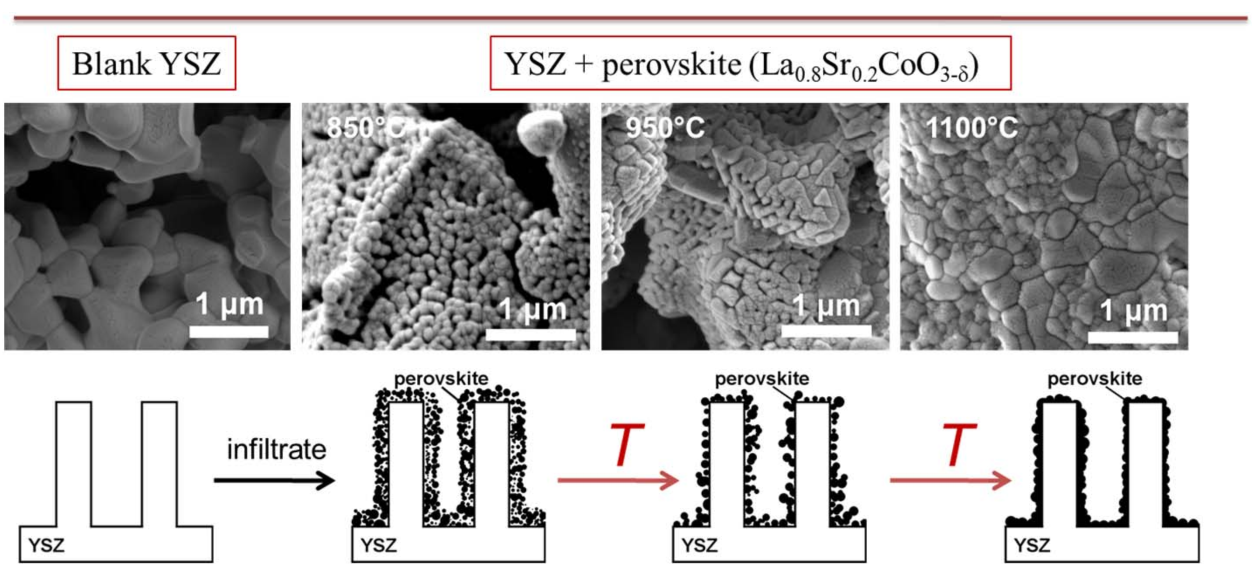
Cathode Issues:

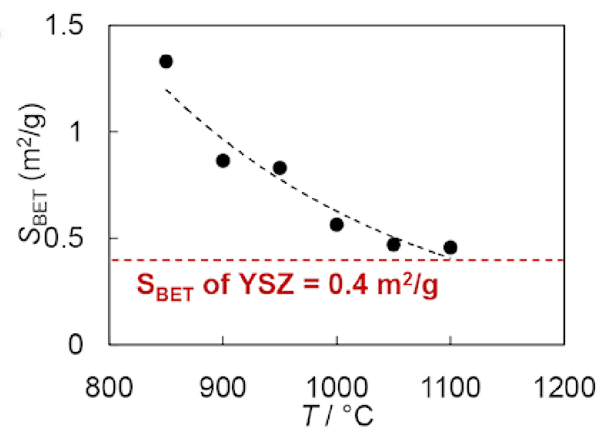
1) Performance and stability depends on surface composition

a) “Surface Catalysts”?

b) SrO segregation?

2) Also by surface structure.





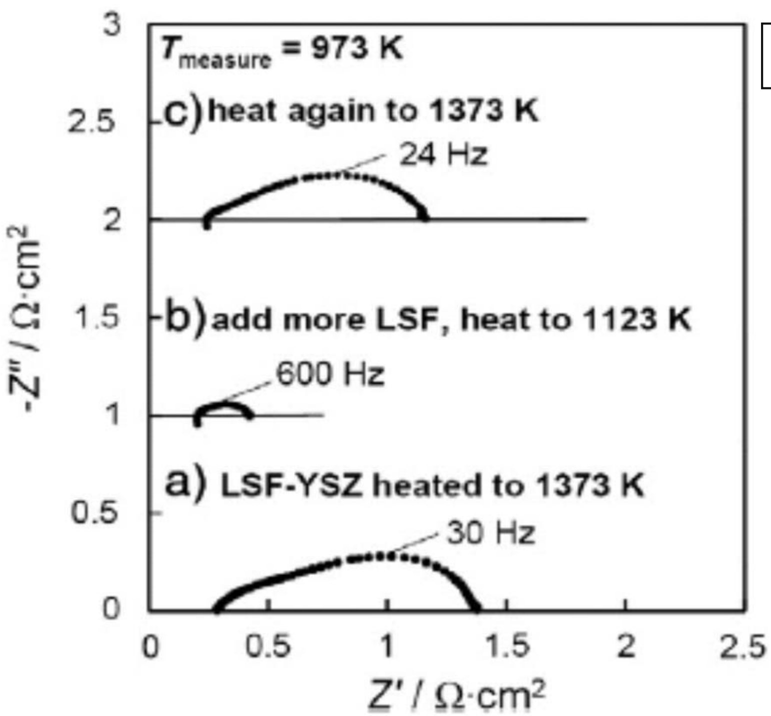
SSI, 225 (2012) 146-150

Infiltration changes composition and structure:

1) LSM, LSF Performance enhanced by infiltration of:
YSZ, Pd, SDC, CaO, and K_2O

J. Power Sources, 195 (2010) 720

2) Performance affected by surface structure.



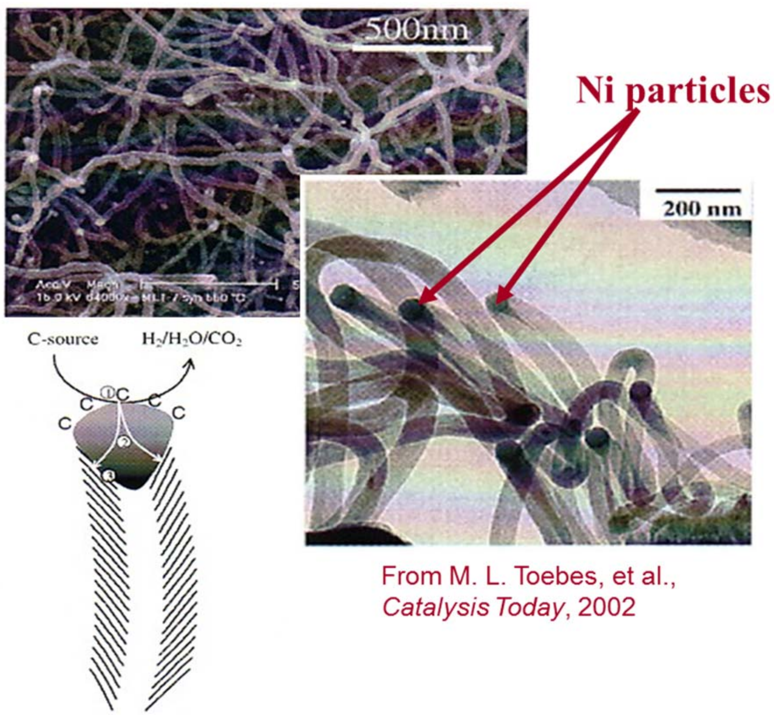
SSI, 225 (2012) 146-150

1) What then is the effect of surface composition separate from structure?
2) Can we optimize composition?

Anode Issues:

1) Hydrocarbon tolerance

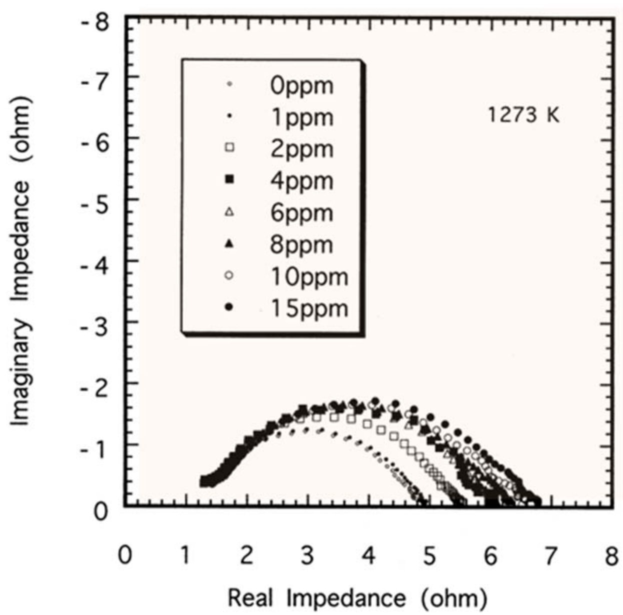
Ni exposed to 20% CO,7% H_2 at 550°C.



