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

DE-FE0031125
Program Officer: Joe Stoffa

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Department of Chemistry and Biochemistry

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Department of Mechanical and Industrial Engineering

2˚ Phase Formation in Ni-based SOFC Anodes

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

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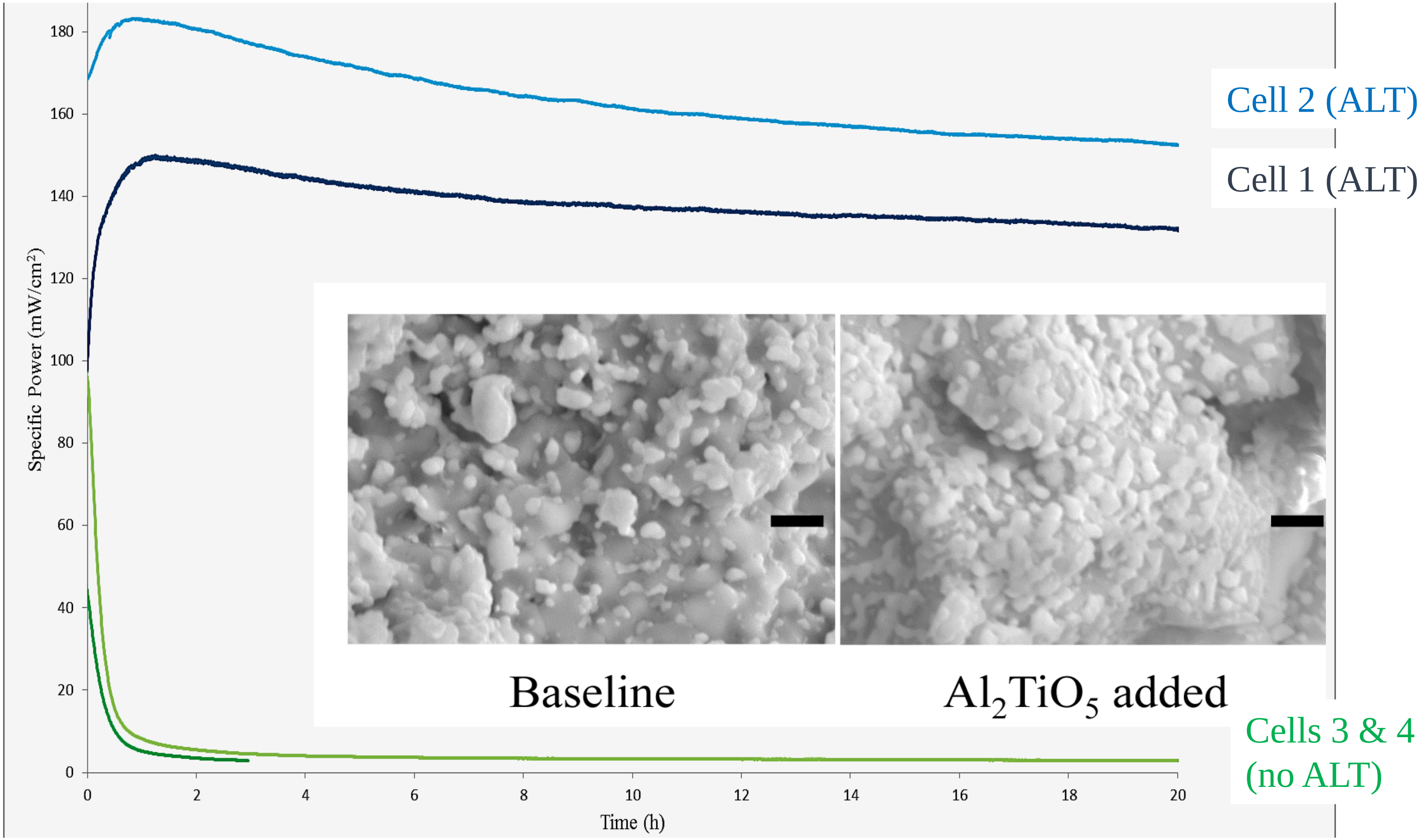

Infiltrated, electrolyte supported MEA's (low Ni loadings, ~20%)

