Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Project ID #P176

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

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Project Partners
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Dr. Olga Marina, PNNL

DOE Hydrogen Program 2024 Annual Merit Review and Peer Evaluation Meeting

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Project Overview

Project Partners
Dr. John Pietras, Saint-Gobain
Dr. Srikanth Gopalan, Boston University
Dr. Olga Marina, PNNL

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

Award #	EE0008377
Start/End Date	10/01/2018 – 12/31/2024
Project Funding*	$1.2M

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

Approach - Summary

Project Motivation

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

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. Alter stoichiometry to prevent interfacial reactions.

Accelerated testing (PNNL)
Development of a protocol which probes the dominant degradation mechanism

Partnerships

Saint-Gobain 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 has demonstrated stable nickelate chemistries and draws on expertise in advancing the chemistry of electrochemical devices

PNNL has developed in-situ characterization capabilities to monitor cells and electrochemical interfaces along with expertise in design and interpretation of acceleration testing

Approach – Safety Planning and Culture*

- There were no incidents or near misses experienced throughout the duration of this project.
  - All relevant personnel were instructed on safe operation of sintering furnaces, as well as the hazards associated with the material chemistries being evaluated.
- Safety was ensured via best practices in material handling, synthesis, and usage.
  - Specialized waste streams were established for nickel-containing or contaminated materials
    - These waste streams are separate of those of other chemistries. This applied to powders and slurries.
- Aqueous ceramic slurry systems were selected to reduce the HSE impact of working with solvent-based systems.

**Safety plan exempted project*

Summary of Approach & Results

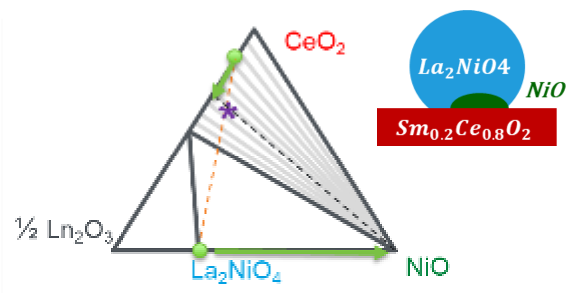
Stabilization

LNO stabilized by heavily doping Ceria

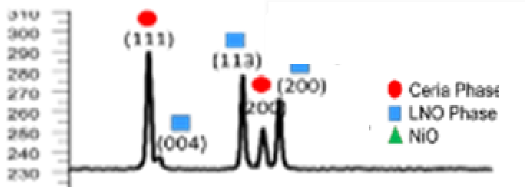
- Decomposition of nickelate phase when in contact with Ceria

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

Resulting Ceria Phase: $La_xSm_{0.2}Ce_{0.8-x}O_{2-\frac{0.2+x}{2}}$

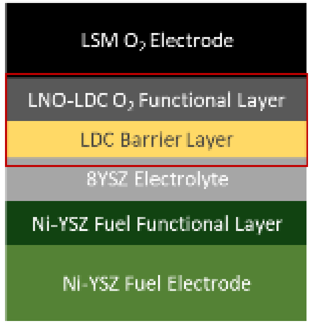


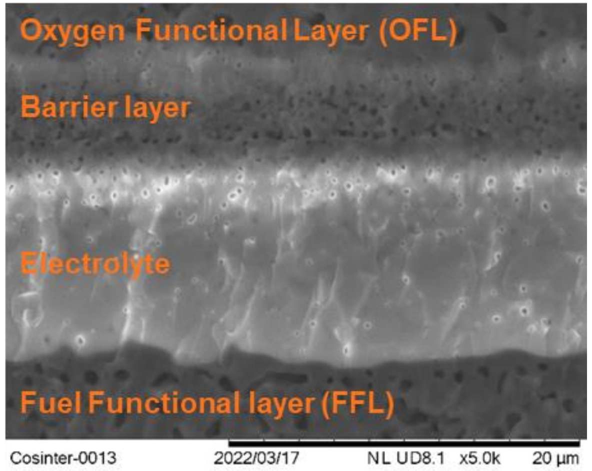
Material stabilized



Co-Sintering

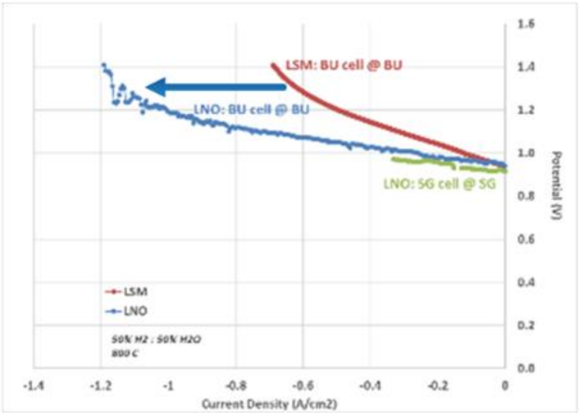
Incorporated nickleate within co-sintered cells





SOEC Performance

Increased SOEC current density at 1.3V



Status vs. 3-year targets

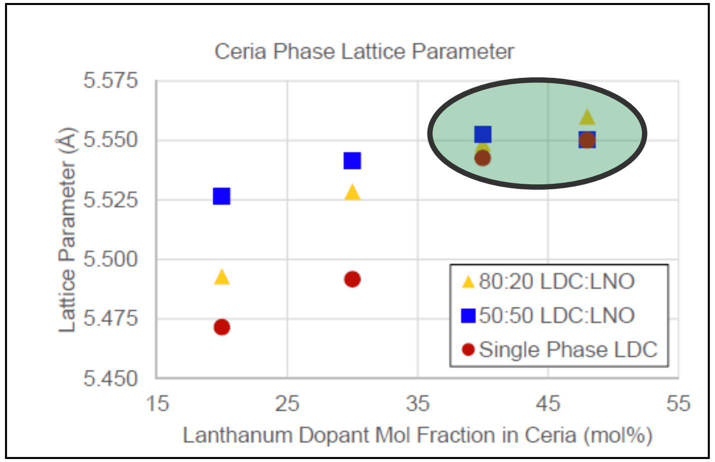
Metric	Target	Current
ASR	≤0.3 ohm cm²	0.24 ohm cm²
Current Density	≥1 A/cm² @ 1.4V	1.2 A/cm² @ 1.4V
Degradation Rate	≤0.3 %/khr	LSM > LNO > 0.3%

