Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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

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SAINT-GOBAIN
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Project ID: p176

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Project Overview

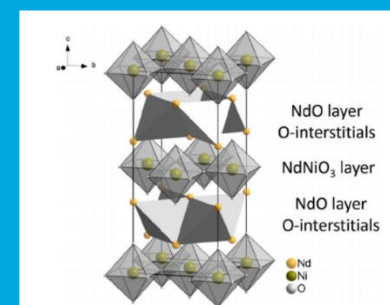
Project Partners

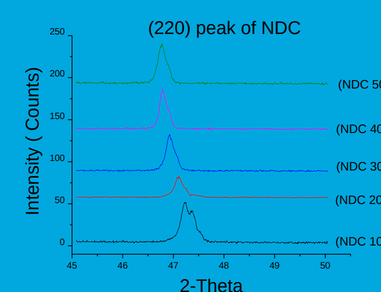
Dr. John Pietras, Saint-Gobain
Dr. Srikanth Gopalan, Boston University
Dr. Jeffry Stevenson, PNNL

Award #	EE0008377
Start/End Date	10/01/2018 – 09/31/2021
Year 1 Funding*	$0.312M

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

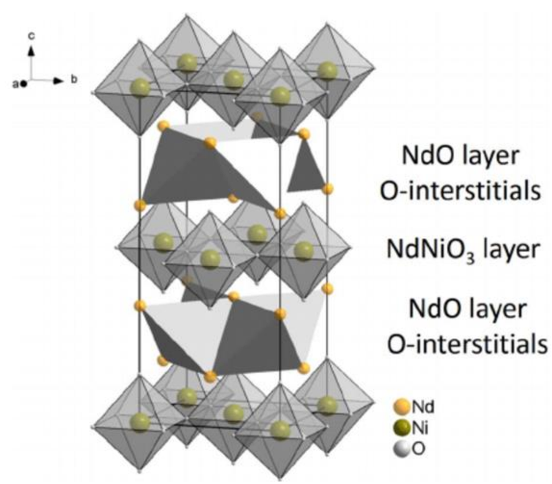
Boston University (Dr. S. Gopalan) has demonstrated stable nickelate chemistries and draws on expertise in advancing the chemistry of electrochemical devices

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

Approach- Problem Definition

The Promise: 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



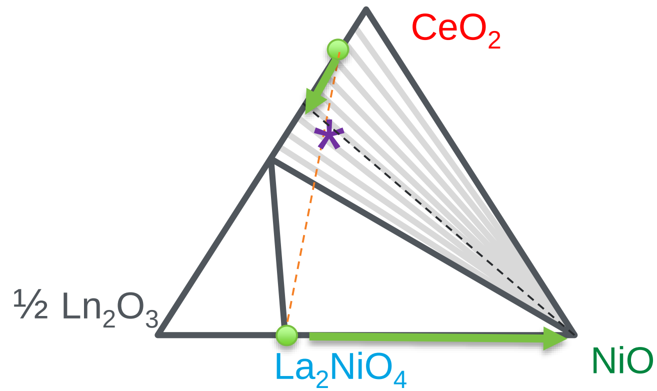
The Issue to Solve:

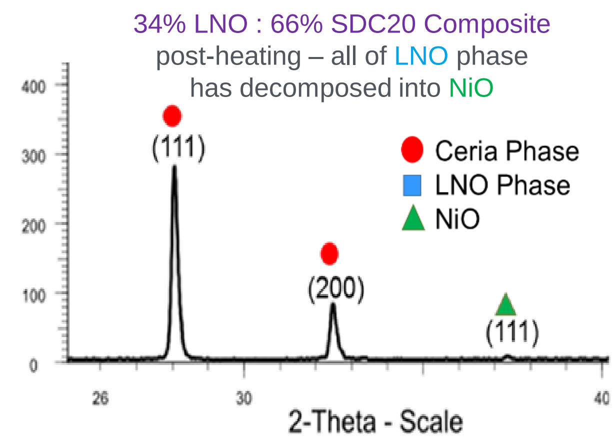
Decomposition of nickelate phase when in contact with doped Ceria

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

Resulting Ceria Phase:

