Development of Durable Materials for cost Effective AWS Utilizing All-Ceramic Solid Oxide Electrolyzer Stack Technology

Dr. John Pietras
Saint-Gobain
5/30/2020

Project ID #P176

Project Overview

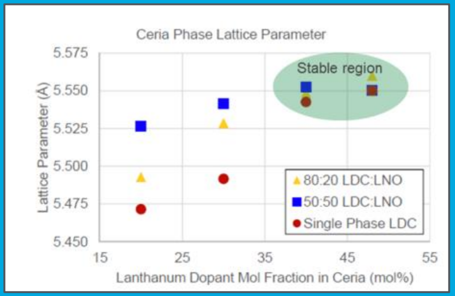
Project Partners

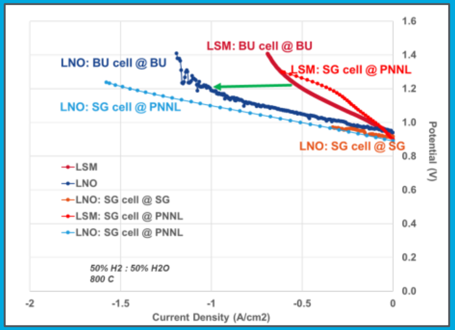
Dr. John Pietras, Saint-Gobain
Dr. Srikanth Gopalan, Boston University
Dr. Jeffry Stevenson, PNNL
Dr. Olga Marina, PNNL

Award #	EE0008377
Start/End Date	10/01/2018 – 9/31/2021
Year 1 Funding*	$0.312M
Cost Share %	20%

Project Vision

Novel chemistries of nickelate-based materials showing enhanced oxygen hyperstoichiometry are being developed to solve the issue of air electrode delamination during SOEC operation





Project Impact

The steady state degradation rate of SOEC stacks will be improved by solving the issue of electrode delamination. The materials developed will be compatible with the highly stable (0.2%/khr degradation rate) co-sintered SOFC stack architecture and result in a cost effective H_2 production platform

** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach: Summary

Project Motivation

A previous project at Boston University funded by Saint-Gobain showed that Lanthanum nickelate – GDC composites could improve SOFC performance.

A solution to the decomposition issue when LNO is in contact with GDC was developed.

This project was initiated to extend this research to SOEC performance and investigate more promising material sets

Key Impact

Metric	State of the Art	Expected Advance
ASR	*0.3-0.5 ohm cm^2*	*$\leq$0.3 ohm cm^2*
Current Density	*0.5 A/cm^2*	*$\geq$1 A/cm^2 @ 1.4V*
Degradation Rate	1-4 %/khr	$\leq$0.3 %/khr

Barriers

Phase stability/performance (Boston University)
Identification of phase stability boundaries with target electrochemical properties
Co-sintering (Saint-Gobain)
Incorporate materials within stacks ensuring porosity, activity, defect free microstructure
Accelerated testing (PNNL)
Development of a protocol which probes the dominate degradation mechanism

Partnerships

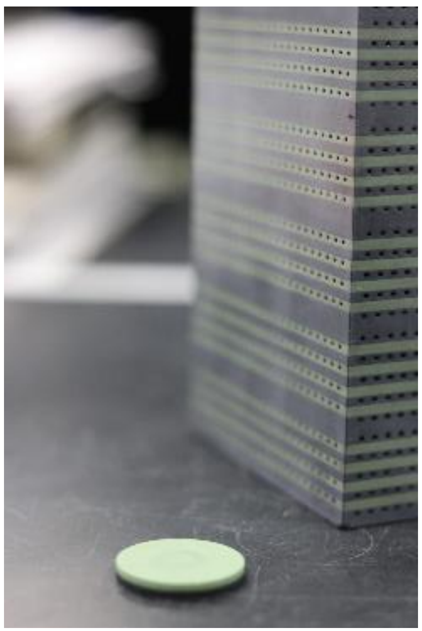
Saint Gobain (Dr. J. Pietras) provides an expertise in materials development and extensive US manufacturing footprint. Has developed an extremely stable all-ceramic, co-fired SOFC solution with a degradation rate of 0.2%/khr

Boston University (Dr. S. Gopalan) has demonstrated stable nickelate chemistries and draws on expertise in advancing the chemistry of electrochemical devices

PNNL (Dr J. Stevenson) has developed in-situ characterization capabilities to monitor cells and electrochemical interfaces along with expertise in design and interpretation of acceleration testing

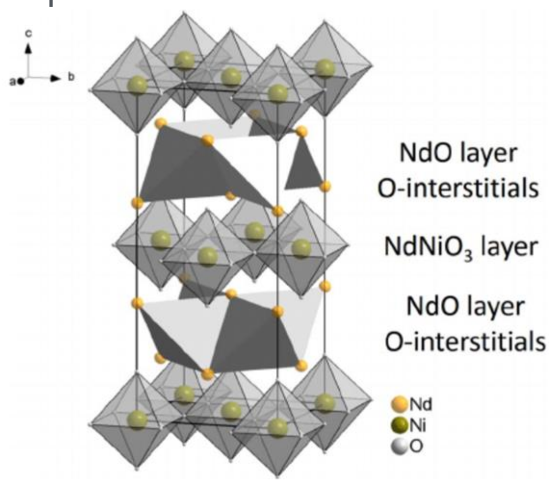
Leverage SOFC Work

- Saint-Gobain has developed a unique co-sintering process to produce SOFCs from button cells to stacks



Potential of Nickelate Family: Performance + Durability

- Rare-earth nickelates have an open alternating crystal structure and thus a large number of oxygen interstitial sites
- Oxygen exchange and transport is higher at higher oxygen pressures than in state-of-the-art perovskite oxides leading to high performance
- Voids and cracks can be avoided by incorporating oxygen in the open lattice



V.V. Kharton, et. al, J.Solid.State.Chem., 181, 1425-1433 (2008)

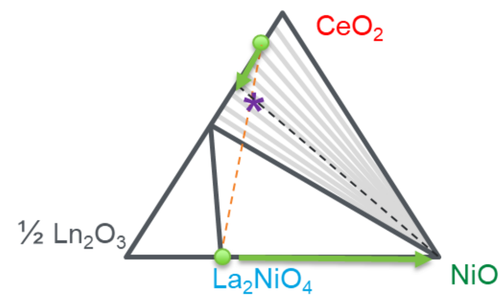
Issue to solve: Reaction with doped ceria

- Decomposition of nickelate phase when in contact with doped Ceria

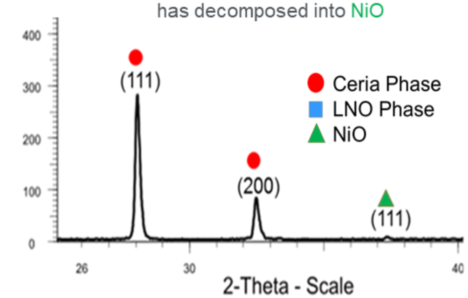
$$La_2NiO4 \rightarrow x\, LaO_{1.5} + 0.5x\, NiO$$

Resulting Ceria Phase:

$$La_xSm_{0.2}Ce_{0.8-x}O_{2-\frac{0.2+x}{2}}$$



34% LNO : 66% SDC20 Composite
post-heating – all of LNO phase has decomposed into NiO

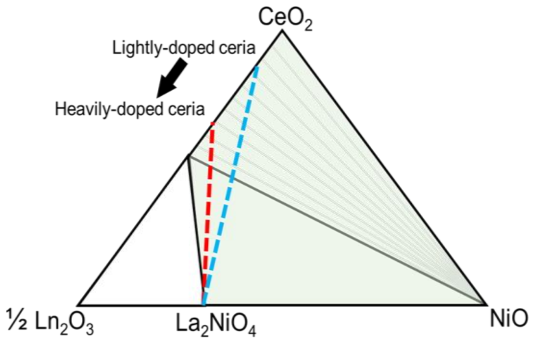


Hrovat, M, et al., Mater. Res. Bull. **33,** 1175–1183 (1998).

