MICHIGAN STATE UNIVERSITY

Degradation and Performance Studies of Atomic Layer Deposition (ALD)-Stabilized Nano-Composite Solid Oxide Fuel Cell (SOFC) Cathodes

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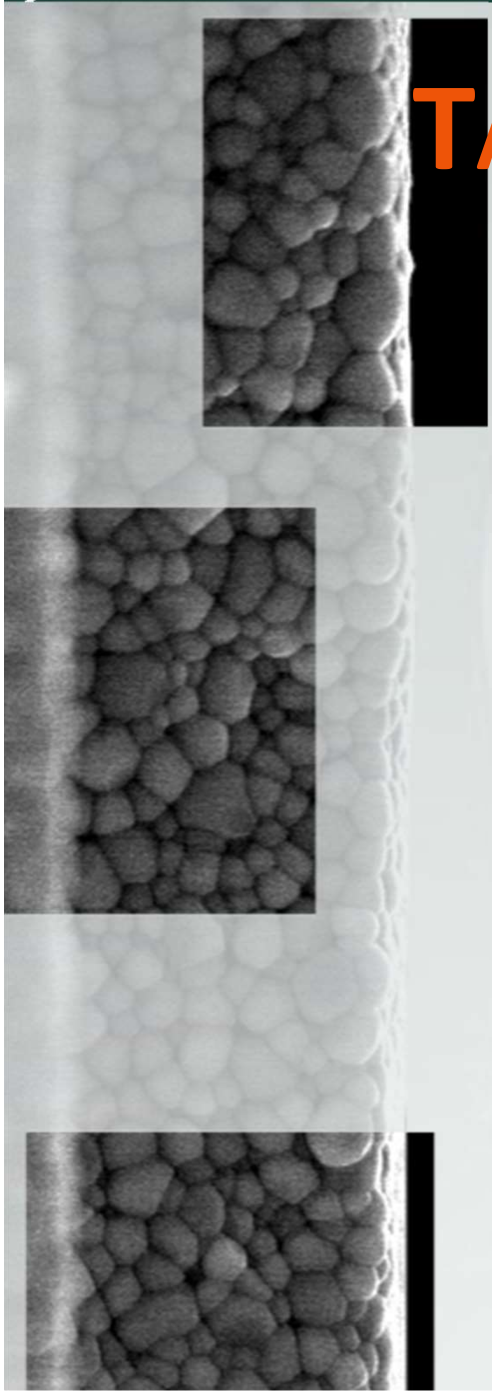


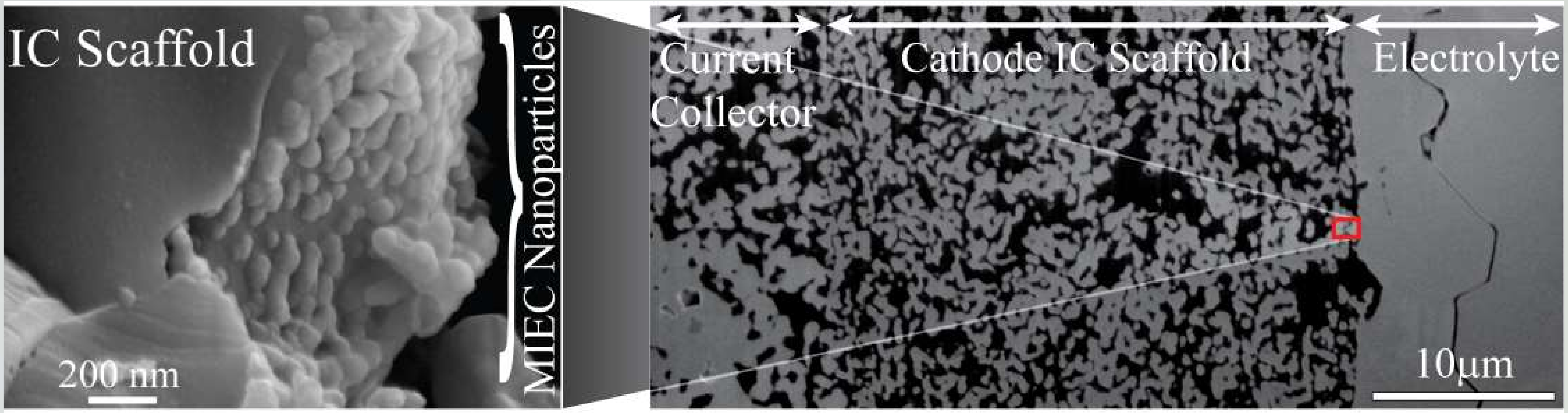
TALK Outline

1. **Background and Motivation**

2. ZrO_2 Overcoat as Sr Getter for Standard LSCF-GDC NCCs

Motivation for MIEC on IC Nano-Composite SOFC Cathodes

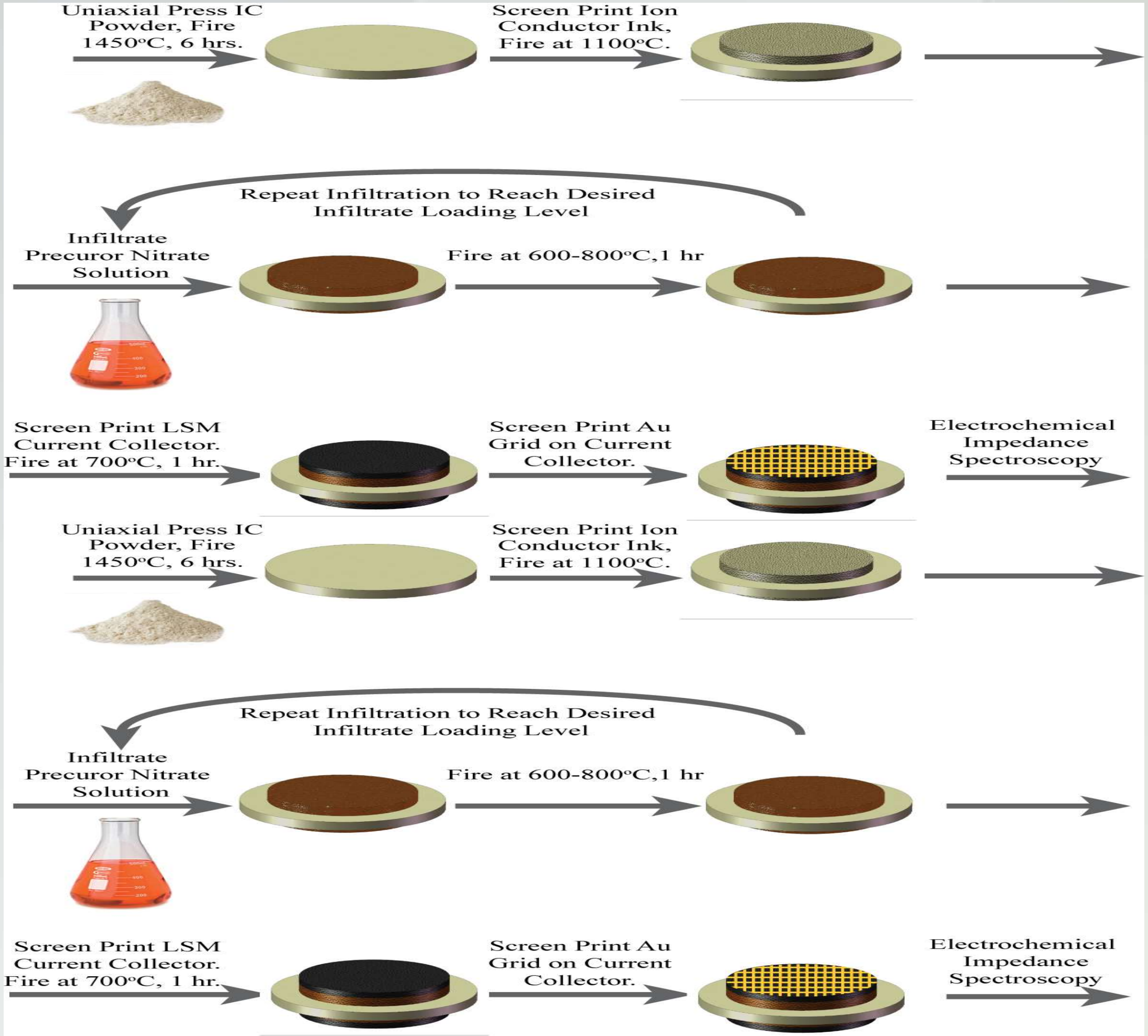
SOFC Cathode Reaction: $1/2O_{2\,(g)} + 2e^- + V_o^{**} = O_o$



Material	Oxygen Surface Exchange Coefficient (k)	Bulk Oxygen Ion Diffusivity (D)	Electronic Conductivity (σ_e)
Mixed Ionic Electronic Conductor (MIEC)	High	Low	High
Ionic Conductor (IC)	Low	High	Low