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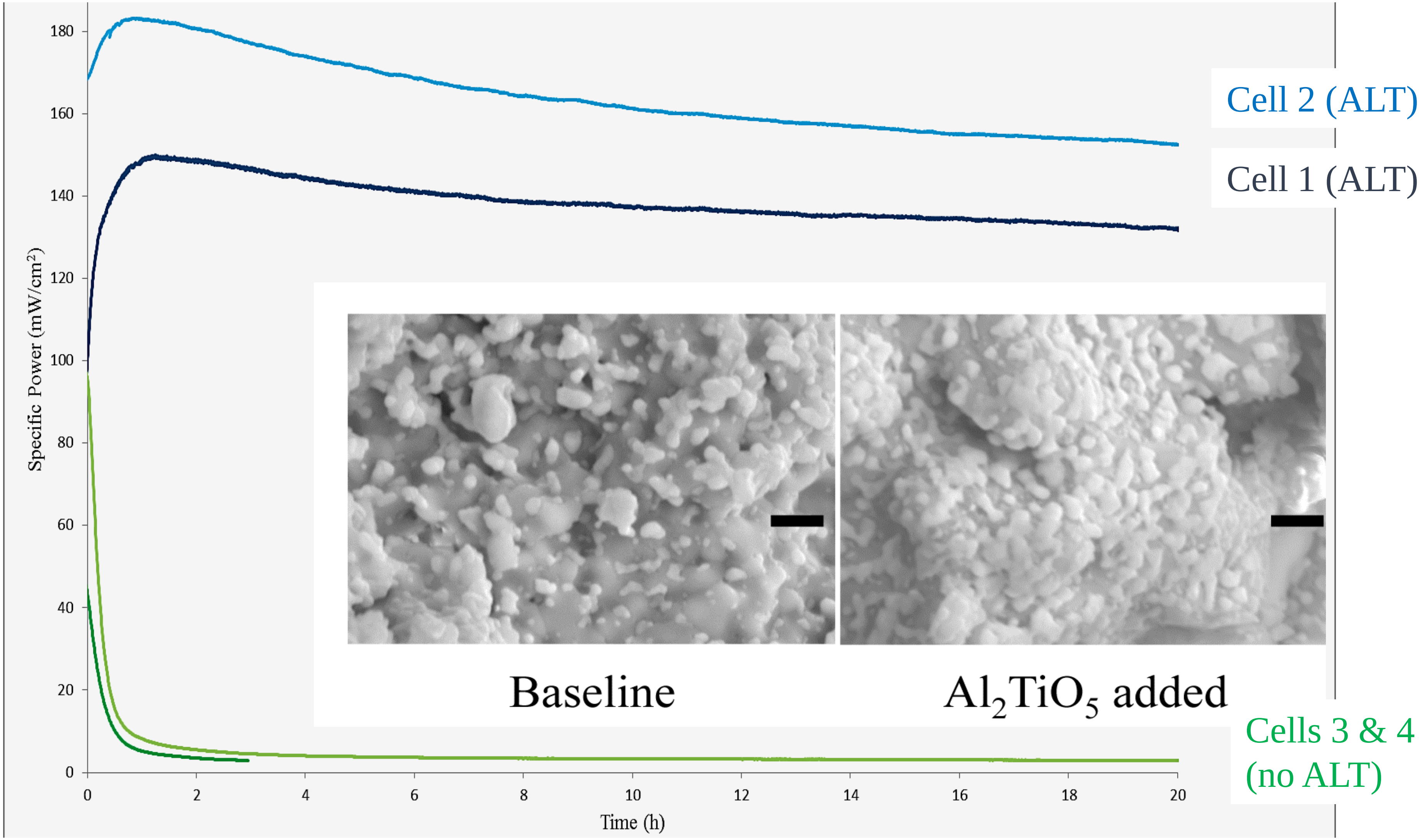


Adapted from C. H. Law and S. S. Sofie *J. Electrochem. Soc.* **158** (2011) B1137)

2° Phase Formation in Ni-based SOFC Anodes

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

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

2° Phase Formation in Ni-based SOFC Anodes

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

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

1. *Mechanical strengthening*
2. *Reduced Ni coarsening*
3. *Improved performance (with H_2)*
4. *Thermal expansion matching*
5. *Sintering aid*
6. *Improved carbon tolerance*

Prior DOE Support: DE-FE0026192 (Phase 1)

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

- 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.

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)

Project Objectives

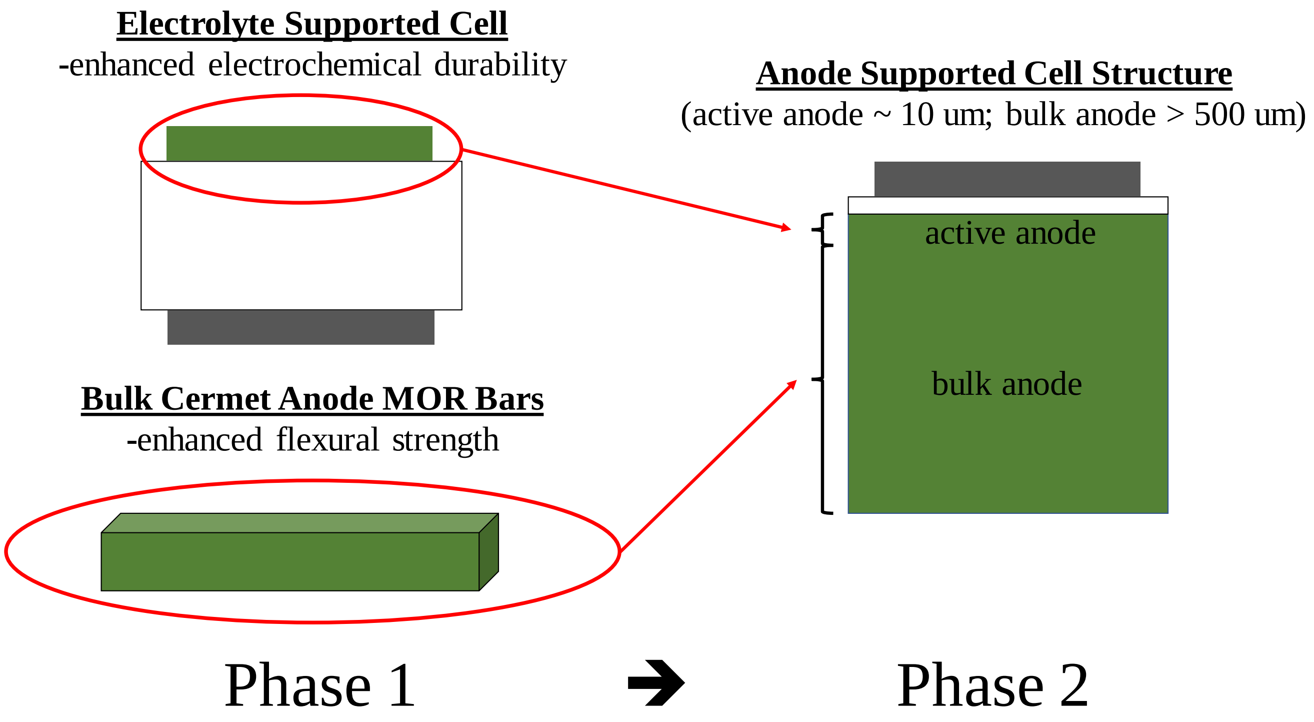
Findings are promising but not well positioned for commercial development.