Approach: Innovative Solution

Strategy to Stabilize LNO Phase

- Push to highly doped Ceria compositions
- Operate on the pseudo-binary tie-line between LNO and the saturated ceria phase
- Prevent incorporation of lanthanides into the ceria structure thus preserving nickelate phase



Project Approach

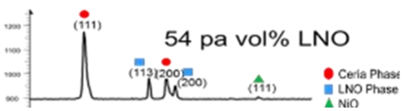
- Synthesize material compositions and utilize XRD to establish phase purity of end compounds
- Create ceria – nickelate mixtures and measure stability & performance characteristics
- Sinter button cells utilizing both conventional and co-sintering techniques, optimizing microstructure
- Electrochemically test button cells for performance and durability

	2018			2019								
Calendar Period	10	11	12	1	2	3	4	5	6	7	8	9
Project Period	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
1.Materials Development and Transport Property Measurements												
1.1 Composite powder production												
1.2 Determine oxygen hyperstoichimetry												
1.3 Measurement of composite properties												
1.4 Point defect chemistry of composites												
M1.1: Phase pure powders (stoichiometry & XRD confirmation)			M									
M1.2: Hyperstoichiometry and identify phase stability boundaries for nickelates & doped ceria								M				
M1.3: ID top 3 candidates (conductivity >96 S/cm, oxygen exchange coefficient 10^{-5} cm/s)												M
2. Degradation Analyses on Materials and Interfaces												
2.1 Preparation of test rig												
2.2 Button cell fabrication, current technology												
2.3 Button cell testing & characterization, current technology												
M2.1: Baseline button cells, He leak <$1x10^{-8}$ $mbarL^{-1}cm^{-2}$						M						
M2.2: Degradation mechanisms confirmed and accelerated testing developed											M	
Go/No-Go Decision Point (Phase I)												G1

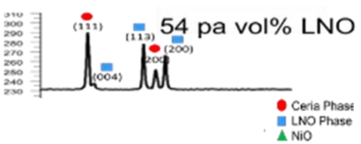
Approach: Summary of Results

Developed, produced and tested advanced electrodes with improved performance over baseline material set

Stabilization

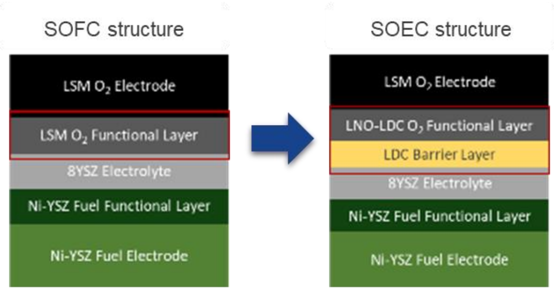


La_2NiO_4 retention

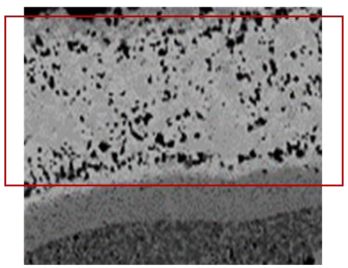


Co-Sintering

Incorporated nickleate within co-sintered cells



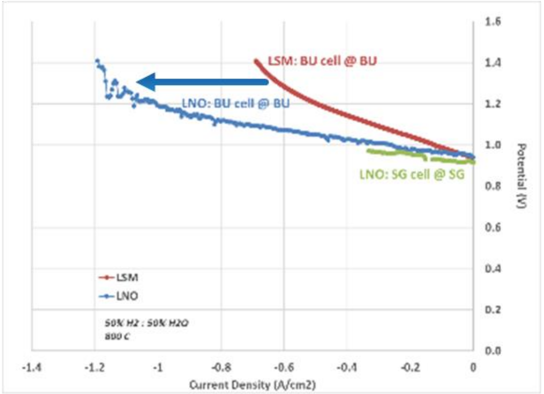
Microstructure achieved



SOEC Performance

Performance Improvement

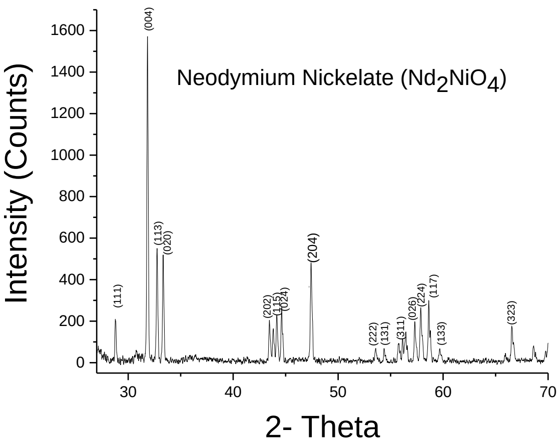
- LNO outperforms LSM electrode
- LNO Cell successfully co-sintered
- Independent of cell design (anode supported and co-sintered cells)



Relevance and Impact

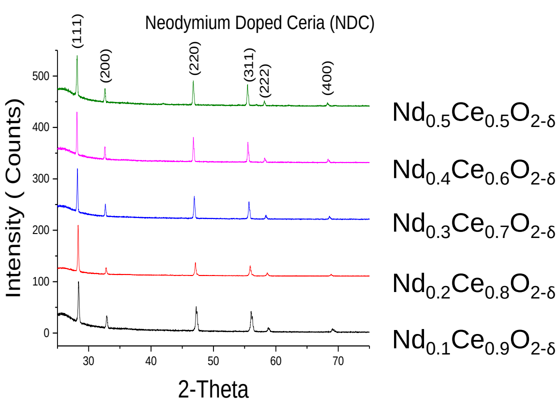
- The goal of the proposed effort is to develop a fundamental understanding of performance degradation and electrode delamination in nickelate based SOEC materials and interfaces, and to develop compositions addressing this degradation while meeting specific performance targets:
    - ASR ≤0.30 ohm-cm2
    - current density >1A/cm2 at 1.4V
    - stack electrical efficiency >95% LHV H2
    - stack lifetime ≥7 years
- High oxygen pressure at the electrolyte-electrode interface has been identified in the literature and in ongoing EERE funded projects as a major cause for degradation within SOEC. The build-up of oxygen pressure can be mitigated by incorporating materials with high oxygen hyper stoichiometries close to the electrolyte-anode interface.
- Thus this project with look to generate solutions based on previous Consortium modeling. In this way the program will push the state of the art and encourage focused discussion on the topic among the Consortium.

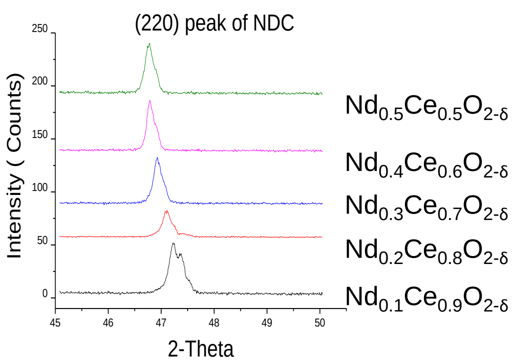
Accomplishments: Powder Synthesis

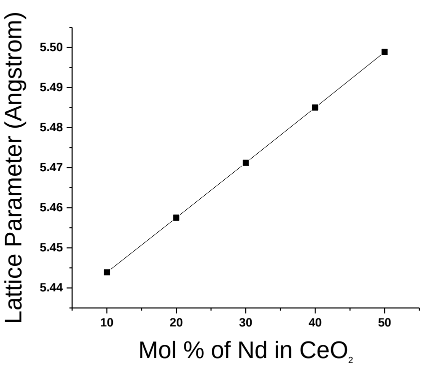


Neodymium System Example

- Synthesis of Neodymium Nickelate (Nd_2NiO_4) and Neodymium Doped Ceria (NDC) by solid state reactions
- 10-50 mol% neodymium was doped into the ceria
- XRD of the NDC powders confirms the fluorite crystal structure even in highly doped ceria
- Peak shift indicates the increase of the lattice parameter with increasing dopant concentration
- Replacement of smaller Ce^{4+} ions with the larger Nd^{3+} ions (the ionic radii of Ce^{4+} and Nd^{3+} are 0.97 and 1.1053 Å respectively) leads to the cubic ceria lattice expansion.





