Enhancing High Temperature Anode Performance with 2˚ Anchoring Phases

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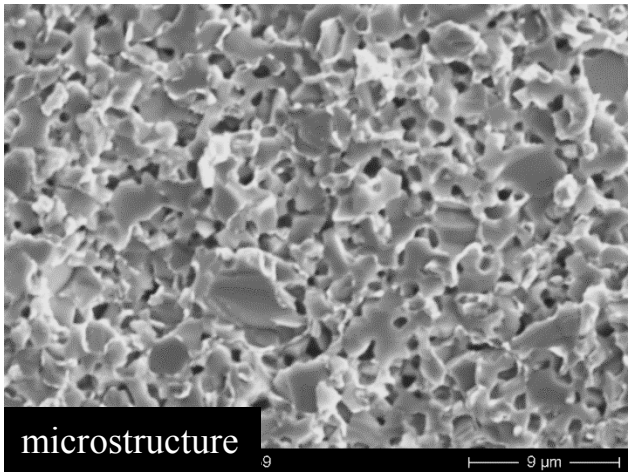

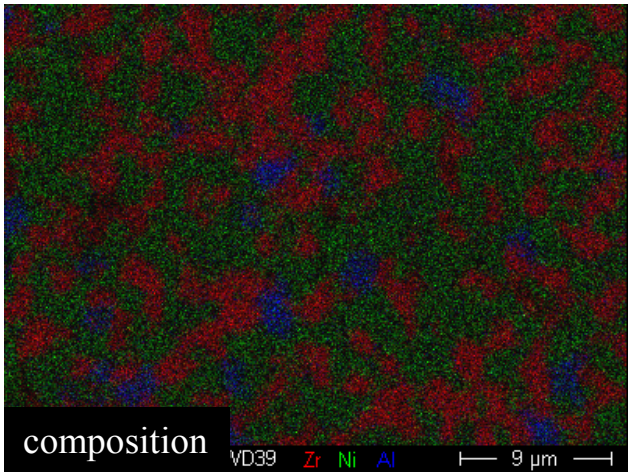

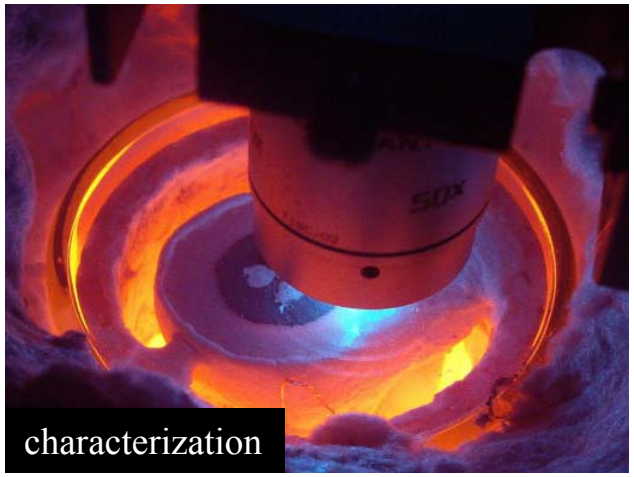

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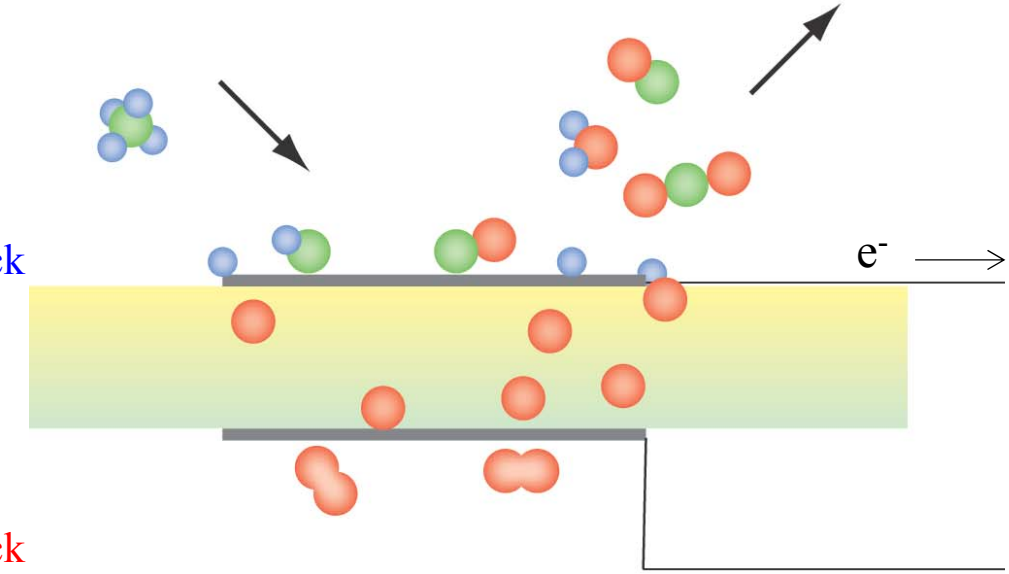
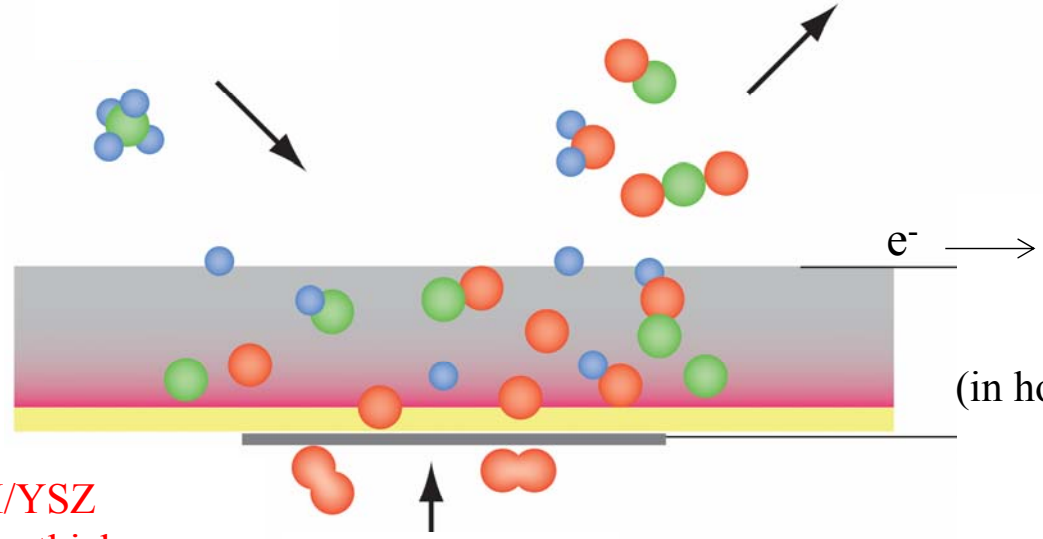
Two types of membrane electrode assemblies



Electrolyte supported
(in-house and FCM)



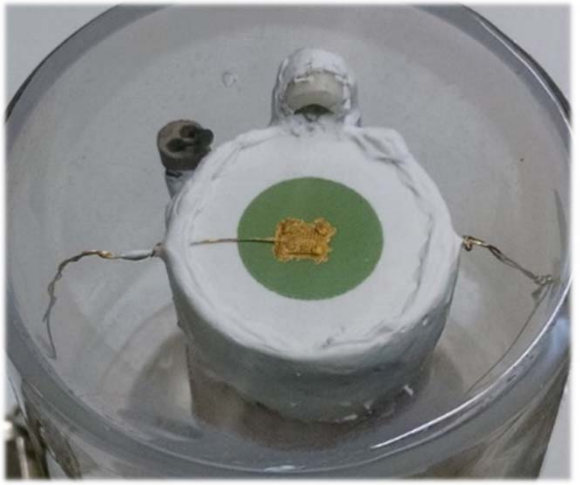
Anode supported
(in house, MSRI, and FCM)

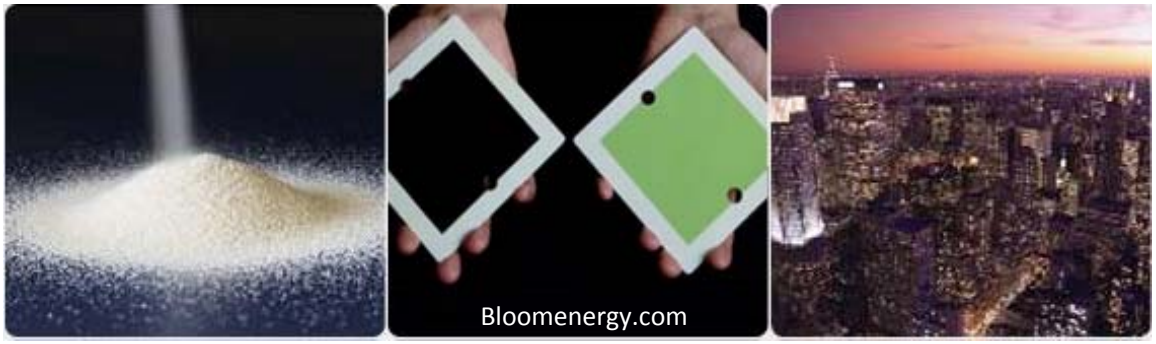
Temp range 650˚C – 800˚C

SOFC Ni-based anodes – the good and the bad:

Advantages:

1. Fuel flexible
2. Efficient
3. Inexpensive
4. Mature technology





Adaptivematerials.com

SOFC Ni-based anodes – the good and the bad:

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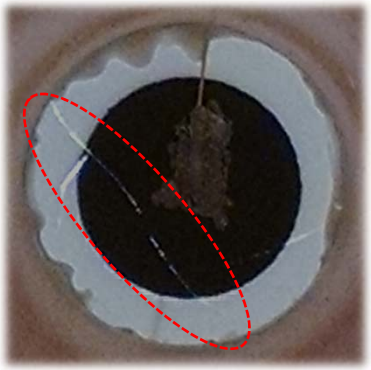
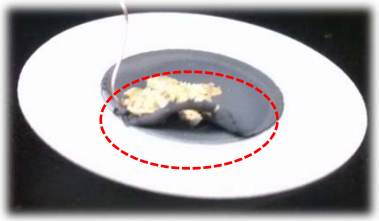
Disadvantages:

1. Mechanical stress (CTE mismatch)





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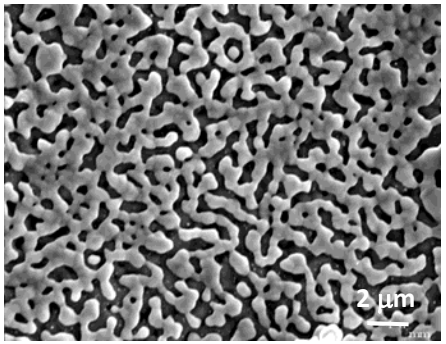
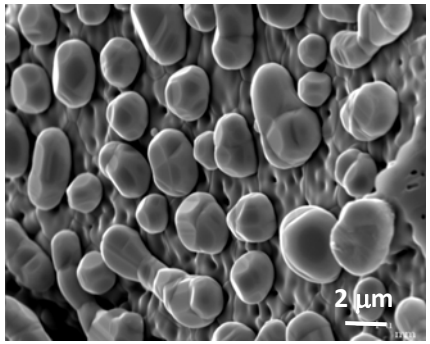
2. Microstructure coarsening



As reduced



After 5 hrs at 800˚C

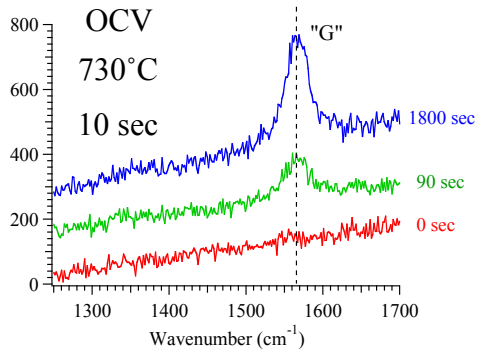
SOFC Ni-based anodes – the good and the bad:

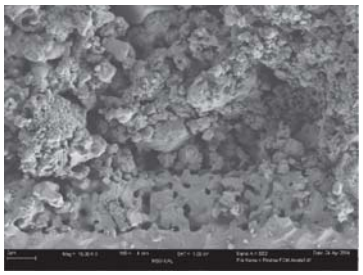
Advantages:

1. Fuel flexible
2. Efficient
3. Inexpensive
4. Mature technology

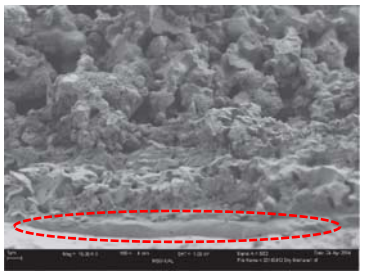
Disadvantages:

1. Mechanical stress (CTE mismatch)
2. Microstructure coarsening
3. Chemical contamination (C, S, Cl)





Pristine anode



Anode following 2 hrs exposure to CH_4

SOFC Ni-based anodes – the good and the bad:

Advantages:

1. Fuel flexible
2. Efficient
3. Inexpensive
4. Mature technology

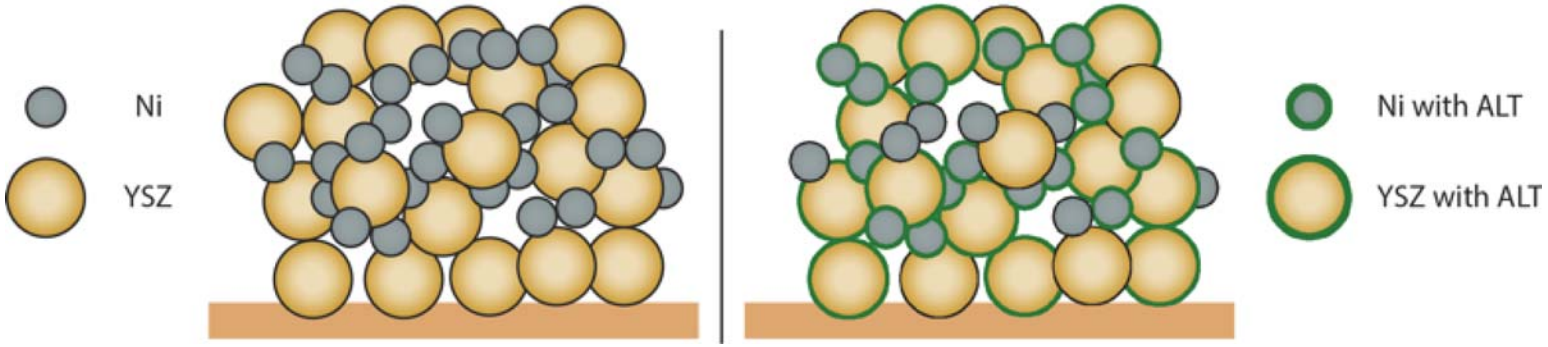
Disadvantages:

1. *Mechanical stress (CTE mismatch)*
2. *Microstructure coarsening*

Improvement through material design

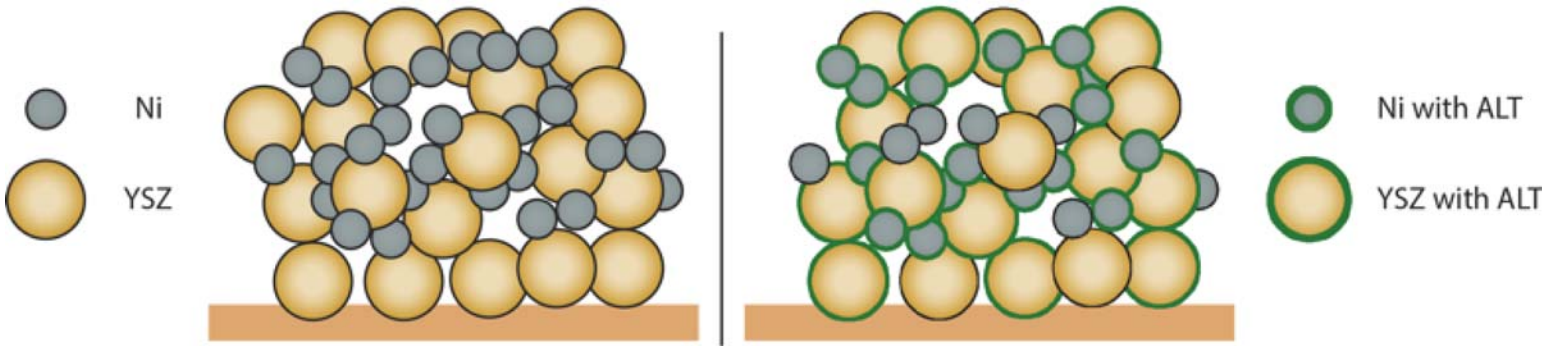
3. Chemical contamination (C, S, Cl)

2˚ phase stabilization of SOFC anode components



This project's goals are to "**develop**, **characterize**, and **refine** electrode preparation methods that **mechanically strengthen** the anode support structure and **facilitate the binding** of sub-micron nickel metal catalysts (diam < 100 nm) to ion conducting ceramic scaffolds. This task will be accomplished through the addition of **reactive materials at low concentrations** that **chemically join** the percolated ion and electron conducting networks that comprise SOFC cermet anodes while simultaneously **immobilizing** metal catalysts to their support."

2˚ phase stabilization of SOFC anode components



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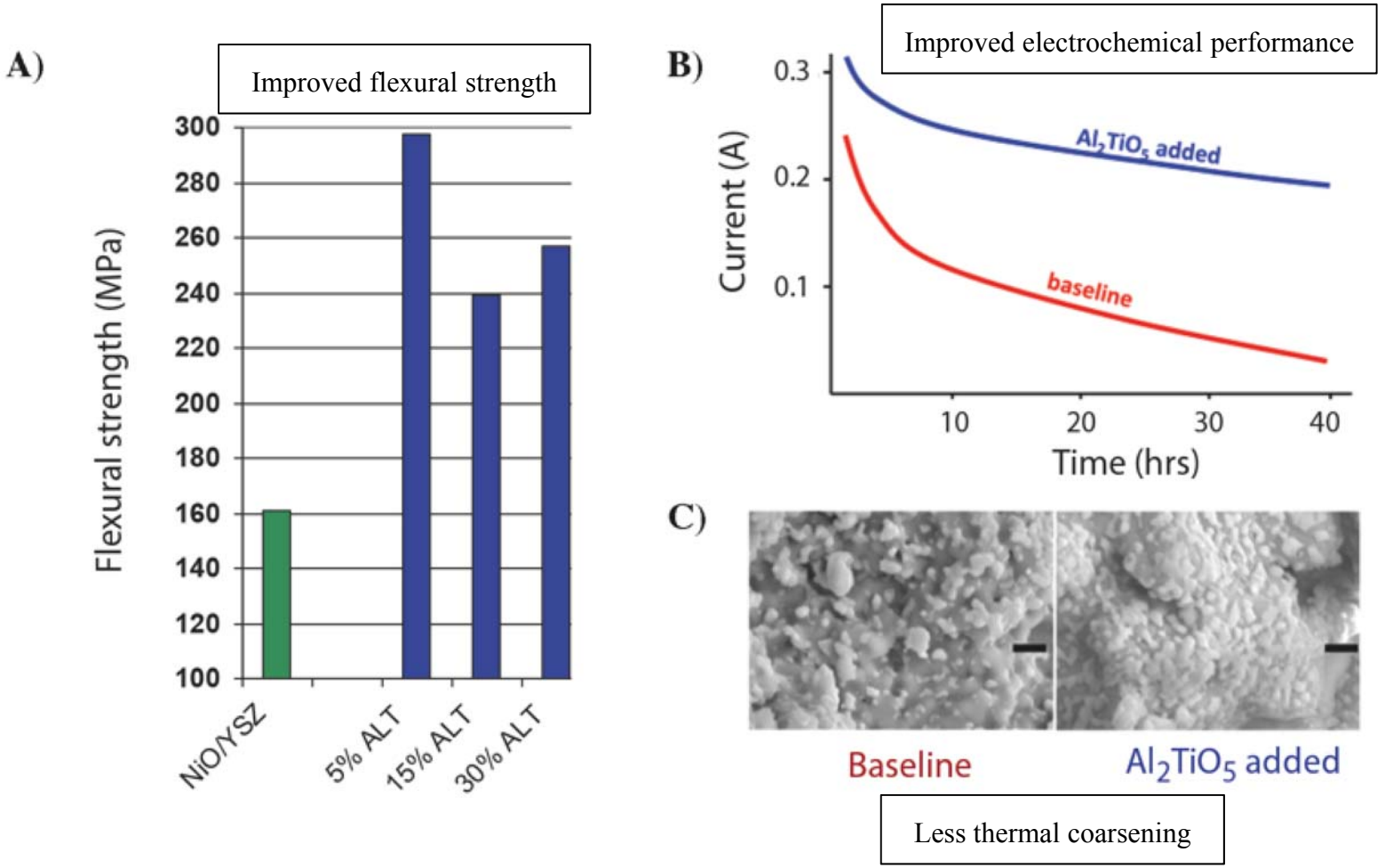
An addendum: These goals should be accomplished using methods that would **introduce minimal disruption** to current commercial fabrication and processing practices.

2˚ phase stabilization of SOFC anode components

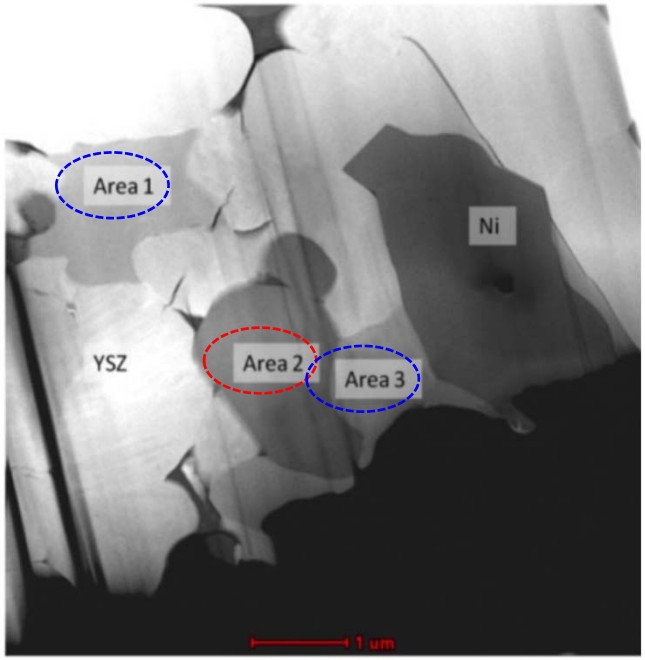
We have reason to believe that our approach has merit. . . .



Law and Sofie, *J. Electrochem. Soc.* **158** (2011) B1137.

2˚ phase stabilization of SOFC anode components

Additional *ex situ* characterization through an EMSL (PNNL) user grant…



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.

These findings support 2˚ phase anchoring mechanism

Project goals – Long term

Overall: Test and refine the hypothesis that judiciously chosen, minority 2° phases can enhance SOFC anode performance and durability by preventing sintering of small particle catalysts and by strengthening the mechanical properties of the anode itself.

- Identifying 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.
- Determining the **optimal thermal conditioning** procedures that promote 2° phase formation while introducing little perturbation or even enhancing anode microstructure.
- **Quantifying the effects of 2° phases on the electrochemical performance** and durability of SOFC anodes using a suite of *in operando* and *ex situ* techniques.

Project goals – Short term

Overall: Test and refine the hypothesis that judiciously chosen, minority 2° phases can enhance SOFC anode performance and durability by preventing sintering of small particle catalysts and by strengthening the mechanical properties of the anode itself.

Task 2.1.1 Fabricate MEAs
Membrane electrode assemblies (MEAs) having Ni-YSZ anodes will be fabricated locally and infiltrated with varying amounts of of ALT including 0.5%, 1%, 2%, 5% and 10% by mass.

Task 2.1.2 Map effects of temperatures and sintering rates on the formation of 2˚ phases
These studies will include conditioning at higher temperatures (≥ 1300˚C) for shorter periods (≤ 6 hrs) and conditioning at lower temperatures (≤ 1100 ˚C) for longer periods (12-36 hrs)

Task 2.2. Testing membrane electrode assembly mechanical strength
To evaluate the macro and micro mechanical behavior of the Ni catalysts impregnated with Ti and Al containing 2˚ phase precursors, the recipient will perform the following subtasks:

Task 2.2.1 Fracture Strength Evaluation
Brittle materials are commonly tested in bending under combined tensile/compressive stresses. Specifically prepared rectangular samples will be tested in a three point flexural fixture (bending test). The assessed fracture strength, along with the Weibull modulus and statistical analyses, will be employed to evaluate the reliability of the mechanical properties and to determine failure probabilities under a given stress situation

Task 2.3.3 Vibrational Raman spectroscopy
Vibrational Raman Spectroscopy will be used to examine chemical and material changes occurring on plain and infiltrated SOFC anodes under polarization. Vibrational signatures from earlier experiments will serve as diagnostics and will be monitored as SOFC polarization changes and as a function of fuel type.

Project goals – Tools available

Technique	Purpose	Surface/Bulk	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*

Enhanced Ni/YSZ Cermet Approaches (Sofie)

NiO/YSZ + ALT Powder (1, 5, 10 wt%)

↓

Ball Milling

↓

Flash Freezing (LN_2) + Freeze Drying

↓

Uniaxial Pressing

- Mechanical mixing yields some ALT is spatial distributions will not bridge YSZ and NiO particles
- Infiltration of ALT will provide a more homogenous distribution at lower dopant concentrations

NiO/YSZ

↓

Ball Milling

↓

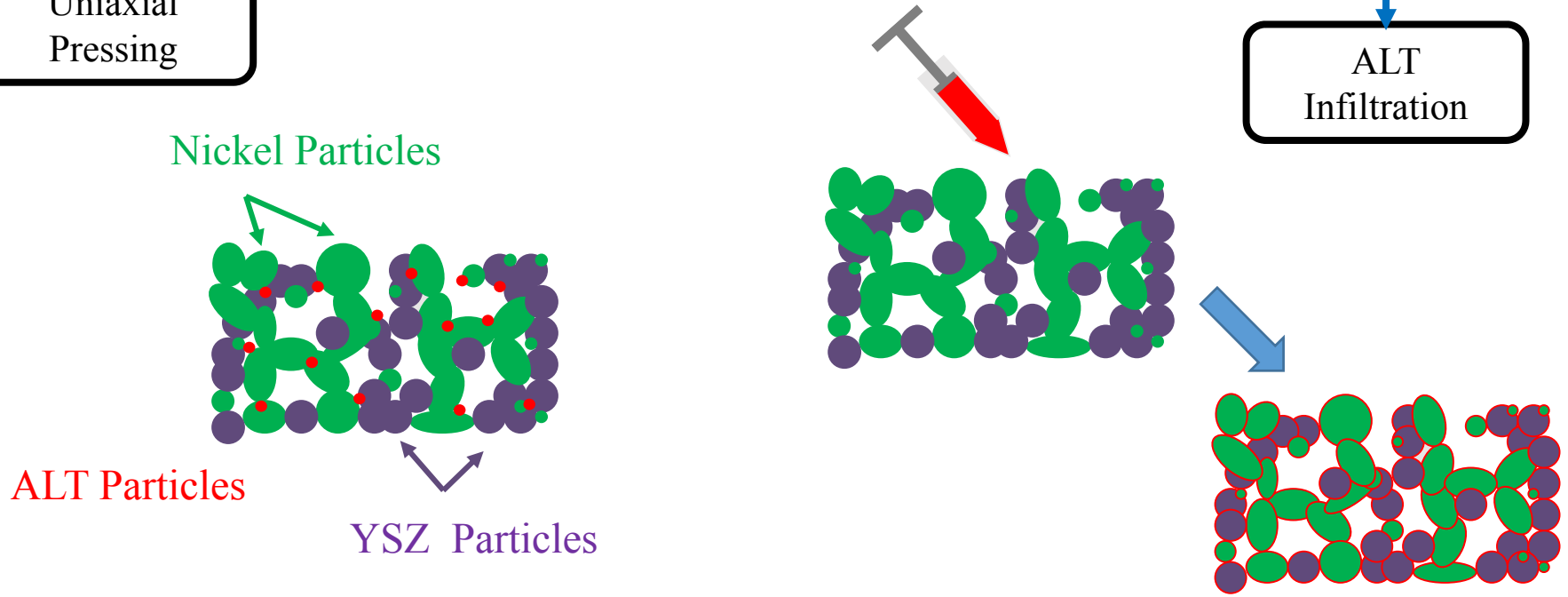
Flash Freezing (LN_2) + Freeze Drying

↓

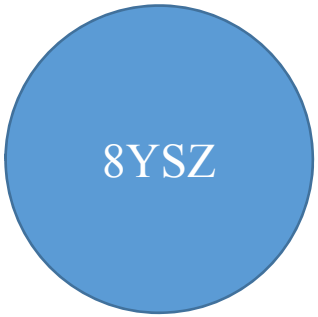
Uniaxial Pressing

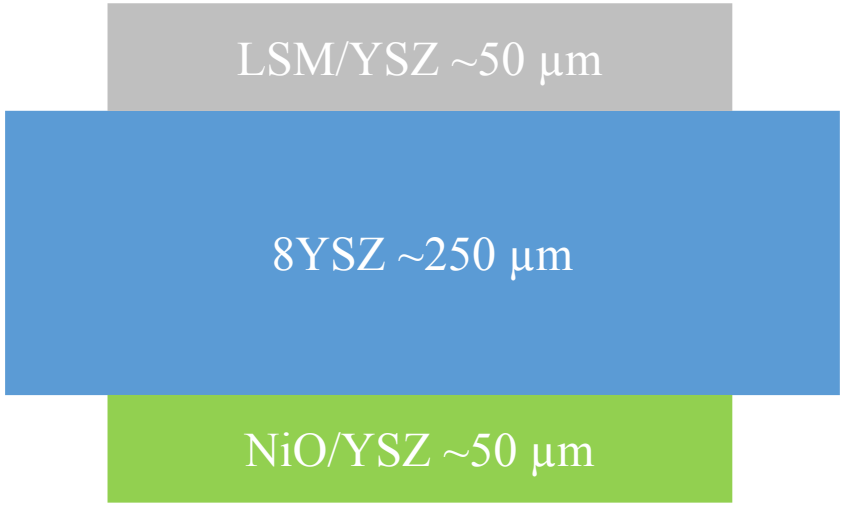
↓

ALT Infiltration



Cell fabrication and cell parameters





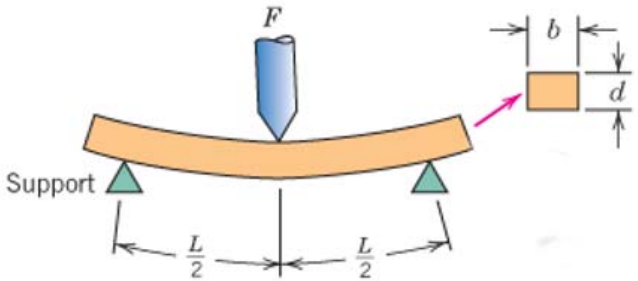
NiO/YSZ Cermets
Tosoh TZ-8Y
NiO options (4 um, 350 nm, 60 nm)