Budget Period 1 Summary

Button cell performance metrics with Nickelate oxygen electrode

- 25% higher electrolyzer current density @ 1.4V than LSM-YSZ (+70%)
- Nickelate electrode well-adhered after a 336 h of continuous operation (stable operation)
- Degradation rate <1.5%/1000 h (performance becoming steadier over time up to 2000 hrs)
  - Degradation mechanisms proposed were out of BP1 scope
    - Contact resistance at cell surface (evidence on at least one cell by disturbing the wires)
    - Contact resistance at Electrode / Bulk electrode interface (potential reactions with LSM)
    - Contact resistance developed between ceria barrier layer and zirconia electrolyte
    - Changes on the Ni/YSZ side of the cell

Stability Map



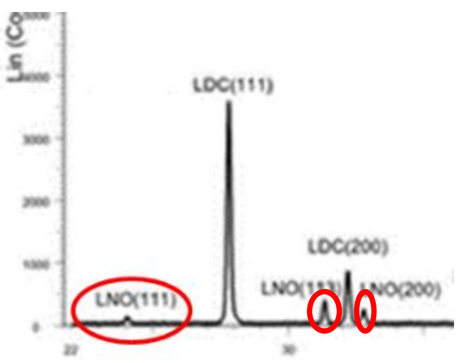
Major Milestone	Description	Metric	Status
M1.1	Powders meet specifications	• Stoichiometry met (ICP) • Phase purity (XRD)	• 100%
M1.2	Identification of stability boundaries	• Decomposition free regions determined for nickelate-ceria mixtures	• 100%
M1.3	Determine top 3 composites	• >96 S/cm @800C, oxygen exchange coefficient $1.2x10^{-5}$ cm/s • Maps of oxygen nonstoichiometry f(T, PO2)	• 100%
M2.1	Button cell fabrication	• Button cells co-sintered and microstructure acceptable	• 100%
M2.2	Accelerated testing	• Baseline degradation rate established in accelerated testing • Degradation mode identified microstructurally	• 100%
G/NG	Button cell test results operating in electrolysis conditions	• 25% higher electrolyzer current density @ 1.4V than baseline well adhered layers after 2 wks of operation • Degradation rate <1.5%/1000 hr	• 100%

Accomplishments: Stoichiometry Control and Stabilization

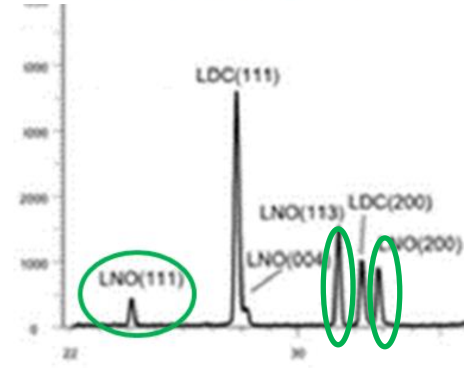
Phase Stability Example

- 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 0.97 and 1.1053 Å respectively) leads to lattice expansion.
- Constant lattice parameter of ceria at high initial dopant levels indicates lack of reaction with nickelate

