Mechanical and Electrochemical Effects of 2° Phase Formation on SOFC Anode Performance

Walker, Sofie and Amendola Research Groups

Chemistry and Biochemistry/Mechanical and Industrial Engineering

Montana State University

Program Officer: Joe Stoffa

DE-FE-0026192

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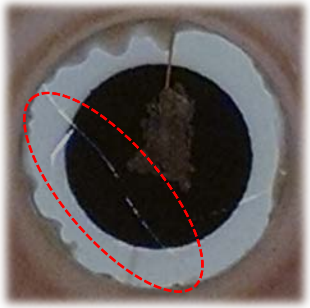
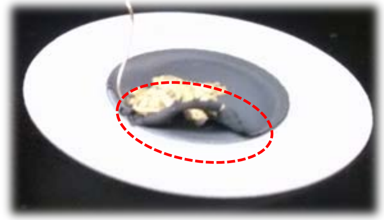
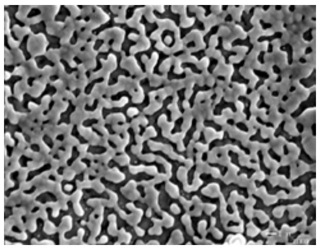
Challenges that limit Ni/YSZ anode performance

1. Mechanical stress induces electrode/electrolyte cracking and delamination

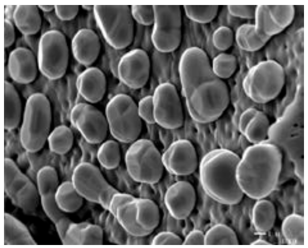




2. High temperatures promote catalyst coarsening

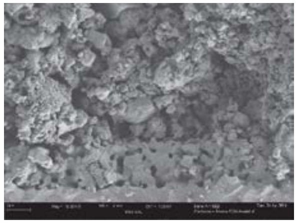


As reduced

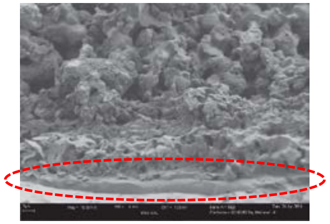


After 5 hrs at 800˚C

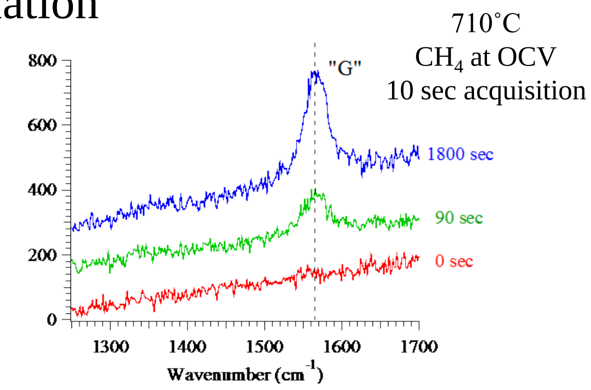
3. Ni catalysts susceptible to contaminants and carbon accumulation



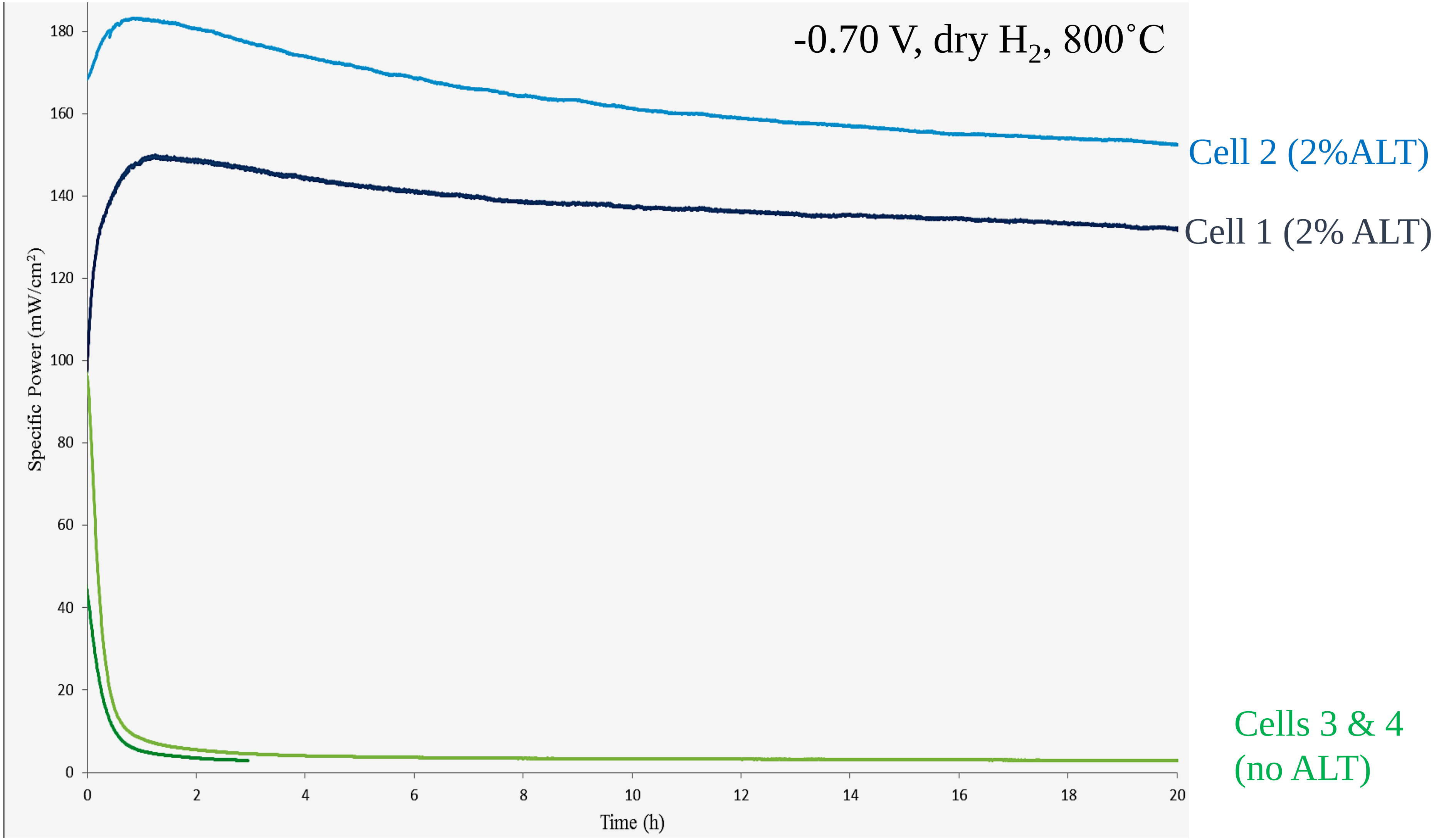
Pristine anode



Anode following 2 hrs exposure to CH_4



A serendipitous observation – Al_2TiO_5 & Ni infiltration withYSZ scaffold

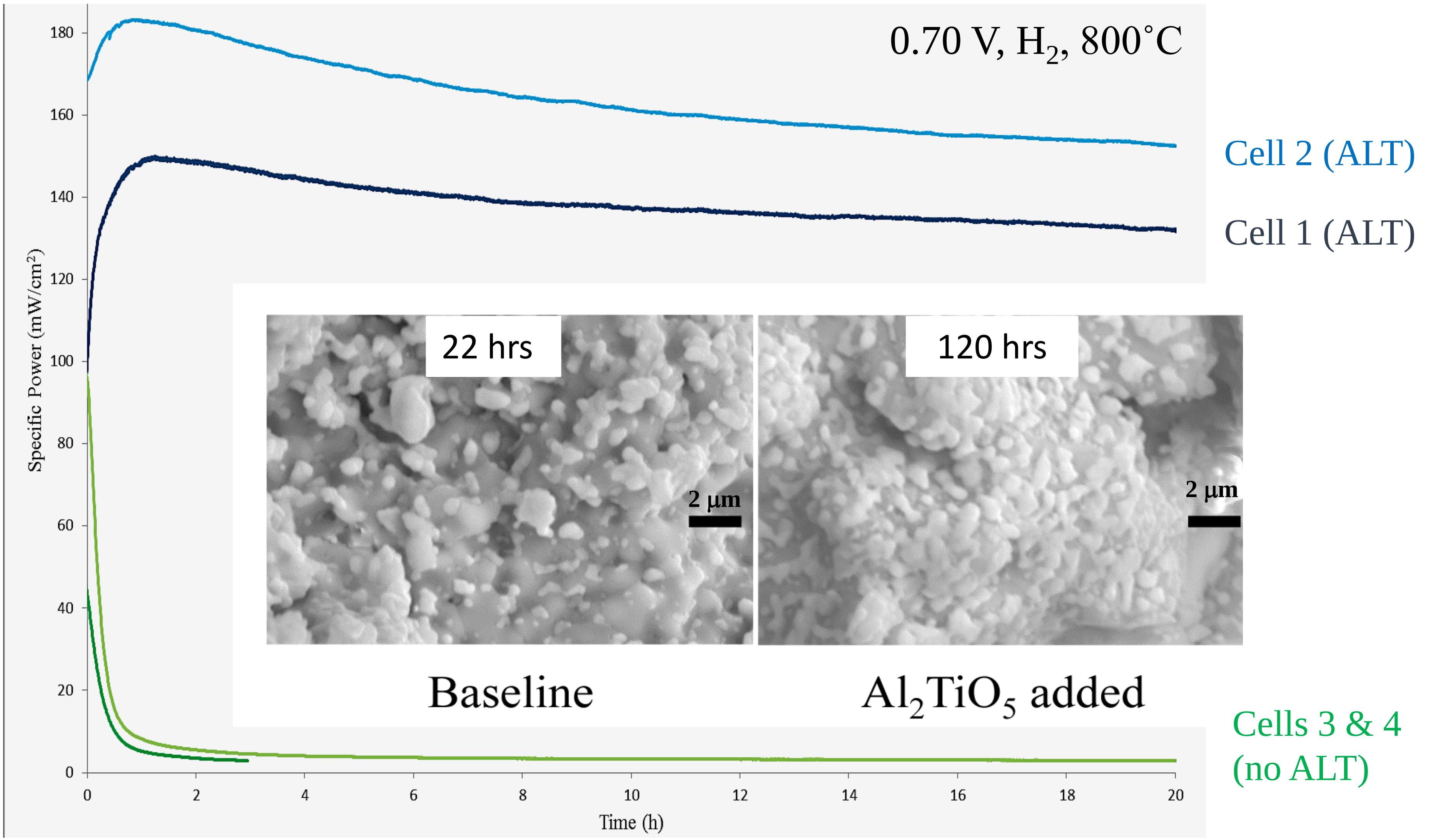


Infiltrated, electrolyte supported MEA's (low Ni loadings, ~20%)

Anodes without ALT failed immediately

Adapted from C. H. Law and S. S. Sofie *J. Electrochem. Soc.* **158** (2011) B1137.

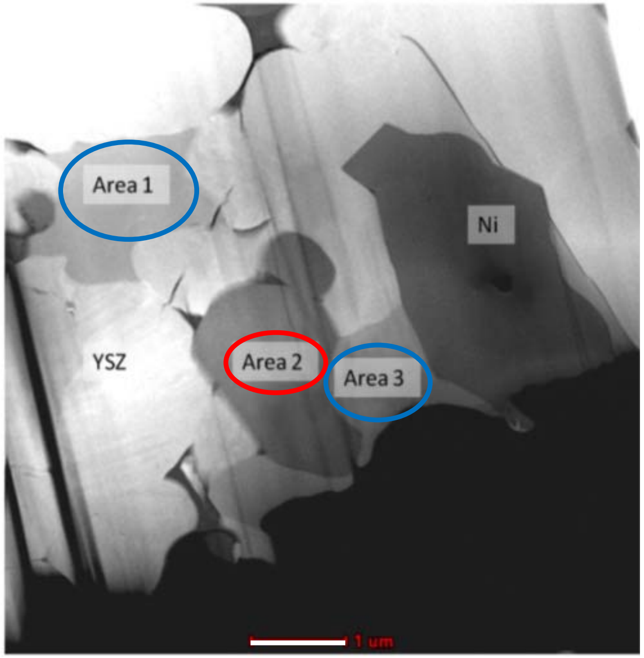
A serendipitous observation – ALT infiltrated Ni-YSZ anode



Less coarsening of Ni particles when ALT is present.

Adapted from C. H. Law and S. S. Sofie *J. Electrochem. Soc.* **158** (2011) B1137)

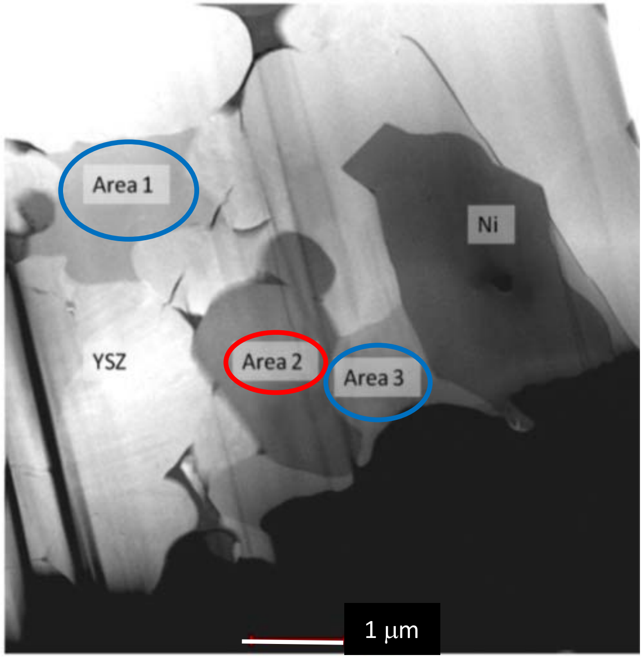
A serendipitous observation – ALT infiltrated Ni-YSZ anode



High resolution TEM/EDS image of Ni/YSZ sample impregnated with Al_2TiO_5 and then heated to 1400˚C. Areas 1 and 3 are rich in both Ni and Al, while Area 2 is rich in Zr and Ti.

Adapted from C. H. Law and S. S. Sofie *J. Electrochem. Soc.* **158** (2011) B1137)

Could ALT (or other materials) serve as chemical anchors?



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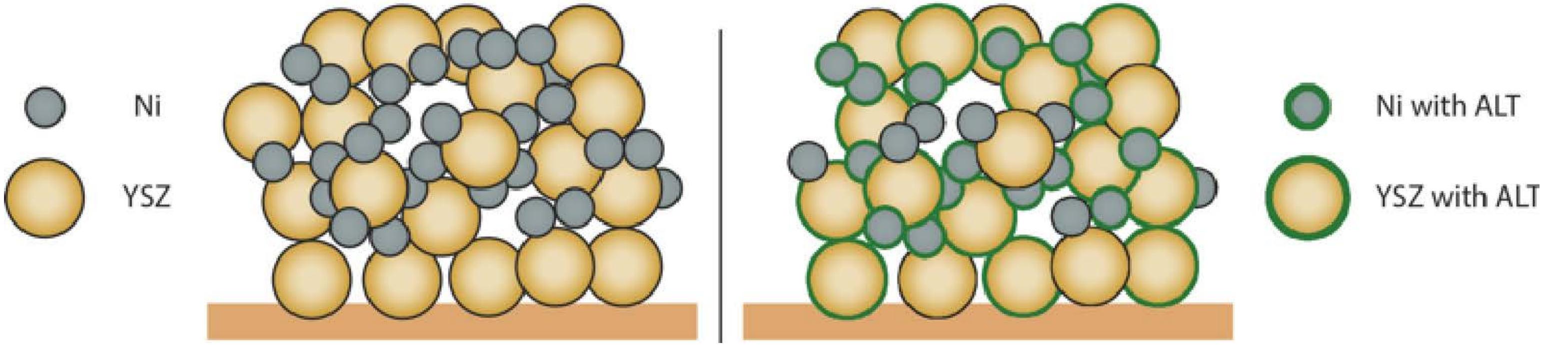
Images support mechanism of 2˚ phase formation



Mechanism(s)?