NiO (350 nm)/8YSZ + 0% ALT
NiO (350 nm)/8YSZ + 1, 5, 10 wt% ALT mechanically mixed
NiO (350 nm)/8YSZ + ~ 1 wt% ALT solution infiltrated
*optional ASC fabrication and testing will follow analysis and optimization of ESC matrix

Mechanical Testing - Initial Tasks

- Manufacturing of initial bars to analyze the fracture surfaces for defects with only NiO-YSZ powders without the addition of ALT
- Iterate through different pressing/sintering conditions to create a flaw-free bar
- Fracture of bars to calculate initial Modulus of Rupture values
- Analyze the fracture surfaces with Electron Microscopy to determine flaw distribution

Flexural Strength (MOR) Evaluation (Amendola)



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

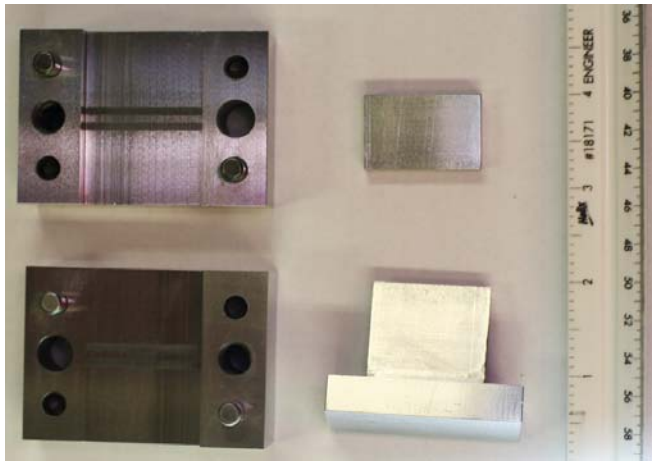
F_f = applied load at failure

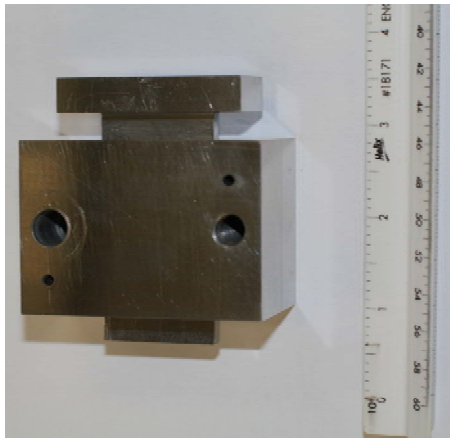
s_{fs} = flexural strength or Modulus of Rupture (MOR)

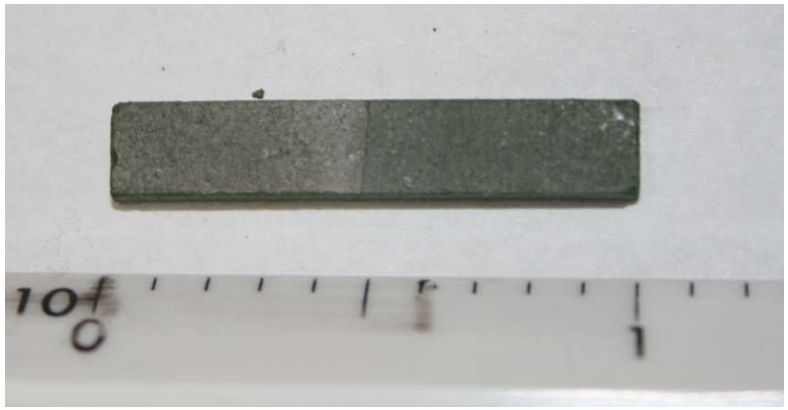
- **ASTM C1161-13**
  Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature
- ***As-Fabricated samples*** —The flexural specimen shall simulate the surface condition of an application where no machining is to be used
- Higher MOR values correspond to a mechanically stronger material
- MOR is dependent on type, size and severity of flaws *(therefore controlling flaws and microstructurally uniformity is critical for a proper comparison between doped and undoped speicmens)*

Sample Preparation

- NiO-8YSZ nanopowder (66%wt NiO 350 nm, 34%wt YSZ 300 nm)
- Specimen size after uniaxial pressing 30 mm x 5 mm x 2 mm



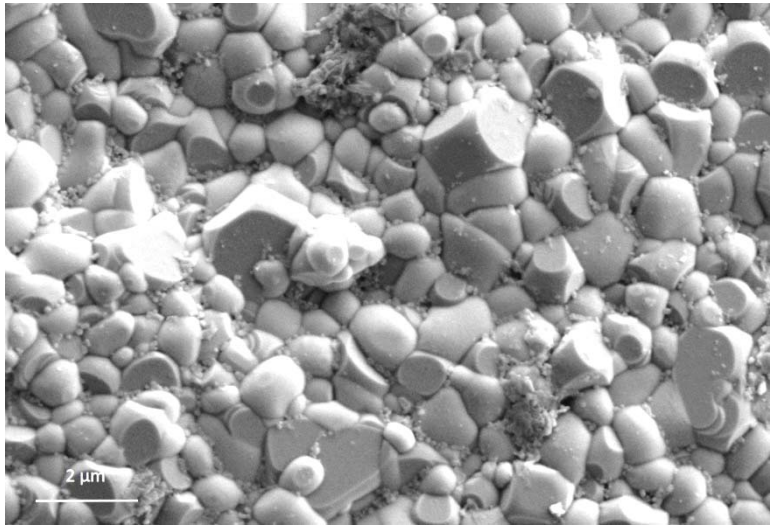


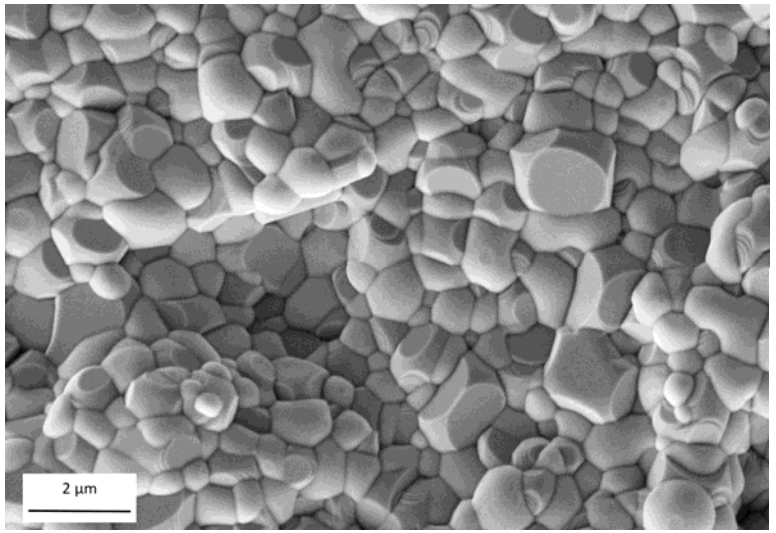


Sintered Bar Surfaces NiO(350nm)/8YSZ

35,590 N (8,000 lbf)

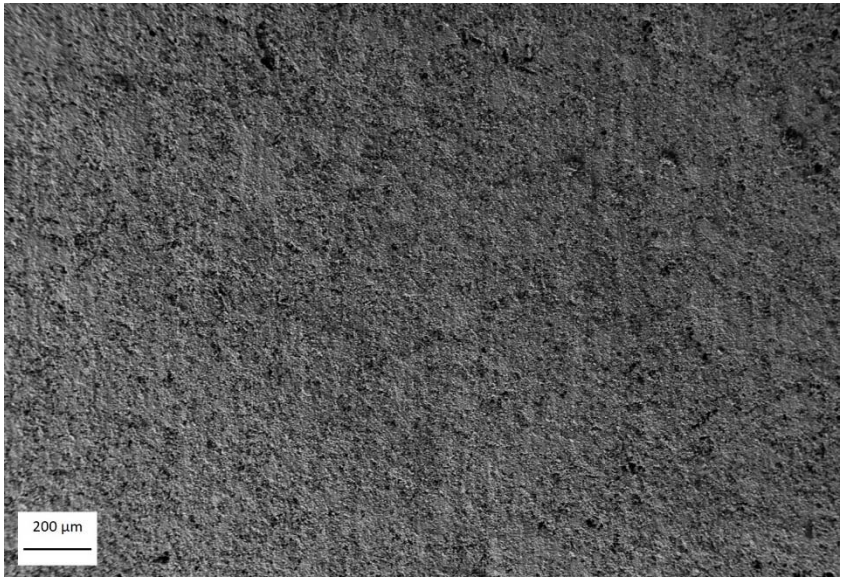
22,240 N (5,000 lbf)