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





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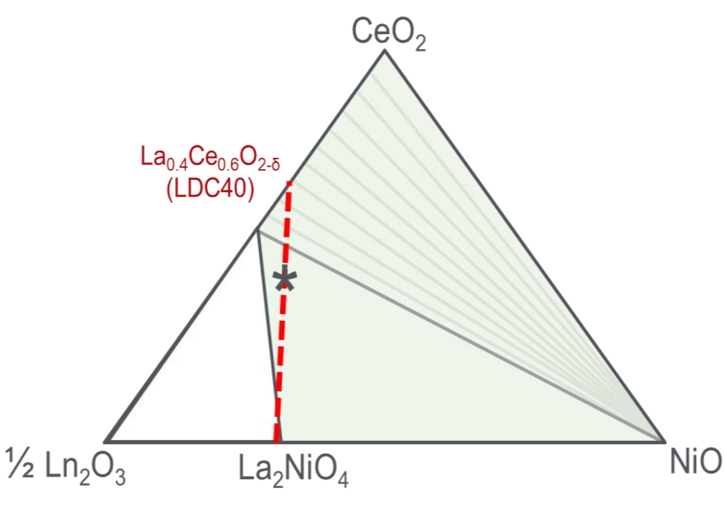
Approach- Innovative Solution

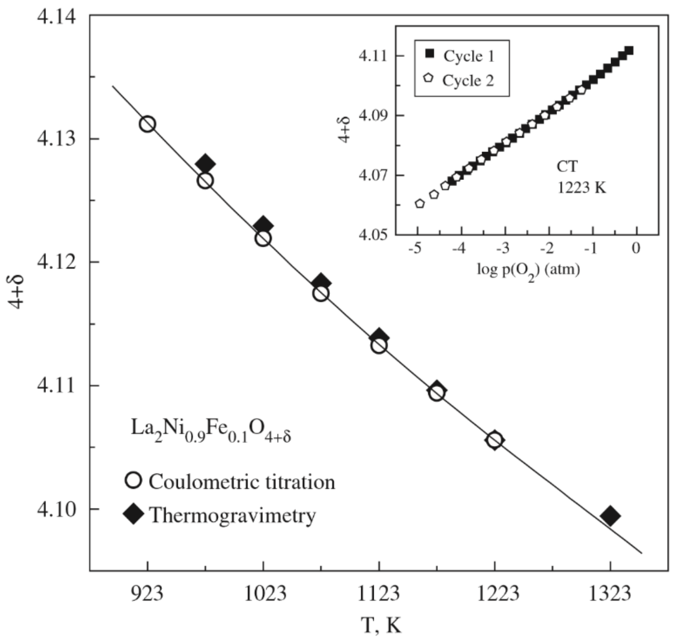
Strategy to Stabilize LNO Phase

- Push to highly doped Ceria compositions
- Operate on the pseudo-binary tie-line between LNO and the saturated ceria phase
- Synthesize material compositions and utilize XRD to establish phase purity of end compounds
- Create mixtures and heat treat followed with XRD to ensure stability during sintering and operation



Strategy to Maximize Performance

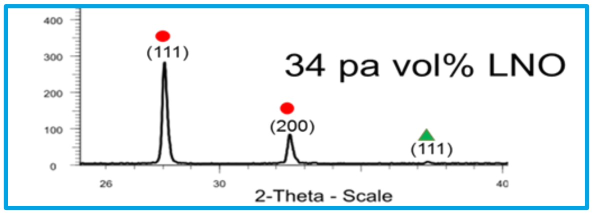
- Utilize Coulometric titration and thermogravimetry to quantify degree of hyperstoichiometry
- Down-select compositions based on stability and hyperstoichiometry for cell testing in SOEC and SOFC modes

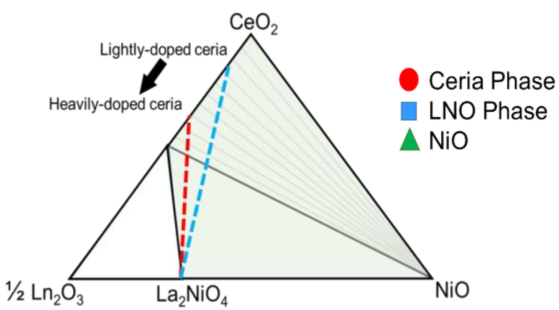


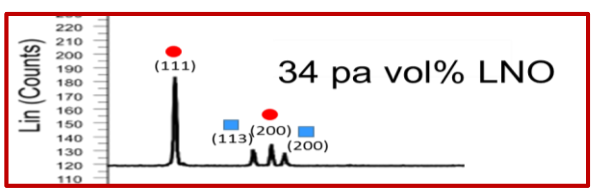
Approach – Building on Past Success

Maximize performance by extending to 3 dopant systems (La, Sm, Nd)