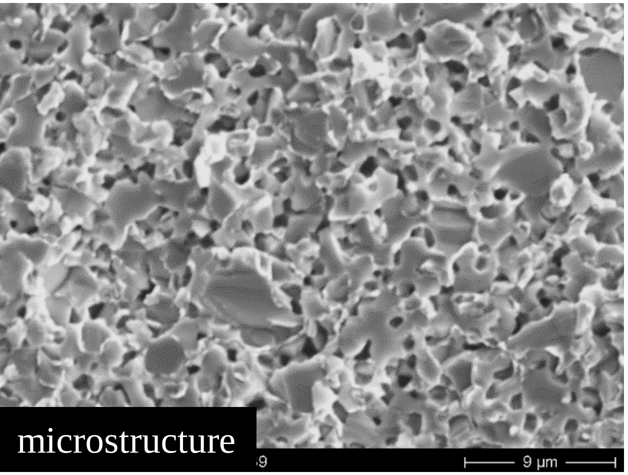
Scalable?

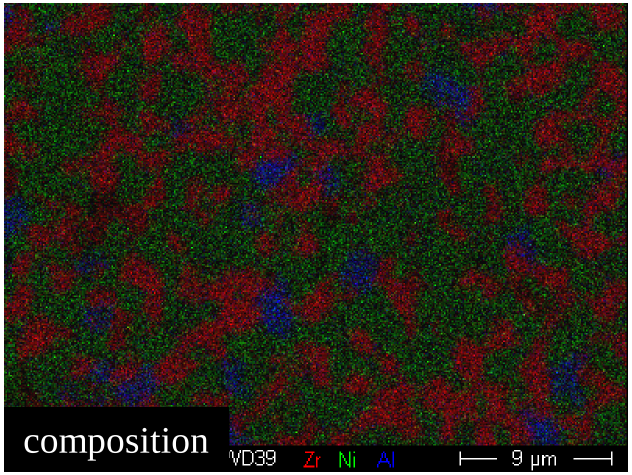
Does processing matter?

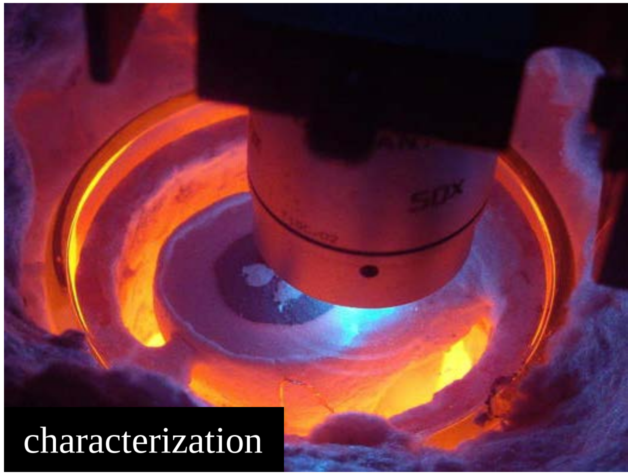
How is performance affected?

Project Objectives of Phase I

- Identifying the most effective means of introducing 2° precursors to traditional Ni-YSZ cermet structures and optimal loadings
- Determining the optimal thermal conditioning procedures that promote 2° phase formation
- Quantifying the effects of 2° phases on the electrochemical performance and durability of SOFC anodes using operando and ex situ techniques.







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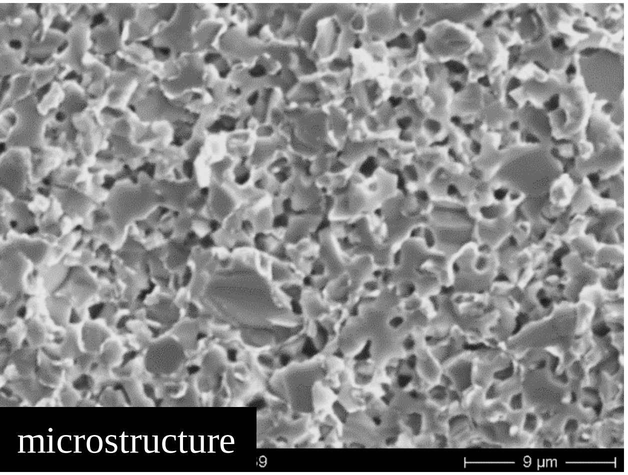
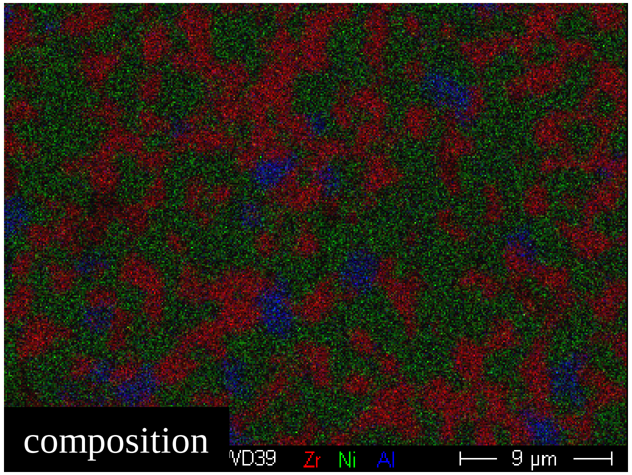
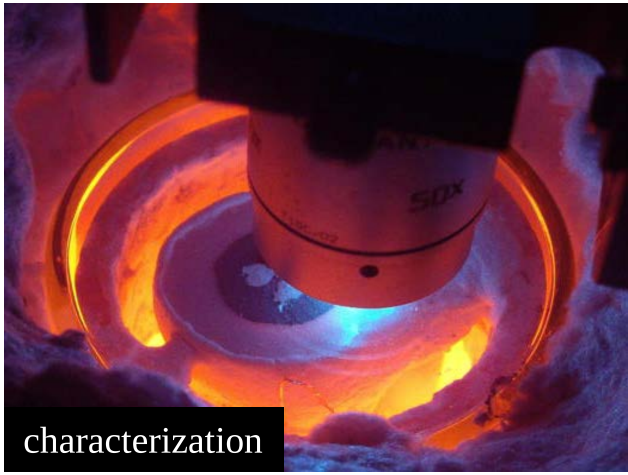
The answer you want depends on the question you ask!

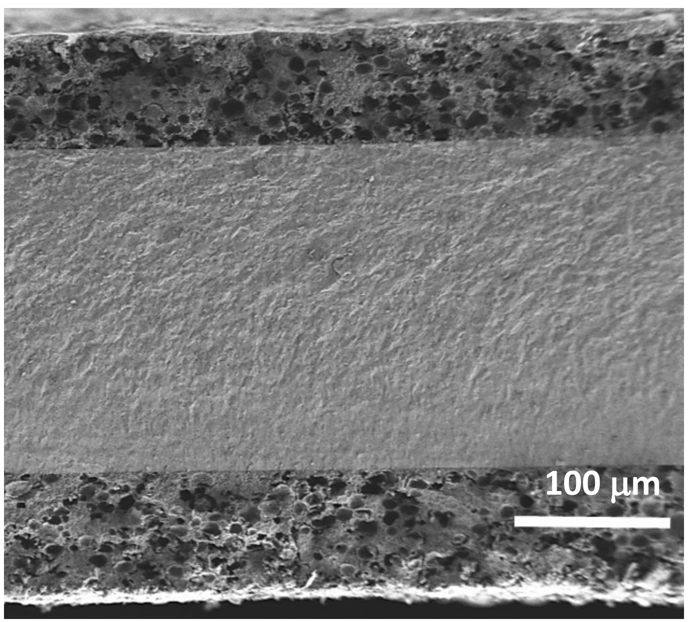


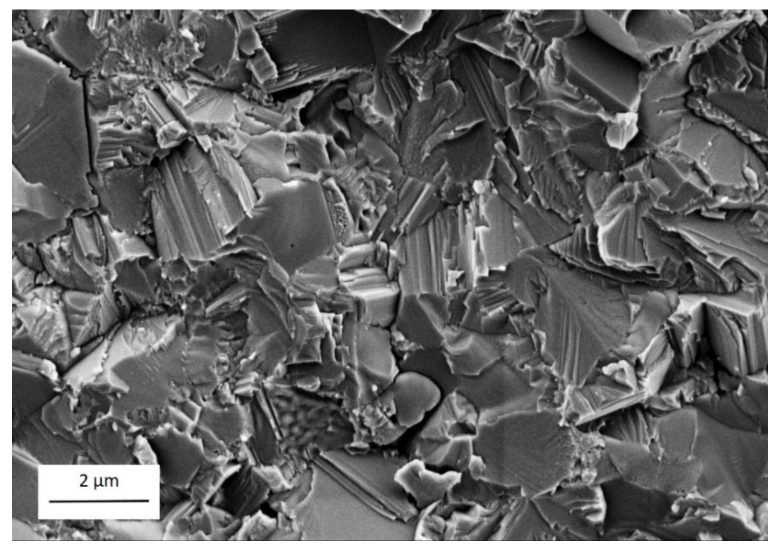




Scope of Work – Phase I

- **Anode fabrication** - Ni-YSZ (8% yttria) seeded with Al_2TiO_5 (ALT) through mechanical mixing and via solution phase infiltration of pre-formed anodes. Both approaches will be tested for different ALT loadings (1-10% by mass)
- **Mechanical and materials testing** - Coefficient of thermal expansion, elastic behavior, and fracture characteristics of both as prepared and chemically reduced samples
- **Operando electrochemical testing and spectroscopic monitoring** – Voltammetry, EIS and Vibrational Raman microscopy will characterize the high temperature behavior of the anchored Ni catalysts X-ray diffraction and ionization techniques will identify stoichiometry, structure, and oxidation state(s).





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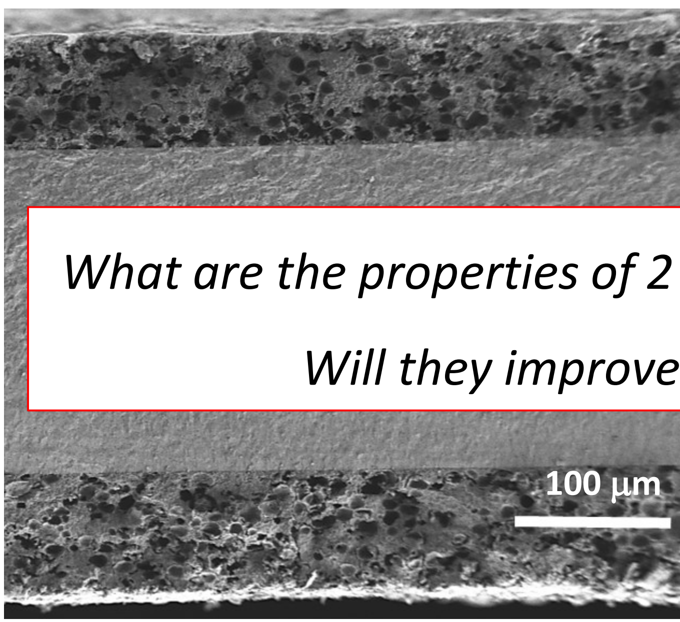
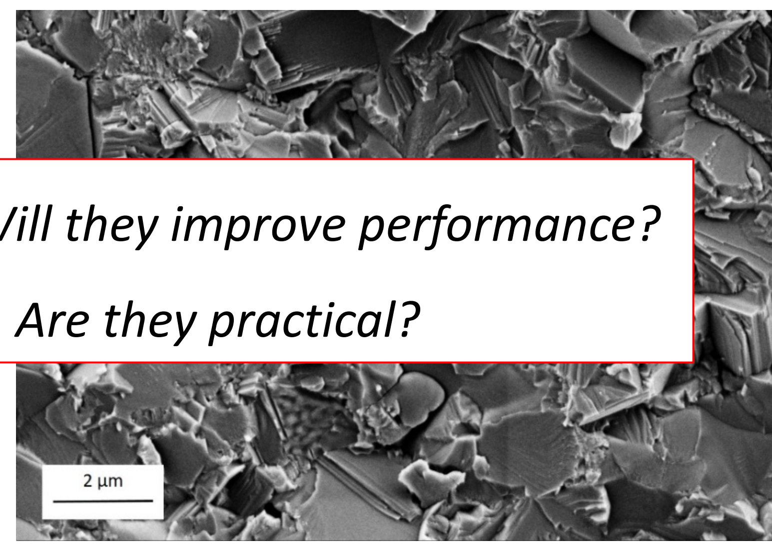


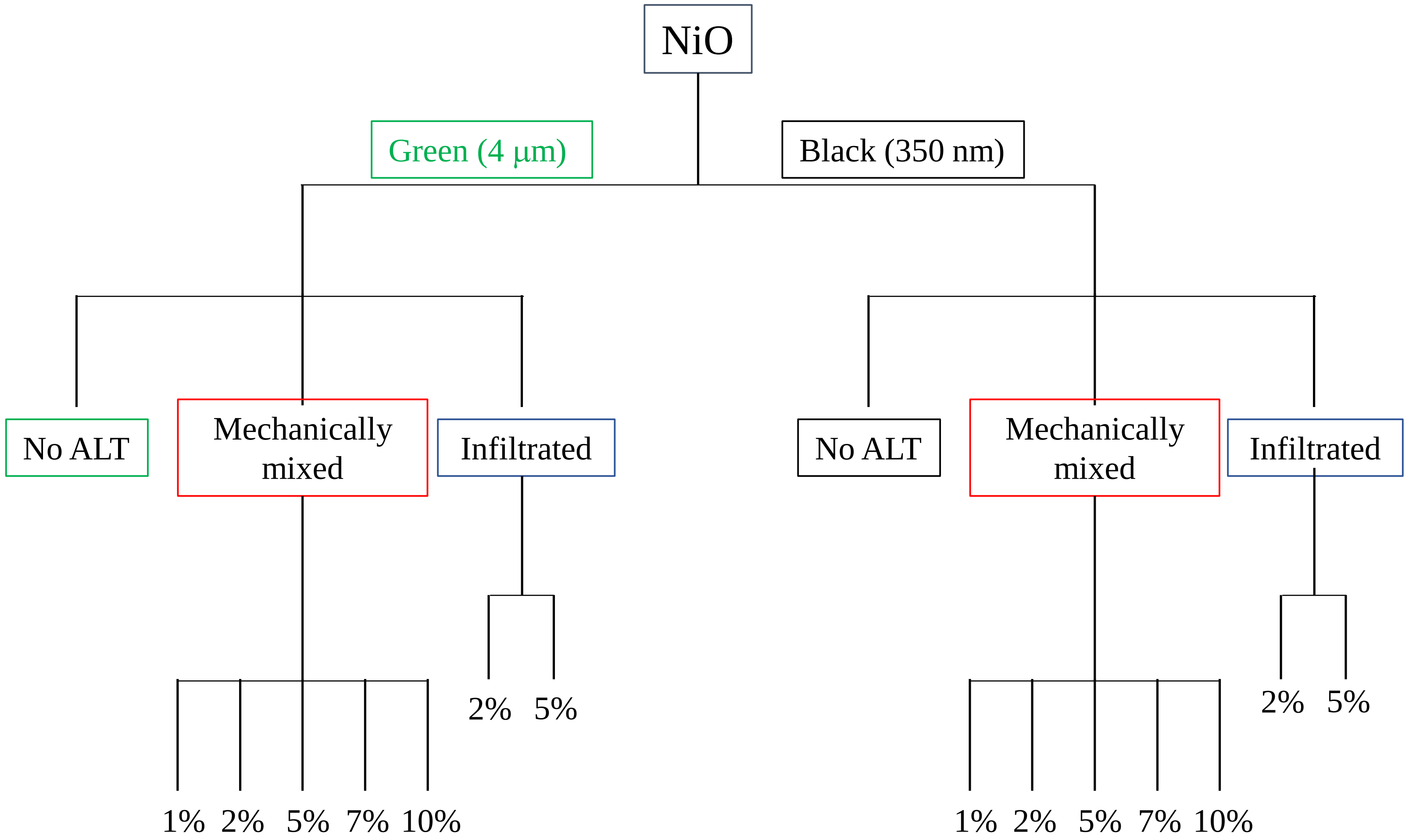


What are the properties of 2˚ phases? Will they improve performance?

Will they improve durability? Are they practical?

An ambitious agenda - a lot of space to explore

- Given: Ni/YSZ cermet anode (50% Ni by mass)
- Electrolyte supported button cells (mostly)
- Dry H_2, 800˚C



Chemistry in ALT-doped Ni-YSZ anodes

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

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Mix (in xylene/EtoH/dispersant)
Ball mill
Spray (50 μm)
1400˚C, 1 hour

$NiO + 8YSZ + ALT\ (1\text{-}10\%) \rightarrow NiO + c\text{-}YSZ + Zr_5Ti_7O_{24} + NiAl_2O_4$

$Zr_5Ti_7O_{24}$: MIEC (?)