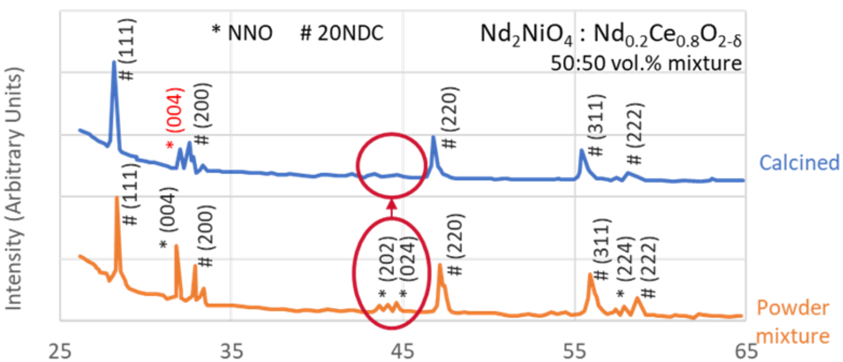


Accomplishments: Stability in Nd System

50/50 MIXTURES OF Nd_2NiO_4 WITH ND DOPED CERIA CALCINED AT 1300 ºC CONFIRM THE STABILITY HYPOTHESIS

Standard Ceria Dopant Level

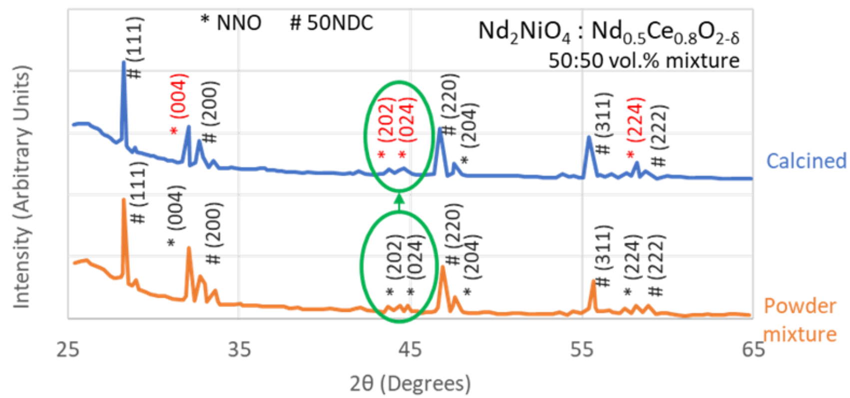
$Nd_{0.2}Ce_{0.8}O_{2-\delta}$



No nickelate phase retained

Heavily Doped Ceria

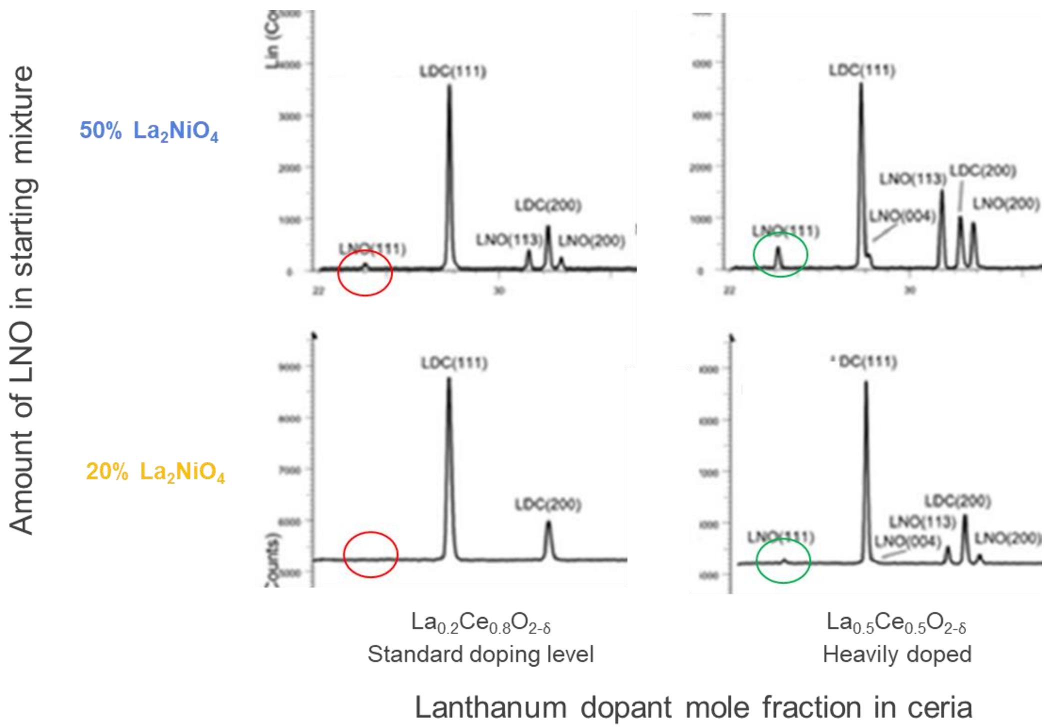
$Nd_{0.5}Ce_{0.5}O_{2-\delta}$



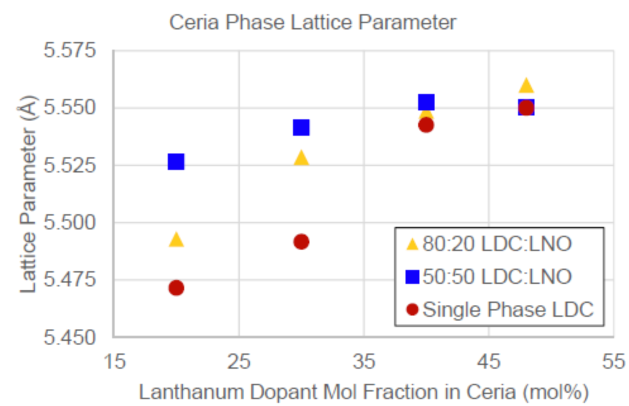
Nickelate phase retained

Accomplishments: Stability in La System

STABILITY HYPOTHESIS DUPLICATED IN THE La SYSTEM



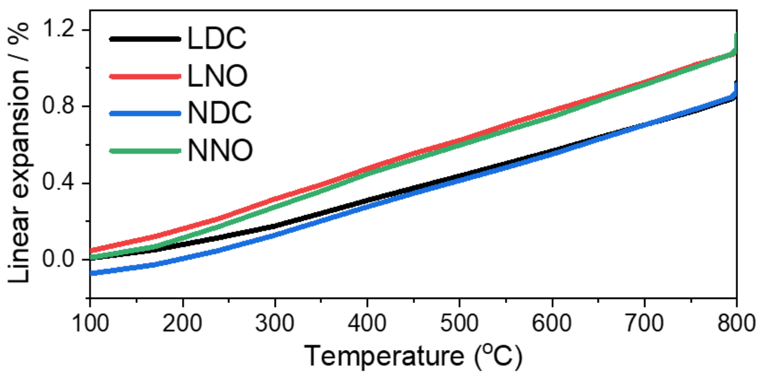
Shift in lattice parameter from starting single phase value indicates incorporation of La into the ceria lattice for dopant concentrations <40 mol%



Accomplishments: Thermal and Chem Expansion

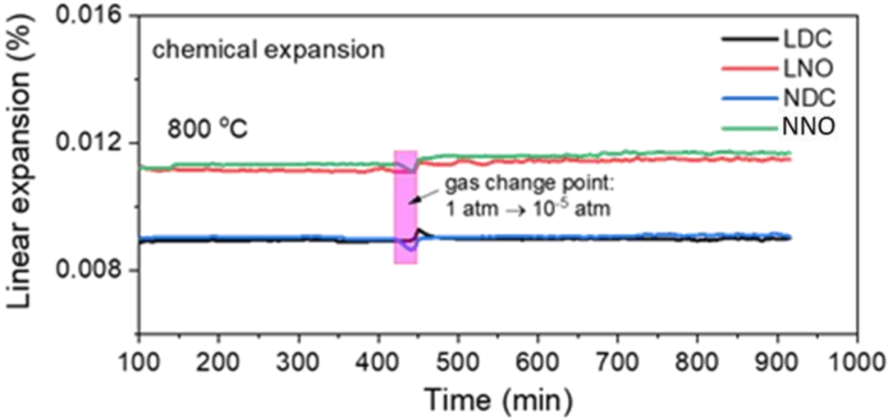
HIGH CTE OF LNO CAN BE REDUCED BY CERIA ADDITION BUT IS AN AREA OF CONCERN

High CTE of LNO can be reduced by ceria addition but remains an area of concern



Coefficient of thermal expansion (1/K)	
LDC	13.2×10^{-6}
LNO	15.1×10^{-6}
NDC	14.4×10^{-6}
NNO	15.9×10^{-6}

Minimal chemical expansion on pO_2 change

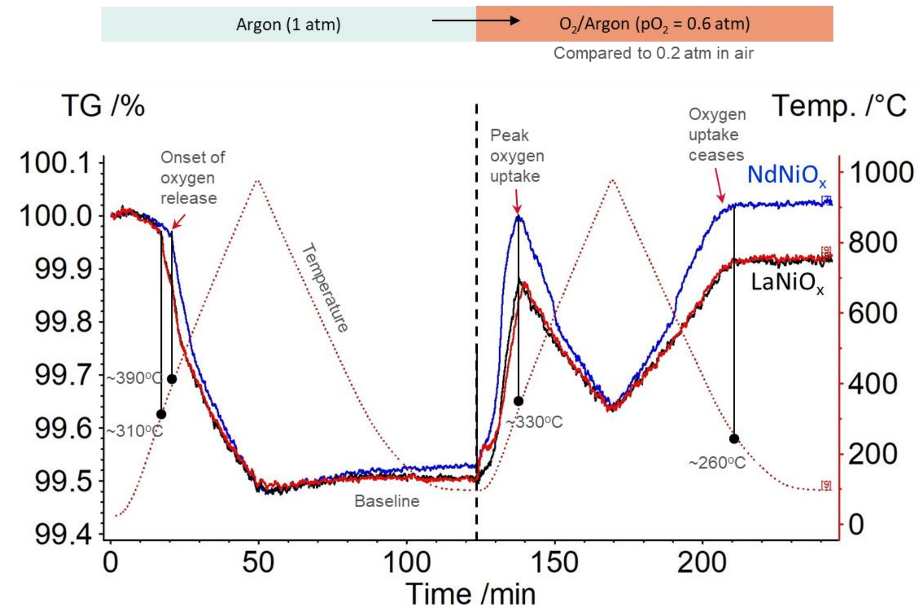


Linear expansion as a function of time at 800ºC showing a transition from 1 atm to 10^{-5} atm pO_2 for LNO, NNO, LDC and NDC. All of the materials show only a small change in dimensions.

Accomplishments: TGA of $LaNiO_x$ & $NdNiO_x$

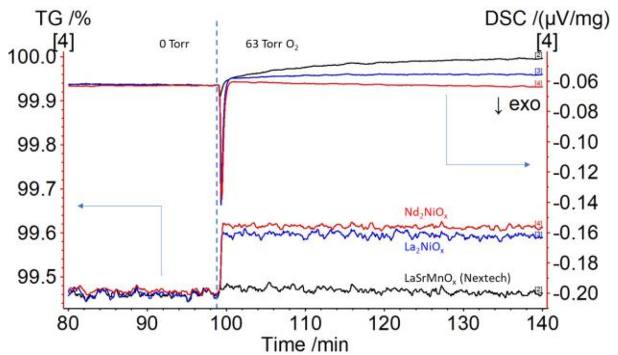
NICKELATES SHOW ABILITY TO STORE AND RELEASE OXYGEN, POSSIBLE GREATER AFFINITY FOR OXYGEN IN Nd BASED NICKELATE THAN La BASED

- As produced powders show very little uptake/release of oxygen
- Samples were pre-conditioned in Ar at 1000°C.
- TGA profile for $LaNiO_x$ virtually independent of $p(O_2)$.
- $NdNiO_x$ shows greater O_2 uptake/release on gravimetric basis.
- Some change at 330°C which causes loss of oxygen with increasing temperature.