From M. L. Toebes, et al., *Catalysis Today*, 2002

2) Sulfur tolerance

Ni-YSZ Anode – 1273 K
H_2 + x ppm H_2S



From Matsuzaki and Yasuda, *Solid State Ionics*, 132 (2000) 261.

Program Goals and Approaches:

Goals

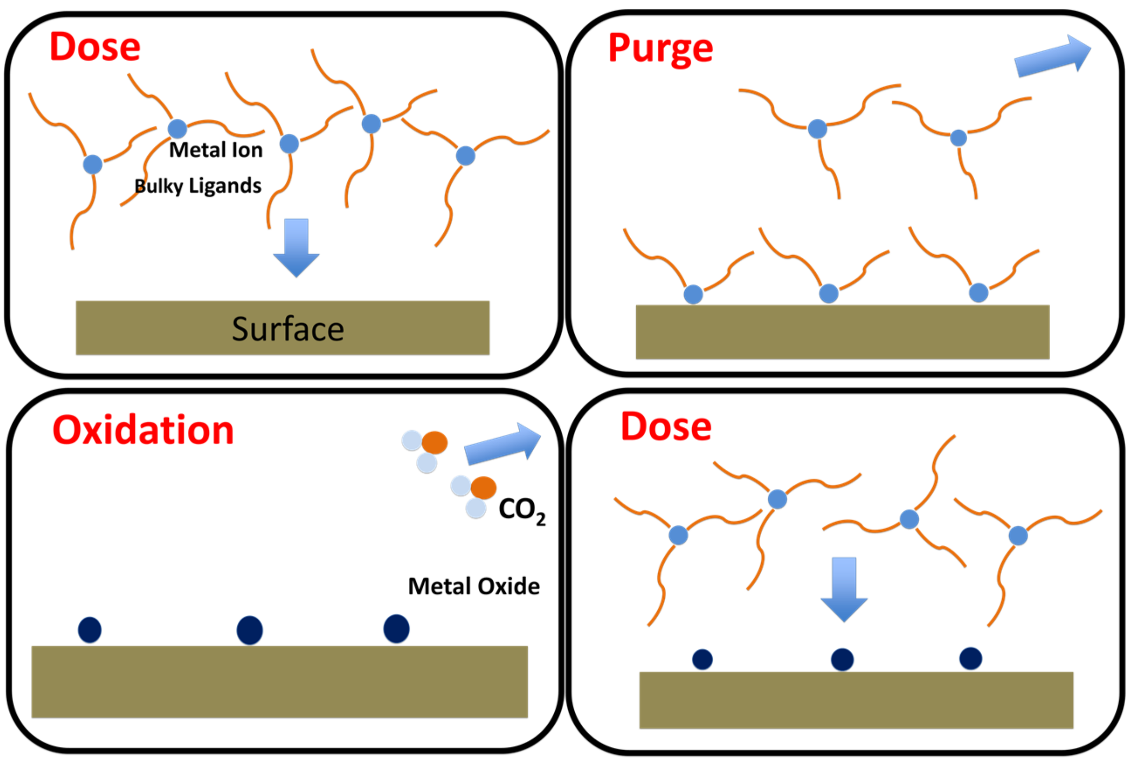
- “Engineer” the surface composition of both electrodes.
- Determine the effect of oxide coatings on electrode performance.
- Transfer the most promising technologies to Atrex and test on commercial scale cells.

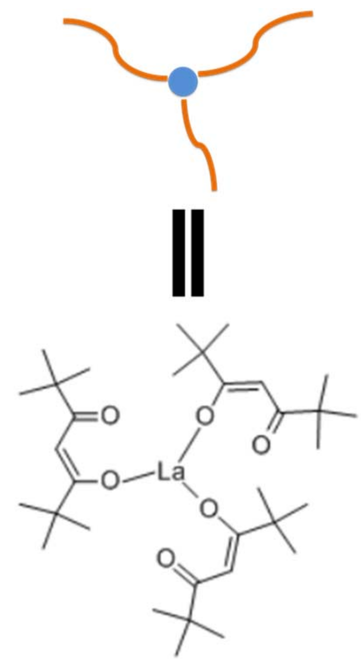
Technical Approach

- Use atomic layer deposition (ALD) to selectively deposit oxide thin films onto both cathodes and anodes.
- Determine the effect of films on electrode performance.

Atomic Layer Deposition (ALD)

- Allows layer-by-layer control
- Can deposit mixed oxides, including perovsites
- Only surface composition is modified.





$La(TMHD)_3$ Precursor

Note:

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

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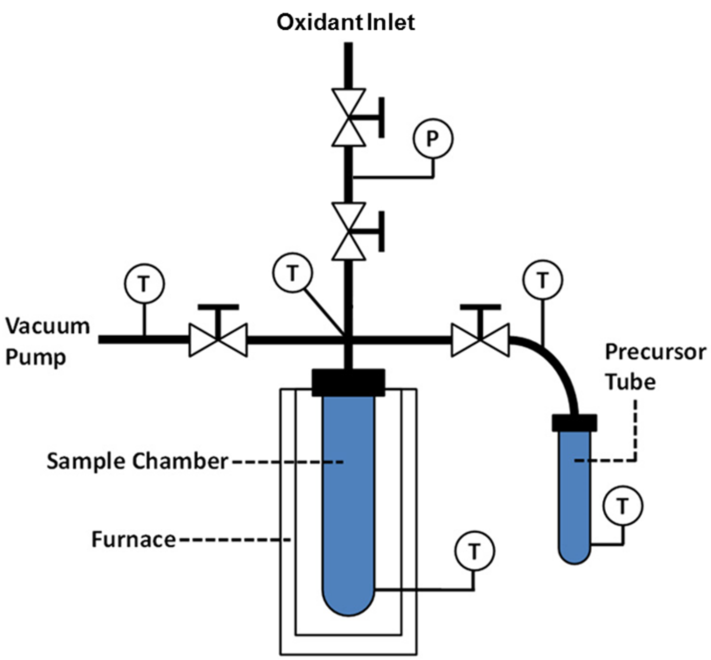
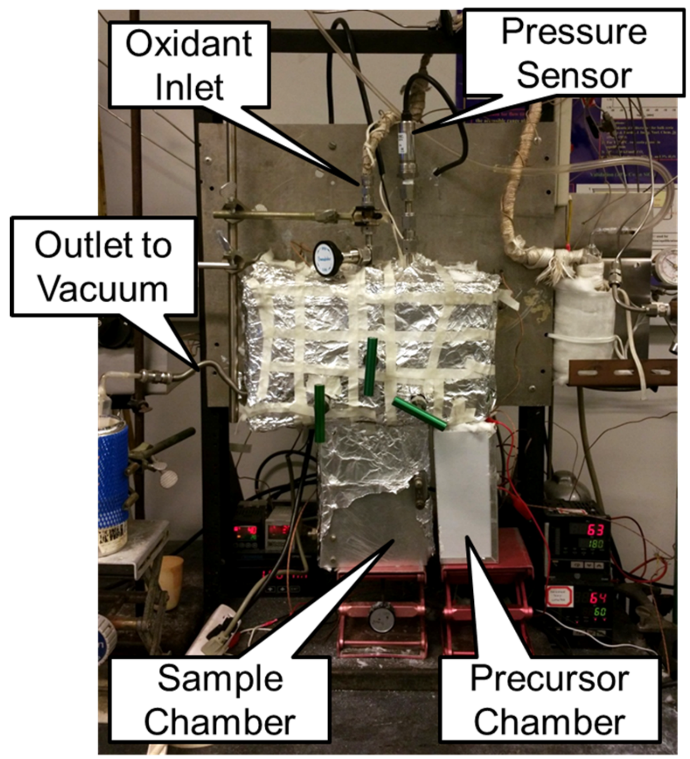
a) **Fast pulsing not required! No need for many cycles.**
b) **Vacuum (millitorr) more effective than carrier gas.**
c) **Easily applied to large cells.**





Growth rates:

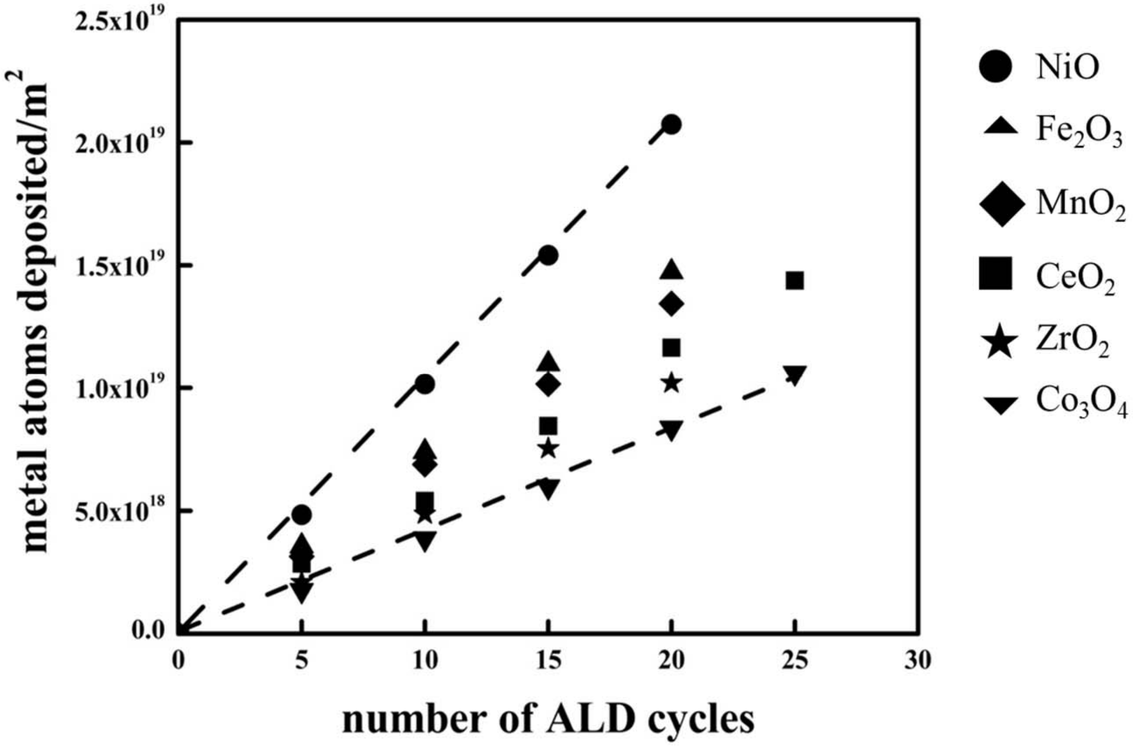
1) Can be measured gravimetrically

1-nm of CeO_2 on 10 m^2/g support is ~7-wt%

2) Similar for different oxides:

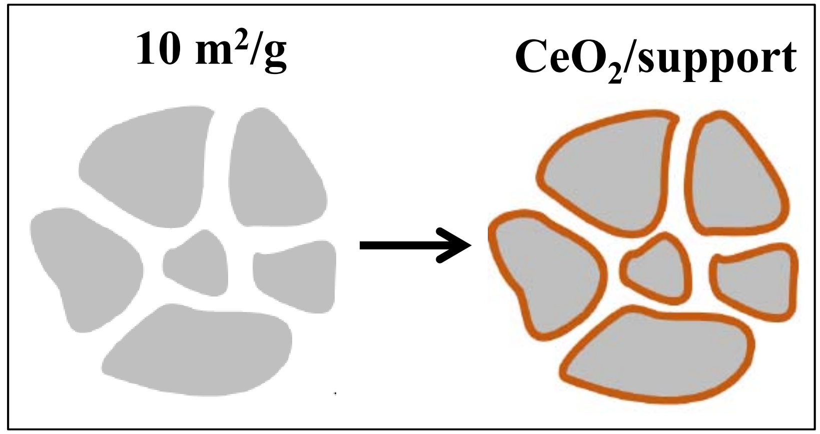
~$1x10^{18}$ metal atoms/m^2-cycle ~ 0.02-nm/cycle

3) 10 ALD cycles ~ 1 monolayer.



Considerations for Electrode Applications:

Coat support with 1-nm CeO_2:



<u>Basis: 10 m^2/g support</u>

1 nm = 10^{-7} cm

10^{-7} cm * 10 m^2/g * 10^4 cm^2/m^2 = 0.01 cm^3 CeO_2/g

0.01 cm^3 CeO_2/g Al_2O_3 * 7.22 g/cm^3 = 0.072 g CeO_2/g

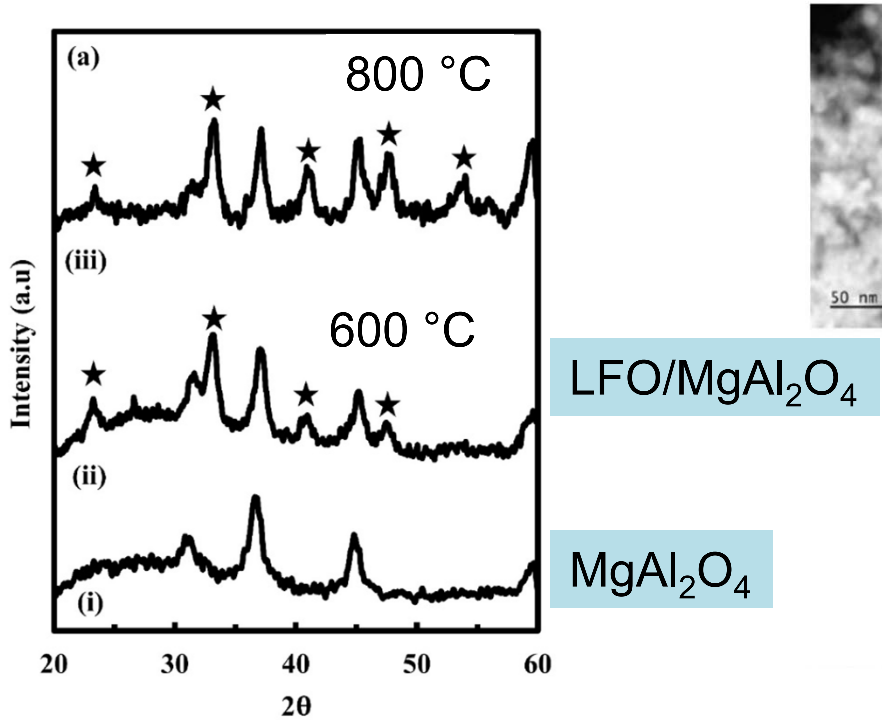
= 7-wt% CeO_2

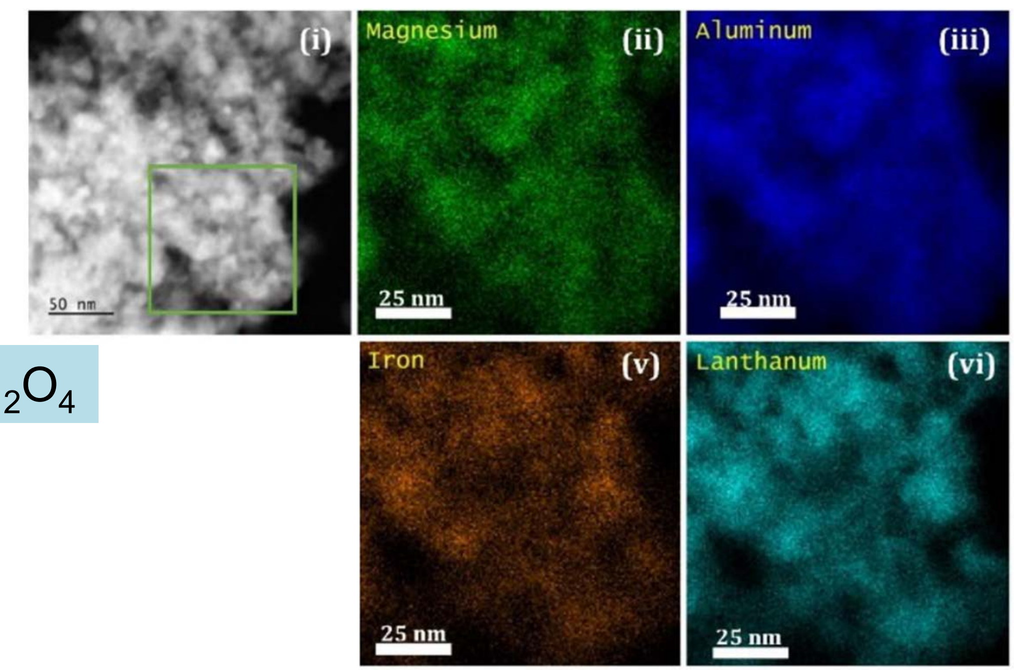
If you had a 10-nm film, it would be 42-wt% CeO_2!