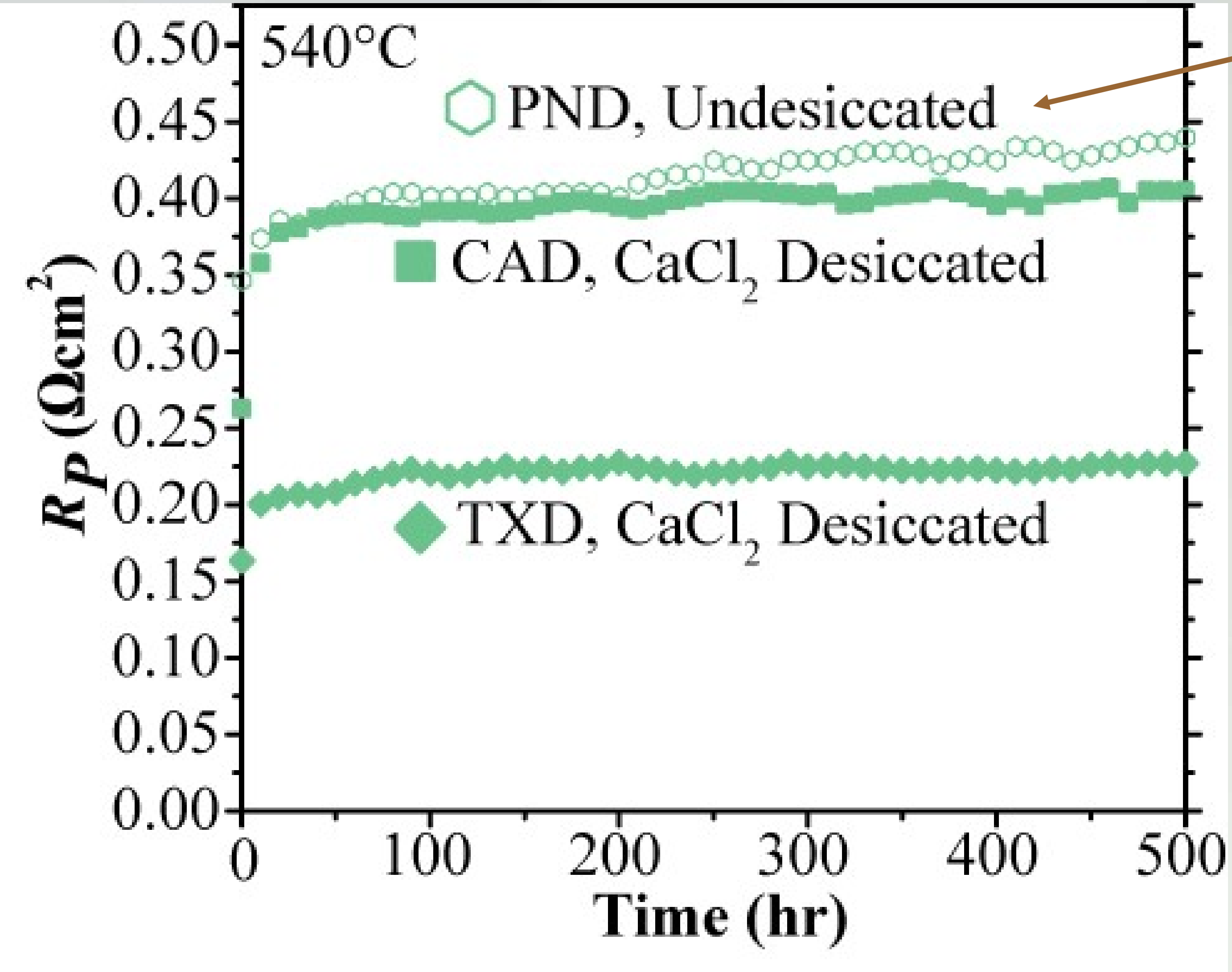
Burye and Nicholas, J Power Sources, 276, 54-61 (2015)

Standard Nano-Composite Cathode (NCC) Fabrication



Burye and Nicholas, J Power Sources, 301, 287-298 (2016)

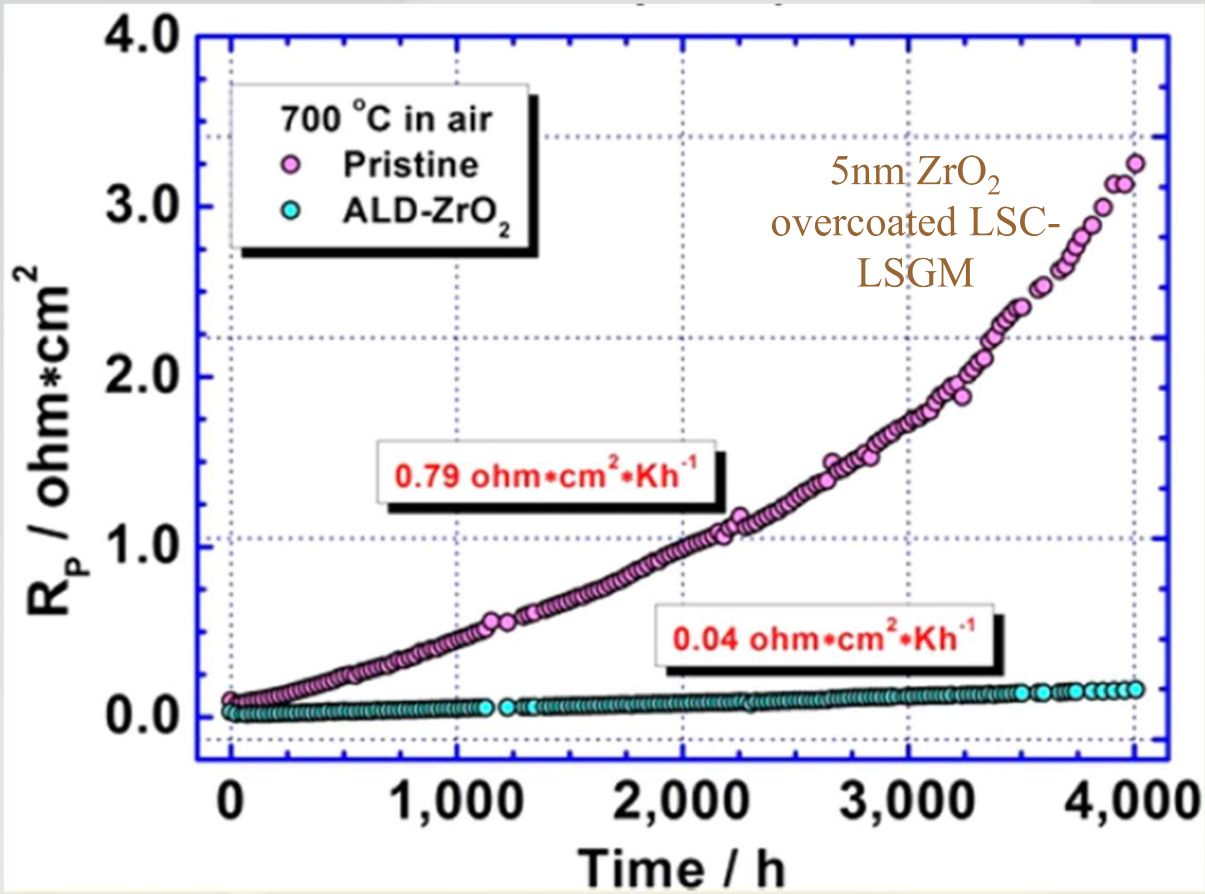
Standard LSCF-GDC NCCs Show Good Low Temperature Performance but Have Stability Problems



Degradation Rate = 35%/khrs after initial "break-in"

Burye and Nicholas, J Power Sources, 301, 287-298 (2016)

Atomic Layer Deposited (ALD) ZrO_2 Thin Films Have Been Reported to Improve SOFC Cathode Durability



5nm ZrO_2 overcoated LSC-LSGM

Standard LSC-LSGM

LSC ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$) nanoparticles supported on a porous LSGM ($La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$) scaffold

These results may be compromised by Ag migration from the current collector into the cathode with time

Gong, *et al*, Nano letters, 13.9 (2013)

