Improving Ni-based SOFC Anode Resilience and Durability through Secondary Phase Formation

DE-FE0031125

Program Officer: Joe Stoffa

PI: Professor Rob Walker, PI
Department of Chemistry and Biochemistry

Co-PI: Professors Stephen Sofie and Roberta Amendola
Department of Mechanical and Industrial Engineering

Improving Ni-based SOFC Anode Resilience and Durability through Secondary Phase Formation

DE-FE0031125

Program Officer: Joe Stoffa

DOE Merit Program Review
29 April – 1 May, 2019
Crystal City, VA

2° Phase Formation in Ni-based SOFC Anodes

$$NiO + 8\text{-}YSZ + Al_2TiO_5 \longrightarrow ??$$

ALT added originally as a sintering aid and to match TCE of NiO and YSZ

2° Phase Formation in Ni-based SOFC Anodes

$$NiO + 8\text{-}YSZ + Al_2TiO_5 \longrightarrow ??$$

$$NiO + 8YSZ + ALT \longrightarrow NiO + c\text{-}YSZ + \boxed{Zr_5Ti_7O_{24}} + \boxed{NiAl_2O_4}$$

Findings:

- ALT-doped anode materials are stronger
- 2° phases segregate – true for mechanically mixed and infiltrated
- ALT is a sintering aid (~90% theoretical density of NiO/YSZ/ALT mixtures)
- 2° phases appear to serve different functions
- Electrochemical degradation is slowed with ALT
- Anodes appear to be less susceptible to carbon accumulation (with CH_4)

Project Objectives

Discoveries are enticing but many questions remain re: strategy's viability…

Project Objectives

Discoveries are enticing but many questions remain re: strategy's viability…

Improving Ni-based SOFC Anode Resilience and Durability through Secondary Phase Formation

- *Refine methods* used to fabricate ALT enhanced anodes into bi-layer anode supports to achieve higher power densities;
- *Compare the effects* of adding ALT mechanically to Ni-YSZ powders prior to anode fabrication with adding ALT through infiltration and co-infiltration of YSZ scaffolds;
- *Test the durability and resilience* of these enhanced anodes to electrochemical and environmental redox cycling and thermal stresses commonly encountered in functioning SOFCs; also test carbon tolerance;
- *Work closely with SOFC manufacturer(s)* to transfer knowledge learned in our laboratories into full sized cell fabrication and testing.

Project Objectives

Discoveries are enticing but many questions remain re: strategy's viability…

Improving Ni-based SOFC Anode Resilience and Durability through Secondary Phase Formation

Today…

- Material consequences of adding ALT to Ni-YSZ cermets
- Mechanical consequences of adding ALT to Ni-YSZ cermets
  - Fracture toughness
  - Hardness
- Electrochemical performance of ALT enhanced Ni-YSZ anodes
- Commercial partnering to independently test anodes with ALT additives

The short version: ALT forms segregated phases with NiO ($NiAl_2O_4$) and YSZ ($Zr_5Ti_7O_{24}$) with Al_2O_3 nanoparticle decorated Ni following reduction; ALT enhanced anodes have improved hardness and fracture toughness in oxidized and reduced forms; ALT enhanced anodes show two-fold improved resilience to redox cycling *and* improved carbon tolerance with CH_4; NDA with Atrex Energy, Inc.

Some details

- Mechanical strength testing with reduced and oxidized coupons
- All YSZ is Tosoh 8%; NiO from various sources
- Mechanically mixed = ball milling; infiltrated = $Al(NO_3)_3$ and Ti lactate
- Most tests with internally fabricated, electrolyte supported cells
- All electrochemical testing at 800˚C with dry fuels

Outcomes (to date)

Amendola, R., McCleary, M. ”Effect of Aluminum Titanate Doping on the Mechanical Performance of Solid Oxide Fuel Cell Ni-YSZ Anodes” *Fuel Cell: From Fundamentals to Systems*: **17** 862-868 (2017).

M. M. Welander, C. D. Hunt, M. S. Zacharaiasen, S. W. Sofie, and R. A. Walker “*Operando* Studies of Redox Resilience in ALT Enhanced NiO-YSZ SOFC Anodes” *J. Electrochem. Soc.* **165** (30) F152-F157 (2018).

C. Hunt, M. Zachariasen, D. R. Driscoll, S. W. Sofie, R. A. Walker “Degradation rate quantification of solid oxide fuel cell performance with and without Al_2TiO_5 addition” *Int. J. Hydrogen Energy* **43** (32) 15531-15536 (2018).

McCleary, M., Amendola, R. ”Reduction Kinetics of Undoped and Aluminum Titanatne Doped NiO-YSZ Solid Oxide Fuel Cell Anodes” *Ceramics International*: **44** 15557-15564 (2018).

M. M. Welander, M. S. Zachariasen, S. W. Sofie, and R. A. Walker “Enhancing Ni-YSZ Anode Resilience to Environmental Redox Stress with Secondary Phases” *ACS Advanced Energy Materials* **1** (11) 6295-6302 (2018).

D. B. Drasbaek, M. L. Traulsen, R. A. Walker, and P. Holtappels “Operando Raman spectroscopy as a tool to investigate coking behavior of SOFC anode materials” *Fuel Cells* **in press** (2019).

M. M. Welander, M. S. Zachariasen, S. W. Sofie and R. A. Walker “Mitigating Carbon Formation with Al_2TiO_5 Enhanced Solid Oxide Fuel Cell Anodes” *J. Phys. Chem. C* **in press** (2019).

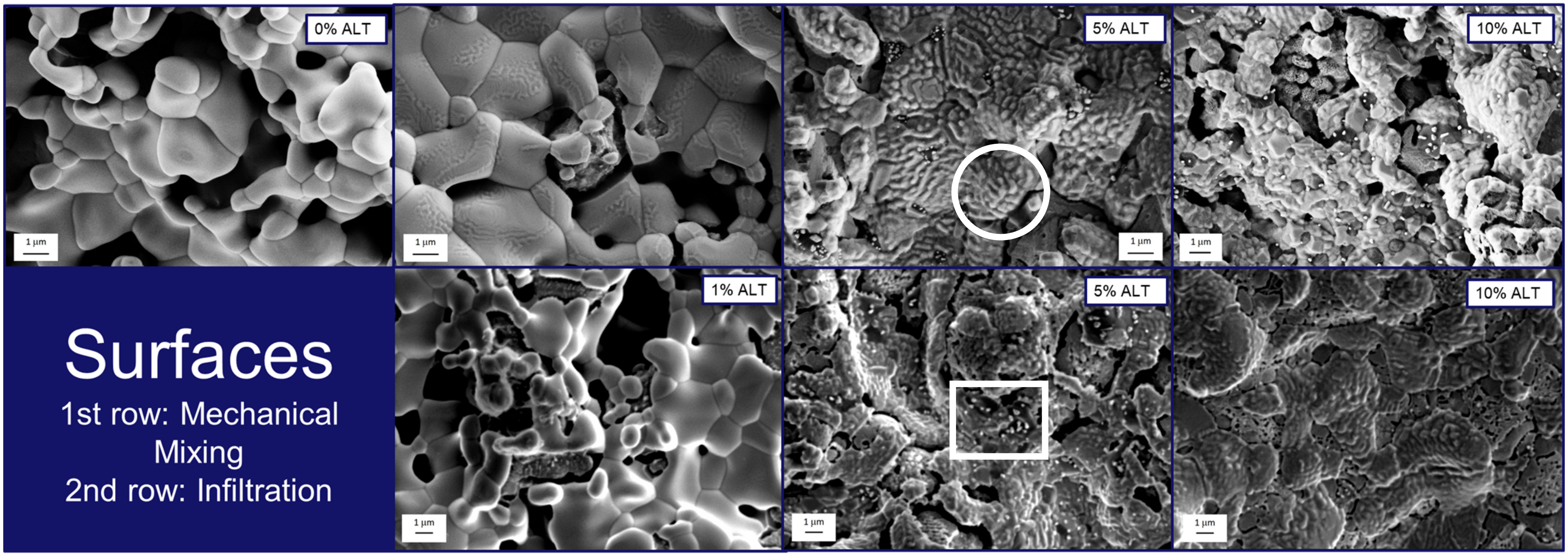
Personnel:

1 Ph.D. conferred (Dr. Madison McCleary); 2 in progress (Martha Welander & Kyle Allemeier)

1 MSE Conferred (John Kent); 1 in progress

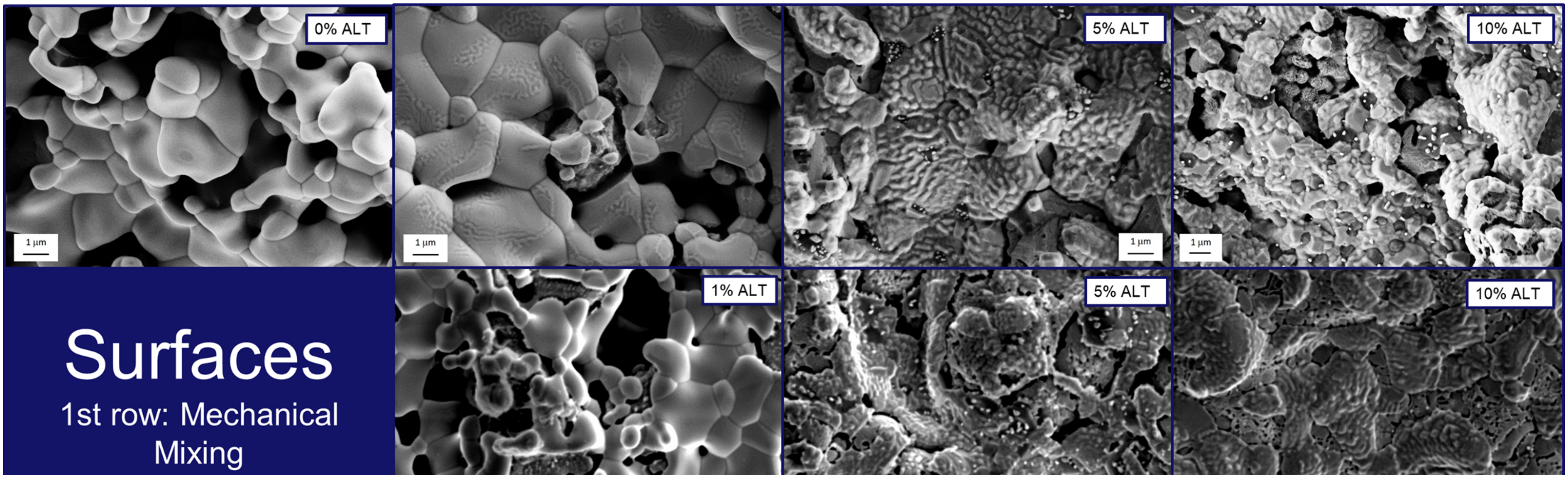
3 B.Sc. conferred (1 to USMC; 1 into Ph.D. program in Materials Science (Boise State), 1 to ZAF Energy)

Material Composition - mechanically mixed and infiltrated

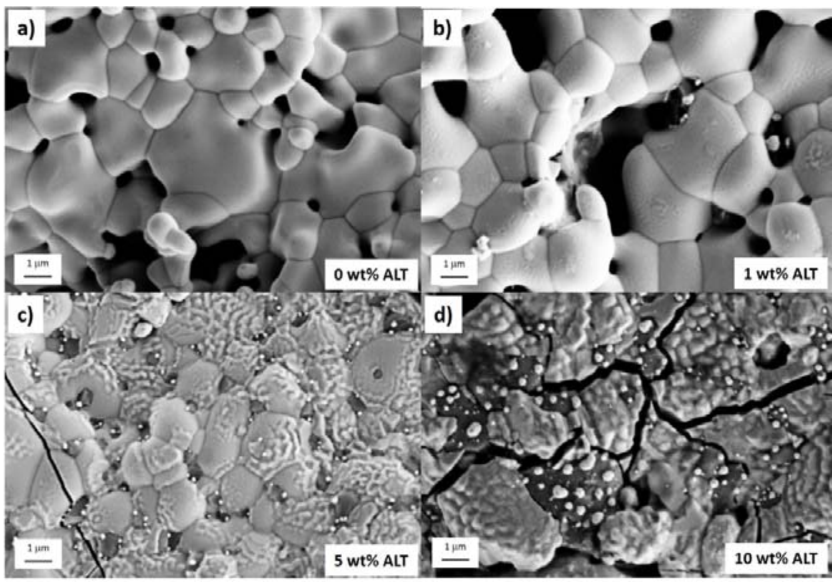


- Oxidized surfaces similar for both doping methods
- Secondary phases present after ALT doping
- Rough phase (circled) and small particle phase (boxed)
- Scale bar = 1 µm

