Apr. 23rd, 2024

Advanced Manufacturing of Solid Oxide Electrodes Using ALD

Dr. Katherine Hansen – RMD Inc.

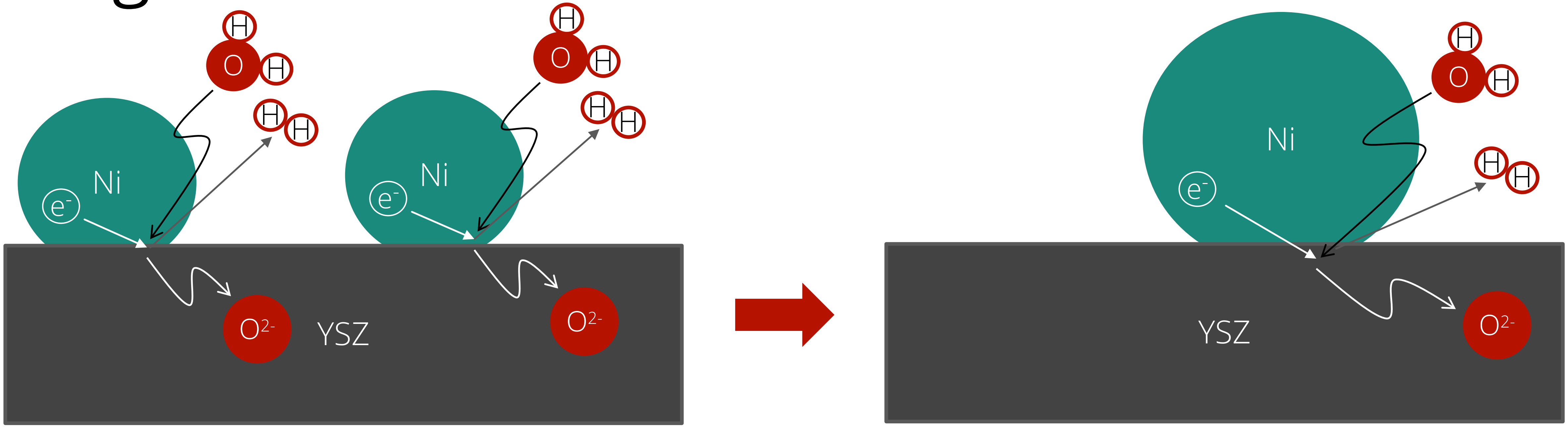
U.S. DOE Office of Fossil Energy and Carbon Management
DOE SBIR Grant #: DE-SC0022769

RMD Inc. and UPenn and OxEon Energy
Collaborators: Prof. John Vohs – UPenn
Dr. Jenna Pike – OxEon Energy

About RMD

- Founded in 1974
- RMD's mission has been to conduct world-class research and develop industry-leading commercial products.
- More than 60 scientists and engineers
- RMD has a growing portfolio of ALD technologies
  - Microelectronic Semiconductor Coatings
  - Gas Barrier Coatings
  - Anti-Corrosion Coatings
  - X-ray and Neutron Supermirror Coatings

Hydrogen Electrode Degradation – Nickel Migration



- As Nickel migrates and agglomerates, density of TPBs is reduced

What's Been Done to Prevent Degradation

- Increasing surface area/density of active TPBs with additional catalysts via infiltration, ALD, PLD, etc.

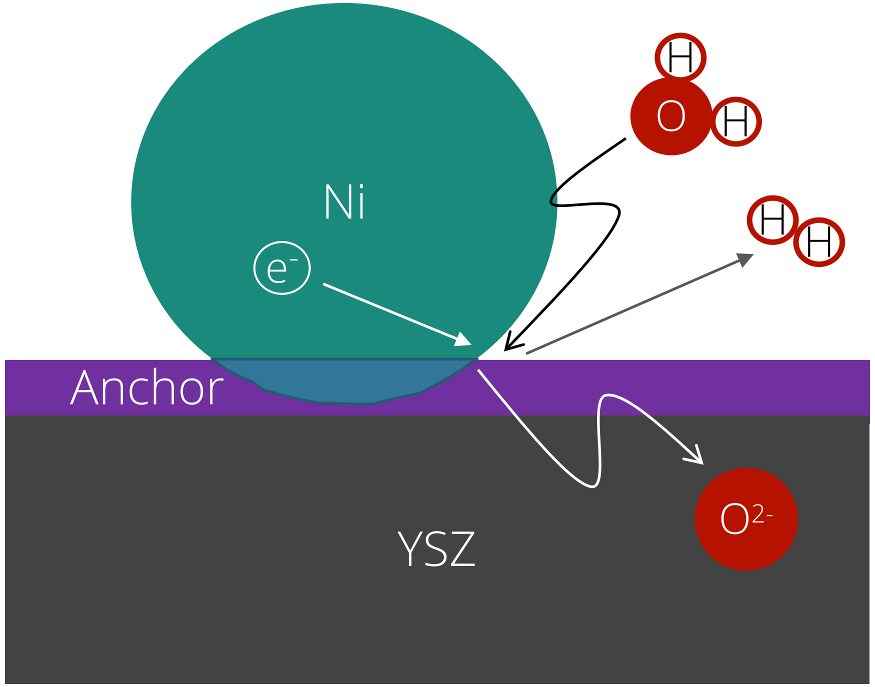
❖ Outlook: Develop robust electrode preventing Ni migration

❖ Challenge: Binding Ni in complex electrode microstructure while preserving TPB density

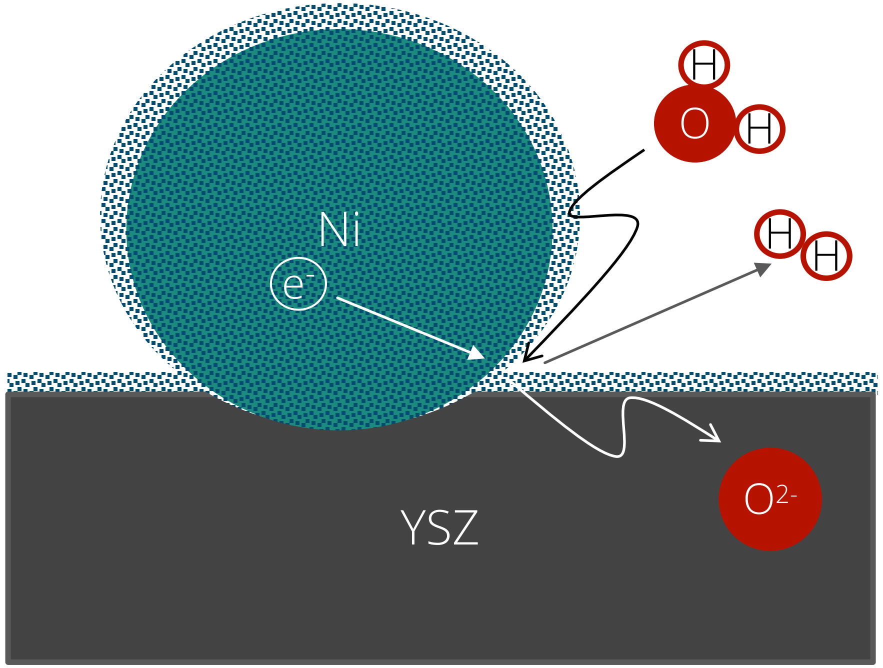
❖ Solution: Conformal ALD coating of chemical anchor compatible with SOC manufacturing

Advantage of Anchoring

- Prevents Ni migration and agglomeration while preserving Ni for TPBs
- Minimized risk of blocking TPB