Phase Retention

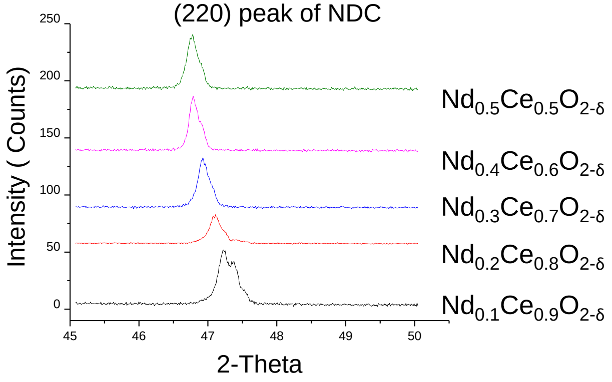


$La_{0.2}Ce_{0.8}O_{2-\delta}$
Standard doping level

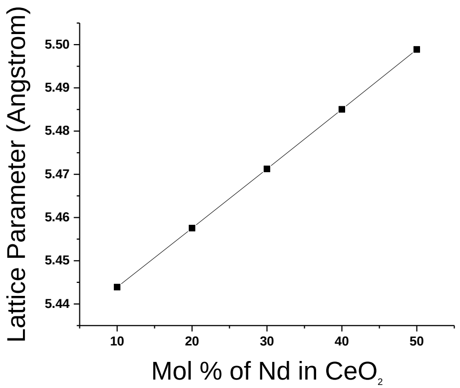


$La_{0.5}Ce_{0.5}O_{2-\delta}$
Heavily doped

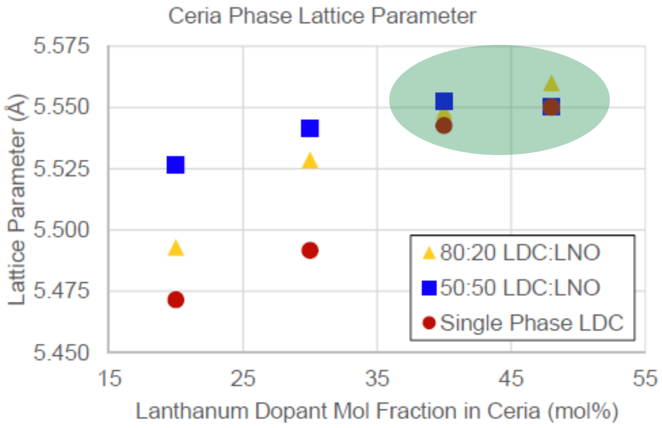
Phase Purity



Lattice Parameter Shift



Stability Map

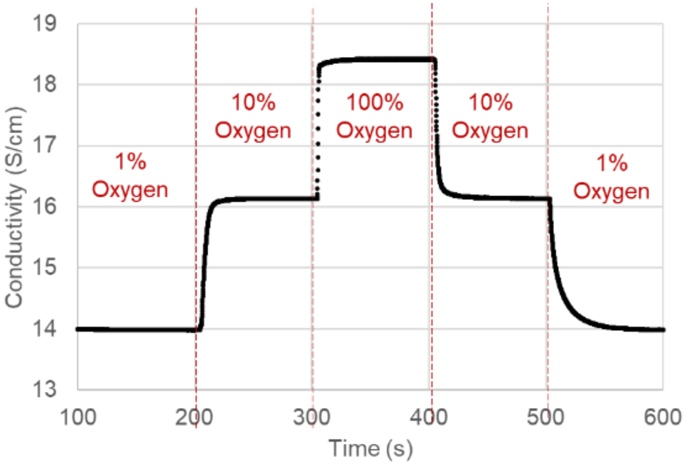


Accomplishments: Performance Targets

Exchange coefficient targets met

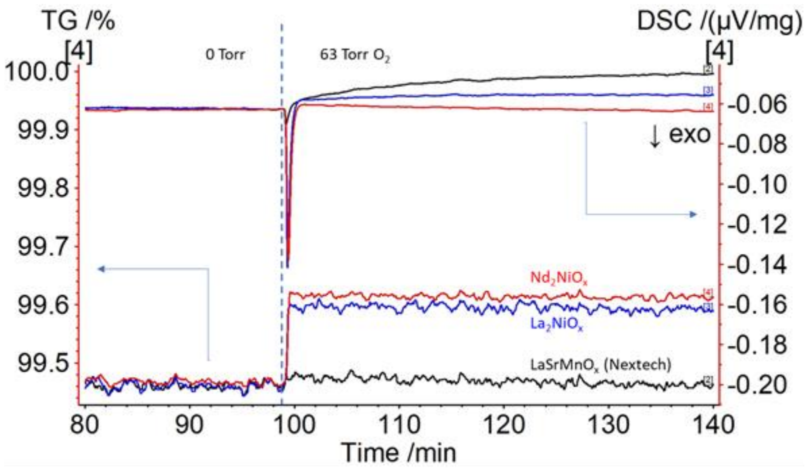
- Conductivity relaxation study completed for LNO & NNO @ 800 °C
- Materials show promising surface exchange activity

	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}



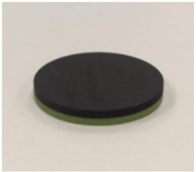
Oxygen uptake verified

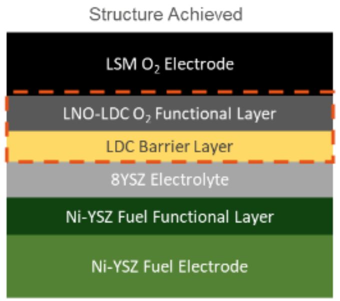
- Weight as a function of partial pressure of O_2 measured
- Nickelate materials show greater affinity for oxygen than LSM

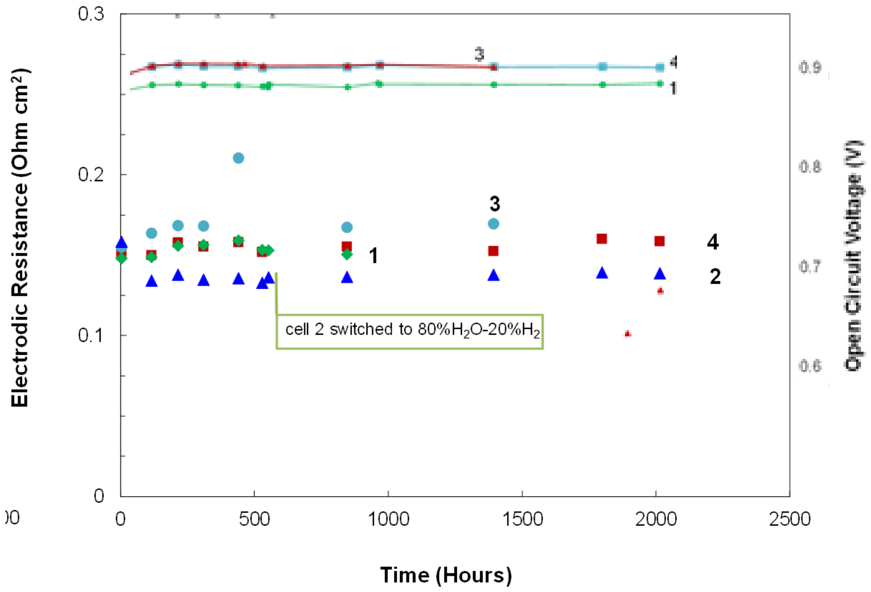


Durability established

- Multiple LNO button cells operated for over 2000 hours with little change in electrode resistance or OCV

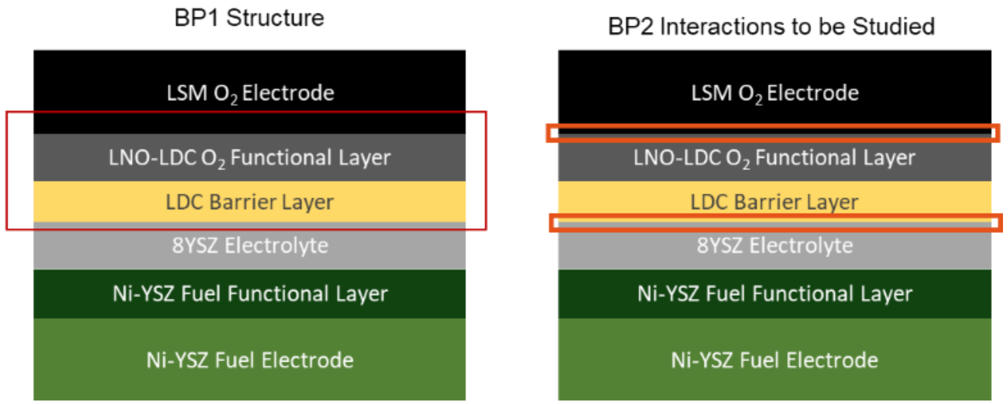






Budget Period 2

- Button cell fabrication and testing of top candidates identified in BP1
- Investigate cross-family **stability and performance**
- Additional **focus on potential interfacial reactions**
    - Detailed interface reactions to be identified at SNL/PNNL
- **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 at INL



Major Milestone	Description	Metric	Status
M3.1 M5.2	Button cell electrochemical performance	• Materials demonstrating >1.5A/cm2 @ 1.3V , 800C • Materials demonstrating >1.4A/cm2 @ 1.3V and deg <1%/khr , 800C	• 100%
M4.1	Barrier layer deposition technique	• Uniform barrier layer <5 µm • Well adhered interfaces	• 100%
M4.2 M6.1	Short stack results	• Scale process to 8x8 cm, 4 cell stack • Demonstrate performance of short stack >1 A/cm2 @ 1.3V, 800C	• 90%