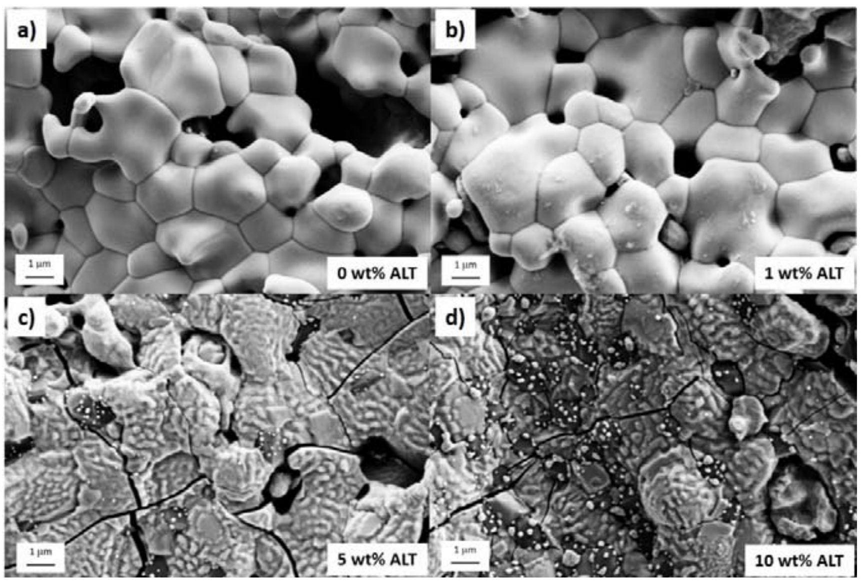
Material Composition – redox cycling leads to little material change



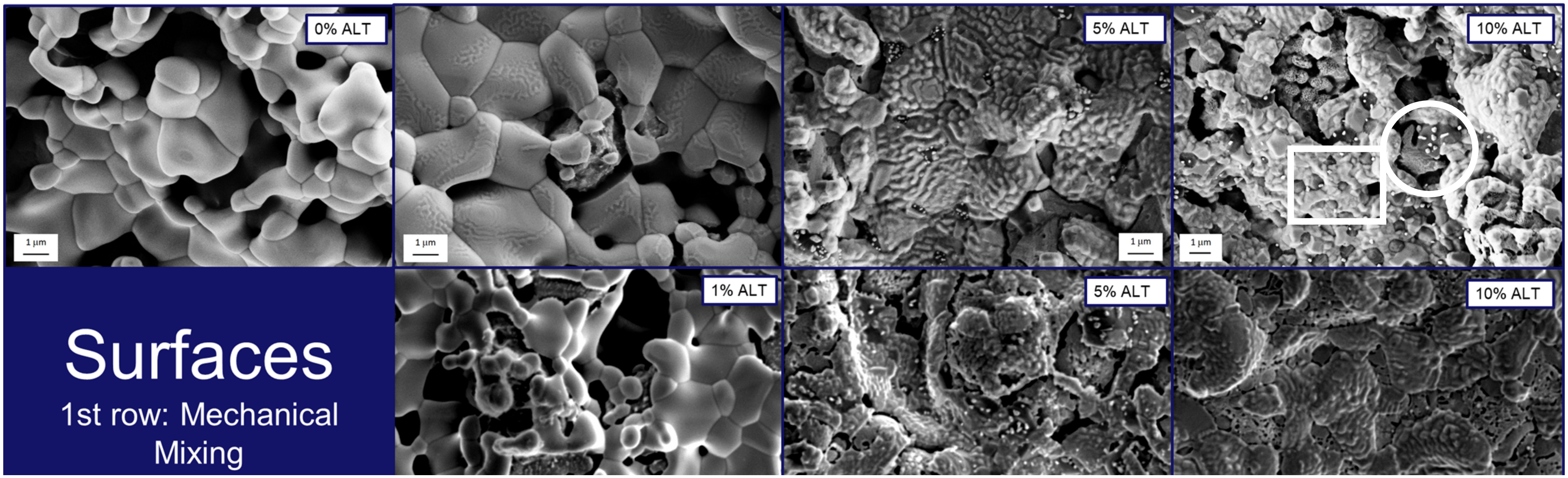
After 1 redox cycle



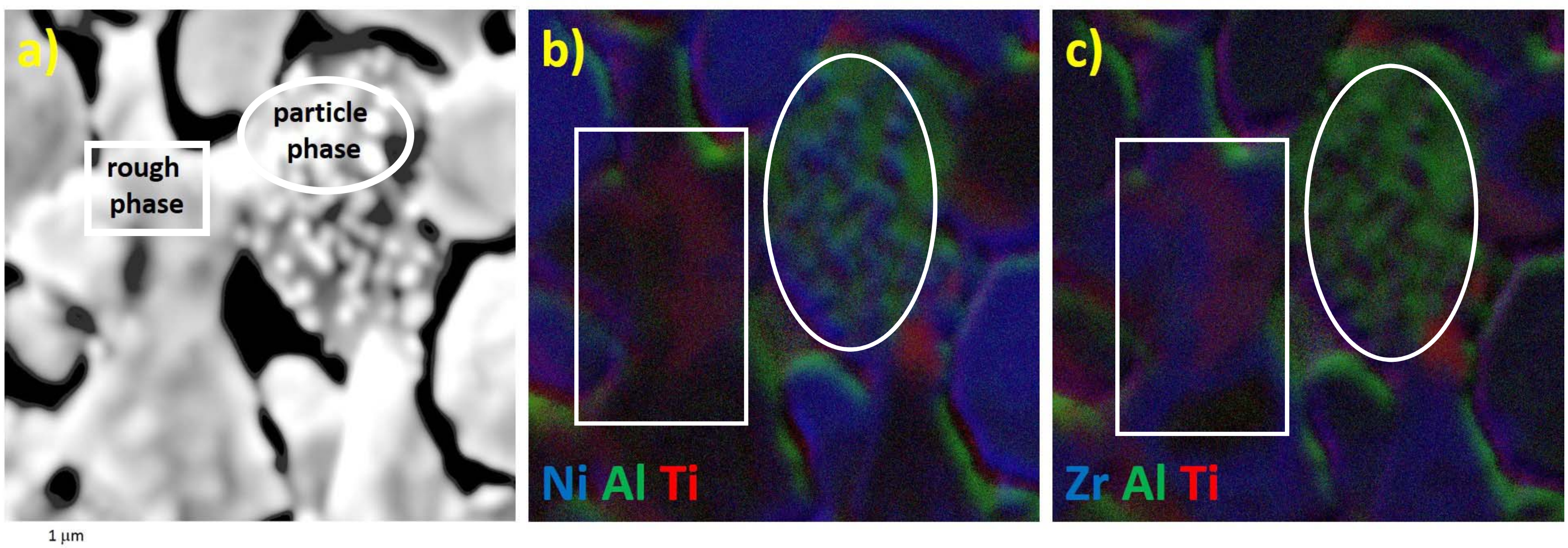
After 5 redox cycles



Material Composition – secondary phase segregation

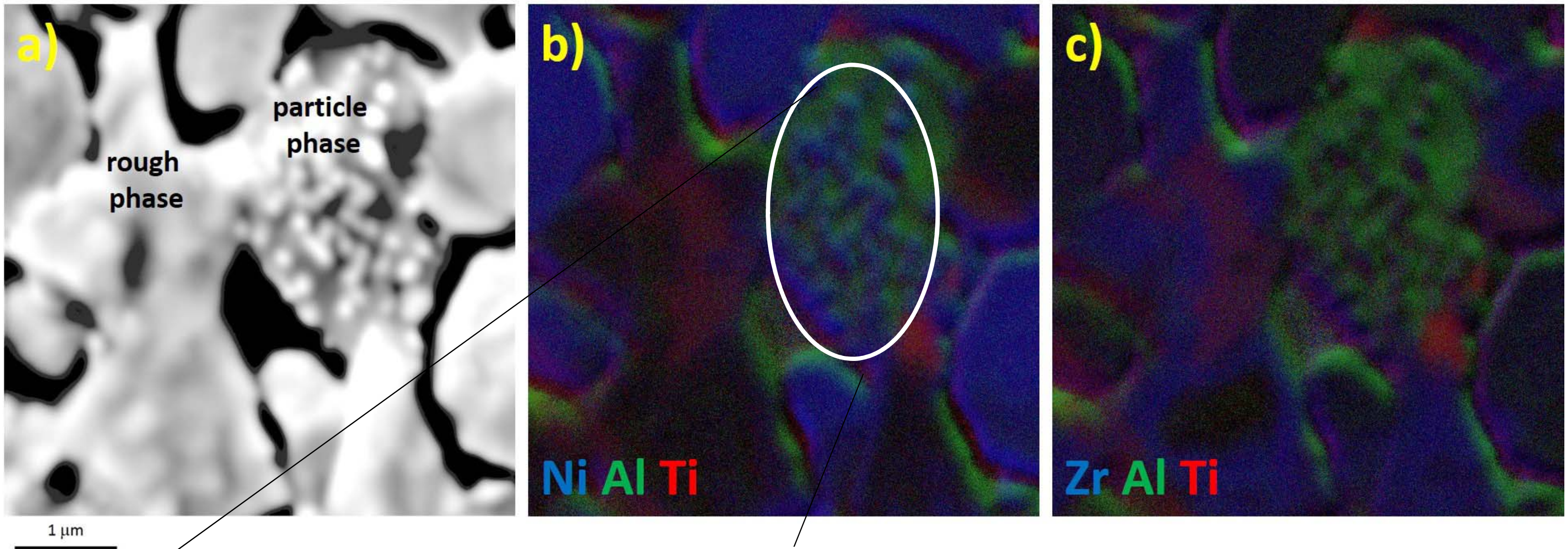


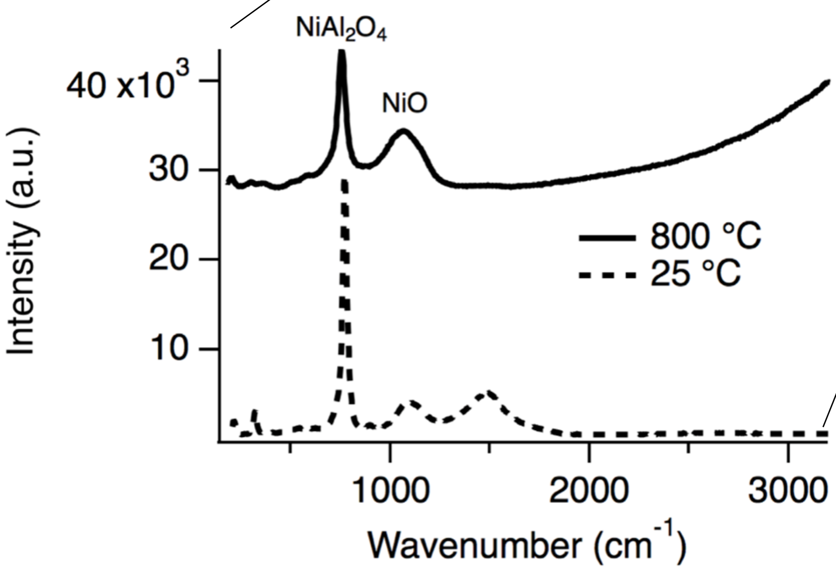
Elemental analysis (nano-Auger) of rough and particle phases (with 10% mechanically mixed)



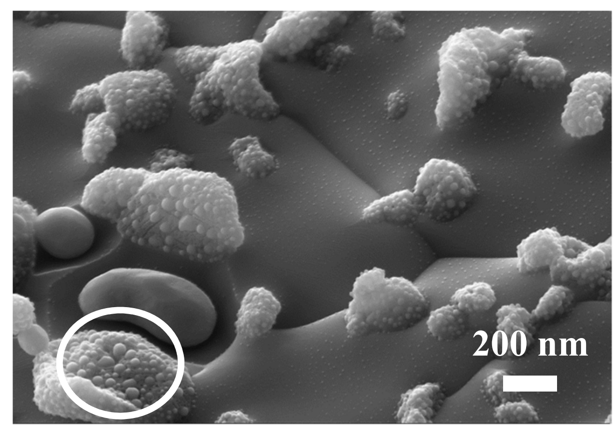
Material Composition

Elemental analysis (nano-Auger) of rough and particle phases (with 10% mechanically mixed)