Why ALD and not simple infiltration?

1) ALD forms uniform films (not particles).
2) ALD does not change the surface area.
3) ALD allows formation of perovskite thin.

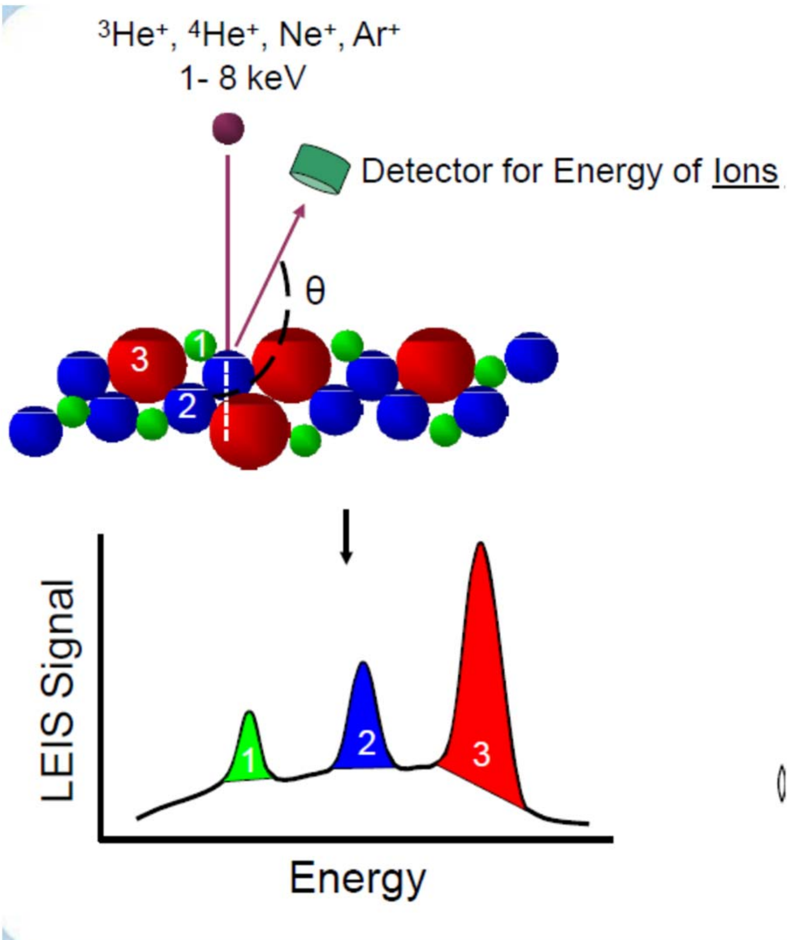
STEM, XRD of 0.5-nm, ALD film of $LaFeO_3$ on $MgAl_2O_4$





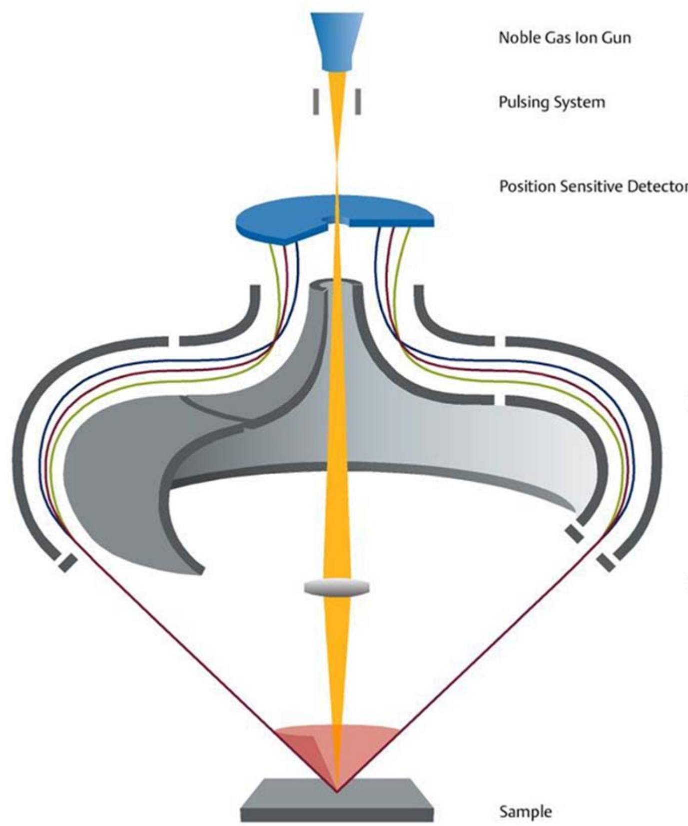
High Sensitivity-Low Energy Ion Scattering:

LEIS



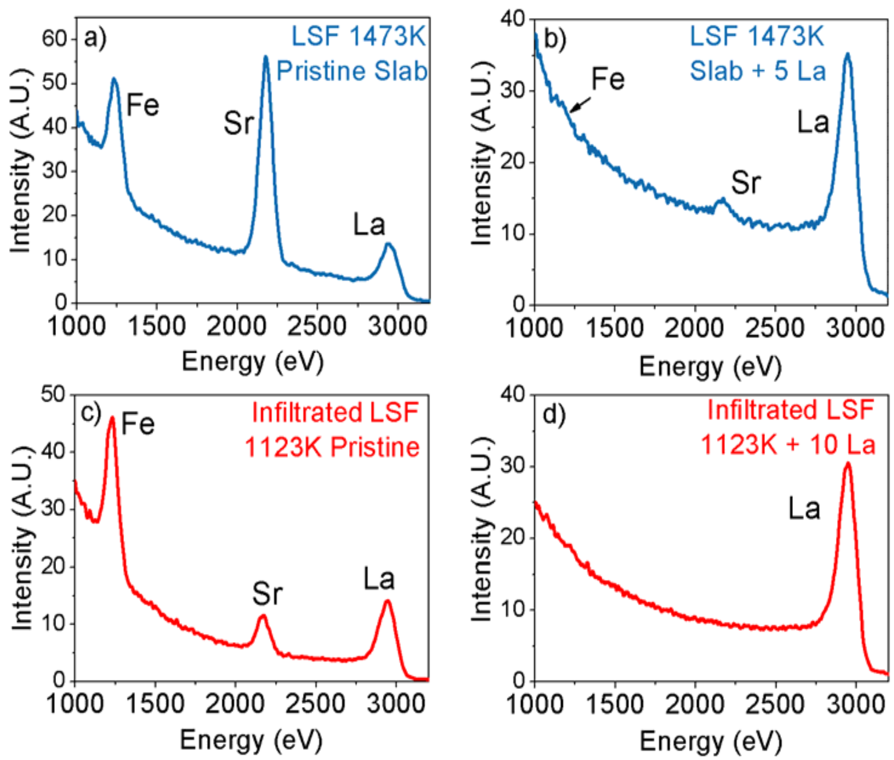
HS-LEIS

- Large acceptance angle (360^o)
- Parallel Energy Detection

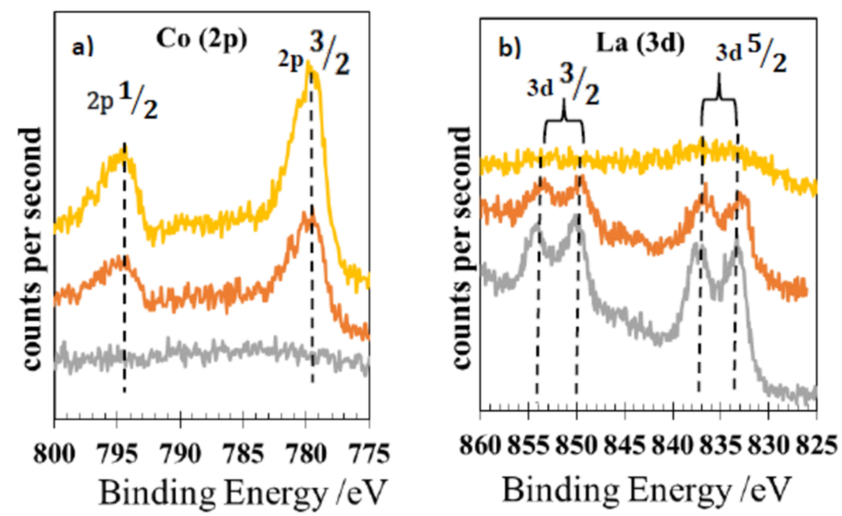


Confirmation of Growth Rates:

LEIS



XPS

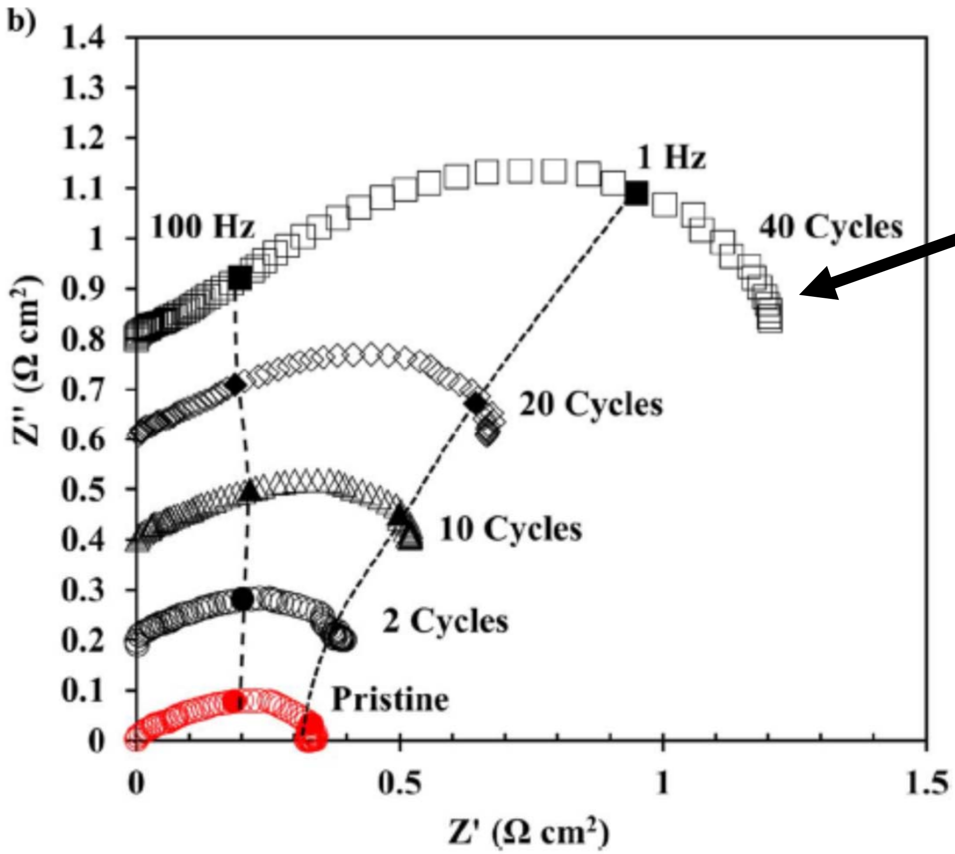


LSF cathode with:

- **0 cycles of Co**
- **10 cycles of Co**
- **40 cycles of Co**

The Effect of ZrO_2 ALD films on LSF cathodes:

650 °C

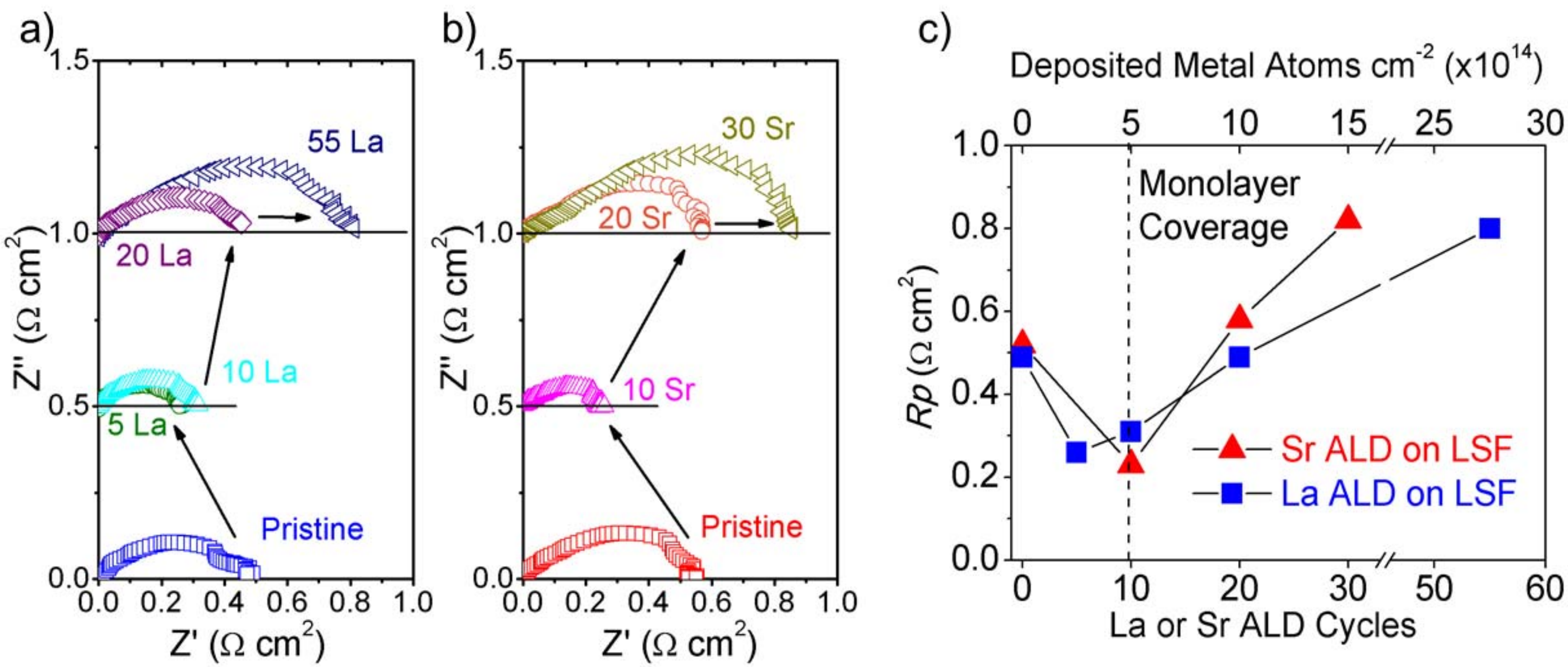


1-nm film!

Uniform ZrO_2 film effectively blocks adsorption sites

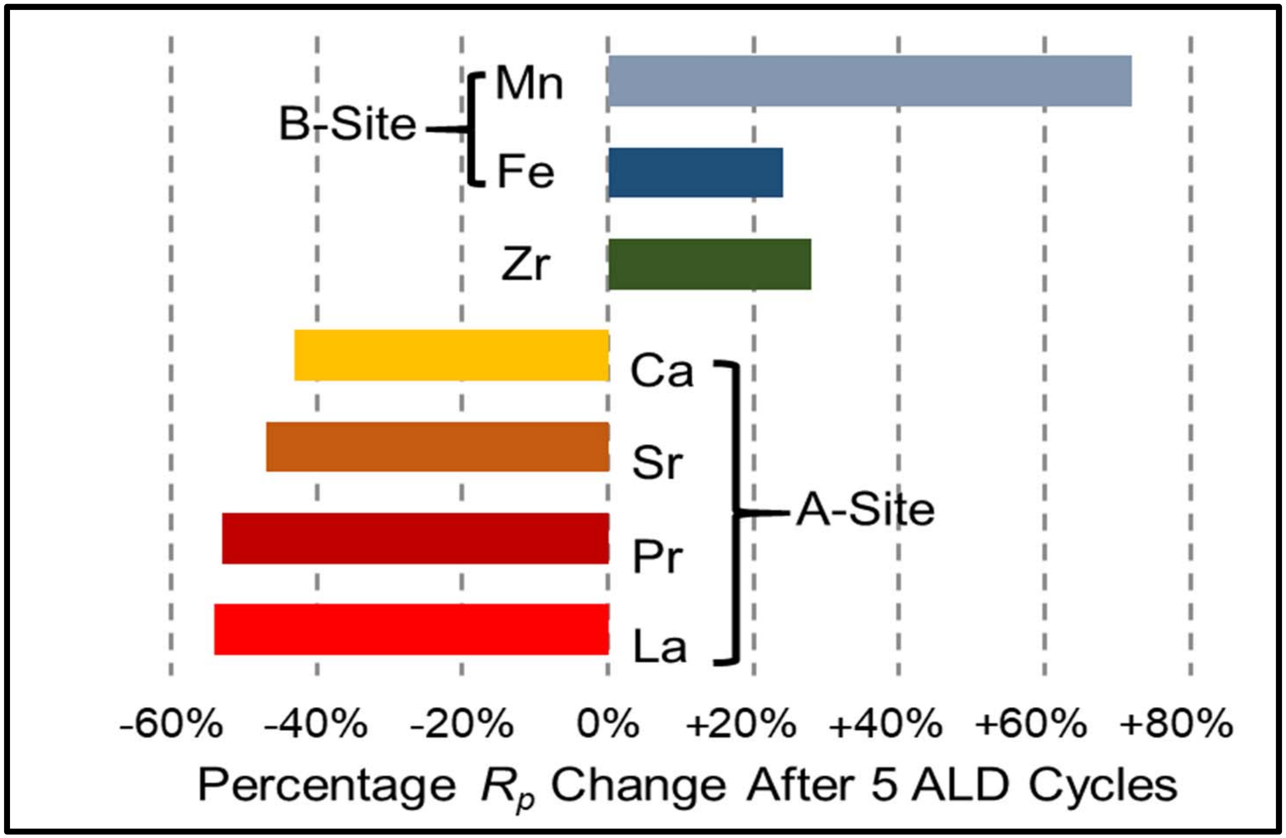
ALD Films of some oxides *promote* performance:

LSF-YSZ, symmetric cells, 650 °C.



Submonolayer coverages of La or Sr significantly enhances cathode performance

LSF Cathodes – ALD Modification with A- And B-site Cations

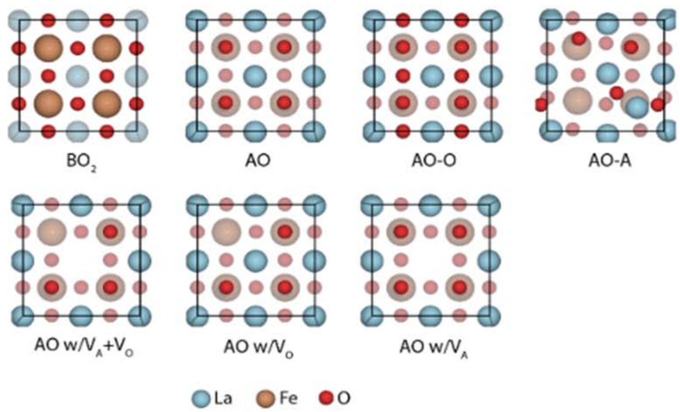


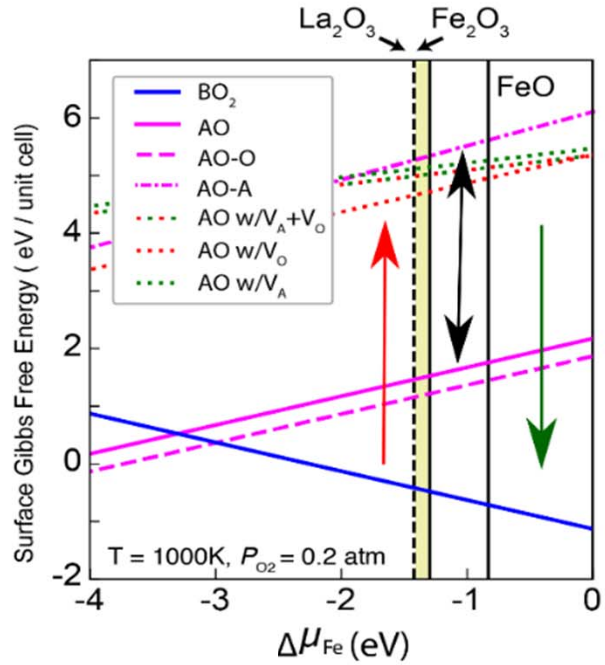
0.5 monolayer
650 °C

A-site addition – enhances performance
B-Site addition – poisons performance

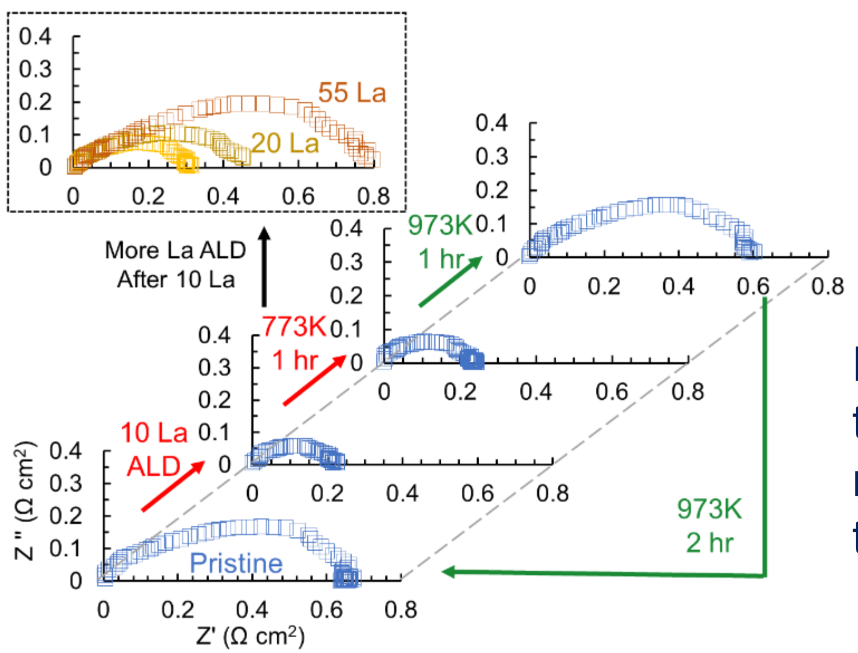
Penn
University of Pennsylvania

LSF Cathodes – ALD Modification with A- And B-site Cations





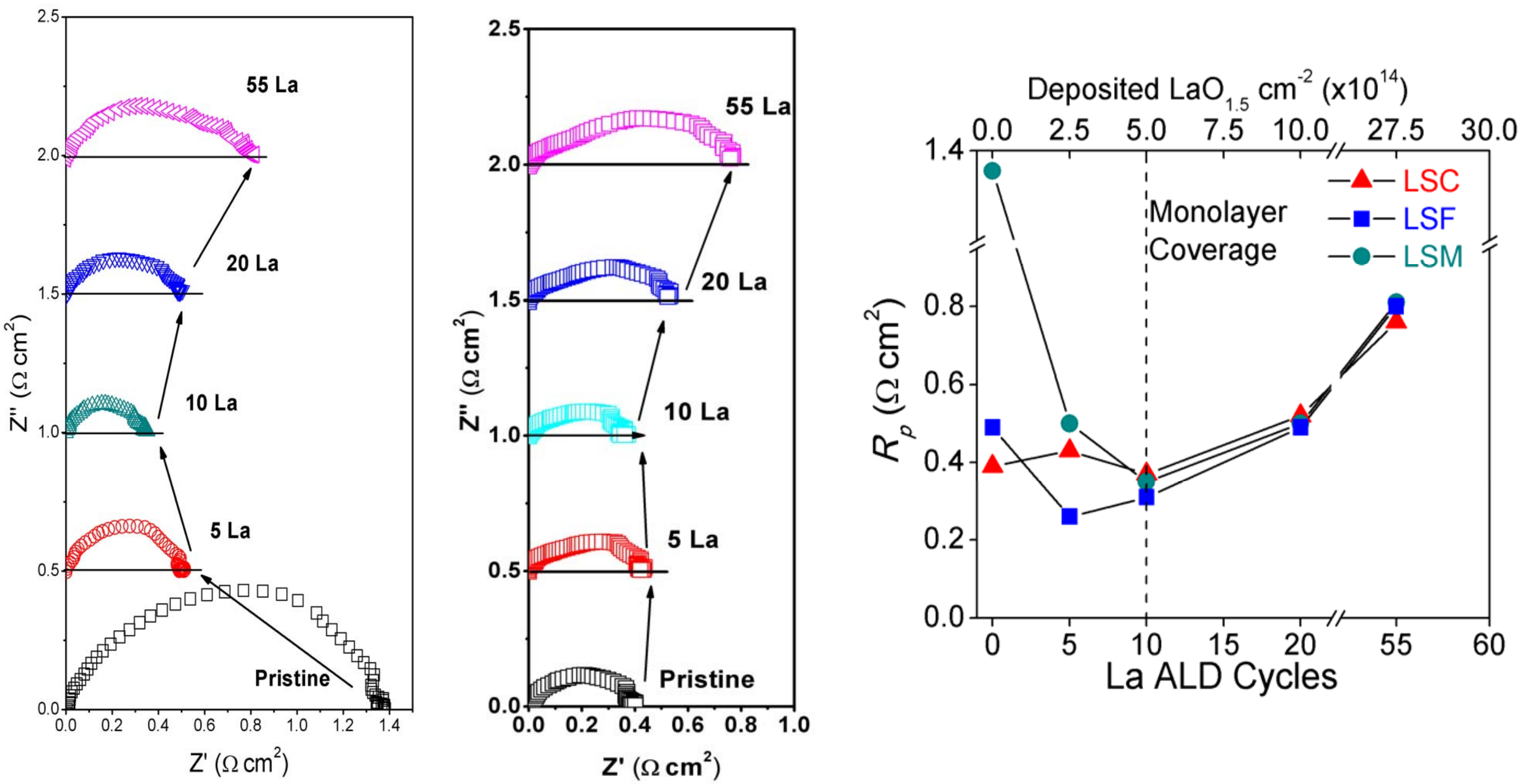
Thermodynamic stability of different surface structures