Electrochemical Performance

Material Improvement

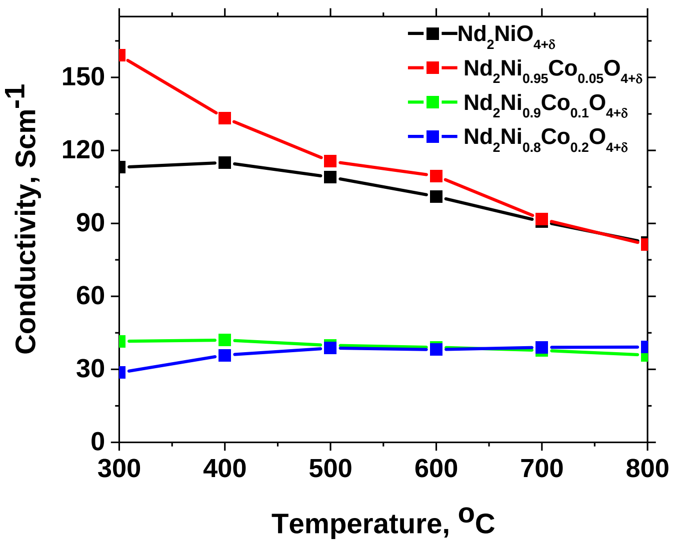
- B-site substitution increases oxygen hyper-stoichiometry and conductivity at small doping level (~ 5 mol%)
- Cells prepared and in testing

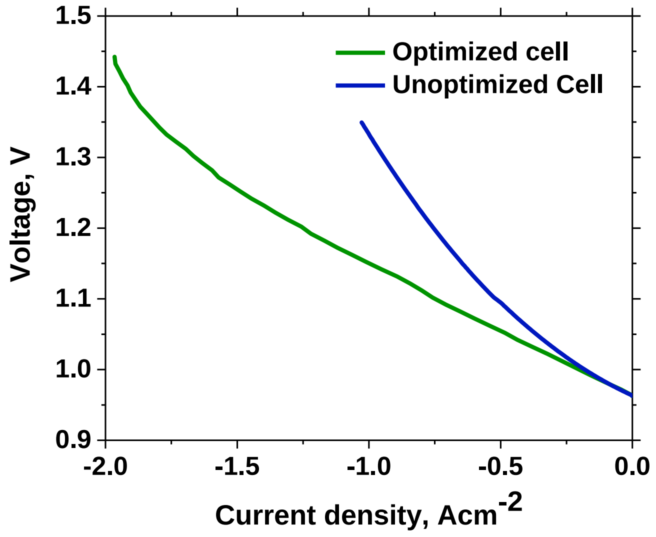
Cell Improvement

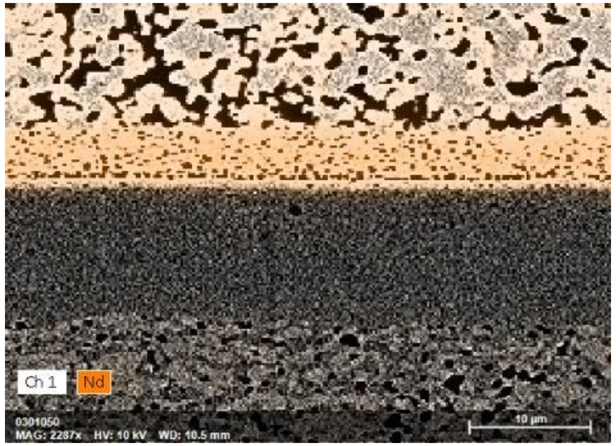
- Oxygen electrode layer thicknesses and architecture optimized on symmetric cells
- Optimized structure utilized in full cells
- 65% performance improvement over baseline cell performance

Interfacial Stability Study

- Initial EDS scans show interdiffusion between barrier layer and electrolyte
- This result kicked off detailed study on layer-to-layer interactions



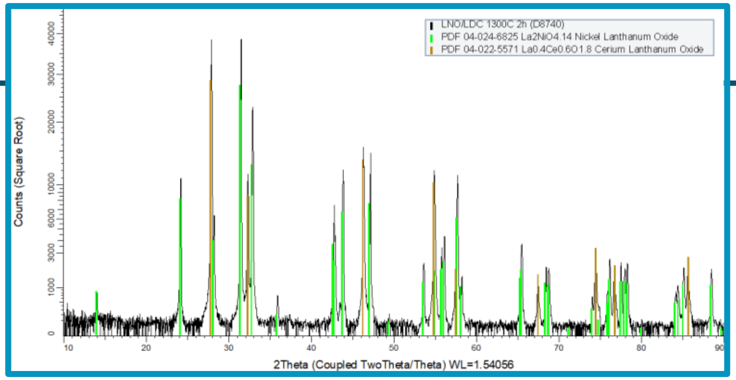


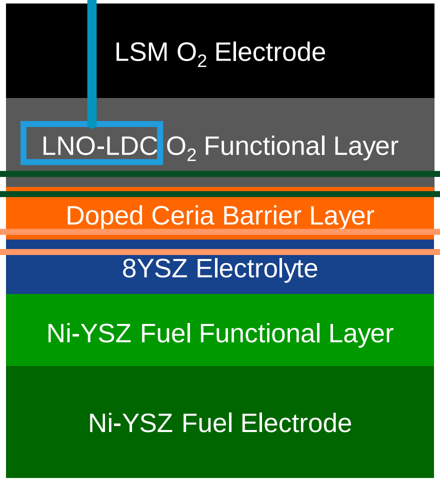


Interfacial Reactions

1. OFL (LNO+LDC)

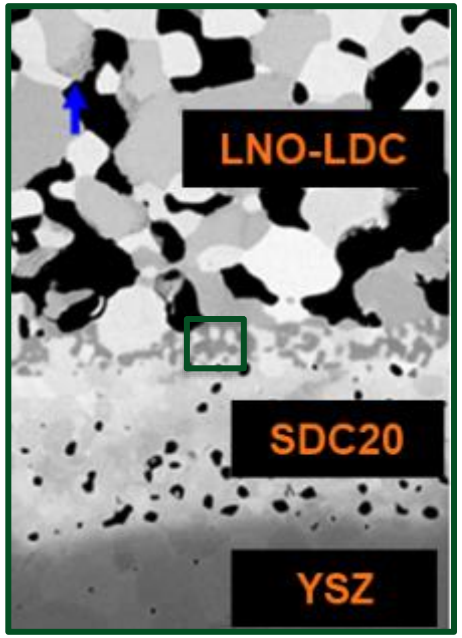
- LNO is stable by itself at 1300C;
- LNO is compatible with LDC at 1300C;