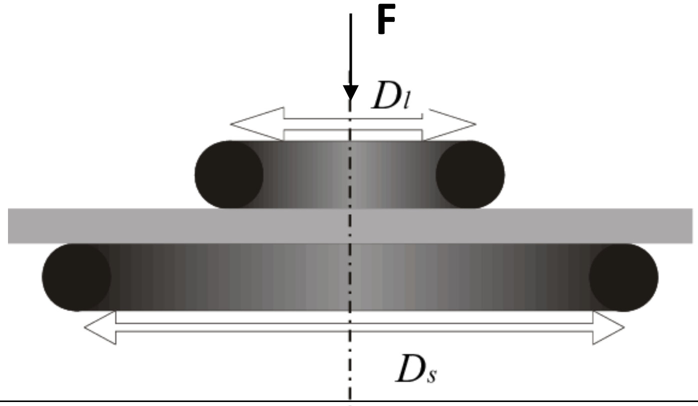
- ALT reacts with NiO-YSZ to form $NiAl_2O_4$
- Upon reduction, $NiAl_2O_4$ forms Ni and nano-Al_2O_3 (measured at (PNNL with TEM and APT))



Mechanical effects of adding ALT to Ni-YSZ - three techniques

- Ring on Ring (equi-biaxial flexure testing)

$$\sigma_f = \frac{3F}{2\pi h^2} \cdot \{(1+\nu) \cdot \frac{D_S^2 - D_L^2}{2D^2} + (1+\nu) ln \frac{D_S}{D_L}\}$$

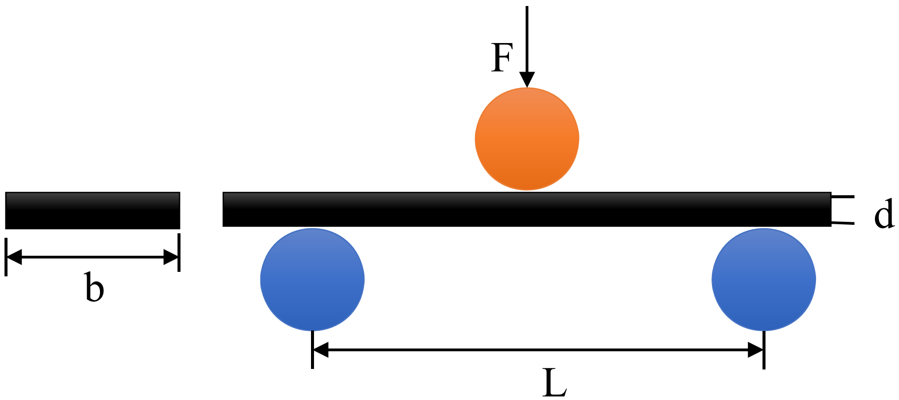


- Modulus of Rupture

$$\sigma = \frac{3FL}{2bd^2}$$

$$p(s) = e^{-(\frac{\sigma}{\sigma_0})^m}$$

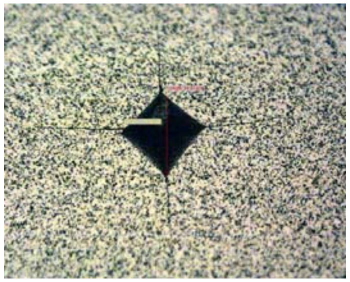
Weibull modulus Equation



- Micro-indentation as strength surrogate (Vickers Hardness)

$$A = \frac{d^2}{2\sin(136^\circ/2)}$$

$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2} \quad [\mathrm{kgf/mm^2}]$$

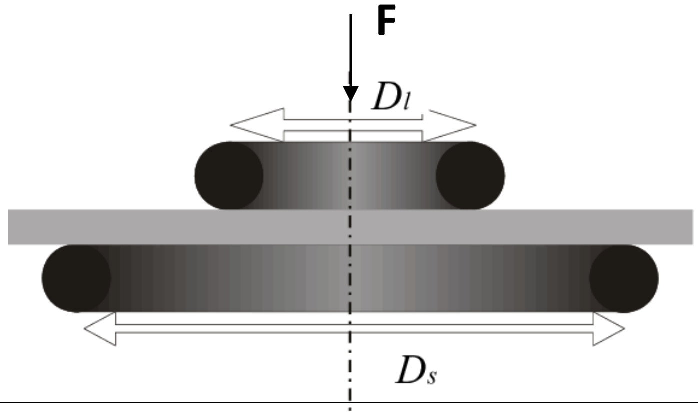


- Rapid assessment
- Non-destructive
- Reuse of same sample after successive thermal/redox cycles

Mechanical effects of adding ALT to Ni-YSZ - three techniques

- Ring on Ring (equi-biaxial flexure testing)

$$\sigma_f = \frac{3F}{2\pi h^2} \cdot \{(1+\nu) \cdot \frac{D_S^2 - D_L^2}{2D^2} + (1+\nu) ln \frac{D_S}{D_L}\}$$

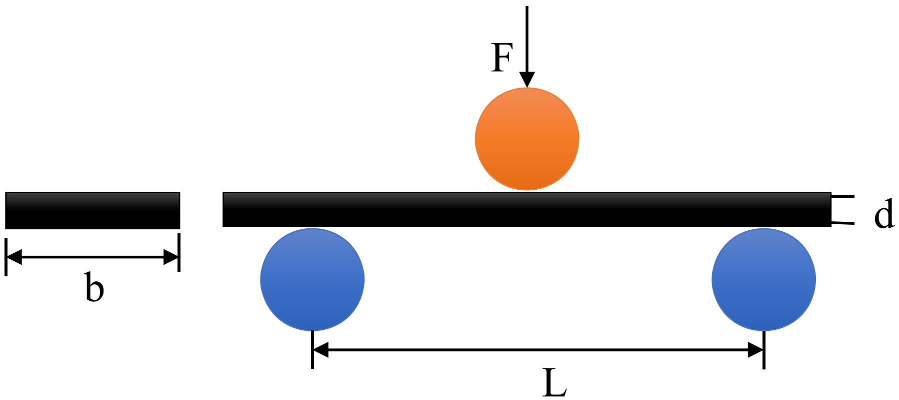


- Modulus of Rupture

$$\sigma = \frac{3FL}{2bd^2}$$

$$p(s) = e^{-(\frac{\sigma}{\sigma_0})^m}$$

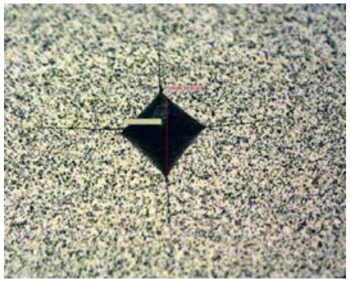
Weibull modulus Equation



- *Micro-indentation as strength surrogate (Vickers Hardness)*

$$A = \frac{d^2}{2\sin(136^\circ/2)}$$

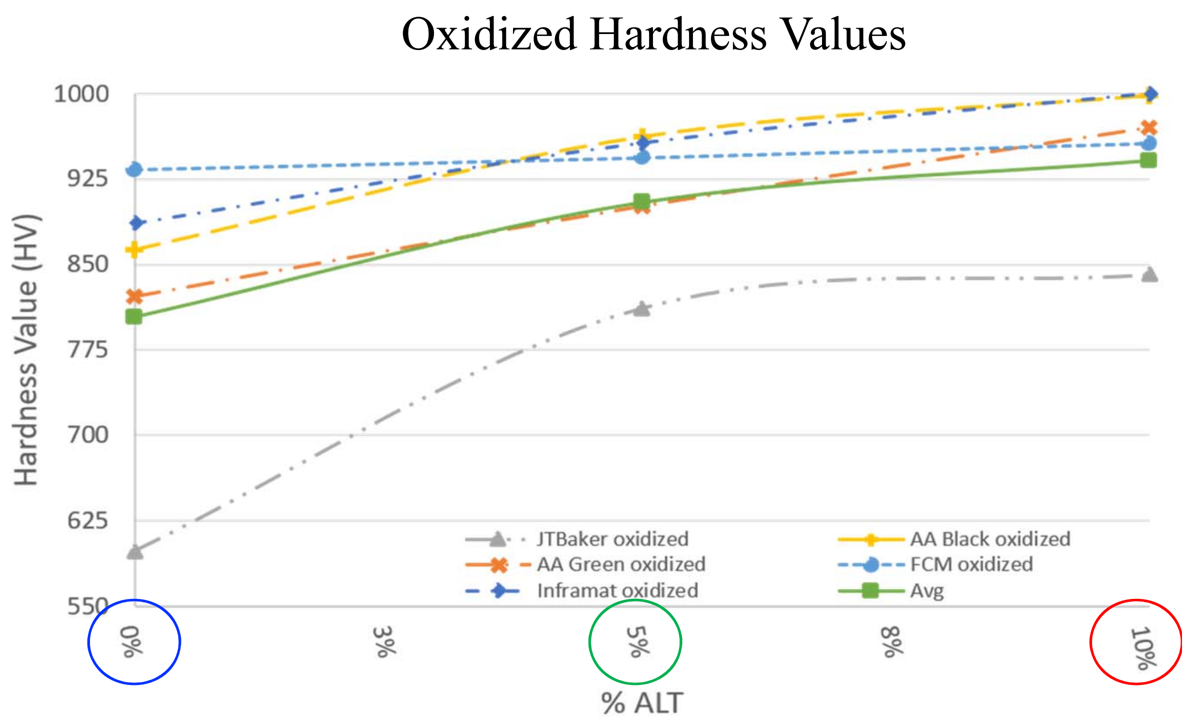
$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2} \quad [\mathrm{kgf/mm^2}]$$

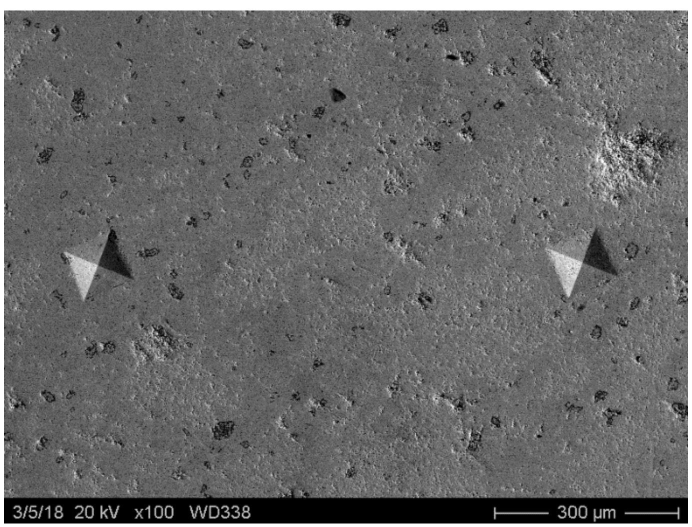


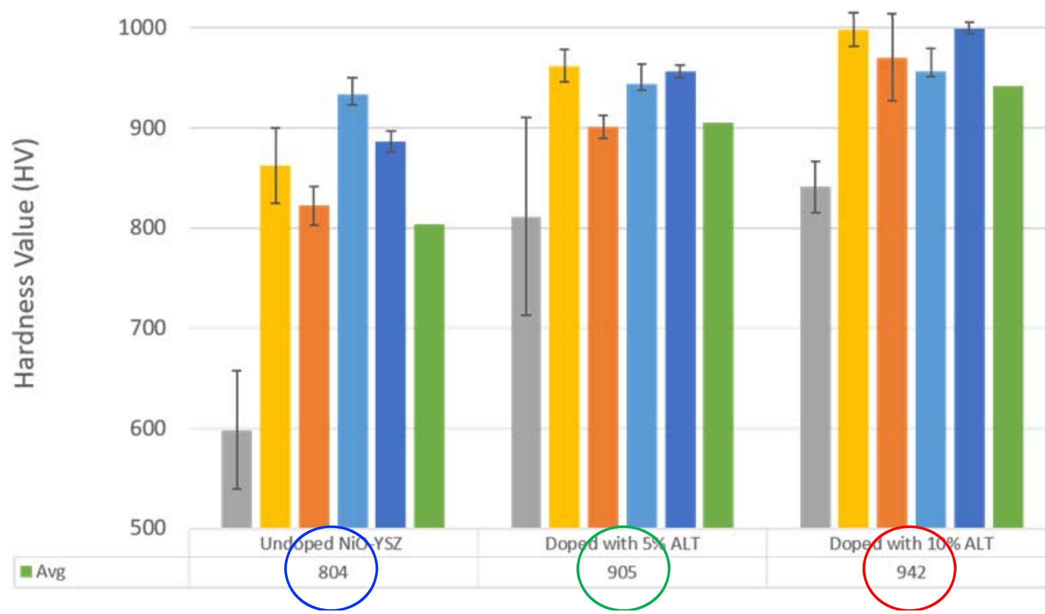
- Rapid assessment
- Non-destructive
- Reuse of same sample after successive thermal/redox cycles