$NiAl_2O_4$: Anchor

D. R. Driscoll, et al. "Enhancement of High Temperature Metallic Catalysts: Aluminum Titanate in the Nickel-Zirconia System" *Applied Catalysis A* **527** 36-44 (2016).

M. D. McIntyre, et al. "*In situ* Formation of Multifunctional Ceramics: Mixed Ion-Electron Conducting Properties of Zirconium Titanium Oxides" *submitted to J. Materials Chemistry A.*

M. M. McCleary, et al. "Effect of Aluminum Titanate (Al_2TiO_5) doping on the mechanical performance of Solid Oxide Fuel Cell Ni-YSZ Anode", " *submitted to Fuel Cells*

D. R. Driscoll, et al. "Aluminum Oxide as a Beneficial Additive to SOFC anodes" *in preparation.*

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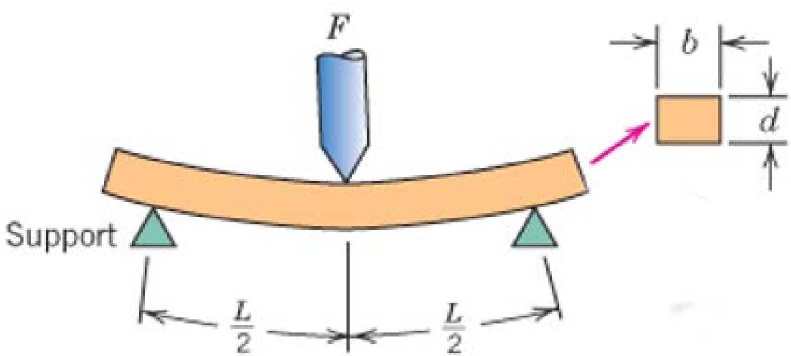
MIEC (?) ($Zr_5Ti_7O_{24}$)   Anchor ($NiAl_2O_4$)

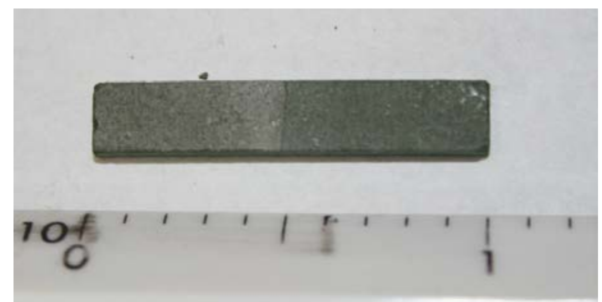
Findings:

- ALT-doped anode materials are 50% 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
- Echem performance depends on processing details (infiltrated v. mech. mixed)

Strength testing

- NiO-8YSZ (66% NiO by mass)
- 400 nm YSZ grains
- 350 nm NiO (**black**) or 4 μm NiO (**green**)
- Oxidized and reduced samples
- 30 mm x 5 mm x 2 mm
- ≥ 30 independent measurements

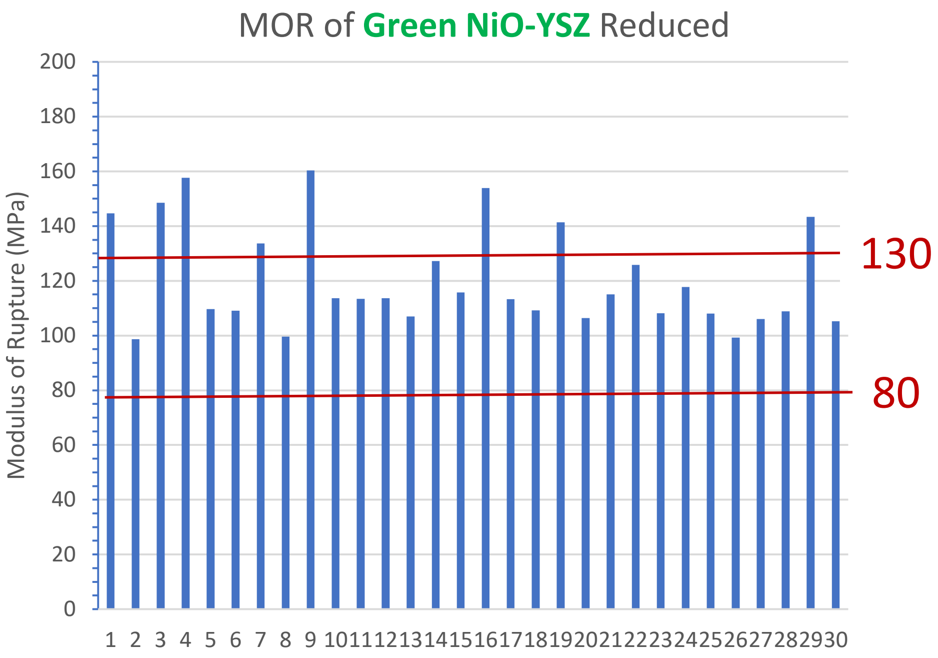


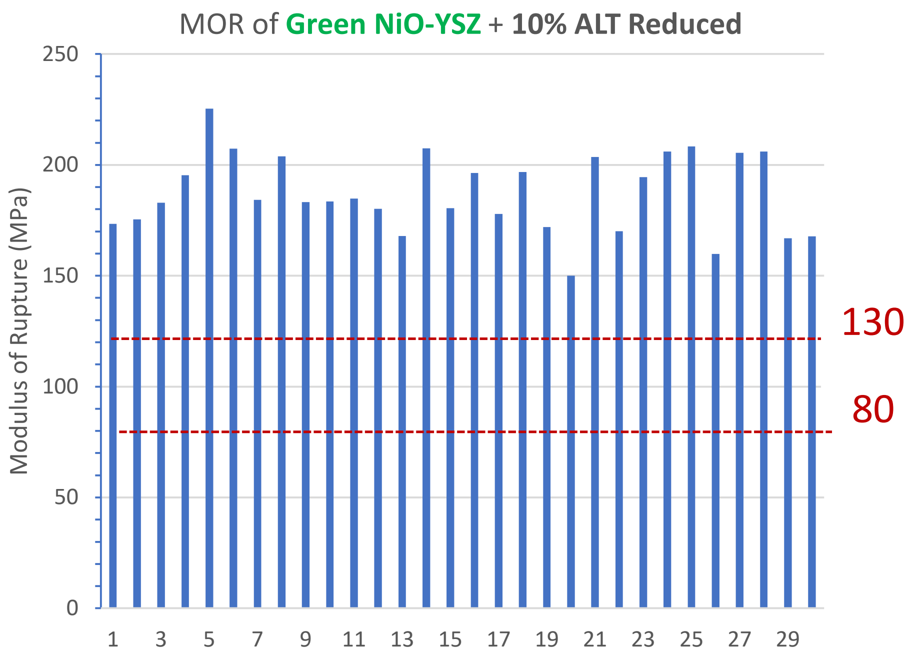


$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

F_f = applied load at failure
σ_{fs} = flexural strength or Modulus of Rupture (MOR)

Modulus of rupture (MOR) results – NiO/YSZ (reduced)





- MOR data fall for reduced samples falls within literature bounds
- MOR for **green** Ni/YSZ coupons is 125 ± 21 MPa
- MOR for '**green**' Ni/YSZ/10% ALT coupons is 187 ± 18 MPa
- MOR for **black** Ni/YSZ behavior similar to **green**

NiO/YSZ and Ni/YSZ cermet MOR is 80-130 MPa
(A. Nakajo, et al. Ceram. Int. 38 (2012) 3907)
(M. Radovic and E. Lara-Curzio, Acta Mater. 52 (2004) 5747)

Strength testing – green NiO/YSZ (mechanically mixed)

GREEN (4 μm)	0 wt% ALT	1 wt% ALT	5 wt% ALT	10 wt% ALT
Oxidized (NiO/YSZ)				
MOR (MPa)	100	136	226	150
Strength Increase (%)	N/A	36	126	50
Standard Deviation	24.9	44.0	29.9	23.4
Weibull Modulus	5.6	6.9	6.9	7.7
Density (g/cm^3)	6.3	6.4	6.2	5.9
Reduced (Ni/YSZ)				
MOR (MPa)	125	151	164	187
Strength Increase (%)	N/A	21	31	50
StandardDeviation	21.3	29.1	22.3	17.6
Weibull Modulus	7.5	5.6	8.6	10.6
Density (g/cm^3)	6.7	6.7	5.5	5.8

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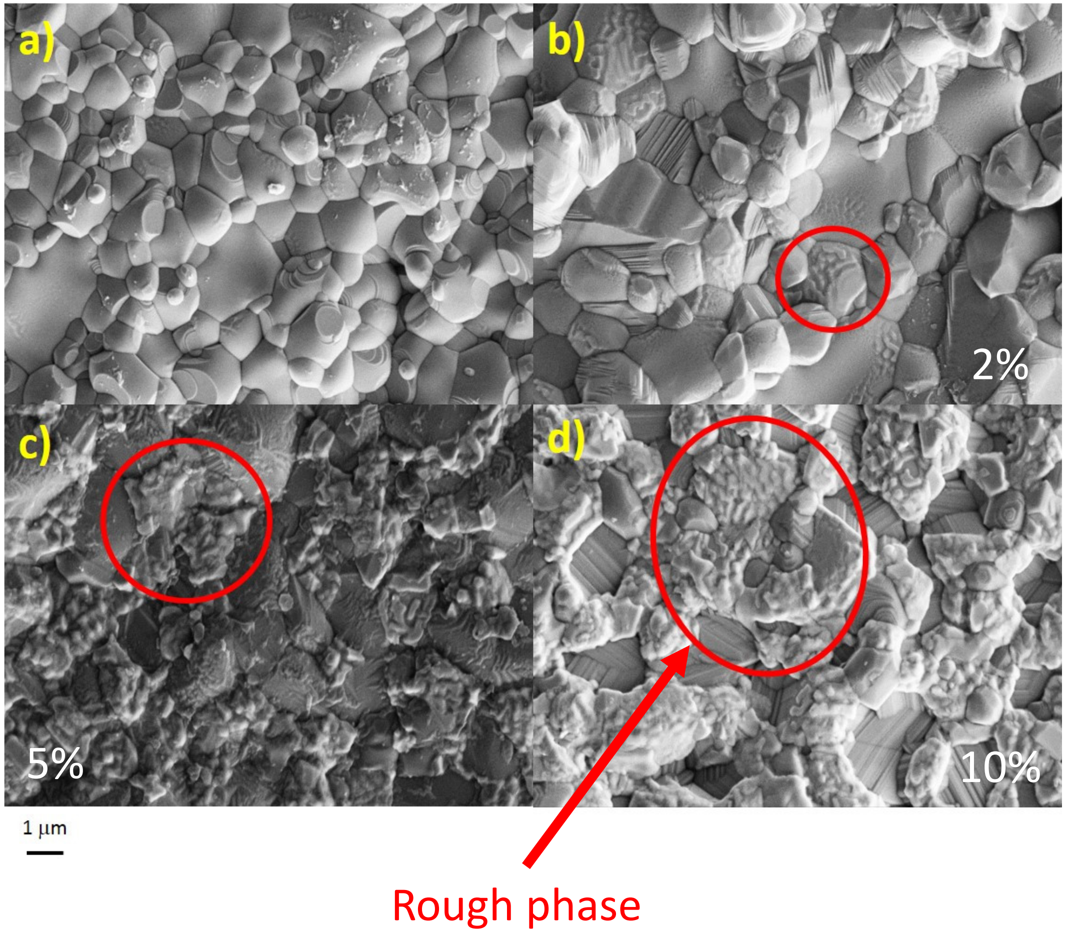
- Mechanical strength benefit due to ALT doping does not dependent on NiO powder size
- MOR scales with ALT amount
- All of the reduced material MOR fall above the maximum value found in literature (130 MPa)

New sub-micron materials on Ni-YSZ surfaces

Micro NiO-YSZ + 0, 1, 5, and 10 wt% ALT **(Oxidized)**



- New phase development with the addition of ALT which persist after reduction
- Phase amount proportional to ALT doping amount

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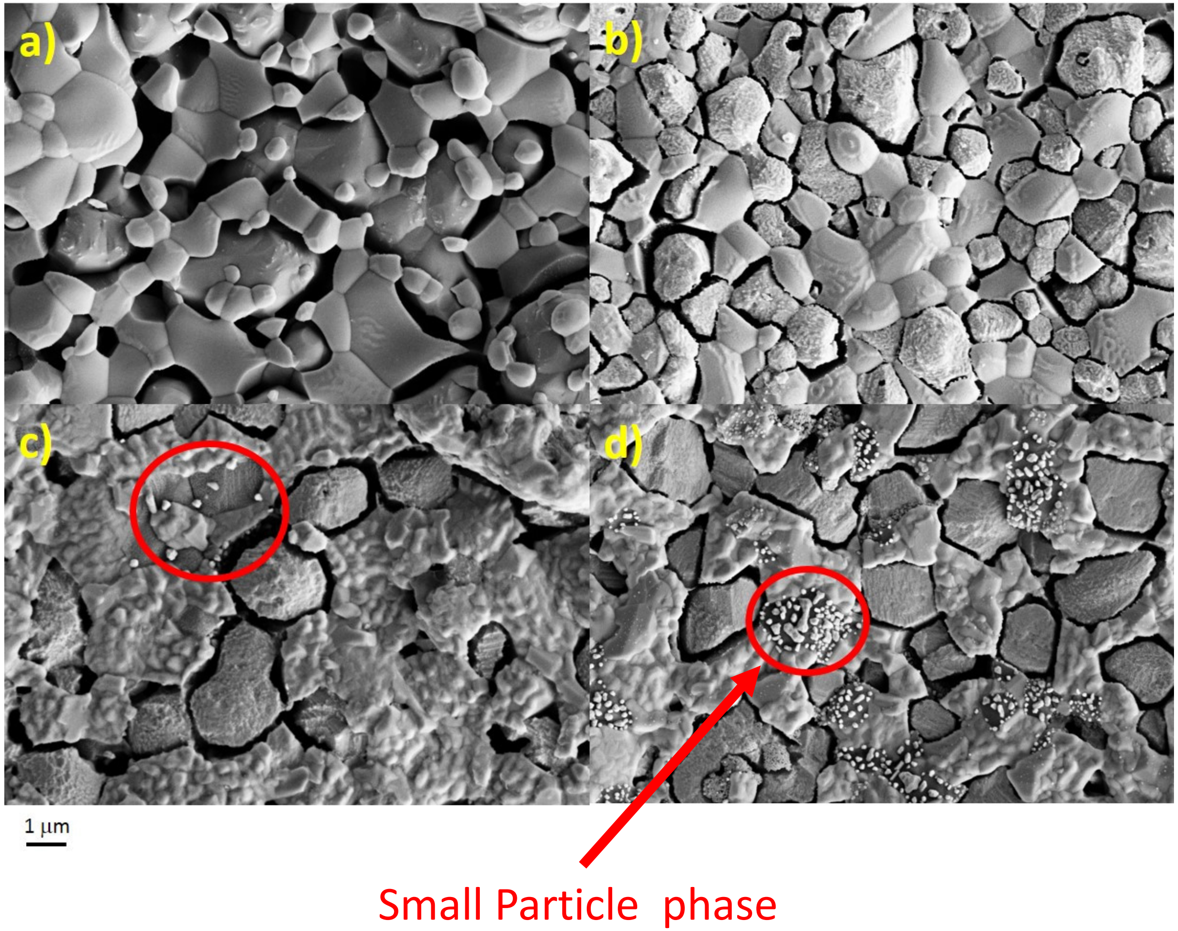