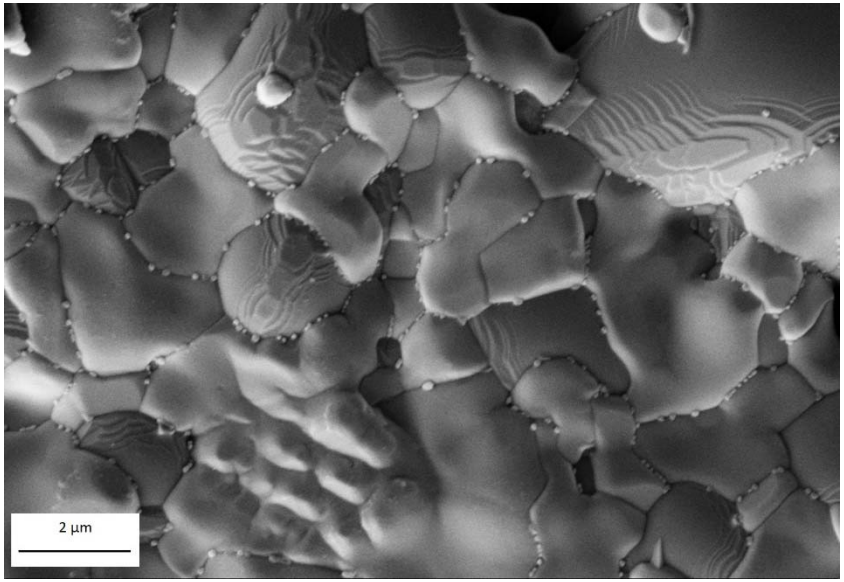




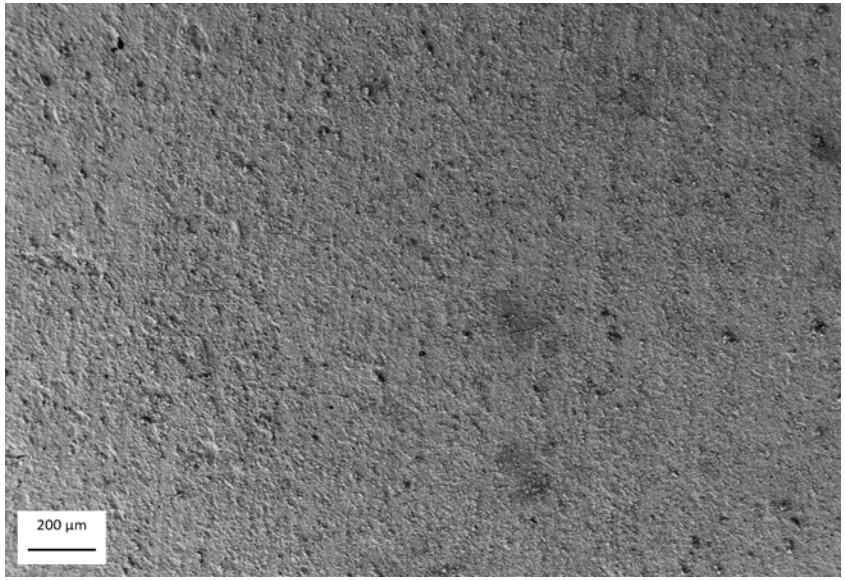
Sintered Bar Surfaces NiO(4µm)/8YSZ

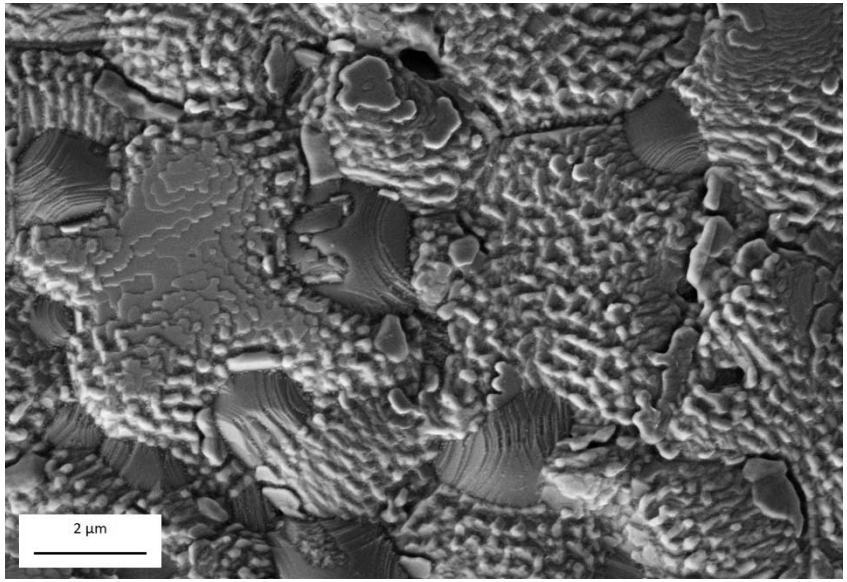
NiO/YSZ





NiO/YSZ + 5% ALT

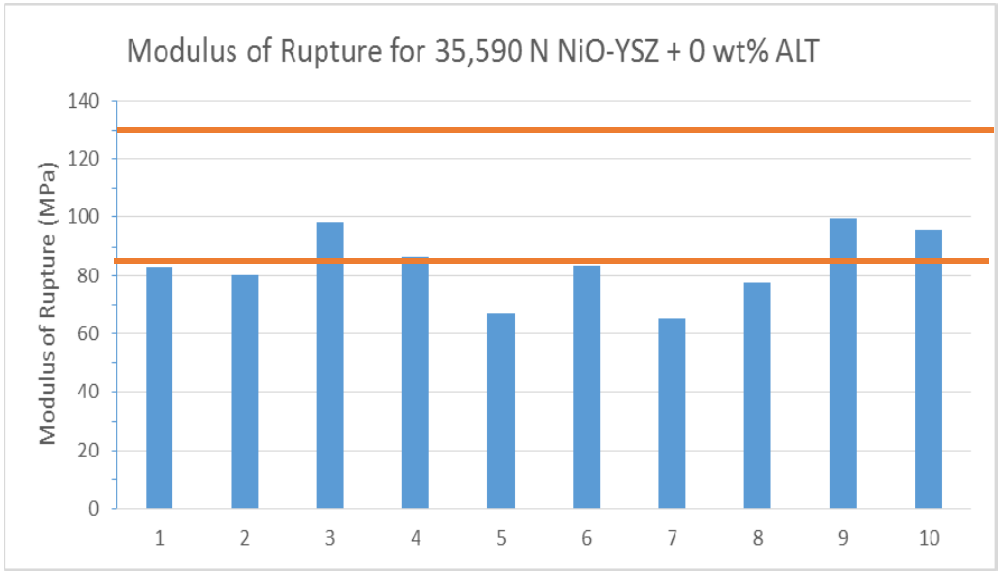


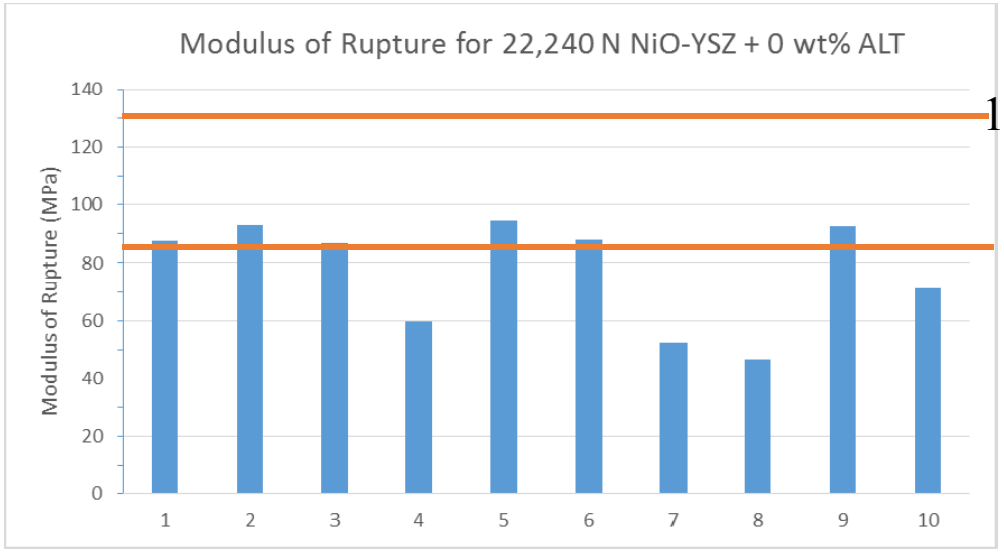


Initial MOR testing - NiO(350 nm)/8YSZ

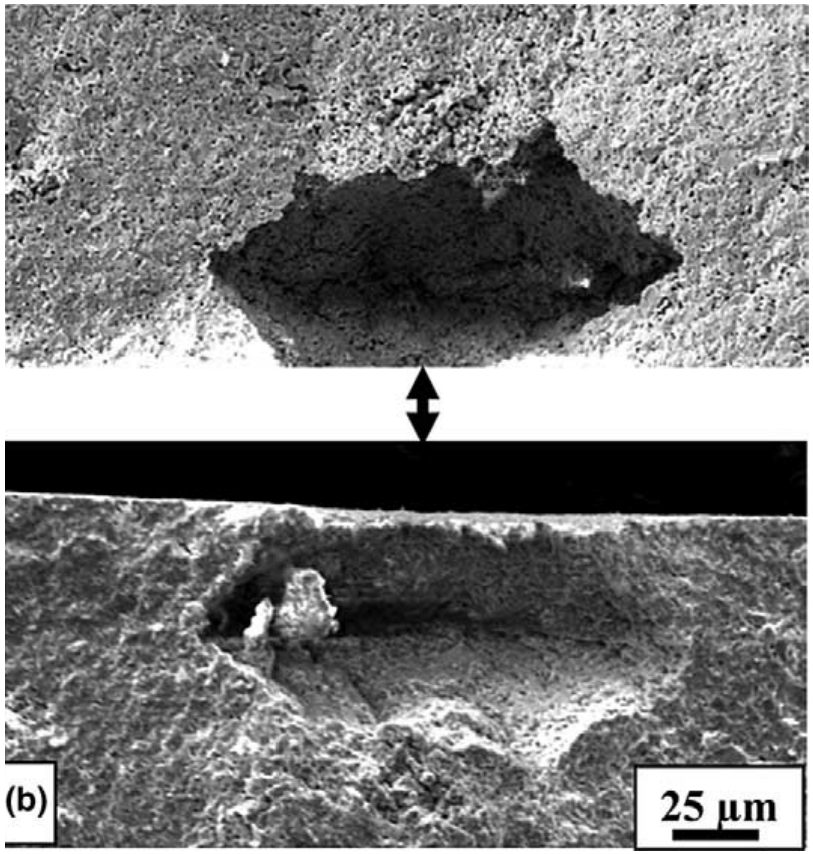
1. The fine nickel oxide powder yields more heterogeneous microstructure
2. Processing optimizations are being performed to yield ideal microstructures for testing

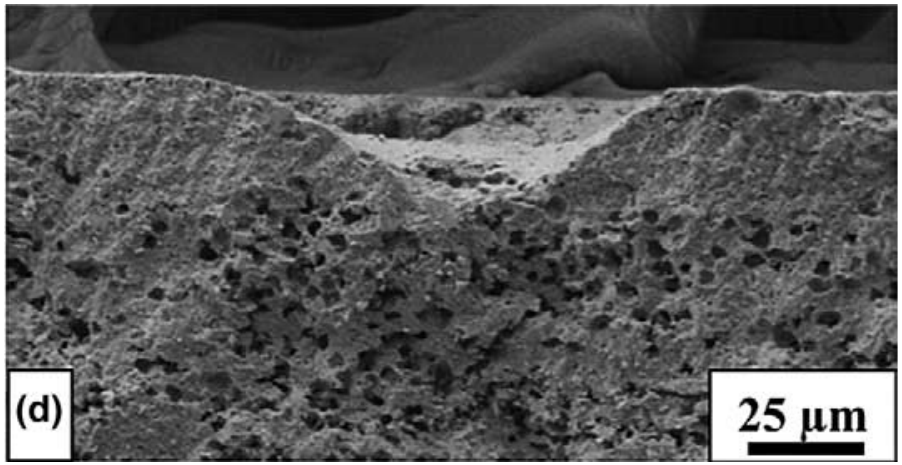
- A total of 41 samples have been produced and 28 have been tested
- 44,480; 35,590; 22,240 N (10,000; 8,000; 5,000 lbf) have been used to press samples
- The influence of pressing time has been investigated for 22,240 N pressed samples
- MOR reference values are in the range 85-130 MPa





Literature reports on NiO-YSZ microstructure

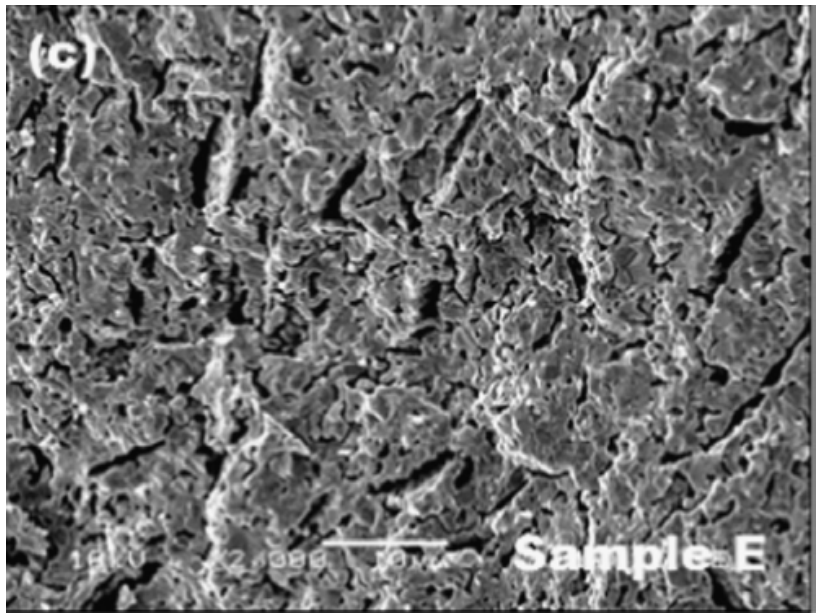


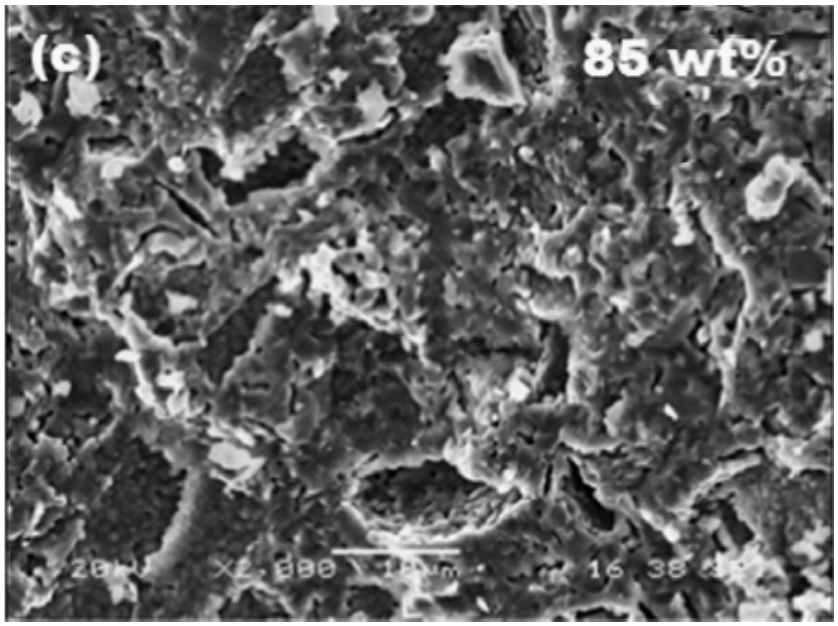


- Large Manufacturing holes in the fracture surface
- Non-homogeneous pore distribution
- Surface dimples
- Particle clusters

Radovic, M., and E. Lara-Curzio. "Mechanical Properties of Tape Cast Nickel-based Anode Materials for Solid Oxide Fuel Cells before and after Reduction in Hydrogen." *Acta Materialia* 52.20 (2004): 5747-756.

Literature reports on NiO-YSZ microstructure



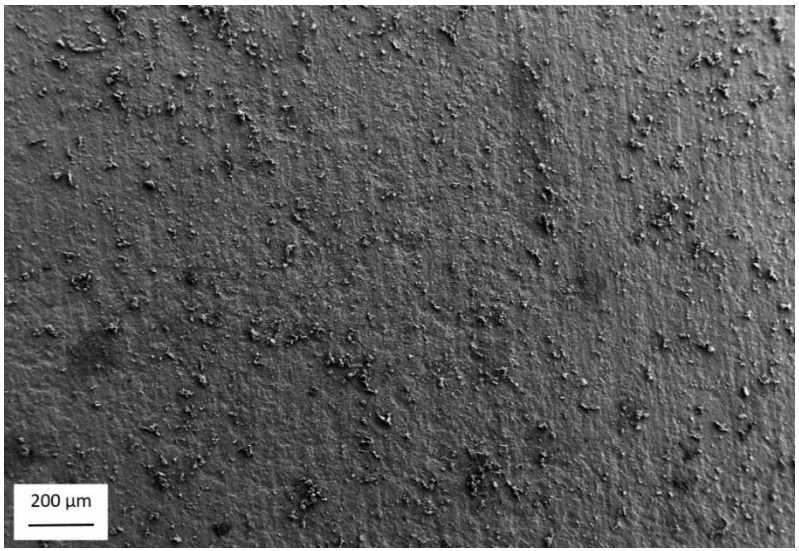


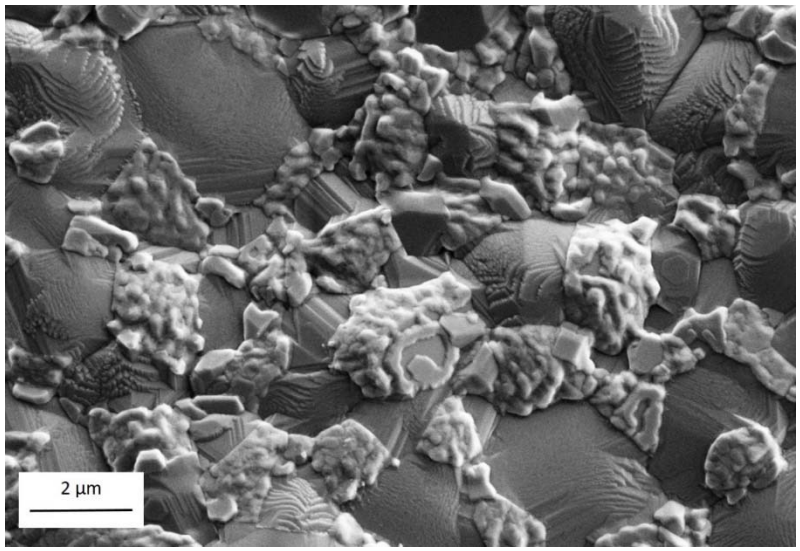
- Non-spherical porosity
- Manufacturing opens microcracks

Casarin, Michele, and Vincenzo M. Sglavo. "Influence of Processing Conditions on the Microstructure of NiO-YSZ Supporting Anode for Solid Oxide Fuel Cells." *Ceramics International* 41.2 (2015): 2543-557.