Mechanical effects of adding ALT to Ni-YSZ

- Positive trend in hardness
- NiO precursor effects
- Average 0 / 5 / 10% ALT:
  804 – 905 – 942 HV
- JT Baker (0.88 µm grain size) poor performance
- FCM (1.12 µm grain size) consistently high







Mechanical effects of adding ALT to Ni-YSZ

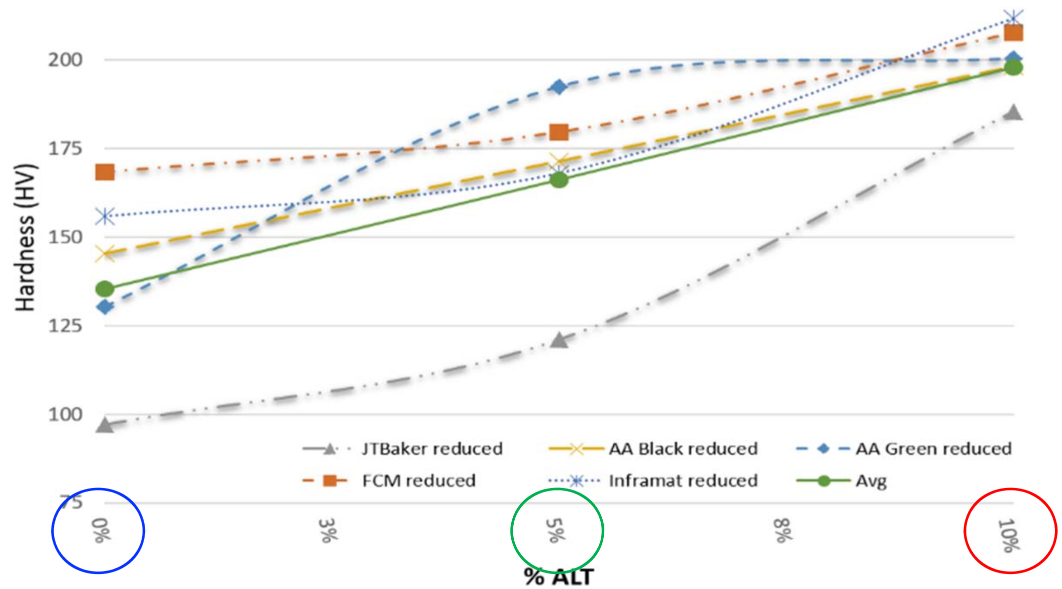
- Positive trend in hardness with ALT loading
- NiO precursor effects
- Average 0 / 5 / 10% ALT:
  135 – 166 – 198 HV

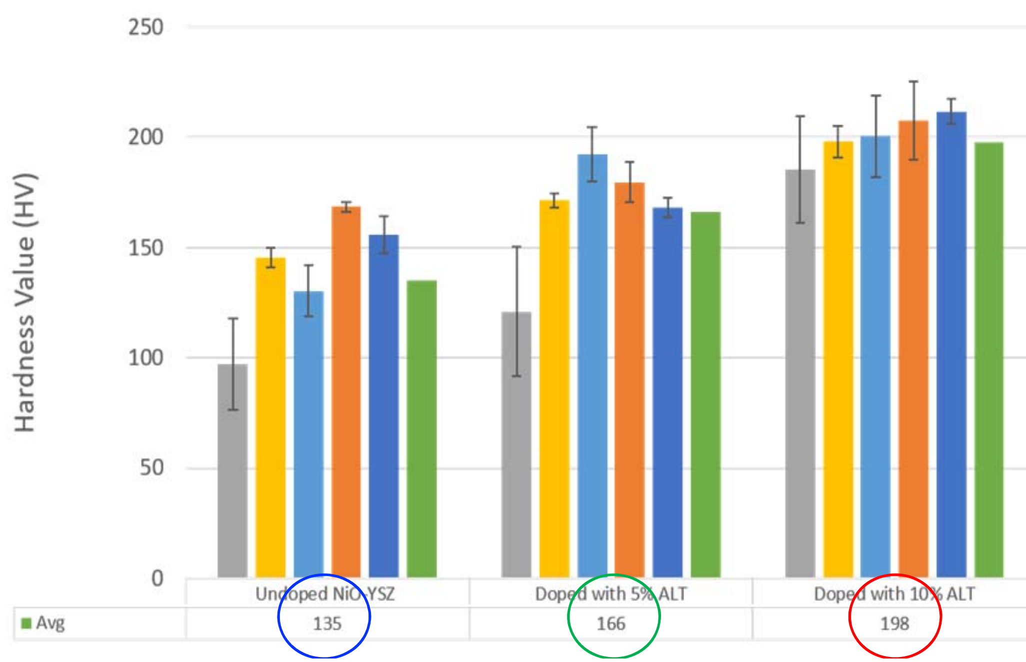
- Hardness scales with modulus of rupture measurements!

Previous Studies	Un-doped (MPa)	5% ALT (MPa)
Ring on Ring	119	157.8
3-pt bending	120	168

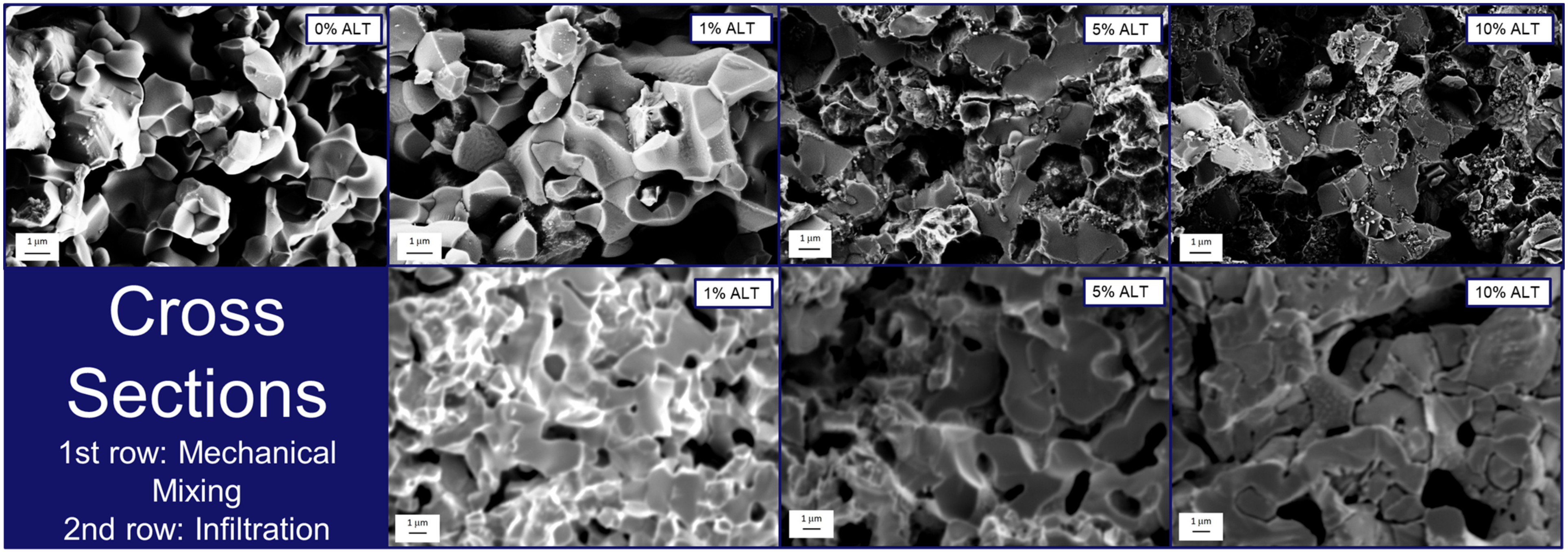
- Trends persist with thermal cycling (5 deep thermal cycles)

Reduced Hardness Values





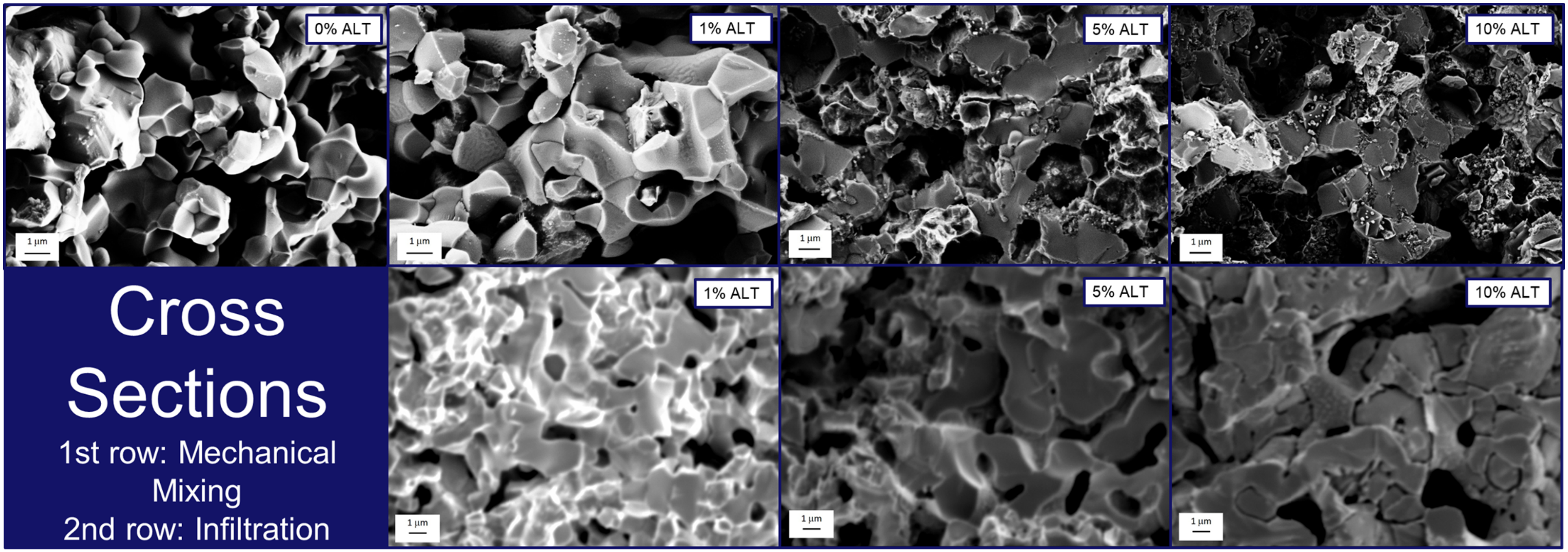
Mechanical effects of adding ALT to Ni-YSZ



(Fractured in reduced state)

- Intergranular fracture (low energy fracture) present for undoped and 1 wt% ALT
- Transgranular fracture (high energy fracture) present for 5 and 10 wt% ALT
- Highest strength at 5 wt% ALT doping for both mechanically mixed and infiltrated samples
- Secondary phases enable the material to better resist the strain buildup due to redox cycling
- 5% ALT loading optimizes balance between strength and electrochemical performance
- Benefits transfer from the bulk materials (2 mm thickness) to the thin layers ($\leq$ 500 µm)