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

- Refining methods used to fabricate ALT enhanced anodes into bi-layer anode supports to achieve high power densities;
- Comparing 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;
- Testing the durability and resilience of these novel materials to electrochemical and environmental redox cycling and thermal stresses commonly encountered in functioning SOFCs;
- Working closely with SOFC manufacturer(s) to transfer knowledge learned in our laboratories into full sized cell fabrication and testing

Project Objectives

- Refining methods used to fabricate ALT enhanced anodes into bi-layer anode supports to achieve high power densities

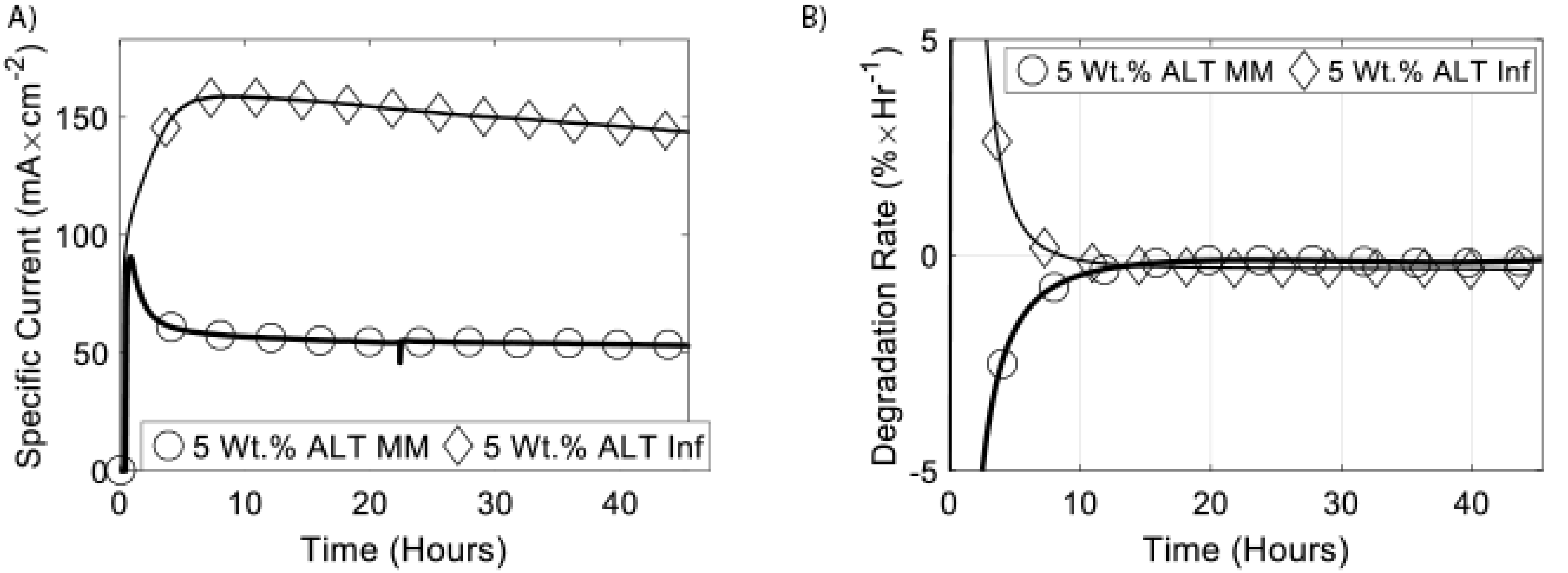


Testing new architectures to improve mechanical strength, current densities and conversion efficiencies

(Sofie & Amendola)

Project Objectives

- Comparing 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



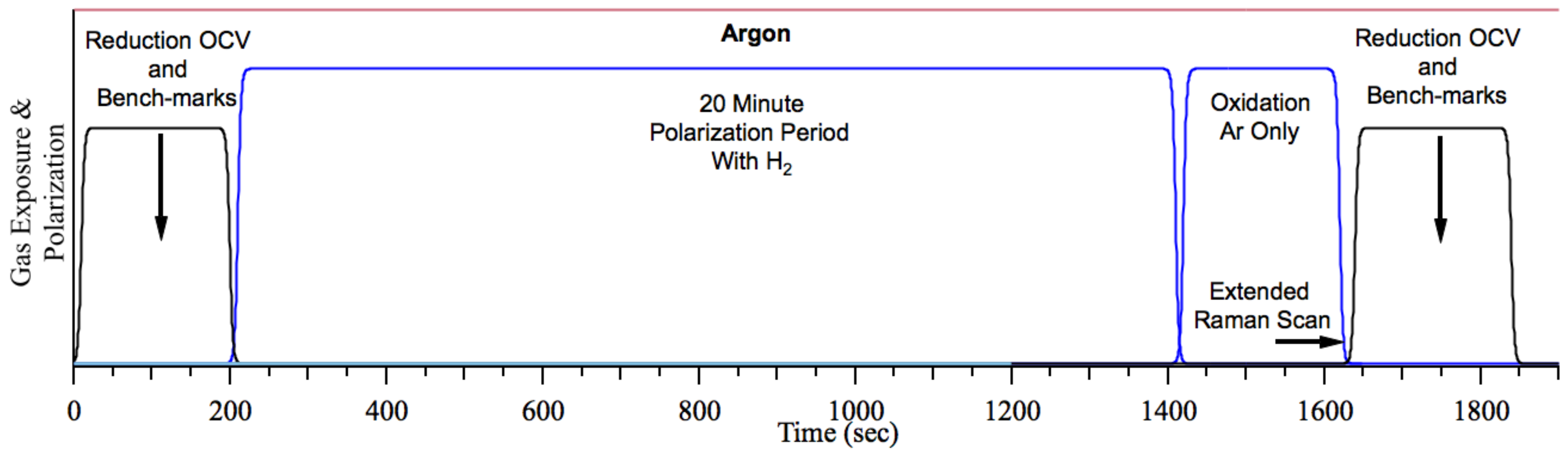
Preliminary measurements suggest that ALT infiltration improves conversion efficiencies