Previous work showed heavily doping ceria can prevent NiO formation





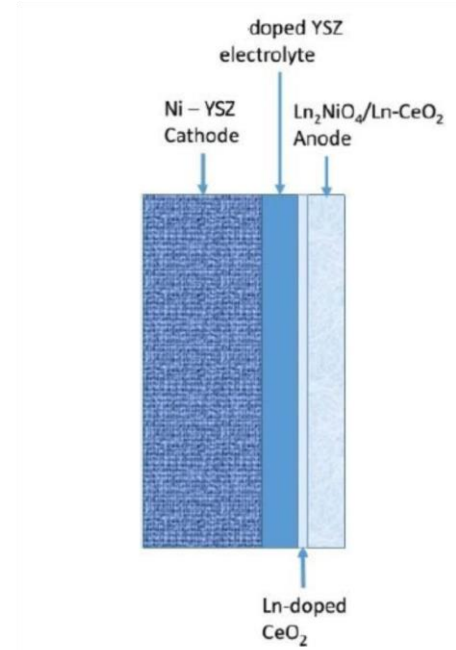


This project will extend to several dopant systems for both nickelate and ceria phases

Electrocatalyst	Ionic conductor
La2NiO4 (LNO)	La-doped CeO2 (LDC)
Sm2NiO4 (SNO)	Sm-doped CeO2 (SDC)
Nd2NiO4 (NNO)	Nd-doped CeO2 (NDC)

Proposed SOEC Cell Architecture

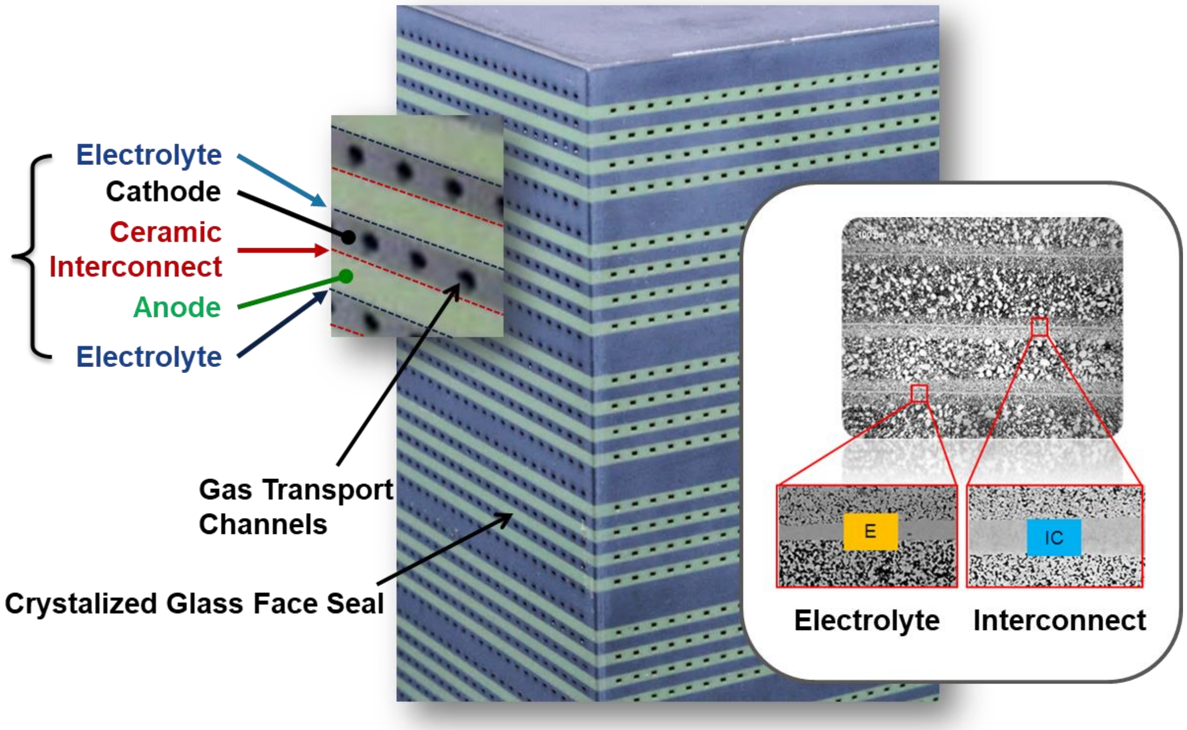
- Mn and/or Ce doped YSZ electrolyte
- Thin layer of heavily Ln-doped CeO_2 (high electronic resistance)
- Composite Ln_2NiO_4 anode with the same heavily Ln-doped CeO_2 as in the thin layer as the ionic conducting phase
- Buffers CTE and effective anode