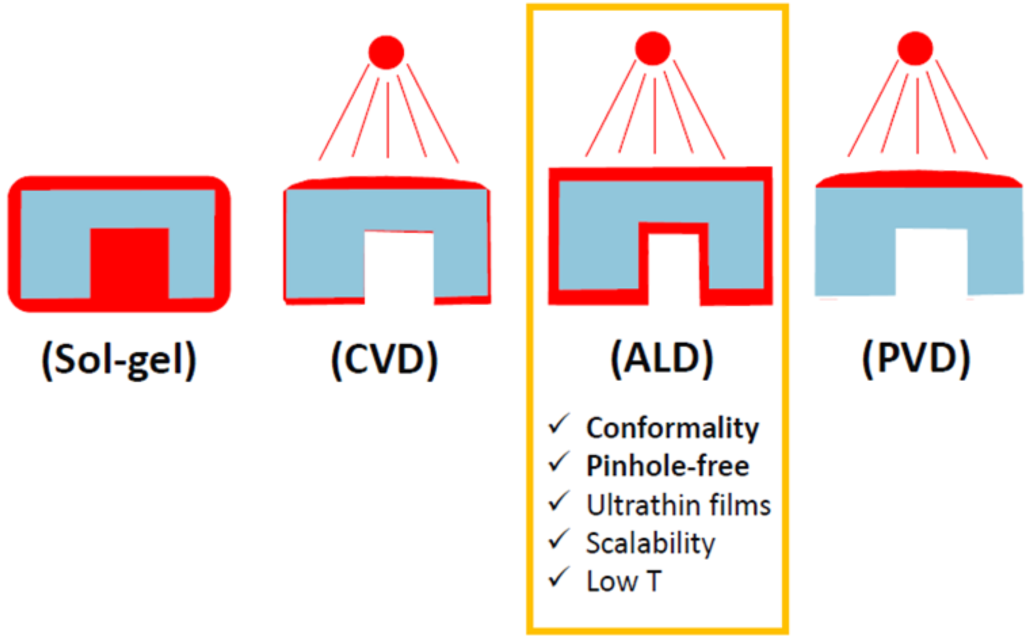
Anchoring



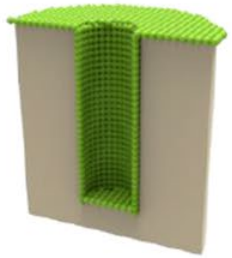
Porous overcoat

Atomic Layer Deposition (ALD)

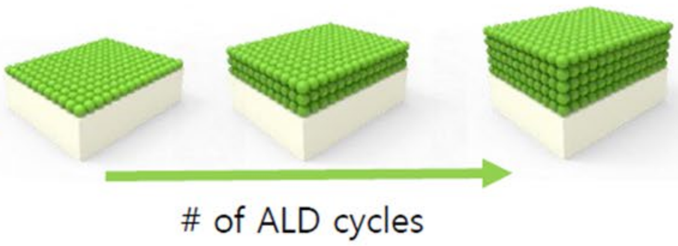
Thin film coating methods



- ALD is driven by surface chemistry
- Requires unique chemical precursors
- Requires careful design of ALD systems



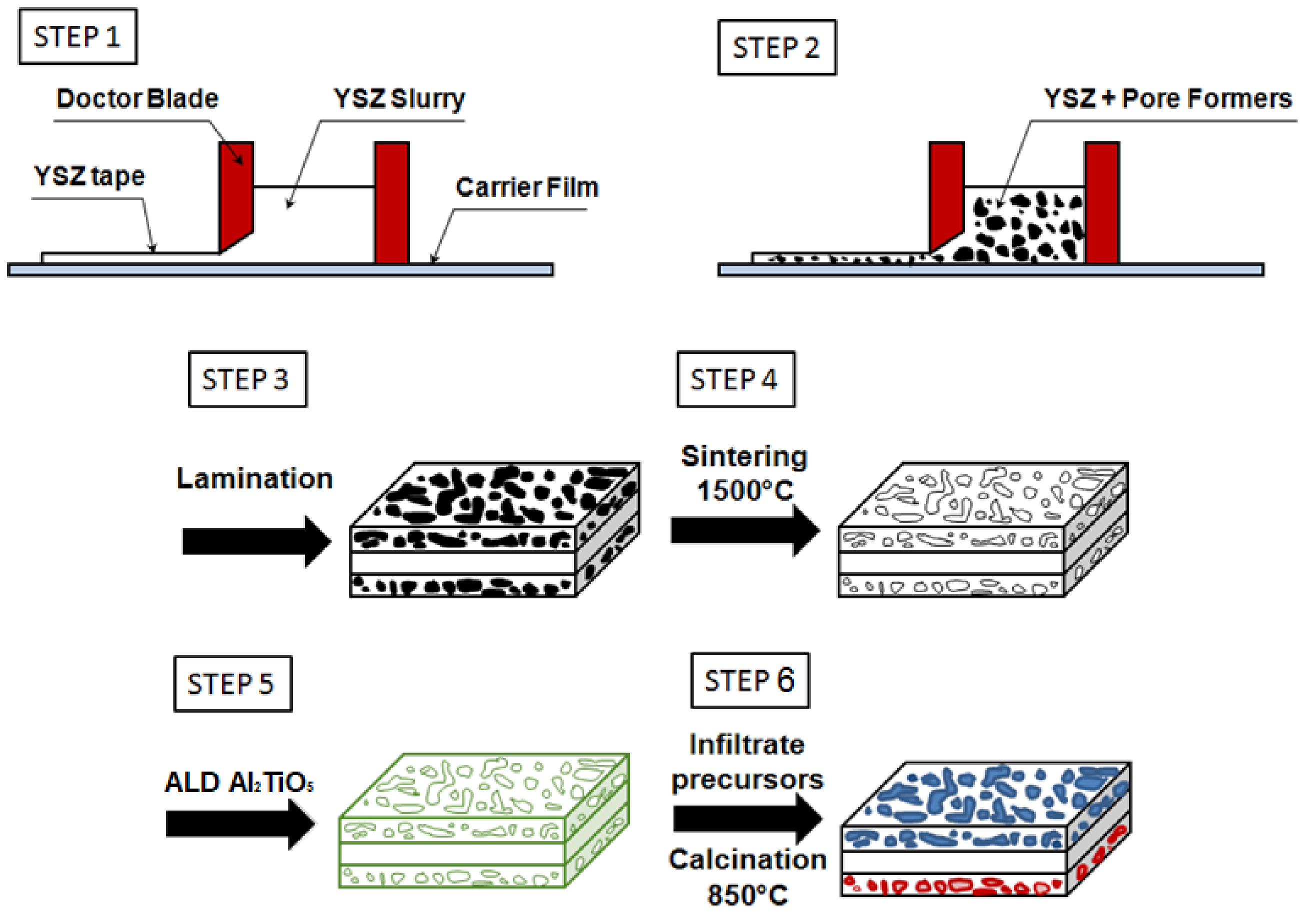
Good conformality



Thickness control

Good uniformity

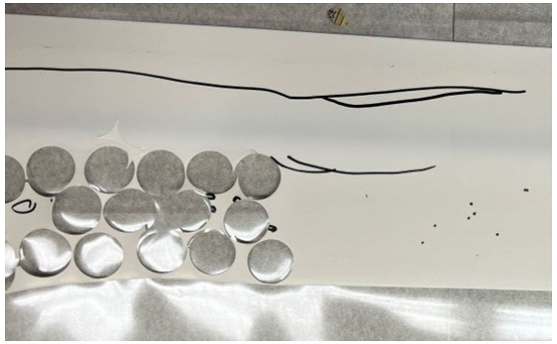
Approach



- Cells fabricated via tape casting
- Al_2TiO_5 anchor will be deposited by ALD into the cell scaffold
- Wet infiltration to add the active components
- Calcination anneal will activate anchor

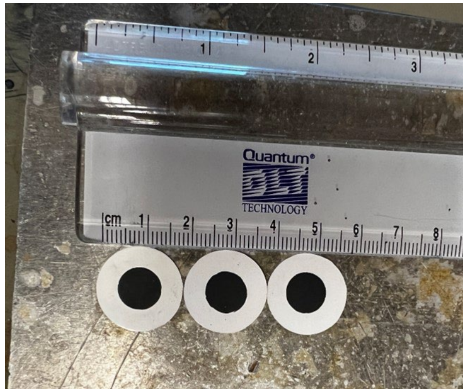
Cell Fabrication – Tape Casting

- Cells are fabricated using tape casting with a slurry containing YSZ or YSZ plus graphite pore formers