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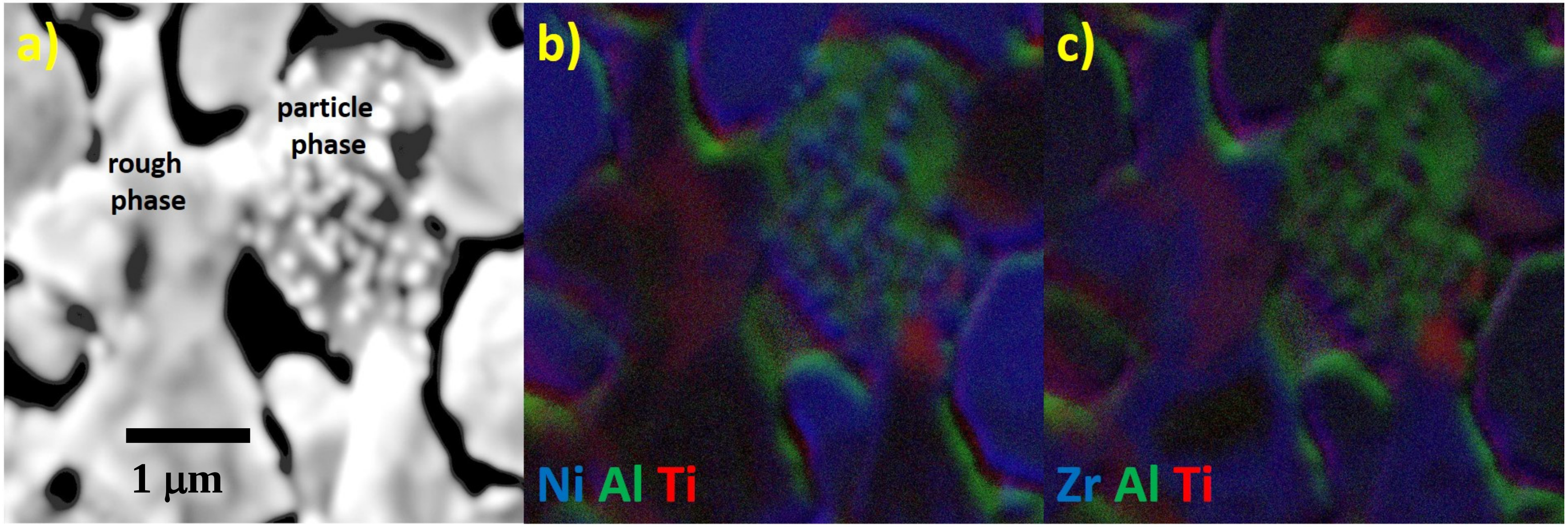
ALT segregates between the NiO and the YSZ (nano-Auger)



- Ti and Zr are spatially associated ($Zr_5Ti_7O_{24}$ from XRD and Raman)
- Al and Ni are associated ($NiAl_2O_4$)

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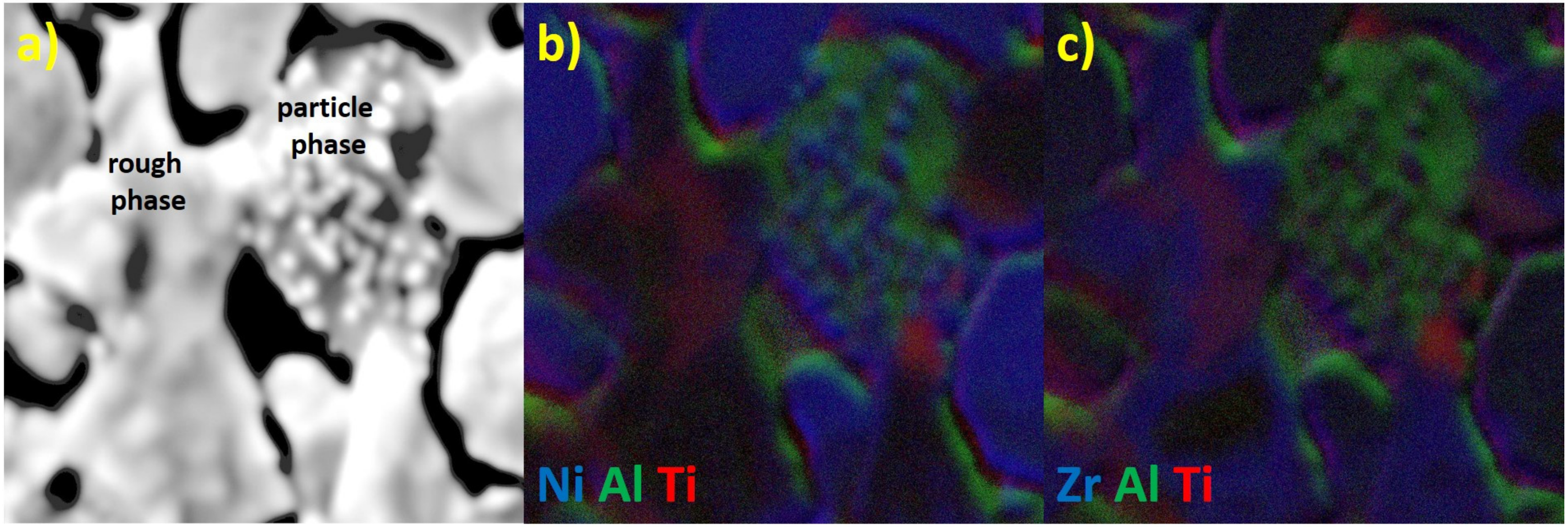
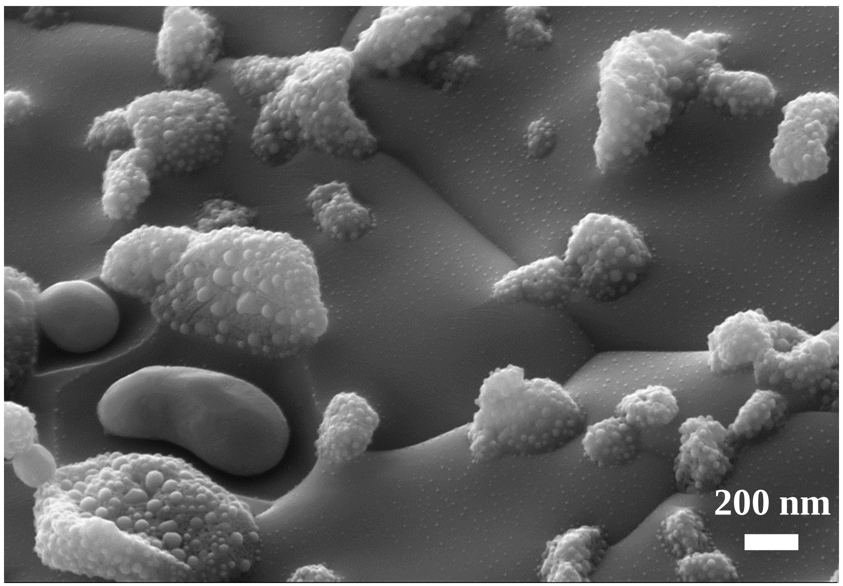
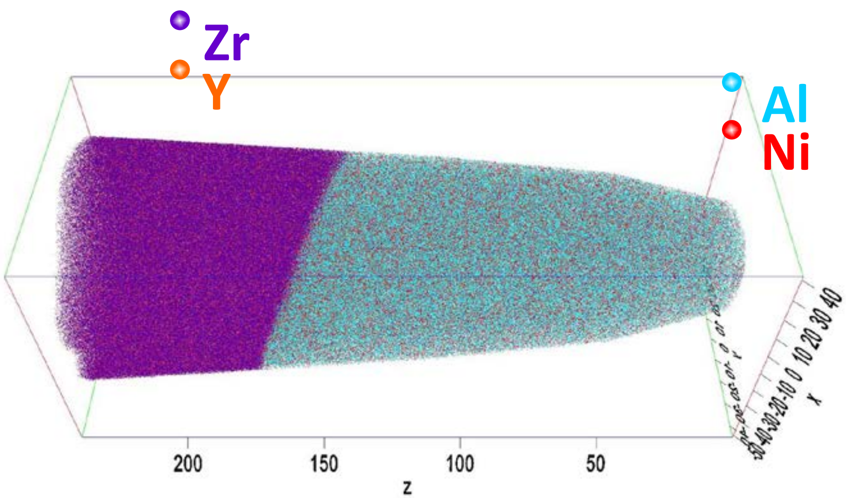


Further evidence from TEM and APT (at EMSL)





Bounding box dimensions: 93.0 × 91.7 × 238.8 nm^3

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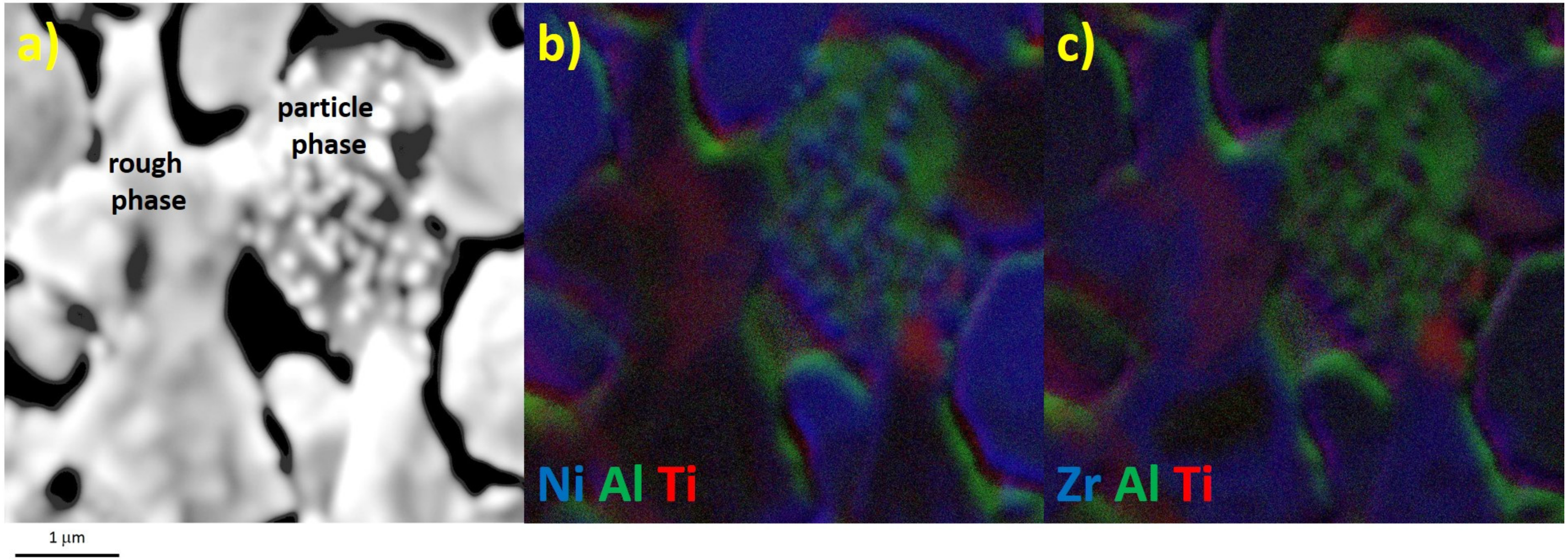
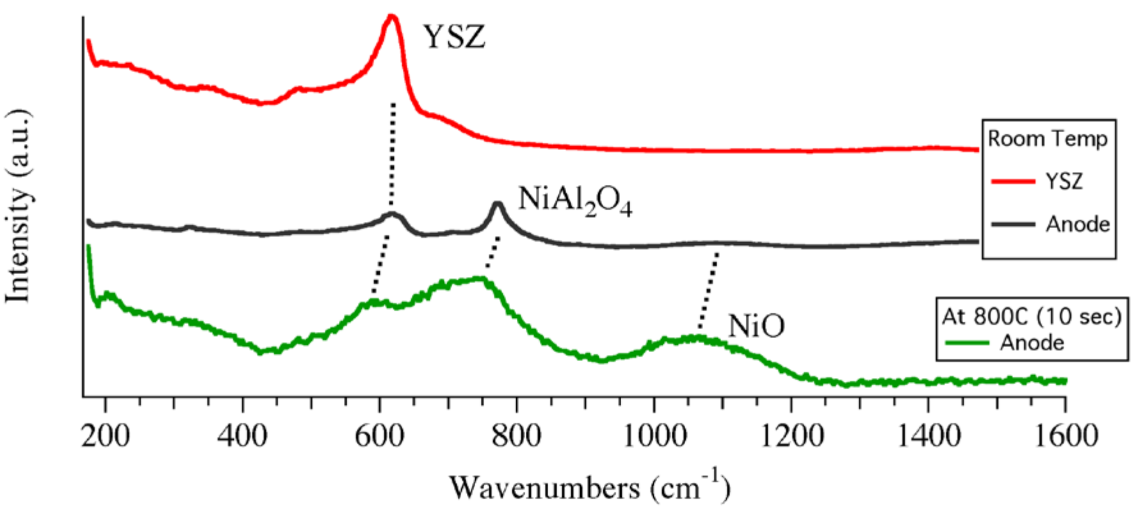
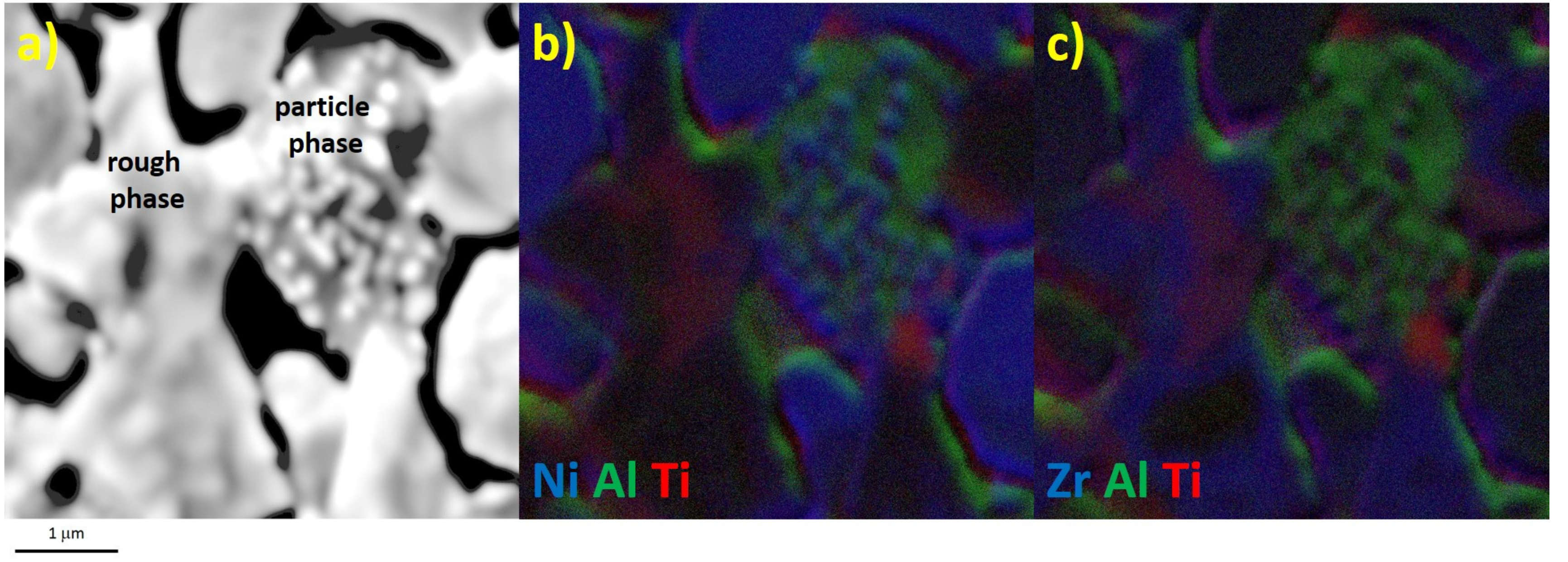


Further evidence from *operando* Raman spectroscopy – Ni/Al rich areas

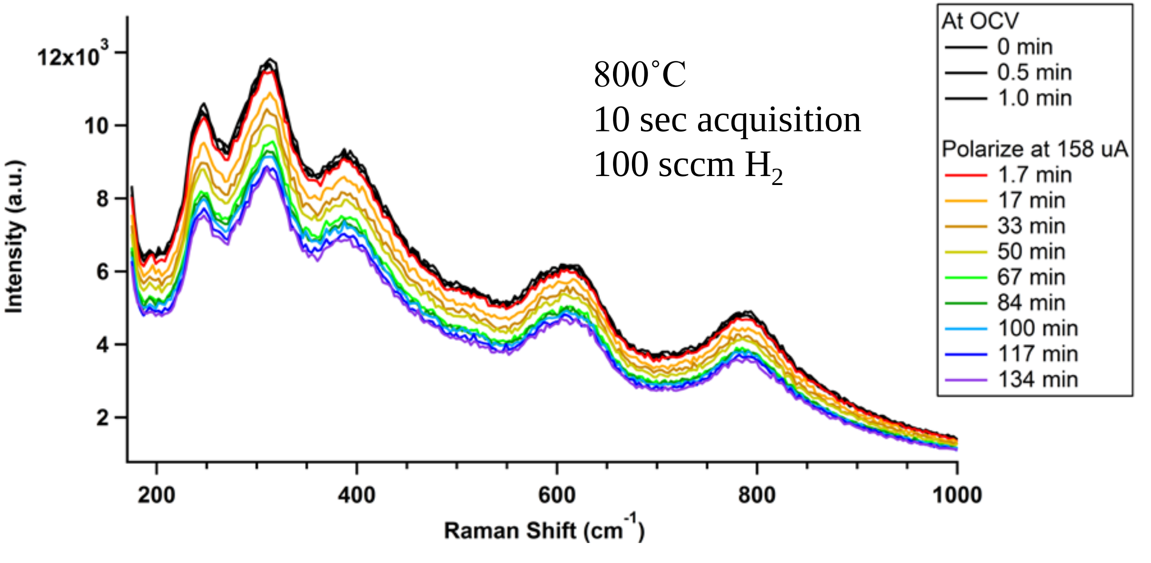


- Raman spectroscopy identifies **$NiAl_2O_4$** as a stable species up to 800˚C in air
- Heterogeneously dispersed across surface