- Electrolyte supported (2.5 cm diam; 300 μm thick)
- 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

(Sofie & Walker)

Project Objectives

- Testing the resilience of these novel materials to electrochemical and environmental redox cycling and thermal stresses commonly encountered in functioning SOFCs



Cycle ALT-enhanced and ALT-free anodes through repeated episodes of electrochemically-induced and atmospheric oxidative stress to test how 2˚ phase formation affects anode resilience

(Walker and Sofie)

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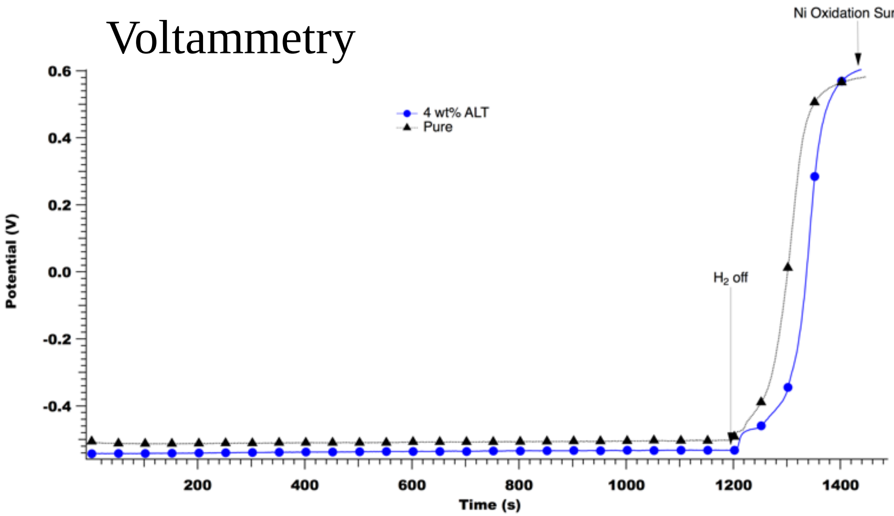
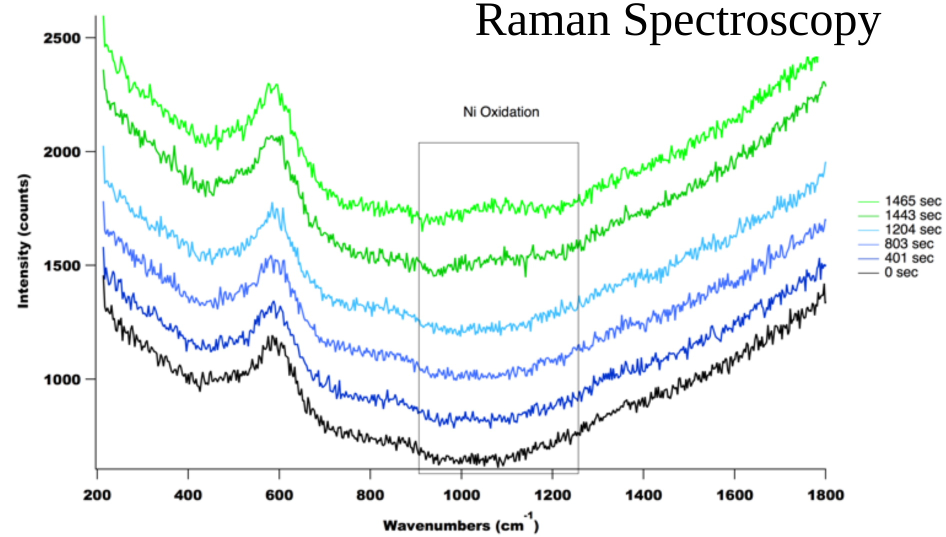
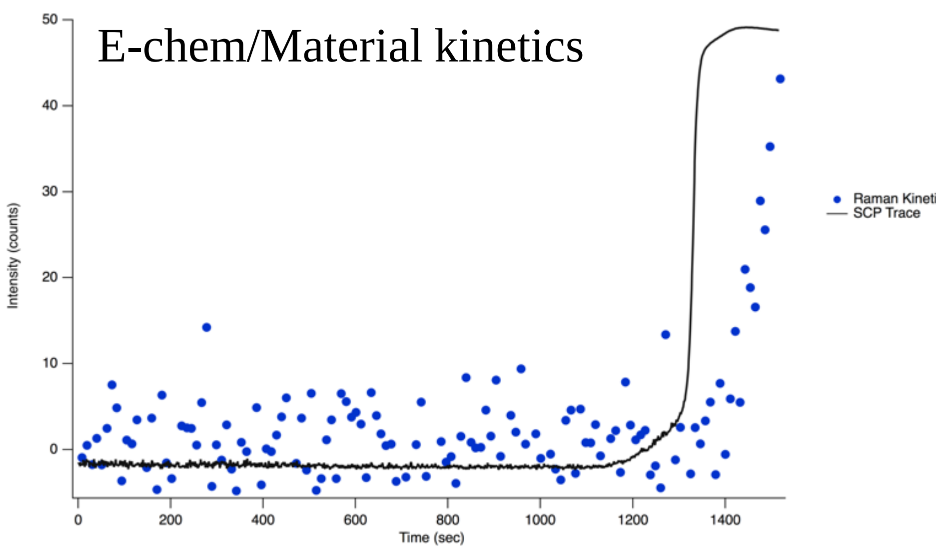
Voltammetry