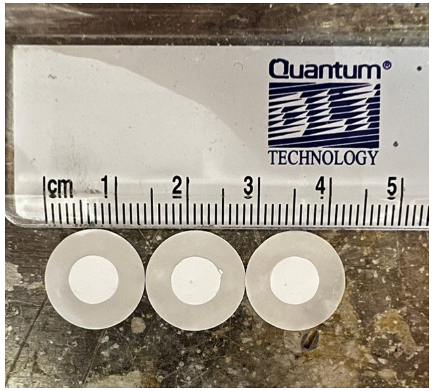


YSZ tape used for making dense electrolyte layer

YSZ tape with graphite pore former used for making electrode layers

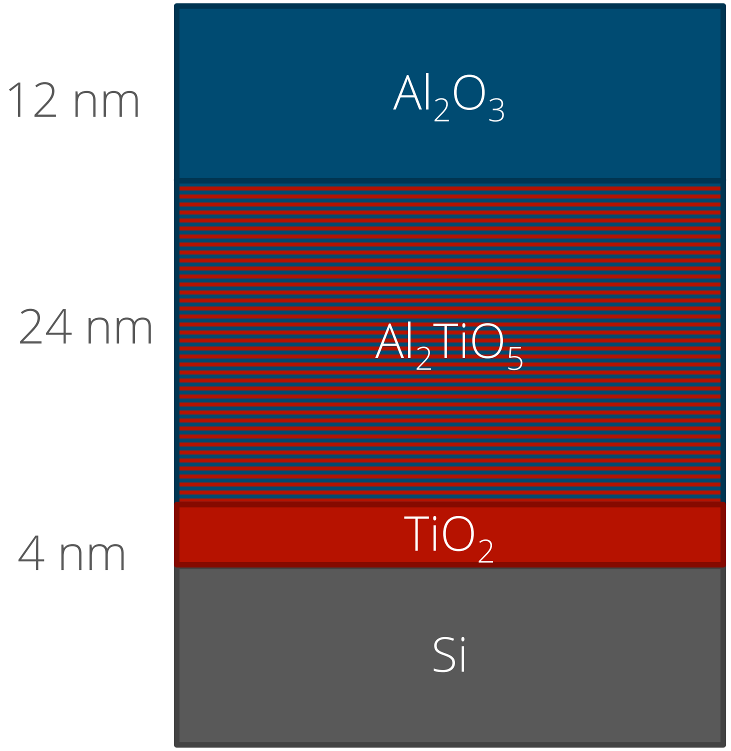


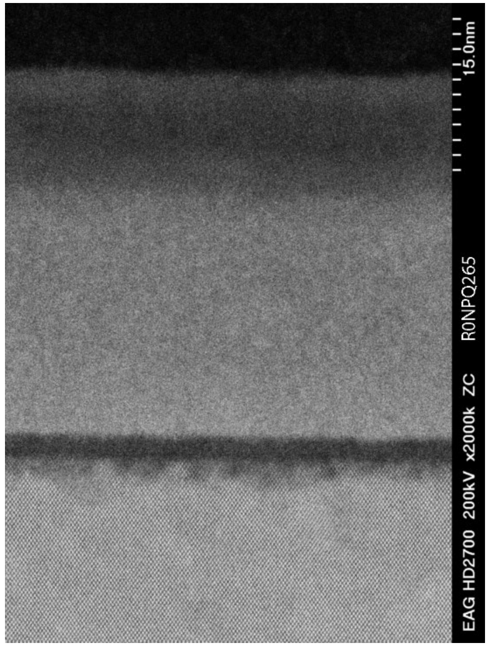
Cells before sintering

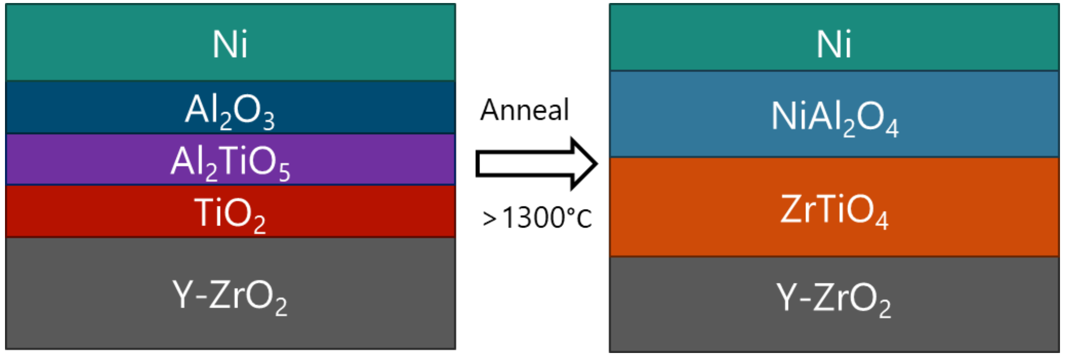


Cells after sintering 1500ºC

Initial Anchor ALD Process Development







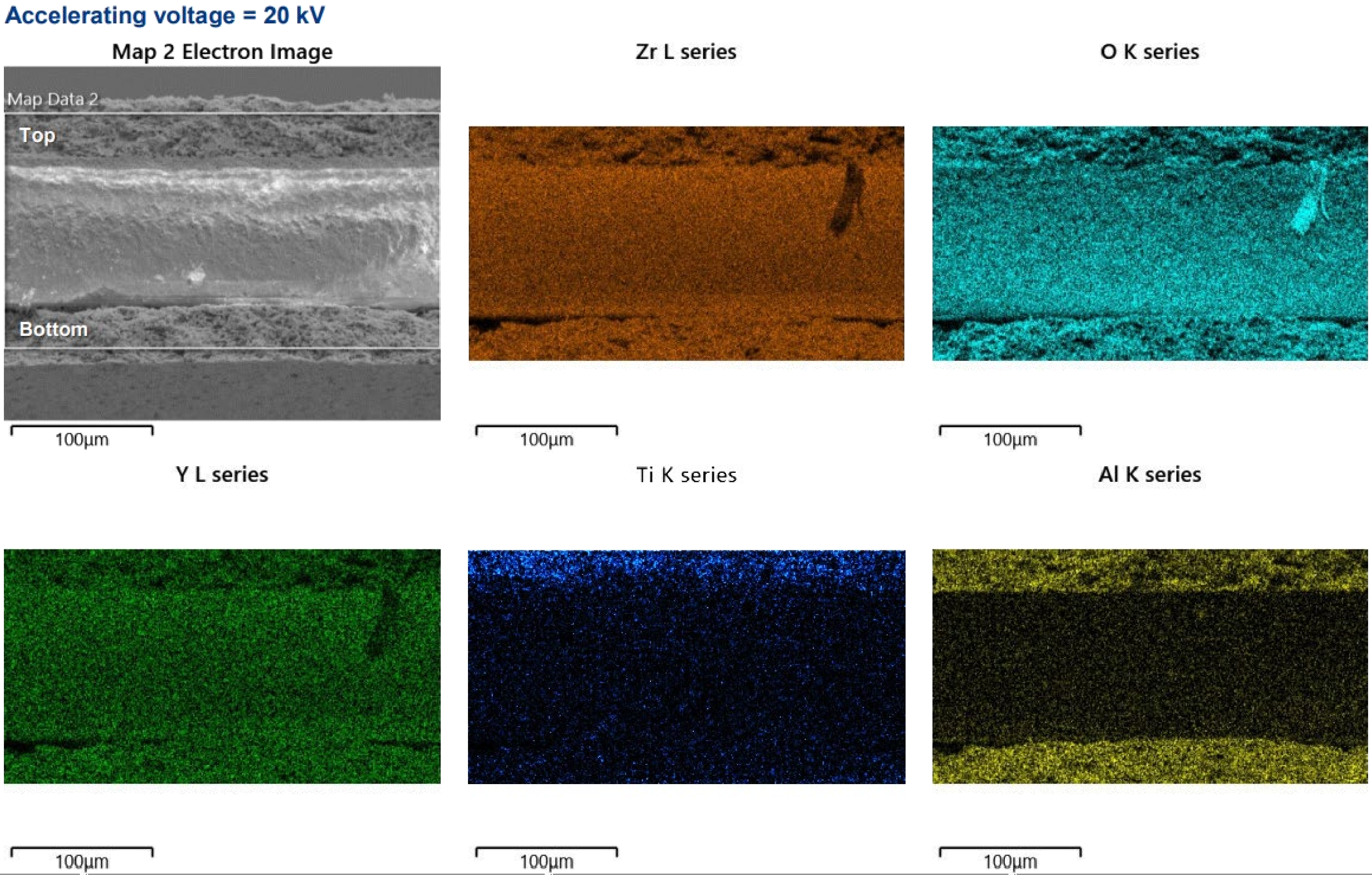
850°C $Al_2TiO_5 \rightarrow Al_2O_3 + TiO_2$