ALT segregates between the NiO and the YSZ (nano-Auger)

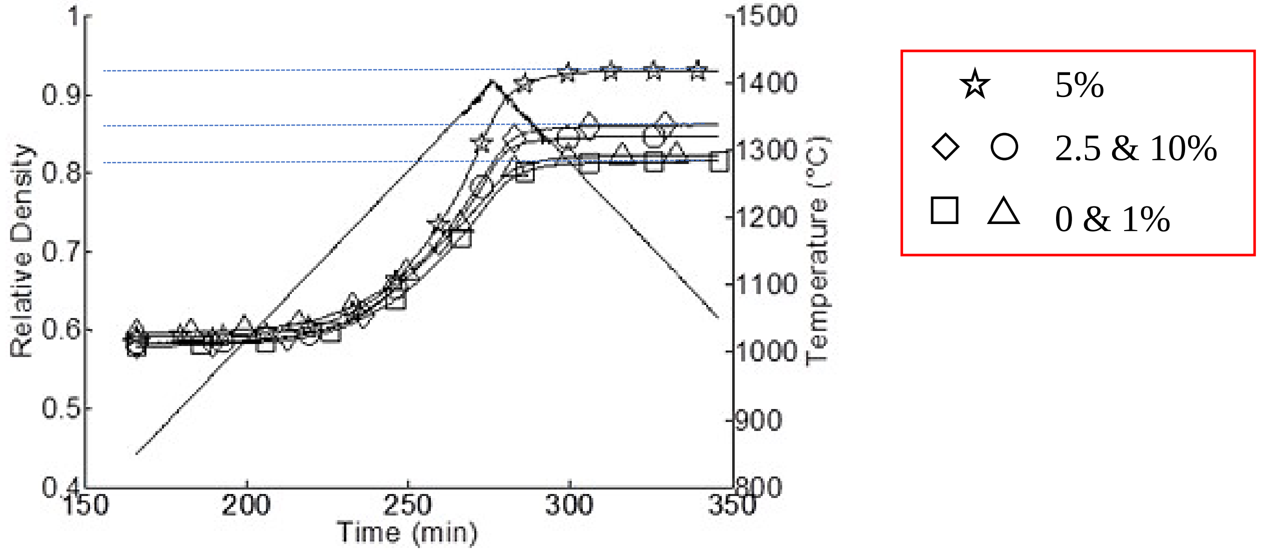


Further evidence from *operando* Raman spectroscopy – Zr/Ti rich areas

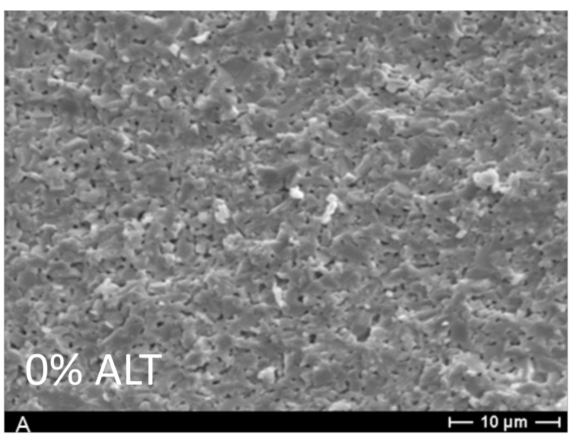


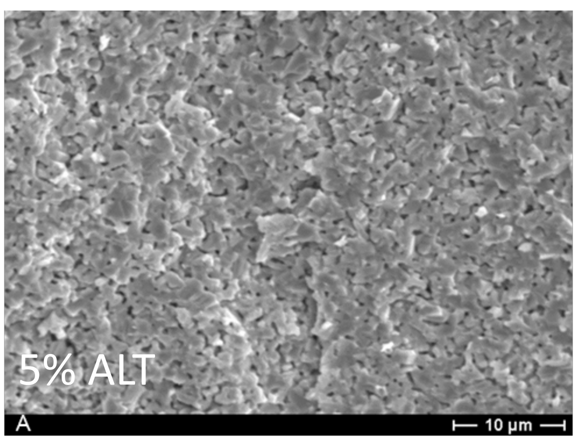
- Raman spectroscopy (and XRD) identifies $Zr_5Ti_7O_{24}$ as a stable species up to 800˚C
- $Zr_5Ti_7O_{24}$ stable under oxidizing and reducing conditions.
- Heterogeneously dispersed across surface

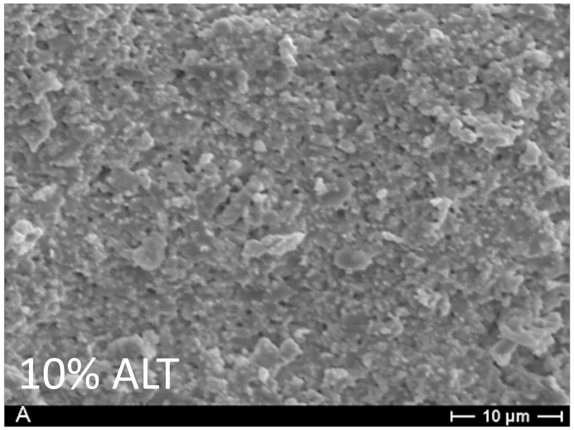
ALT as a sintering aid for NiO-YSZ:



- Ni-YSZ cermet anodes with ALT mixed in mechanically
- Sintering density v. temperature measured via dilatometry
- Absolute density changes with composition; most enhanced effects with 5% ALT
- No dramatic changes observed in microstructure.







How do the ALT-doped anodes behave?

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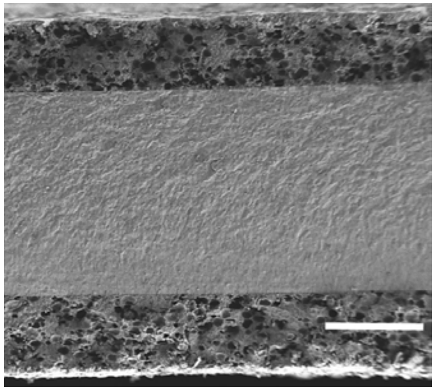
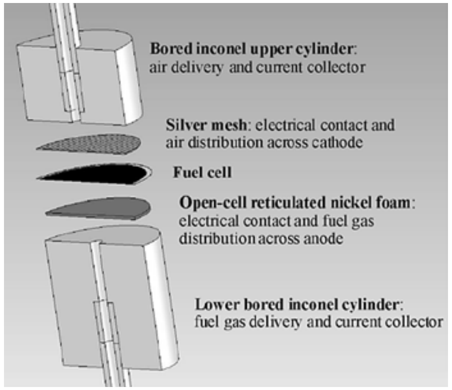
Details:

- Electrolyte supported (2.5 cm diam; 300 µm thick)
- Mechanically mixed anode material (NiO, YSZ, ALT)
- Xylene/Ethylene glycol suspension; ball milled
- Sprayed, Sintered to 1400˚C (~50 µm thick)
- LSM/YSZ cathode
- Operate at 800˚C and dry H_2

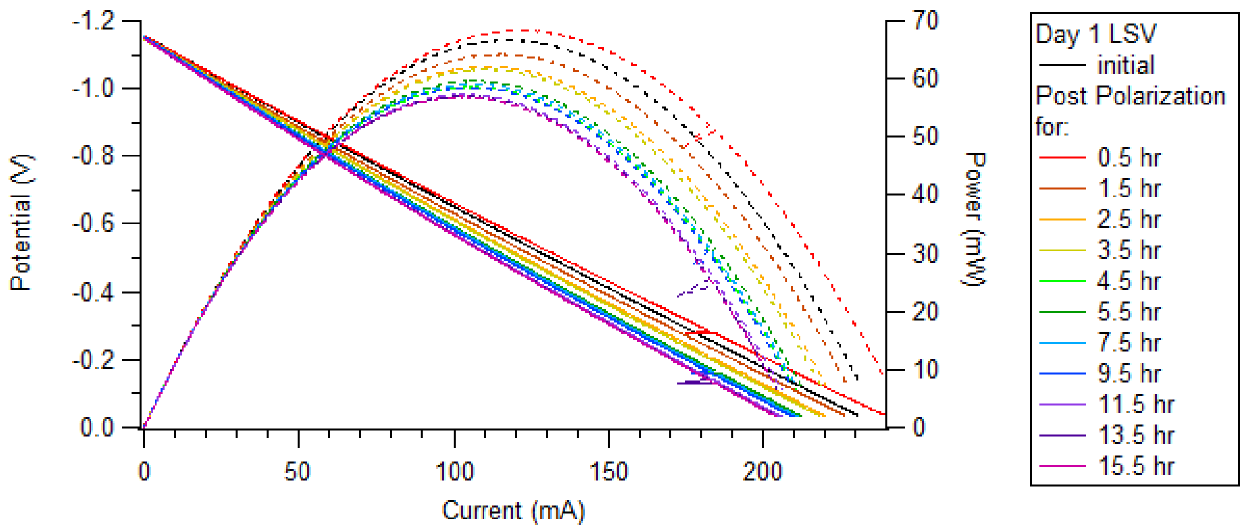
Experiments:

- Linear sweep voltammetry
- Constant polarization (0.7 V)
- Degradation at constant polarization (24-120 hrs)
- Electrochemical impedance spectroscopy (EIS)
- *Operando* Raman spectroscopy





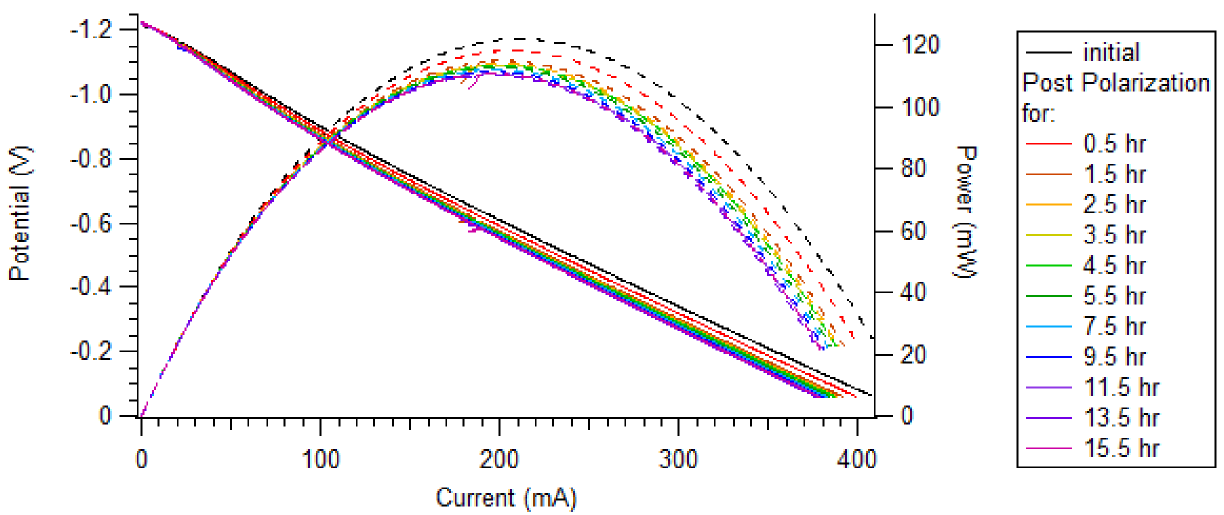
Performance (0% vs. 2% ALT)



Pure Cell

I_{max} = 239 mA/cm^2 → 204 mA/cm^2

P_{max} = 68 mW/cm^2 → 57 mW/cm^2



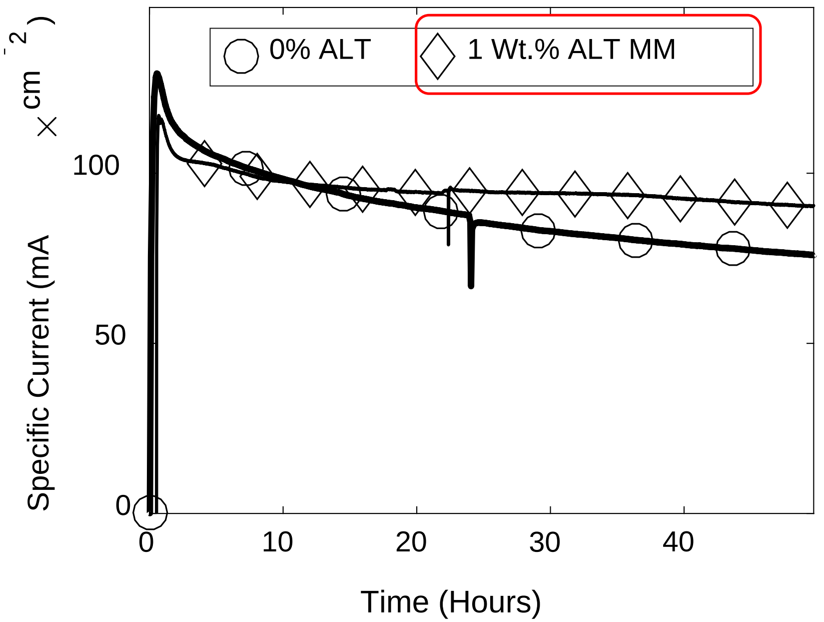
2 mol% ALT Cell

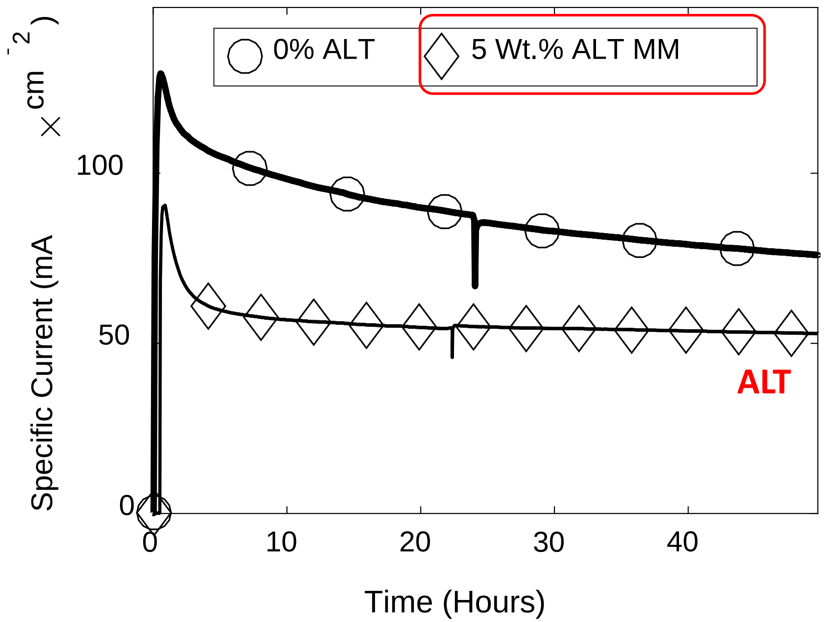
I_{max} = 379 mA/cm^2 → 408 mA/cm^2

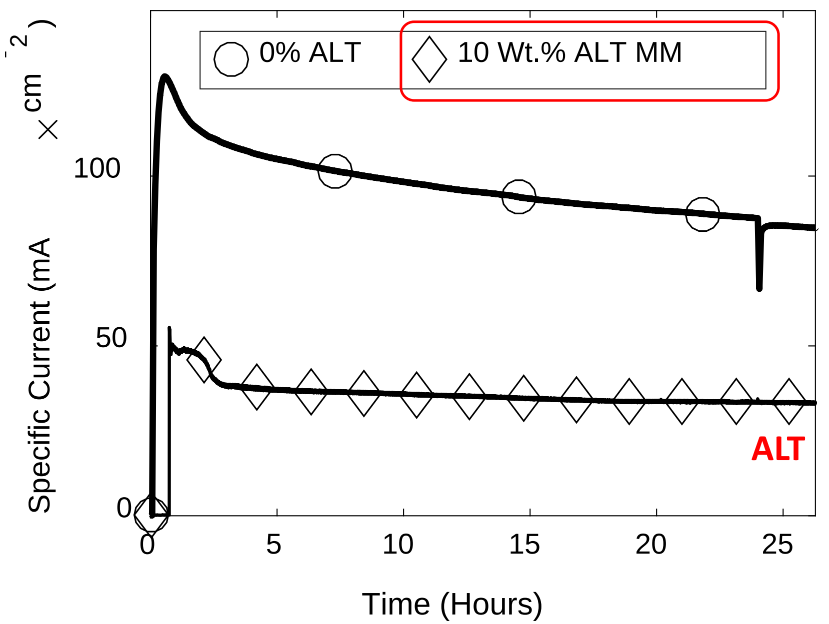
P_{max} = 122 mW/cm^2 → 110 mW/cm^2

2% ALT cell shows ~2x better performance & less degradation

Performance vs. % loading (mechanically mixed)