Mechanical effects of adding ALT to Ni-YSZ

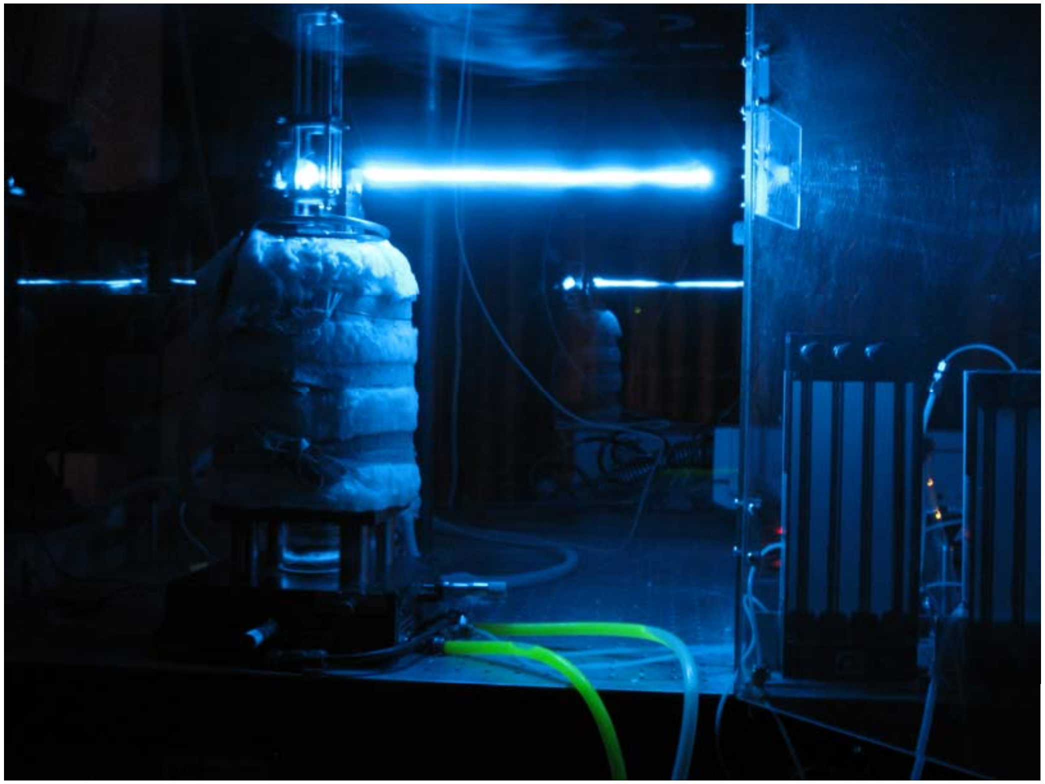


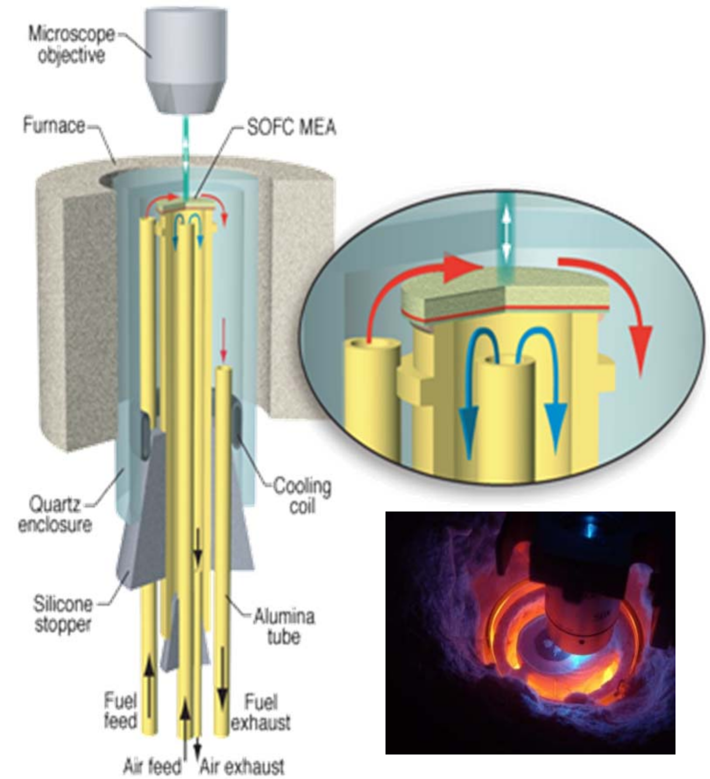
(Fractured in reduced state)

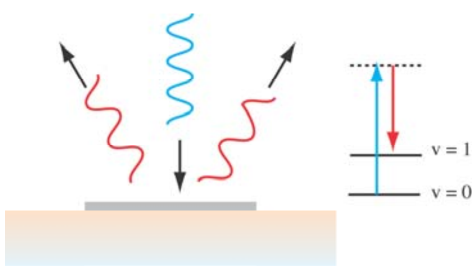
- Intergranular fracture (low energy fracture) present for undoped and 1 wt% ALT
- Transgranular fracture (high energy fracture) present for 5 and 10 wt% ALT
- Highest strength at 5 wt% ALT doping for both mechanically mixed and infiltrated samples
- Secondary phases enable the material to better resist the strain buildup due to redox cycling
- 5% ALT loading optimizes balance between strength and electrochemical performance
- Benefits transfer from the bulk materials (2 mm thickness) to the thin layers (≤ 500 µm)

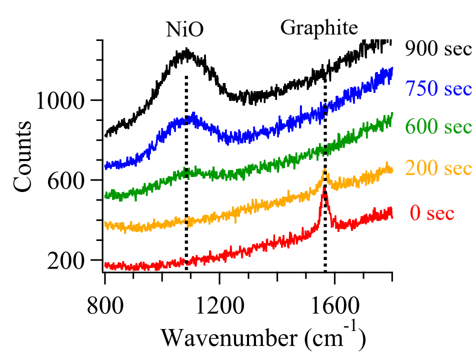
Electrochemical performance of ALT-enhanced anodes

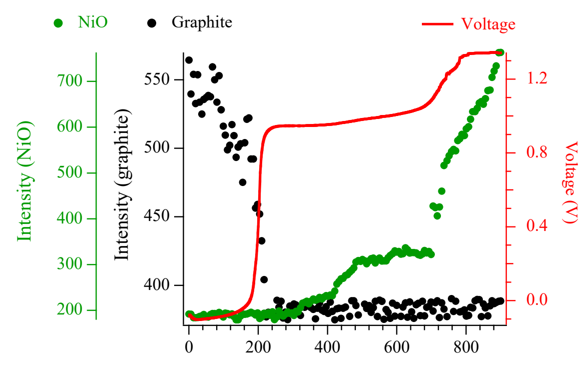
Correlate electrochemical data with *operando* materials specific Raman spectra





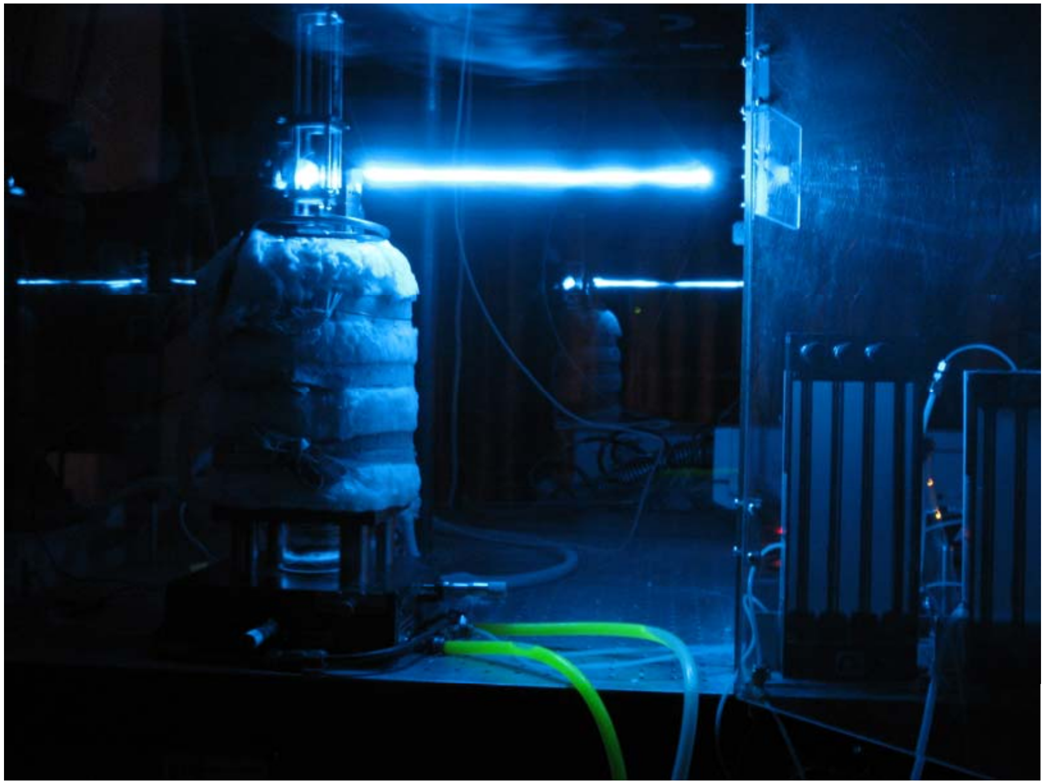


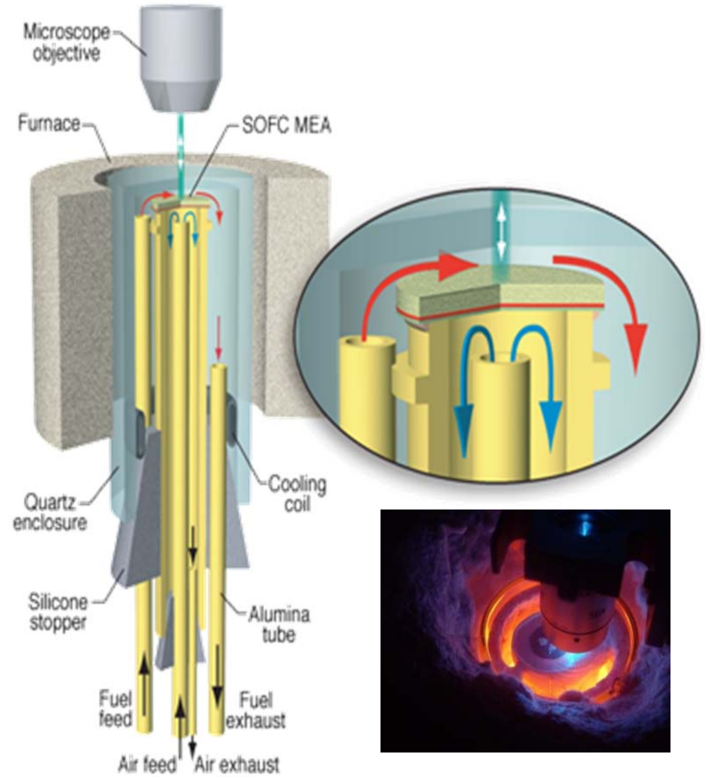




Electrochemical performance of ALT-enhanced anodes

Correlate electrochemical data with *operando* materials specific Raman spectra



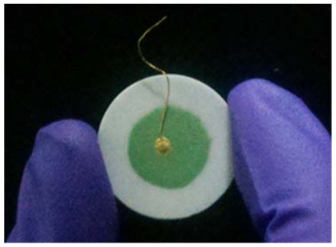


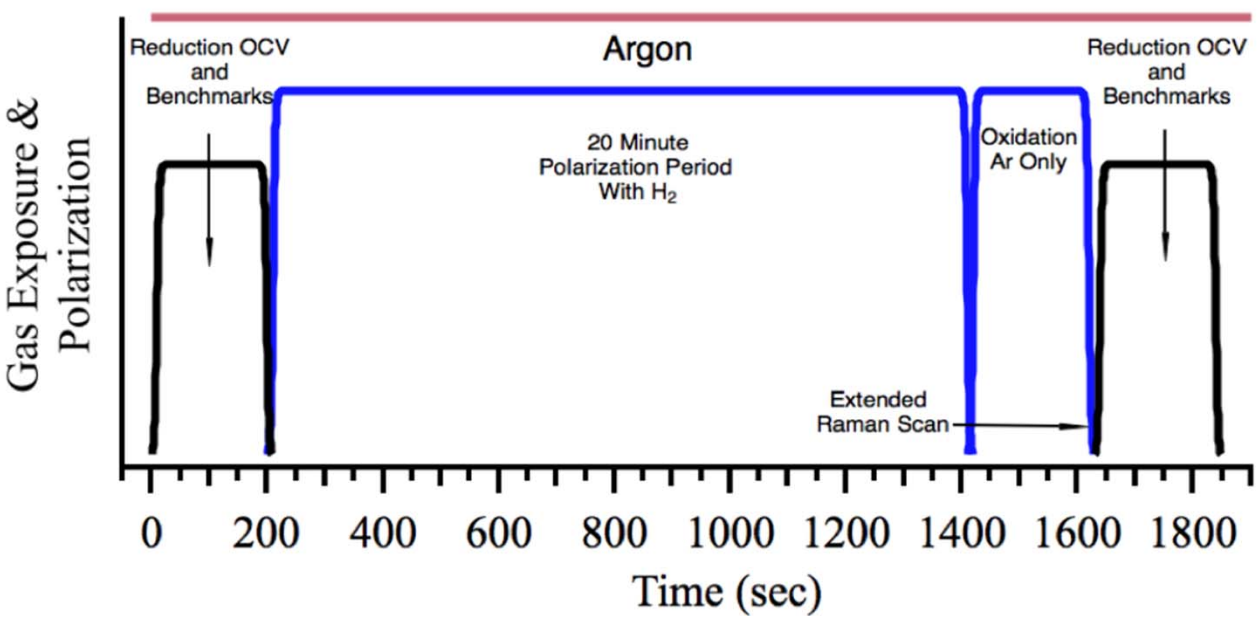
Does ALT improve resilience to reduction/oxidation cycling?