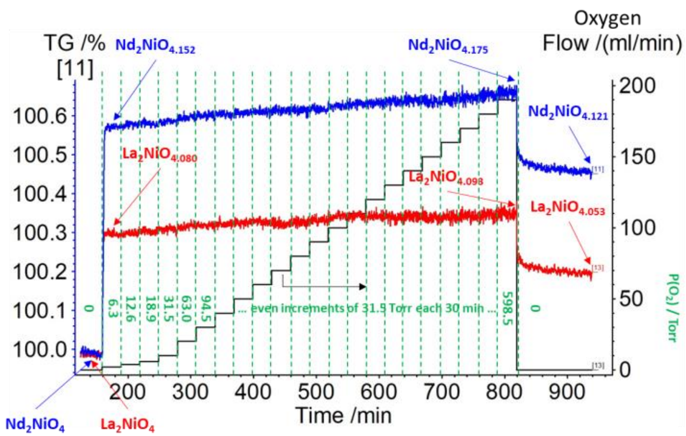


Accomplishments: Oxygen Uptake

Greater oxygen update for nickelates compared to LSM

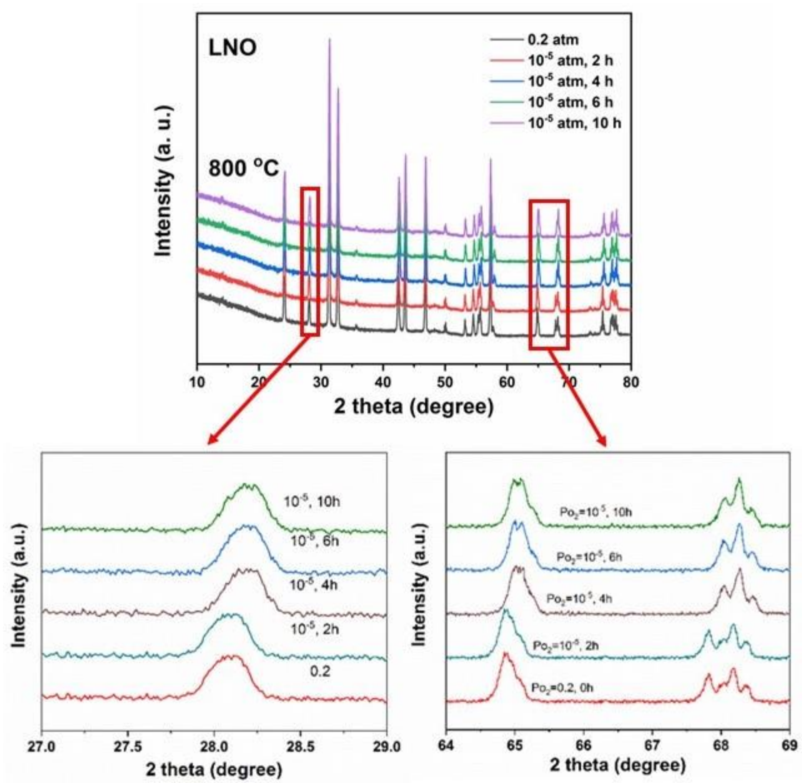


Step-wise pO2 change confirms Nd has more open structure then La nickelate



Results confirmed through peak shift

Shift towards right indicates unit cell shrinkage under low pO_2

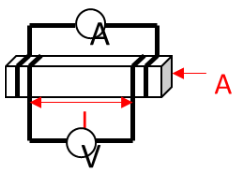


Sandia National Laboratories

Accomplishments: Conductivity Relaxation

PROCEDURE DEVELOPED TO ISOLATE SURFACE EXCHANGE REACTION

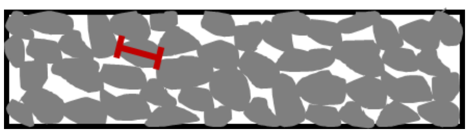
Constant current of 1 A is applied and voltage is measured



$$\sigma = \frac{LI}{AV}$$

Porous bars are used to reduce the diffusion length

- Oxygen Diffusion no longer rate limiting
- Relaxation time, $t = l^2/D \sim 2$ sec



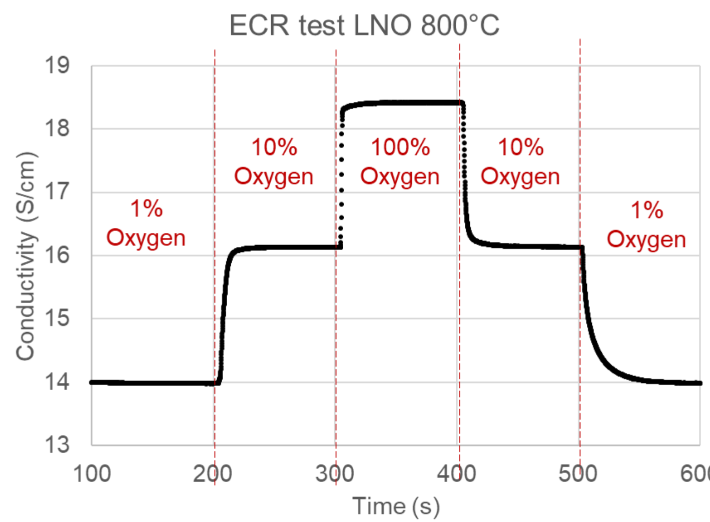
l = diffusion length = 5 µm $D = 1.5 \times 10^{-7}\ cm^2/s$

LNO @ 800°C

Surface exchange is the only rate limiting step

$$\sigma_n = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = 1 - \exp(-\frac{kt}{l})$$

Testing Sequence



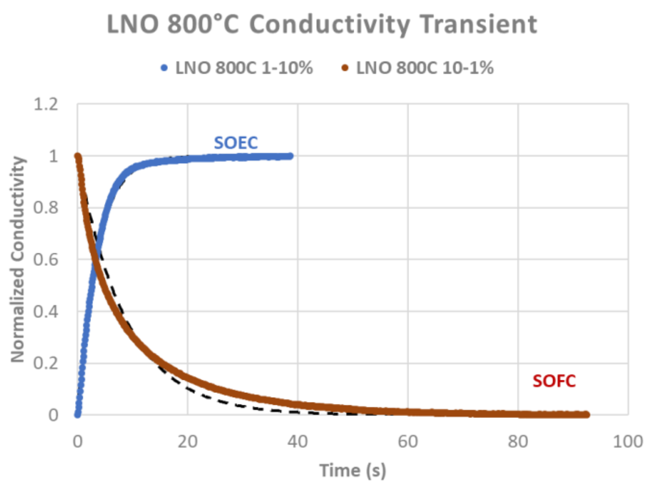
Accomplishments: Conductivity Relaxation

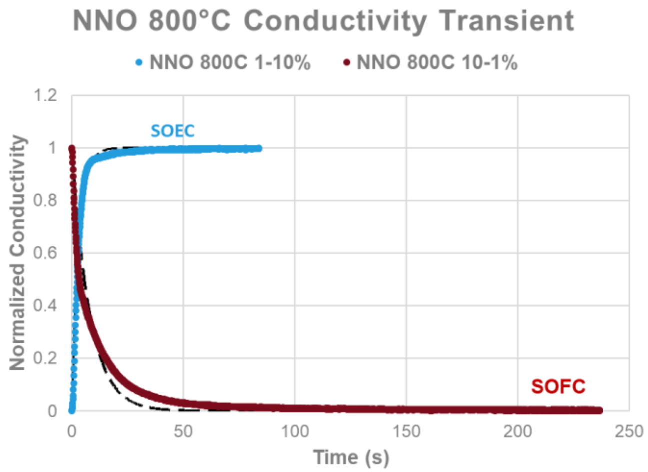
NORMALIZED CONDUCTIVITY RESULTS SUGGEST NICKELATES WILL OUTPERFORM LSM

- Both LNO & NNO show 5 orders of magnitude improvement over LSM
- Transitions occur faster when going from low pO_2 to higher pO_2 aka in SOEC mode
- Faster oxygen transport kinetics in SOEC mode

	Exchange coefficient (m/s)	
	1-10%	10-1%
LNO	1.40×10^{-6}	5.66×10^{-7}
NNO	1.59×10^{-6}	6.19×10^{-7}

LSM = 1×10^{-12} (m/s)
*Phys. Chem. Chem. Phys. 2013, **15**, 2298*
Effect of A and B-site cations on surface exchange coefficient for ABO_3 perovskite materials
Eric N. Armstrong,[a] Keith L. Duncan[a] and Eric D. Wachsman[b]*