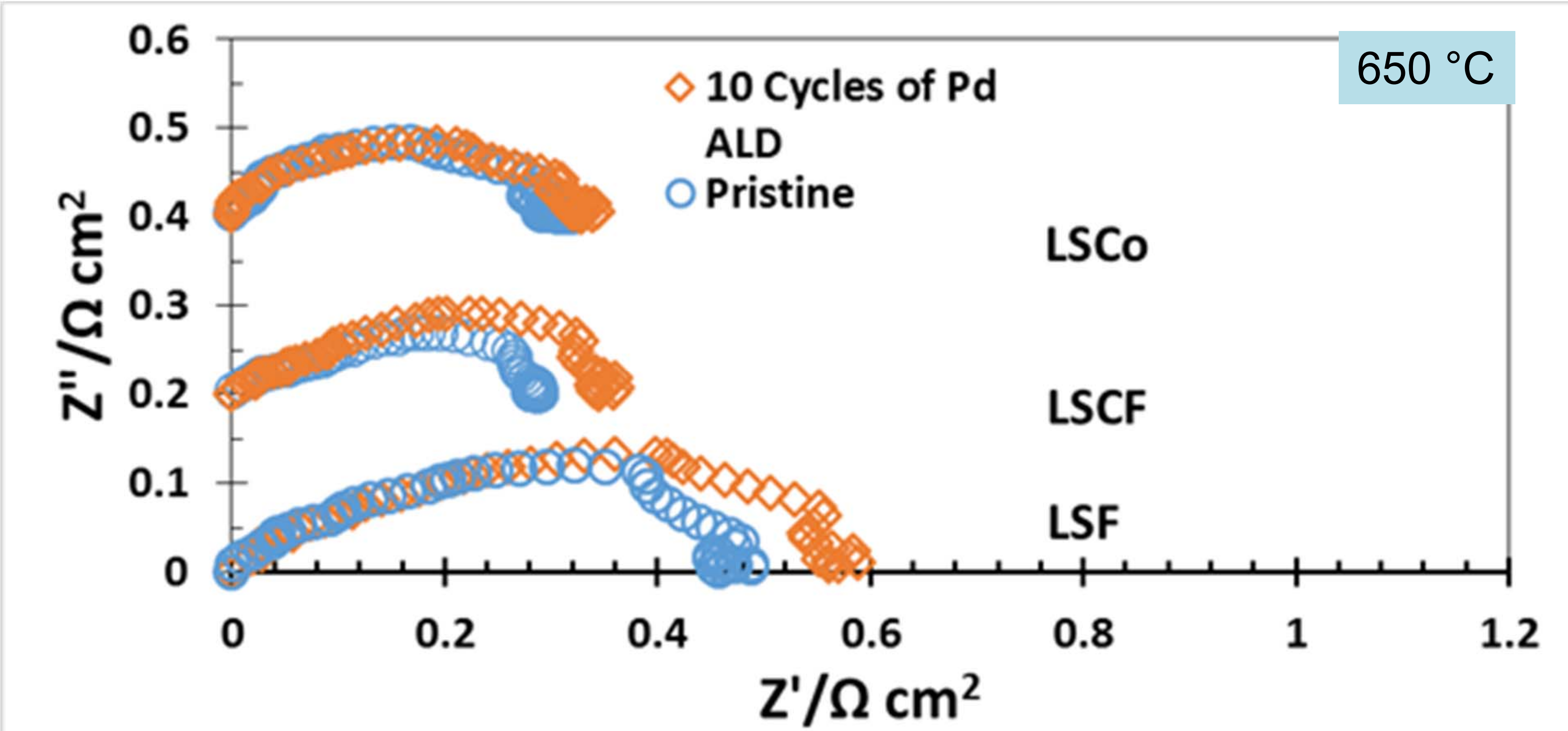
Highly active surfaces are not thermodynamically stable but may be metastable at intermediate temperatures

LSM also promoted by A-site cations; LSCo is not.