Electrochemical performance of ALT-enhanced anodes

Procedure:

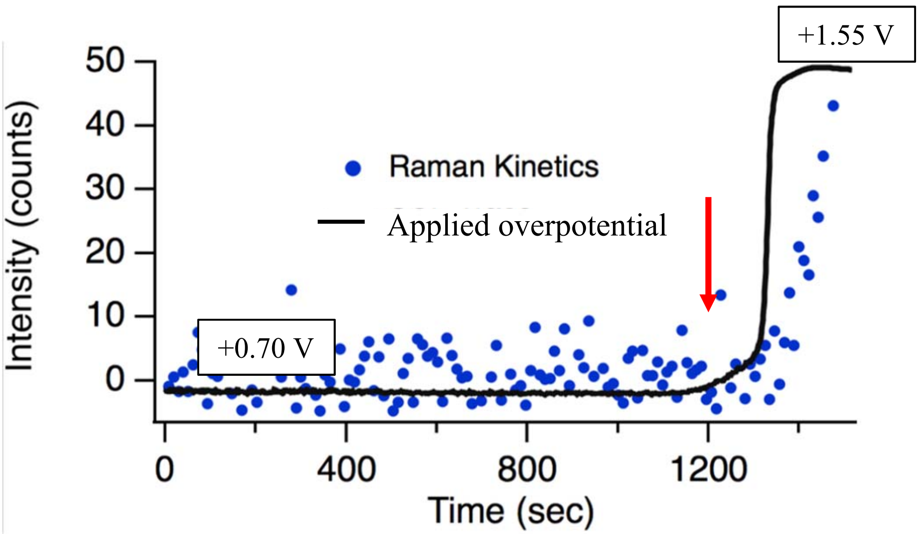
- 800˚C, dry H_2
- Measure LSV and EIS benchmarks
- Operate galvanostatically for 20 min with H2
- Eliminate H_2 while still drawing current
- Stop operation when anode begins to oxidize
- Re-reduce anode, make benchmark measurements and repeat
- Device ‘failure’ defined as being unable to produce 50% original I_{max}

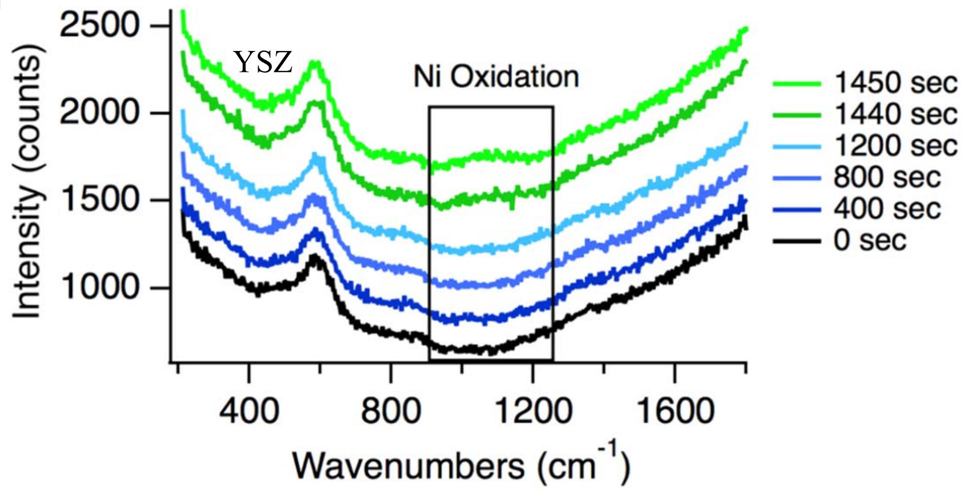




Welander, M. M.; Zachariasen, M. S.; Hunt, C. D.; Sofie, S. W.; Walker, R. A. *J. Electrochem. Soc.* **2018**, *165* (3), F152–F157.

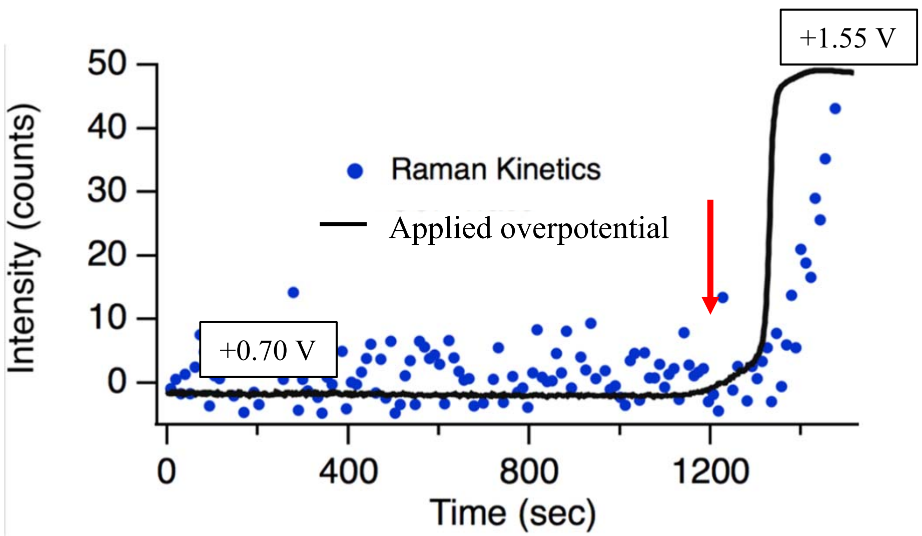
Electrochemical performance of ALT-enhanced anodes

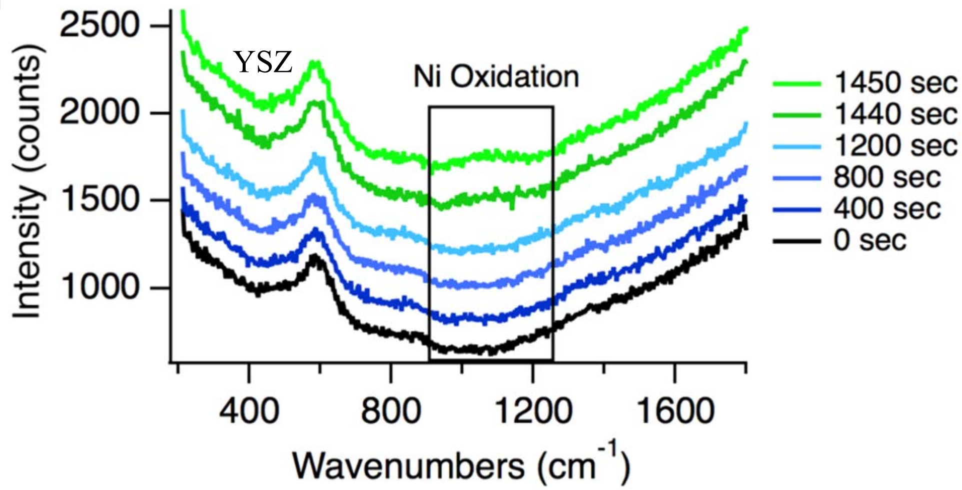


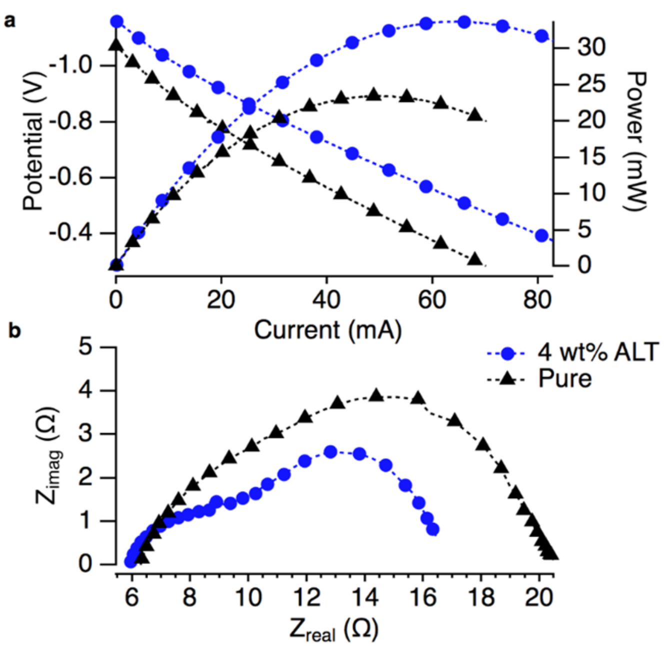


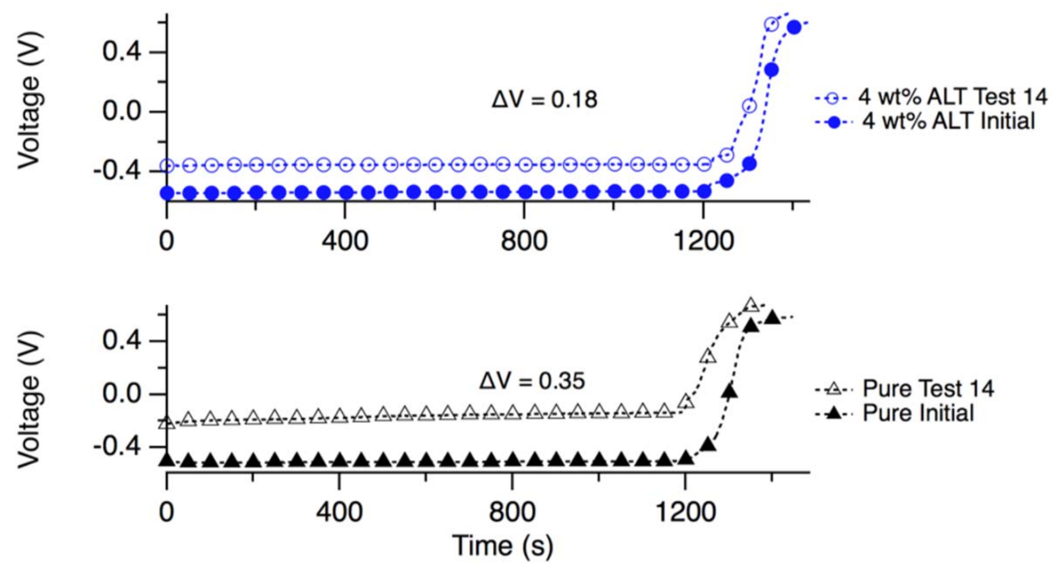
- Steep rise in overpotential correlates with appearance of NiO