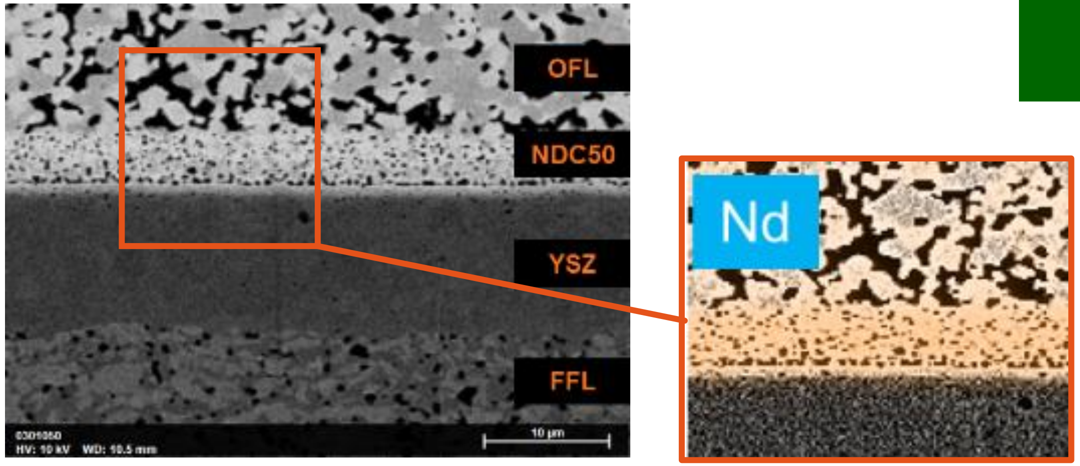
2. OFL/Barrier Layer

- Surveyed various combinations of oxygen functional layers with different barrier layers
- Identified instable combinations which lead to secondary phase formation



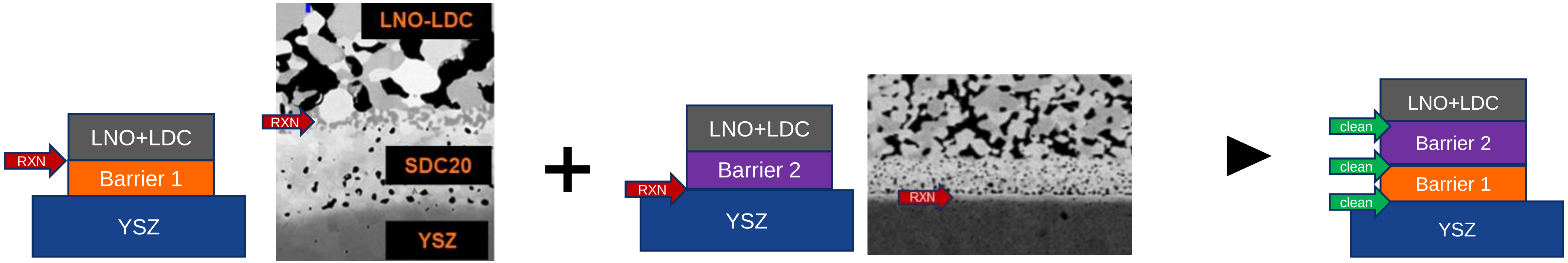
3. Barrier Layer/YSZ

- Surveyed various combinations of barrier layers with YSZ electrolyte
- Identified instable combinations which lead to excessive diffusion

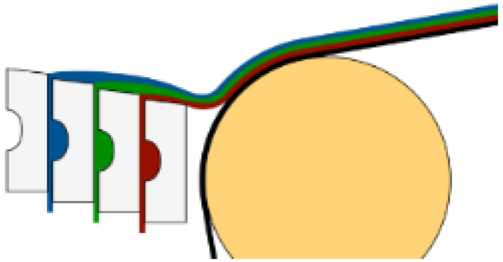


Implementation of Stable Interfaces

Summary of Learning

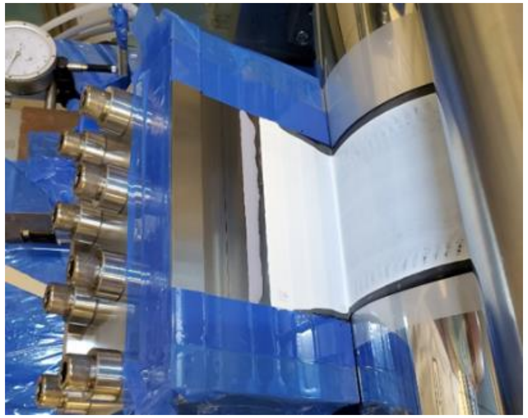


Simultaneous Multilayer Coating Development



Development Results

- Modification of slurry properties
- Very thin barrier layer possible
- Elimination of punching, stacking, lamination
- Sharp interfaces maintained
- Improved interface integrity

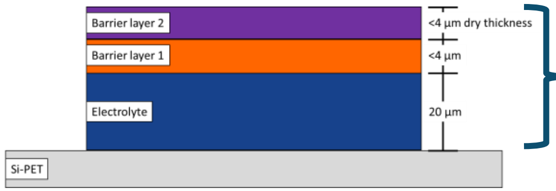


Successful Simultaneous Casting

Trial results – excellent control of film homogeneity and microstructure

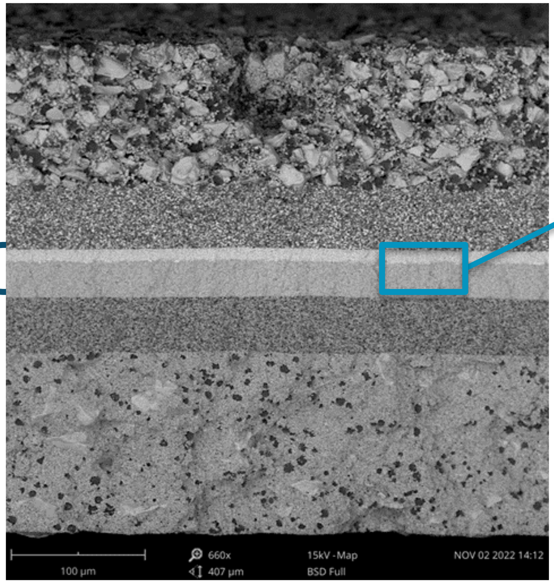
- Stable coating – good separation of 3 layers, smooth coating
- Confirmation of fluid handling approach and workflow strategy
- Layer thickness & architecture were on target
- High quality interfaces and degree of uniformity