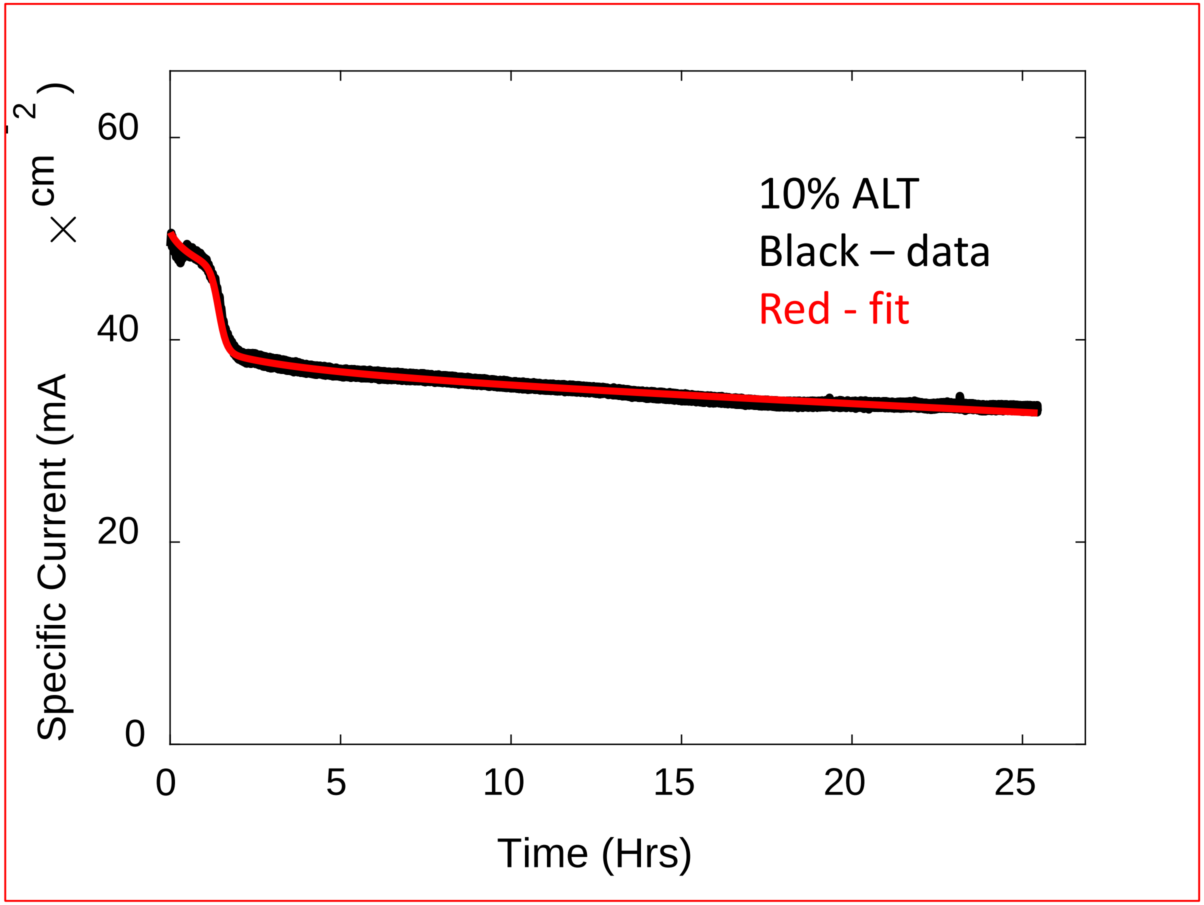


- Polarized to 0.7 V (800˚C, dry H_2)
- ALT adversely affects performance in (MM)
- Lower current densities for ALT > 3%
- Degradation rate appears slower with ALT

Quantifying degradation

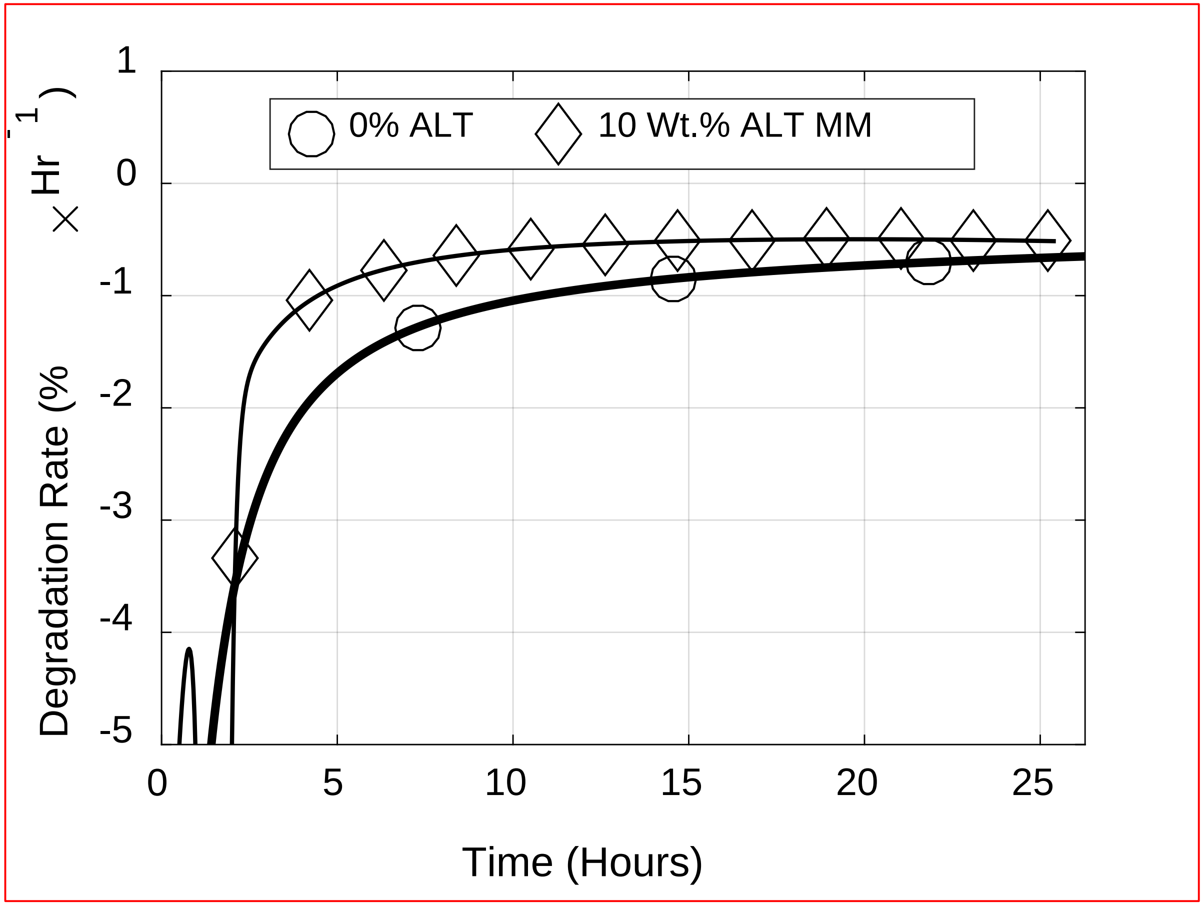
- Develop empirical curve-fitting algorithm
- Fit all degradation plots with R-squared value of 0.95 or better.
- Degradation rates are determined from curve fit, and normalized with respect to current output of fuel cell at that time…
- Curve-fitting equation
  - $I(t) = a_0 c_0 \cdot \frac{1}{t} + a_1 c_1 \cdot \sqrt{\frac{t}{t_0 - t}} + a_2 c_2 \cdot \tan(at - b)^{-1} + a_3 c_3 \cdot \frac{I_{Max}}{1+\exp(-at+b)}$
- Derivative
  - $R(t) = \frac{-a_0 c_0}{t^2} + \frac{a_1 c_1 \cdot t_0 \sqrt{t_0 - t}}{2\sqrt{t} \cdot (t - t_0)^2} + \frac{a_2 c_2 \cdot a}{(b - at)^2 + 1} + \frac{a_3 c_3 \cdot a \cdot I_{Max} \cdot \exp(b - at)}{(1 + \exp(b - at))^2}$
- Normalized Degradation Rate: $\frac{dI_{Norm}}{dt} = \frac{R(t)}{I(t)}$
- Positive ‘degradation’ rates = performance improvement
- Negative degradation rates = performance decline

Quantifying degradation



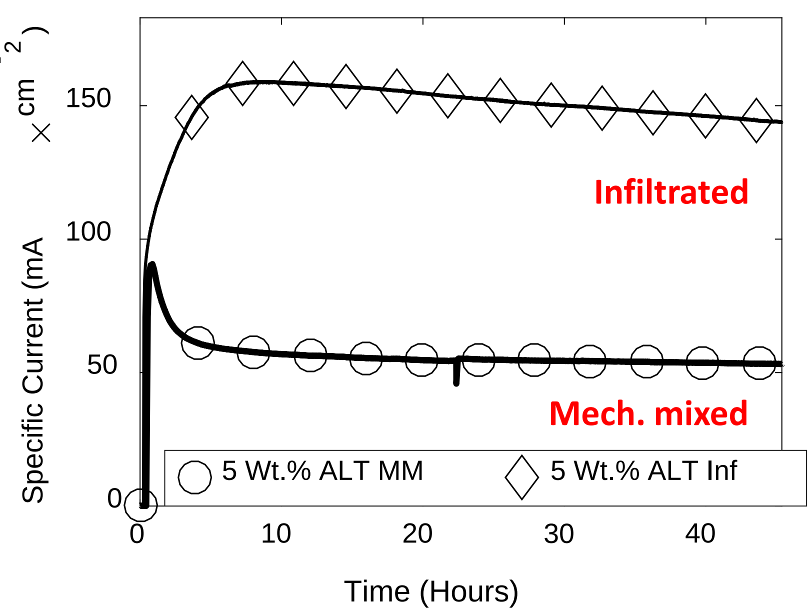
Empirical fit & iteration converge to observed behavior

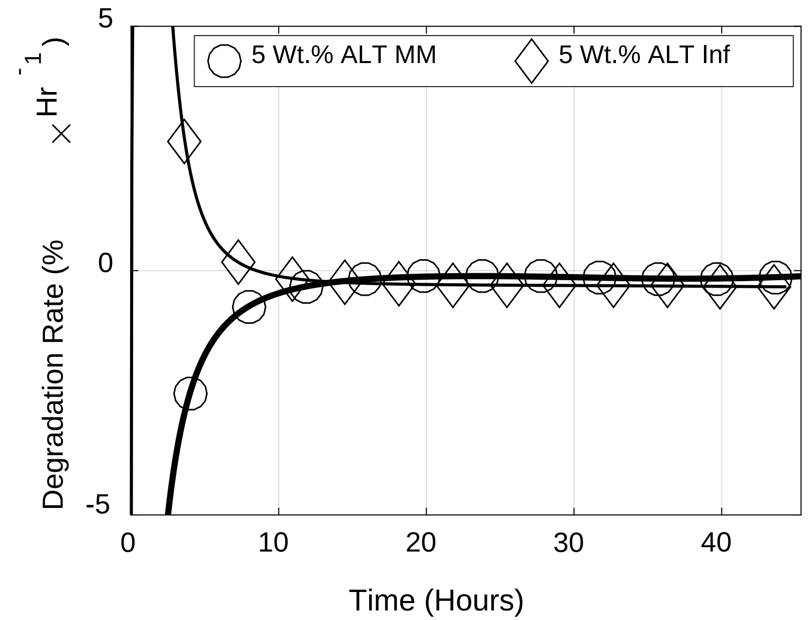
Quantifying degradation



Degradation rates can be reported accurately and updated

Mechanical mixing vs. infiltration

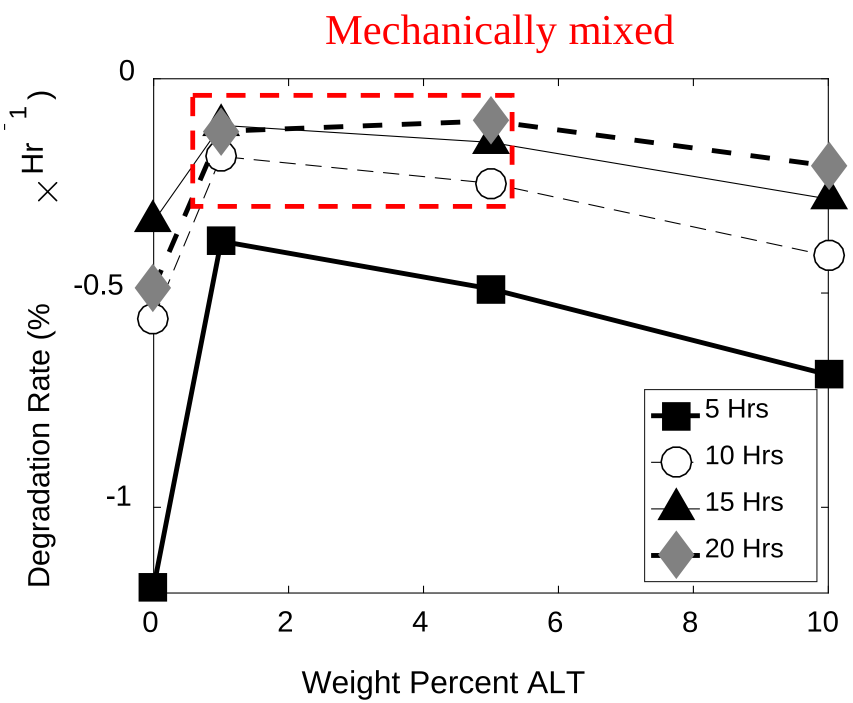




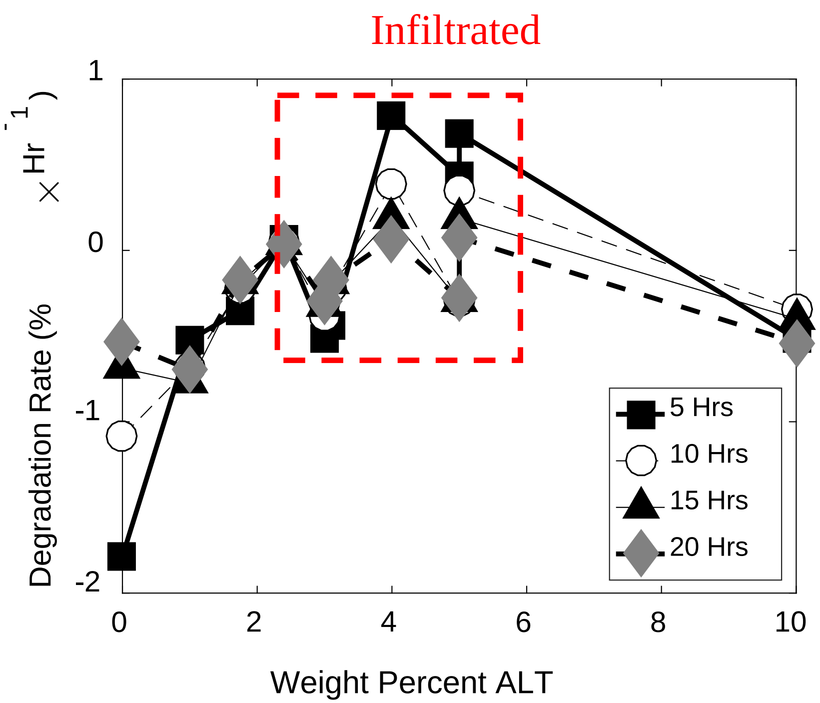
- Infiltrated cells show improved electrochemical performance
- Degradation rates both converge to ~-0.25%