Electrochemical performance of ALT-enhanced anodes



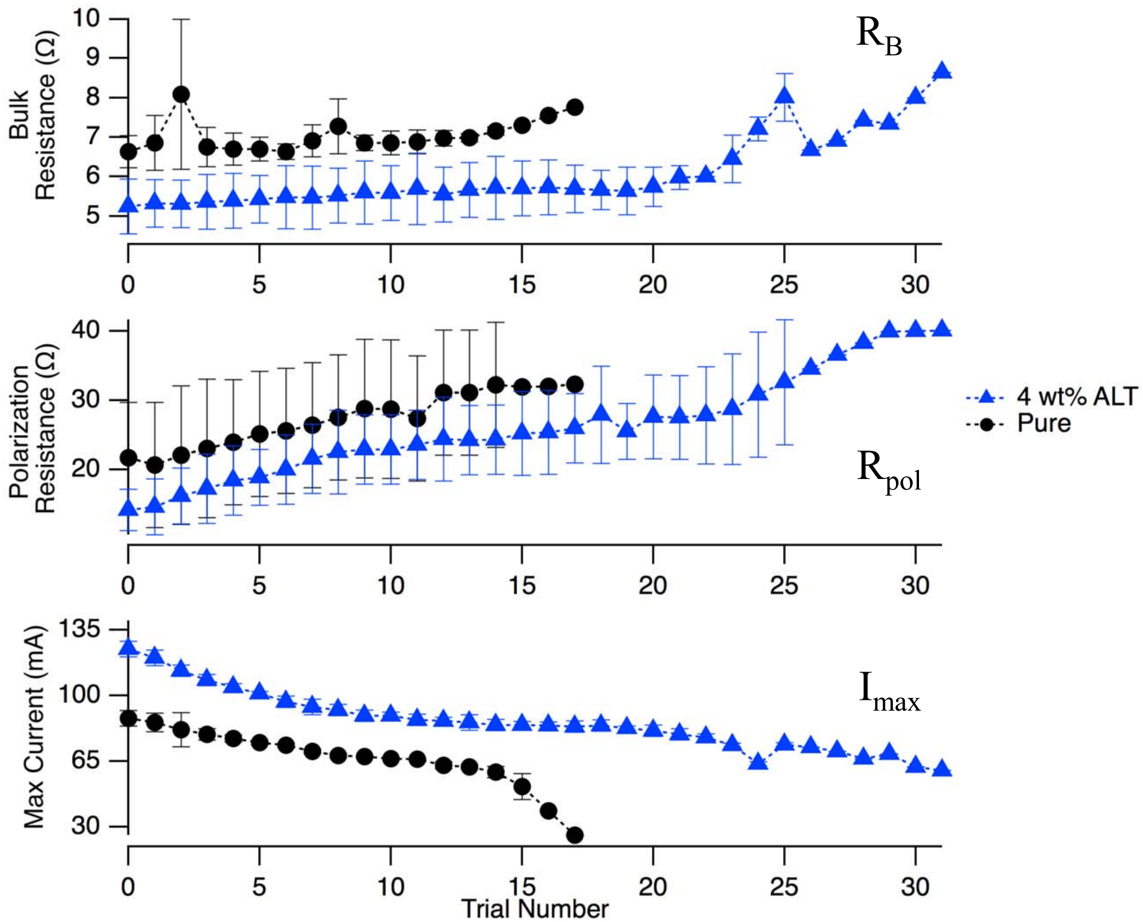


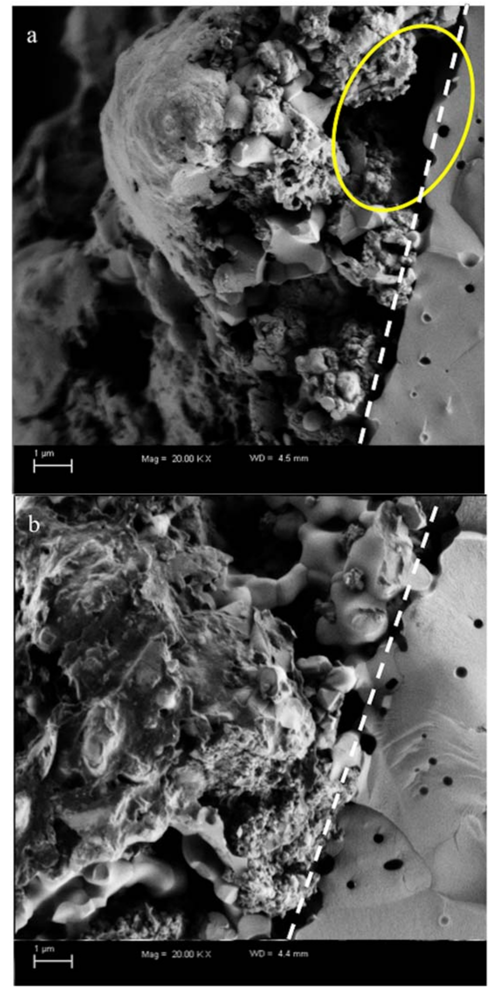




- Better initial performance with ALT
- Better performance with ALT after cycling

Electrochemical performance of ALT-enhanced anodes





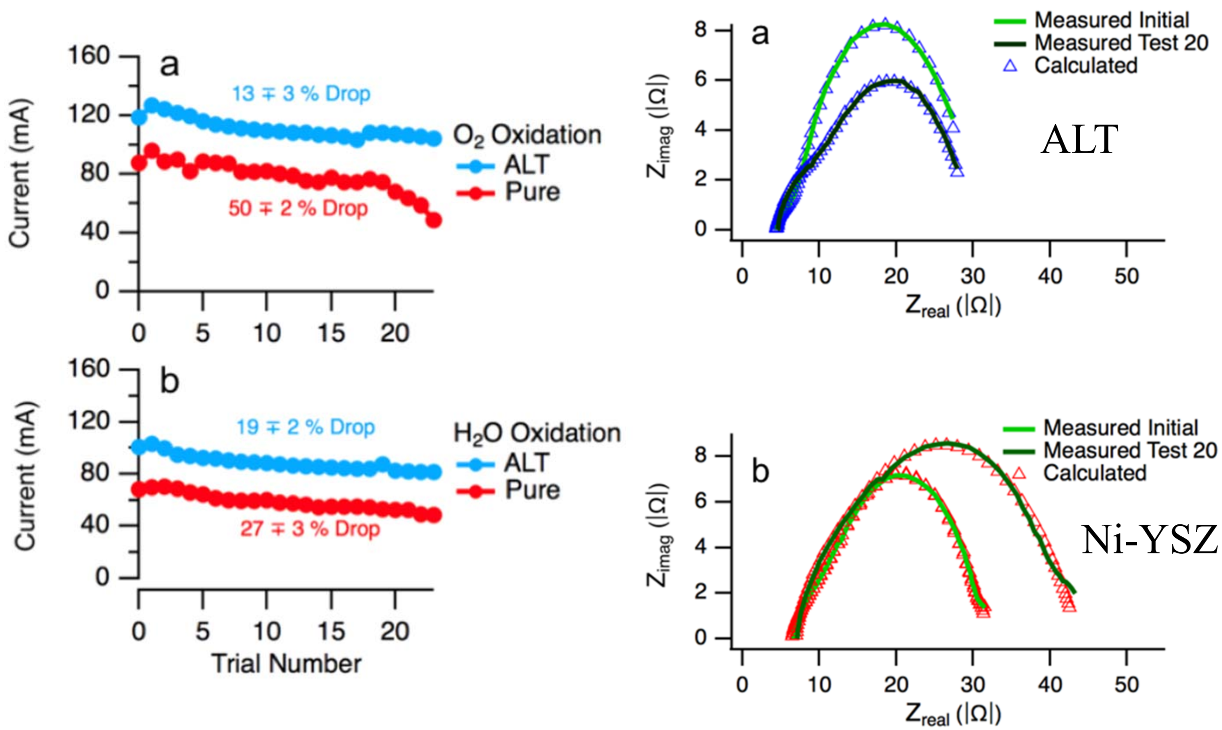
Pure Cell

ALT Doped Cell

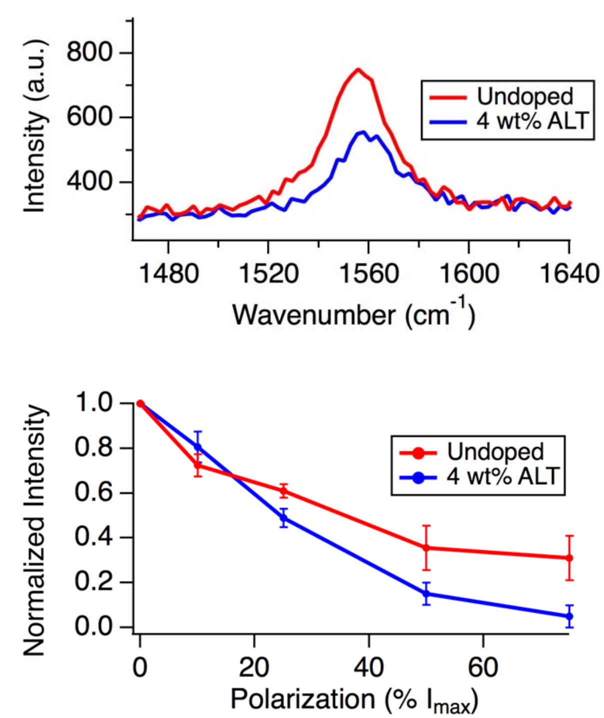
- ALT enhanced Ni-YSZ anodes >2x more resilient
- Biggest change is in bulk (or series) resistance (R_B)
- *Ex situ* SEM show loss of material from electrode/electrolyte boundary

Electrochemical performance of ALT-enhanced anodes

- ALT enhanced Ni-YSZ anodes >2x more resilient to *electrochemical* redox cycling
- ALT enhanced Ni-YSZ anodes ≥3x more resilient to *environmental* O_2 redox cycling
- Steam redox cycling eventually leads to Ni-YSZ anode failure; ALT anodes don't fail
- ALT enhanced anodes are less susceptible to coking (with CH_4).