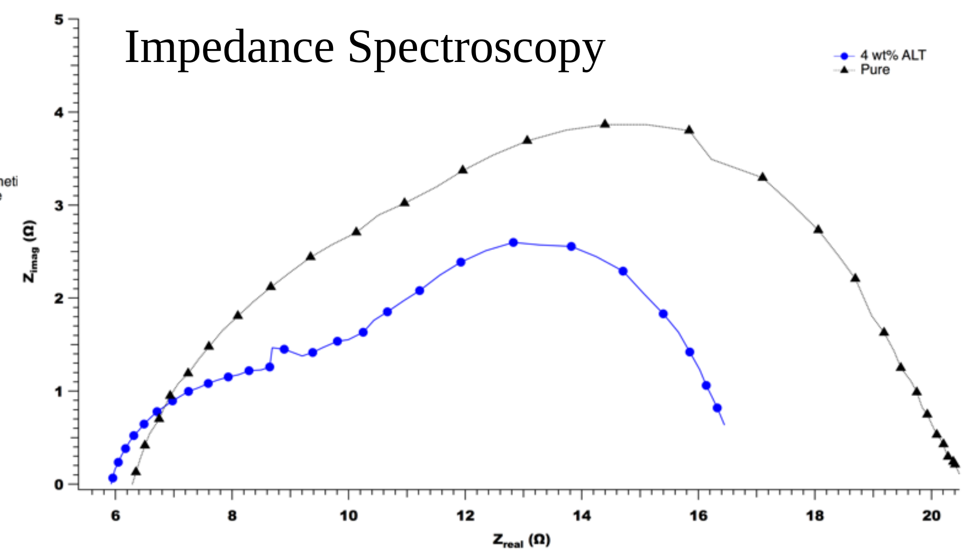
Raman Spectroscopy



E-chem/Material kinetics



Impedance Spectroscopy



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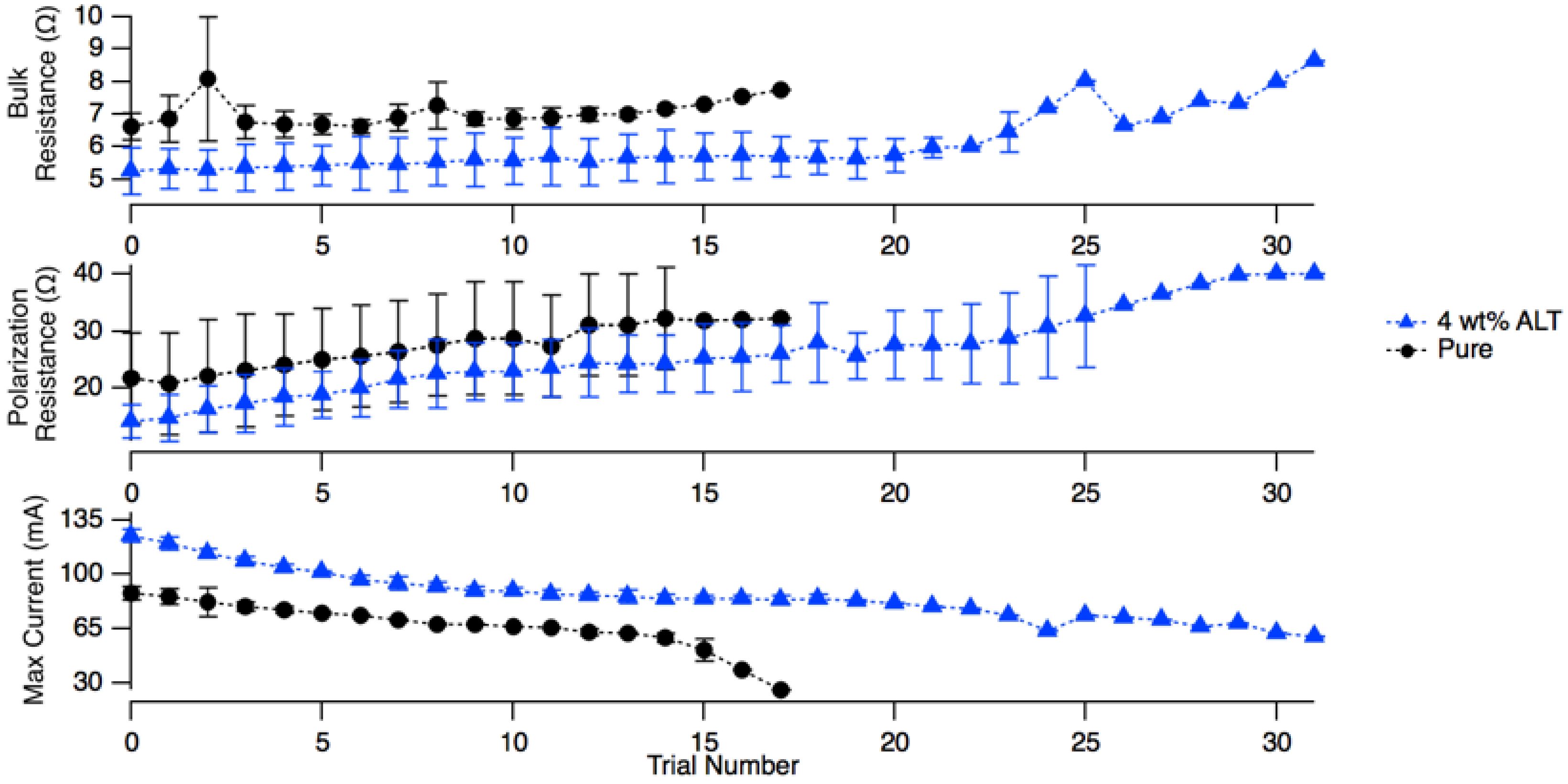


ALT doped anodes appear to be twice as resilient as undoped anodes

So where are we?