Green Ni-YSZ		Degradation Rate (%-Hr^{-1})					
	I_{max} (mA/cm^2)	5 Hr	10	15	20	30	40
0% ALT	129	-1.62	-1.03	-0.85	-0.81		
5% ALT MM	52	-1.39	-0.51	-0.27	-0.20	-0.24	-0.21
5% ALT Inf	157	+1.60	-0.05	-0.27	-0.24	-0.26	-0.23

Degradation mechanically mixed vs. infiltrated

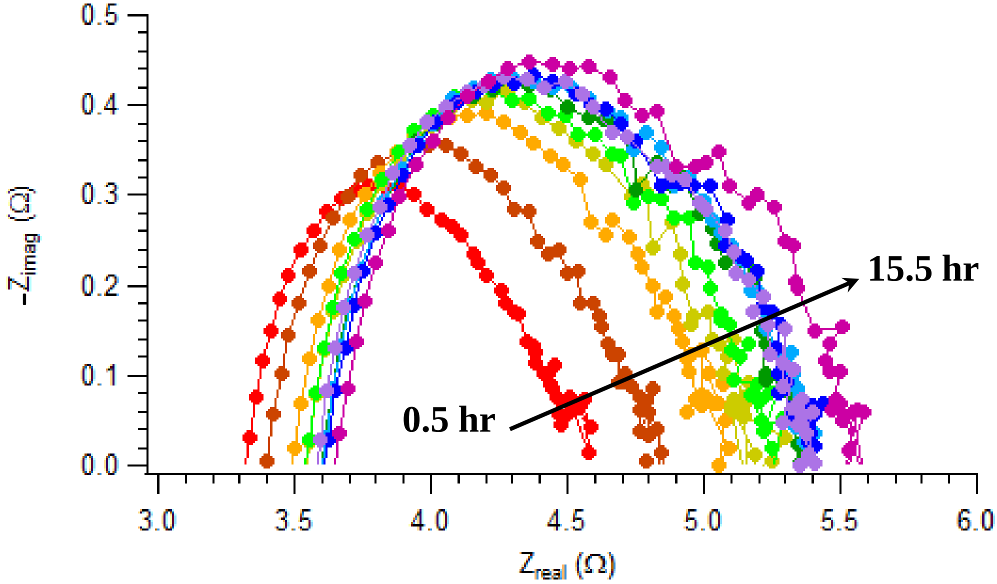


ALT added by mechanical mixing predicts optimal concentration ~1–4 wt.% ALT



ALT added by INFILTRATION predicts optimal concentration ~3-6 wt.% ALT

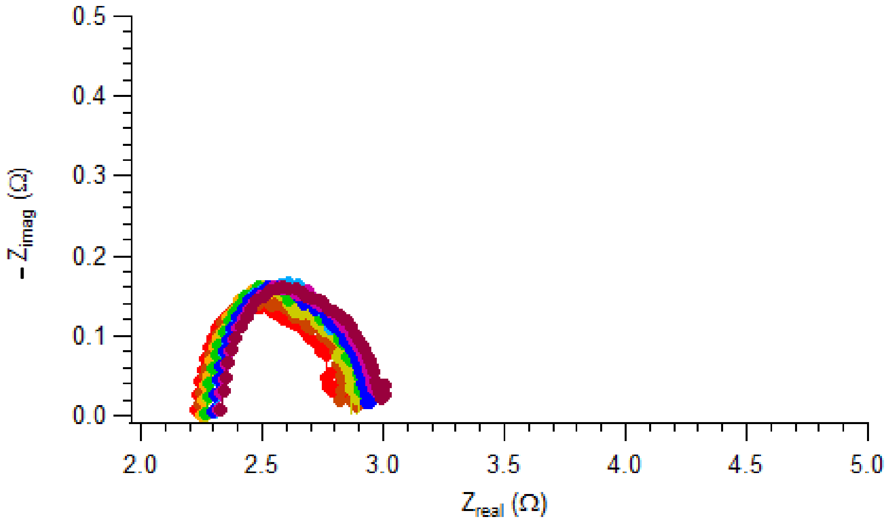
Performance (0% vs. 2% ALT)



Pure Cell

$R_B = 3.34\ \Omega \rightarrow 3.76\ \Omega$

$R_P = 1.24\ \Omega \rightarrow 1.86\ \Omega$



2 mol% ALT Cell

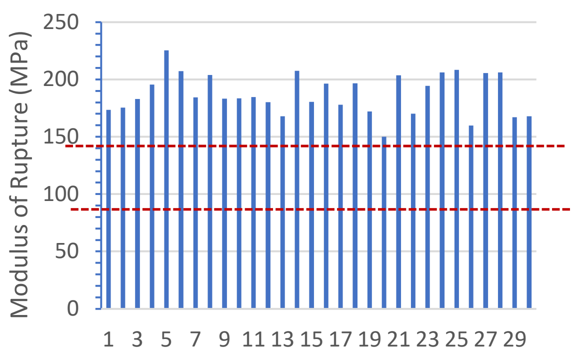
$R_B = 2.22\ \Omega \rightarrow 2.33\ \Omega$

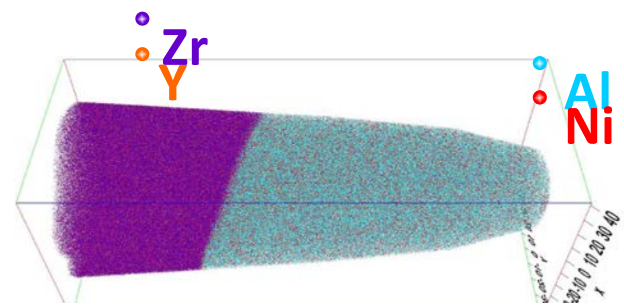
$R_P \approx 0.62\ \Omega \rightarrow 0.66\ \Omega$

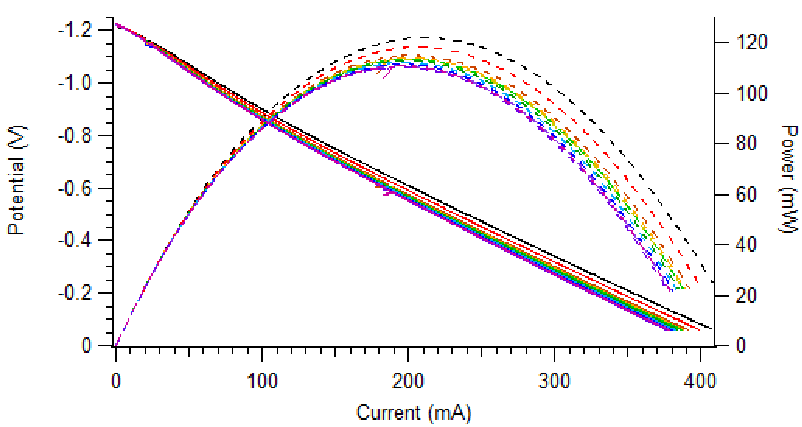
Qualitative differences in EIS imply different charge transfer mechanisms

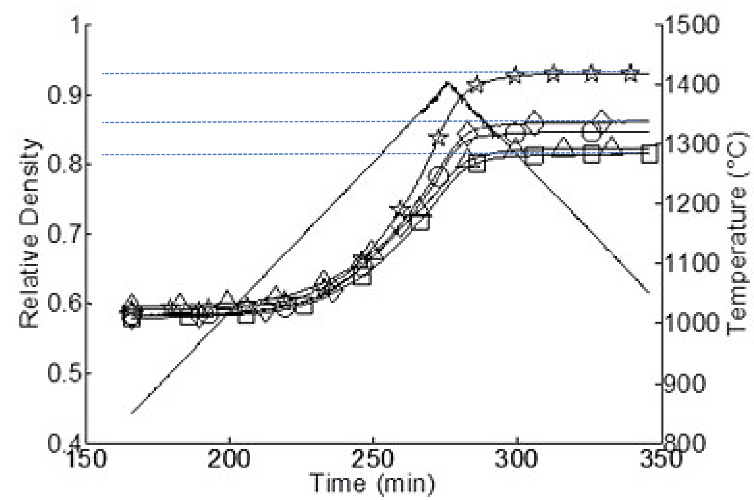
Phase I - Accomplishments

- Stronger anode materials - 50% enhancement with ALT
- Denser anode materials (optimized at 5% ALT mech. mixed)
- *Operando* electrochemical studies (enhanced at low % ALT if mech. mixed)
- *Operando* electrochemical studies (enhanced at medium % ALT if infiltrated)
- (*Test commercial materials*)



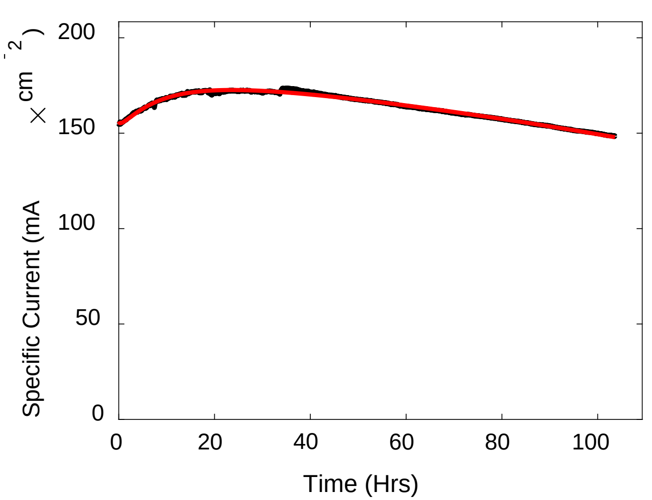


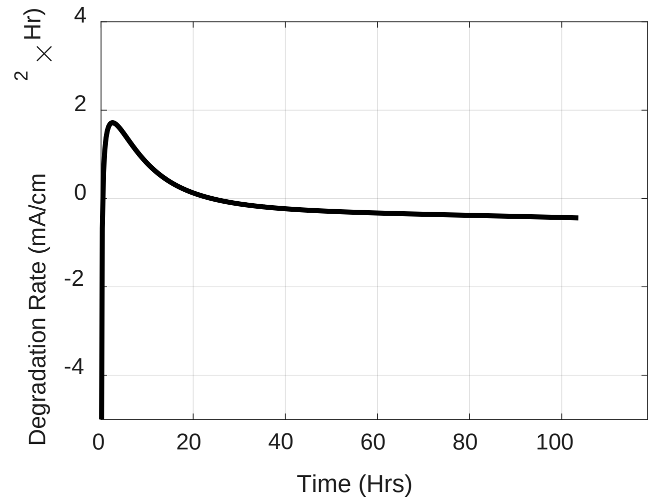




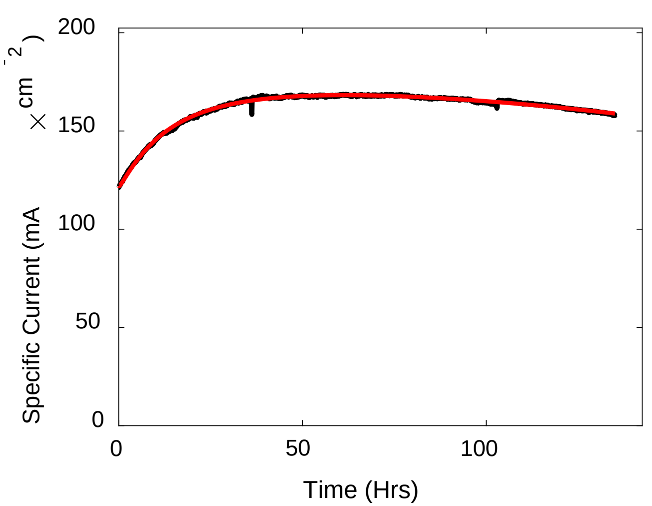
Raw materials from Fuel Cell Energy

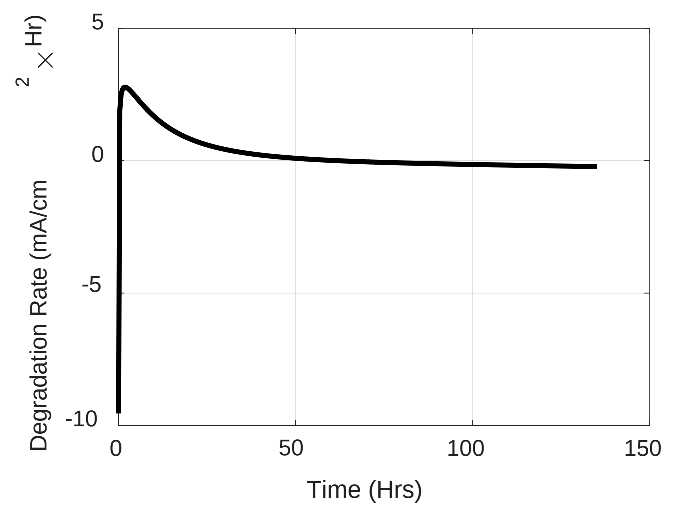
0% ALT (8 YSZ & 3 μm NiO)





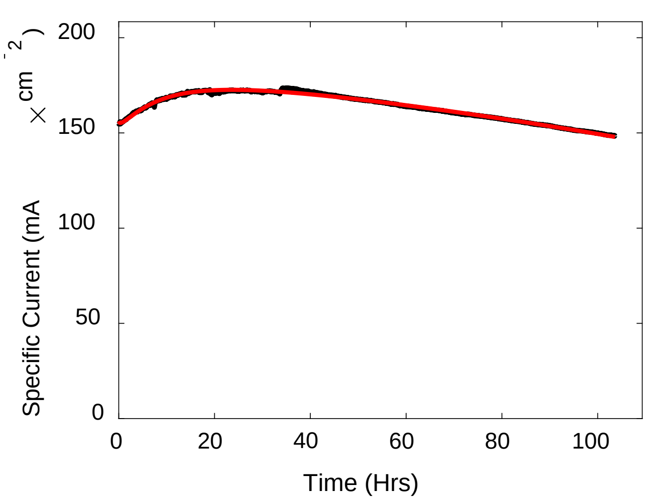
4% ALT mech mixed (8 YSZ & 3 μm NiO)

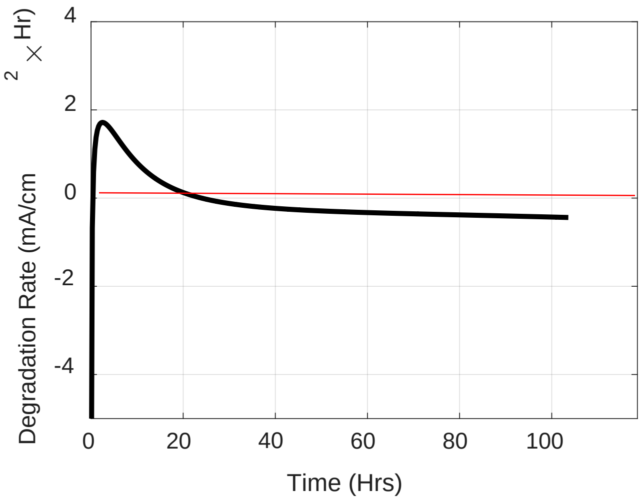




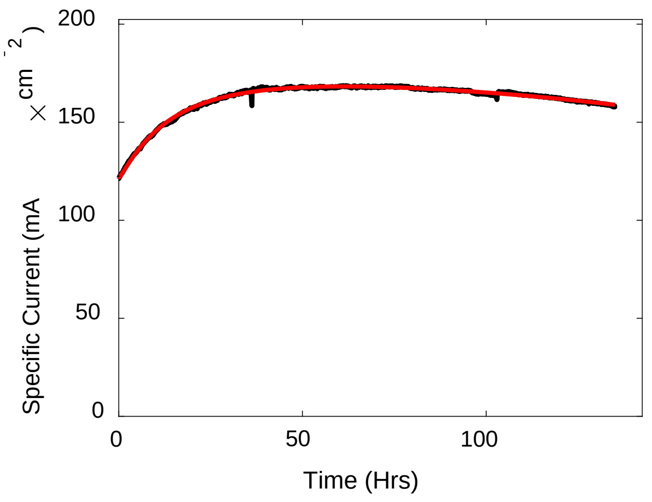
Raw materials from Fuel Cell Energy

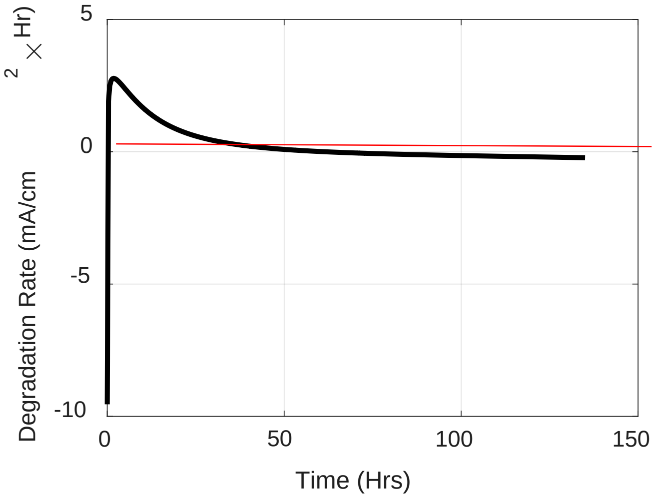
0% ALT (8 YSZ & 3 μm NiO)