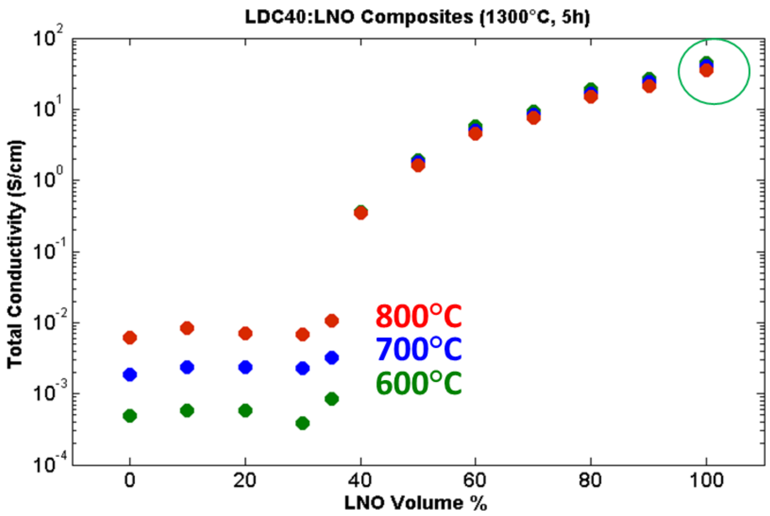


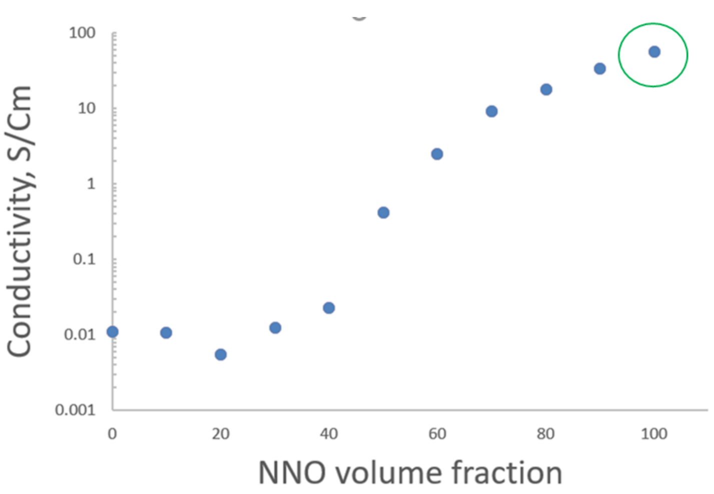
Accomplishments: Electrical Conductivity

CONDUCTIVITY MATCHES THE TARGET OF >96 S/cm

Conductivity variation as a function of vol% nickelate

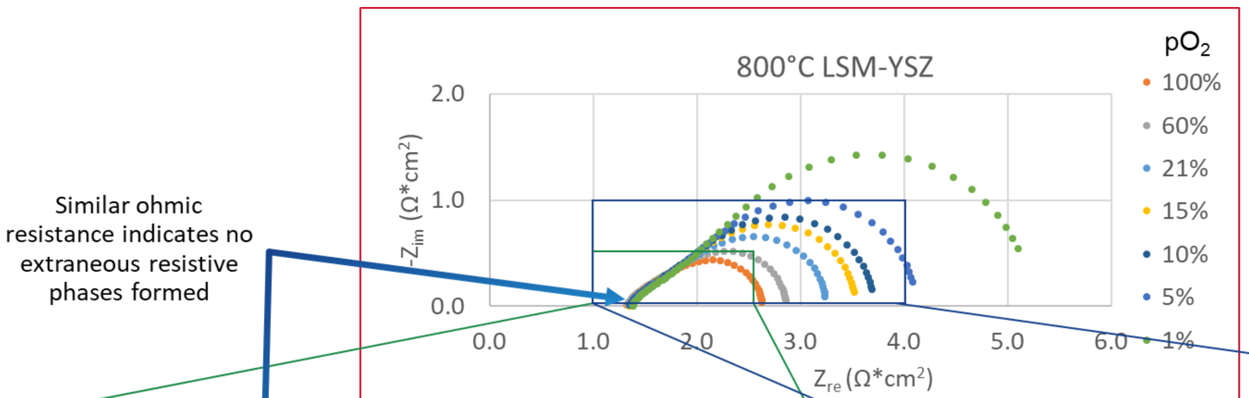
- Percolation limit in these mixtures occurs at ~ 40 vol%
- Below nickelate percolation limit conductivity is controlled by ceria (ionic conductivity)
- Above nickelate percolation limit conductivity is controlled by nickelate (electronic conductivity)





Accomplishments: Symmetrical Cells

NICKELATE STRUCTURES SHOW MUCH LOWER POLARIZATION RESISTANCE THAN LSM BASED ELECTRODES



600 µm YSZ electrolyte

LSM sym cell:

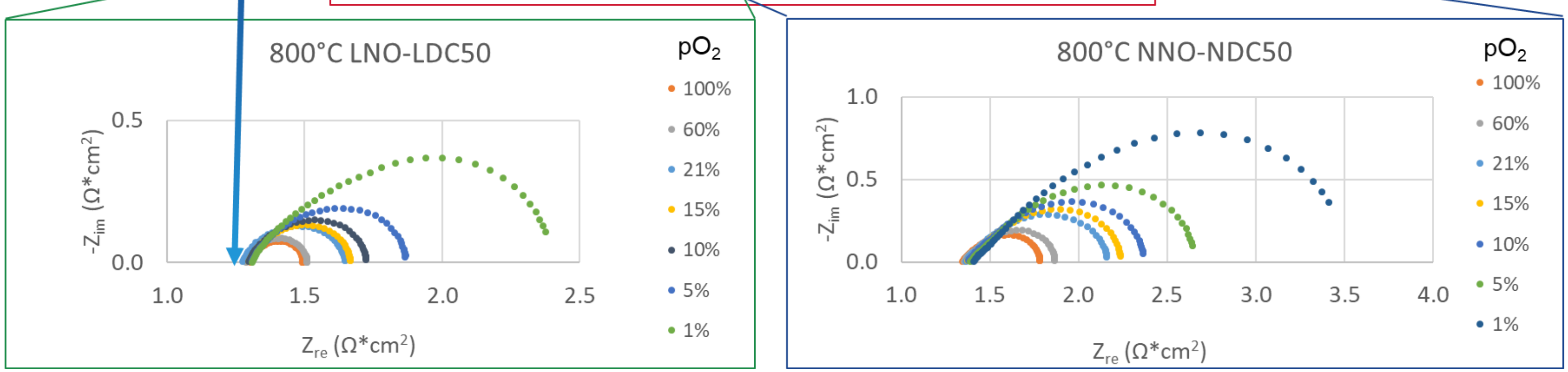
- Cathode 50-50 wt% LSM-YSZ

LNO sym cell:

- Cathode: 65-35 vol% LNO-LDC50 (50 mol% lanthanum doped ceria)
- Barrier Layer: 10 mol% gadolinium doped ceria

NNO sym cell:

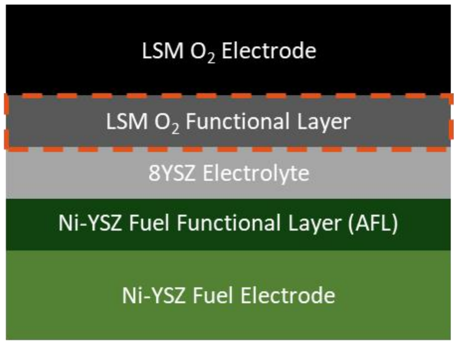
- Cathode: 65-35 vol% NNO-NDC50



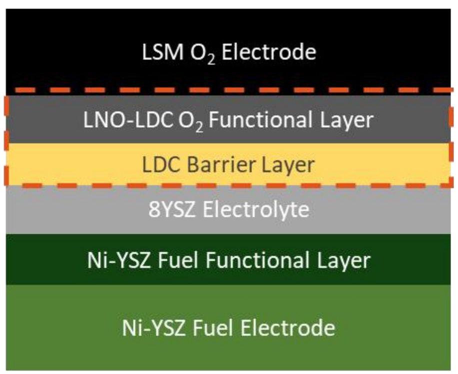
Accomplishments: Button Cell Fabrication