650 °C

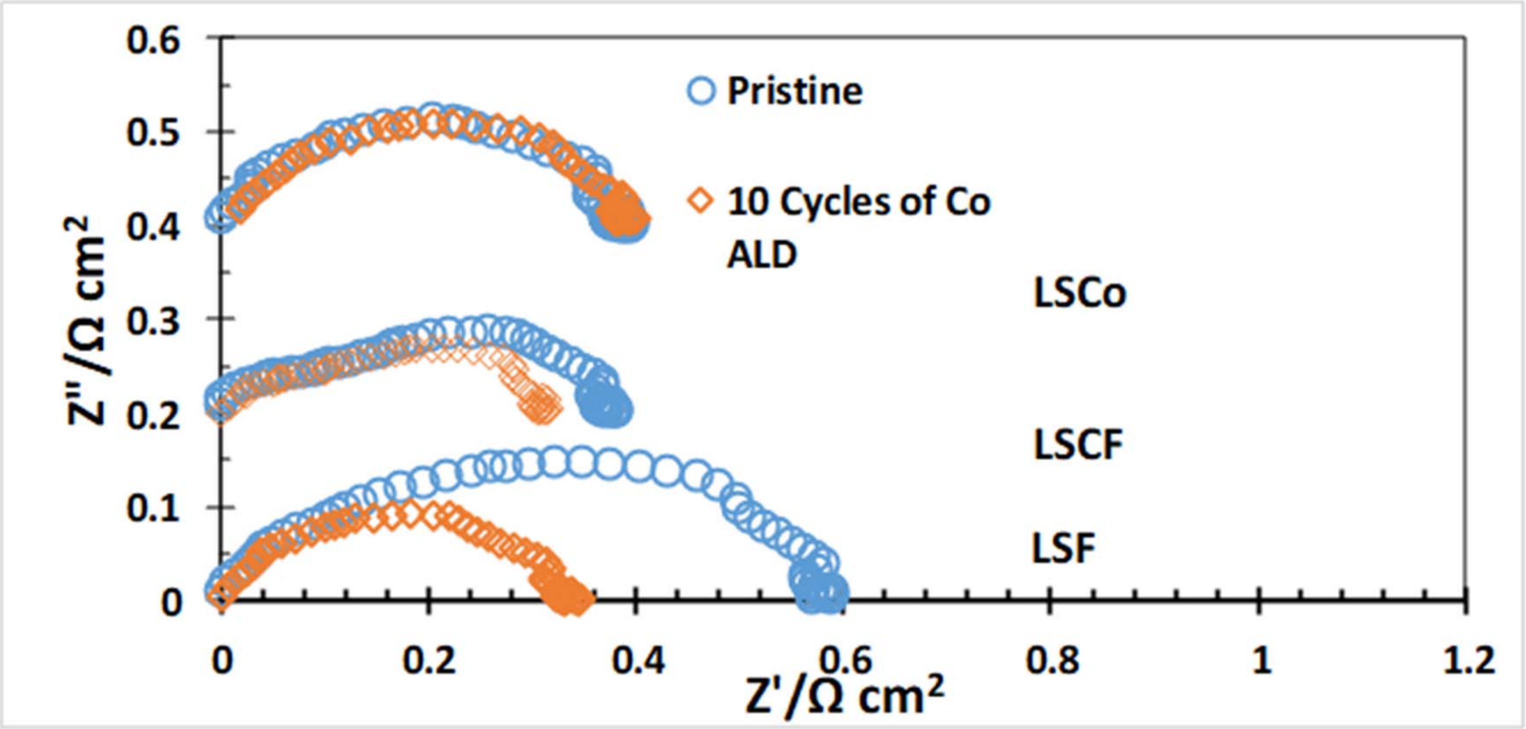


What about “catalyst” addition? Pd



Conclusion: No advantage for adding a catalyst for enhanced O_2 dissociation

Effect of Co ALD

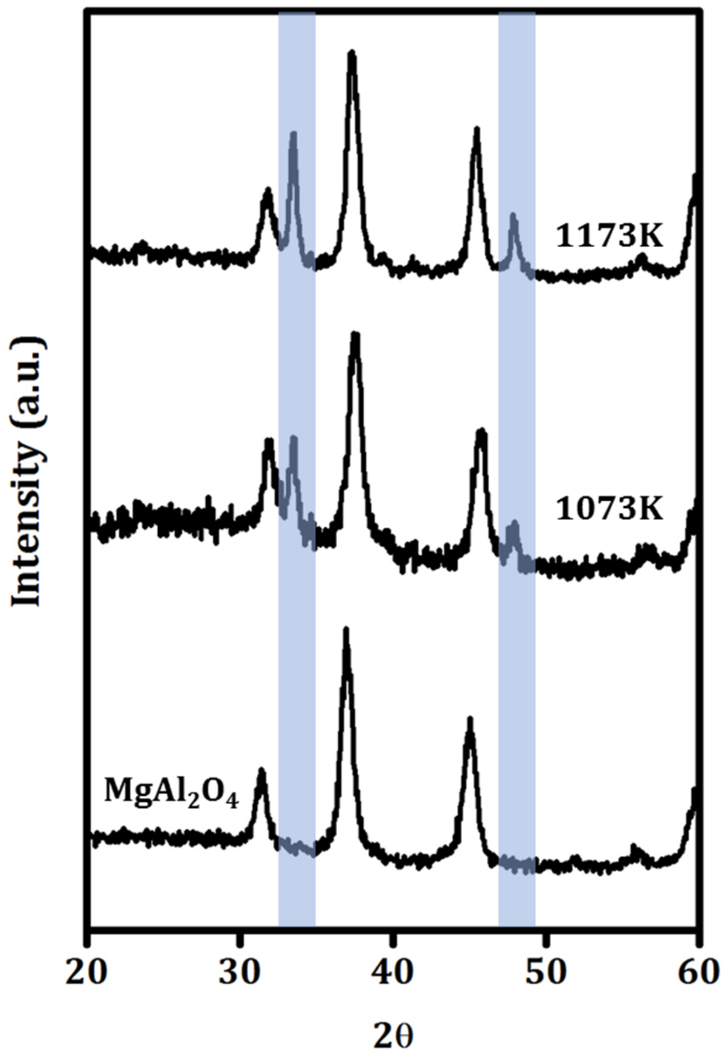


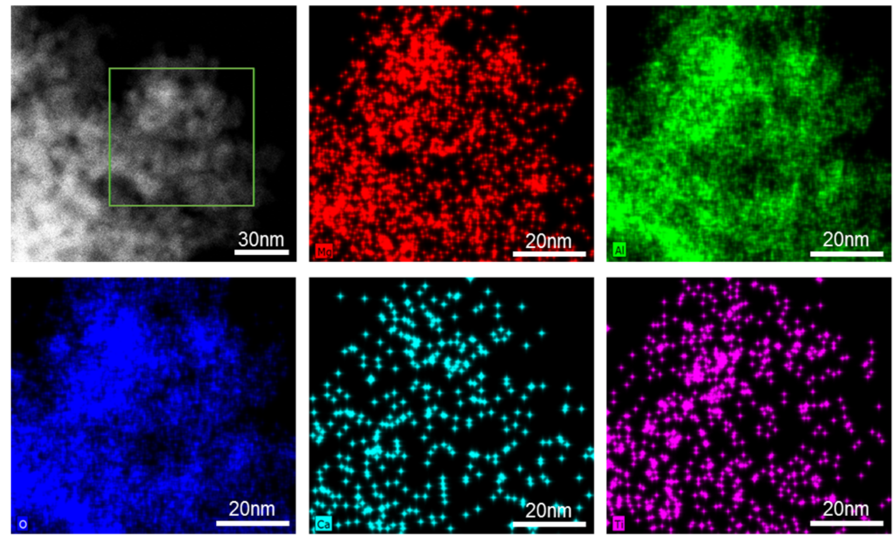
Conclusions:

1) Co addition to LSF makes the surface look like LSCo or LSCF

Modification of Anodes: Grow $CaTiO_3$ on $MgAl_2O_4$:

30-wt% $CaTiO_3$ on $MgAl_2O_4$:



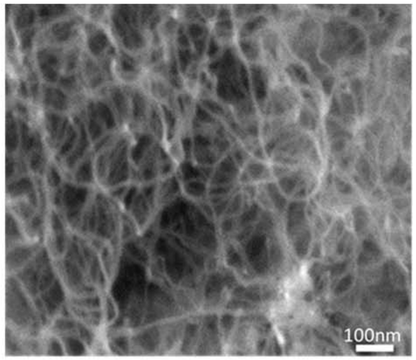


Surface area comparison(m^2/g)	
Bulk $CaTiO_3$	5
$CaTiO_3$ ALD-$MgAl_2O_4$	87
$MgAl_2O_4$	118

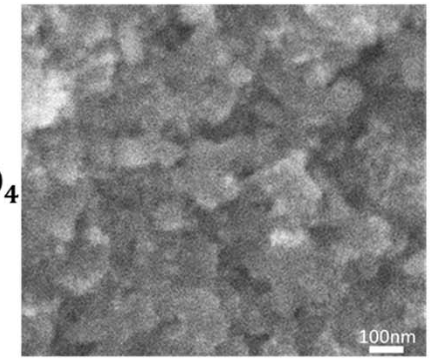
ACS Catal., 8 (2018) 7679.

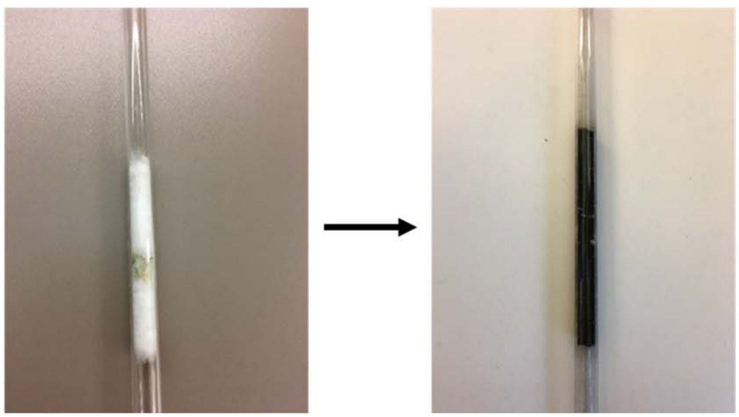
Expose $Ni/CaTiO_3/MgAl_2O_4$ to 10% CH_4-He at 800 °C for 12 h

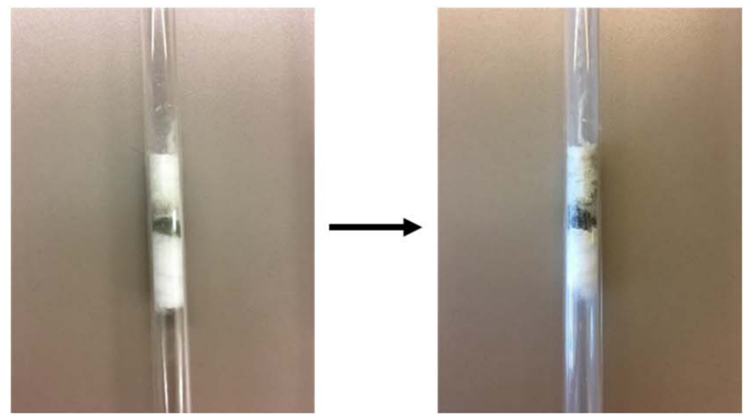
$Ni/MgAl_2O_4$



$Ni/CaTiO_3$-$MgAl_2O_4$







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