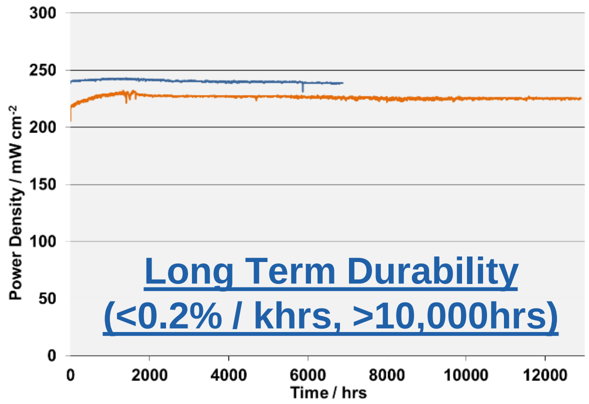


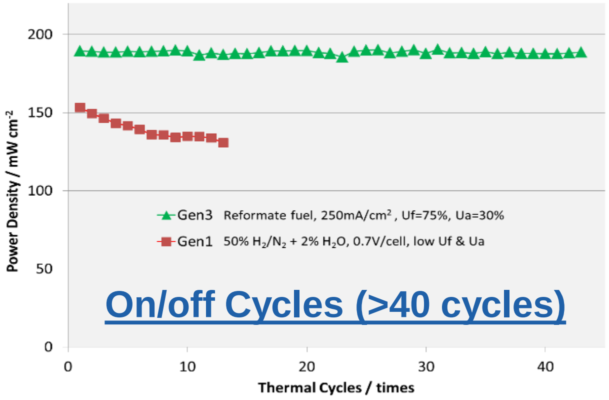
Approach – Utilize Stable Stack Design

All-ceramic stack technology has been developed for SOFC operation

- Leverage Saint-Gobain's extremely durable all-ceramic SOFC stack
- Co-sintering multiple repeat units has been proven and demonstrates very low degradation
- Replace air-side electrode with newly developed compositions tuned for SOEC







Approach- Scope of Work

Budget Period 1 Scope of Work

- Synthesize and characterize proposed materials which satisfy the target properties
- Develop the degradation analysis platform
- Analyze button cells for performance and durability
- Identify key material properties leading to degradation
- Identify top material sets for short stack integration in budget period 2

Today

	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 $<1\times10^{-8}$ $mbarL^{-1}cm^{-2}$						M						
M2.2: Degradation mechanisms confirmed and accelerated testing developed											M	
Go/No-Go Decision Point (Phase I)												G1

Relevance & 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.

Relevance & Impact

Contributions to the project via utilization of the HydroGEN national lab nodes

Materials Development

- **Quantification of hyperstoichiometry (SNL)** – important for both durability and performance, this is a key metric to understand how the novel materials react to changing oxygen partial pressure
- **Measurement of thermal and chemical expansion (INL)** – physical length change mismatch between cell components leads to stress and if too great, can create internal cracks leading to premature failure. Compatibility is required during sintering, heat and cooling, and during operation when the partial pressure of oxygen can change by several orders of magnitude

Degradation Analysis

- **CT Scanning (INL)** – the prevention of electrode delamination is a key component to this project. The non-destructive ability of CT scanning to sample the entire button cell will be critical to evaluating the successful implementation of the mitigation strategy
- **Consultation (INL & SNL)** – in-depth data interpretation will enable the team to react to project results and greatly increase the odds of success. The background brought by the members of the HydroGEN nodes will provide experienced sounding board throughout the project