NiO/8YSZ + ALT Sintered Surface

Black NiO-YSZ + 5% ALT mechanically mixed

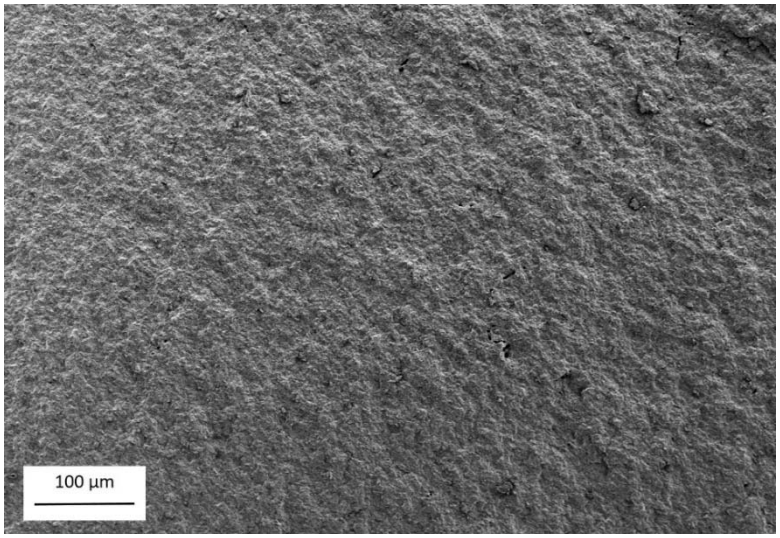


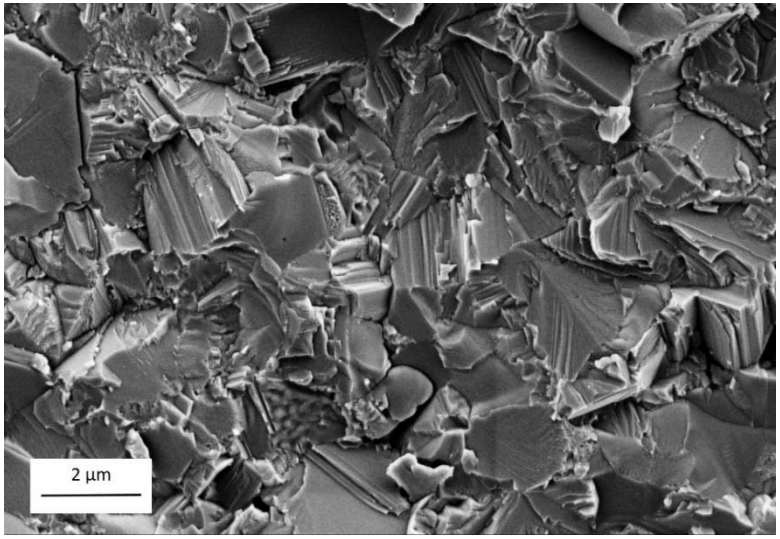


- Significantly more homogeneous microstructure
- Apparent material migration and heterogeneous distribution across surface

NiO/8YSZ + ALT Fracture Surface Microscopy

Black NiO-YSZ + 5% ALT mechanically mixed





- Homogeneous microstructure extends throughout the material!
- Fractures occur *through* grains, not at grain boundaries
- MOR of 222 MPa (>2x larger than undoped!)

- **Task 2.2.1 Fracture Strength Evaluation and 2.2.3 Fractography (Current – June 2016)**

  - **Sample Manufacturing**
    - Optimize sample preparation and sintering parameters (binder, pressure, and sintering conditions effect on the densification of the bars
    - Investigation of NiO particle size (~4 μm vs. 350 nm) effect on bars' densification
    - Comparison of Infiltration of ALT with ALT powder mechanical mixing
    - Reduction of NiO-YSZ bars
  - **Fracture strength evaluation**
    - Once the parameters to manufacture flaw-free samples will be identified, statistical analyses on over 30 samples per batch will be performed
    - Comparison of NiO-YSZ and Ni-YSZ samples with and without ALT addition

- **Task 2.2.2 Fracture toughness evaluation and 2.2.4 Microindentation (August – December 2016)**

ALT as a sintering aid (Sofie)

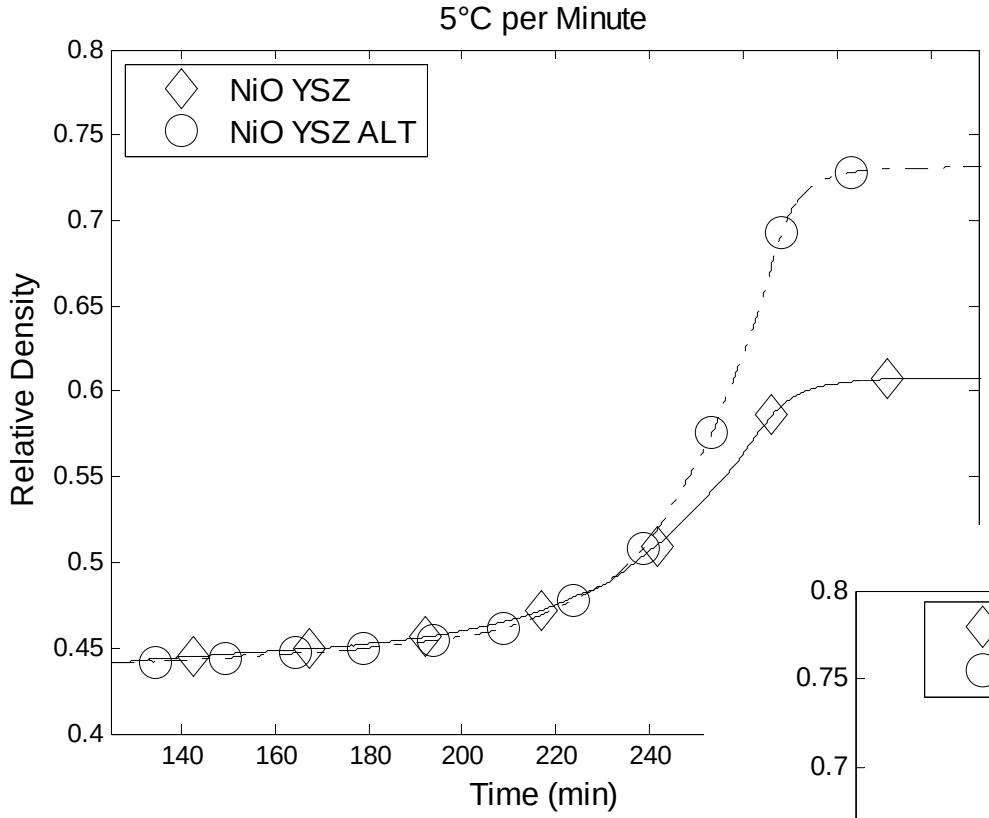
Initial fabrication studies identified that ALT additions yielded enhanced densification of NiO/YSZ cermets.

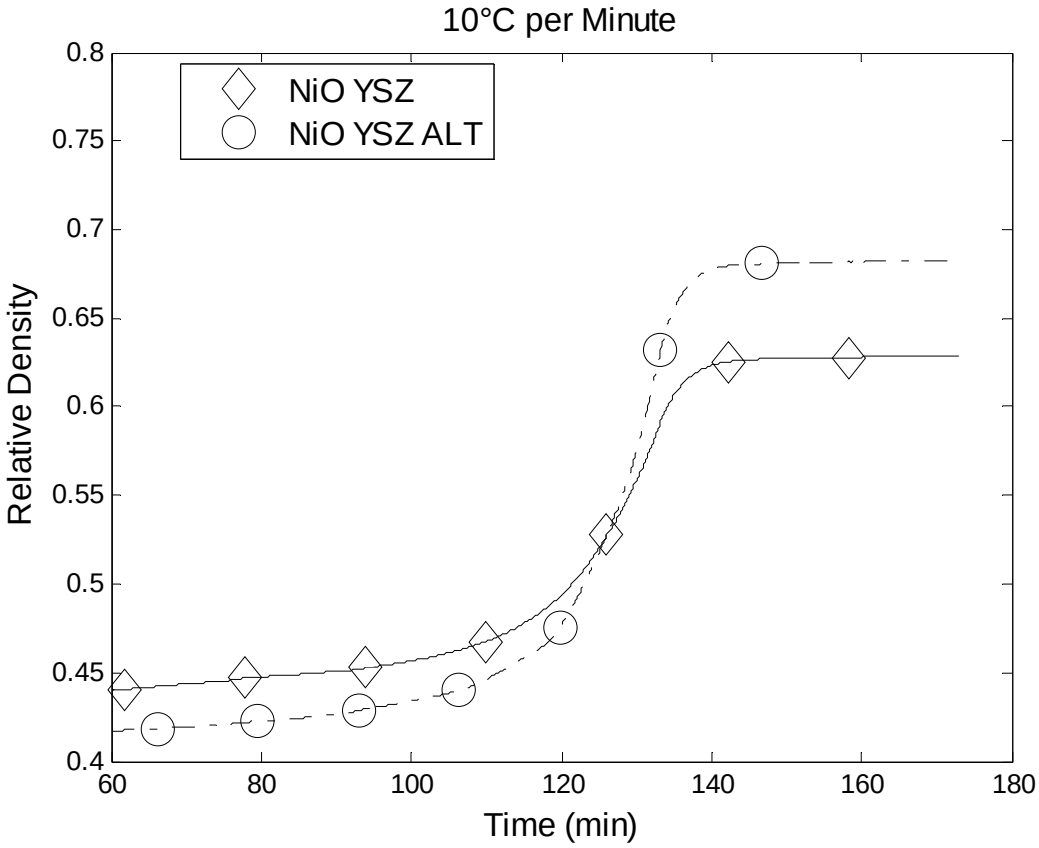
The influence of ALT as a sintering aid was evaluated by dilatometry to provide a path to processing equivalent microstructures for comparative electrochemical performance and durability evaluation.

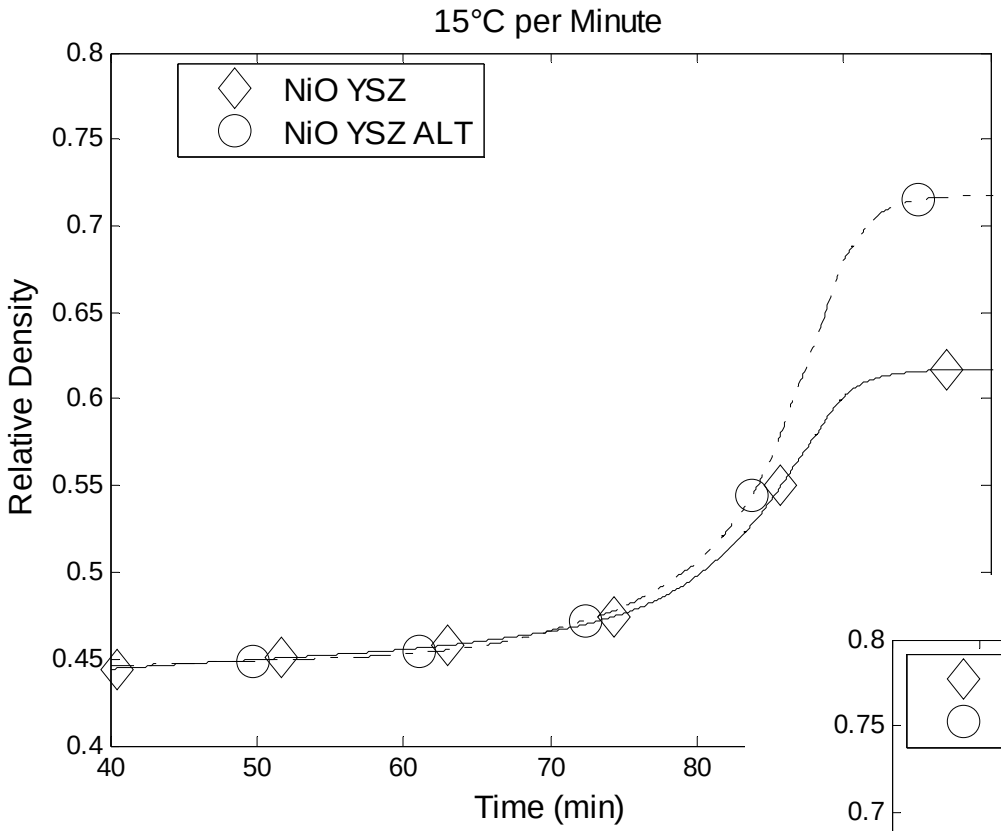
- Lower temperature sintering of ALT doped anodes
- Addition of pore former to ALT doped anodes

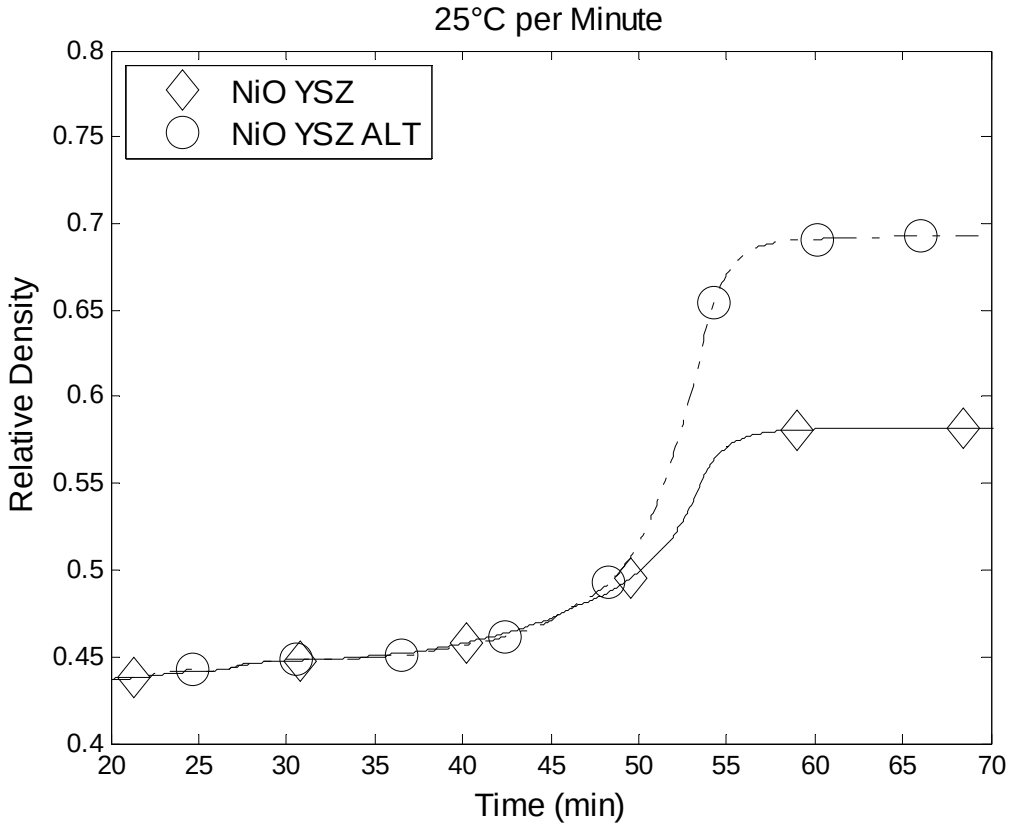
The effect of ALT as a sintering aid for processing has an important impact in SOFC fabrication as secondary phases traditionally hinder electrochemical performance.

