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

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Program Officer: Joe Stoffa
DE-FE-0026192

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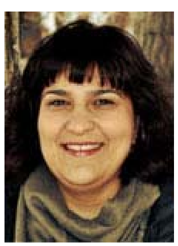
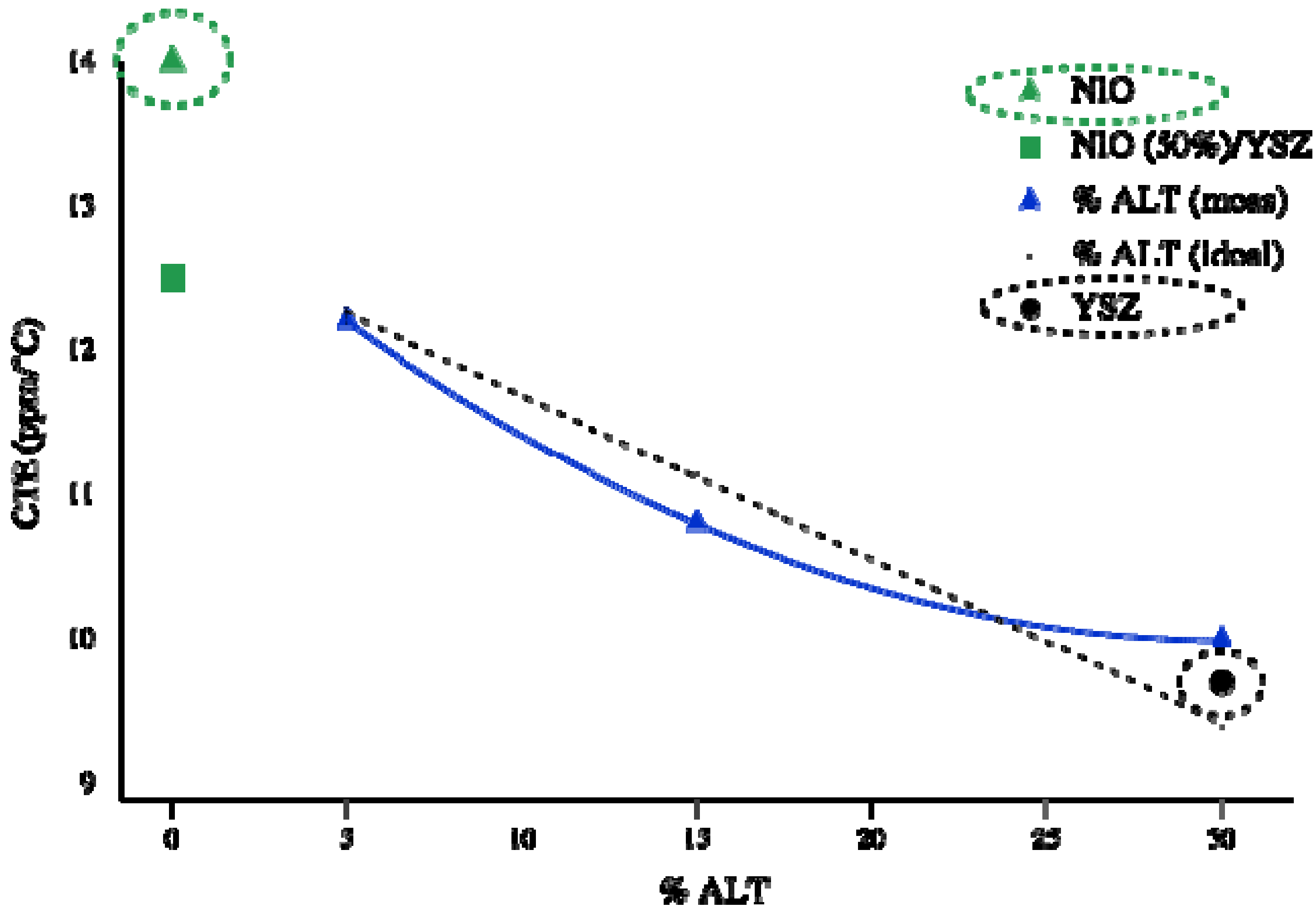


& Clay Hunt
Madisen McCleary
Martha Welander

A serendipitous observation . . . .

- NiO and YSZ have a mismatch in CTE that causes stress and structural failure.
- Aluminum titanate (ALT, Al_2TiO_5) has a CTE of $< 1 \times 10^{-6}$
- *Can ALT be added as a dopant to better match anode and electrolyte CTEs?*

Serendipitous observations . . . .

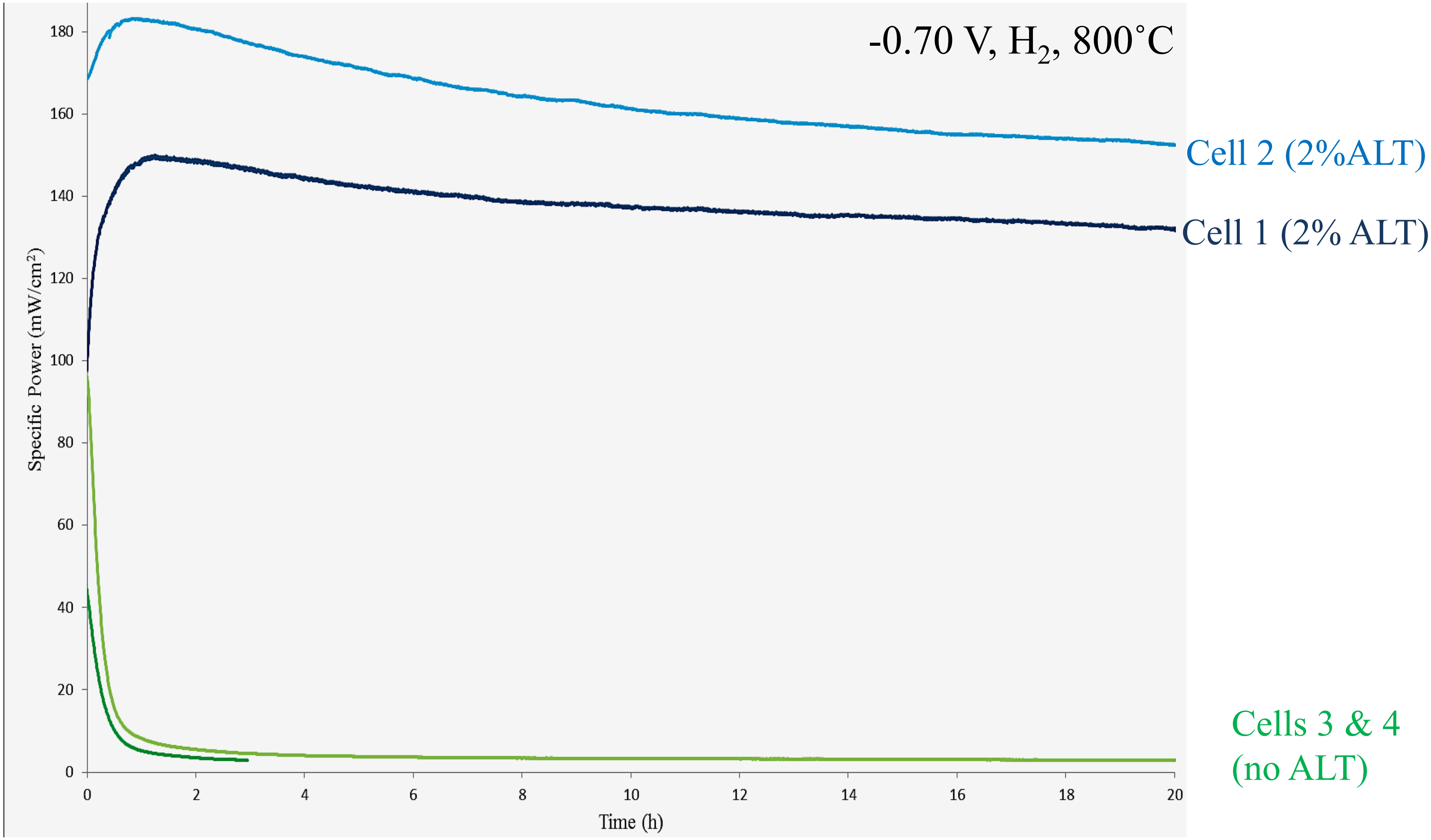


Simple Rule of Mixtures Model: volume fraction weighting

$$\alpha_{Total} = \alpha_{YSZ} * V_{YSZ} + \alpha_{Ni} * V_{Ni} + \alpha_{ALT} * V_{ALT}$$

Sofie

Serendipitous observations . . . .(infiltrated anodes, e-lyte supported)

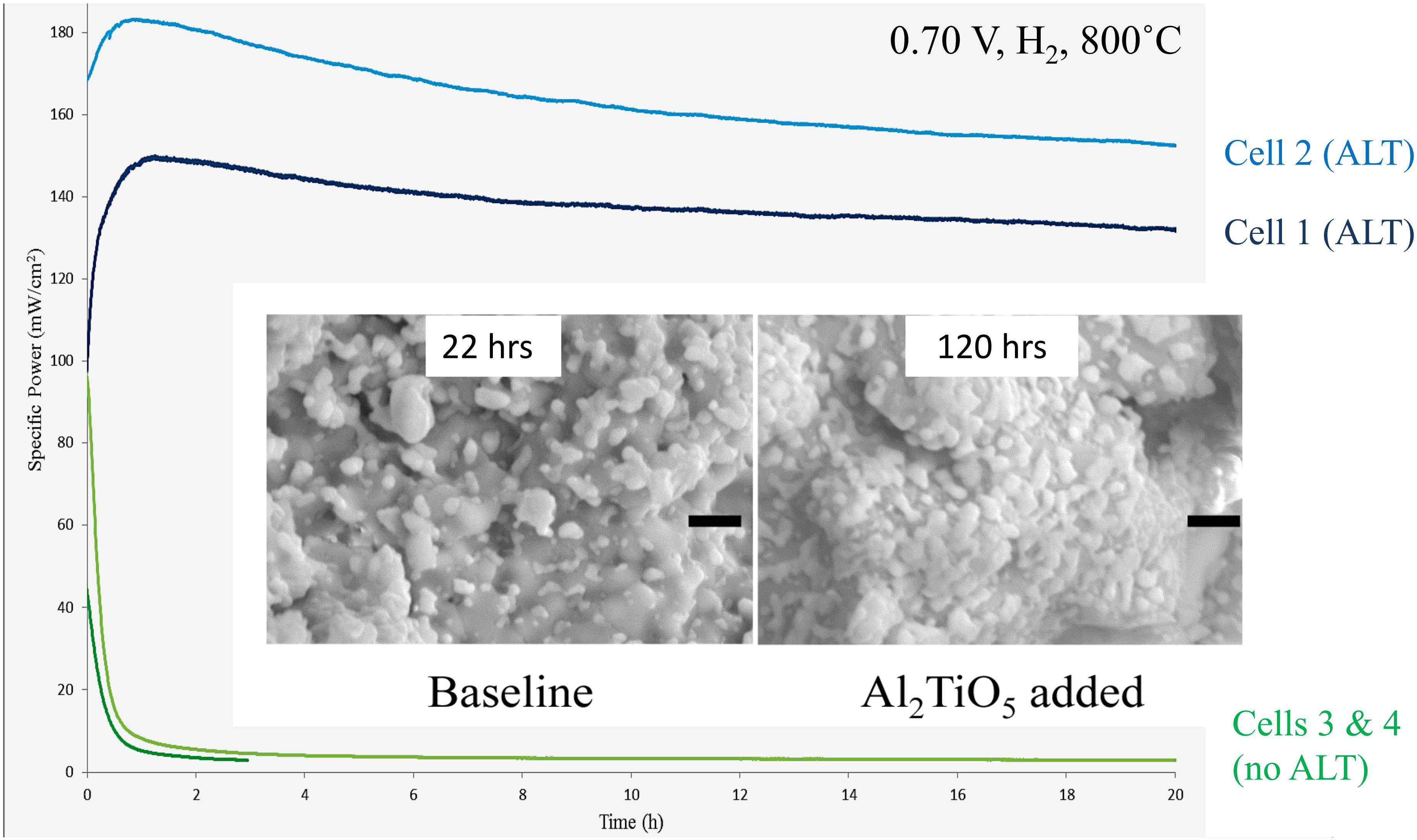


Infiltrated, electrolyte supported MEA's (low Ni loadings, ~20%)

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

Sofie

Serendipitous observations . . . .



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

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Questions. . . .

1. What’s going on?

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   - **A lot**

Questions. . . .

1. What's going on?
   - **A lot**
2. Mechanical effects of ALT doping?
3. ALT compositional changes with processing?
4. New electrochemical mechanisms?

Statement of Project Objectives

- Identify the most effective means of introducing 2° phase precursors to traditional Ni-YSZ cermet structures (**mechanical mixing or solution phase infiltration**) and the optimal 2° phase loadings

- Determine the **optimal thermal conditioning procedures** that promote 2° phase formation while introducing as little perturbation as possible to anode microstructure.

- Quantify the effects of 2° phases on the electrochemical performance and durability of SOFC anodes using a of **in operando and ex situ techniques**

- Recommend strategies for **scaling-up fabrication practices**

Many methods, many conditions, many answers . . . .

Table 1. Primary methods to be employed in the proposed research

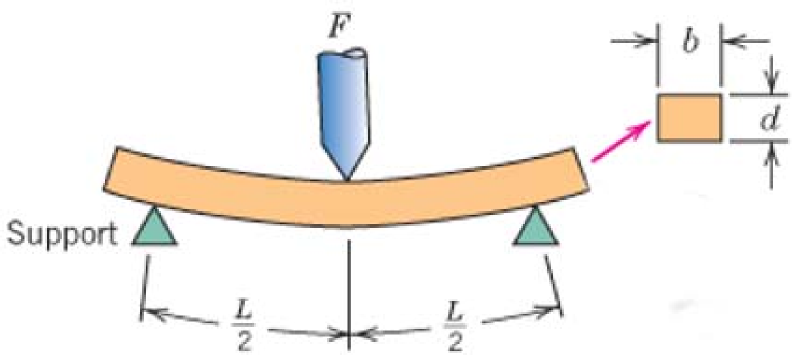
Technique[a]	Purpose	Surface/Bulk[b]	In /Ex situ	Composition (spatial resolution)	Kinetics (temporal resolution)	Performance/ Durability
XRD	*Phase composition*	*Bulk*	*Both*	*Y*	*N*	*n/a*
XPS	*Elemental composition and redox state*	*Surface*	*Ex situ*	*Y (50 μm)*	*N*	*n/a*
Raman	*Material vibrational structure*	*Both*	*Both*	*Y (1-2 μm)*	*Y (1-2 sec)*	*n/a*
NIR Thermal Imaging	*Thermal changes across anode surface*	*Surface*	*In situ*	*Y (20 μm laterally)*	*Y (< 1 sec)*	*n/a*
Flexural strength testing	*Measure mechanical stability*	*Bulk*	*Ex situ*	*N*	*N*	*Y*
SEM	*Structure and morphology*	*Bulk*	*Ex situ*	*N (0.5 μm)*	*N*	*n/a*
EDX	*Elemental composition and mapping*	*Bulk*	*Ex situ*	*Y (0.5 μm)*	*N*	*n/a*
DTA/TGA-MS	*Redox behavior, chemical interactions and volatility*	*Bulk*	*Both*	*N*	*Y (3-5 sec)*	*Y*
Voltammetry	*Electrochemical Catalytic Performance*	*n/a*	*In situ*	*N*	*Y (5 sec)*	*Y*
Impedance Spectroscopy	*Catalyst Degradation*	*n/a*	*In situ*	*N*	*Y (2 min)*	*Y*

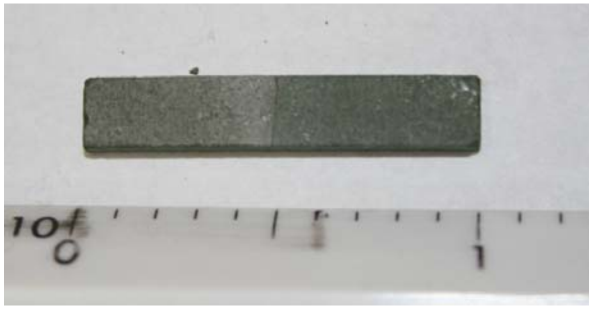
Questions. . . .

1. What's going on?
   - **A lot**
2. Mechanical effects of ALT doping?
   - **Up to 50% enhancement in mechanical strength**
   - **No strong dependence on Ni particle size**
3. ALT compositional changes with processing?
   - **Extensive 2° phase formation**
   - **Strong dependence on processing conditions**
4. New electrochemical mechanisms?
   - **MIEC properties in 2° phases?**
   - **Improved anode performance**
   - **Carbon tolerance?**

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





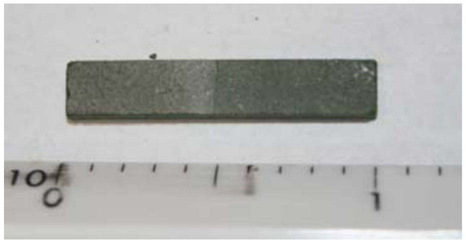
$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

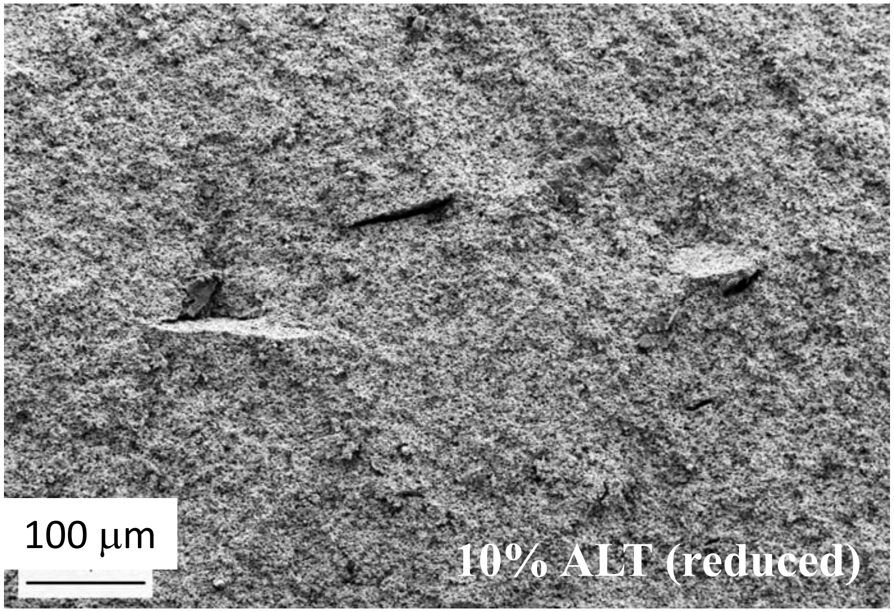
F_f = applied load at failure
σ_{fs} = flexural strength or Modulus of Rupture (MOR)

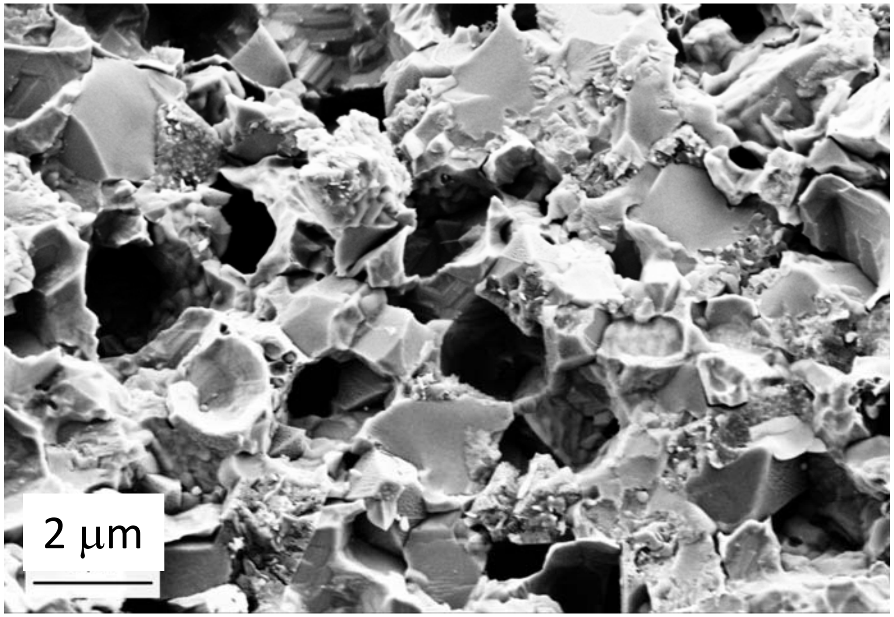
Amendola/McCleary

Coupon preparation

- Green and Black NiO-YSZ
- Green and Black NiO-YSZ with 1%, 5%, and 10% ALT
- Mechanically mixed; sintered at 1400˚C
- Oxidized and Reduced
- Literature window between 80 – 130 MPa[1-4]
- Trans-granular fracture in all samples