Target Design

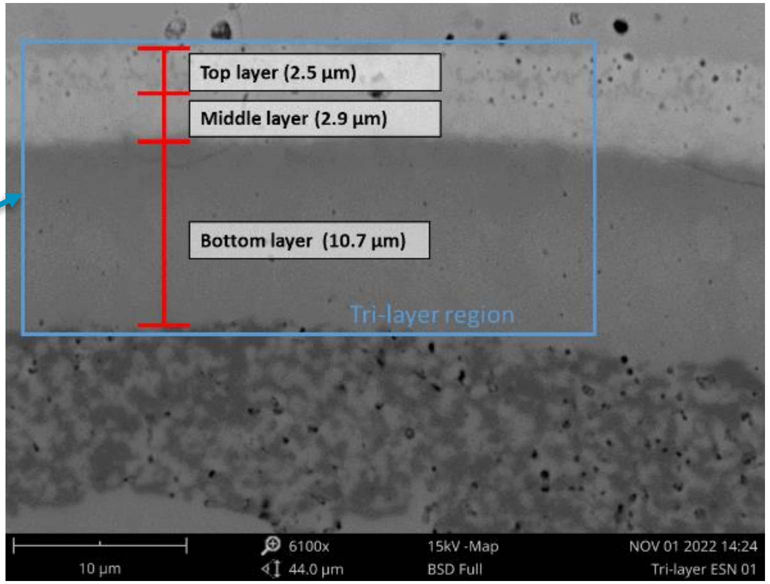


Multilayer Wet Coating

Laminated Green Structure



Final Sintered Microstructure

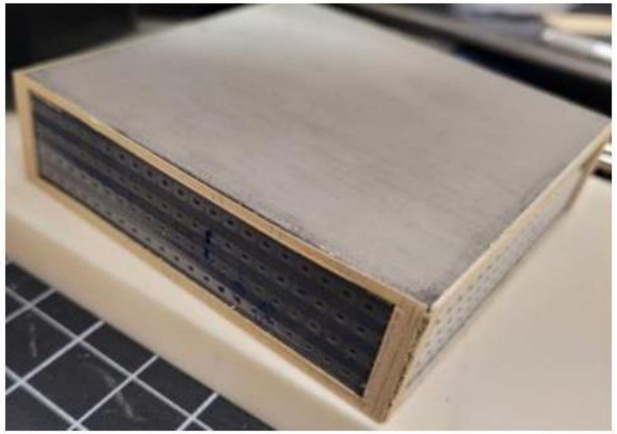


Stack Testing at Idaho National Labs

- Stack testing equipment including a furnace, electrochemical testing equipment, and fixtures shipped and installed at Idaho National Labs
- A baseline 4-cell short stack prepared and tested at INL
- Excellent lab-to-lab reproducibility in performance in SOFC mode
- Modifications to test stand ongoing to enable SOEC testing
- Materials recently tested at the button cell level will be scaled to the short stack which will be subsequently shipped to INL for evaluation

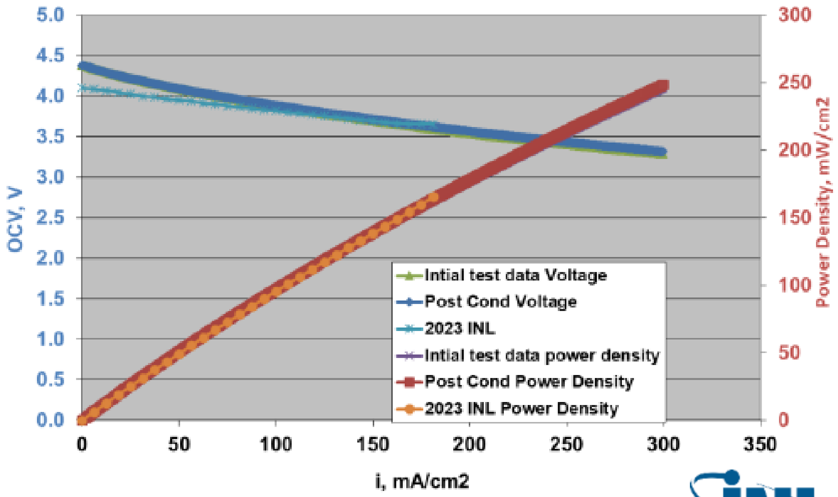
Installed Equipment

Co-sintered All-Ceramic Stack



Manifolded Stack

Test Data



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

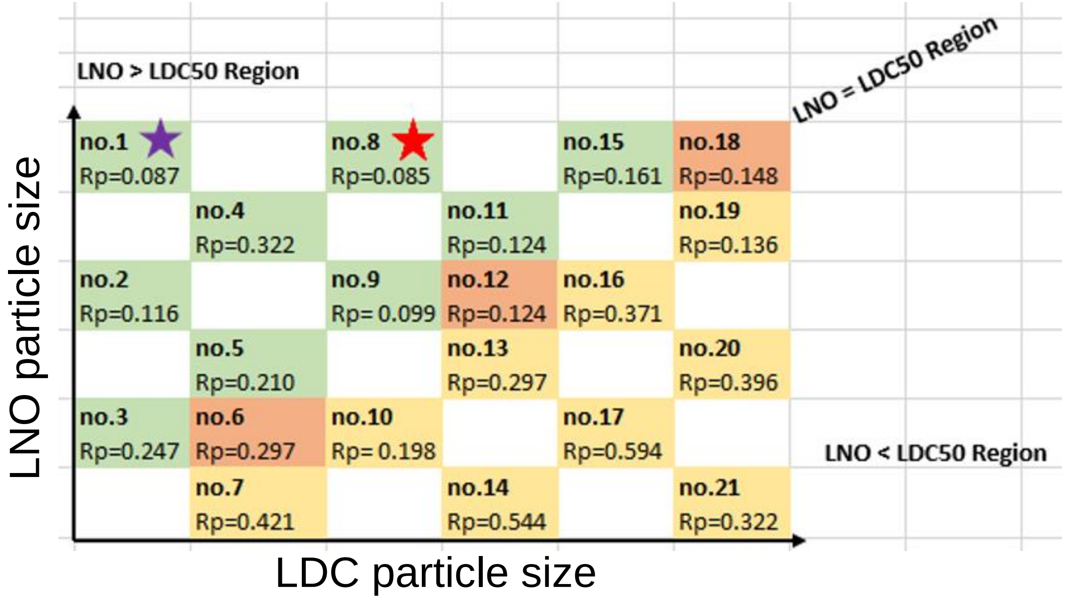
Idaho National Laboratory

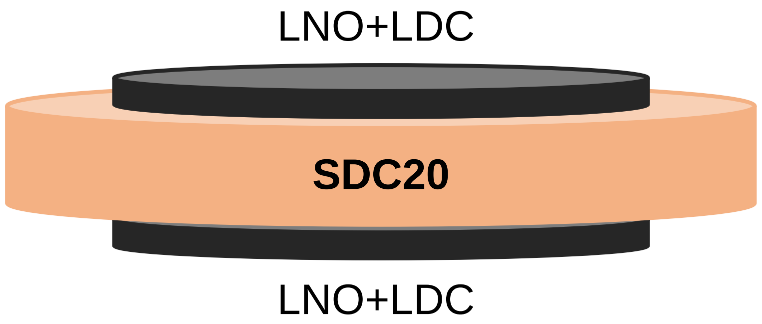
Optimization of Air Electrode Microstructure