Priority	Node	Work	Comment
1	INL – Adv. Electr. Dong Ding	Chemical expansion measurement of new materials on sintered bars at isothermal temperature of 800°C as PO_2 varies from 1 atm to 10^{-5} atm	Critical & Unique
2	SNL-High-Temp XRD Eric Coker	High temperature XRD in controlled atmosphere at nominally 800°C to investigate the oxygen hyperstoichiometry of novel materials	Critical & Unique
3	INL – Electrochem James O-Brien	CT scan of as-tested cells looking for signatures of degradation including delamination of electrode from electrolyte	Critical & Unique
4	INL – Adv. Electr. Dong Ding	Thermal expansion measurement of new materials on sintered bars at temperatures from RT to 1400°C	Critical
5	INL – Electrochem James O-Brien	Consultation regarding interpretation of results with regard to existing degradation model	Critical

Relevance & Impact

Enhancement of the broader HydroGEN Consortium

- The development of accelerated degradation profiles can be utilized by other research teams
- Protocols developed to link CT scans of as-tested button cells to durability measurements will be published – these can be utilized by other research teams in the future

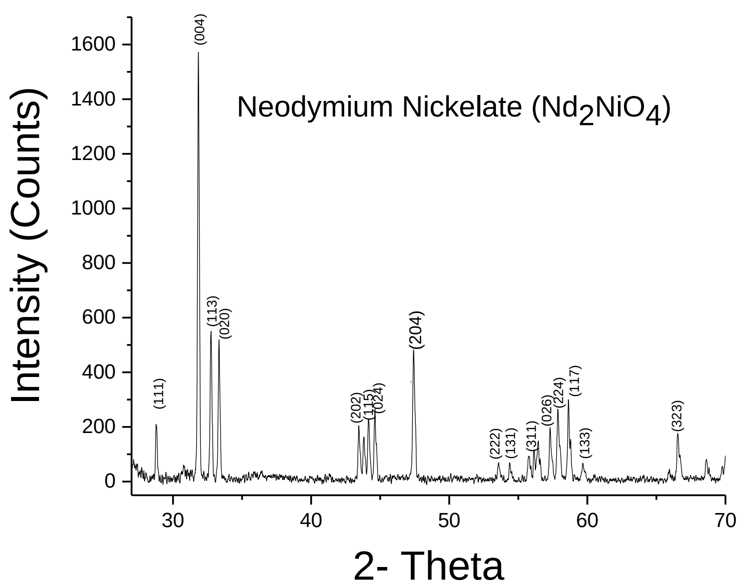
Other types of resources currently not in the HydroGEN Consortium might be valuable to your research area

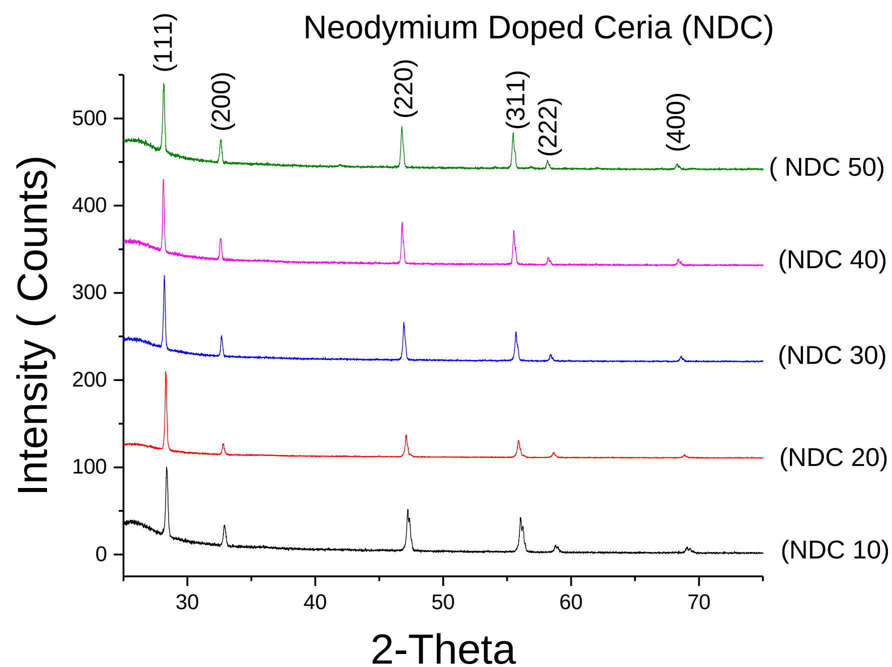
- SOEC testing under pressurized operation conditions – would allow the quantification of performance improvement that can be expected and thus lead to a reduction in material usage and total system cost