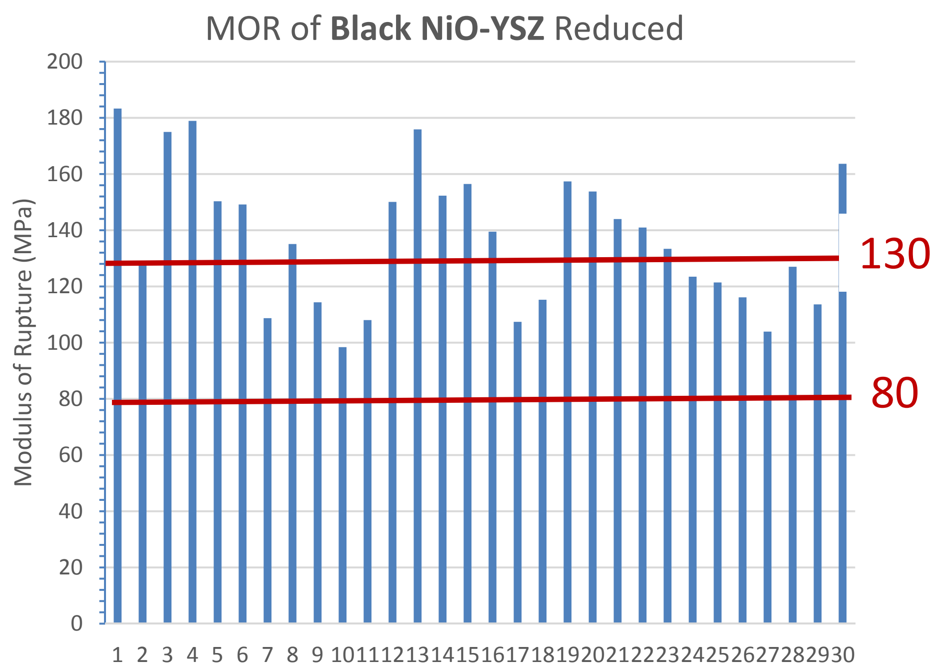


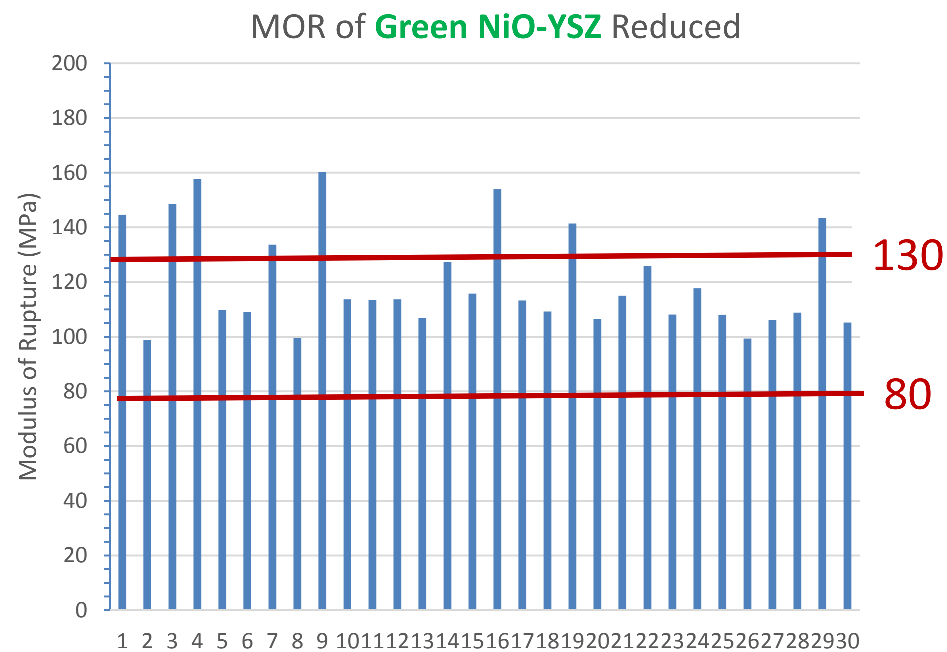




1. A. Nakajota, et al. *Ceramics International* 38.5 (2012): 3907-927.
2. J. H. Yu, et al. *Journal of Power Sources* 163.2 (2007): 926-32.
3. M. Radovic and E. Lara-Curzio *Acta Materialia* 52.20 (2004): 5747-756.
4. M. Casarin, et al. *Ceramics International* 41.2 (2015): 2543-557.

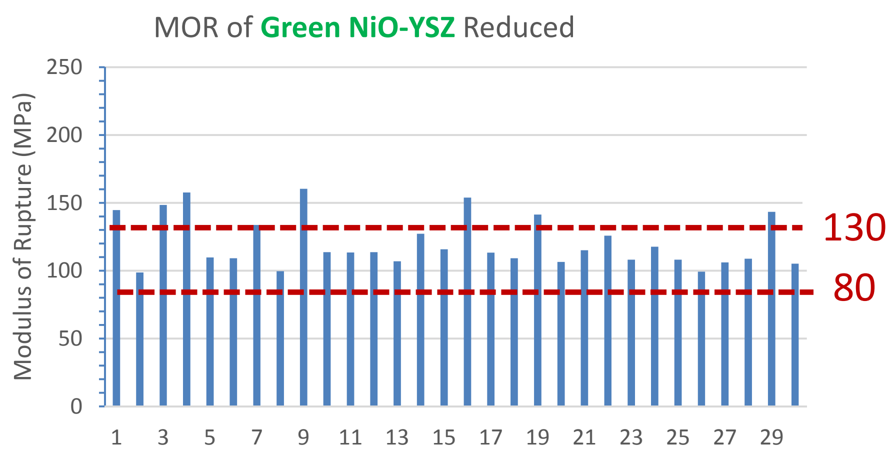
Modulus of rupture (MOR) results – NiO/YSZ (reduced)

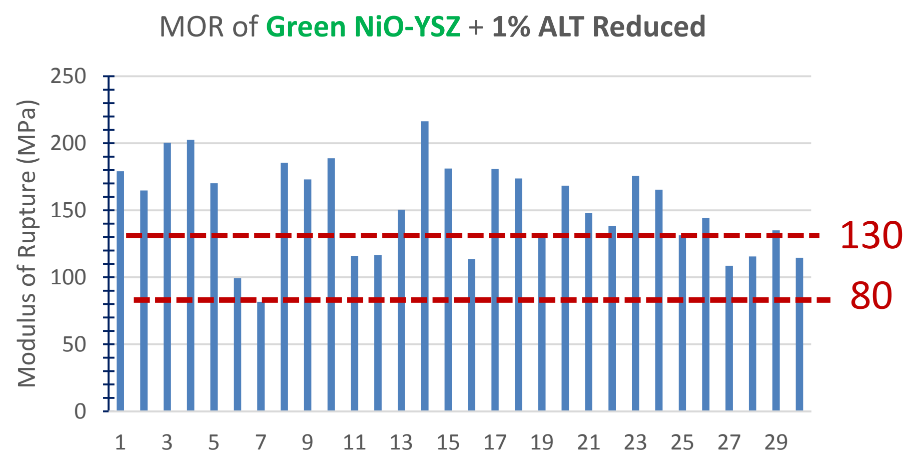


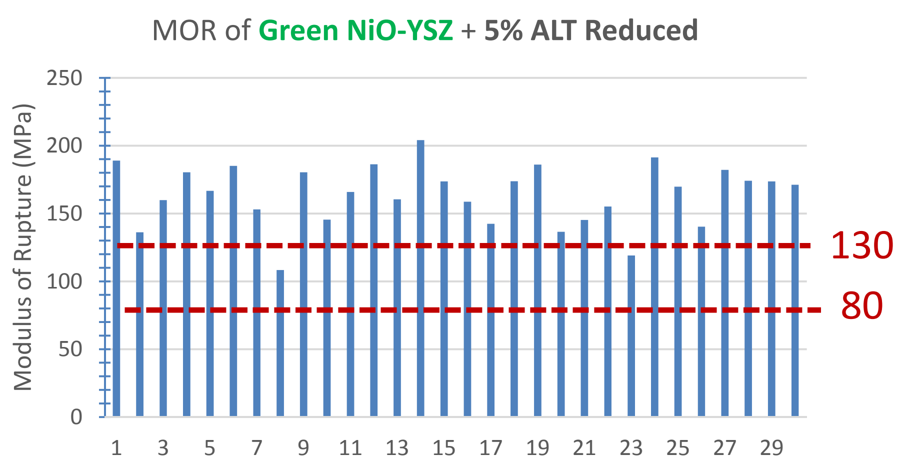


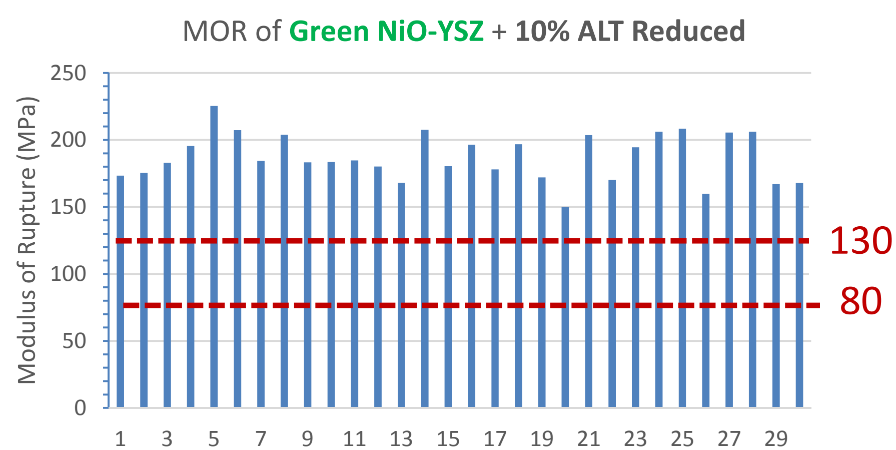
- MOR data fall for reduced samples falls within literature bounds
- MOR for **black** NiO coupons is 137 +/- 24 MPa
- MOR for **green** NiO coupons is 125 +/- 21 MPa

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









- Increasing ALT content increases material strength

Modulus of rupture (MOR) with ALT

	Black NiO-YSZ Reduced	Green NiO-YSZ Reduced	Green NiO-YSZ + 1% ALT Reduced	Green NiO-YSZ + 5% ALT Reduced	Green NiO-YSZ + 10% ALT Reduced
Average MOR	137 MPa	125 MPa	161 MPa	164 MPa	187 MPa
Standard Deviation	24	21	39	22	18

With 10% loading, MOR is ~50% larger than undoped sample.

Modulus of rupture (MOR) with ALT

	Black NiO-YSZ Reduced	Green NiO-YSZ Reduced	Green NiO-YSZ + 1% ALT Reduced	Green NiO-YSZ + 5% ALT Reduced	Green NiO-YSZ + 10% ALT Reduced
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ELSEVIER
Solid State Ionics
Volumes 101–103, Part 2, November 1997, Pages 1127-1133
International Symposium on the Reactivity of Solids

Aluminum titanate-tetragonal zirconia composite with low therm... expansion and high strength simultaneously

Tadashi Shimada [a], Masatoshi Mizuno [a], Kouji Katou [a], Yukio Nurishi [b], Minoru Ha... ...amu Sakurada [b], Daisuke Mizuno [b], Teruaki Ono [b]

3YSZ in ALT strengthens ALT

Effects are largely independent of Ni particle size

	Black NiO-YSZ Reduced	**Green NiO-YSZ Reduced**	**Green NiO-YSZ + 1% ALT Reduced**	**Green NiO-YSZ + 5% ALT Reduced**	**Green NiO-YSZ + 10% ALT Reduced**
Average MOR	137 MPa	125 MPa	161 MPa	164 MPa	187 MPa
Standard Deviation	24.3	21.3	38.9	22.3	17.6
			Black NiO-YSZ + 1% ALT Reduced	**Black NiO-**YSZ + 5% ALT Reduced	**Black NiO-**YSZ + 10% ALT Reduced
			138 MPa	152 MPa	199 MPa

What is responsible for this improved mechanical strength?

Materials testing as a function of processing temperature

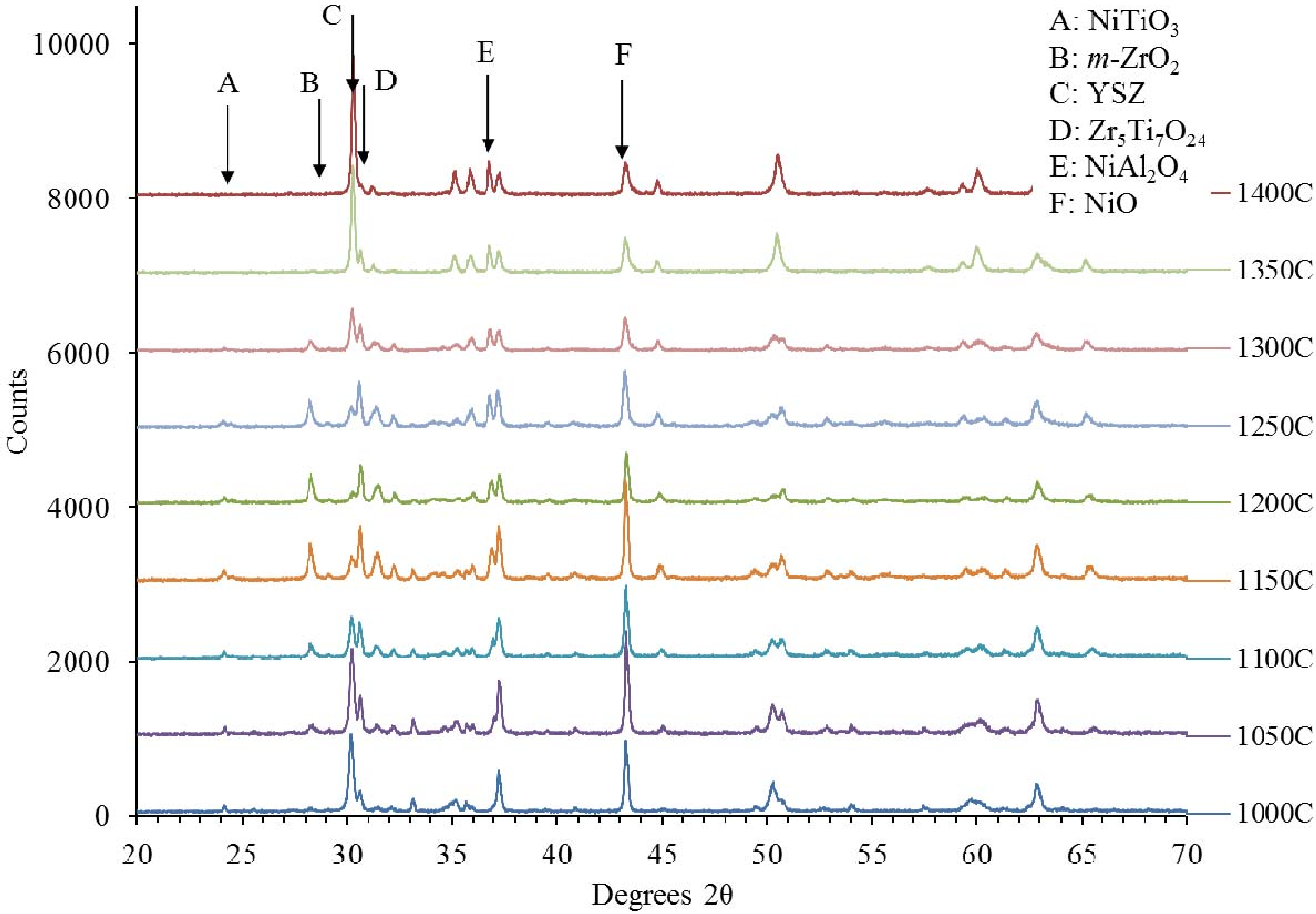
- NiO-8YSZ-ALT discs (33% by volume mixtures, green NiO)
- Mixed, sonicated, dried, re-ground, pressed (27 MPa)
- Sintered with 5˚C/min ramp; 1 hour dwell; 10˚C cool
- Dwell temperatures 1000 ˚C – 1400˚C in 50˚ increments

NiO + 8-YSZ + ALT ⟶ ??