Microstructure Optimization of Nickelate Air Electrode

Process LNO, LDC, NNO, NDC powders by milling to create a set of microstructure combinations and down-select the optimal be symmetric cell screening

- Synthesis of LNO, LDC, NNO and NDC at SG
  - ➢ **Single phase confirmed for all compositions**
- **LNO** and **LDC** powders were processed for particle size, 21 LNO+LDC combinations created in symmetric cells;
- **NNO** and **NDC** powders were processed for particle size, 21 NNO+NDC combinations created in symmetric cells;
- Tests completed, clear impact of microstructure on Rp;





Symmetric cell schematic

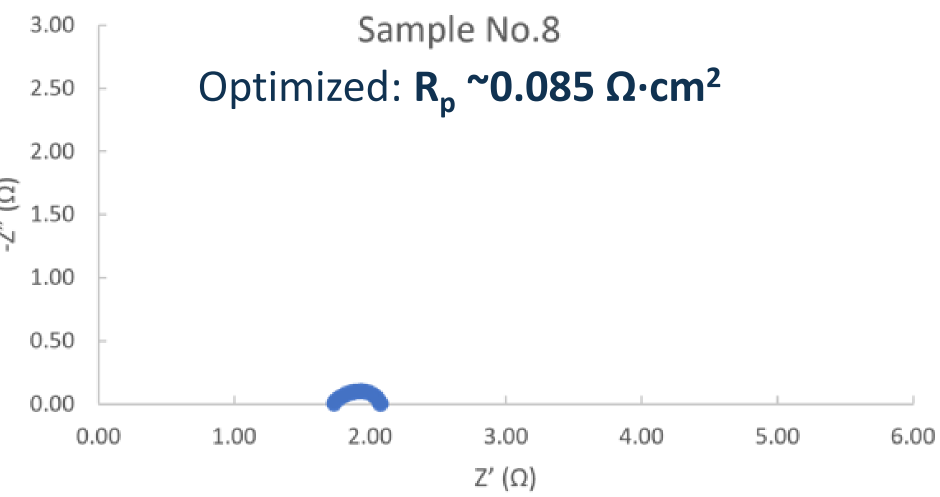
Optimized: **R_p ~0.085 Ω·cm^2**

Current BU data: **R_p ~0.240 Ω·cm^2**

Optimization of Air Electrode Microstructure – EIS

LNO + LDC

a



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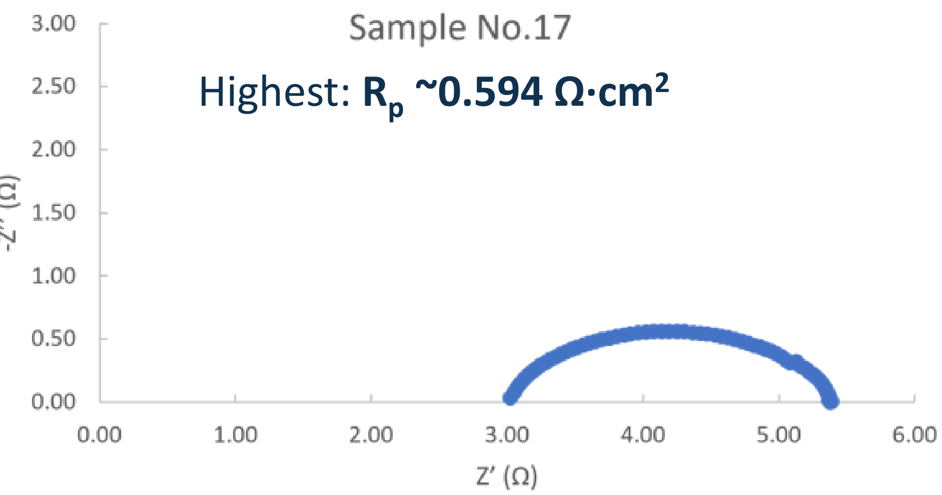

NNO + NDC

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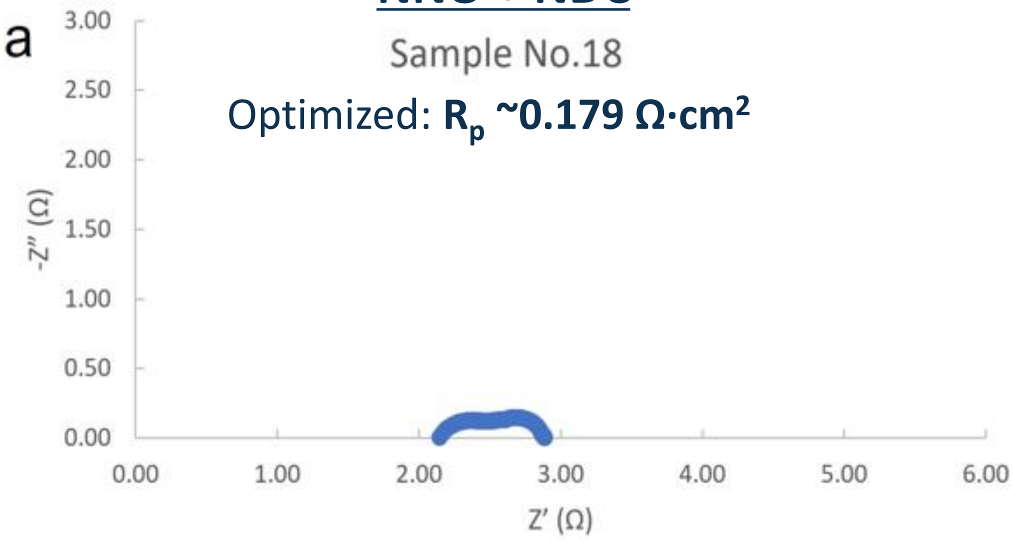