TRL	Definition	Description
3	Analytical and experimental critical function and/or characteristic proof-of-concept validated	Proof-of-Concept Validated. Performance requirements that can be tested in the laboratory environment have been analytically and physically validated. The core technology should not fundamentally change beyond this point. Performance attributes have been updated and initial performance requirements have been established.
4	Basic technology components integrated and validated in a laboratory environment	Technology Validated in a Laboratory Environment. The basic technology components have been integrated to the extent practical (a relatively low-fidelity integration) to establish that key pieces will work together, and validated in a laboratory environment. Performance attributes and requirements have been updated.

- Proof of concept validated and core technology will not change
- Initial performance requirements have been established (V-I, impedance, resilience)
- Anodes have been integrated into low-fidelity SOFC and performance validated
- Refinement and characterization still needed

Where do we want to be in 2 years?

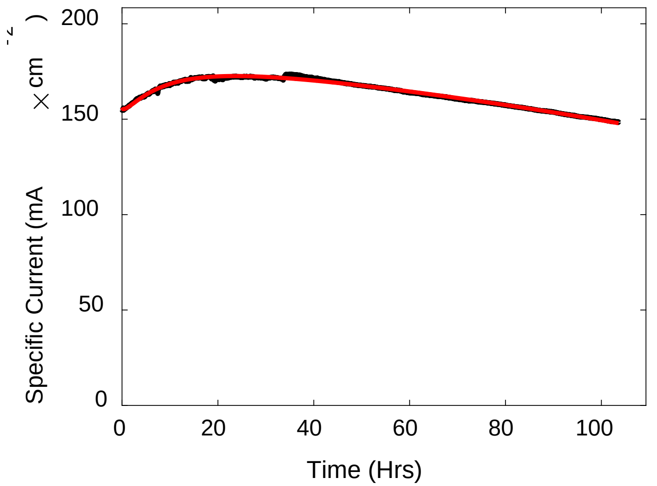
TRL	Definition	Description
5	Basic technology components integrated and validated in a relevant environment	Technology Validated in a Relevant Environment. Basic technology component configurations have been validated in a relevant environment. Component integration is similar to the final application in many respects. Data sufficient to support planning and design of the next TRL test phase have been obtained. Performance attributes and requirements have been updated.
6	Prototype validated in a relevant environment	Prototype Validated in Relevant Environment. A prototype has been validated in a relevant environment. Component integration is similar to the final application in most respects and input and output parameters resemble the target commercial application to the extent practical. Data sufficient to support planning and design of the next TRL test phase have been obtained. Performance attributes and requirements have been updated.

- Functioning cells with ALT-enhanced anodes validated in relevant environment
- Prototype validated and tested for reproducibility
- Test stack?
- Need commercial partner

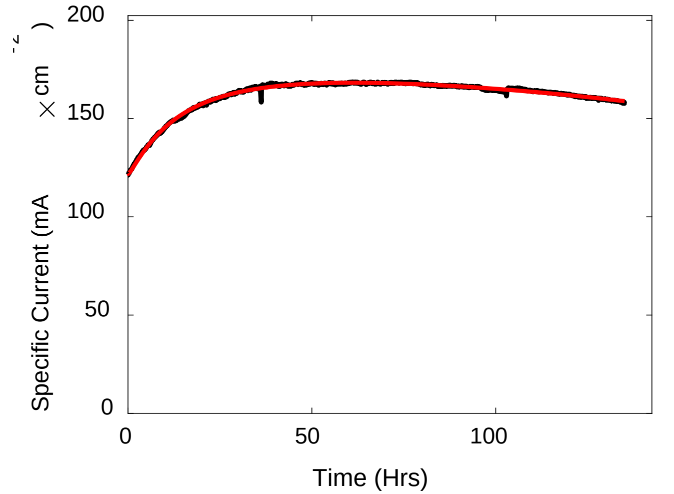
Project Objectives

- Working closely with SOFC manufacturer(s) to transfer knowledge learned in our laboratories into full sized cell fabrication and testing

Using raw anode materials from FCE (8 YSZ & 3 μm NiO)



undoped



4% ALT

Similar performance

fuelcellenergy

Dr. Ali Torabi, Fuel Cell Energy

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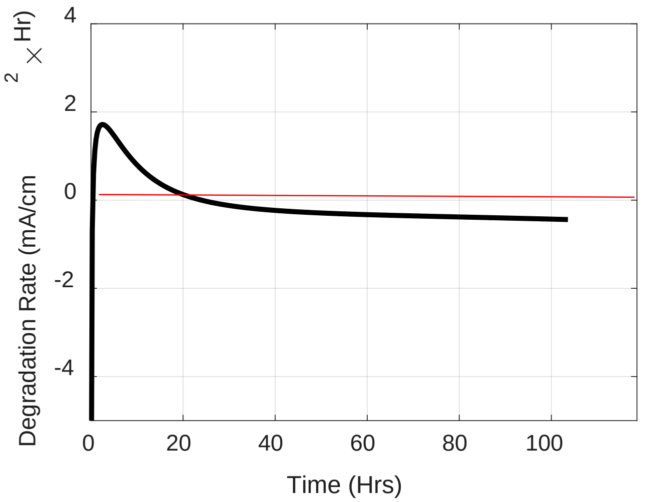
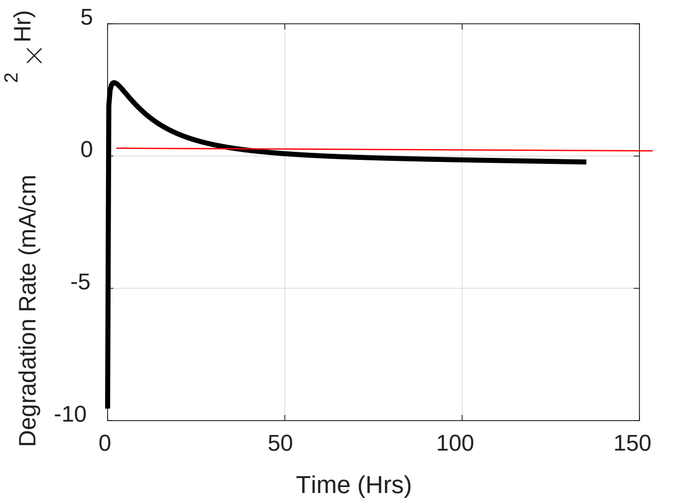