Ex situ XRD & Raman

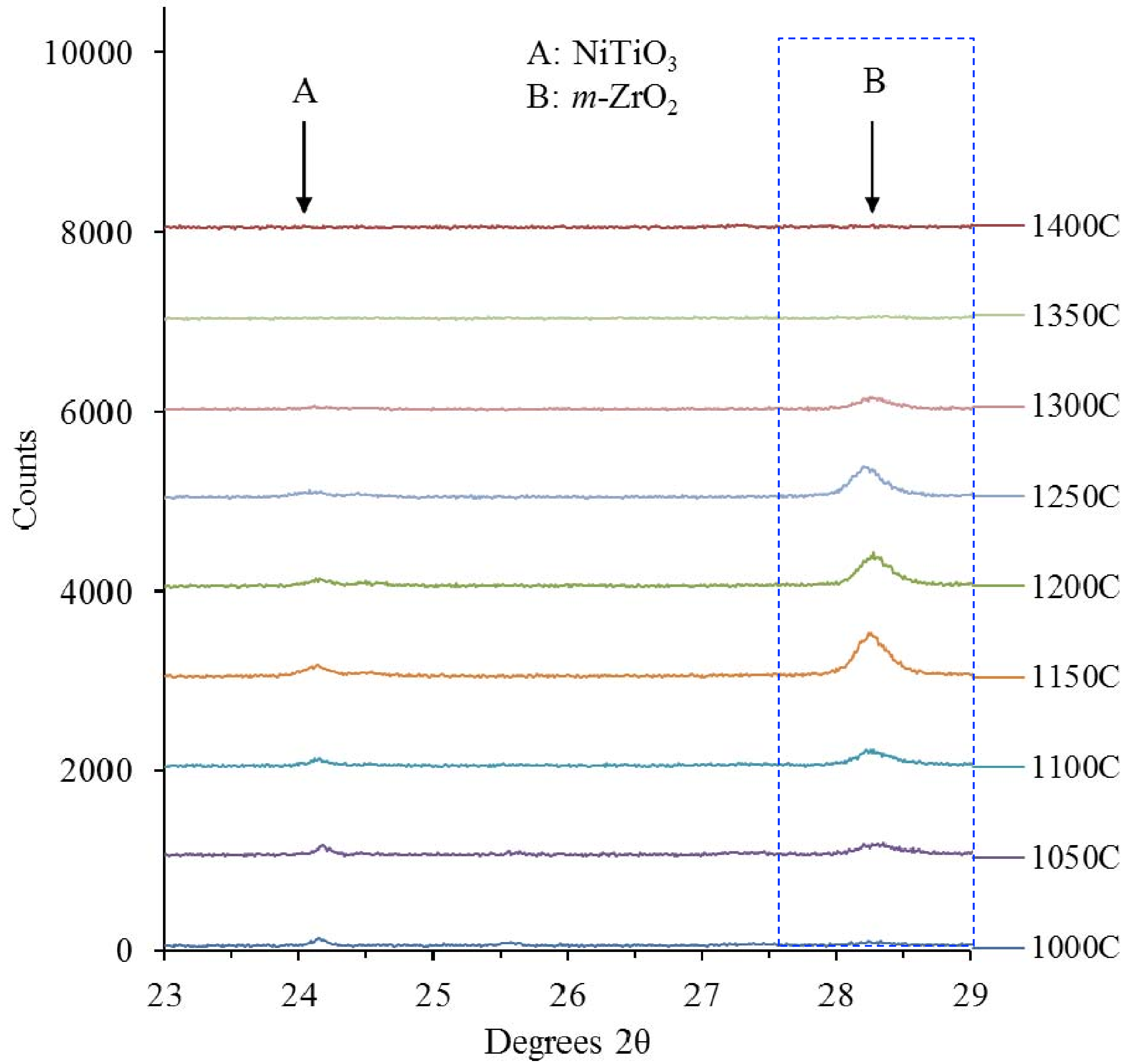
Sofie/Hunt/Driscoll

Materials testing as a function of processing temperature



Sofie/Hunt/Driscoll

Materials testing as a function of processing temperature



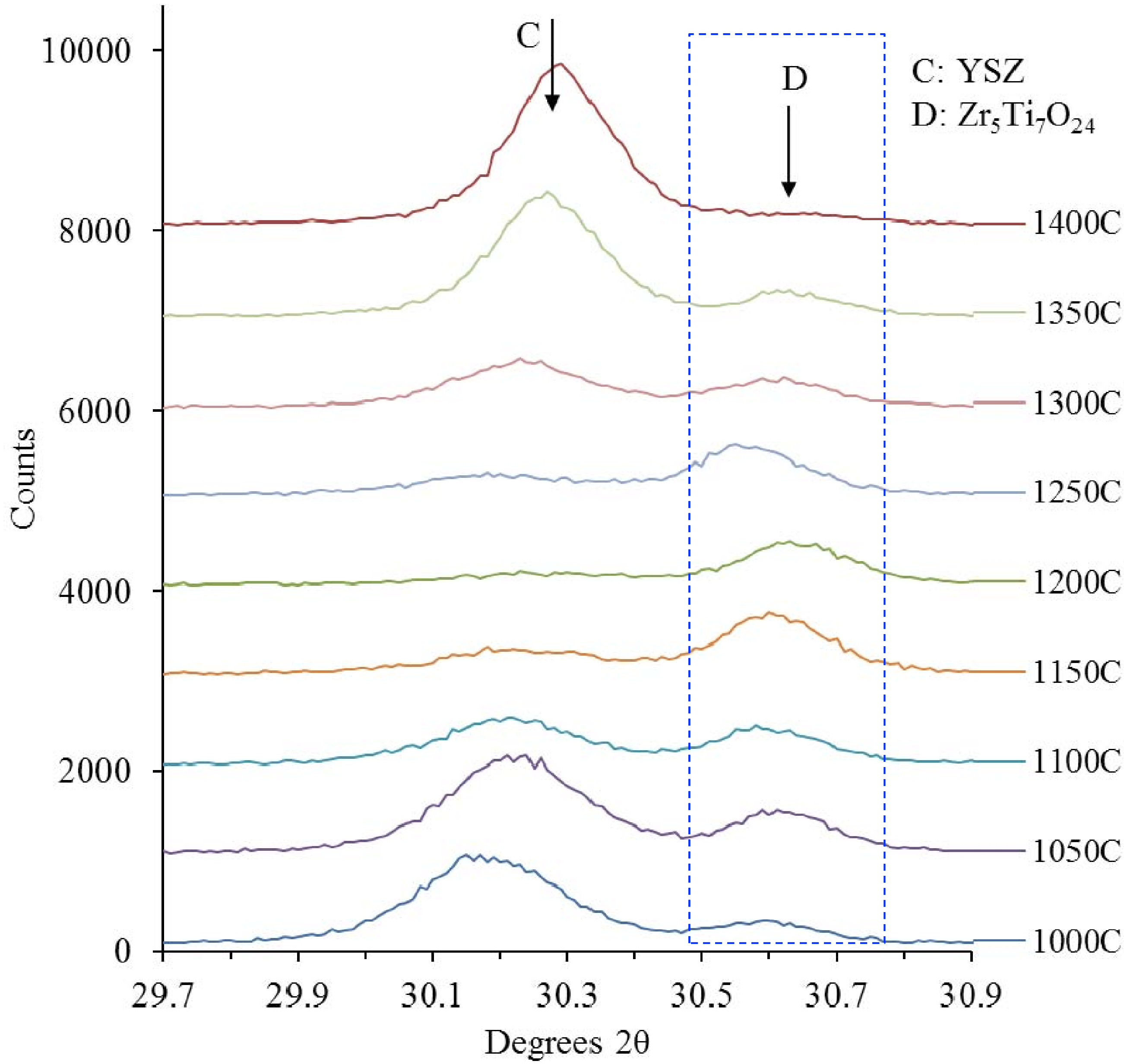
At intermediate sintering temperatures, c-YSZ diminishes and m-YSZ appears.

At higher sintering temperatures, m-YSZ disappears and only c-YSZ remains.

(No $NiTiO_3$ remains at high sintering temps)

Sofie/Hunt/Driscoll

Materials testing as a function of processing temperature



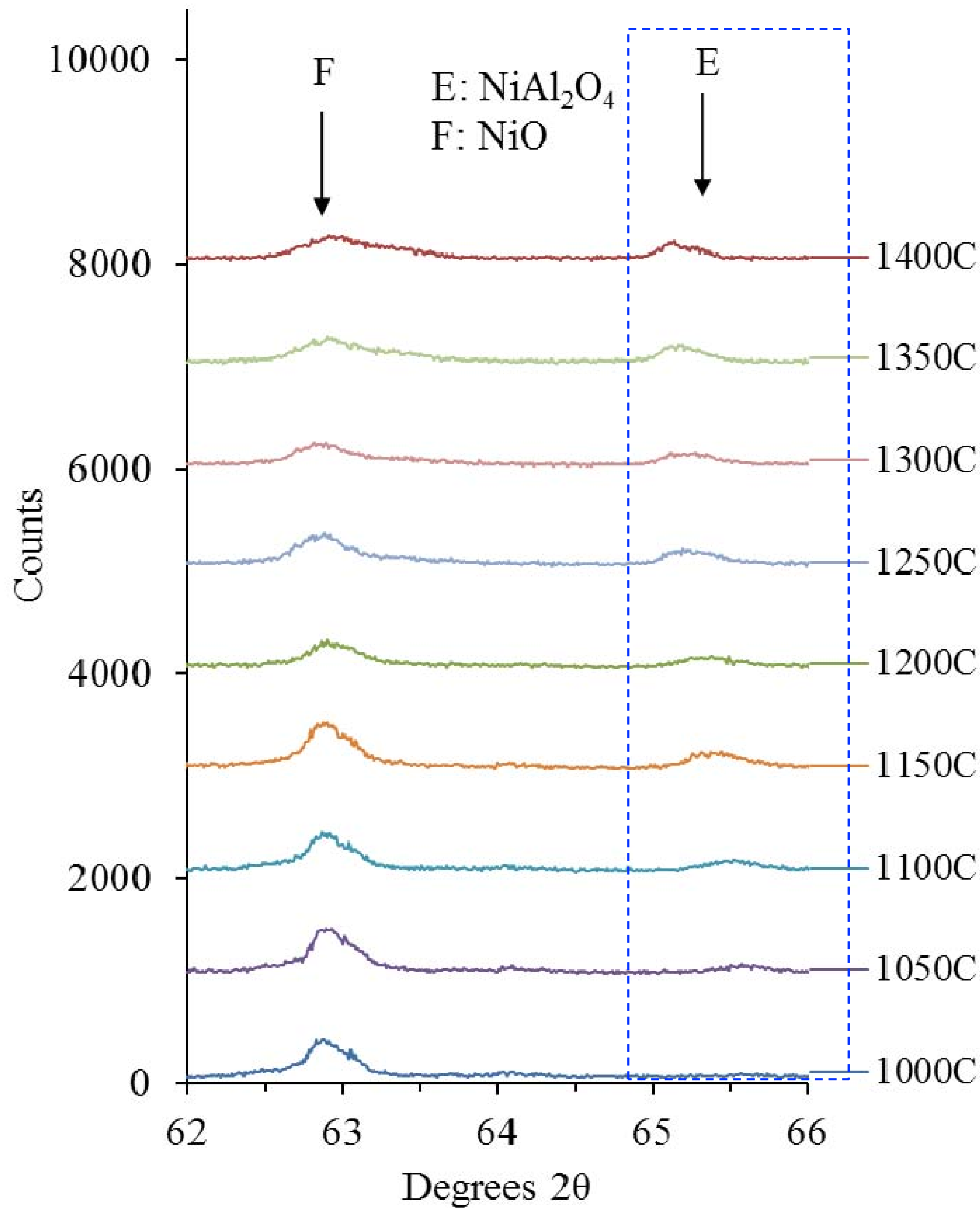
Loss of c-YSZ coincides with the appearance of $Zr_5Ti_7O_{24}$ superlattice

Return of c-YSZ coincides with the loss of $Zr_5Ti_7O_{24}$ superlattice

R. Christoffersen, P. K. Davies, *J. Am. Cer. Soc.* **1992**, *75*, 563.

Sofie/Hunt/Driscoll

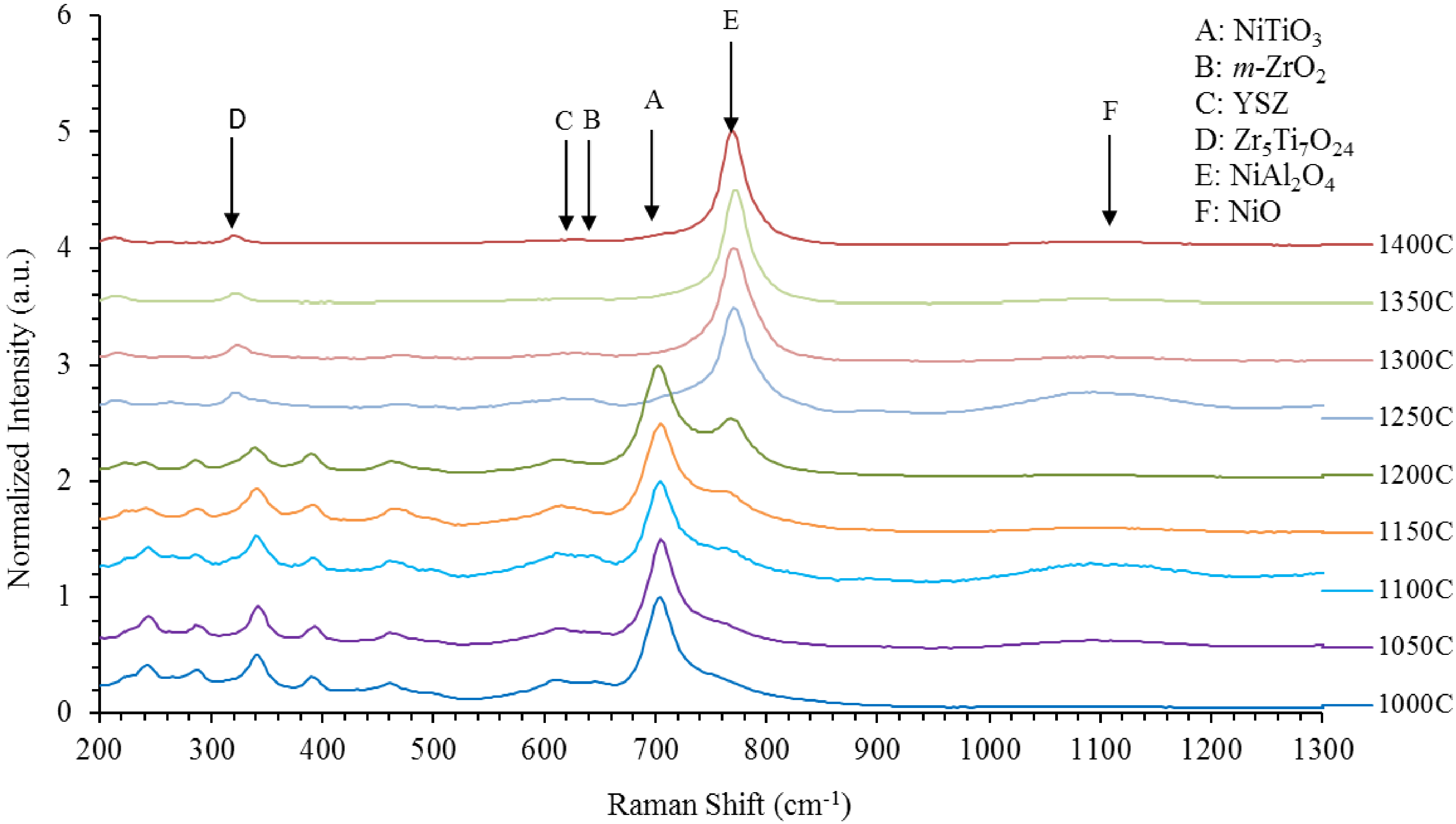
Materials testing as a function of processing temperature



NiO and $NiAl_2O_4$ present at all temperatures.

Sofie/Hunt/Driscoll

XRD data supported by *ex situ* Raman spectra



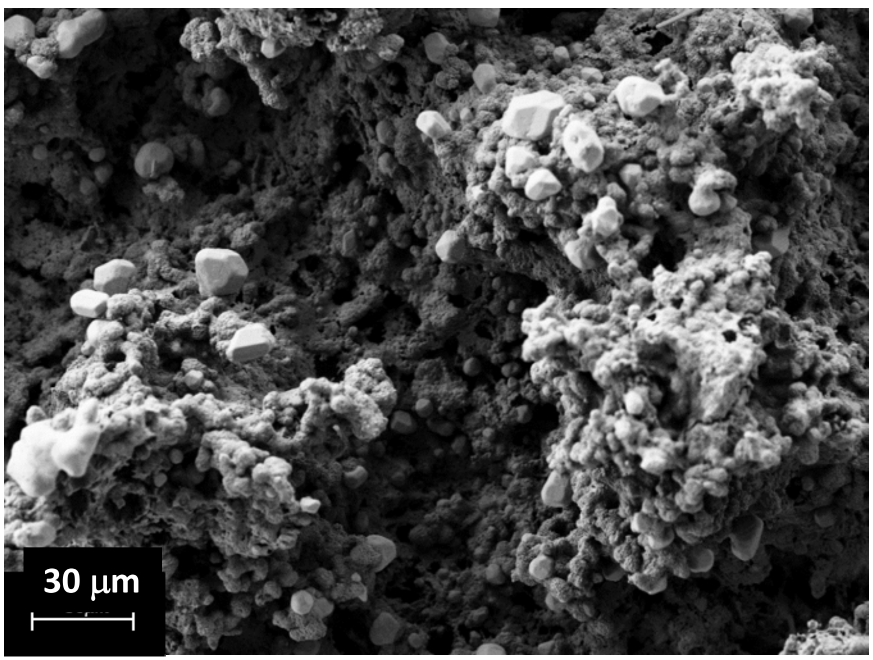
$$NiO + 8YSZ + ALT \longrightarrow NiO + c\text{-}YSZ + Zr_5Ti_7O_{24} + NiAl_2O_4$$

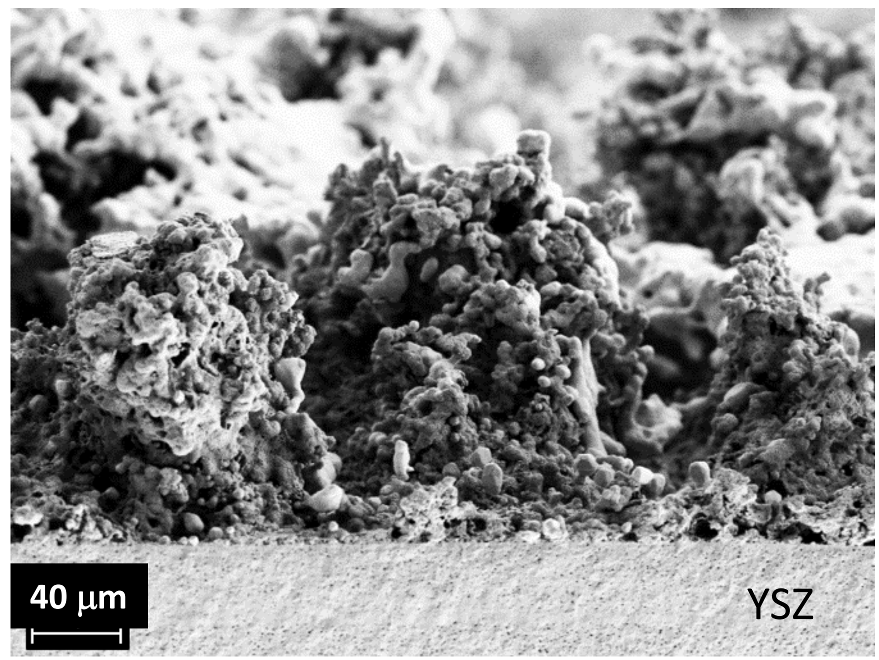
Walker/Welander

Now what?

Cell testing

- NiO-8YSZ (66% green NiO by mass)
- Mechanically mixed with 10% ALT
- Anode mixture sprayed onto commercial 8-YSZ electrolyte (300 μm thick; 32 mm diam)
- Anode sintered at 1400˚C
- LSM cathode sprayed and cured at 900˚C
- Cells operated at 800˚C, dry H_2, polarized to -0.7 V

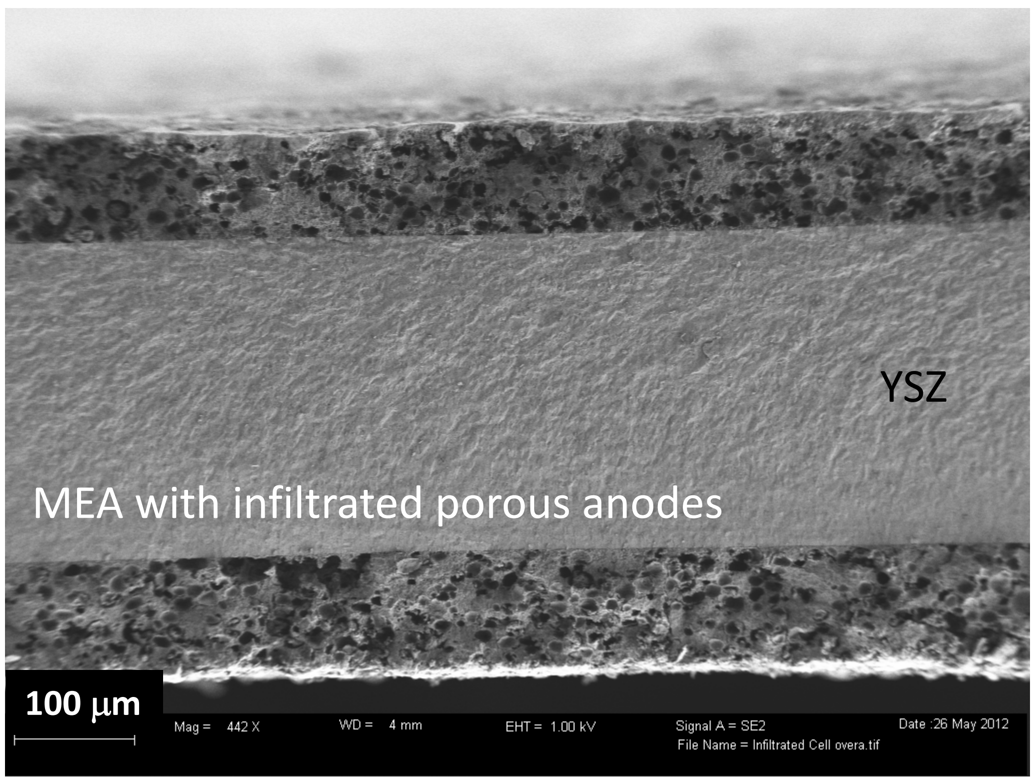




Walker/Sofie/Hunt/Welander

Cell testing (testing other architectures)

- NiO-8YSZ (66% by volume mixtures pre-reduced, green NiO)
- Mechanically mixed with 10% ALT
- Anode mixture sprayed onto commercial 8-YSZ electrolyte (300 μm thick; 32 mm diam)
- Anode sintered at 1400˚C
- LSM cathode sprayed and cured at 900˚C
- Cells operated at 800˚C, dry H_2, polarized to -0.7 V