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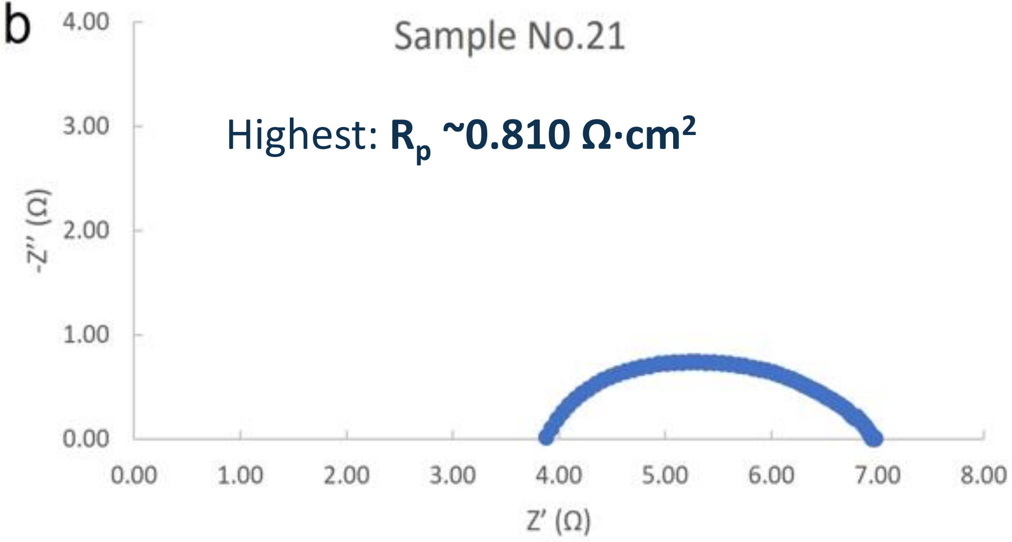


PNNL Collaboration on Cells Characterization

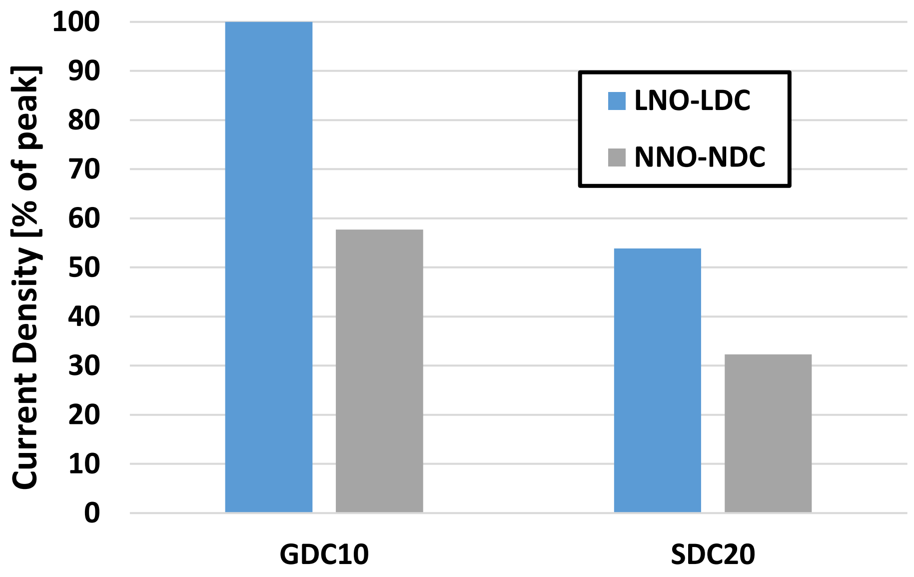
Button Cells Testing for Determining Barrier Layer

All cell components are identical except barrier layer and oxygen functional layer.

Bi-layer barrier layers:
1. SDC20+NDC50 (with NiO)
2. GDC10+NDC50 (with NiO)

Oxygen Electrode:
1. LNO+LDC50 (microstructure unoptimized)
2. NNO+NDC50 (microstructure unoptimized)

SOEC Operation: 800 ^oC in 50% H_2O-50% H_2



The results above are being used to prepare optimized cells for the final round of testing

Publications & Future Work

1) J. Banner, A. Akter, R. Wang, J. Pietras, S. Sulekar, O.A. Marina, and S. Gopalan, "Rare earth nickelate electrodes containing heavily doped ceria for reversible solid oxide fuel cells", J. Power Sources 507 (2021) 230248

2) A. Akter, J. Pietras, and S. Gopalan, "Heavily neodymium doped ceria as an effective barrier layer in solid oxide electrochemical cells", Int. J. Hydrogen Energy

Next steps

- Investigate microstructural changes occurring during operation
- Determine operational and microstructural improvements to reduce degradation rate
- Deliver a short stack containing the optimized microstructure for electrochemical testing.

Final project targets

- Demonstrate a cell operating at >1.5A/cm2 @ 1.3V, <0.75 %/1000 hr post break-in
- Demonstrate a short stack at >1.2 A/cm2 @1.3V, <1%/ 1000 hr

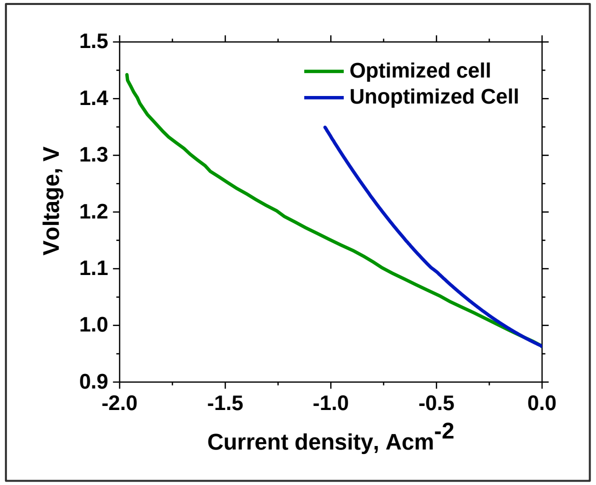
Any proposed future work is subject to change based on funding levels

Project Summary

The project is progressing well along the milestones for budget period 3 and is on track to reach the program goals.

Key Achievements

- Microstructure optimized for electrode supported button cells surpassing year 3 goals
- Uniform 5 μm barrier layer production demonstrated to be reproducible and scalable.
- Sintering kinetics modified to produce dense barrier layer during co-sintering
- No cracking due to thermal expansion mismatch has been found
- An optimal oxygen functional layer PSD (microstructure) has been identified to minimize R_p



On-going Efforts

- Stability characterization and optimization is ongoing
  - Stability during co-sintering at electrolyte-barrier layer interface
  - Stability during operation within air electrode
- Scaling to short stack underway
- B-site doping to improve performance is ongoing

Acknowledgements

- ***INL***: *D. Ding, J. O'Brien, J. Gomez*
- ***SNL***: *E. Coker, J. Sugar*
- ***BU***: *J. Banner, A. Aktar*
- ***SG***: *S. Soulekar, R. Wang, B. Oistad, X. Qian, G. Vincentelli, I. Jones, M. Sugimoto*
- **EERE**: *Dave Peterson, William Gibbons*

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