1100°C $Al_2O_3 + NiO \rightarrow NiAl_2O_4$

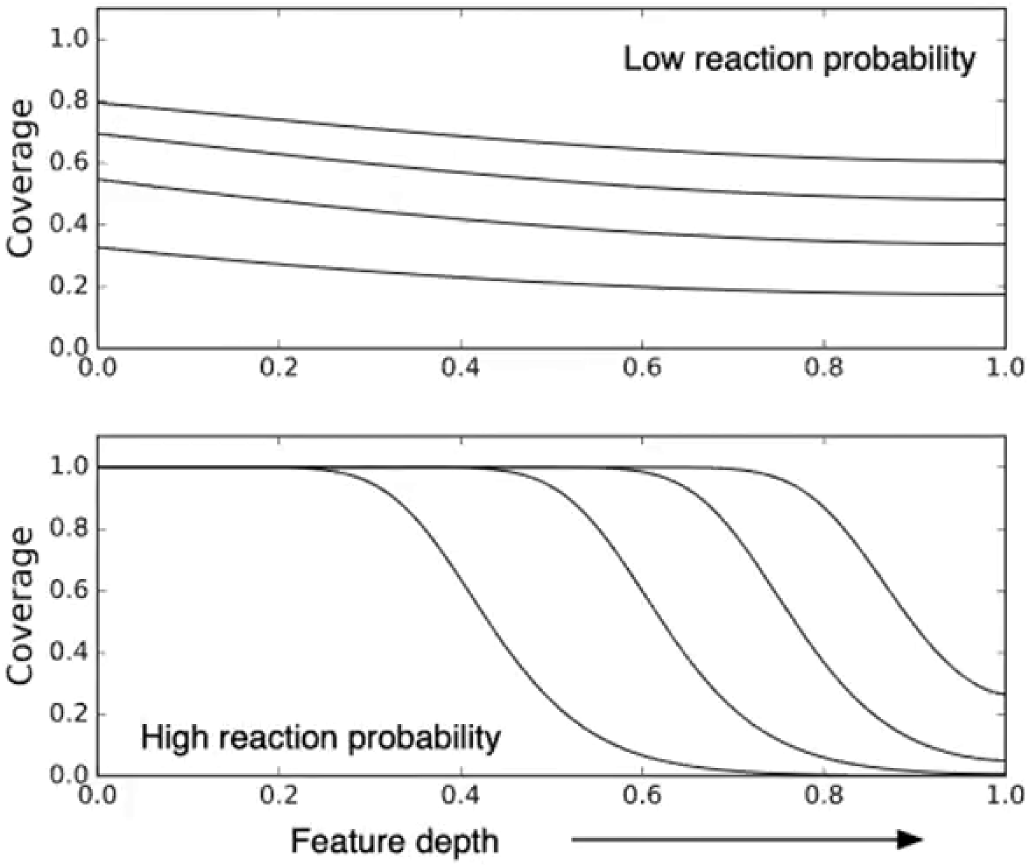
1300°C $TiO_2 + ZrO_2 \rightarrow ZrTiO_4$

* SEM image is of film deposited on flat Si wafer substrates at same time as infiltration into cell

Elemental Mapping of Anchor in Button Cell

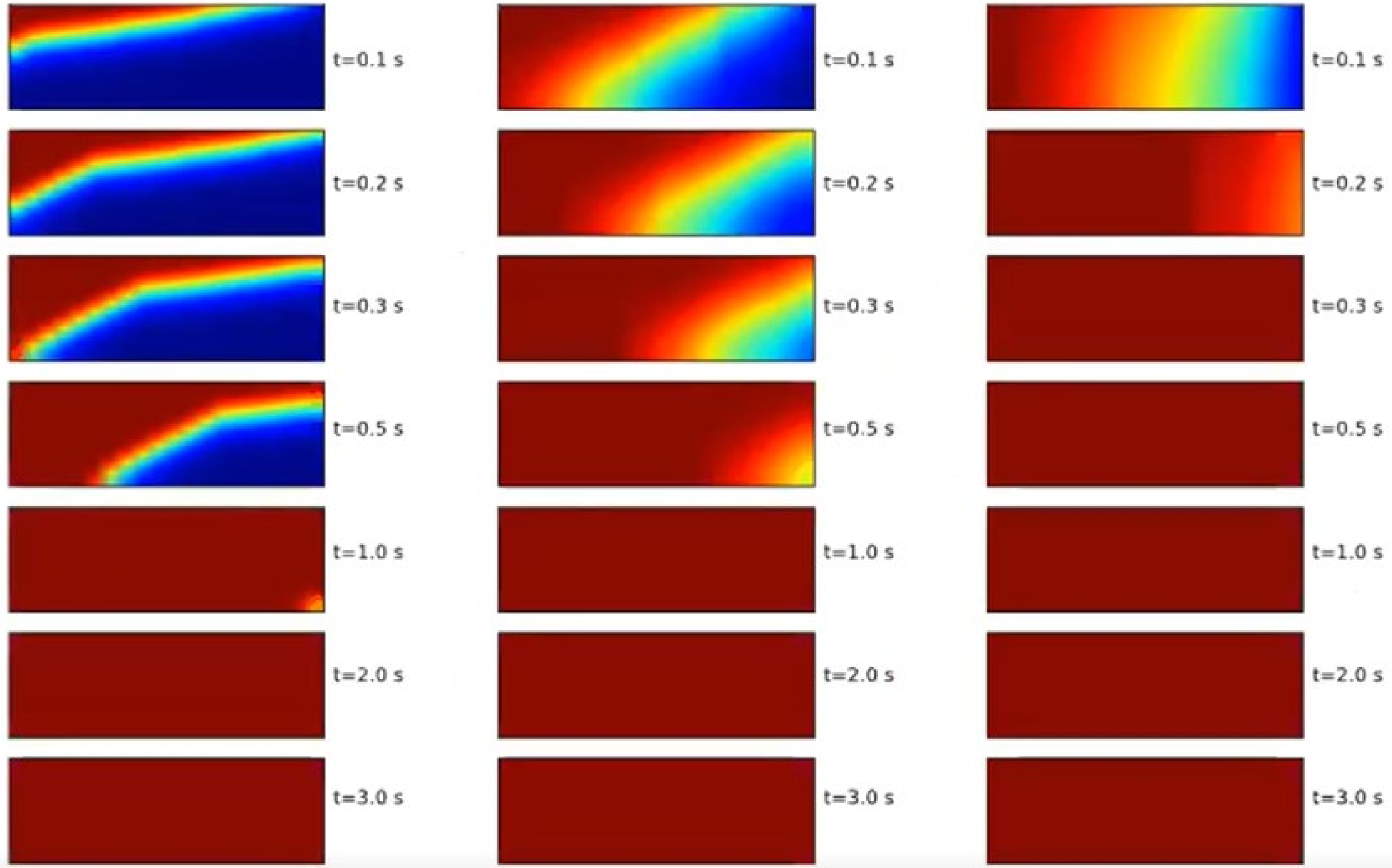


ALD in Porous Materials

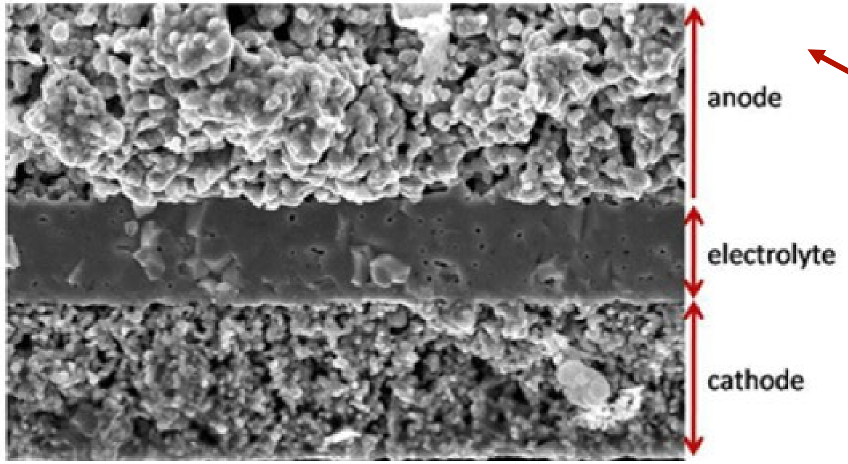


High Aspect Ratio Substrate

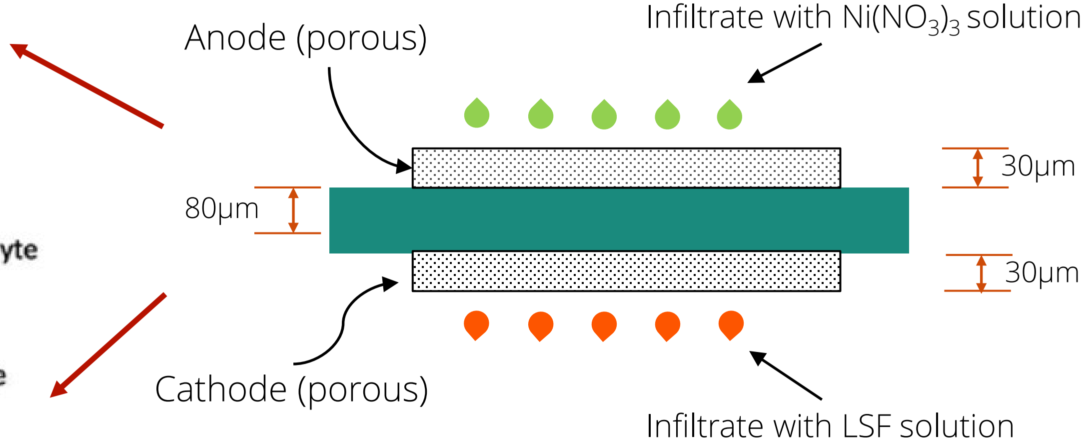
Decreasing sticking probability



Cell Fabrication: Electrode Infiltration – Post ALD



Cross-section micrograph showing a typical cell structure



Anode infiltrated with $Ni(NO_3)_3$ solution and heated to 1300 °C

Cathode infiltrated with LSF solution followed by drying.