TALK Outline

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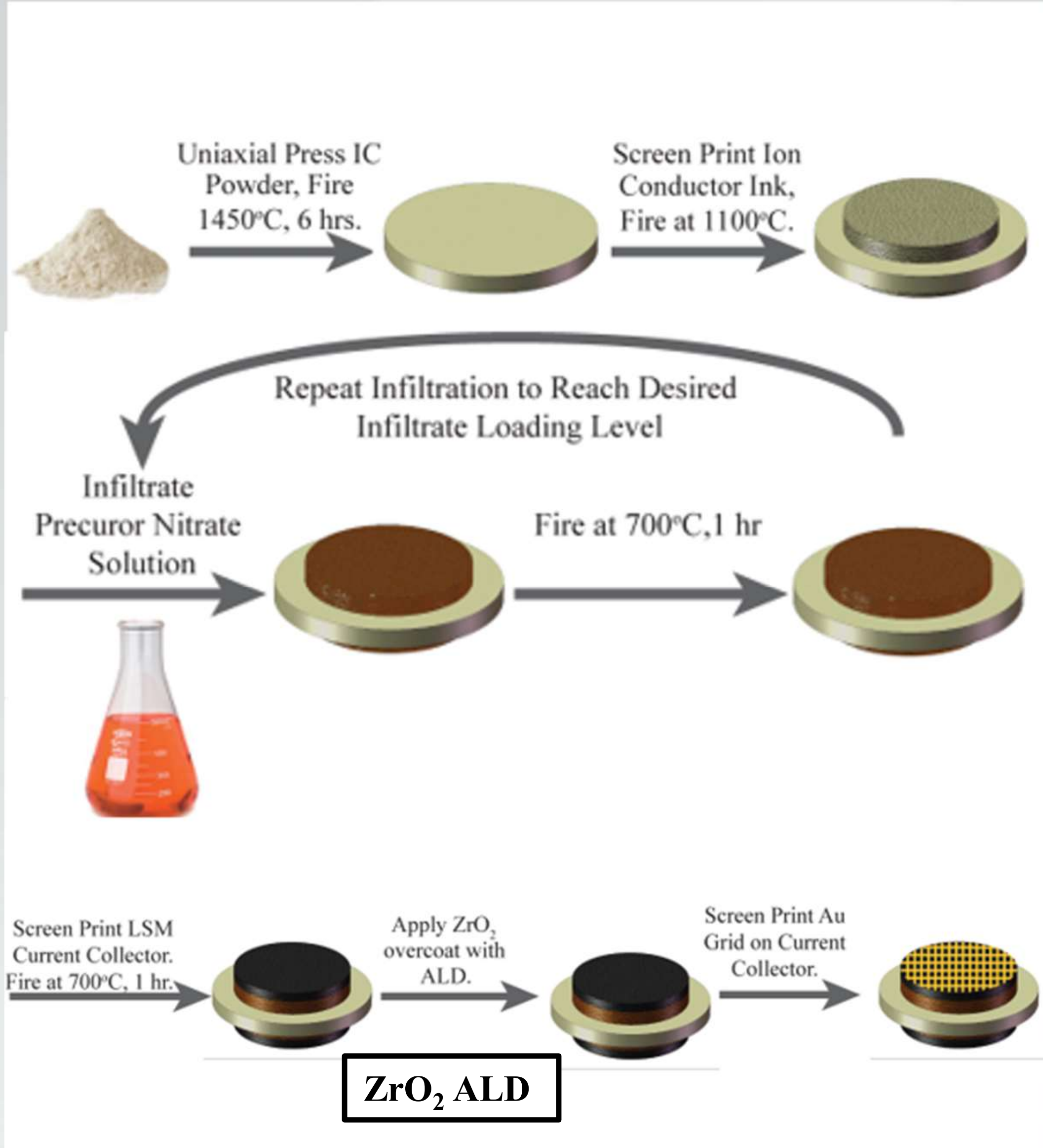
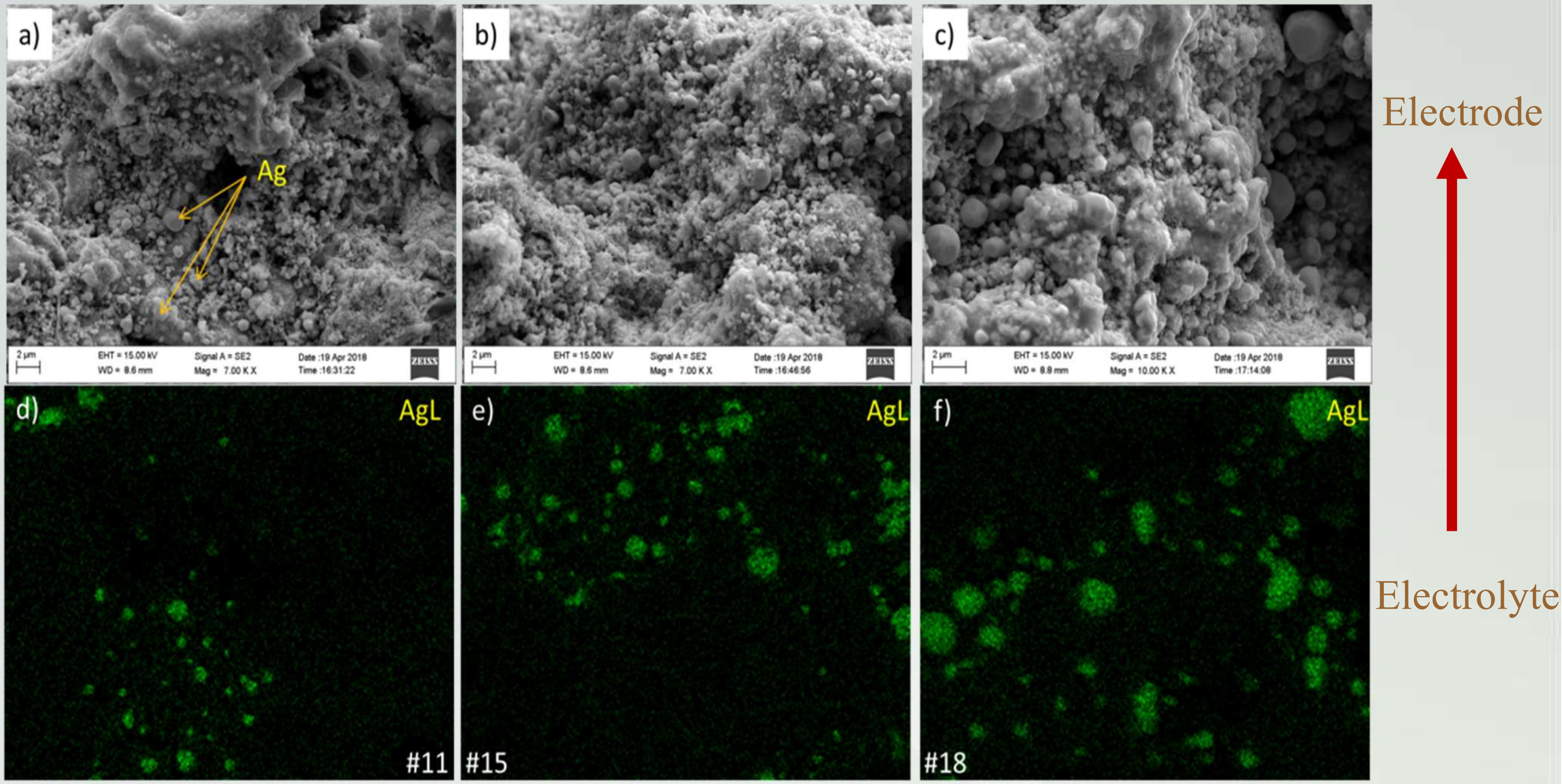
2. **ZrO_2 Overcoat as Sr Getter for Standard LSCF-GDC NCCs**

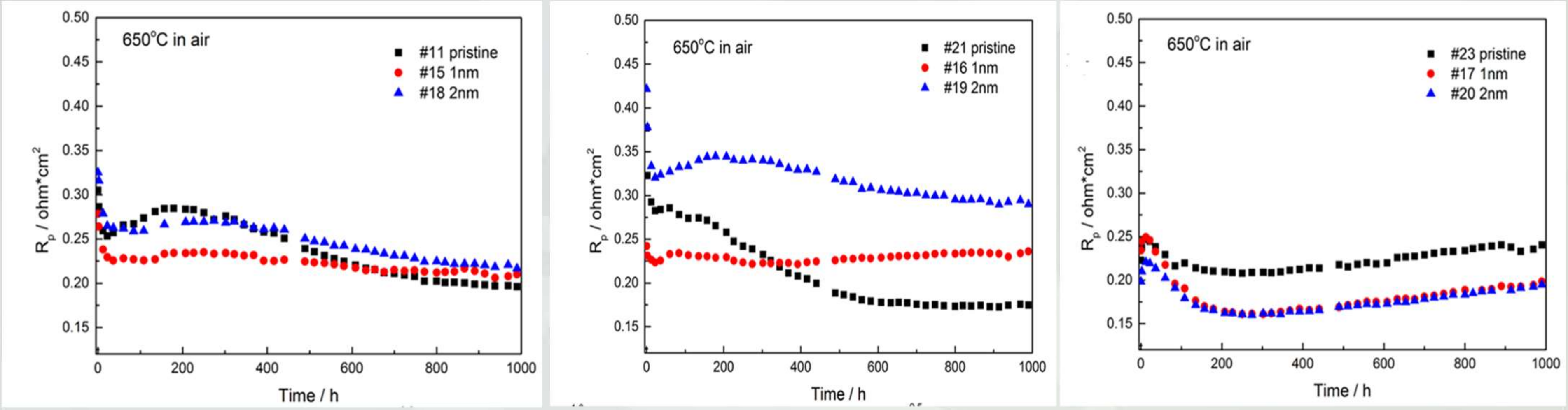
ZrO_2 Coated Nano-Composite Cathode Fabrication



Silver Shouldn’t Be Used as Current Collector Because of Its Electro-Migration at Elevated Temperature



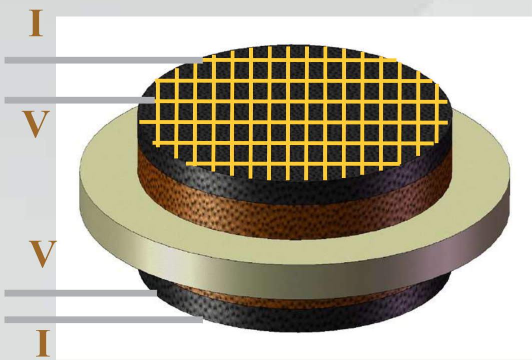
Silver Current Collectors Unpredictably Alter Standard LSCF-GDC NCC R_p Aging Behavior