undoped



4% ALT

ALT slows degradation

fuelcellenergy

Dr. Ali Torabi, Fuel Cell Energy

Project Objectives

FuelCell Energy
Ultra-Clean, Efficient, Reliable Power

July 13, 2017

Dr. Robert A. Walker, Professor
Department of Chemistry and Biochemistry
Montana State University

Re: Fuel Cell Energy support for SOFC Core Technology Phase I proposal

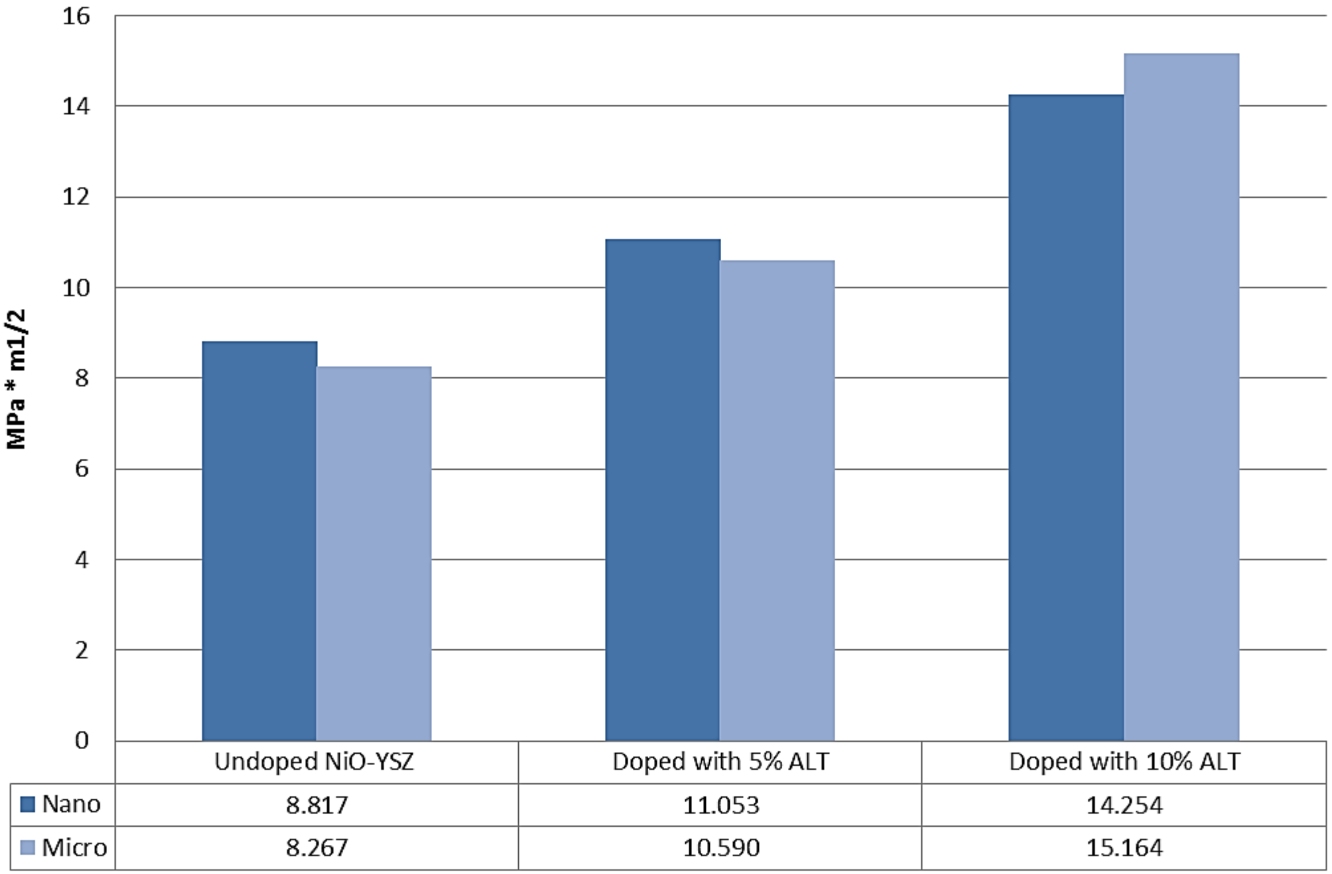
Dear Dr. Walker,

We recognize that one of the elements required for a successful proposal is for the researchers to partner with SOFC manufacturers and that projects selected under this topic area will culminate in testing of full size cells by the participating SOFC manufacturer. Our company policy does not enable us to provide academic/industrial partners with samples for method development and testing. We recommend that you use commercial cells purchased from a vendor such as Fuelcellmaterials to develop and refine your materials and method development. Once your team has zeroed in on optimal dopant loading and processing, we could provide your team with a few cells to infiltrate and return to us for testing. We would then run the cell tests here at our facility for no charge. Should the modified FCE devices deliver on their promising performance benchmarks, we will then work with your team to establish methods for scaling up material synthesis and device fabrication.