Dilatometry was performed at various heating rates from 5 – 25 degrees C per minute up to 1400°C to establish the rate of anode densification. Samples consisted of ¼" diameter uniaxially pressed NiO (350 nm)/8YSZ + 5 wt% ALT

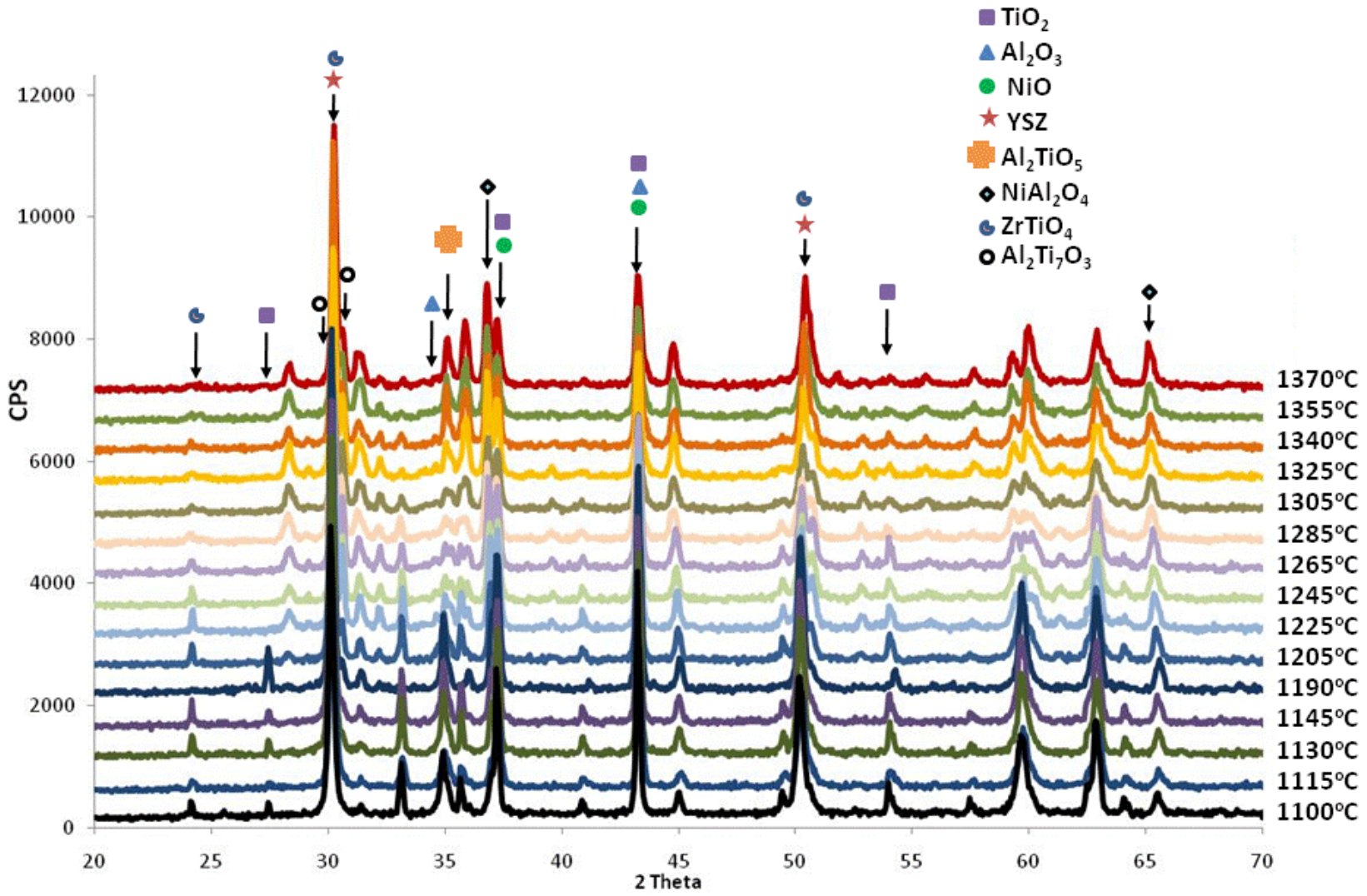

5°C per Minute
NiO YSZ
NiO YSZ ALT
Relative Density
Time (min)
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
140
160
180
200
220
240


10°C per Minute
NiO YSZ
NiO YSZ ALT
Relative Density
Time (min)
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
60
80
100
120
140
160
180


15°C per Minute
NiO YSZ
NiO YSZ ALT
Relative Density
Time (min)
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
40
50
60
70
80


25°C per Minute
NiO YSZ
NiO YSZ ALT
Relative Density
Time (min)
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
20
25
30
35
40
45
50
55
60
65
70

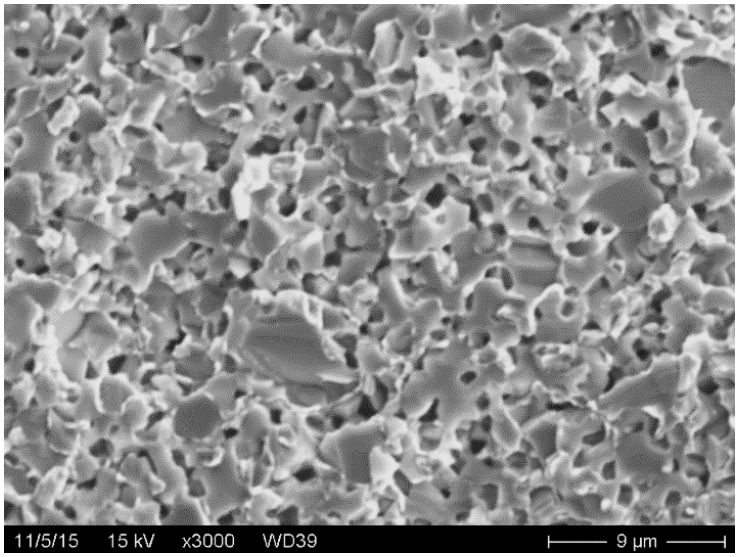
XRD Analysis of Phase Formation in NiO/8YSZ/TiO_2/Al_2O_3 System

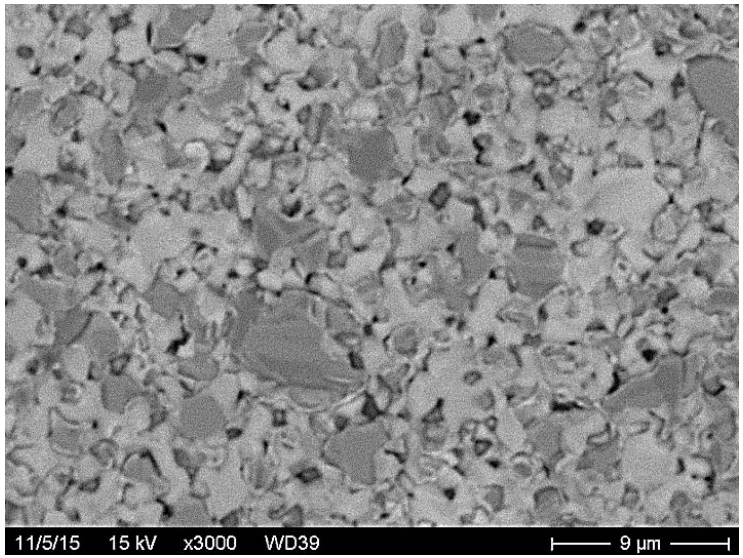


NiO/8YSZ Microstructure – 1400°C, 5 hrs

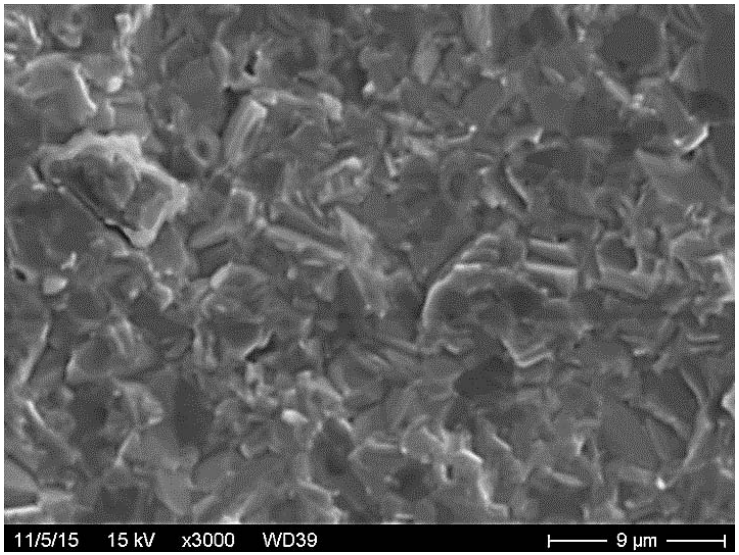
Zr – dark, Ni - light

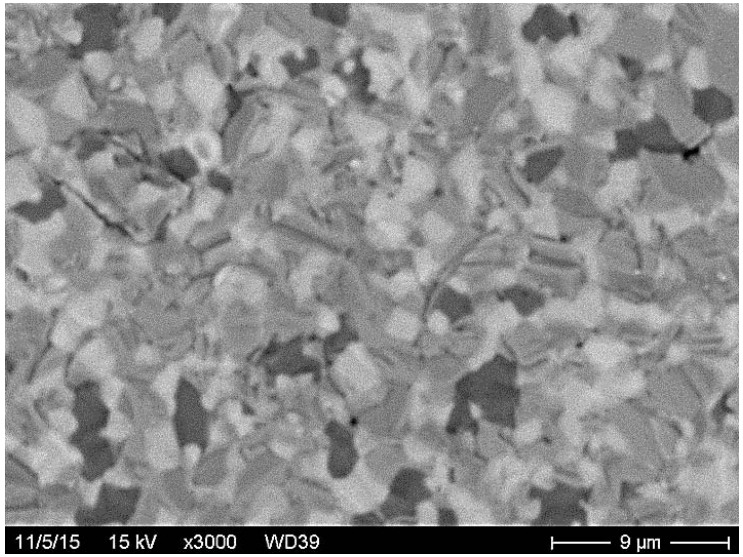
baseline





5wt% ALT (added mechanically)





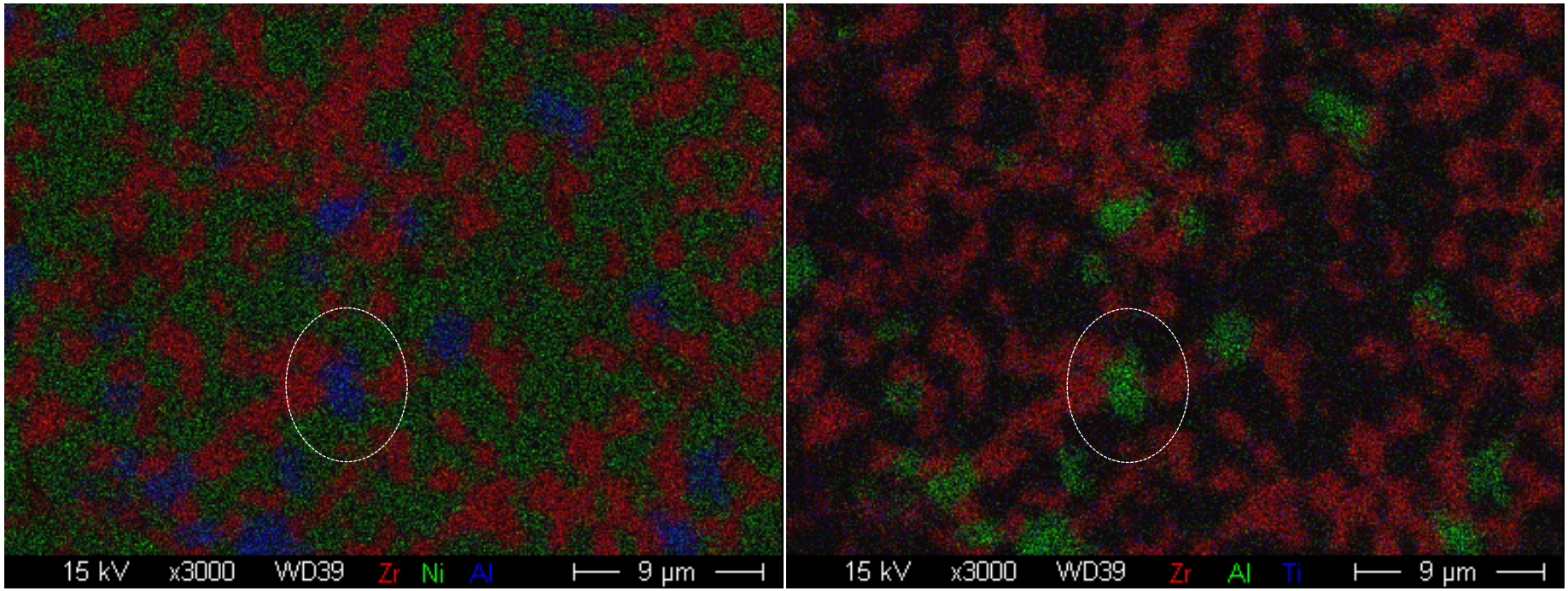
SEI (secondary electron)

BEI (backscatter electron)

NiO/8YSZ Elemental Mapping (EDS)

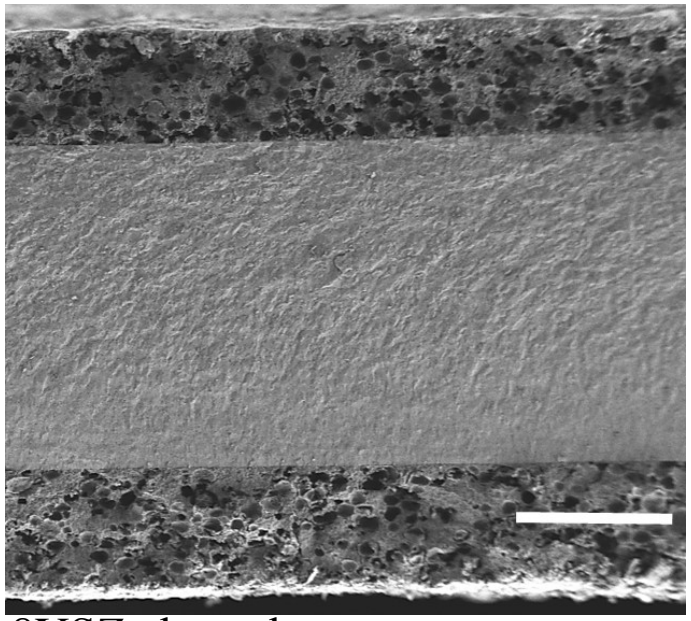
Mechanically mixed ALT – 5 wt%

- Good Ti uniformity
- Some Al clustering, however some Al may also come from Al2O3 furnace setters
- Improved Ti/Al homogeneity from ALT solution infiltration?