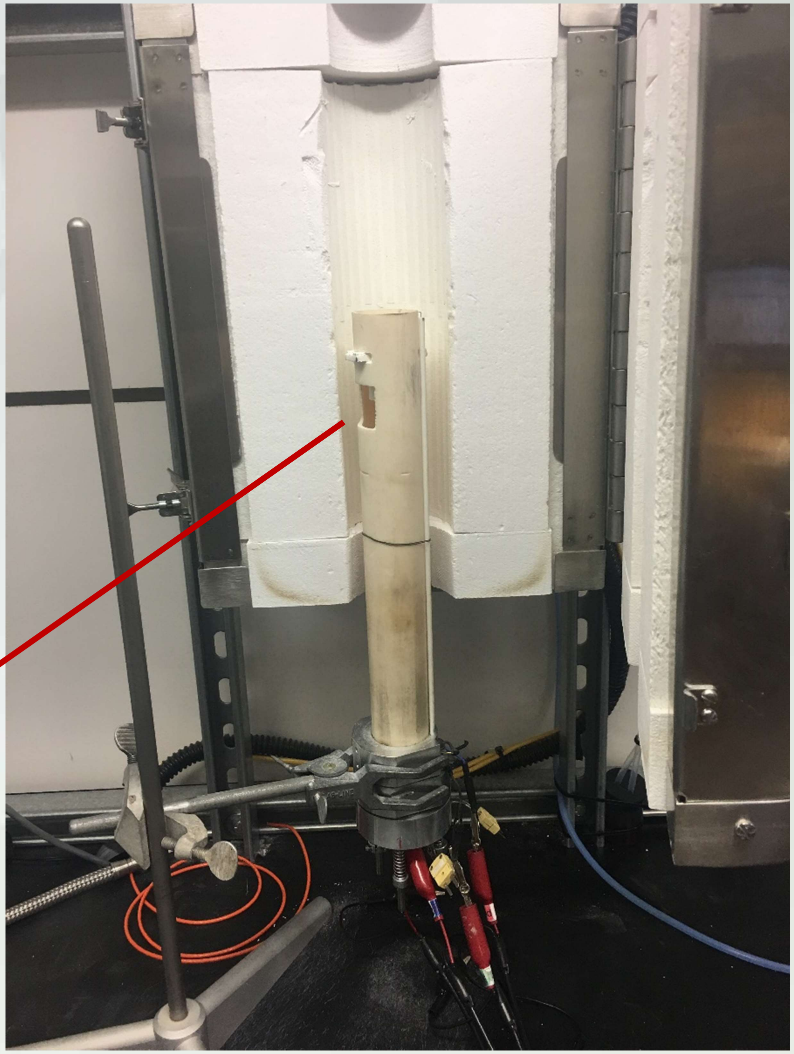


The polarization resistance vs time for three uncoated (left), three 1nm ZrO_2 coated (center) and three 2nm ZrO_2 coated (right) standard LSCF-GDC NCCs tested using silver mesh as a current collector.

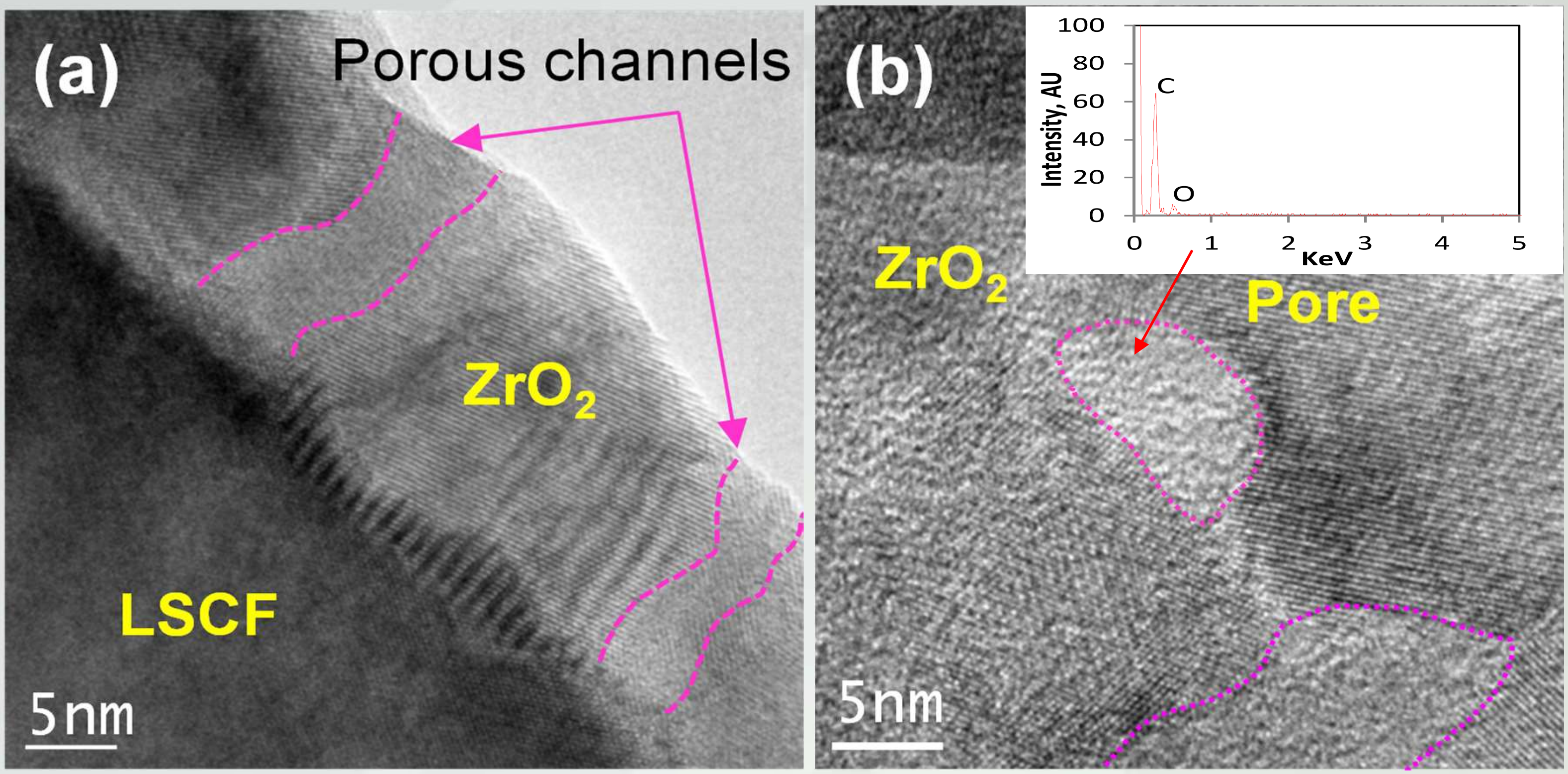
Zhang, *et al*. ACS Applied Energy Materials 3.4 (2020).

Screen Printed Gold Current Collector Grids and a Pt Plate Push-Contact Setup Was Used for the Measurements Here



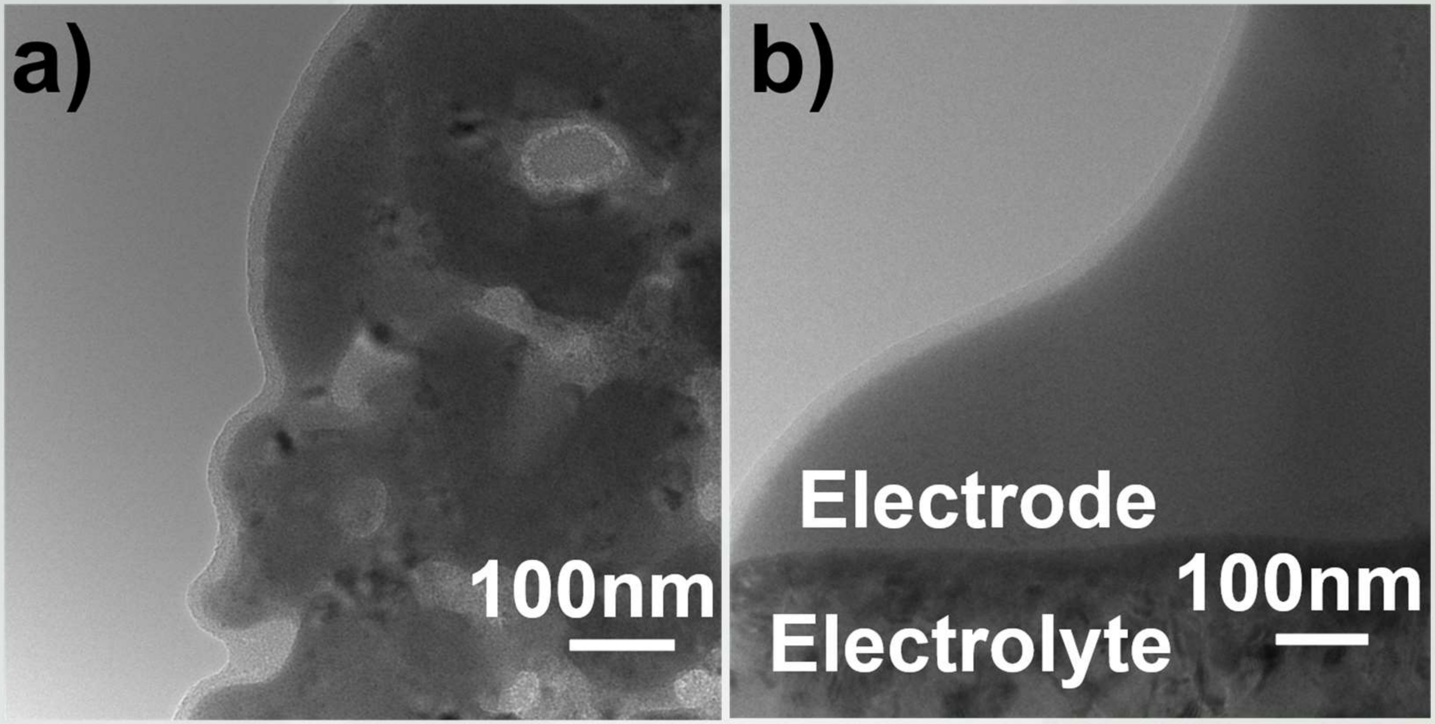


Porous ZrO_2 Overcoats Were Produced Using the ALD Recipes Employed Here



Gong, *et al*. Chem. Mater. (2013)