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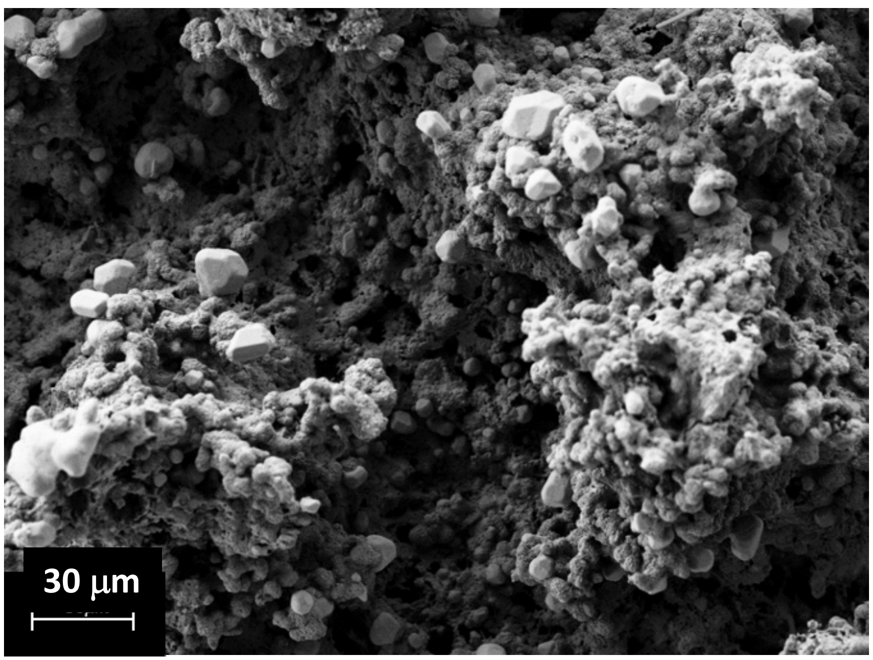
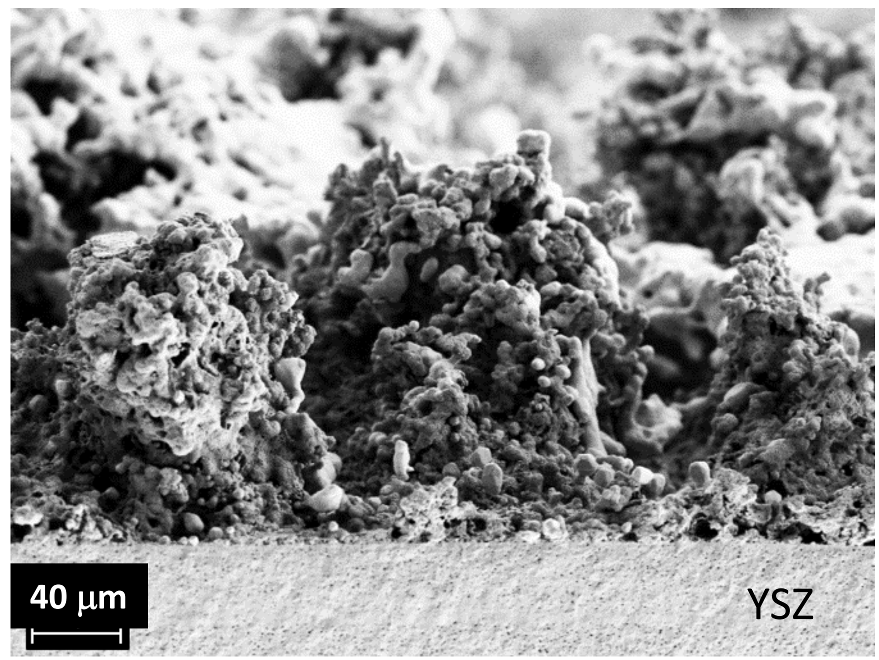
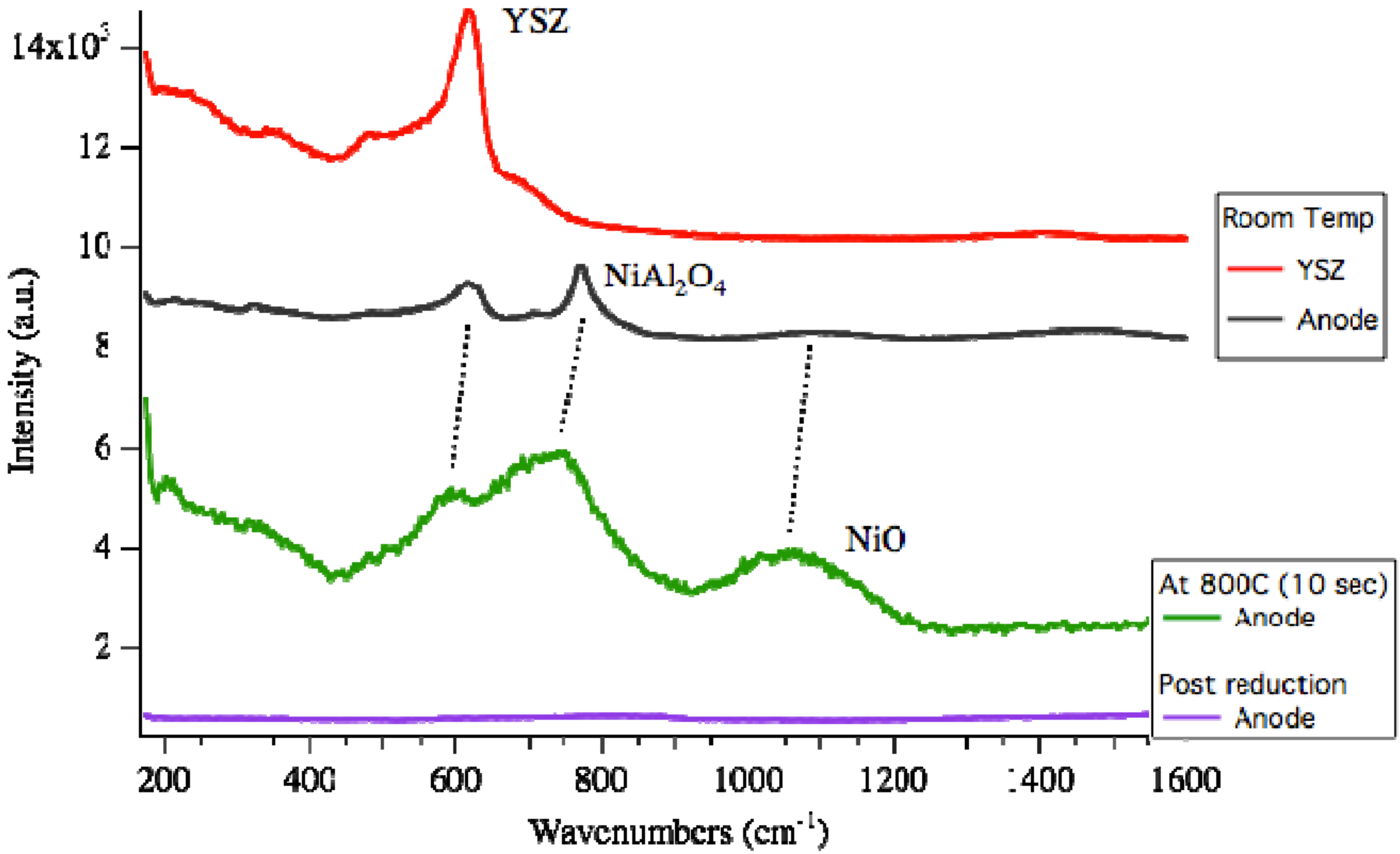




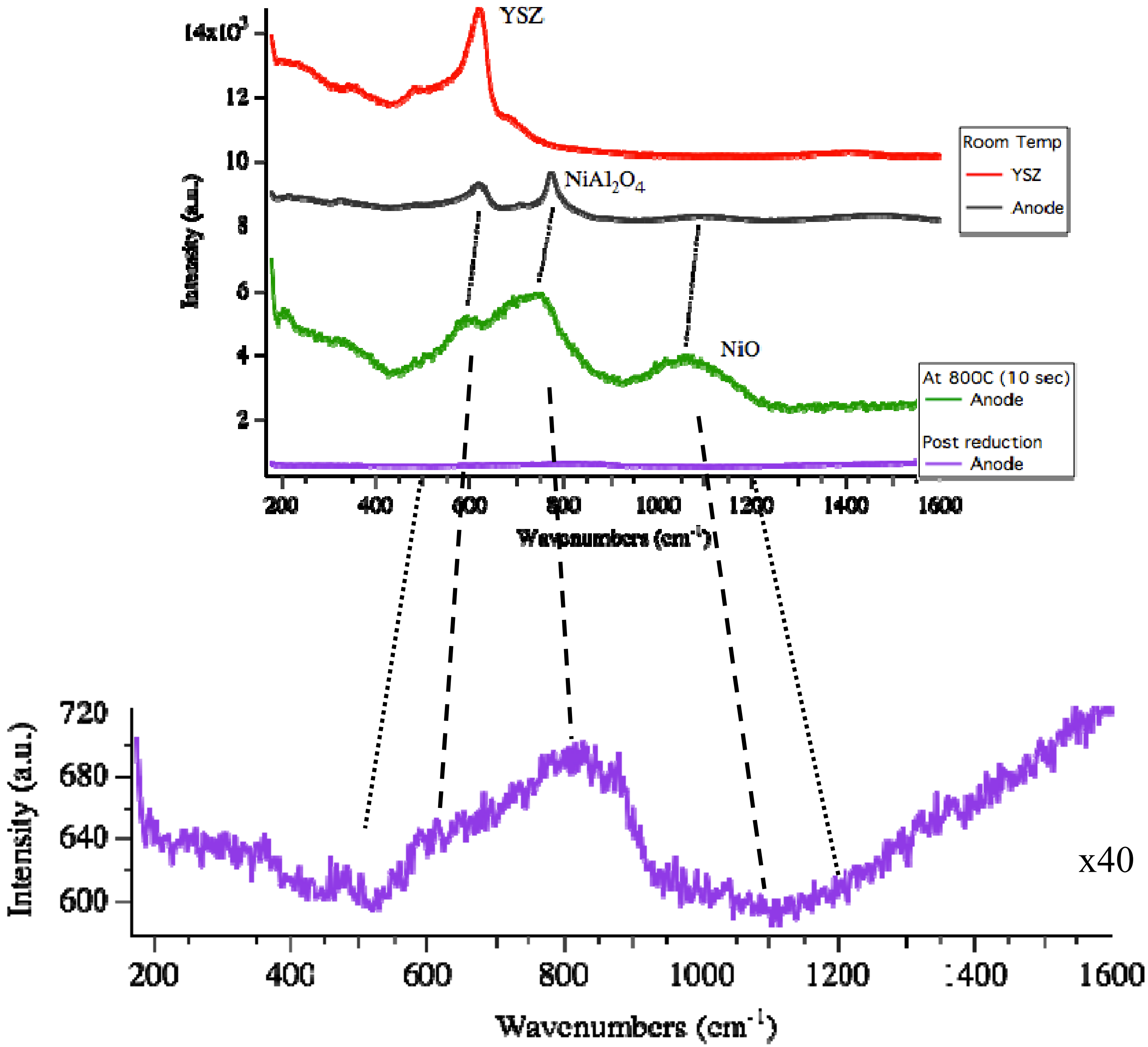
Walker/Sofie/Hunt/Welander

<u>Cell testing – anode reduction (800˚C, 10 sec acquisition)</u>

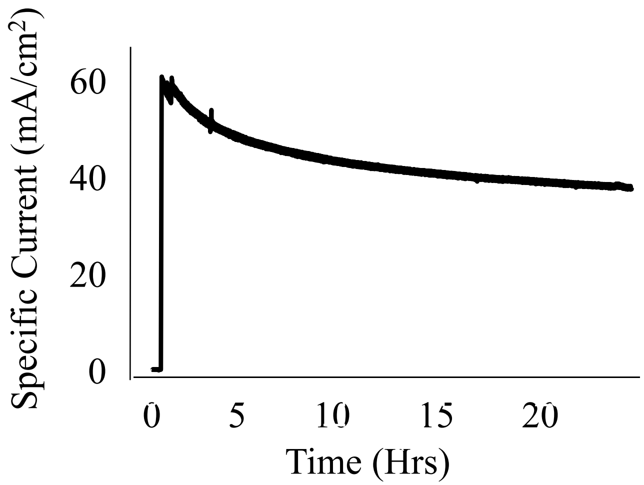


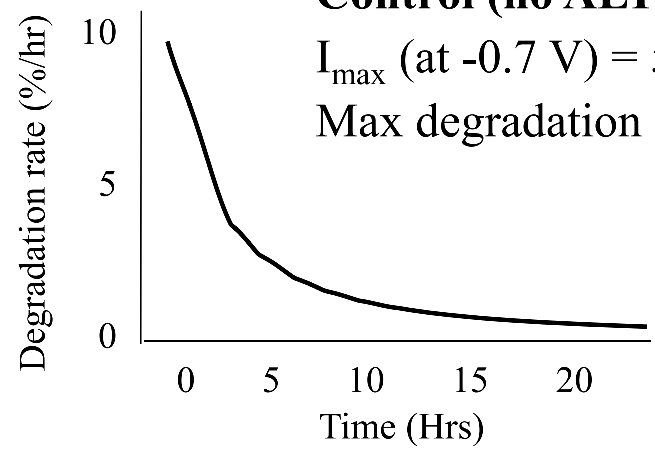
NiO and $NiAl_2O_4$ appear to be reduced within 20 sec.

Cell testing – anode reduction (800˚C, 10 sec acquisition)

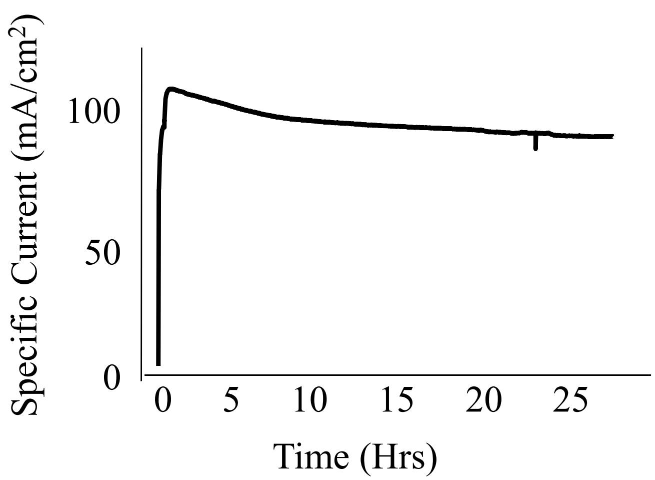


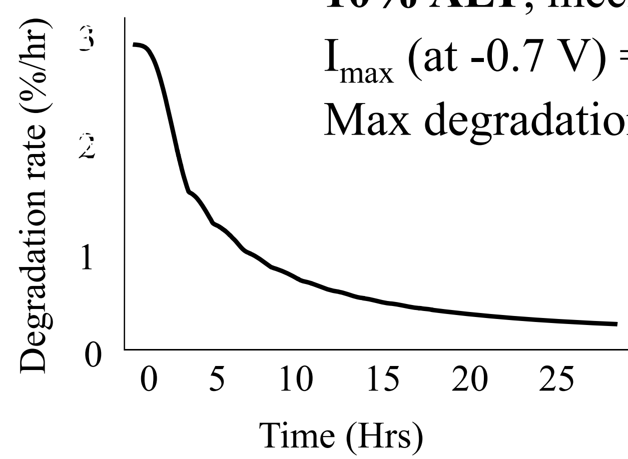
Cell testing – (800˚C, dry H_2, -0.7V)





Control (no ALT)
I_{max} (at -0.7 V) = 58.6 mA/cm^2
Max degradation = 9 %/hr

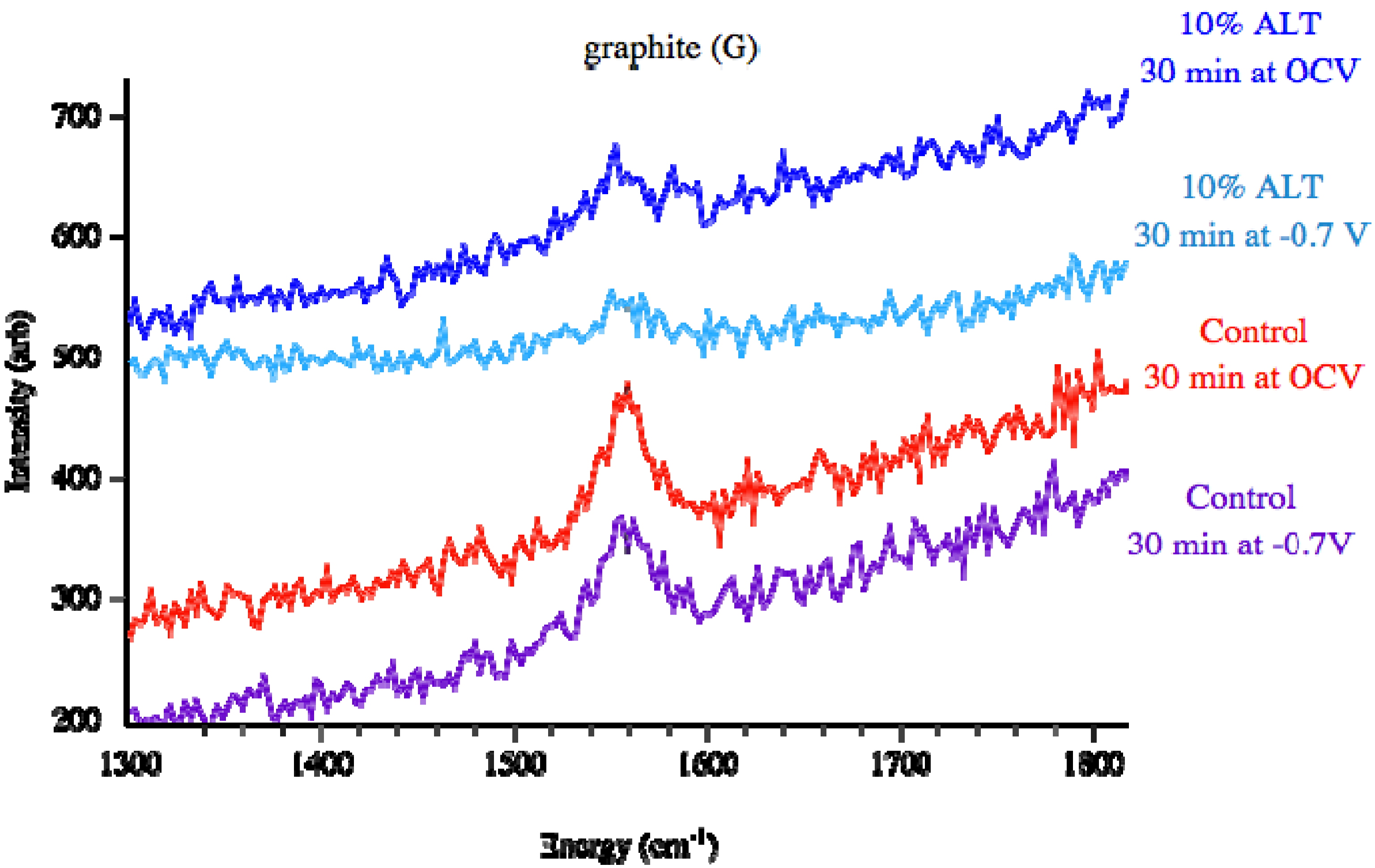




10% ALT, mechanically mixed
I_{max} (at -0.7 V) = 109 mA/cm^2
Max degradation = 3 %/hr