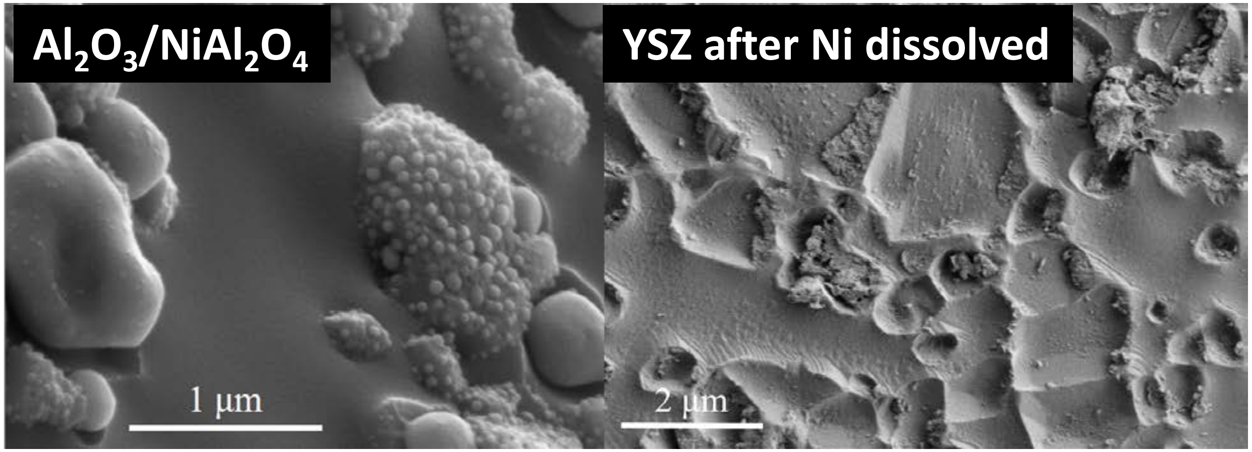
Similar performance over 120 hours;
ALT slows degradation.

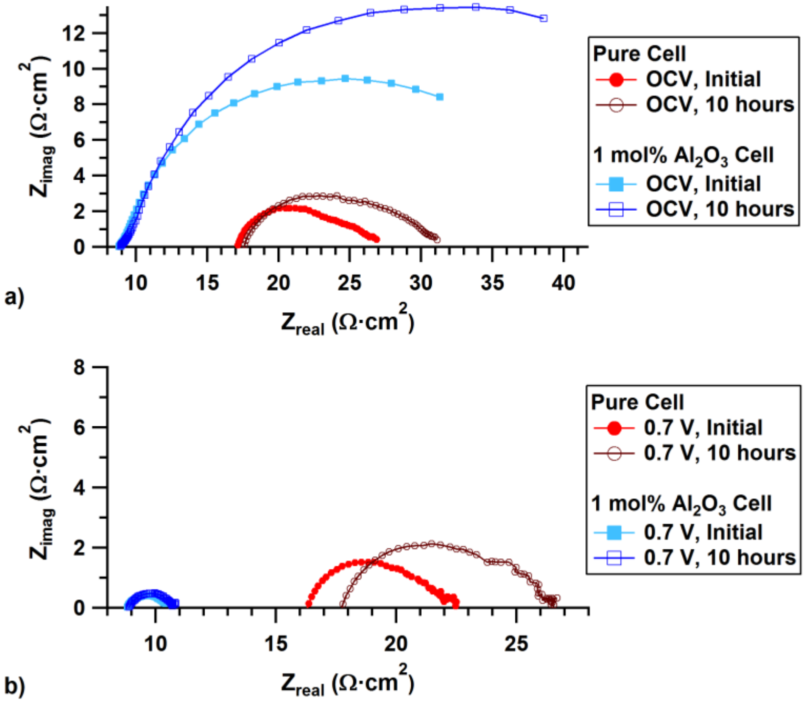


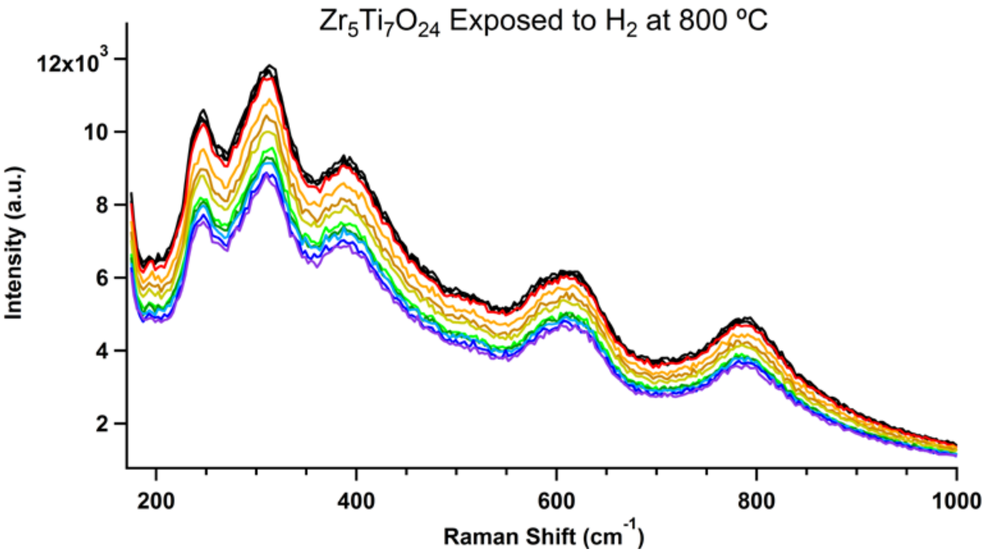


Future work

1. Role of individual additives? (Al_2O_3 vs. TiO_2)

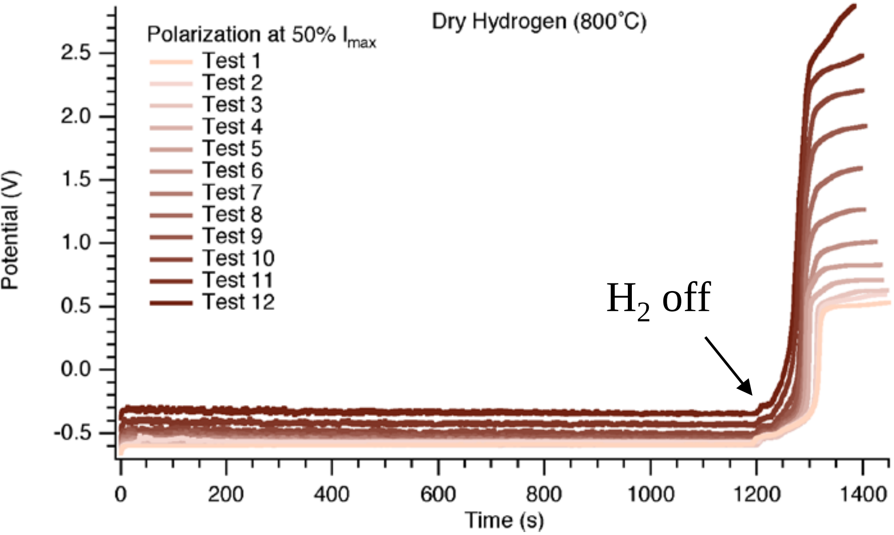


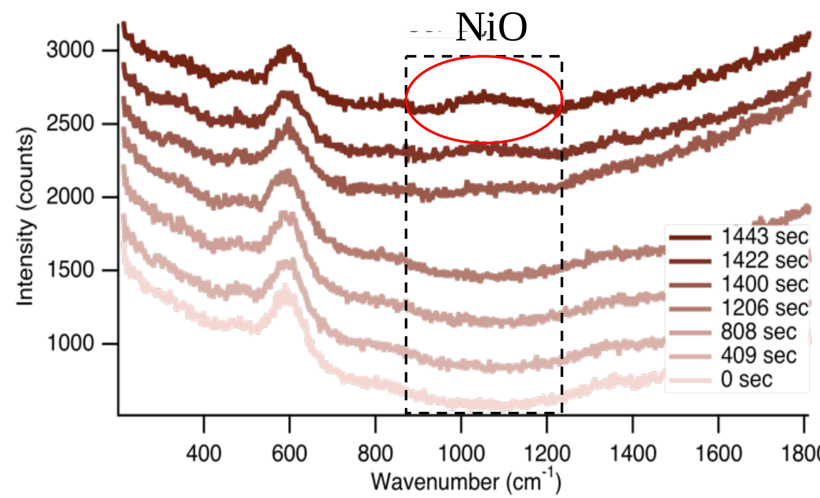


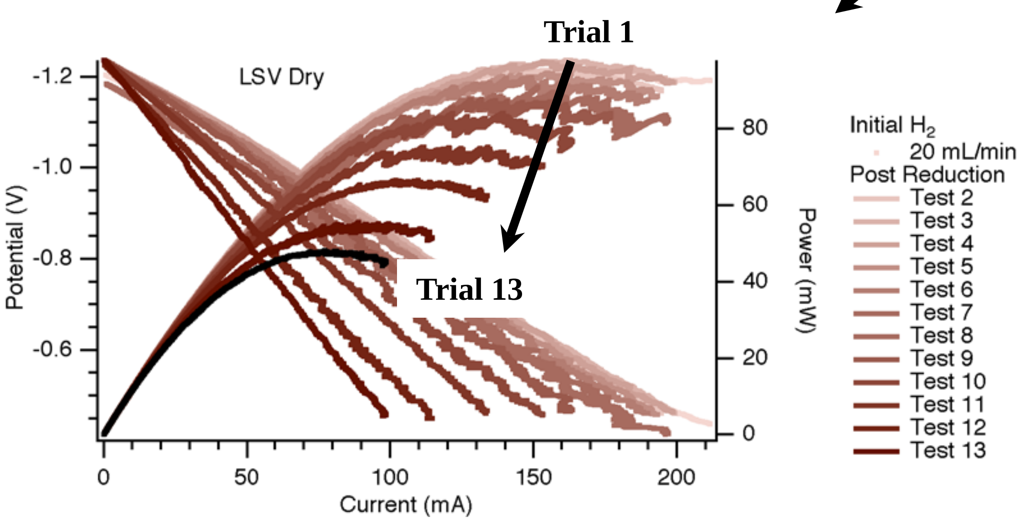


Future work

2. Resilience to electrochemical and environmental redox cycling







Ni-YSZ only (no ALT)

- Operate for 20 min at const current
- Turn off H_2 at 20 min
- Monitor potential
- Vibrational spectra
- Stop current when NiO appears
- Re-reduce anode & measure LSV

Acknowledgements

Joe Stoffa & NETL-SOFC staff

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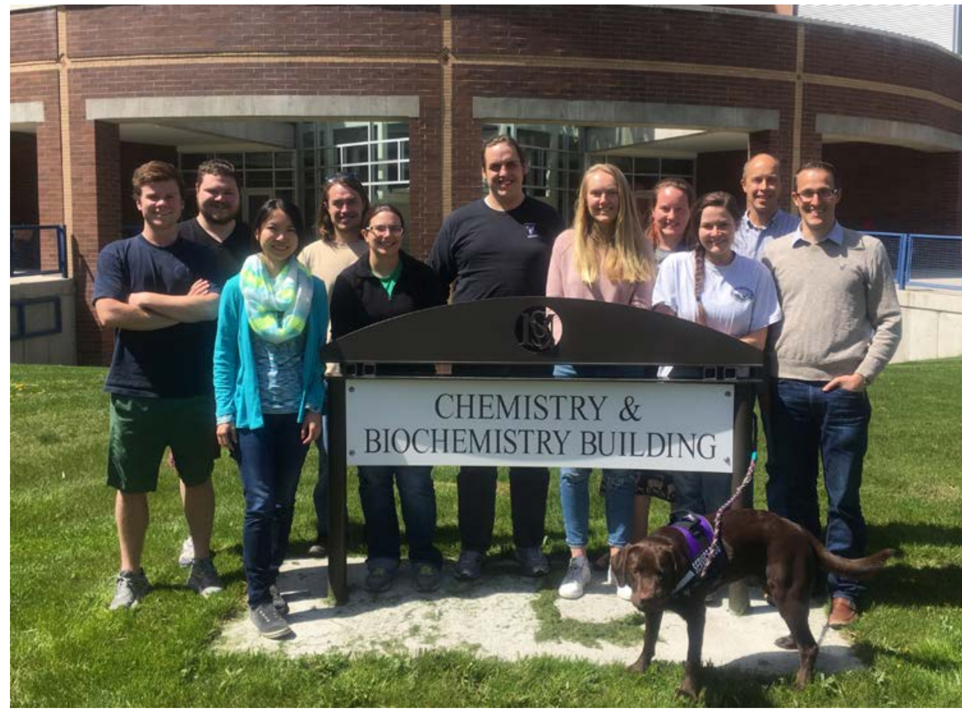
Kyle Reeping (Walker)

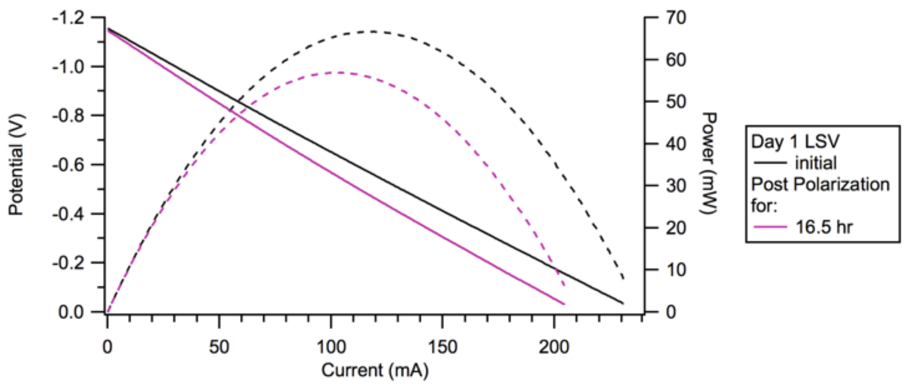
Märtha Welander (Walker)

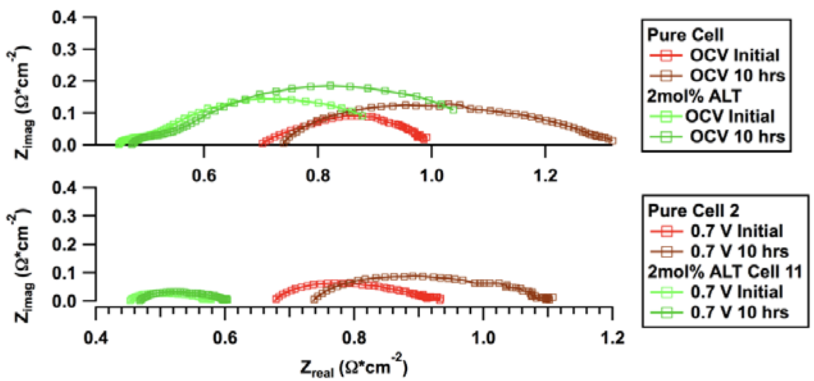


Dr. Ali Torabi, Fuel Cell Energy

Tasks – Phase I

- Fabricating anodes with ALT (0 – 10%)
- Map effects of temp and sintering rates on 2˚ phases
- Test mechanical strength
- Identify new materials that form
- *Operando* electrochemical studies
- *Operando* vibrational Raman spectroscopy
- (Test commercial materials)





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