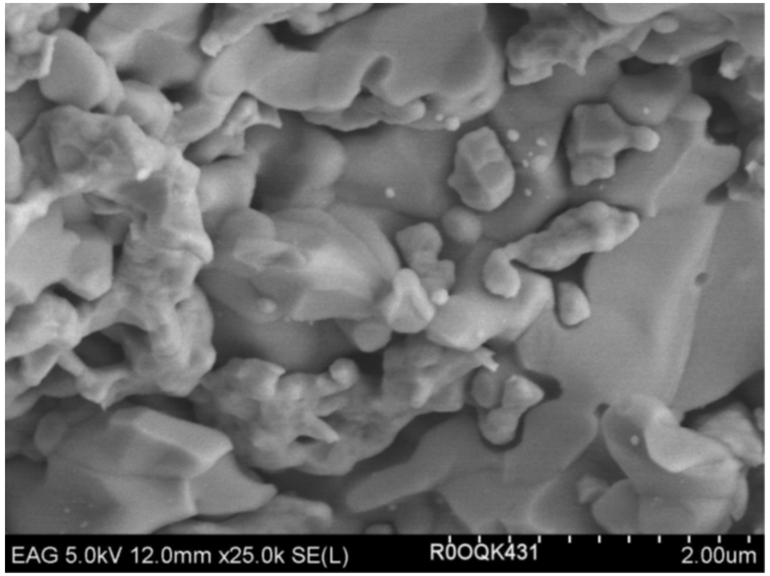
Further testing with cells coated by ALD

- Calcinate cell at 1400°C for 1 hour (with a ramp rate of 3°C /min) to activate ALT to form $ZrTiO_4$
- NiO added to anode with 4.5 M $Ni(NO_3)_2$ solution for 8 cycles. And then calcinate cell at 1100°C for 1 hour (with a ramp rate of 3°C/min) to activate ALT to form $NiAl_2O_5$
- $La_{0.8}Sr_{0.2}Fe_2O_3$ added to cathode using 15 cycles of wet infiltration. And then calcinate cell to 850°C to form perovskite phase
- Infiltrate another 7 cycles of $Ni(NO_3)_2$ solution to load the same amount of Ni on the anode as the uncoated cell (total 15 infiltrations)
- Complete cell and test by measuring performance at 700°C, heating to 800°C for 1 hour, re-testing at 700°C, then heating to 900°C for 1 hour, and re-testing at 900°C

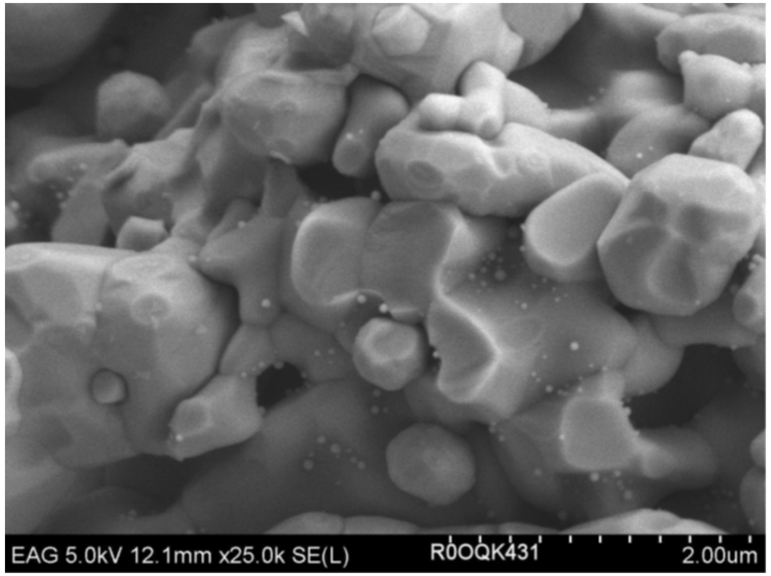
Cell infiltrated by $Ni(NO_3)_3$ on the anode side and heated up to 1100℃

1100°C	$Al_2O_3 + NiO \rightarrow NiAl_2O_4$
1300°C	$TiO_2 + ZrO_2 \rightarrow ZrTiO_4$

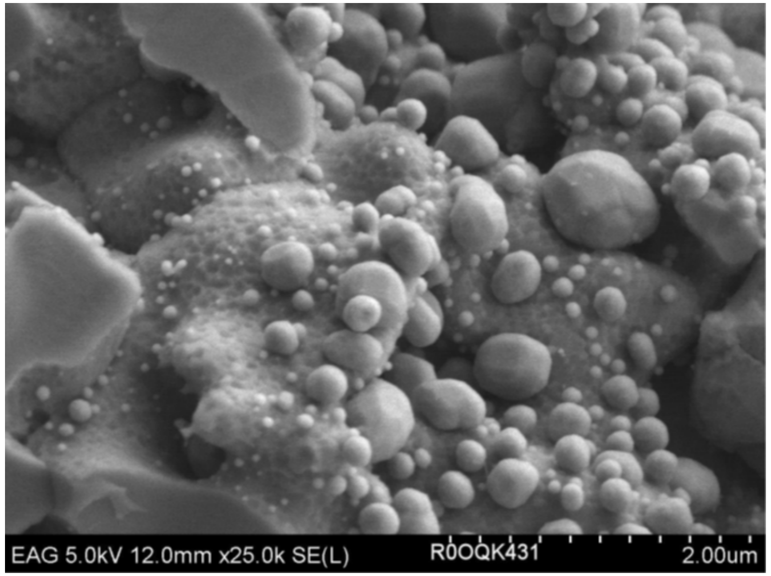
SEM Cross-Section of Electrode Before and After Stressing