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

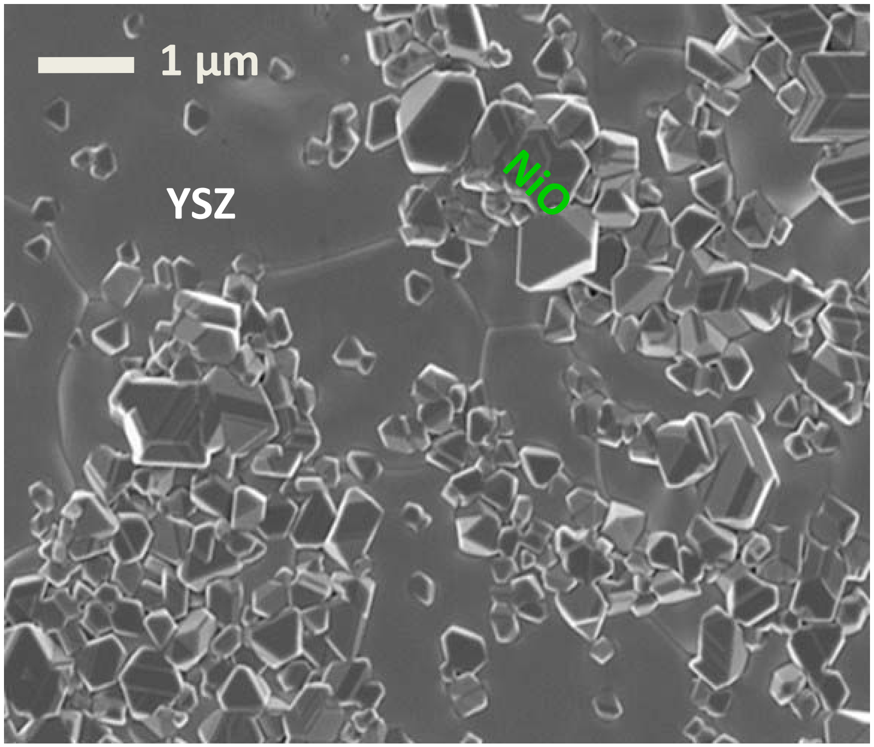
Cell testing for carbon tolerance – (800˚C, dry CH_4, -0.7V)



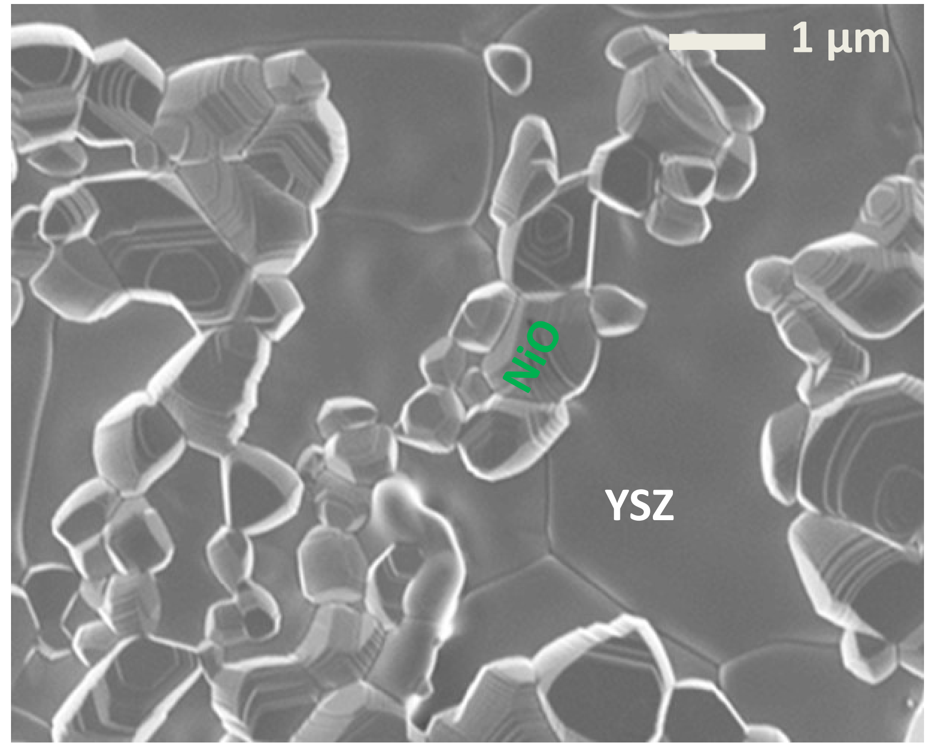
ALT containing cell shows resistance to carbon accumulation

Infiltrated anodes (~20% Ni loading, ~2% ALT)

ALT Doped



Baseline



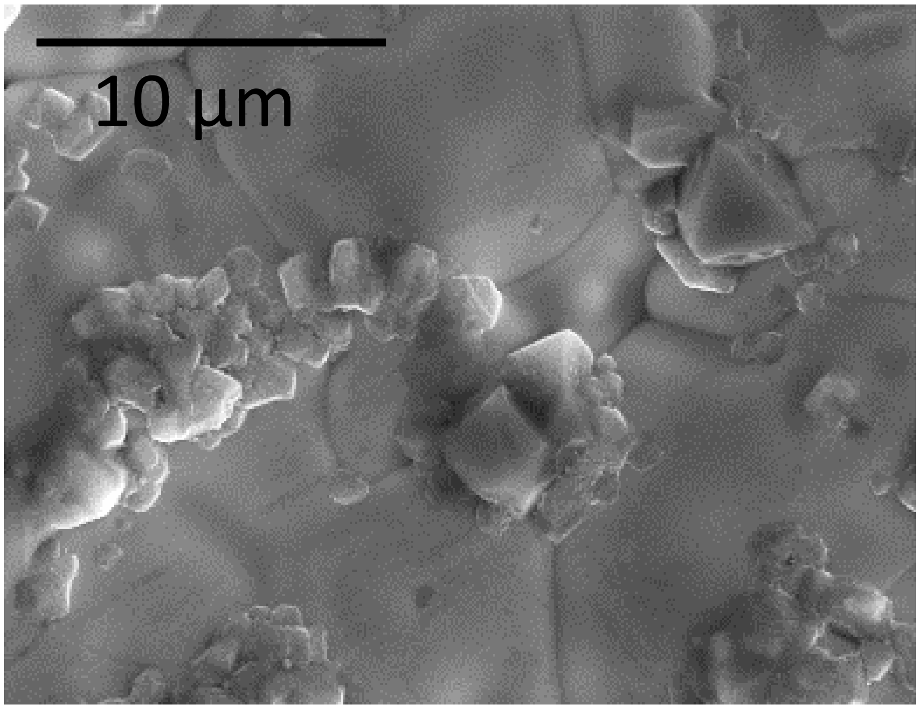
1400°C post ALT addition heat treatment

ALT infiltrated cell shows less coarsening

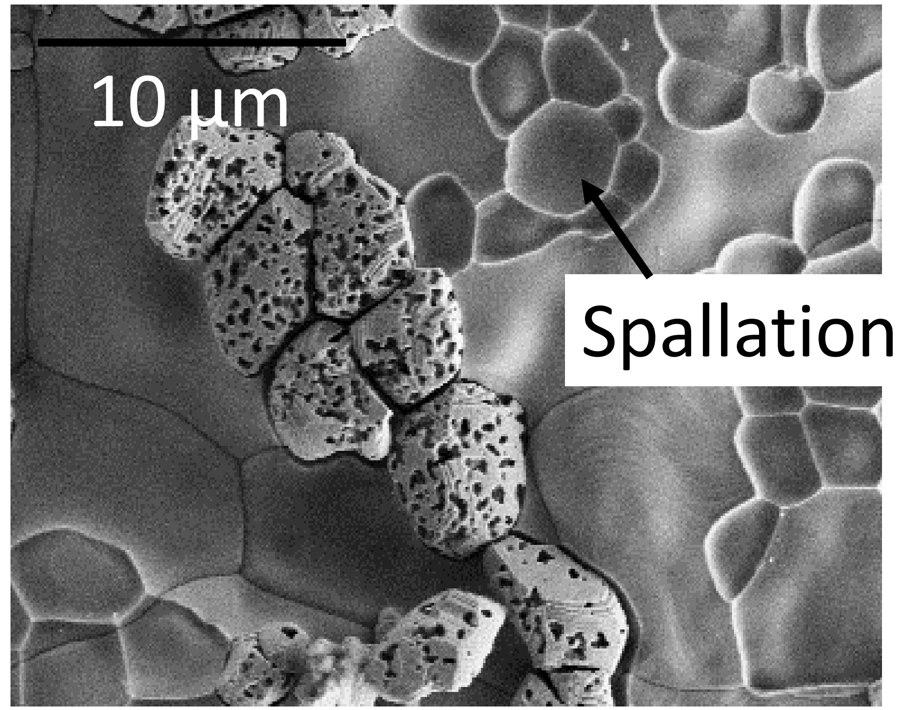
(Infiltrated with Ti-lactate and Al-nitrate)

Infiltrated anodes (~20% Ni loading, ~2% ALT)

ALT Doped



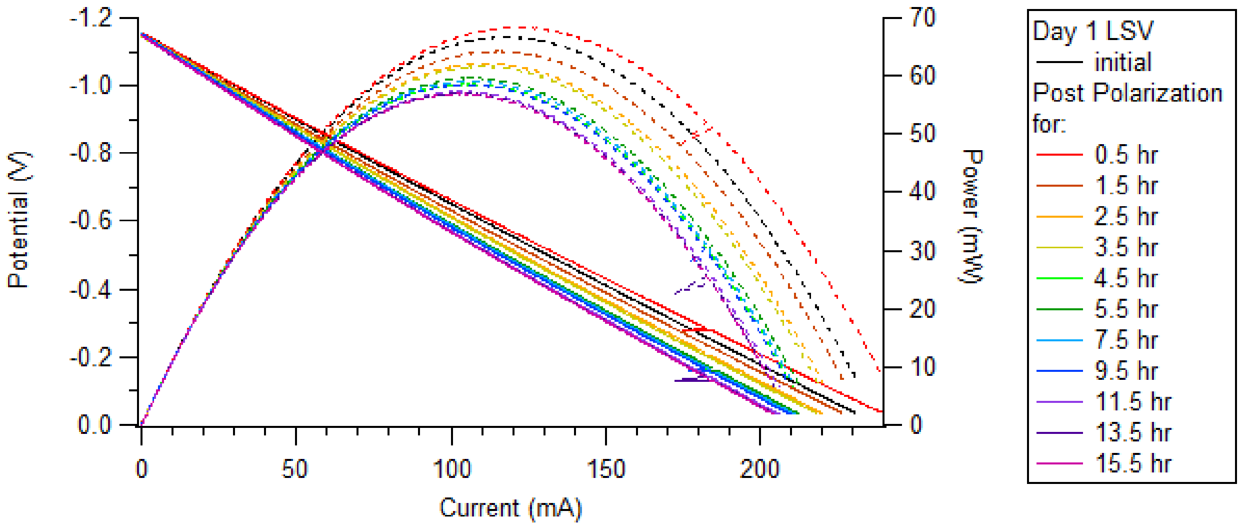
Baseline



150 hour thermal treatment in H_2/N_2 at 800°C

ALT infiltrated cell shows less coarsening after reduction

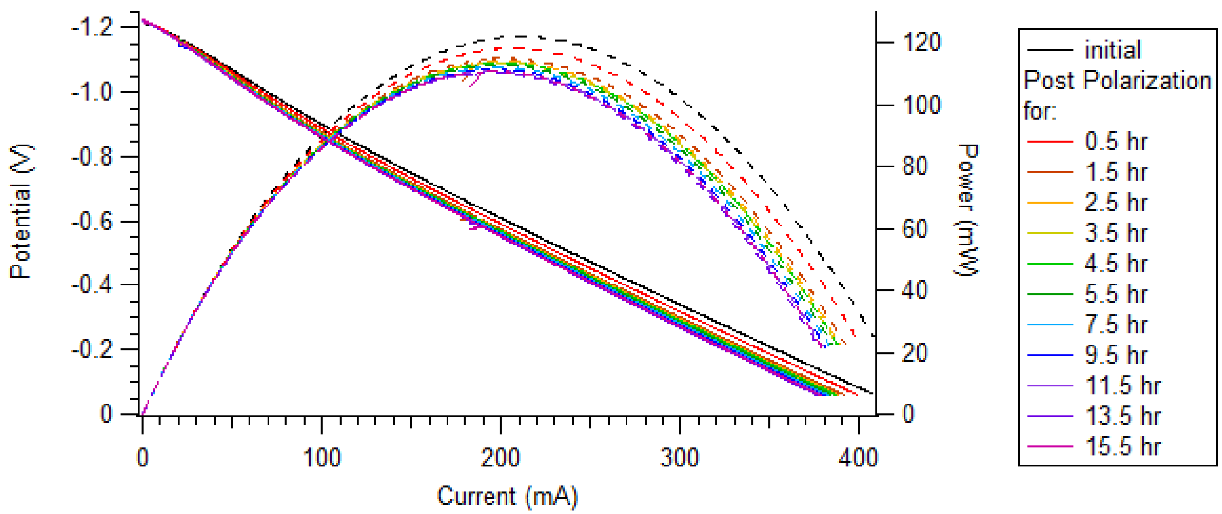
Additional cell testing – (800˚C, dry H_2, -0.7V, **Infiltrated anodes**)



Pure Cell

I_{max} = 239 mA → 204 mA

P_{max} = 68 mW → 57 mW



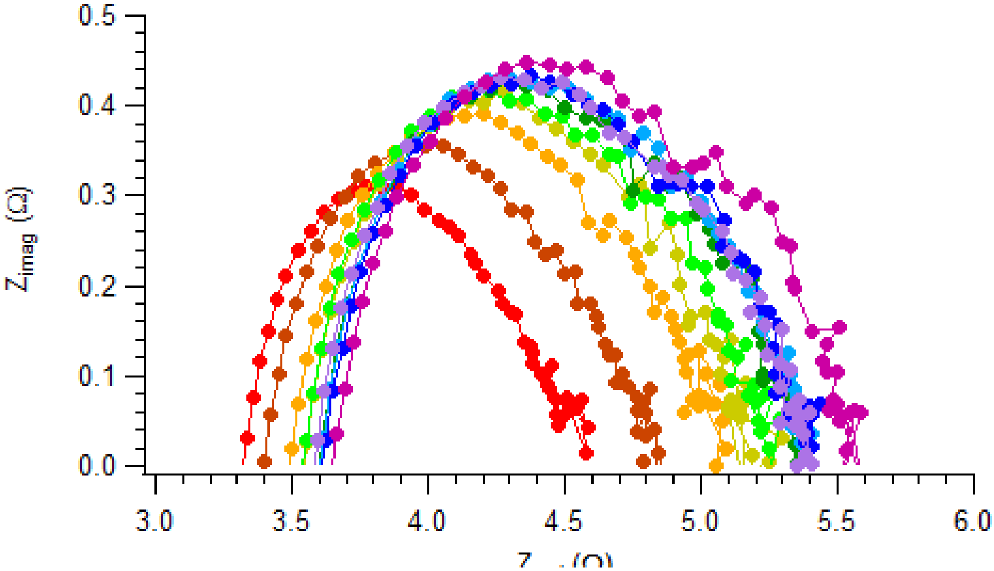
2 mol% ALT Cell

I_{max} = 379 mA → 408 mA

P_{max} = 122 mW → 110 mW

ALT **infiltrated** cell shows ~2x better performance & less degradation

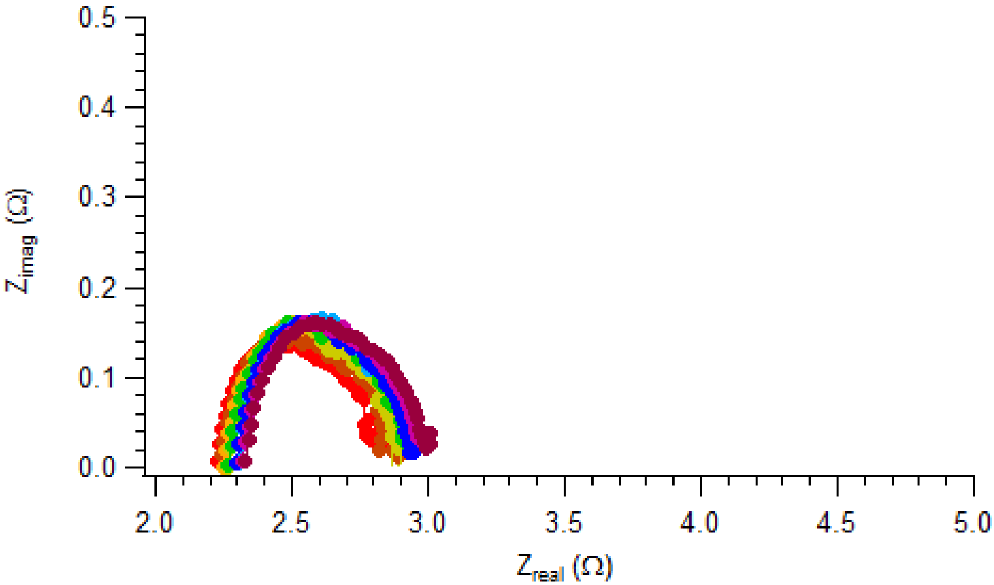
Additional cell testing – (800˚C, dry H_2, -0.7V, **Infiltrated anodes**)



Pure Cell

R_B = 3.34 Ω → 3.76 Ω

R_P = 1.24 Ω → 1.86 Ω



2 mol% ALT Cell

R_B = 2.22 Ω → 2.33 Ω

R_P ≈ 0.62 Ω → 0.66 Ω

We started with questions. Now we have (some) answers.

Mixing ALT with NiO/8YSZ enhances mechanical strength

- Up to 50% enhancement in mechanical strength
- No strong dependence on Ni particle size

Composition of the doped anode is complicated and heterogeneous

- Extensive 2° phase formation ($NiAl_2O_4$, $Zr_5Ti_7O_{24}$)
- Strong dependence on processing conditions

Electrochemical performance is enhanced

- MIEC properties in 2° phases? ($Zr_5Ti_7O_{24}$)
- Improved (= slower) degradation under H_2
- Carbon tolerance under CH_4

We started with questions. Now we have (some) answers.

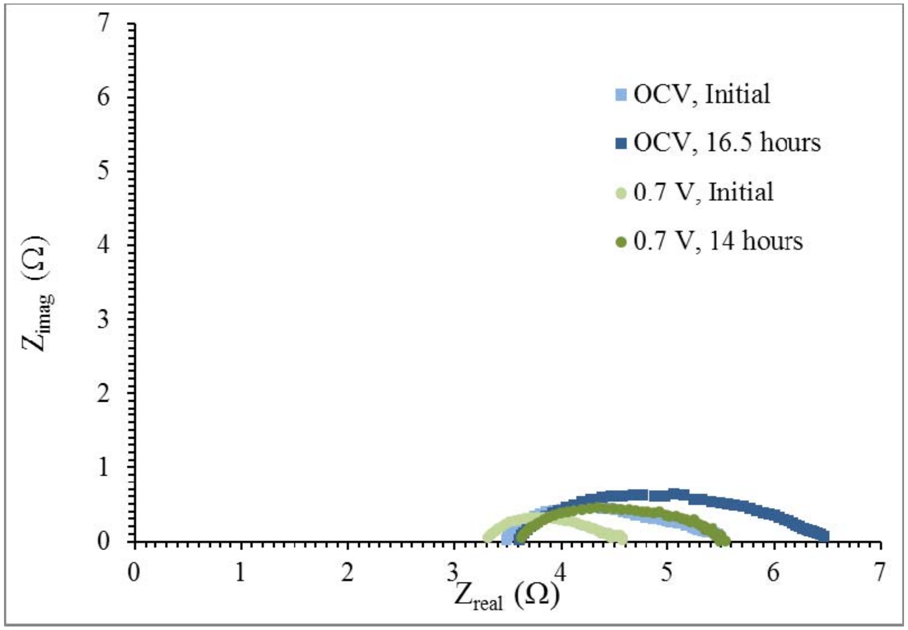
Where next?

- Work to improve performance with mechanically mixed cells.
- Electrochemical and spectroscopic characterization of 2° phases
- Carbon tolerance under CH_4, syn-gas, biogas
- Infiltrate commercial MEAs– do advantages confer to prefab cells?
- Can fabrication methods scale up for commercial manufacture.