No ZrO_2 Thickness Variation with Cathode Thickness Was Observed

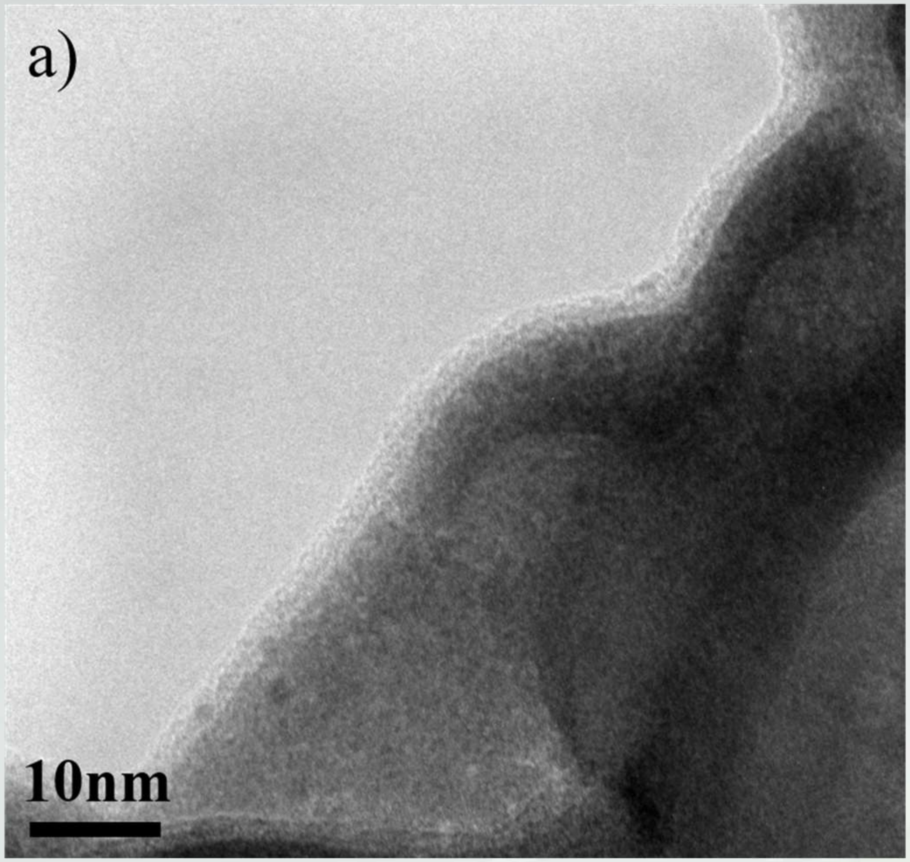


Near electrode surface

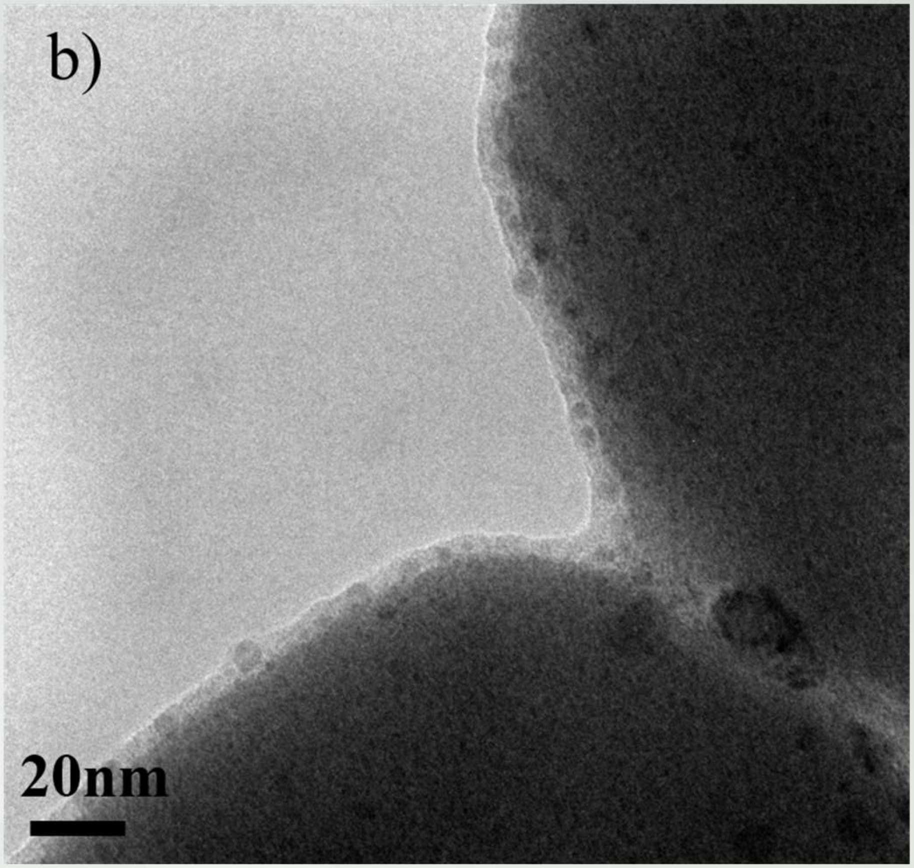
Near electrode/electrolyte interface

Zhang, *et al*. ACS Applied Energy Materials 3.4 (2020).

The ZrO_2 Overcoat Remained Conformal and Maintained the Target Thickness After 1000 Hours at 650°C



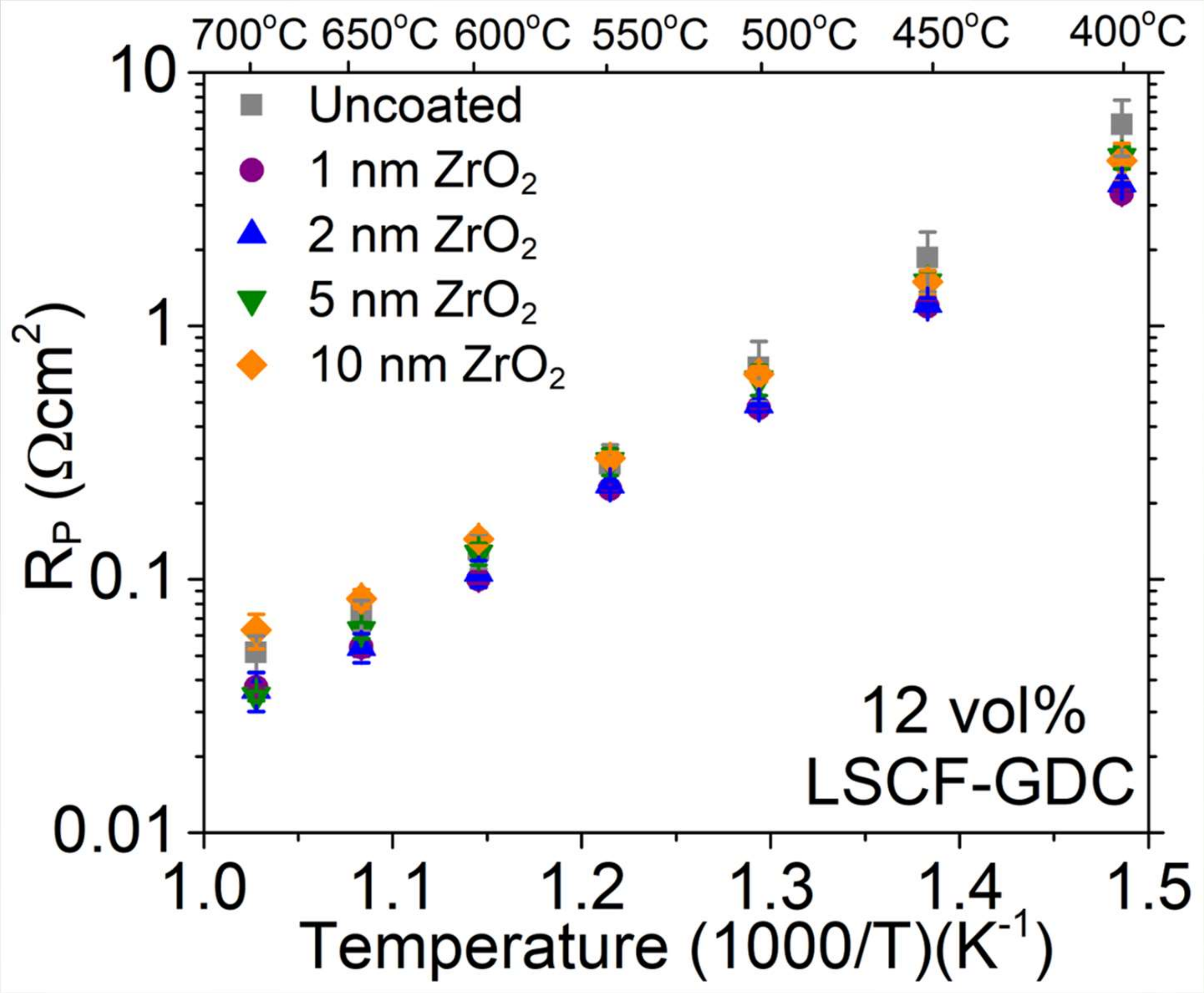
Tested cell with 3nm ZrO_2 overcoat (actual thickness ~3.2nm)



Tested cell with 5nm ZrO_2 overcoat (actual thickness ~5.3nm)