ABLE TO INCORPORATE NEW MATERIALS INTO THE CO-SINTERING PROCESS

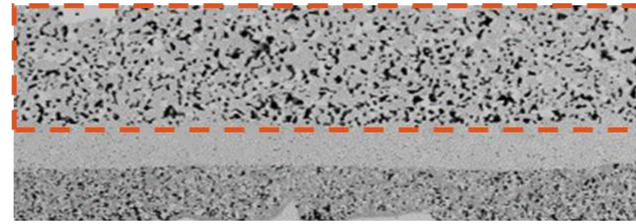
SOFC Structure



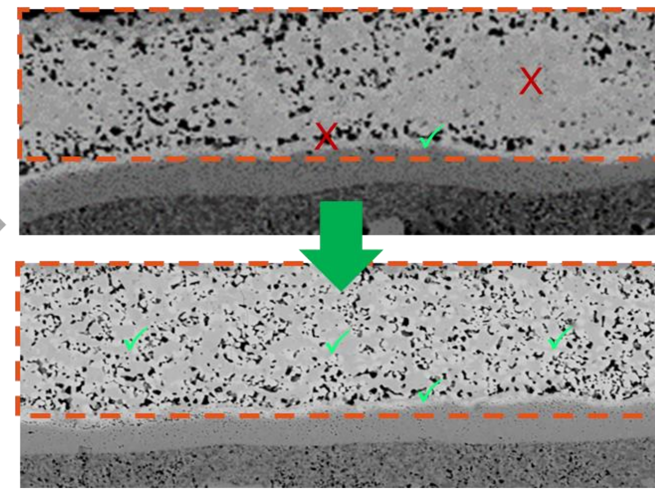
Structure Achieved



Uniform baseline microstructure



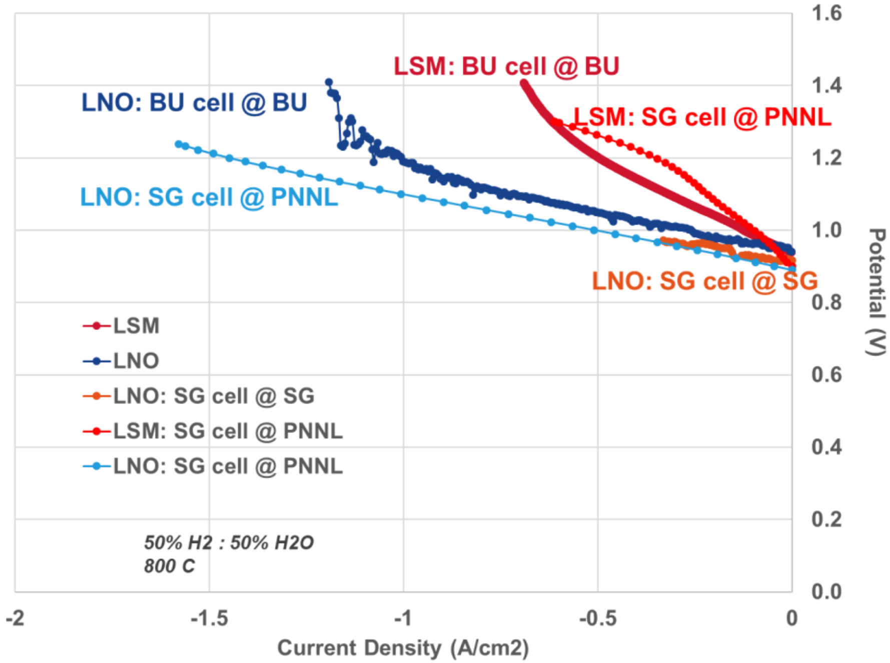
Improved LNO/LDC electrode microstructure



Accomplishments: Electrochemical Performance

STABILIZED NICKELATES SHOW IMPROVEMENT IN PERFORMANCE OVER BASELINE

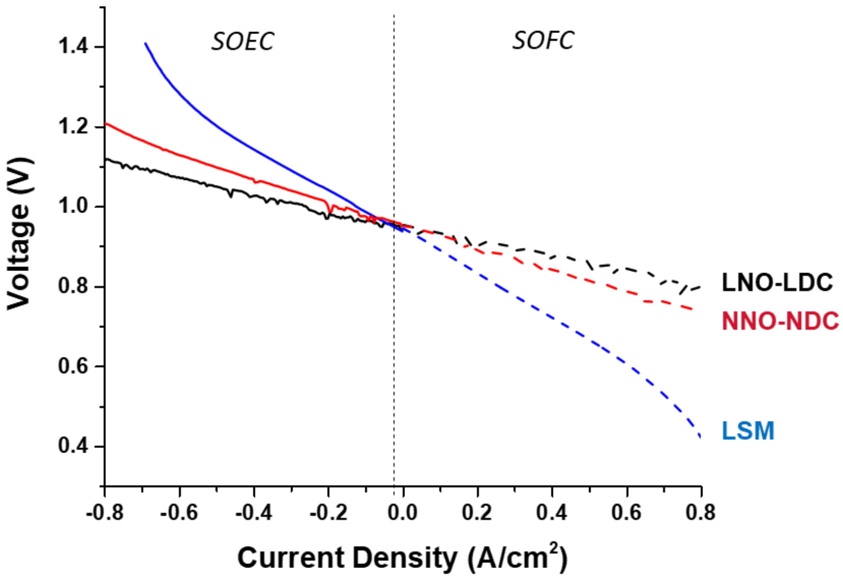
- >80% improvement in current density
- Good agreement between 3 labs
- Performance improvement shown on:
  - Anode supported cells (BU cell)
  - Co-sintered cells (SG cell)
- Solution can be utilized industry wide



Accomplishments: Reversible Performance

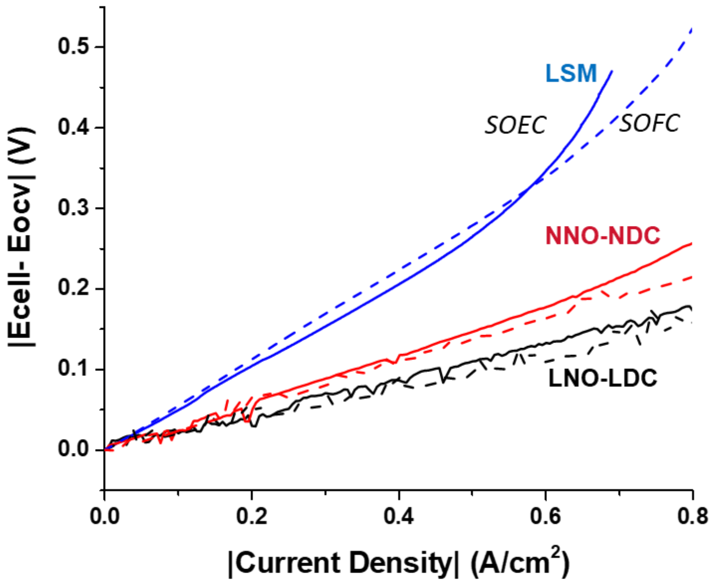
STABILIZED NICKELATES SHOW ABILITY TO FUNCTION IN SOEC AND SOFC MODES

Nickelate structures outperform LSM in both SOFC an SOEC mores



Anode supported cells

Overpotential analysis show LSM performs worse in SOEC than SOFC mode



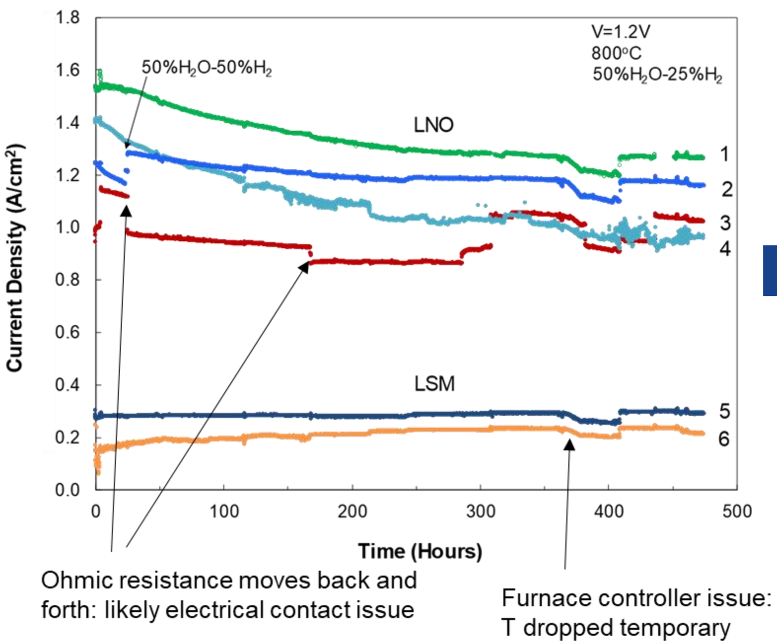
Anode supported cells

Accomplishments: Durability Testing

NICKELATE SYSTEM SHOWS A 250 HR BREAK-IN PERIOD FOLLOWED BY STABILIZATION

Raw data analysis from long term testing

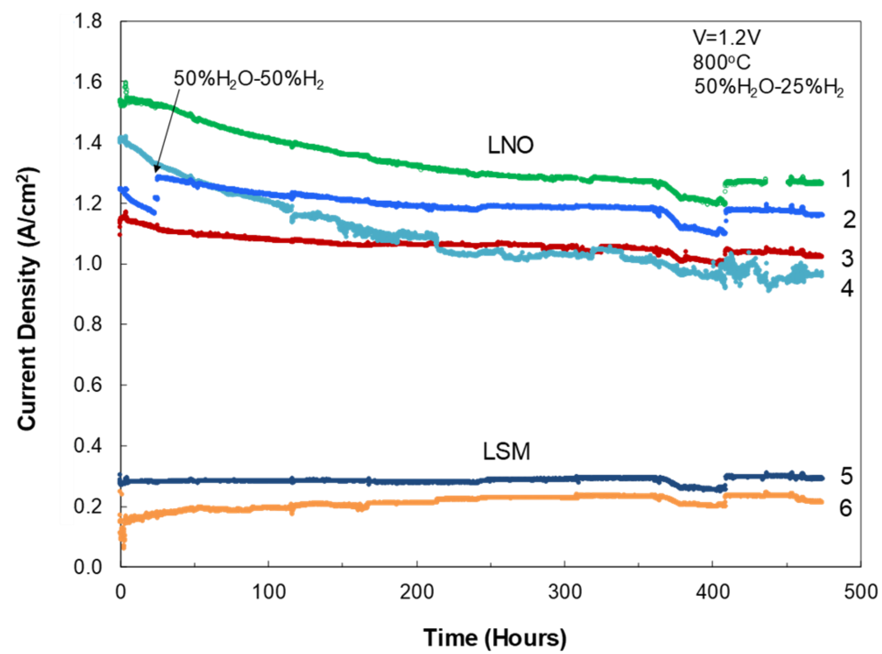
- Cell 3 shows R_{Ω} instability, likely electrical contact issue (can be corrected for)
- Cell 2 change in performance due to gas composition (OCV) change
- Furnace controller issue at 375hr