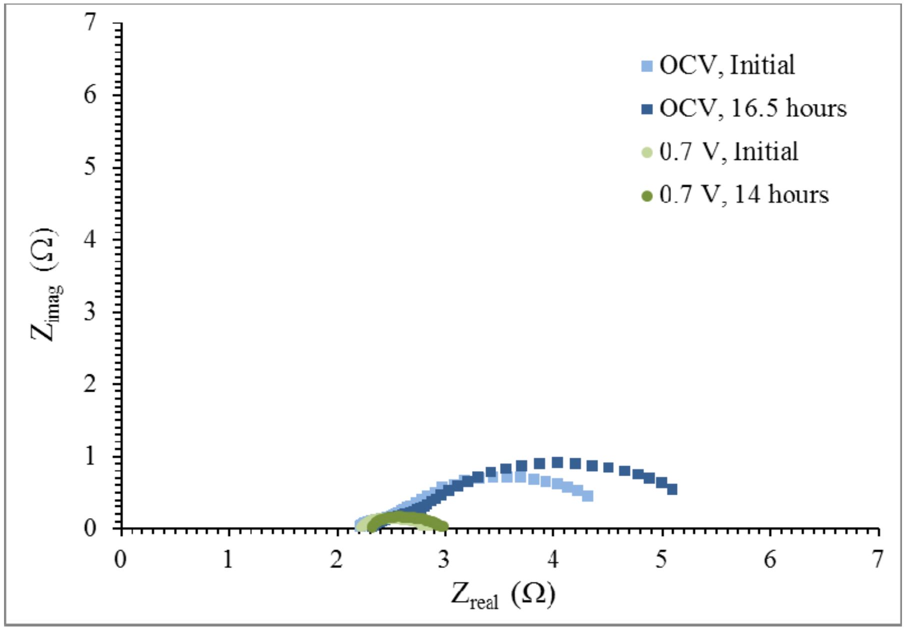
Thanks

Additional cell testing – (800˚C, EIS at OCV and under polarization)

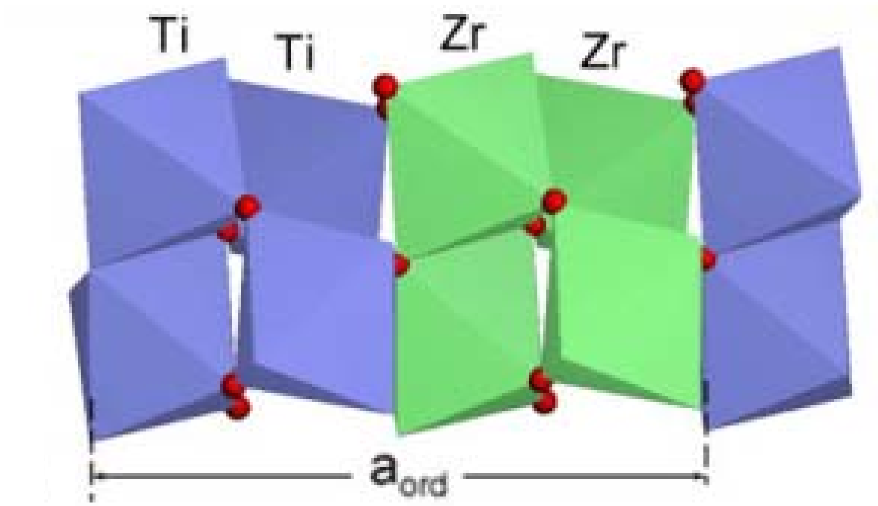
Undoped



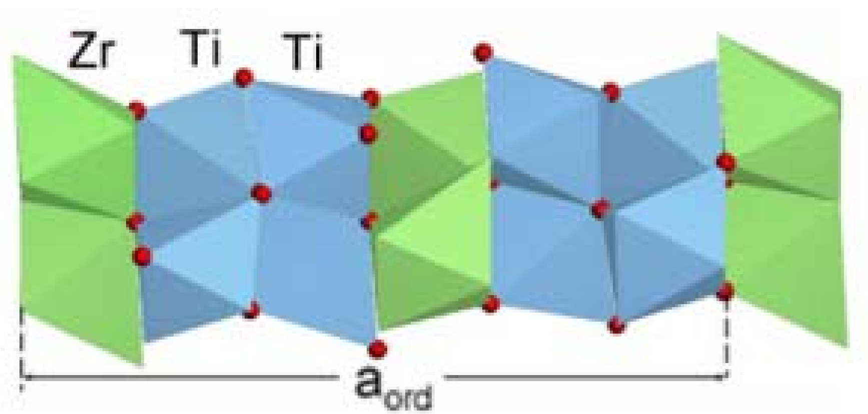
Infiltrated with ALT



Could $Zr_5Ti_7O_{24}$ be the answer?



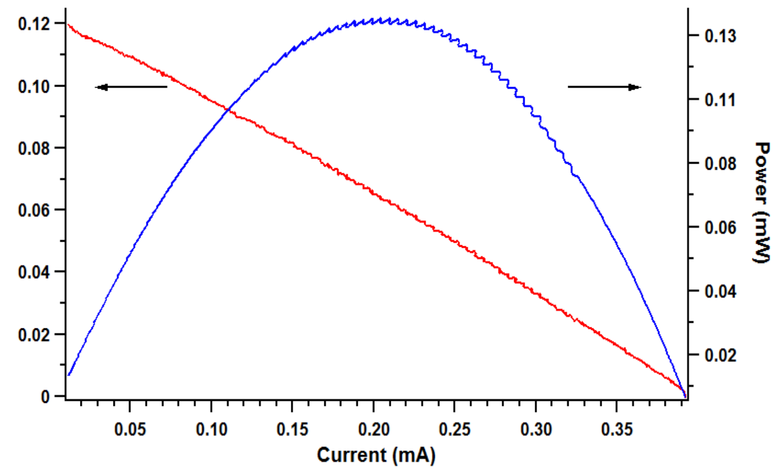
$ZrTiO_4$
→Distorted Zr polyhedra, octahedral Ti polyhedra



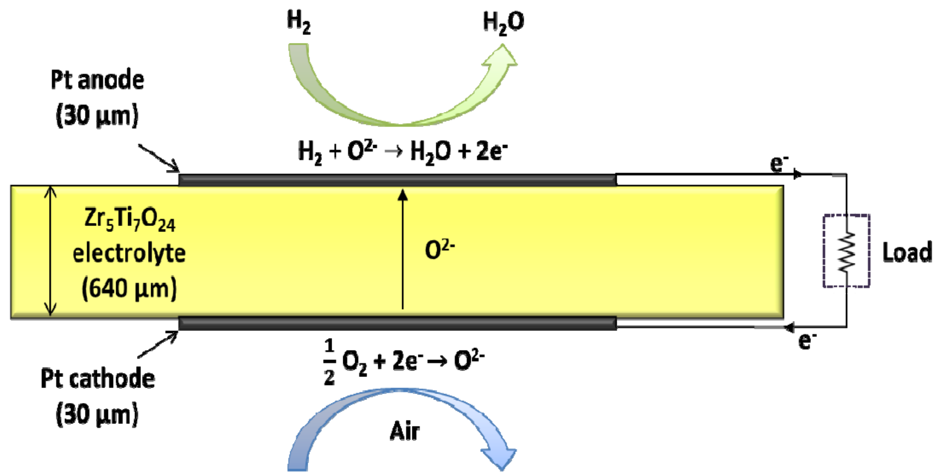
$Zr_5Ti_7O_{24}$
→Zr is hosted in 1 of every 3 cation layers (pushing from distorted octahedral towards cubic coordination)

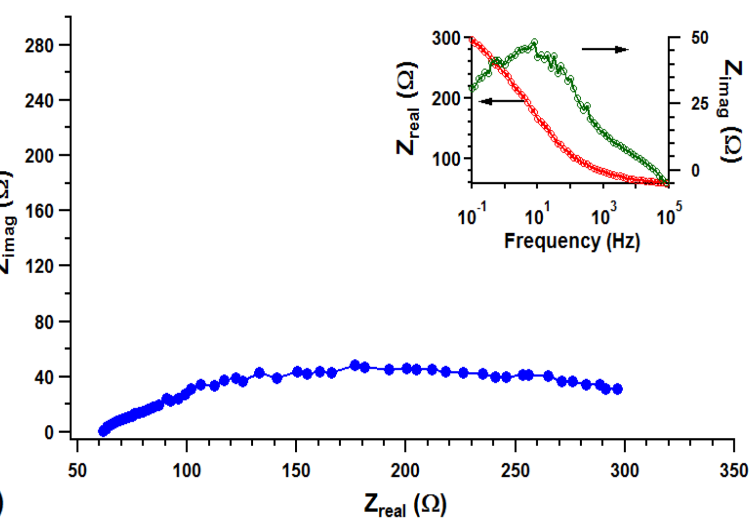
Phase evolution, Raman spectroscopy and microwave dielectric behavior of (Li1/4Nb3/4) doped ZrO2-TiO2 system
Li-Xia Pang · Hong Wang · Di Zhou · Yue-Hua Chen ·Xi Yao
Appl Phys A (2010) 100: 1205–1209

5-7-24 electrochemical activity

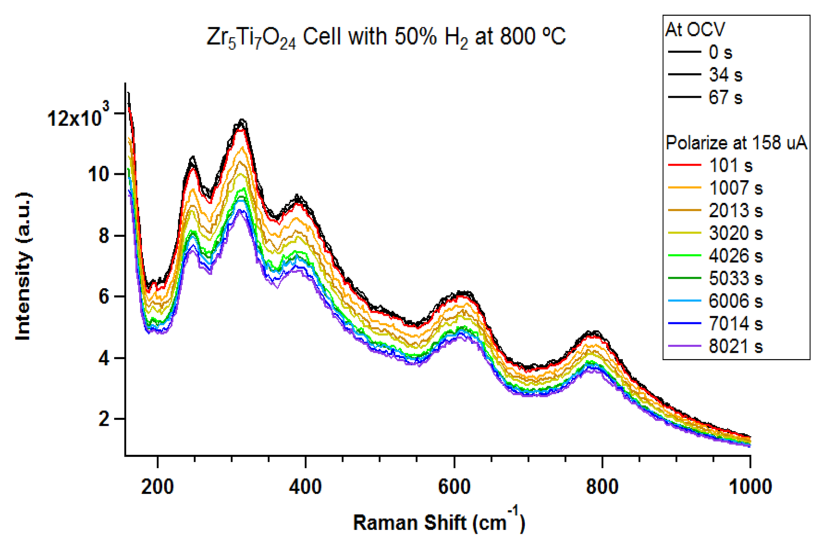


a)

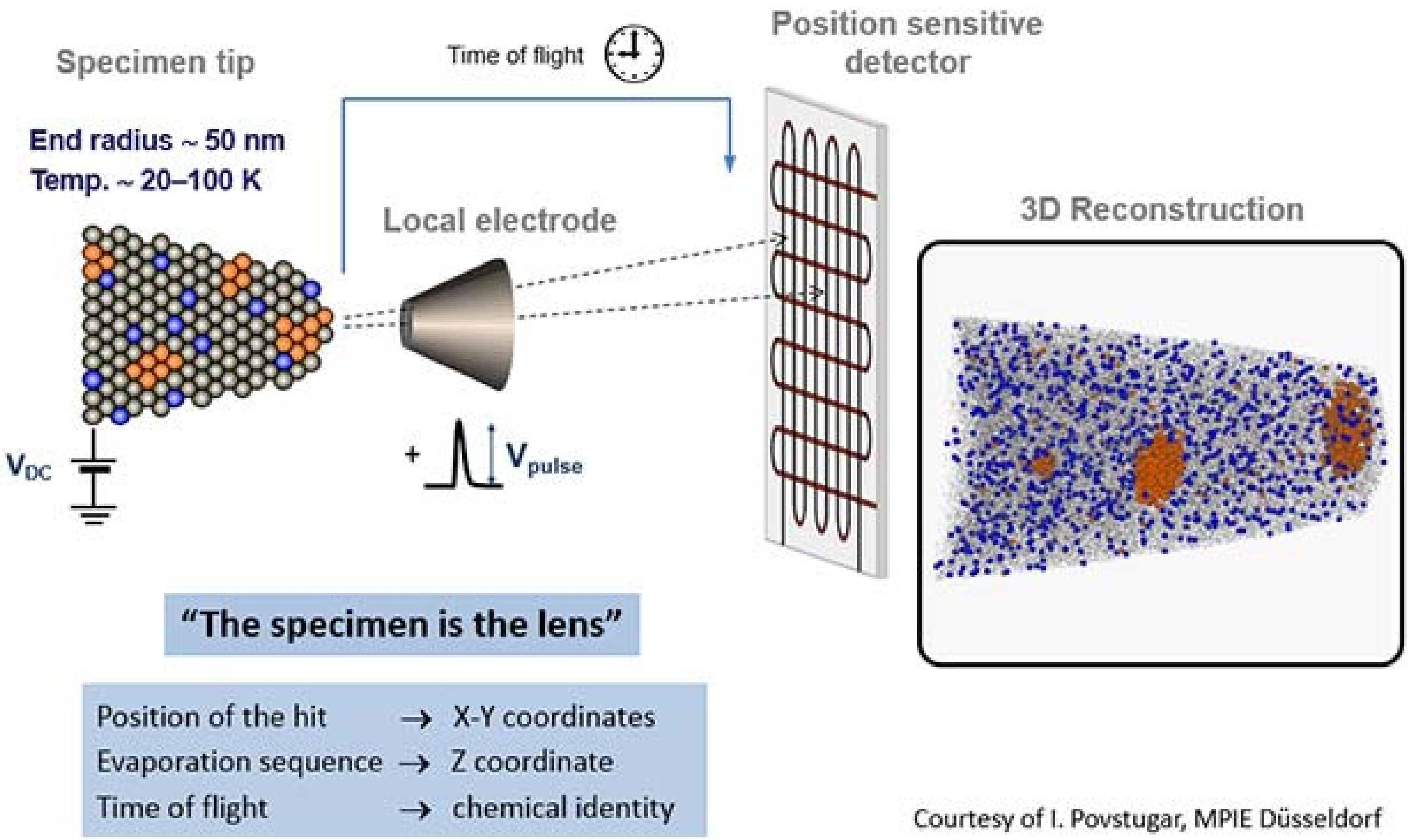




b)



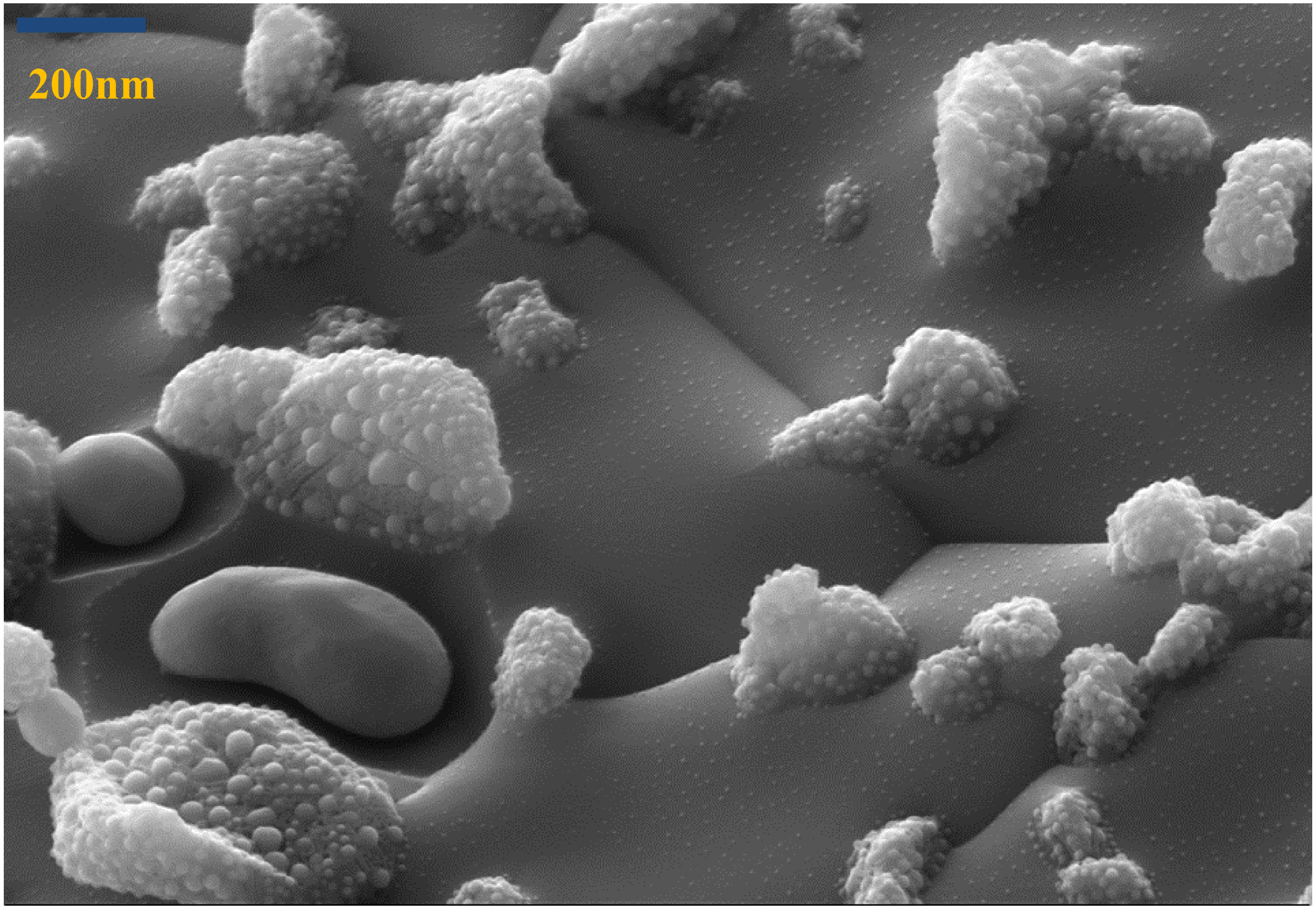
Atom Probe Tomography (APT) - EMSL



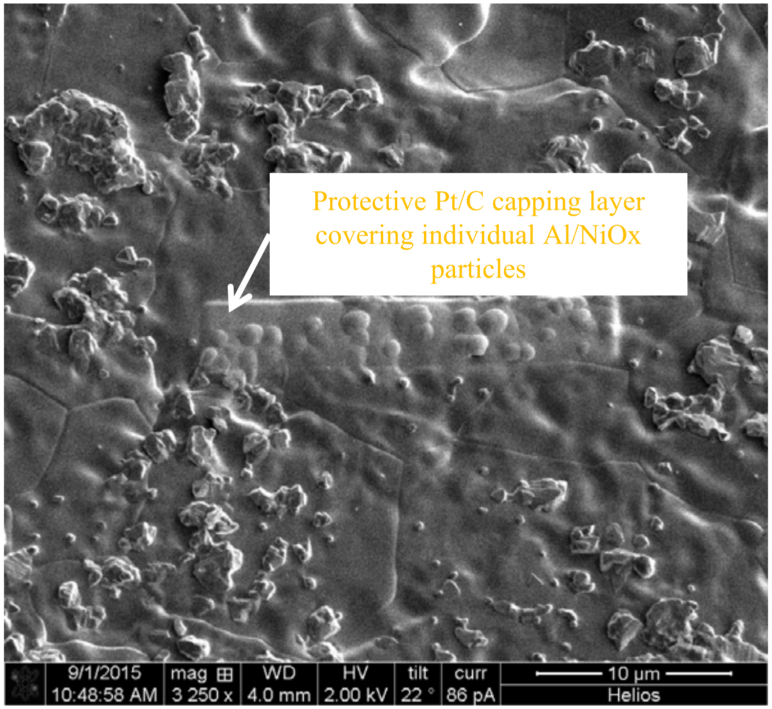
3-15 kV (10's of V per nm) near the point of atom evaporation

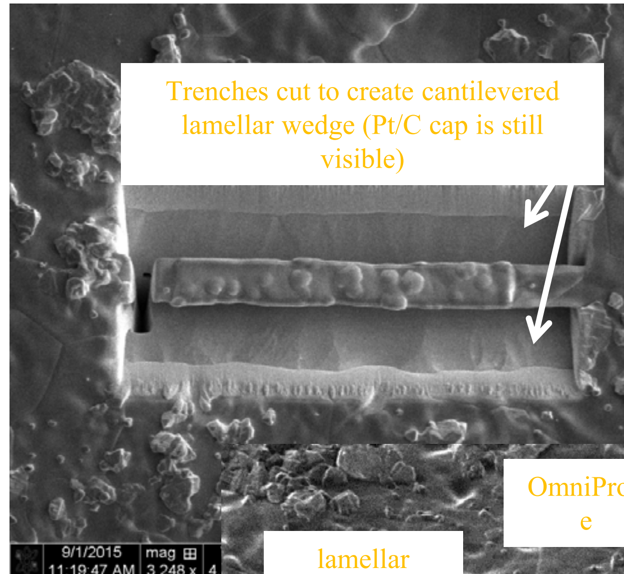
Laser or HV pulse for evaporation and TOF measurement