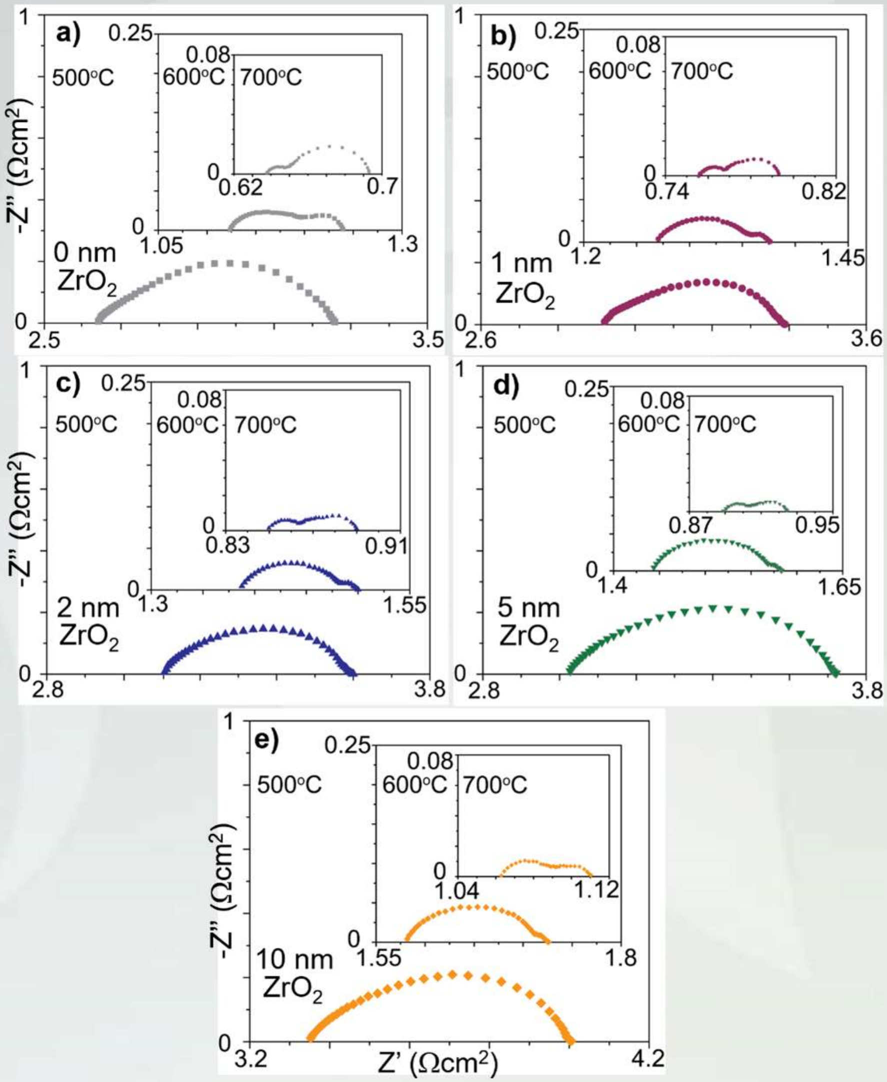
Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

ZrO_2 Overcoating Did Not Significantly Alter the Initial Performance of Standard LSCF-GDC NCCs



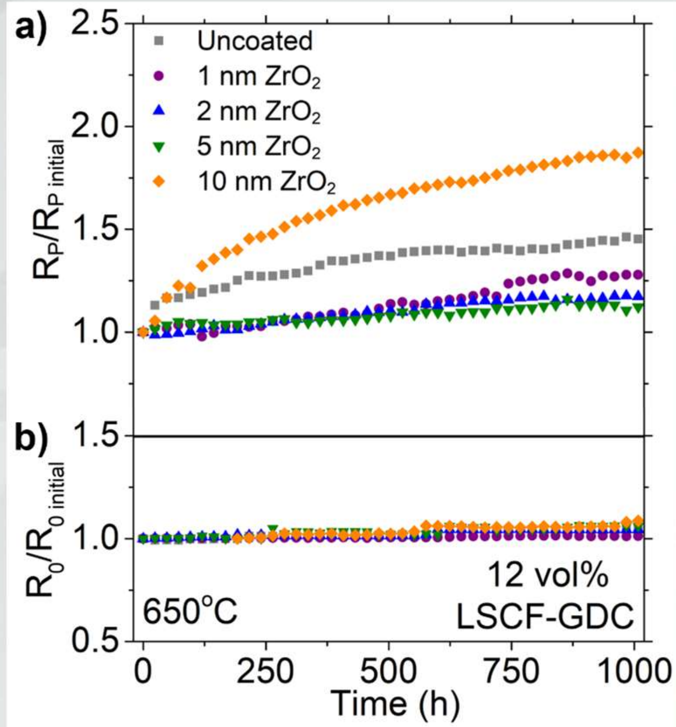
Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

ZrO_2 Overcoating Did Not Significantly Alter the Initial Performance of Standard LSCF-GDC NCCs



Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

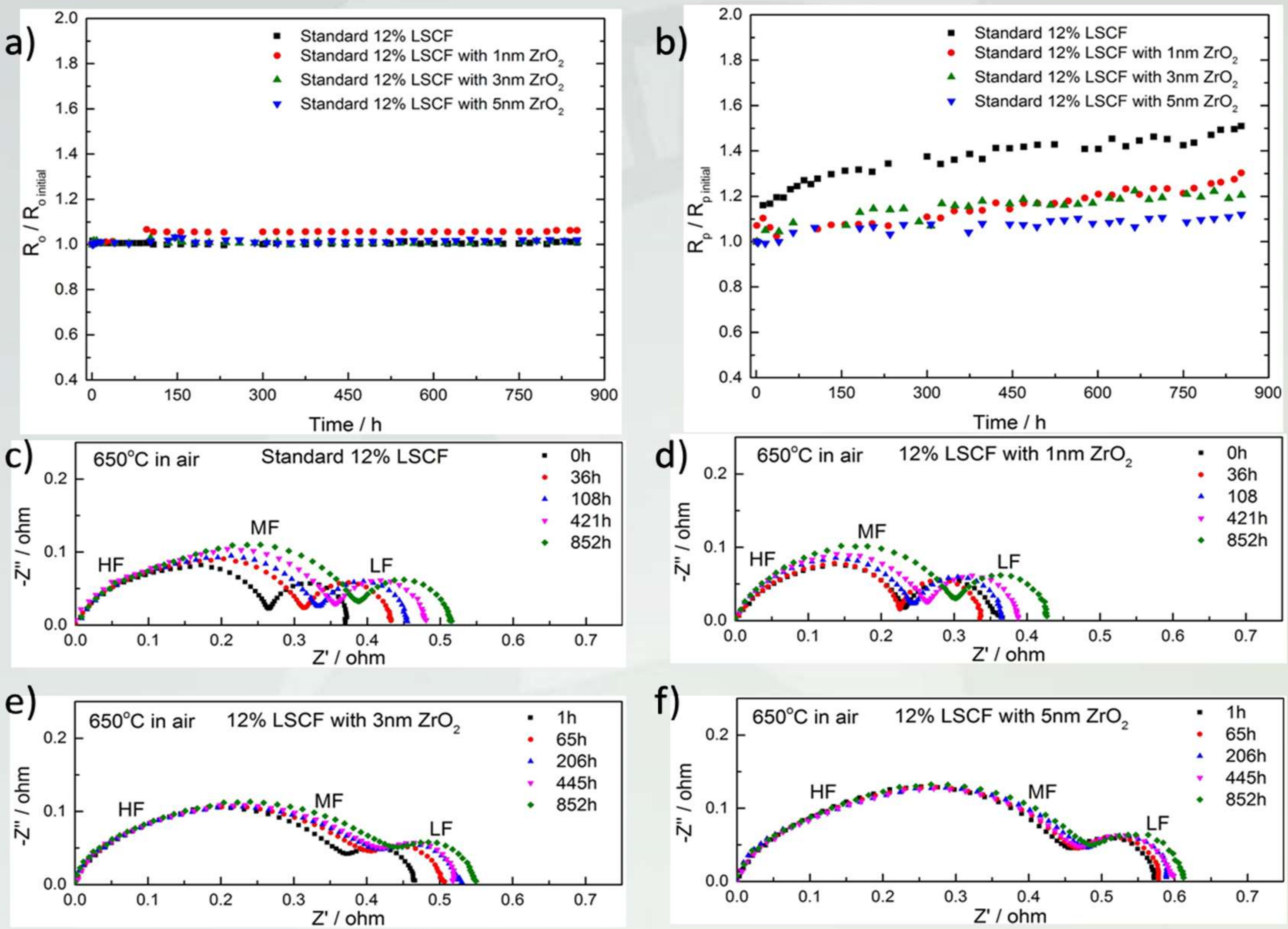
Different Rp Degradation Rates Were Observed for Standard LSCF-GDC NCCs with Different ALD ZrO_2 Thicknesses



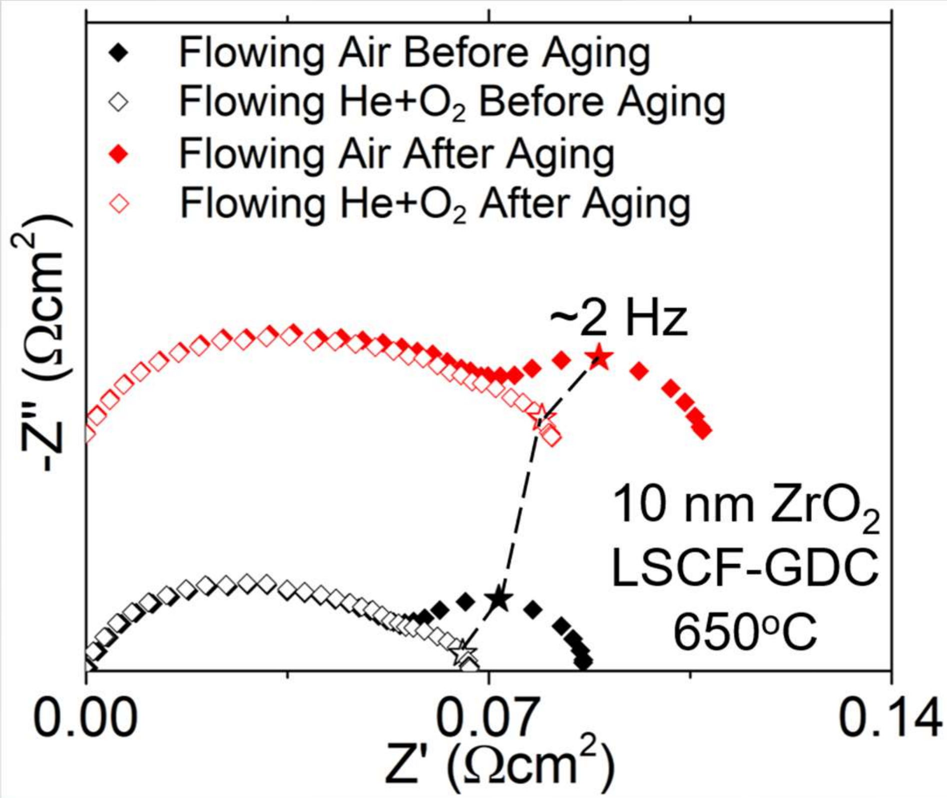
	R_p degradation rate (/khrs)	R_0 degradation rate (/khrs)
12% Standard LSCF	36%	2%
1nm ZrO_2 coated 12% LSCF	28%	1%
2nm ZrO_2 coated 12% LSCF	18%	4%
5nm ZrO_2 coated 12% LSCF	12%	4%
10nm ZrO_2 coated 12% LSCF	87%	5%