Before Stressing

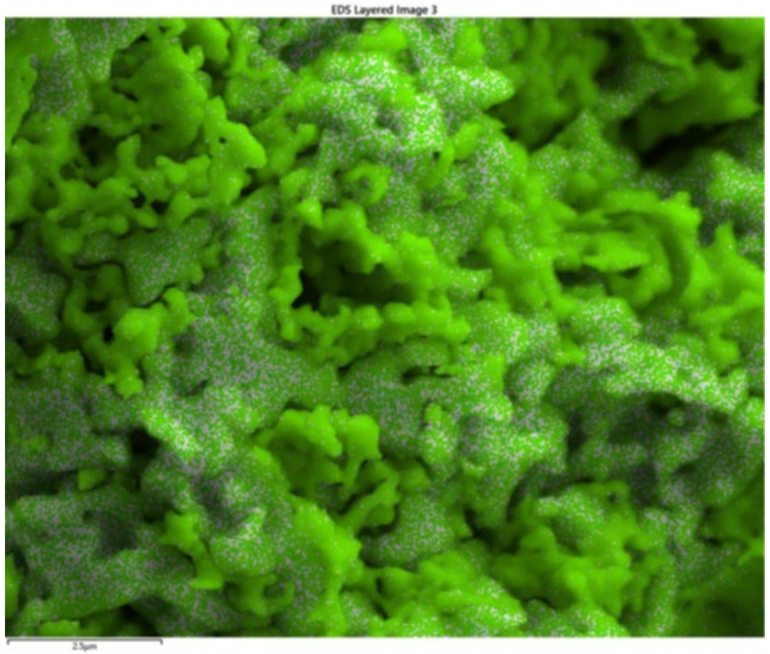


Without ALD coating

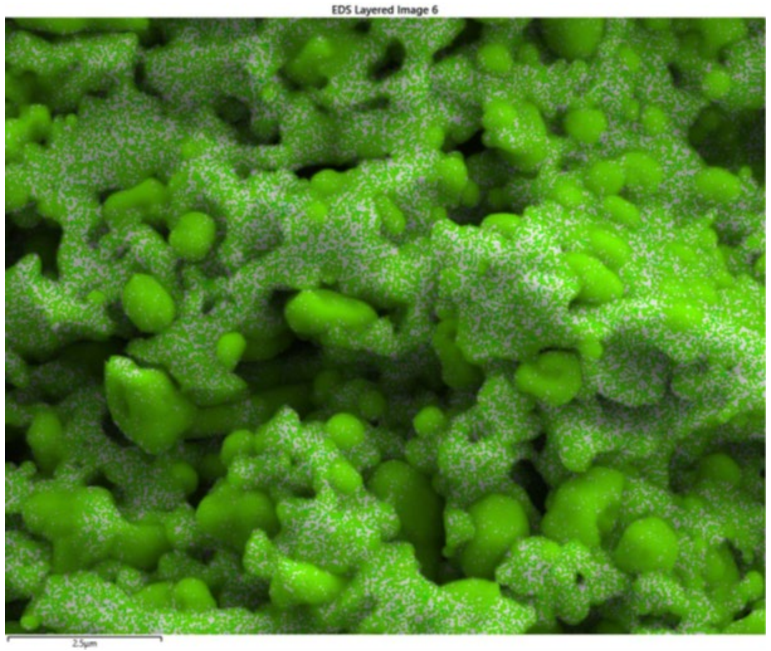


With ALD coating

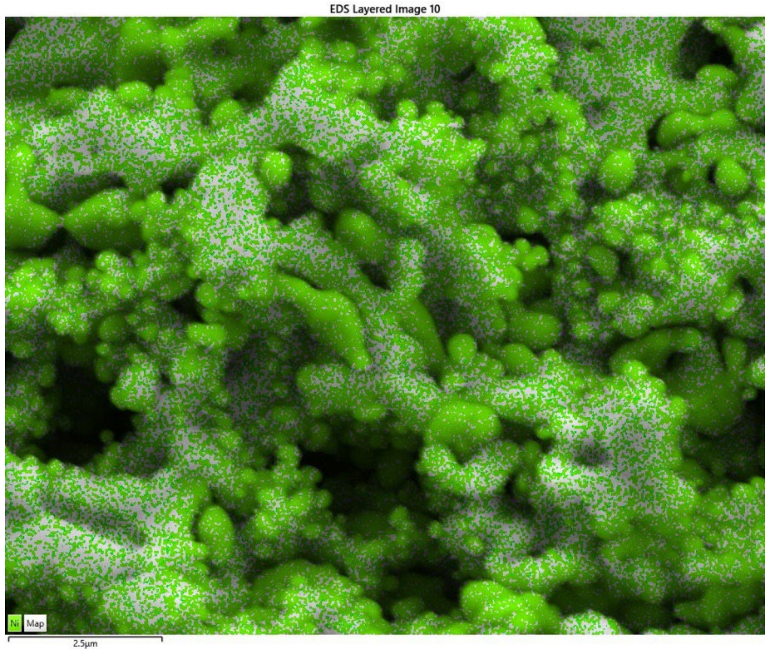
Addition of Ni EDS Overlay



Before Stressing

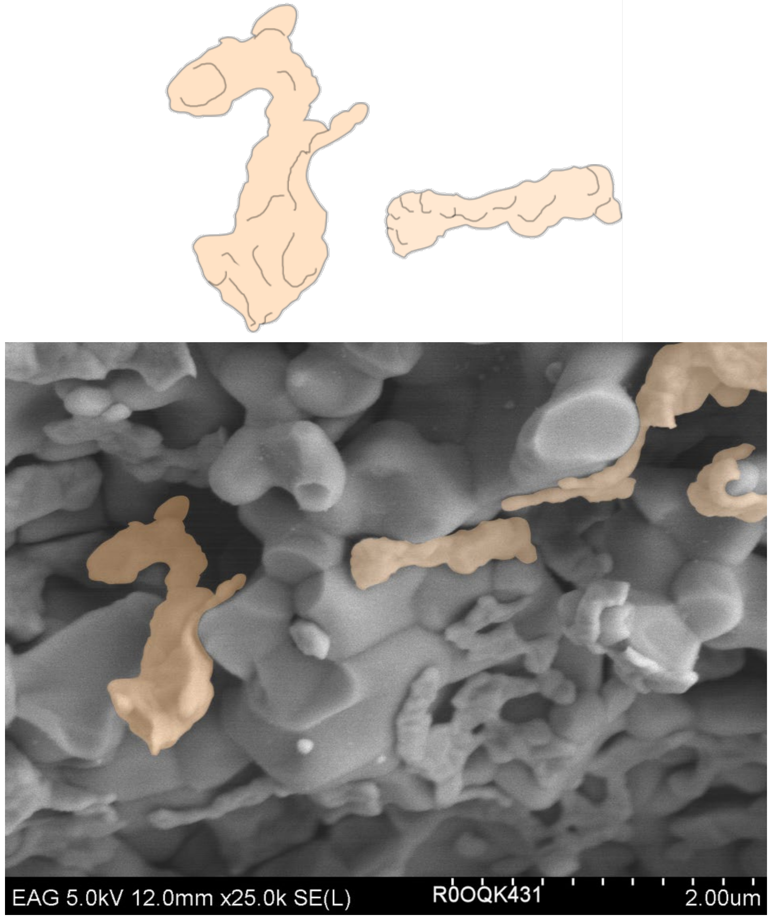


Without ALD coating

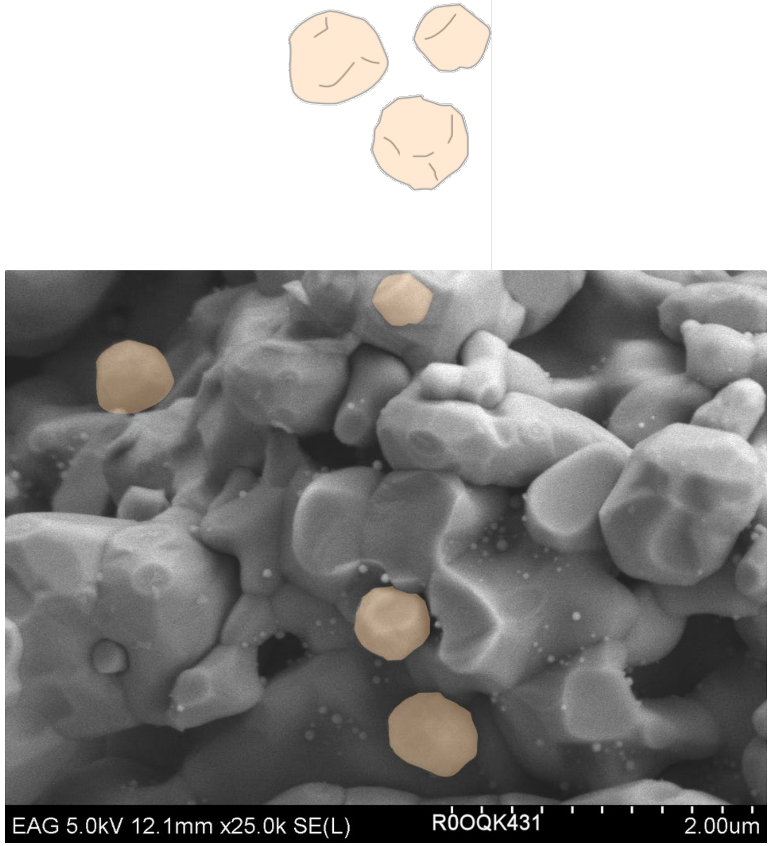


With ALD coating

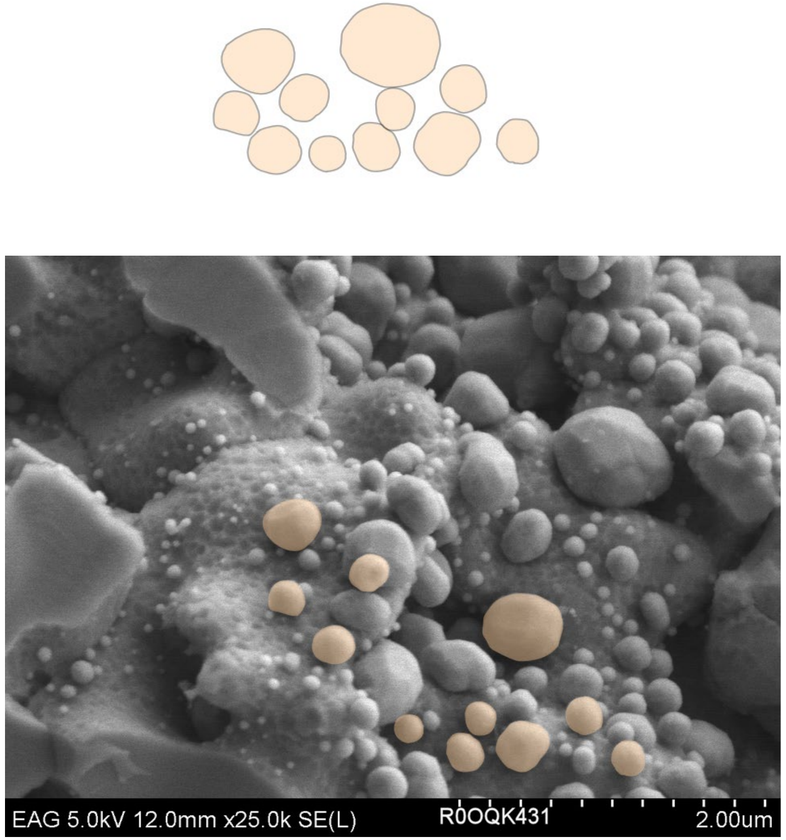
Ni in the Electrode Before and After Stressing