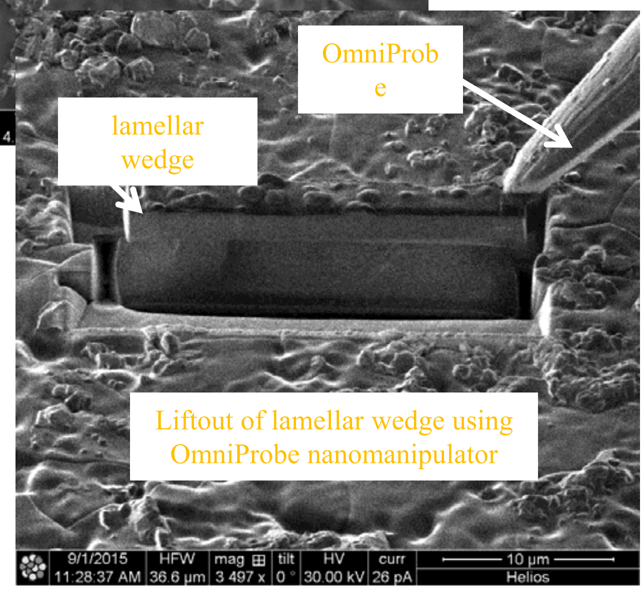
Investigating Al in the Ni-YSZ system: $NiAl_2O_4$



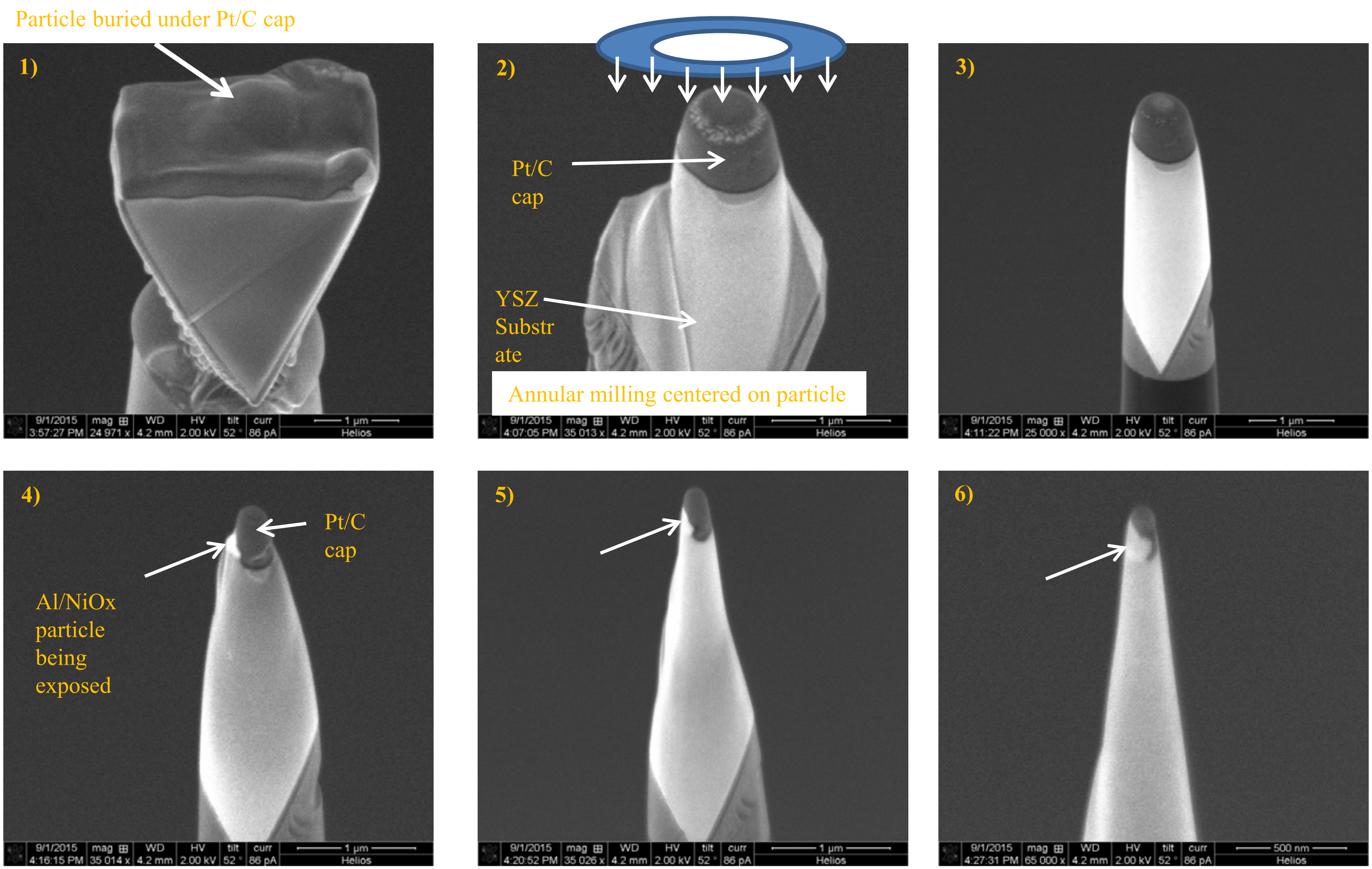
FIB/SEM Specimen Prep (1)



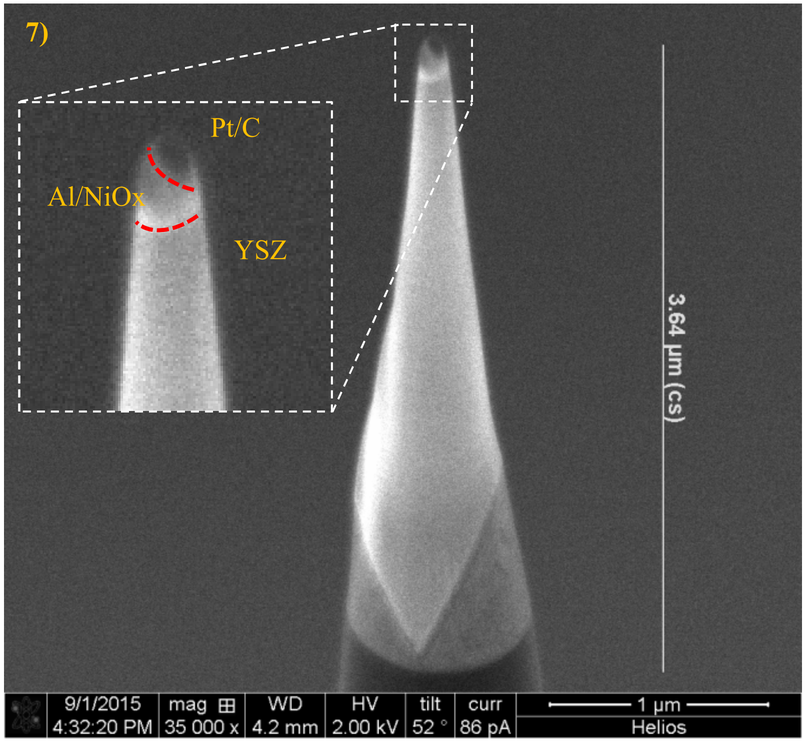


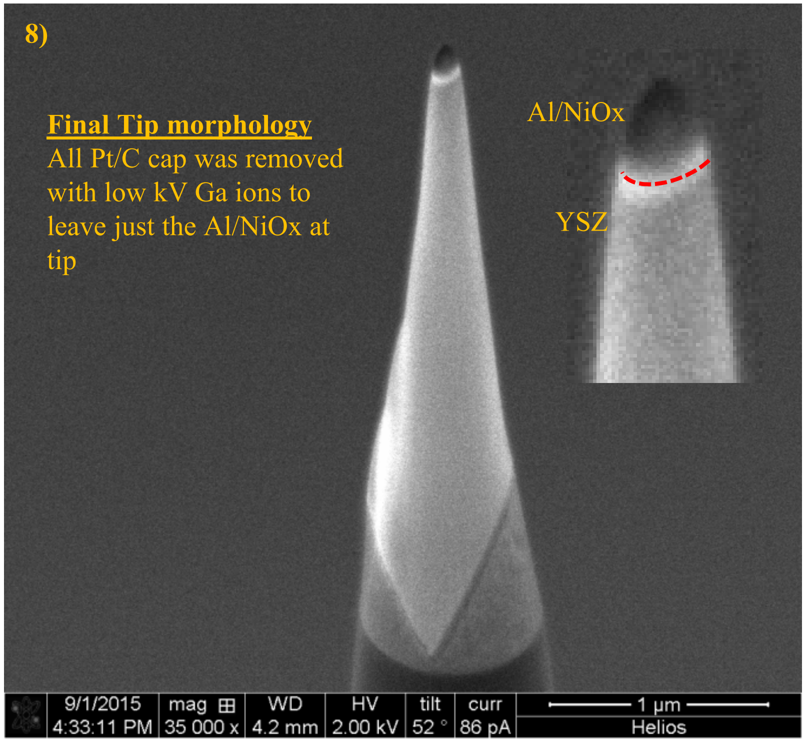


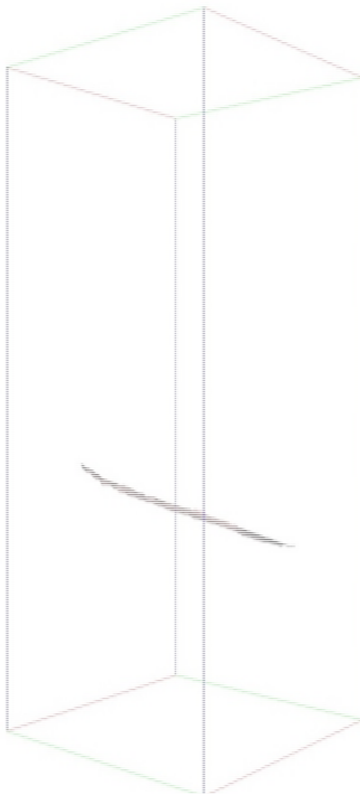
FIB/SEM Specimen Prep (2)



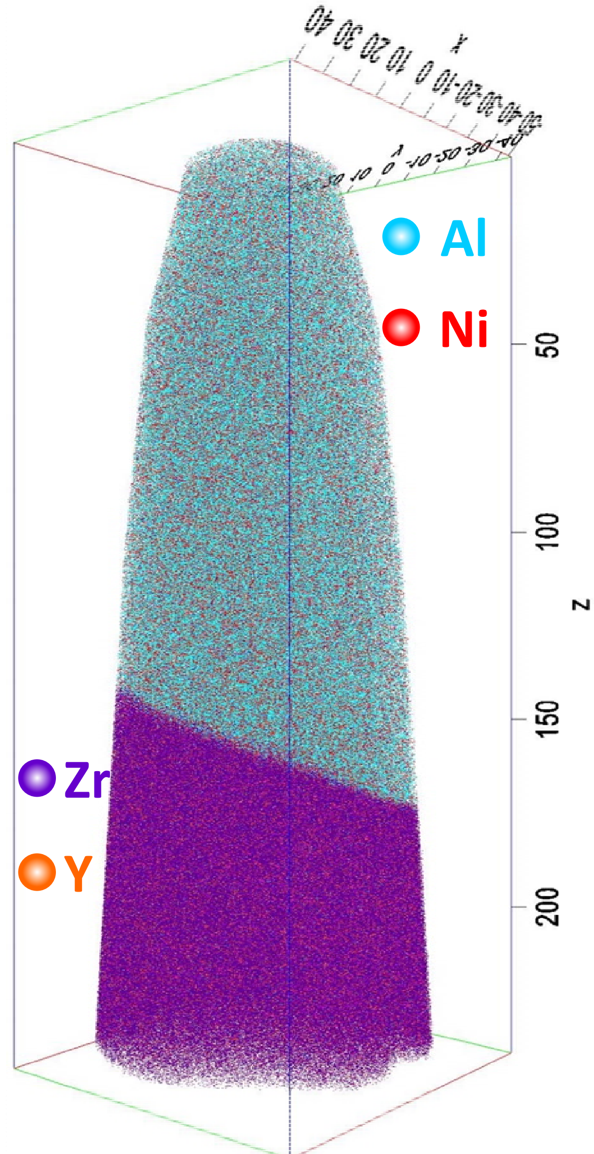
FIB/SEM Specimen Prep (3)





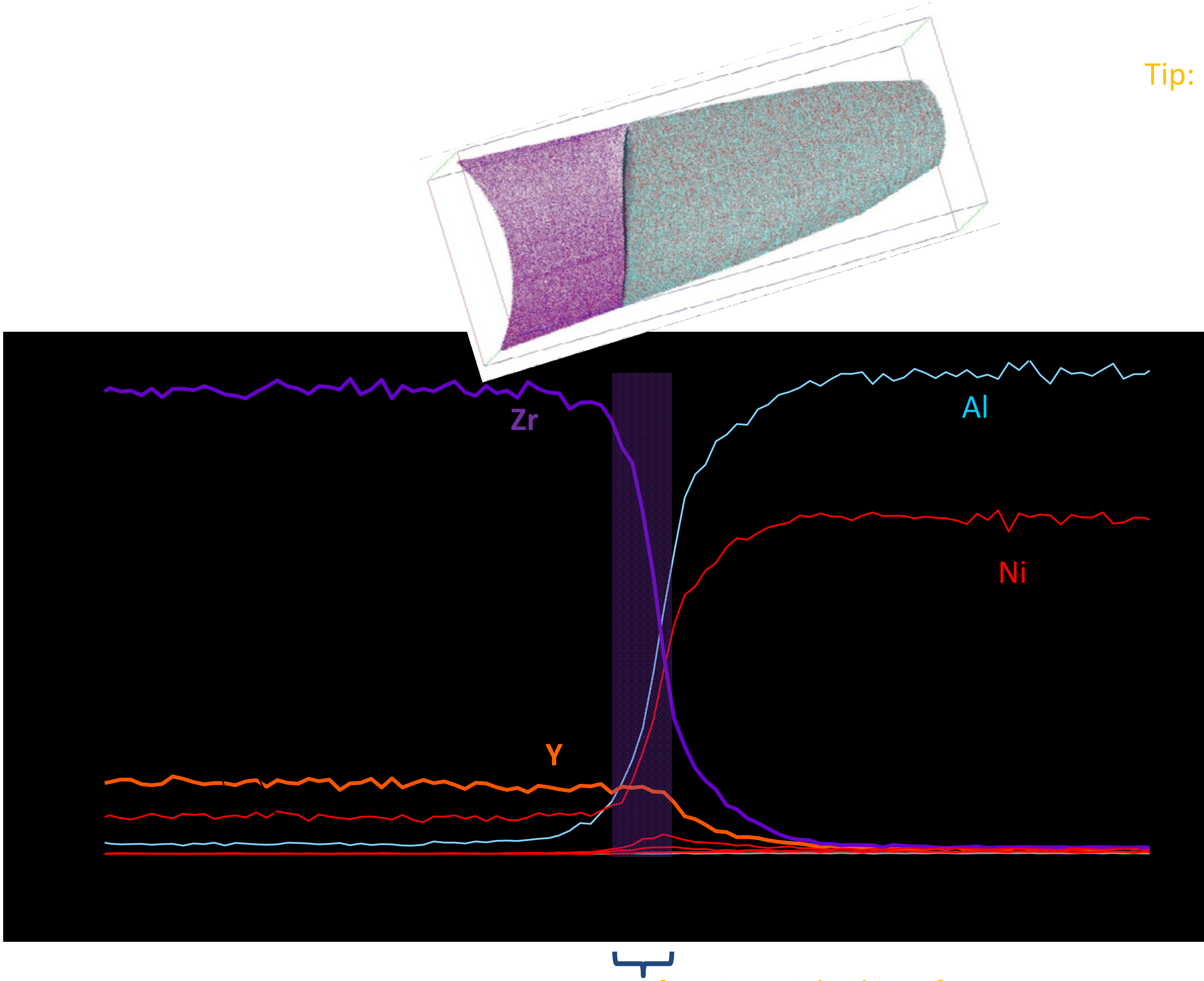


10% Al isoconcentration surface used to delineate the interface between Al/NiOx and YSZ



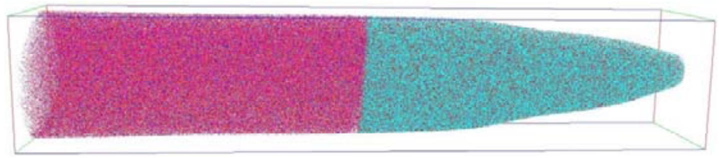
Bounding box dimensions: 93.0 × 91.7 × 238.8 nm^3