Accomplishments

During the 1st quarter of the program the powder synthesis process has been successfully designed

- Synthesis of Neodymium Nickelate (Nd_2NiO_4) and Neodymium Doped Ceria (NDC) by solid state reactions as evidenced by XRD
- 10-50 mol% neodymium was doped into the ceria
- XRD of the NDC powders confirms the fluorite crystal structure even in highly doped ceria

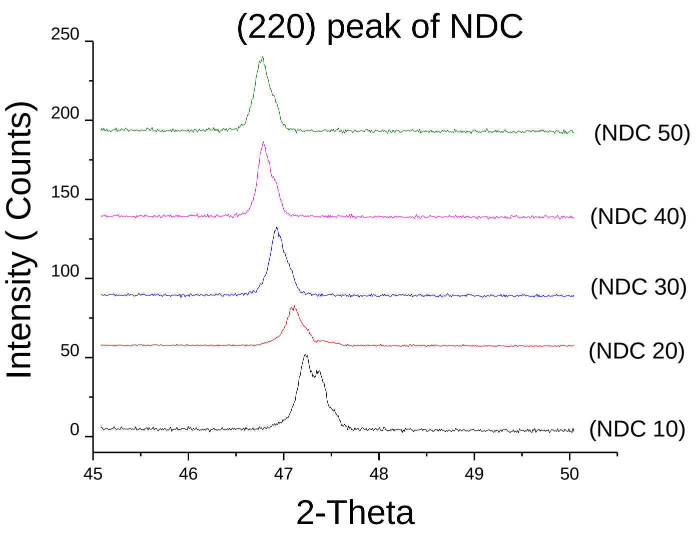


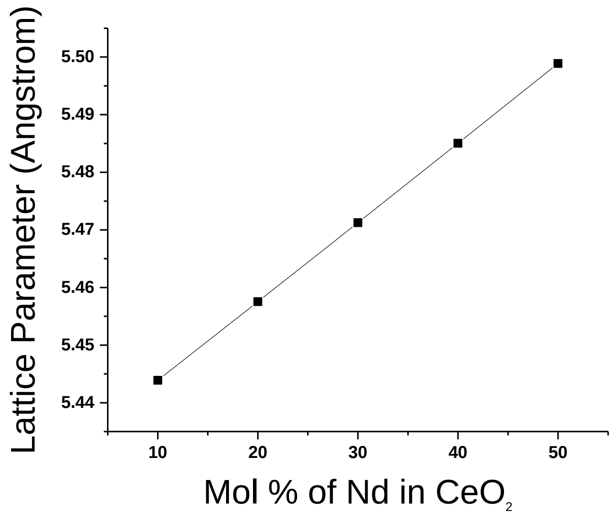


Accomplishments

XRD peak shift was measured to be directly proportional to mol% Nd

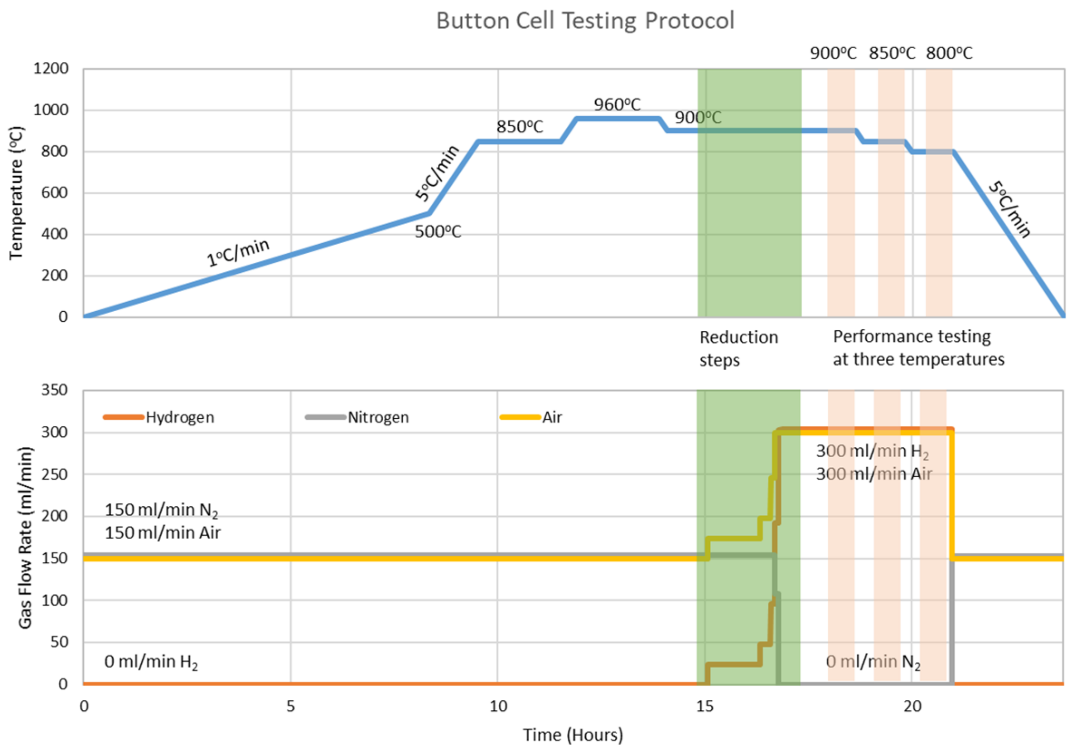
- Further investigation of the NDC XRD patterns reveals peak shifting
- Peak shift indicates the increase of the lattice parameter with increasing dopant concentration
- Replacement of smaller Ce^{4+} ions with the larger Nd^{3+} ions (the ionic radii of Ce^{4+} and Nd^{+3} are 0.97 and 1.1053 Å respectively) leads to the cubic ceria lattice expansion.





Accomplishments

Button cell testing protocol developed and baseline button cells prepared



- Button cell testing planned at varying temperatures: 900ºC, 850ºC, and 800ºC.
- Varying the current density for the 6 cells (two replicates at each condition)
  - LSM (6 cells)
  - LNO (6 cells)

Accomplishments – (Oct '18 through Feb '19)

On schedule to meet project objectives through 1.5 quarters

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 complete, others started
M1.2	Identification of stability boundaries	8	• Decomposition free regions determined for nickelate-ceria mixtures	• Work started
M1.3	Determine top 3 composites	12	• >96 S/cm @800C • Oxygen exchange coefficient 1.2×10^{-5} cm/s • Maps of oxygen nonstoichiometry f(T, PO2)	• Planned to start Q3