Before Stressing

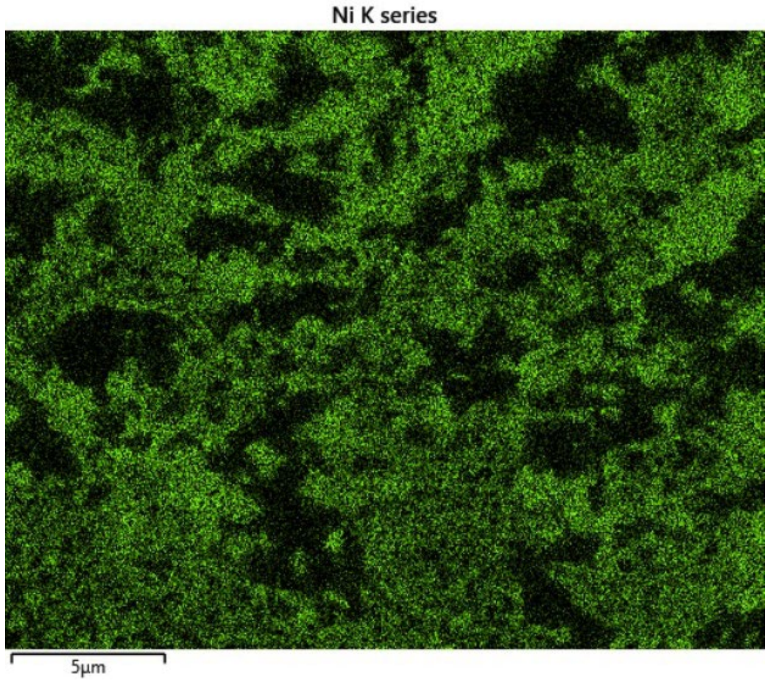


Without ALD coating

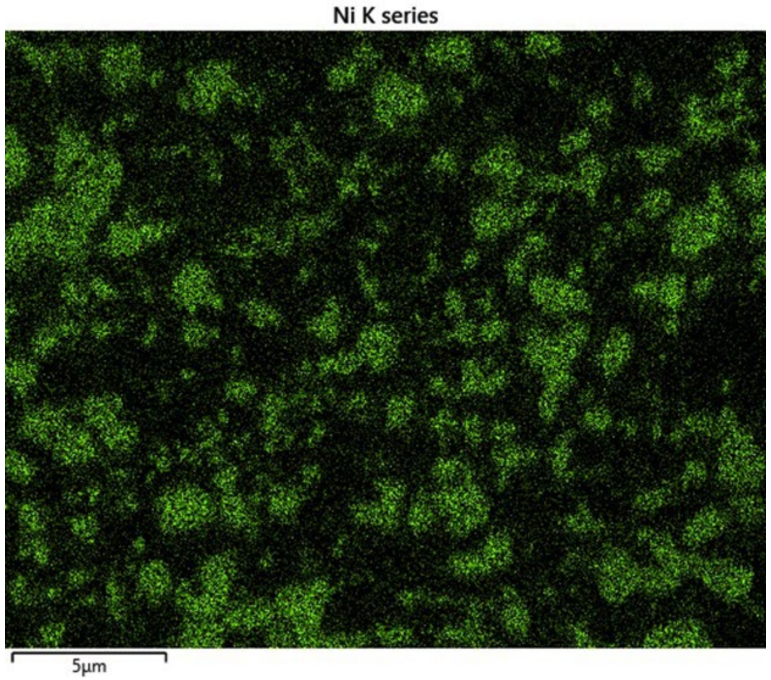


With ALD coating

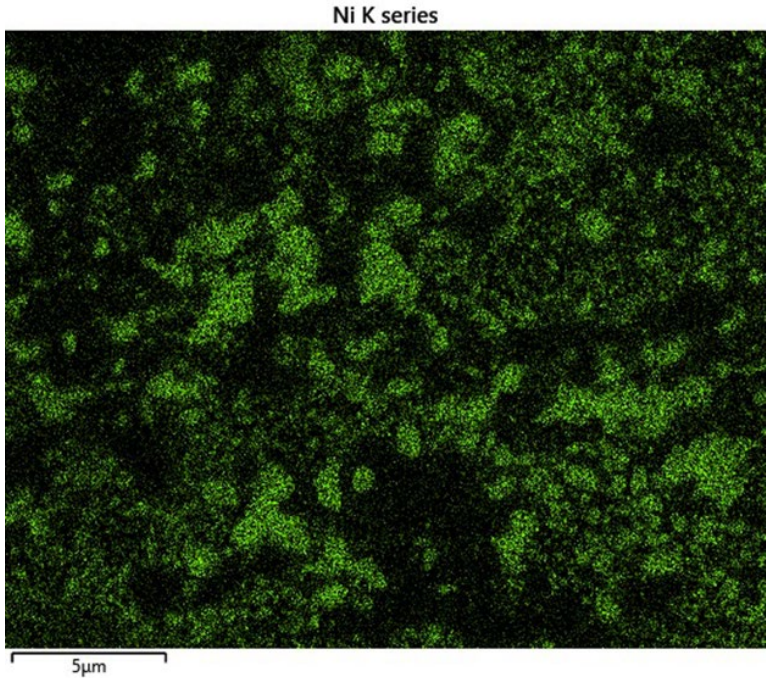
And At the Macro Level



Before Stressing

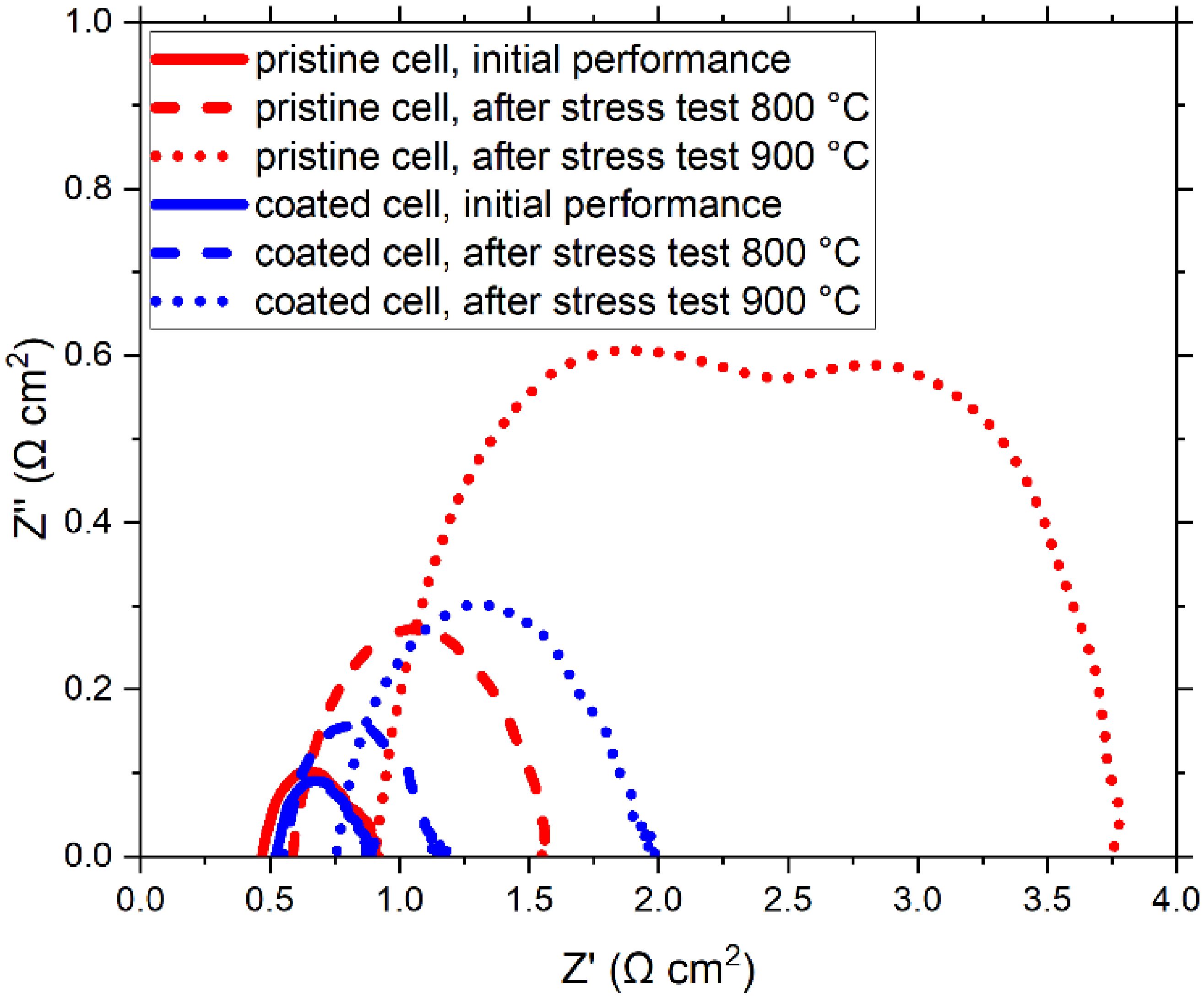


Without ALD coating



With ALD coating

Electrochemical Impedence Spectra Confirmation



Early Success!

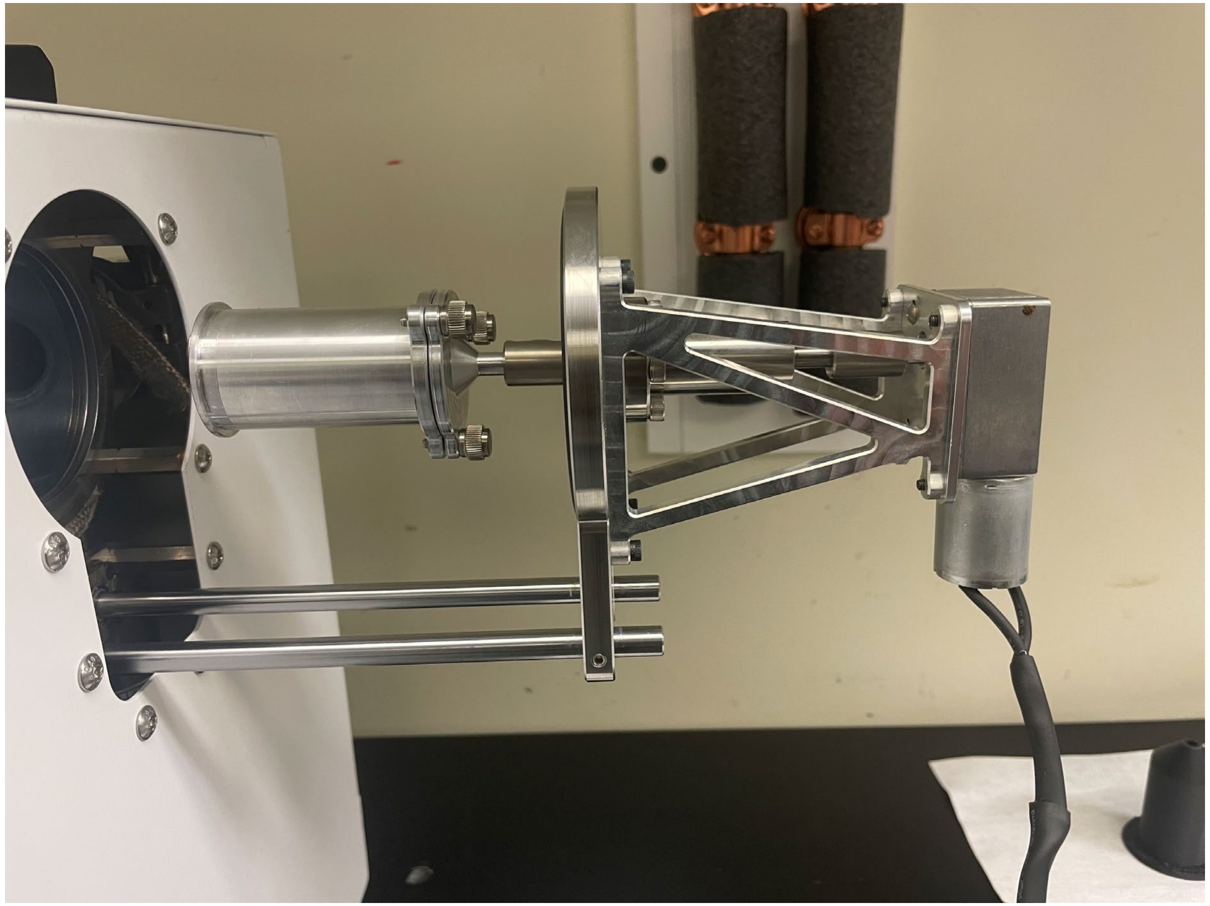
Cells were tested in fuel-cell mode using humidified H_2 (3% H_2O)

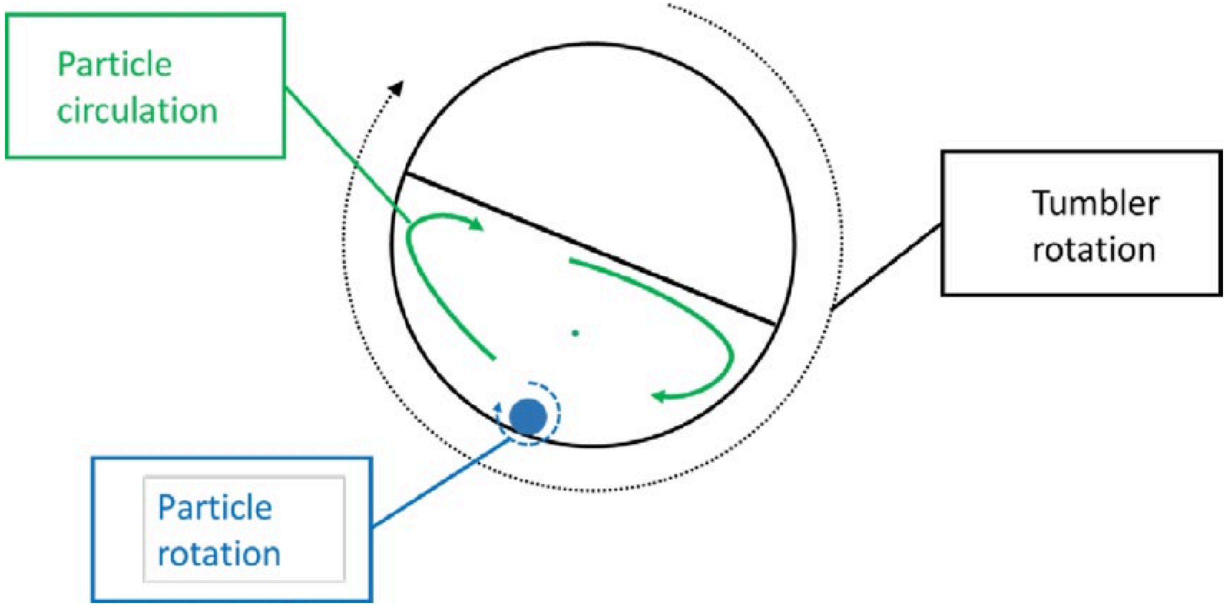
Next Steps

1. Optimize and demonstrate the repeatability of the anchoring by ALT in Ni-YSZ button cells ensuring
   a) A process in which all the nickel is properly anchored,
   b) 5 identical cells show the same performance preventing nickel migration and agglomeration

2. Develop and validate the performance of ALD within current SOEC manufacturing

Particle ALD for Scale Up





As the tumbler rotates, the powder material circulates, and individual particles rotate exposing all surfaces for even ALD coating

Conclusion

- We developed an ALD process for depositing ALT conformally on high aspect ratio surfaces

- We successfully demonstrated that a thin ALT anchor coating deposited by ALD significantly enhances the thermal stability of Ni in an infiltrated Ni-YSZ electrode button cell and have on-going experiments to further validate the results

- We are working with SOEC manufacture OxEon Energy to evaluate scale up through a method compatible with current processing

OxEon energy
Beyond Current Potential

Acknowledgements

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

Program Managers Debalina Dasgupta and John Homer

Penn UNIVERSITY of PENNSYLVANIA

OxEon energy Beyond Current Potential

Collaborators Prof. John Vohs (UPENN), Zhouming Feng (UPENN), Dr. Jenna Pike (OxEon) and Dr. Elango Elangovan (OxEon)