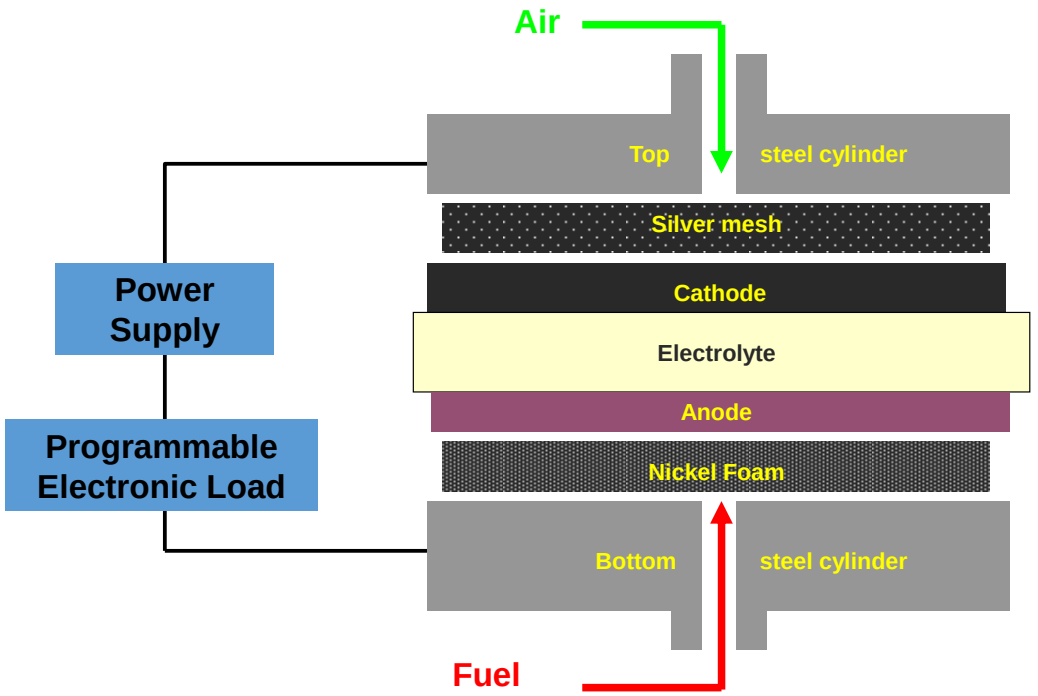


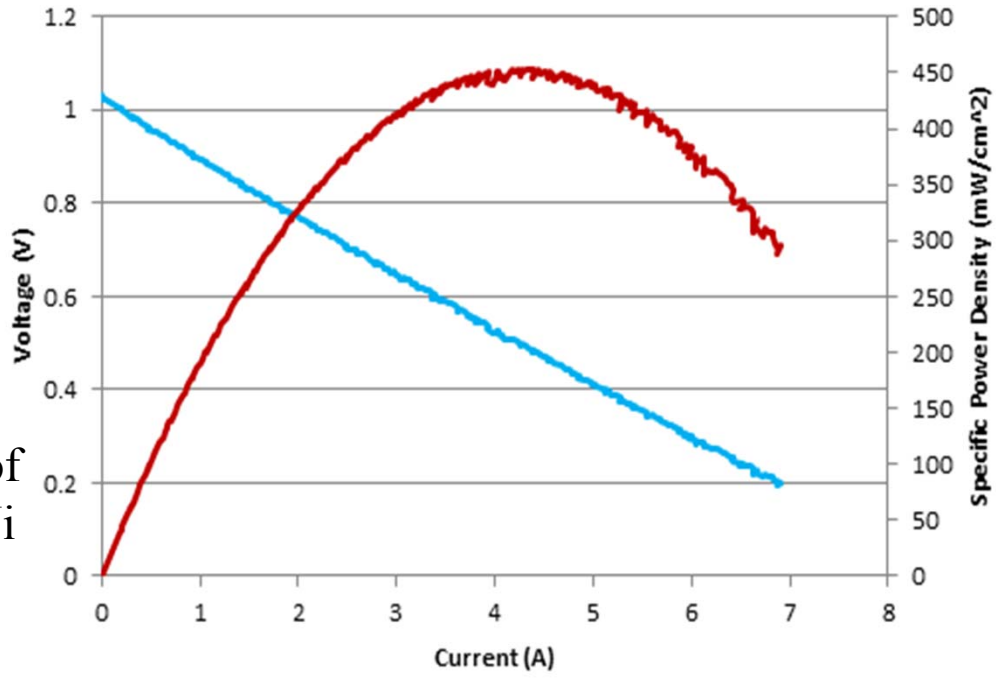
***Anode densification with ALT and XRD data indicate 1300-1400°C anchoring treatment temperature.**

Cell testing:



8YSZ electrolyte supported SOFC, bar = 100 µm





VI scan for initial operating point of infiltration based cell ~20-80 nm Ni with 32mm 8YSZ supports

MSU test stand features – Rig 1





- Seal-less design
- Up to 3” ESC or ASC cells
- 8%YSZ electrolyte supported cells
- Tests conducted at:
  - 750 - 850°C
  - Constant current/constant voltage testing
  - Voltammetry
  - EIS (equipment acquired for this project is being integrated with existing apparatus)

Electrochemical testing

- Independent control of:
  - N_2 flow
  - H_2 flow
  - Air flow
  - Temperature
  - Voltage or current

Representative LSV/EIS (Nyquist or Bode plot)?

- **Task 2.1.1, 2.1.2, and 2.1.3 (Current – June 2016)**

SOFC Fabrication,Testing, and Analysis

-Optimize anode sintering temperature and anchor activation temperature in NiO/YSZ cermet anode on ESC.

-Fabricate comparative cermet microstructures given the sintering aid effect of ALT

-Identify anchoring phase formation in solution vs. mechanically mixed ALT

-Compare SOFC performance with 1, 5, and 10 wt% ALT added by mechanical mixing

-Compare distribution of anchoring phases with solution infiltrated ALT

-Compare electrochemical performance of infiltrated ALT

-Analyze Ni/YSZ microstructure as a function of operational time and performance degradation.

Correlating Material Changes with Performance *in operando* (Walker)

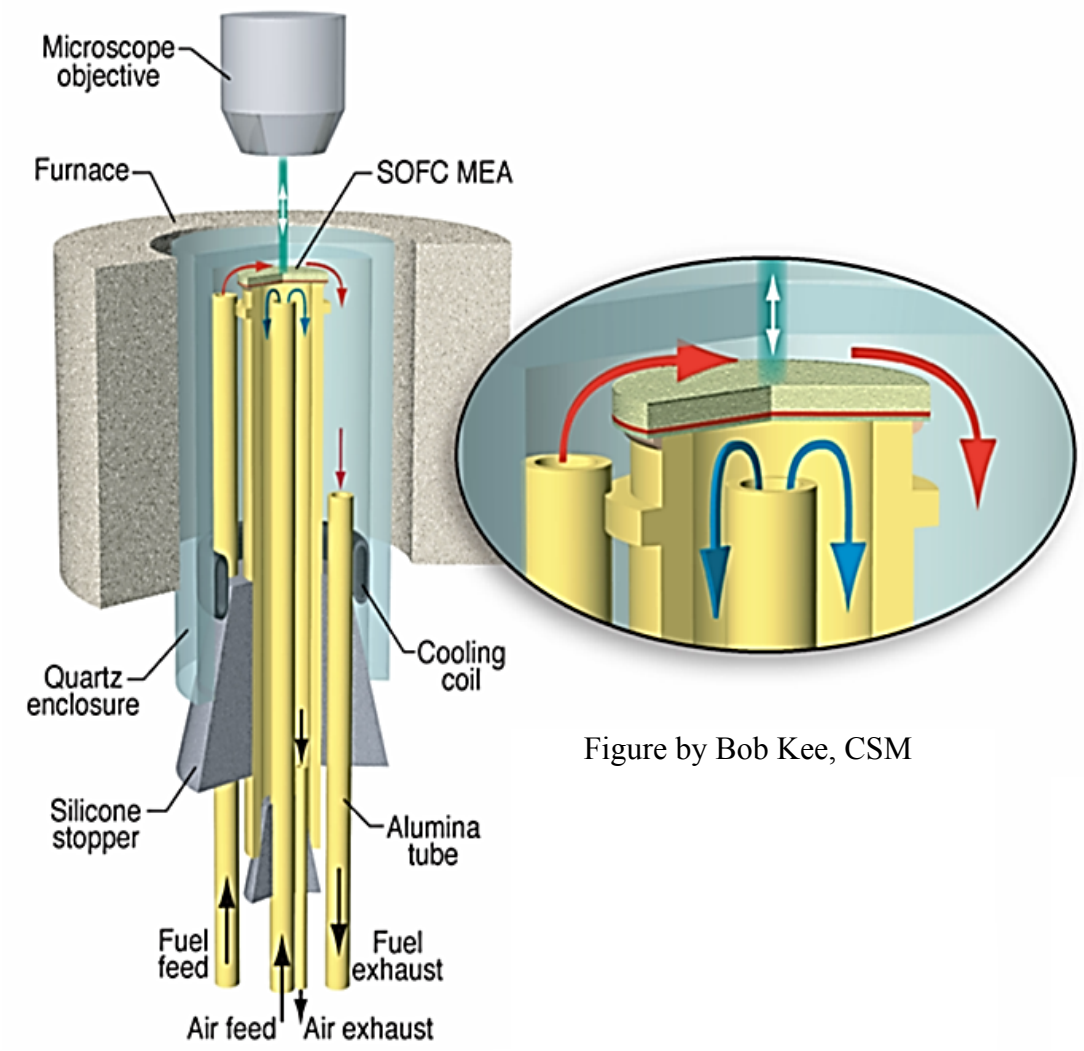
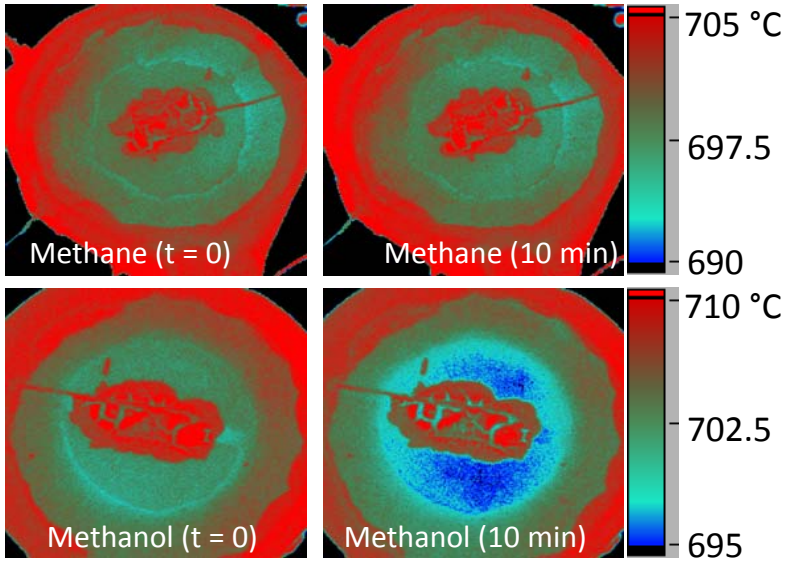
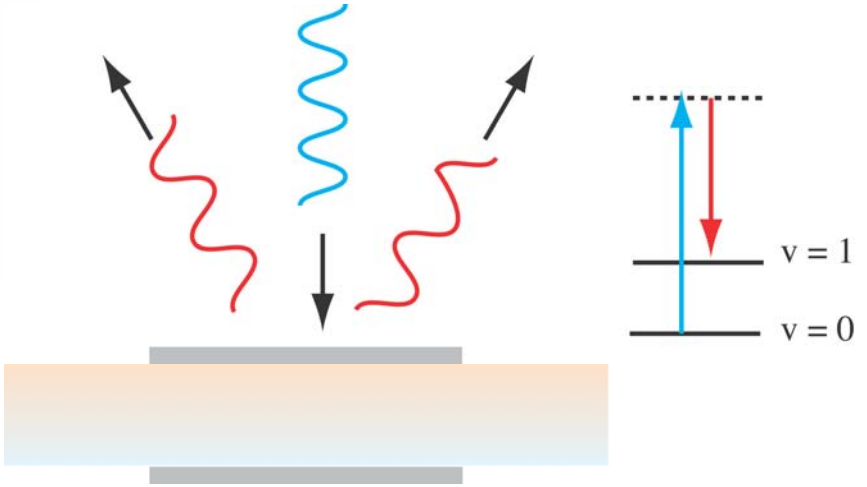


Figure by Bob Kee, CSM



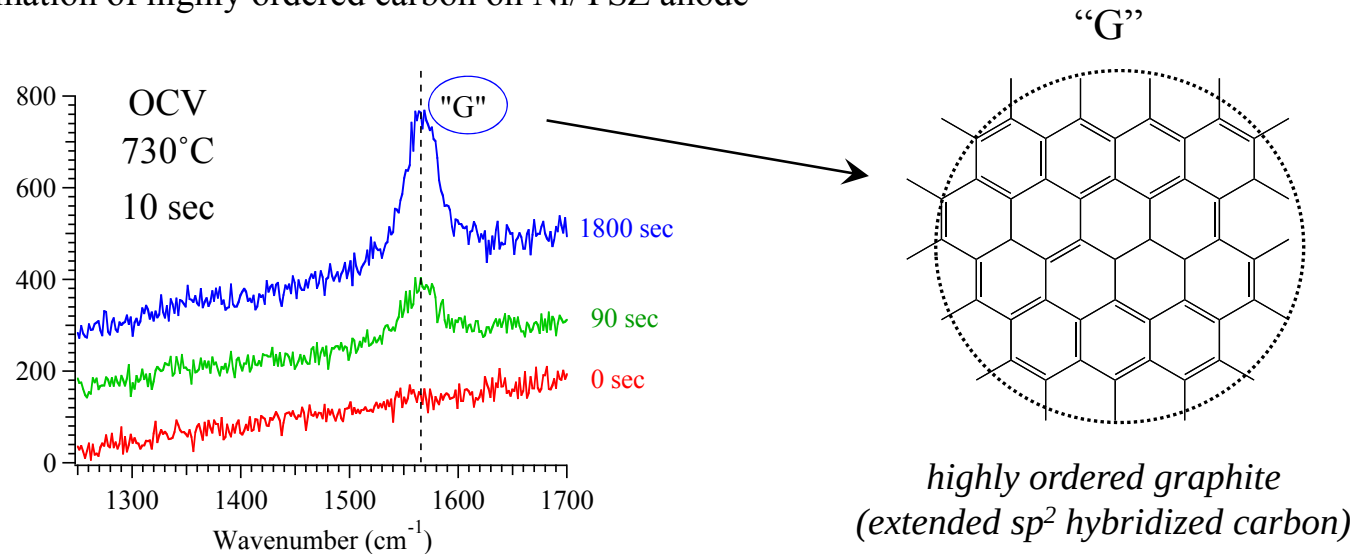


- ~2 μm spatial resolution
- 2-10 sec. temporal resolution
- materials specific assignments
- up to 850˚C

Vibrational Raman Scattering – Observables

1. **Can a response be observed?**
2. **Is the response strong or weak?**
3. How do optical measurements correlate with electrochemical condition?
4. Does the response change with time and/or conditions?