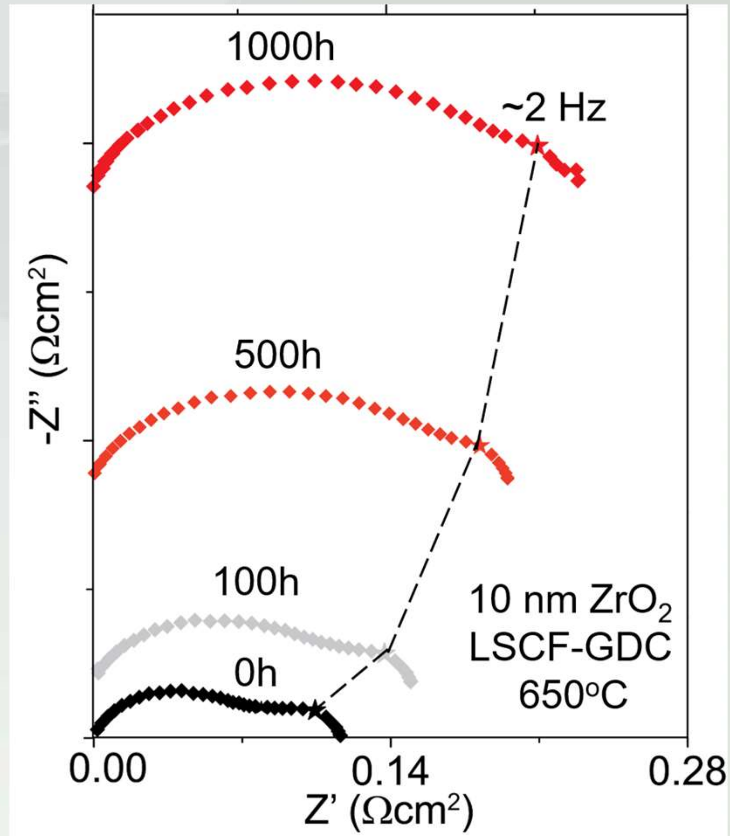
Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

Independent Degradation Tests at the University of South Carolina Showed Similar Degradation Behavior to Those Taken at Michigan State and Reported on the Previous Slides



Gas Diffusion Limitation Changes Were Not the Main Degradation Mechanism for ZrO_2 Coated LSCF-GDC NCCs





- The ~2 Hz curve in Nyquist plots is associated with gas diffusion
- This curve did not change during aging for ZrO_2 coated LSCF-GDC NCCs

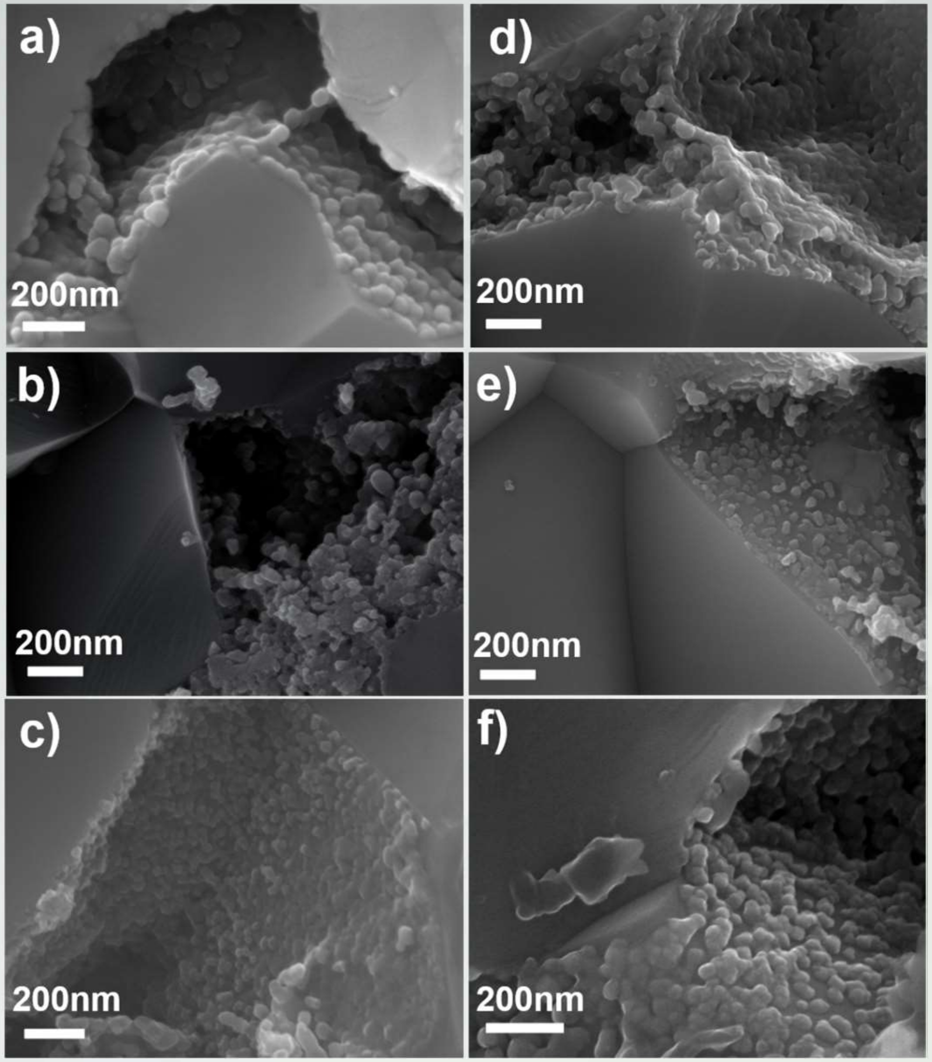
Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

No Obvious Particle Coarsening Was Observed in Any NCCs after 1000 Hours of 650^{o}C Degradation