Data Correction

Durability trends identified

- LNO stabilizing after 250 hrs
- Cells 1, 2, 3 show reproducible behavior (cell manuf. and testing reliability)
- Cell 4 shows stability issues, unclear if internal or external



Collaboration: Effectiveness

Collaboration with EMN project node experts

- Monthly conference calls with the full team including EMN project node experts
- Discussions with team at INL (James O'Brian, Dong Ding, Hanping Ding) refined post-testing analysis plan including CT scanning of button cells
- Discussions with Eric Coker at SNL focused on quantification of oxygen hyperstoichiometry. Through this discussion atmosphere controlled TGA was added to the project plan to supplement atmosphere controlled XRD. In this way the risk of being able to measure this property was reduced
- Data analysis discussions after significant testing milestones were used to share progress, interpret results, and plan next steps

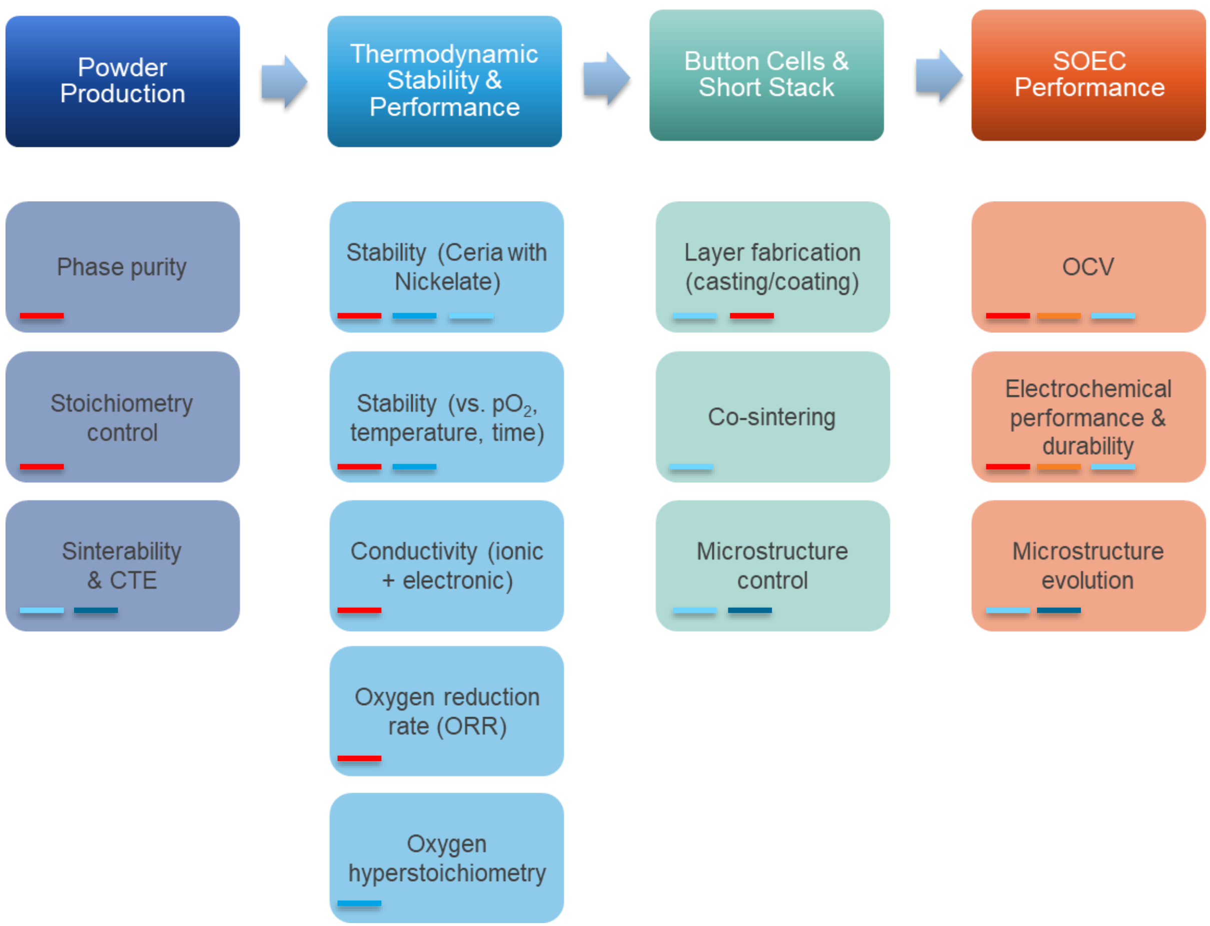
Collaboration: Effectiveness

PROJECT TASKS WERE SPREAD ACROSS THE TEAMS, TAKING FULL ADVANTAGE OF BOTH EXPERTISE AND RELEVANT UNIQUE CAPABILITIES

Project Teams

- SAINT-GOBAIN
- BOSTON UNIVERSITY
- Pacific Northwest NATIONAL LABORATORY
- INL Idaho National Laboratory
- Sandia National Laboratories

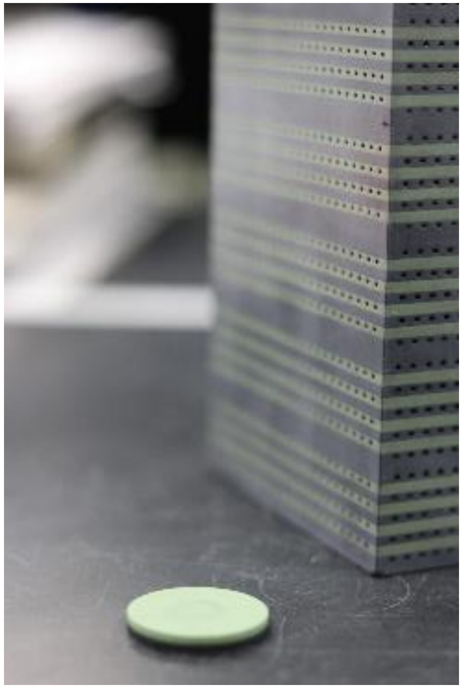
Areas of Collaboration

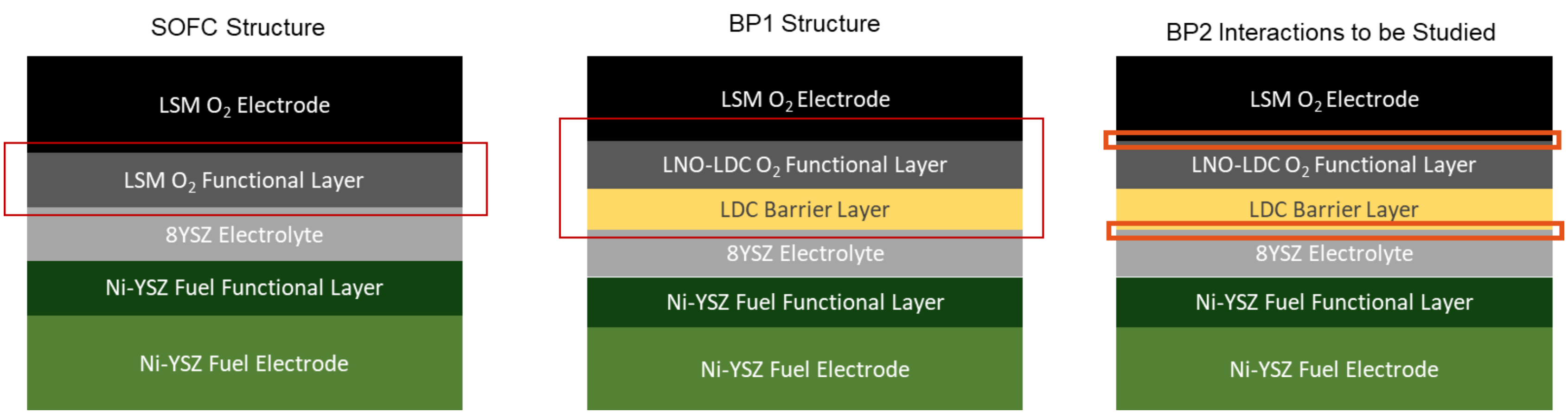


Proposed Future Work

Next Steps

- Button cell fabrication and testing of top candidates
- Investigate cross-family stability and performance
- Engage with additional Nodes for modeling support
- Additional focus on potential interfacial reactions
- Optimization of stoichiometry and sintering to maximize performance and minimize degradation
- Down selection of electrode compositions for integration into short stacks
- Initial short stack performance and durability testing