Formation of highly ordered carbon on Ni/YSZ anode

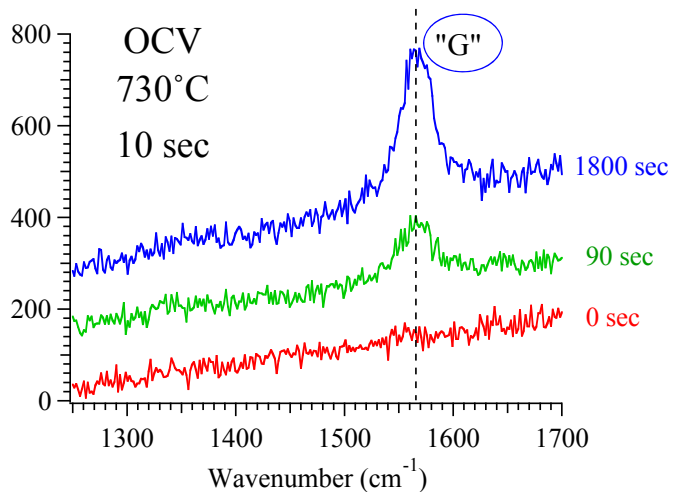


With strong scattering response, temporal resolution is ~2-5 sec; spatial resolution is ~1-2 μm

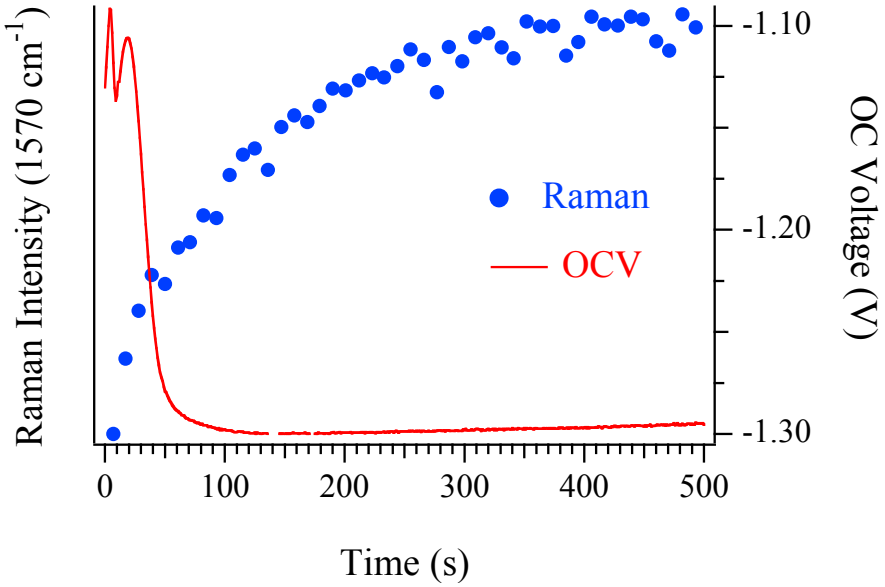
Vibrational Raman Scattering – Observables

1. Can a response be observed?
2. Is the response strong or weak?
3. **How do optical measurements correlate with electrochemical condition?**
4. Does the response change with time and/or conditions?

Formation of highly ordered carbon on Ni/YSZ anode



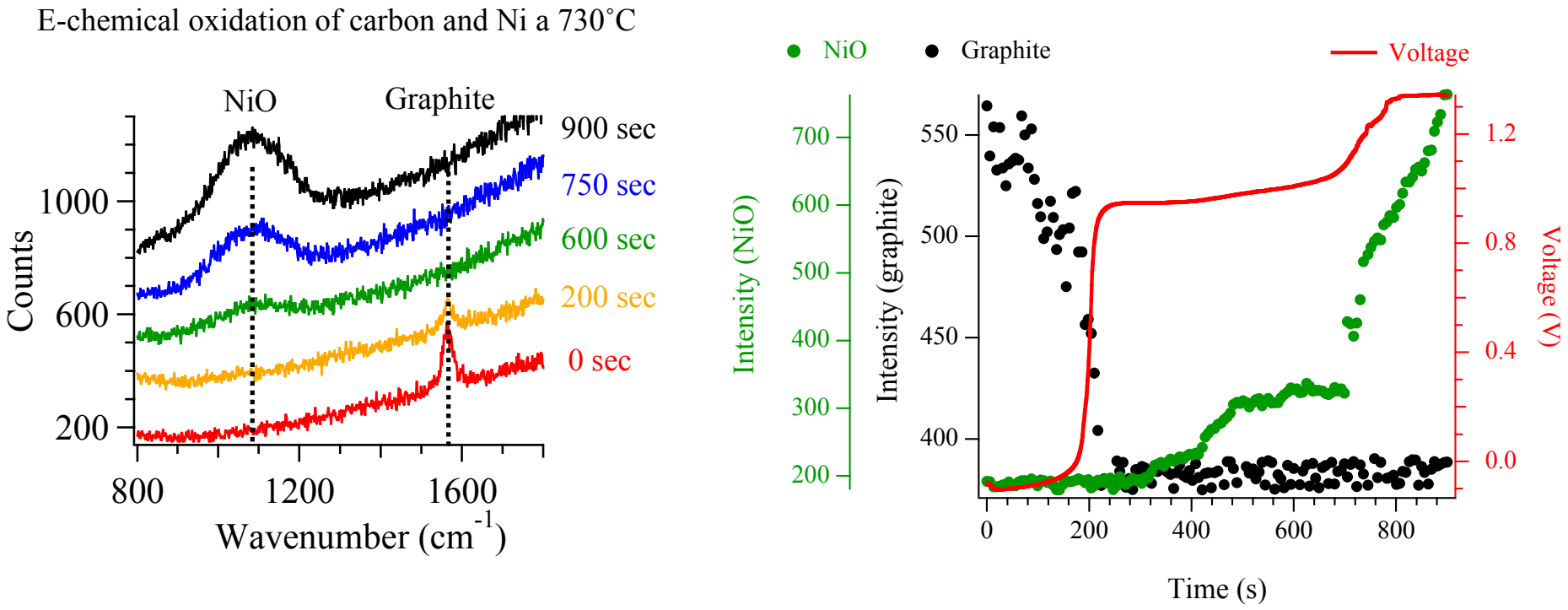
Coking and OCV



With strong scattering response, temporal resolution is ~2-5 sec; spatial resolution is ~1-2 μm

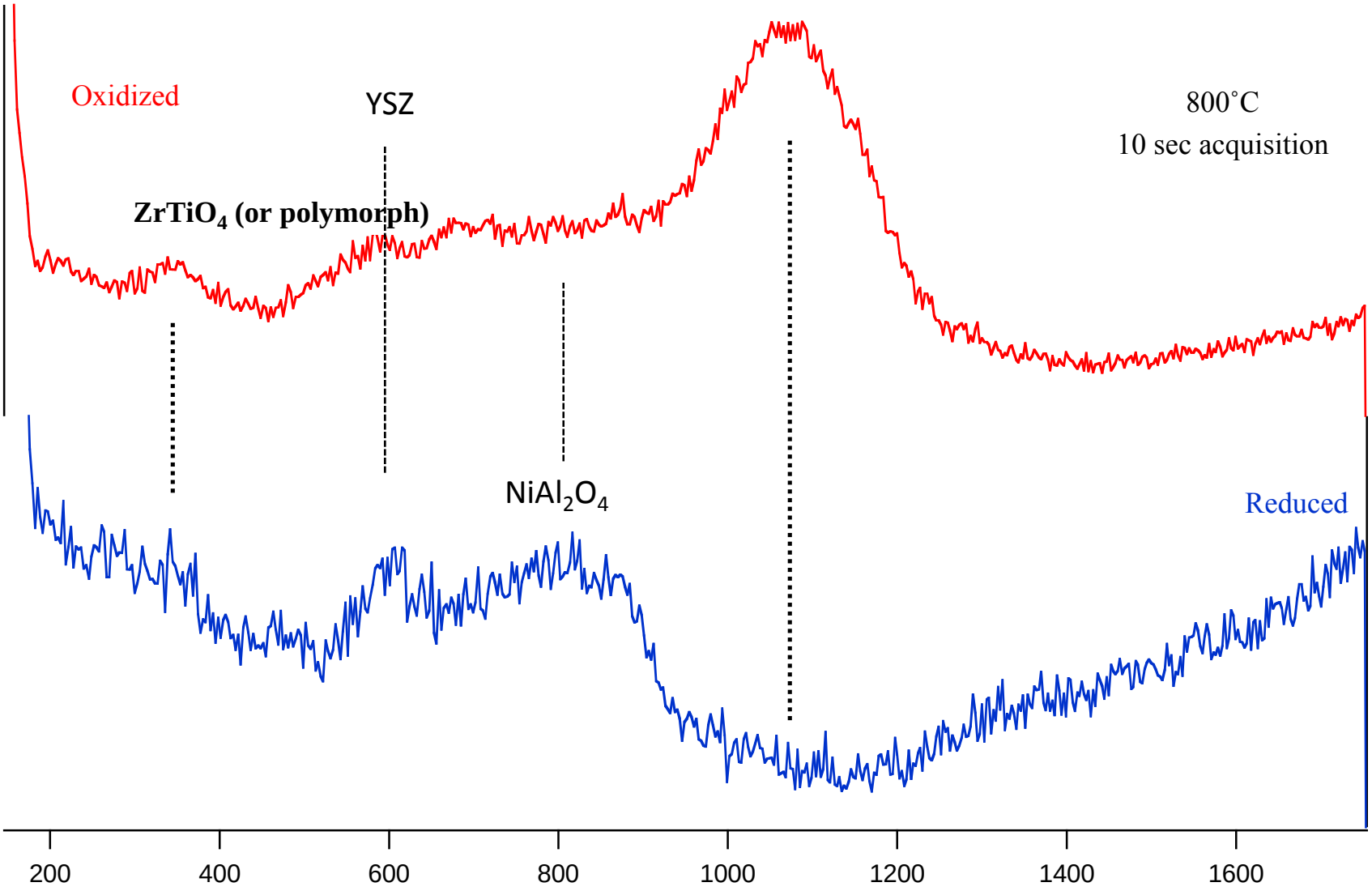
Vibrational Raman Scattering – Observables

1. Can a response be observed?
2. Is the response strong or weak?
3. How do optical measurements correlate with electrochemical condition?
4. **Does the response change with time and/or conditions?**

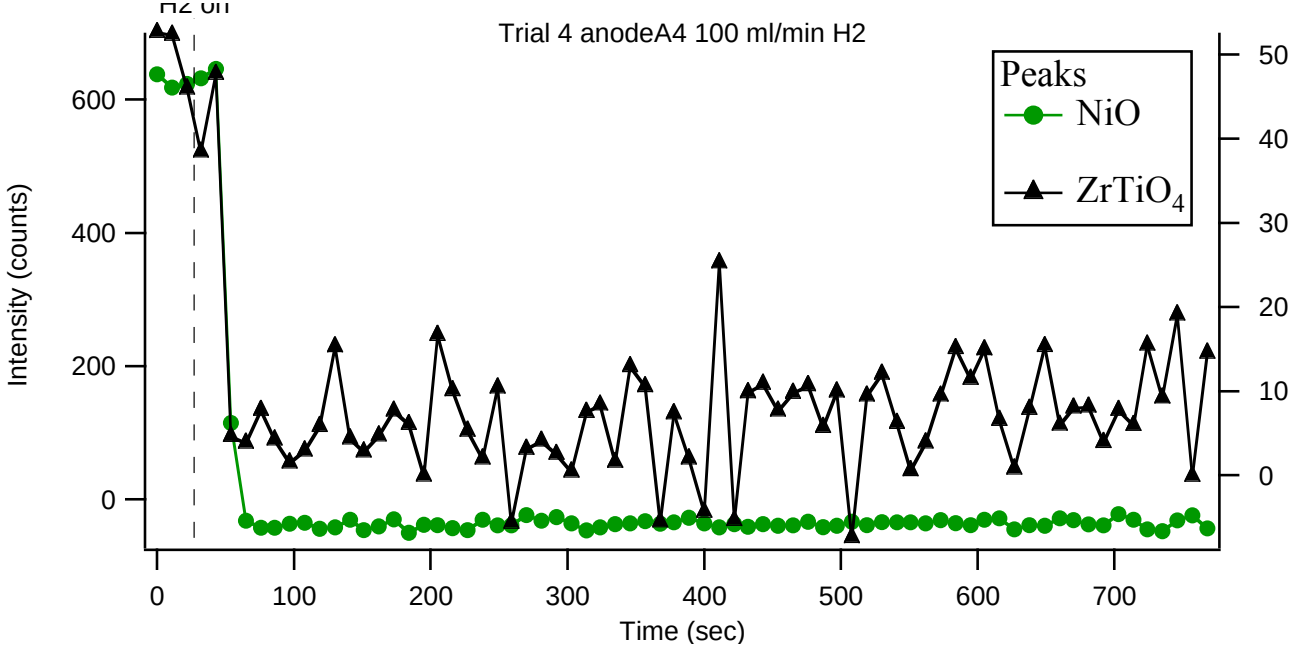


Operating at costant current leads to sequential changes in spectra that correlate with cell voltage

Vibrational Raman scattering – Chip studies of infiltrated anodes



Vibrational Raman scattering – Chip studies of infiltrated anodes



- **Task 23.1 and 2.3.3 (Current – June 2016)**

Vibrational Raman Spectroscopy

-Identify and quantify signatures from 2˚ phases
-Determine response of 2˚ phases to oxidizing/reducing conditions
-Characterize material heterogeneity across anode surface
-Resolve whether or not material changes are reversible
-Correlate material changes with polarization conditions

Near Infrared (NIR) thermal imaging

-Construct thermal imaging assembly
-Calibrate thermal imaging assembly in functioning devices
-Optmize NIR performance re: thermal and spatial resolution