0 nm
As produced

1nm
After aging

5nm
After aging



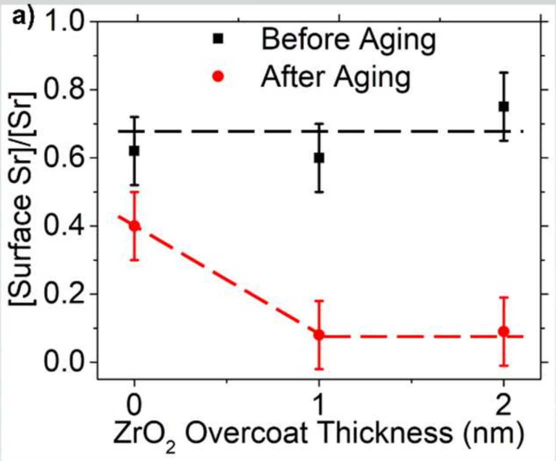
0 nm
After aging

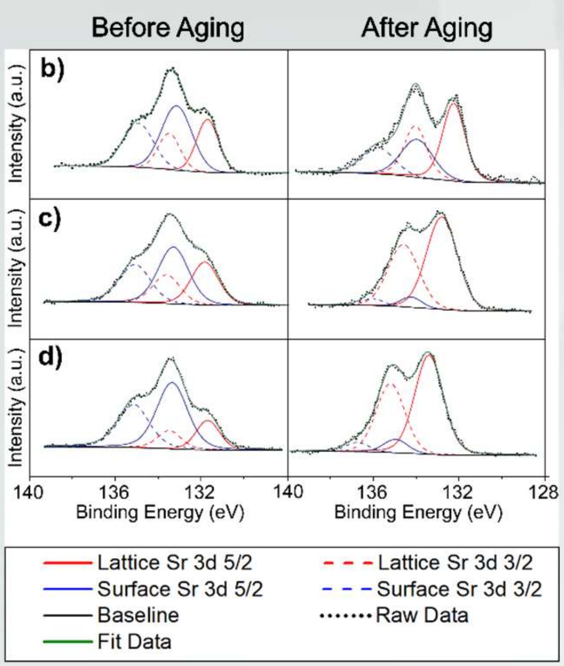
2 nm
After aging

10 nm
After aging

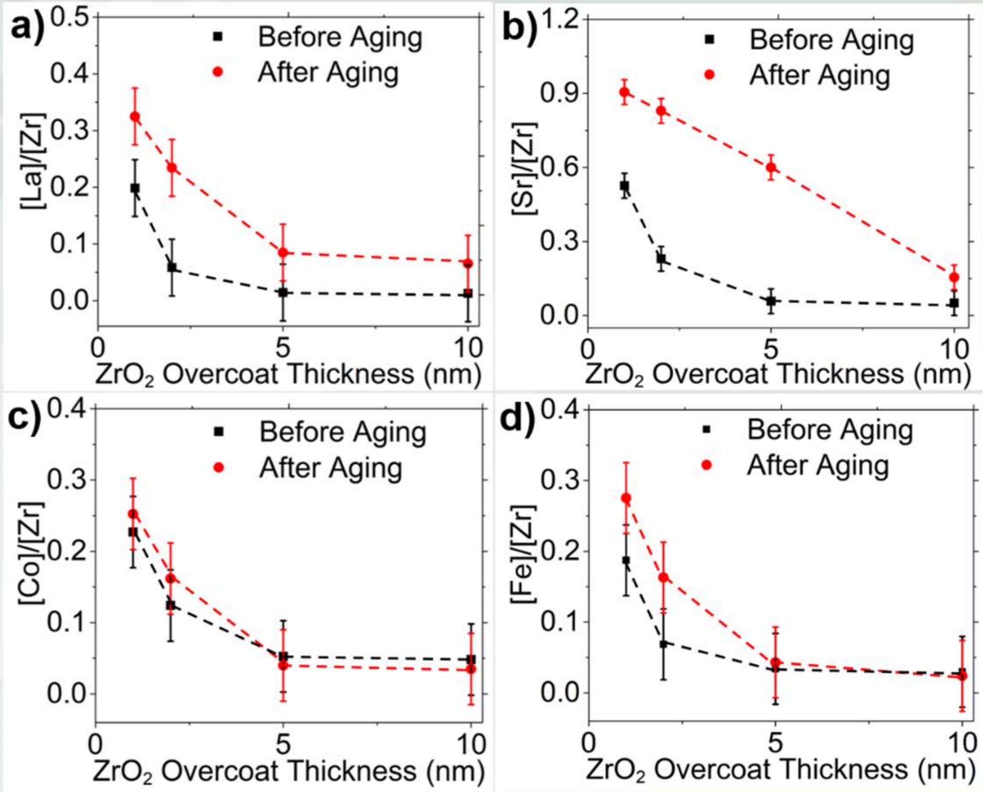
Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

XPS Showed ZrO_2 Coatings Reduced the Amount of Inactive "Surface" Sr on the LSCF-GDC NCC Surface After Aging



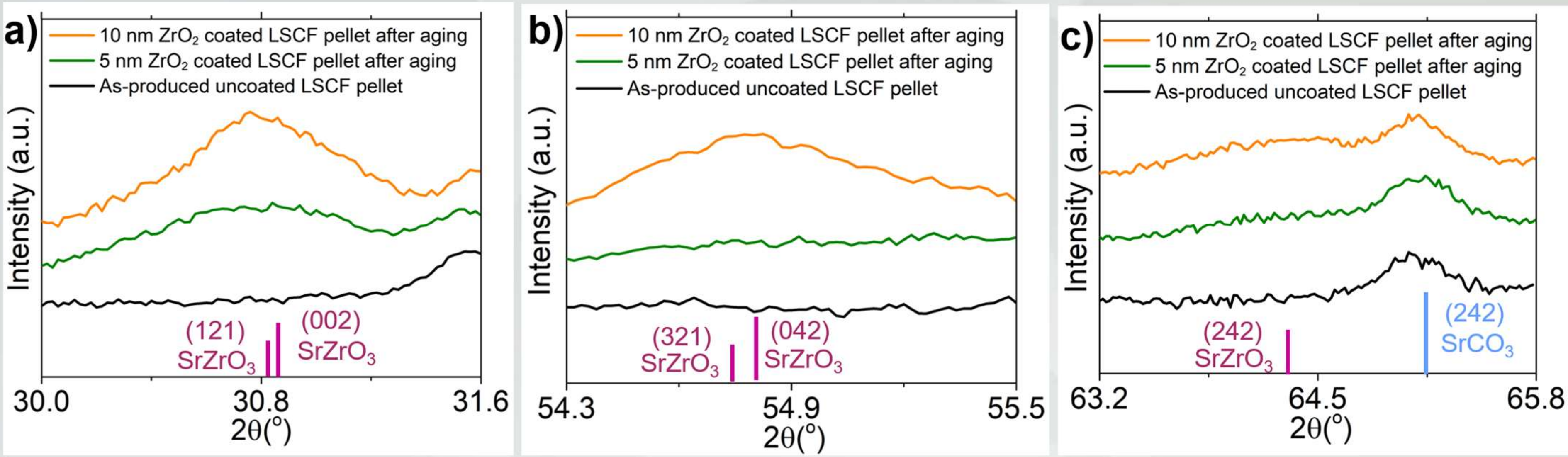


Even though there was more Sr on the surface after aging, the fraction of "Surface" Sr was lower with ALD ZrO2 overcoats.



Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

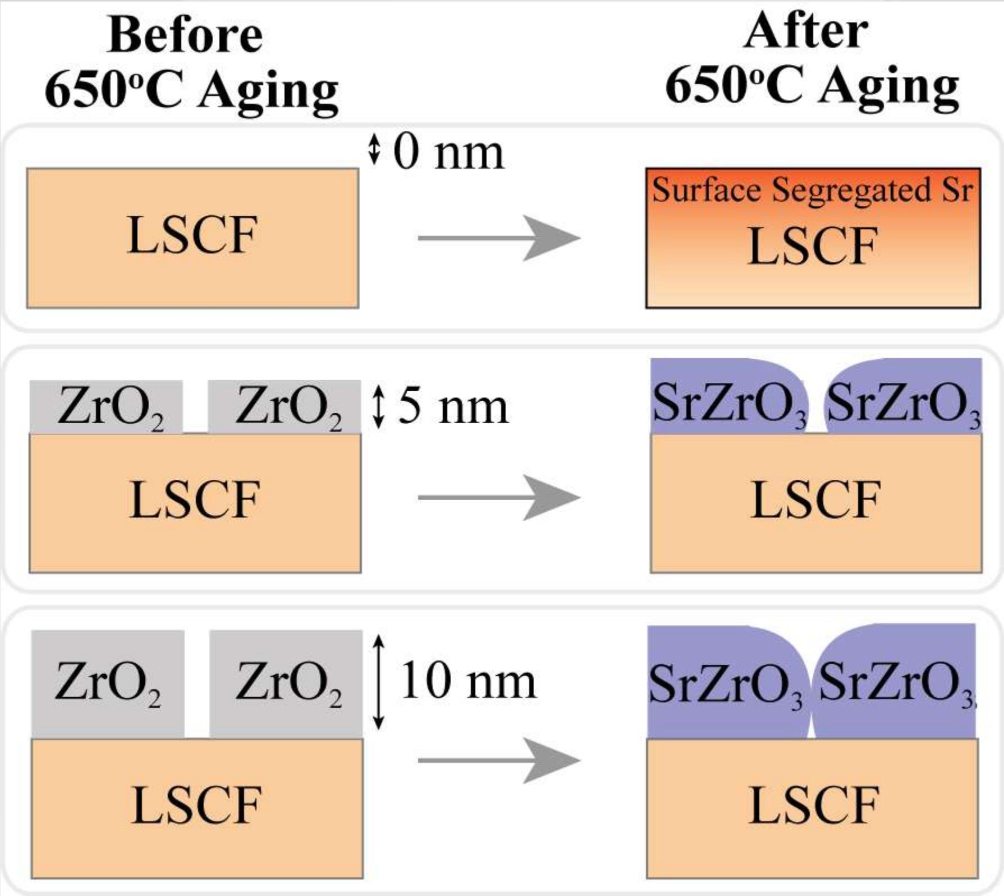
Detailed XRD Showed the Existence of $SrZrO_3$ in 5 nm and10 nm ZrO_2 Coated Cells after Aging



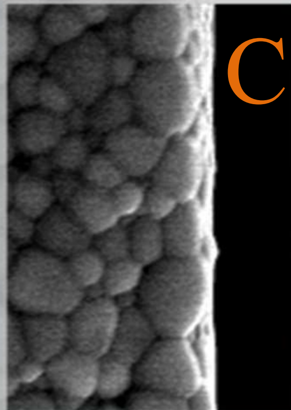
$SrZrO_3$ is expected to form during aging for 1 and 2 nm ZrO_2 coated LSCF-GDC NCCs as well, but was hard to detect due to the low $SrZrO_3$ concentration.

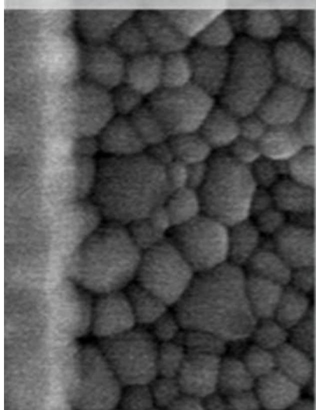
Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).

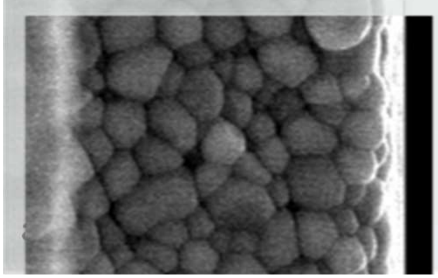
Mechanism Hypothesis: ZrO_2 Overcoats Serve as a "Sr Getter" and Clean up the LSCF Surface During Aging



Zhang, *et al.* ACS Applied Energy Materials 3.4 (2020).







Conclusions

1. ZrO_2 ALD overcoats 1-5 nm in thickness improved the long-term stability of standard LSCF-GDC NCCs without significantly altering their R_p between 400°C and 700°C.

2. Higher degradation rates, and similar initial performance, were observed for LSCF-GDC NCCs with 10 nm ZrO_2 overcoats

3. ZrO_2 overcoats served as “Sr getters” and reacted with inactive “Surface” Sr to form $SrZrO_3$ during aging. This reaction cleaned up LSCF surface and resulted in improved stability for ZrO_2 overcoats ≤ 5 nm thick. For LSCF-GDC NCCs with 10 nm ZrO_2 overcoats, too much $SrZrO_3$ accumulated on the LSCF surface, blocking oxygen exchange and increasing the measured degradation rate.

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