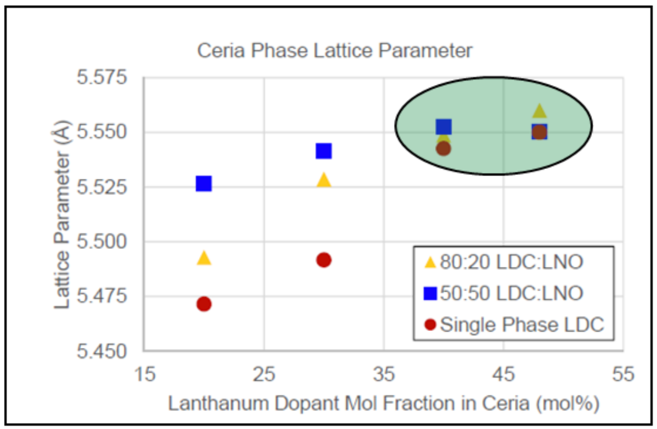


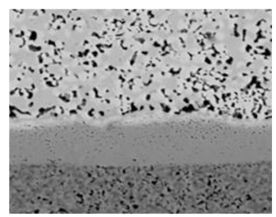
Any proposed future work is subject to change based on funding levels

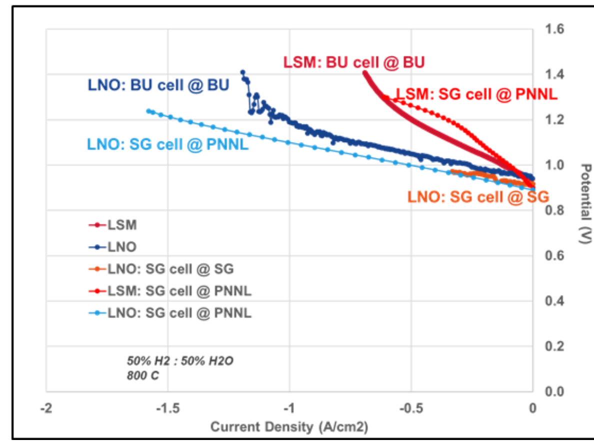
Project Summary

Performance of button cells with a Nickelate oxygen electrode

- Dramatic performance increase
  - 70% higher electrolyzer current density @ 1.4V than LSM-YSZ
  - Indicates Nickelate – ceria interactions prevented during sintering
- Interface stable/well-adhered after 336 hr of continuous operation







Status vs. 3-year targets

Metric	Target	Current
ASR	*≤0.3 ohm cm²*	*0.24 ohm cm²*
Current Density	*≥1 A/cm² @ 1.4V*	*1.2 A/cm² @ 1.4V*
Degradation Rate	≤0.3 %/khr	LSM > LNO >> 0.3%

Acknowledgements

- ***INL**: D. Ding, J O'Brien*
- ***SNL**: E. Coker*
- ***PNNL**: J. Stevenson, O. Marina*
- ***BU**: J. Banner, A. Aktar*
- ***SG**: S. Soulekar, R. Wang*

Technical Backup Slides

(optional)

Accomplishments

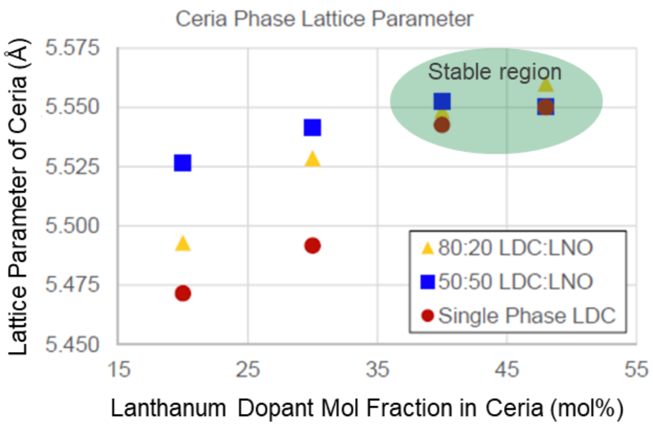
Summary of milestones and progress

Milestone	Description	Month	Metric	Progress
M1.1	Powders meet specifications	3	• Stoichiometry met (ICP) • Phase purity (XRD)	• √ Process defined • √ Stoichiometry and purity confirmed • √ NNO, NDC , LNO, LDC, complete
M1.2	Identification of stability boundaries	8	• Decomposition free regions determined for nickelate-ceria mixtures	• √ Completed
M1.3	Determine top 3 composites	12	• >96 S/cm @800C • Oxygen exchange coefficient $1.2x10^{-5}$ cm/s • Maps of oxygen nonstoichiometry f(T, PO2)	• √ Measurements completed
M2.1	Button cell fabrication	5	• Baseline button cells co-sintered with He leak (in air) <1x10-8 $mbarLs^{-1}cm^{-2}$ • Microstructure acceptable	• √ Baseline cells prepared • √ Initial characterization started • √ Tapes of nickelate prepared • √ Nickelate microstructure to be improved
M2.1	Accelerated testing	11	• Baseline degradation rate established in accelerated testing • Degradation mode identified microstructurally	• √ Baseline cells tested • √ Baseline cells examined • √ Nickelate cells to be tested • Nickelate cells to be examined
G/NG	Button cell test results operating in electrolysis conditions	12	• 25% higher electrolyzer current density @ 1.4V than baseline LSM-YSZ • Well adhered layers after 2 wks of operation • Degradation rate <1.5%/1000 hr	• Discussion

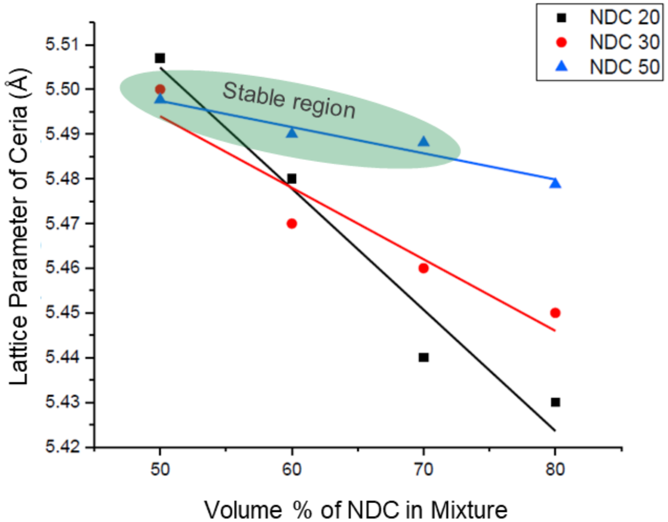
Accomplishments: Stability Boundaries

STABLE REGIONS HAVE BEEN IDENTIFIED FOR FURTHER WORK, IN THESE DOMAINS THE REACTION BETWEEN NICKELATE AND CERIA PHASES IS MINIMIZED OR ELIMINATED. THIS PREVENTS LOSS OF THE ACTIVE NICKELATE PHASE AND ELIMINATION OF RESISTIVE GRAIN BOUNDARY PHASES.

Electrocatalyst	Ionic Conductor	Stability of System
La_2NiO_4 (LNO)	La-doped CeO_2 (LDC)	✓
Sm_2NiO_4 (SNO)	Sm-doped CeO_2 (SDC)	✗
Nd_2NiO_4 (NNO)	Nd-doped CeO_2 (NDC)	✓



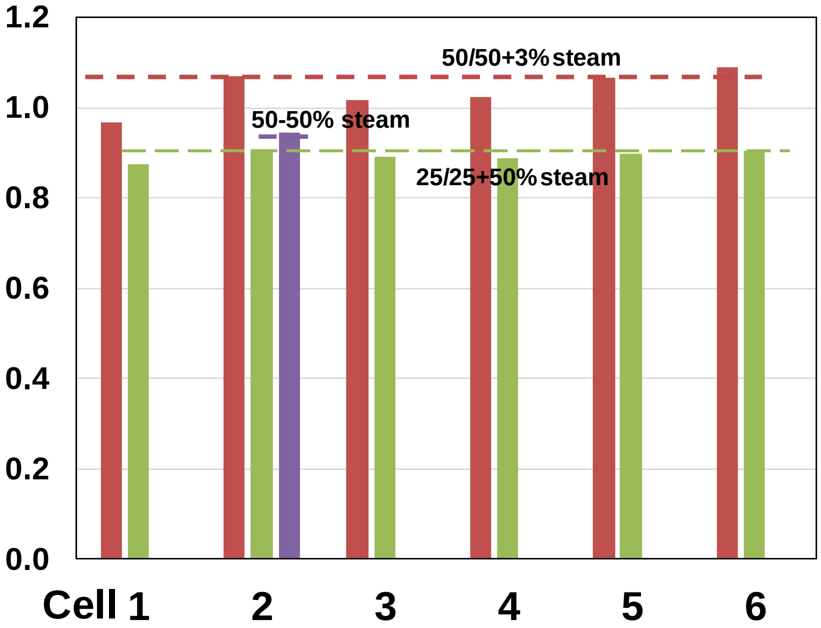
- Identified that a relatively high level of doping is required to prevent ceria from decomposing the nickelate phase
- Was not able to effectively utilize Sm during Phase 1 testing
- Did not investigate cross family stabilization – potential Phase 2 investigation



Accomplishments: Good Cell Integrity

CTE DIFFERENCES DID NOT MANIFEST AS ELECTROLYTE CRACKS, THIS WAS A CRITICAL RESULT IN TERMS OF ENABLING CO-SINTERING WHICH RESULTS IN WELL BONDED INTERFACES THROUGHOUT THE CELL

Initial OCVs are close to predicted values



OCV is stable over time