fuelcellenergy

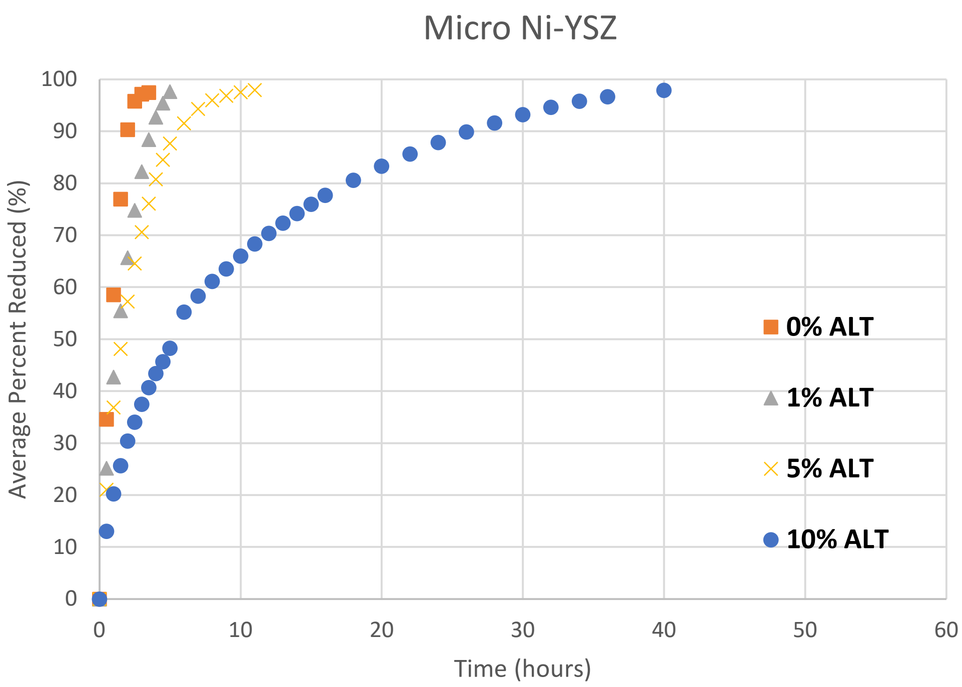
Dr. Ali Torabi, Fuel Cell Energy

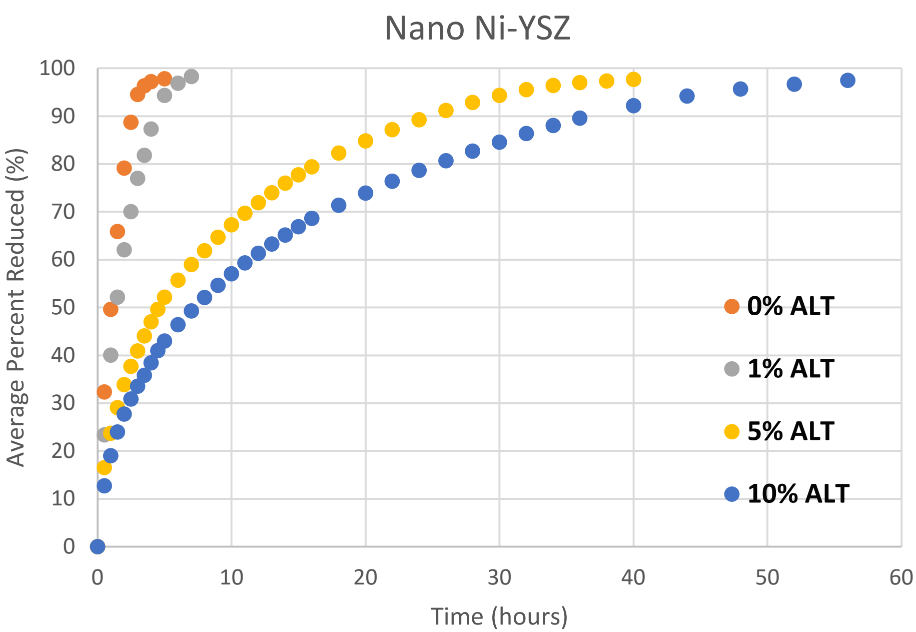
Recent findings – fracture toughness from micro-indentation



No real difference in fracture toughness between nano and micro NiO particles

Recent findings – anode conditioning





Anodes made with micron sized NiO particles reduce more quickly than those fabricated with nano-sized NiO.

(800˚C, forming gas (5% H_2))

Diffusion limitations?

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
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
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?

Timeline

E. Project Timeline

The milestones listed above can also be represented on a Gantt chart:

Task/Subtask	September '17 – August '18	September '18 – August '19
1. Project management and planning		
1.1 Project Management	RW[a]	RW
2. Optimizing anode fabrication		
2.1. Anode fabrication and testing	SS/RA	
2.2 Comparing effects of mechanically mixed vs. infiltrated ALT	SS/RA	
3. Testing anode resilience		
3.1. *Operando* Raman and electrochemical	RW	RW
3.2 Fracture testing of cycled cells	RA	RA
3.3 Thermal and electrochemical analysis	SS	SS
4. Scale up and testing by commercial partners		
4.1. Coordinate fabrication methods and specifications	RW/SS/RA	
4.2. Modify commercially supplied cells with ALT		SS/RA
4.3. Independent testing at commercial facility		RW/SS/RA
4.4. Technology transfer/IP negotiations; Follow-on		RW/SS/RA