Environmental redox cycling with O_2 and H_2O

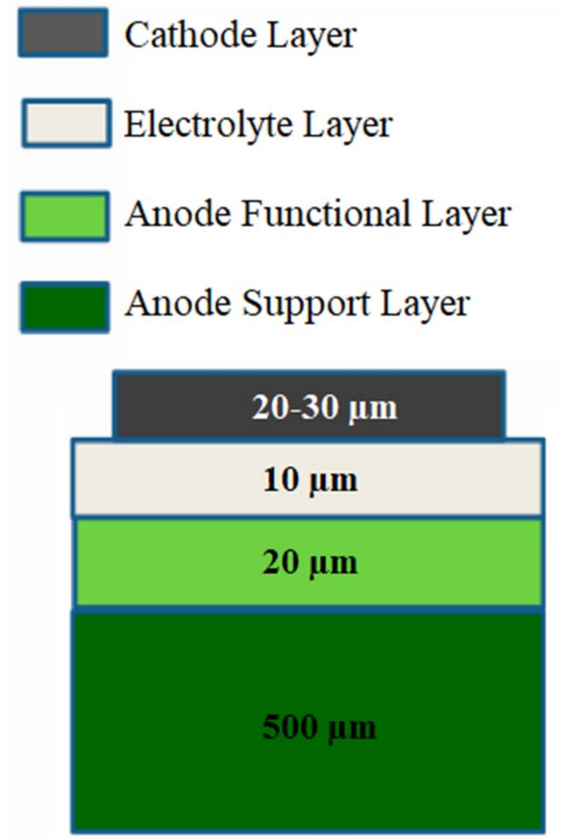


Carbon tolerance with CH_4

Current efforts – developing anode supported assemblies with ALT

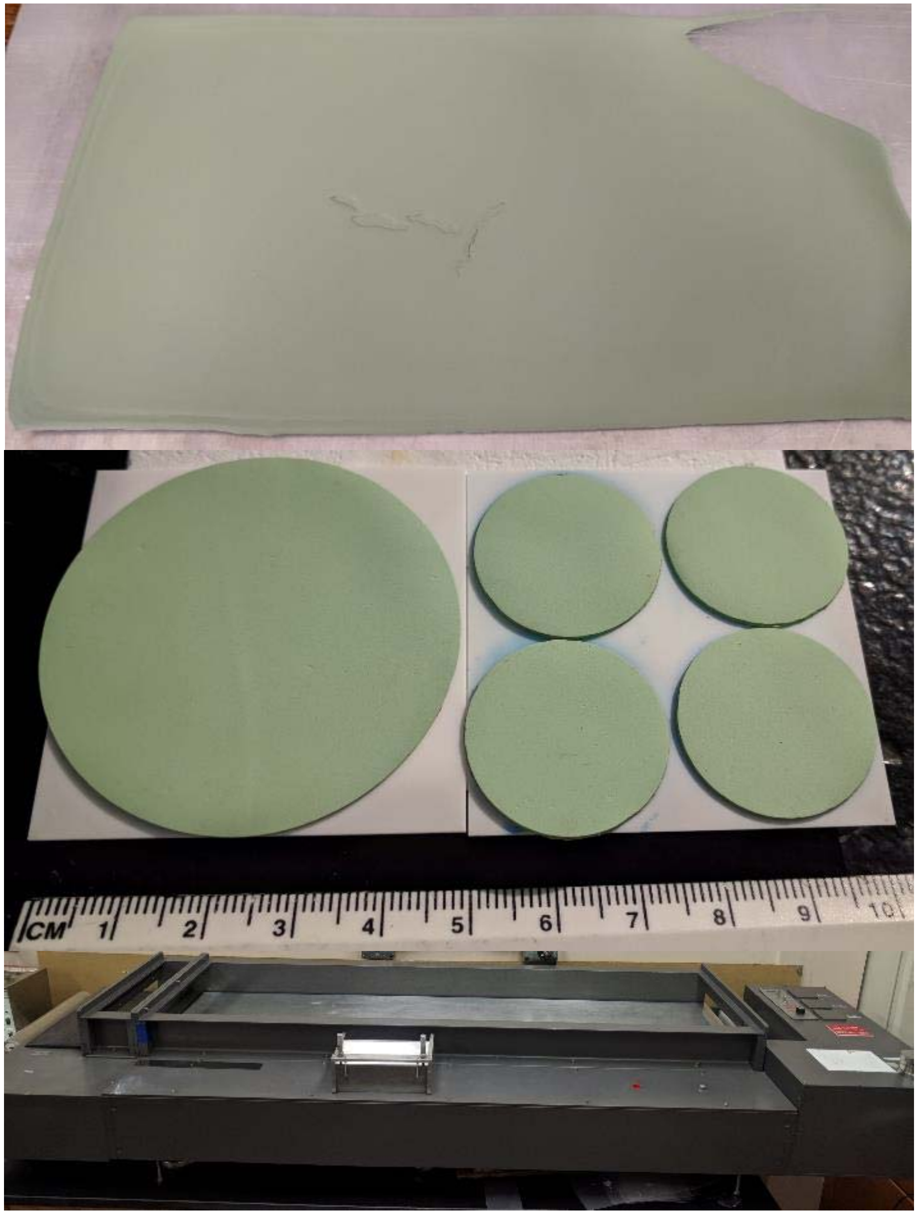
3 Layers

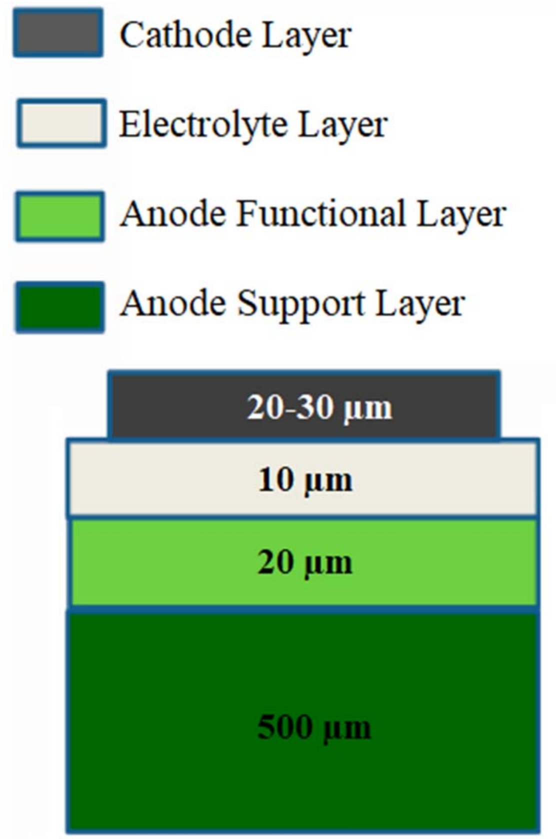
- Anode
  - Porous NiO+YSZ
    - Functional and bulk layers
- Electrolyte
  - Dense
    - Yttria-Stabilized Zirconia (YSZ)
- Cathode
  - Porous
    - Lanthanum strontium manganite (LSM)



- ALT enhanced Ni-YSZ anodes >2x more resilient
- Biggest change is in bulk (or series) resistance (R_B)
- *Ex situ* SEM show loss of material from electrode/electrolyte boundary

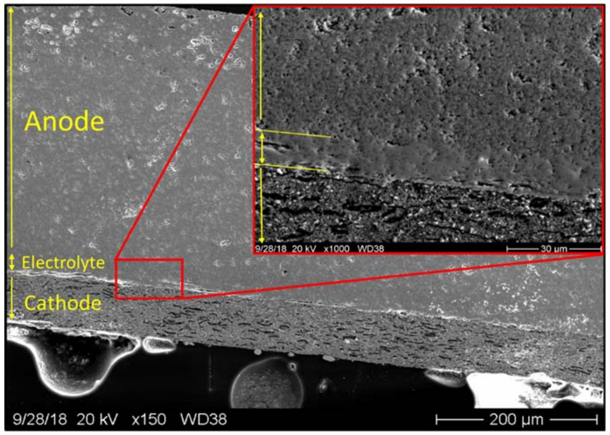
Current efforts – developing anode supported assemblies with ALT



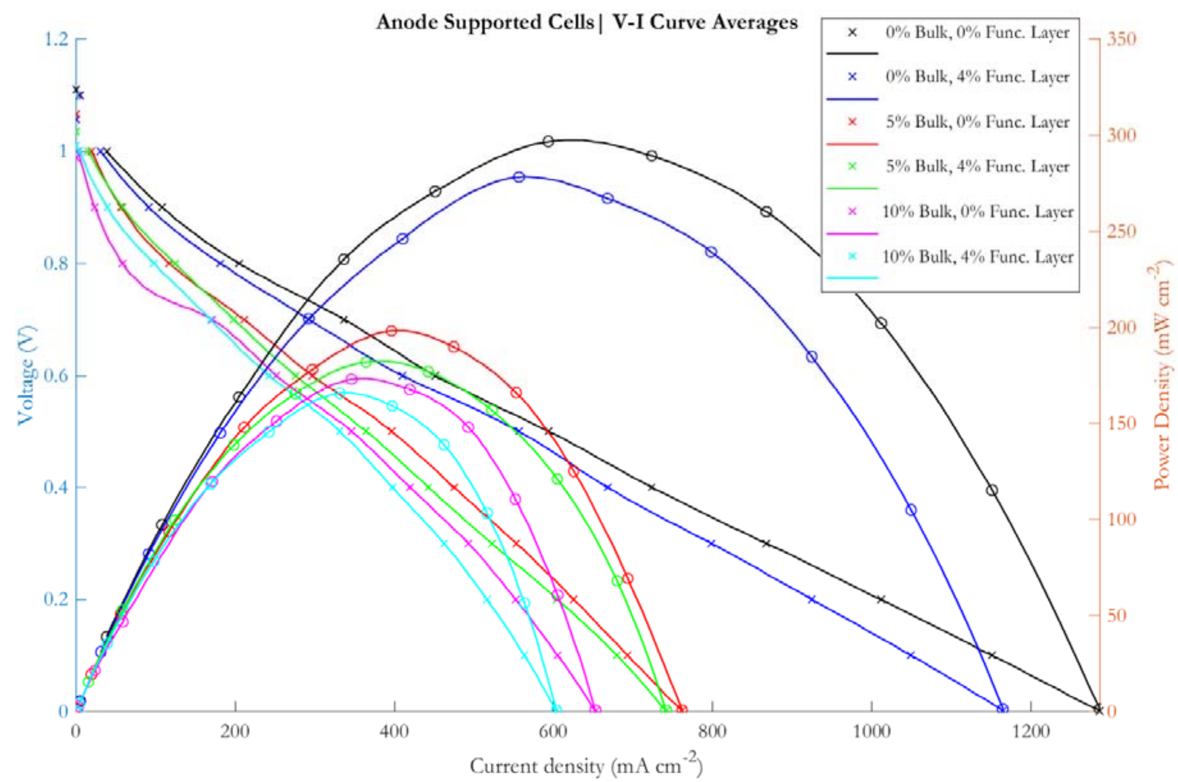


- Tape casting
- Anode support: 0.5 ± 0.1 mm
- Functional layer: 30 ± 10 µm
- Electrolyte: 10 ± 5 µm
- Cathode: 40 ± 20 µm

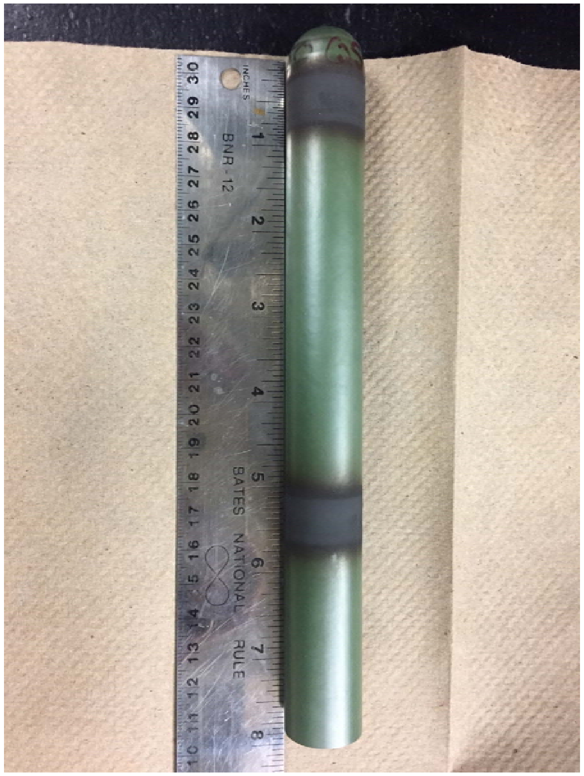
Current efforts – developing anode supported assemblies with ALT



- ASC: > $1 A/cm^2$
- ALT in functional layer leads to small loss of performance
- ALT in support layer leads to larger loss in performance
- Early indicators are that support and functional layers need higher Ni loadings



Current efforts – Developing strategies for infiltrating tubular SOFCs



ATREX ENERGY
POWERFUL POSSIBILITIES

- Atrex Ni-YSZ anode material shows similar mechanical enhancements with ALT
- ALT slows degradation in anodes made with Atrex supplied Ni-YSZ in ESCs
- Working out kinks for homemade ASCs before infiltrating Atrex units
- ALT-enhanced tubular ASCs to be tested at Atrex Energy

Timeline

C. Milestone Log

Task	Milestone title	Planned Completion Date	Verification method	
1.0	Project Management Plan	10/31/17	PMP file approved	
1.0	Kickoff Meeting	11/30/17	Presentation file	
2.1	Planar anode fabrication and testing	5/30/18	Laboratory benchmarks for mechanical strength and initial performance	✓ (in progress)
2.2	Completion of mechanically mixed v. infiltration studies	8/31/18	Recommendation for method of introducing ALT *and* % loading by mass	✓
3.1.	*Operando* Raman and electrochemical testing	2/28/19	Correlations between performance, composition and history to guide Tasks 2.1, 2.2 and 4.2	✓
3.2	Fracture testing	5/31/19	Correlations between strength, composition and history to guide Tasks 2.1, 2.2 and 4.2	✓
3.3	Thermal and electrochemical analysis	5/31/19	Correlations between stability, composition and history to guide Tasks 2.1, 2.2 and 4.2	✓
4.1	Coordinate fabrication methods and specifications	8/31/18	Methods and procedures for large cell fabrication	(in progress)
4.2	. Fabricate cells & benchmark testing	11/30/18	First 500 hour tests on planar assemblies at FCE	
4.3.	Independent testing at commercial facility	6/30/19	500 hour tests for planar and tubular assemblies	
4.4.	Technology transfer/IP negotiations; Follow-on	8/31/19	Patents and/or Licensing agreements STTR/SBIR?	


Thanks