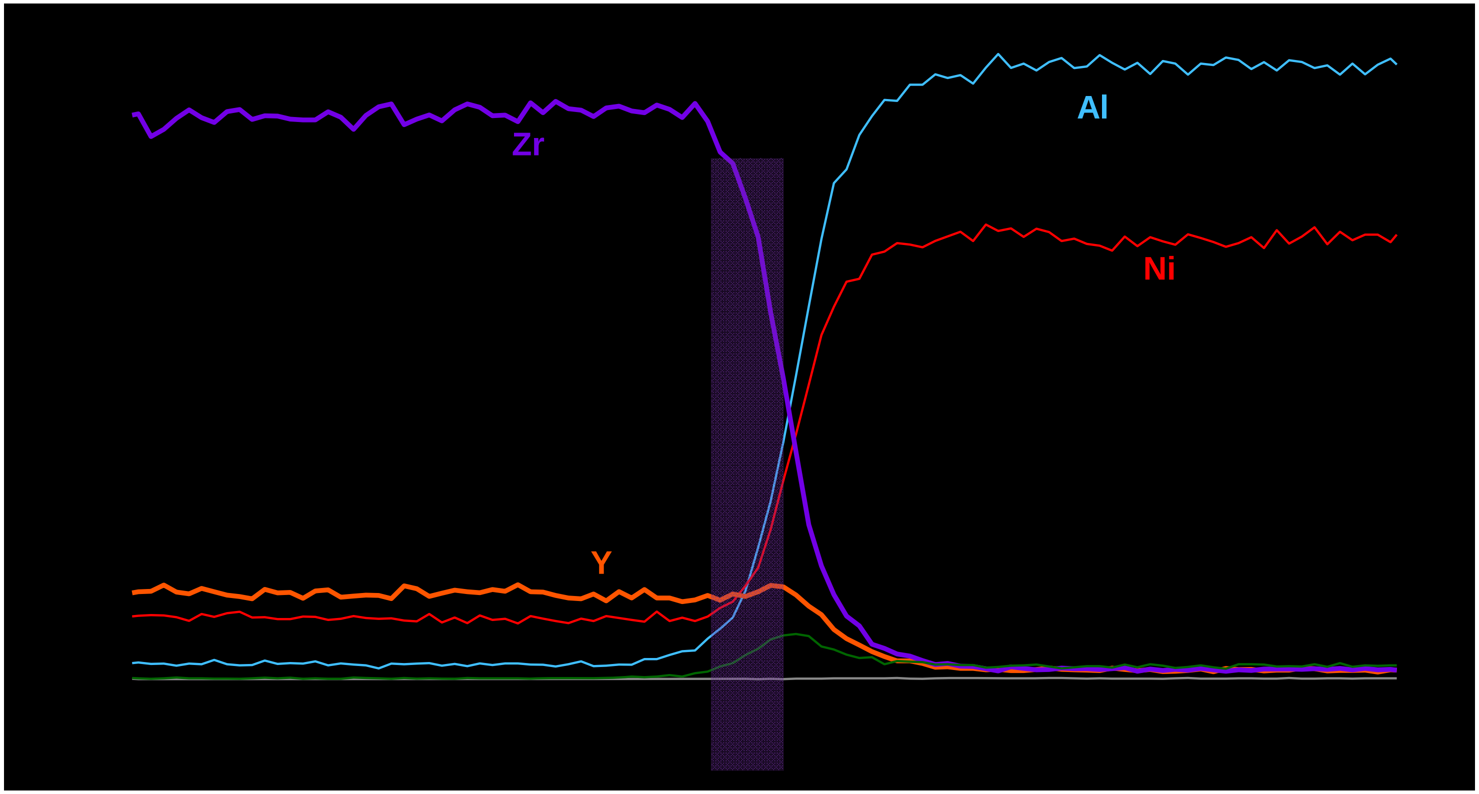
Tip: M04



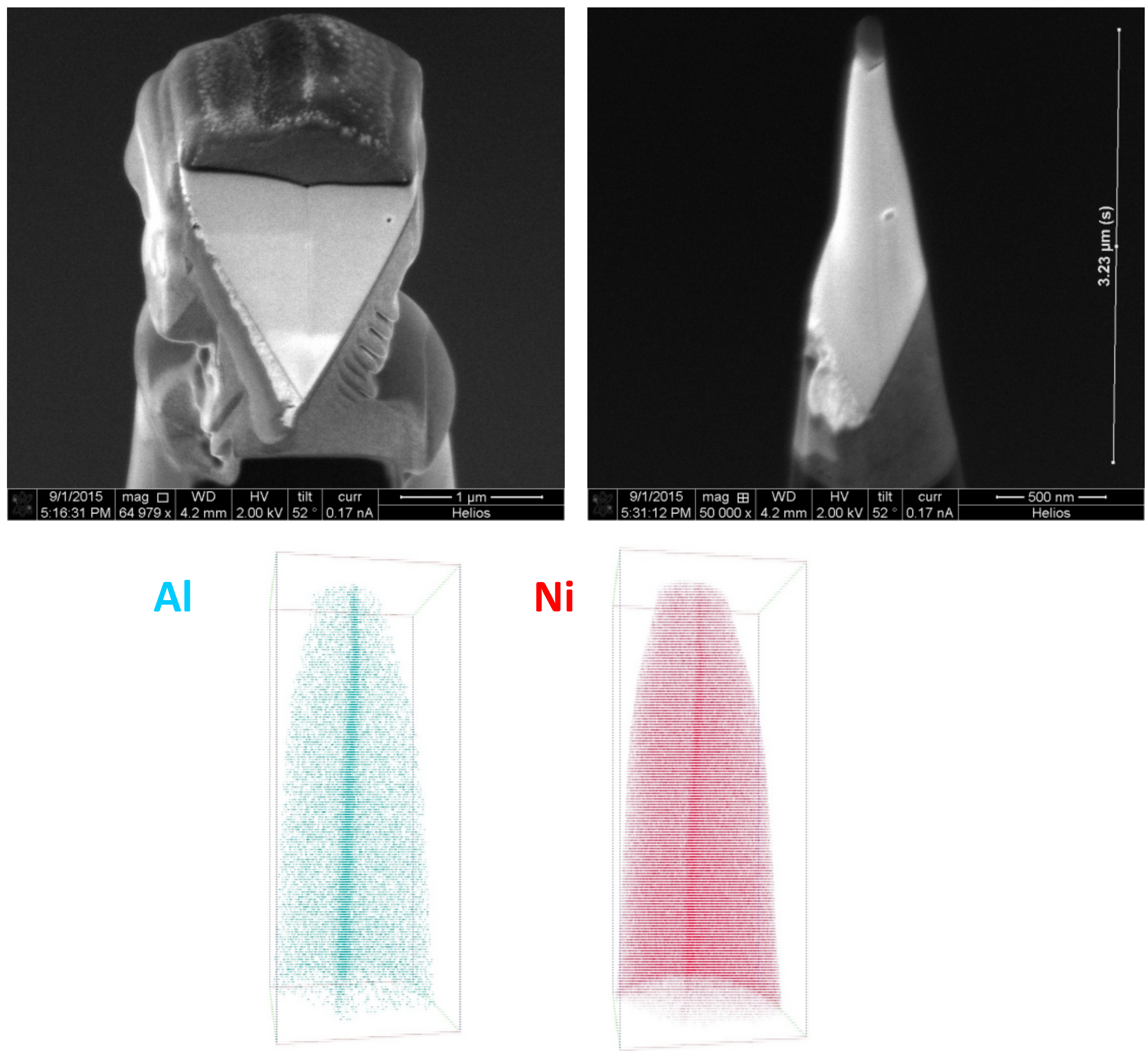
Interface is enriched in Y for ~1nm

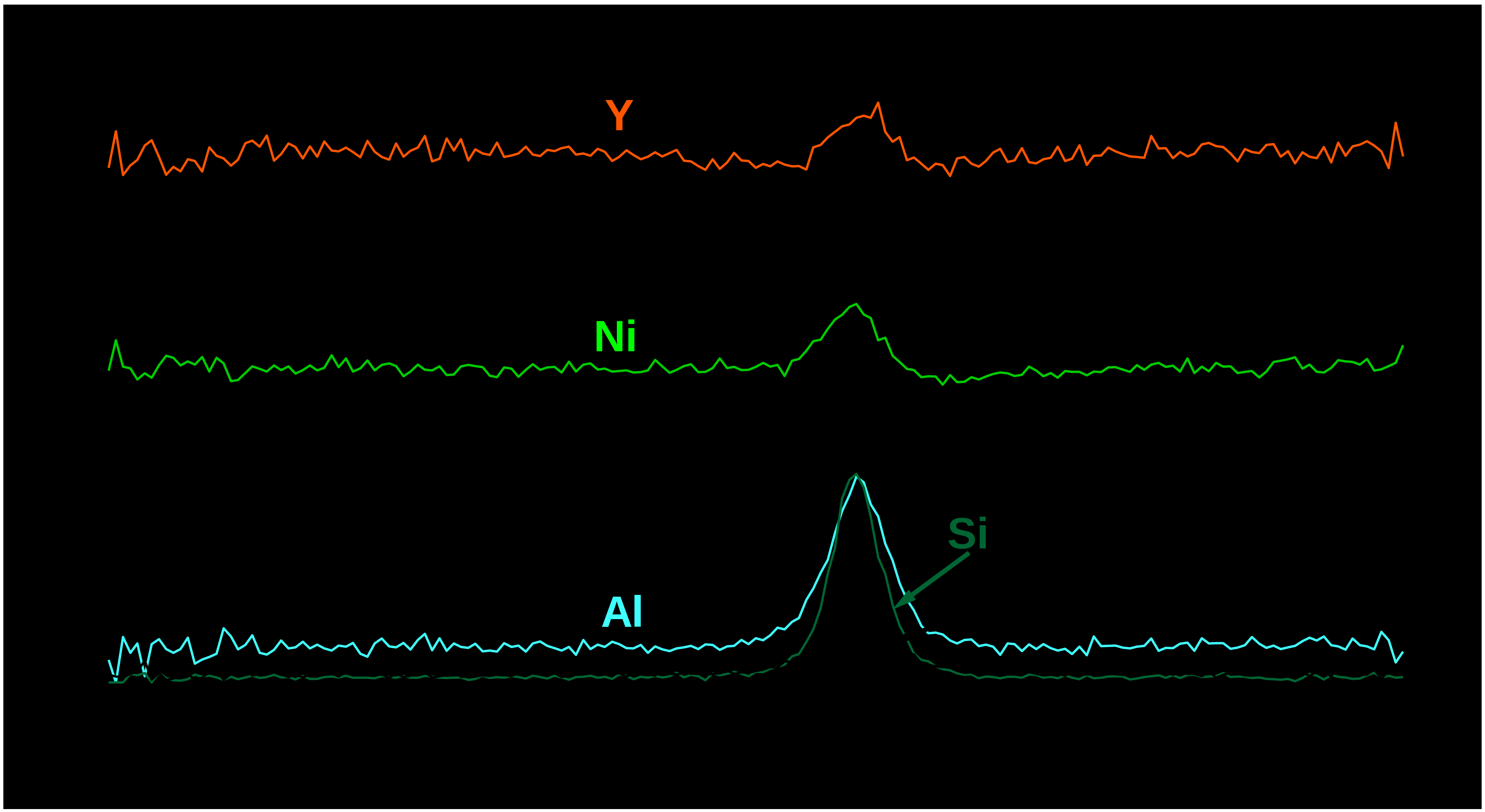
Tip: M05

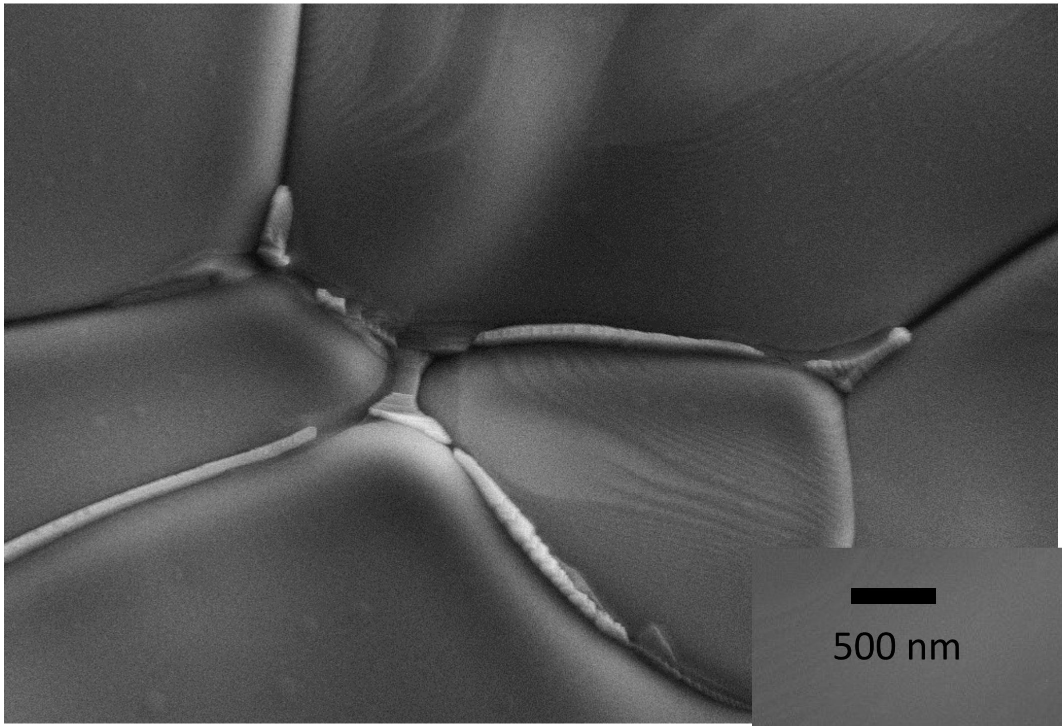




*no interfacial phases are present at the YSZ/Ni interface
(Fully dispels hypothesis of composition grading – chemical binding of catalyst)

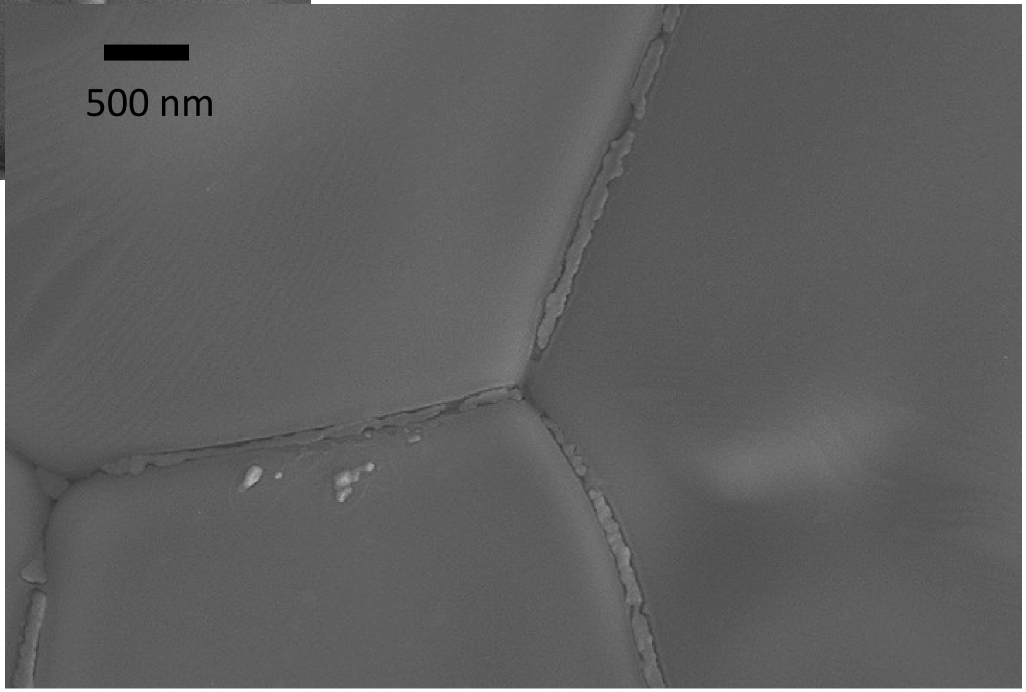

9/1/2015
5:16:31 PM
mag
64 979 x
WD
4.2 mm
HV
2.00 kV
tilt
52 °
curr
0.17 nA
1 μm
Helios
3.23 μm (s)
9/1/2015
5:31:12 PM
mag
50 000 x
WD
4.2 mm
HV
2.00 kV
tilt
52 °
curr
0.17 nA
500 nm
Helios
Al
Ni

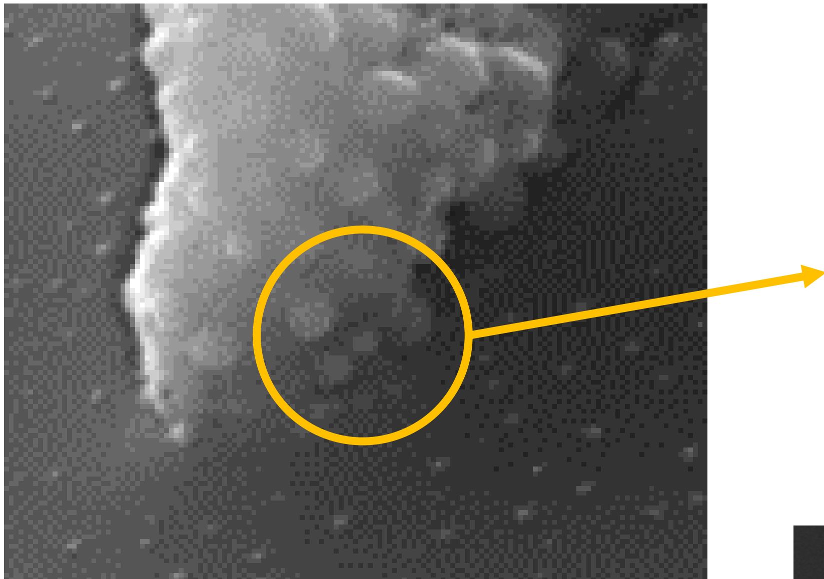

Y
Ni
Si
Al



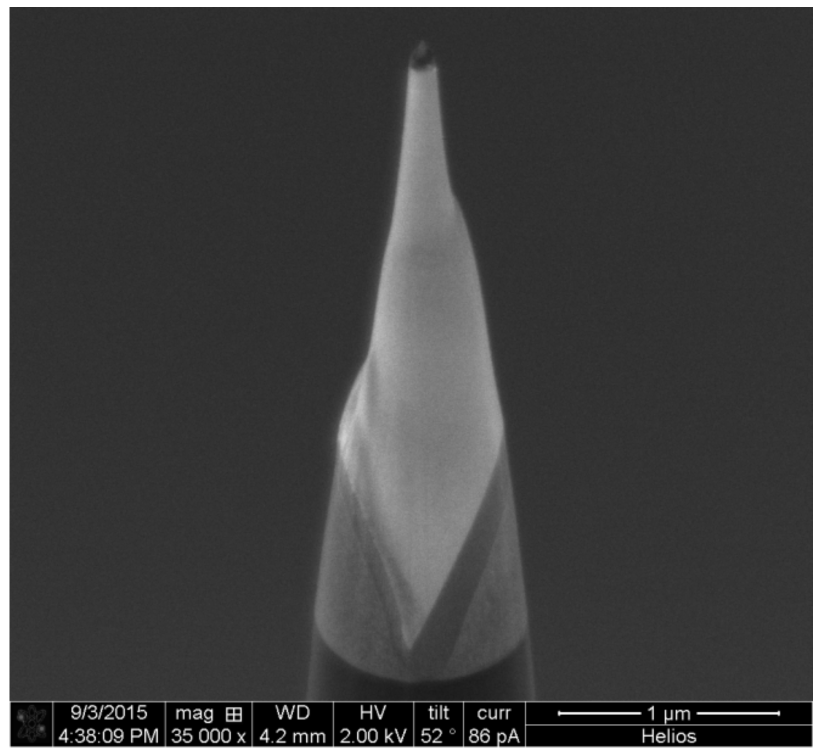
Al enrichment at grain boundary promotes formation of Ni nano-ribbons at GB

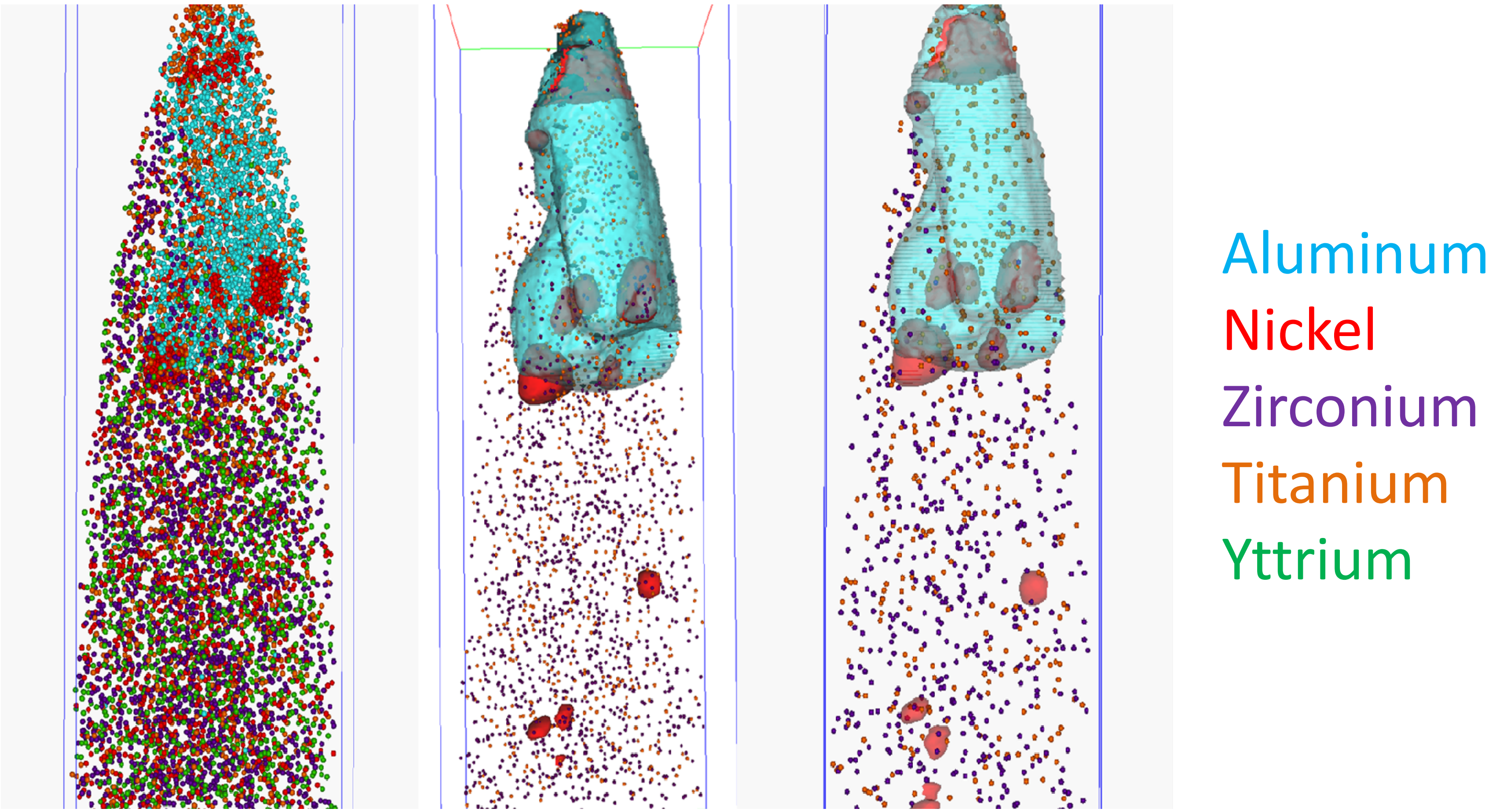
Enhanced wetting of Ni in Al rich regions, aided by precipitation of dissolved Ni upon cooling





Targeting regions of Al rich nodules
on Ni catalyst particles




Aluminum
Nickel
Zirconium
Titanium
Yttrium