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
M2.1	Accelerated testing	11	• Baseline degradation rate established in accelerated testing • Degradation mode identified microstructurally	• Planned to start Q3
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	• End Q4

Analysis of Risks Remaining

Phase stability/performance (Boston University)

Medium: Good initial progress achieved, working through compositions and characterizing performance

Co-sintering (Saint-Gobain)

Medium: Previous successful experience with LNO suggests porosity, activity, defect free microstructure are achievable

Accelerated testing (PNNL)

Low: Major degradation mechanisms proposed in literature and testing protocol discussed

Collaboration: Effectiveness

Collaboration with EMN project node experts

- Monthly conference calls scheduled with the full team including EMN project node experts
- Discussions with team at INL (James O'Brian, Dong Ding, Hanping Ding) have refined post-testing analysis plan including CT scanning of button cells; as-prepared cells sent in March as baseline
- 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

Interactions with the HydroGEN research community

- Major interaction thus far was at the initial kickoff meeting in Sept
- As the team moves into cell testing during Q3, discussion with the protocol team will be critical to ensure comparable data sets across HydroGEN working groups.
- Use of the data hub will ease collaboration and provide a repository for the team

Collaboration: Effectiveness

A common sample preparation and testing protocol can be devised to get comparable results between the different organizations

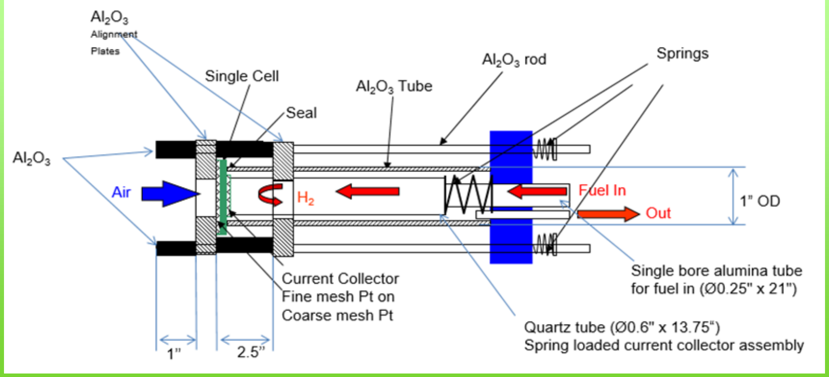
Minor points that still need to be resolved are:

- Sample dimensions and active area
- Current collector used

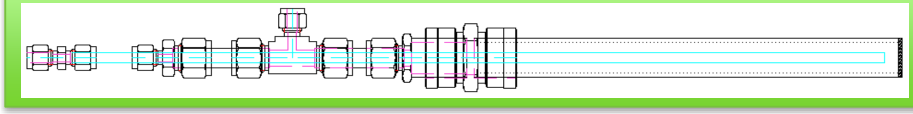
Comparison of Test Rigs

Team	SG	BU	INL	PNNL
Gases	H_2, N_2, Air	H_2, N_2, Air	H_2, N_2, Air	H_2, N_2, Air
Seal	Mica gasket, glass sealant (in-situ 900°C curing)	Mica gasket, glass sealant (in-situ 900°C curing)	Ceramic sealant (dried at room temperature)	Ceramic sealant (dried at room temperature)
Anode	Pt paste/mesh (100°C drying; spring load in-situ to improve contact resistance)	Ni paste/mesh (700°C curing; load to improve contact resistance)	Ni paste/mesh	Ni paste/mesh (Dried at 80°C and cured at 1200/1100/1000°C)
Cathode	Pt paste/mesh (100°C drying; spring load in-situ to improve contact resistance)	Ag paste/mesh (700°C curing; load to improve contact resistance)	Ag paste/mesh	Au paste/mesh (Dried at 80°C and cured at 875°C in air)
Button Cell - Active Area	2.85 cm^2 (equal to cell diameter)	2 cm^2 (dictated by small cathode)	1.26 cm^2 (dictated by small cathode)	Area as per cathode size

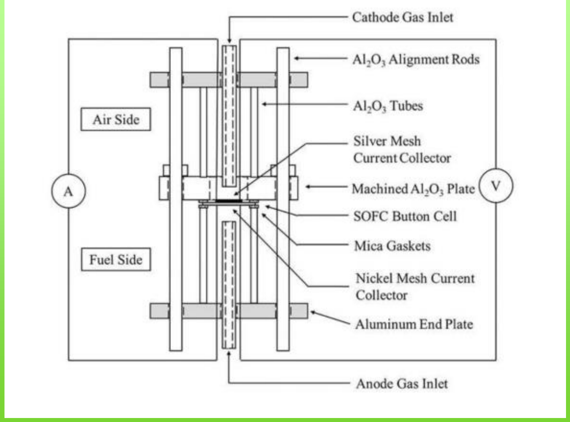
Schematic of the all alumina button cell test stand used at SG



Schematic of the button cell test stand used at INL



Schematic of the button cell test stand used at BU



Proposed Future Work

Budget Period 2 ($479k funding proposed)

- Button cell fabrication and testing of top candidates identified in BP1
- Optimization of stoichiometry and sintering conditions to maximize performance and minimize degradation
- Down selection of electrode compositions for integration into short stacks
- Initial short stack performance and durability testing

Budget Period 3 ($238k funding proposed)

- Stack production of top performing candidate
- Stack testing under pressurized conditions
- SOEC performance and durability testing at stack level
- Production cost and sensitivity analysis

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

Project Summary

- The nickelate family of materials has a potential for high performance in SOEC operation due to its open structure
- This open structure can also solve the electrode delamination problem clearly identified in the literature by its ability to hold oxygen ions
- The use of these materials is limited due to its reactivity and subsequent decomposition when in contact with ceria
- A solution to the decomposition problem has been identified and is the root of this program

- Stable nickelate-doped ceria composites will be prepared as air electrodes in co-sintered button cells
- These button cells will be tested for SOEC performance and durability utilizing an accelerated testing protocol
- As-prepared and as-tested button cells will be analyzed to confirm the degradation mechanism and degree of degradation compared to the state of the art

Publications & Presentations

No publications or presentations through the first 4 months of the project