
HydroGEN Seedling: Development of Durable Materials for Cost-Effective Advanced Water Splitting Utilizing All Ceramic Solid Oxide Electrolyzer Stack Technology

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- PNNL, Richland WA

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Project End Date: September 30, 2019

Overall Objectives

- Develop a fundamental understanding of performance degradation and electrode delamination in nickelate based solid oxide electrolysis cell (SOEC) materials and interfaces.
- Develop compositions addressing this degradation while meeting specific performance targets:
 - ASR ≤ 0.30 ohm-cm²
 - Current density > 1 A/cm² at 1.4V
 - Stack electrical efficiency $> 95\%$ LHV H₂
 - Stack lifetime ≥ 7 years.

Fiscal Year (FY) 2019 Objectives

- Synthesize and characterize proposed materials that satisfy the target properties.
- Develop the degradation analysis platform.
- Identify decomposition-free regions determined for nickelate-ceria mixtures.

- 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.
- Demonstrate 25% higher electrolyzer current density @ 1.4V than baseline LSM-YSZ.
- Demonstrate well-adhered layers after 2 weeks of operation.
- Demonstrate a degradation rate of $< 1.5\%$ /1000 h.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (L) Operations and Maintenance
- (G) System Efficiency and Electricity Cost.

Technical Targets

This project is investigating novel air electrodes in the rare-earth nickelate system. These nickelates promise improved performance and thus system efficiencies if their reactivity with other cell components can be eliminated. Solutions to these issues in combination with the all-ceramic stack design can lead toward meeting the future DOE hydrogen production targets with the following metrics:

- Cost: \$4/kWh net
- Specific energy: 1.5 kWh/kg
- SOEC stack degradation rate of 0.25%/1,000 h.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

FY 2019 Accomplishments

- Synthesized phase pure Neodymium Nickelate (NNO) and Lanthanum Nickelate (LNO) (Nd_2NiO_4), (La_2NiO_4).
- Synthesized and determined solubility limit of corresponding Neodymium and Lanthanum doped ceria (NDC, LDC).
- Proved Nickelates do not decompose when in contact with heavily doped ceria.

INTRODUCTION

High oxygen pressure at the electrolyte-electrode interface has been identified in the literature as a major cause of degradation within SOEC. The build-up of oxygen pressure can be mitigated by incorporating materials with high oxygen hyperstoichiometries close to the electrolyte-anode interface, thus providing a path for oxygen diffusion throughout the three-dimensional network of the electrode and minimizing delamination. This project will develop a high-temperature electrolysis technology that combines a new anode material with a novel all-ceramic stack design.

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 to meet specific performance targets: ASR ≤ 0.30 ohm-cm², current density $> 1\text{A}/\text{cm}^2$ at 1.4 V, stack electrical efficiency $> 95\%$ LHV H₂, and stack lifetime ≥ 7 years. Specific objectives are to optimize material stoichiometry and to demonstrate their capability in SOEC cells and stacks through modeling, fabrication, and testing of an all-ceramic stack architecture. A major innovation and key to the project's effort is the identification and development of nickelate-based materials with high oxygen hyper stoichiometries for the anode in solid oxide electrolysis cells (SOECs) in an effort to prevent degradation modes associated with the build-up of oxygen partial pressure at the electrolyte-electrode interface.

APPROACH

The use of nickelate-based materials has been limited due to their strong reactions with electrolyte materials such as ceria. The diffusion of the rare-earth into the ceria phase at processing and operation temperatures decomposes the nickelate into nickel oxide, thus creating inactive and resistive phases on the surface of the material. The project focuses on stabilizing this material set through stoichiometry control in the doped ceria layer. The use of a heavily doped ceria barrier layer between the anode and electrolyte will be investigated to reduce reactivity and increase the electronic transfer resistance at this interface, which should lead to improved cell durability and performance.

In addition, the nickelate-based materials that will be investigated in this project have the ability to incorporate more oxygen (i.e., oxygen hyperstoichiometry) than conventional perovskite cathodes such as LSM and LSCF. Accommodation of oxygen hyperstoichiometries close to the electrolyte-anode interface will increase anode stability by mitigating the build-up of oxygen pressure. Understanding the factors that govern this stability will provide critical insights into their use as hydrogen production materials, and their ability to drive long-term performance and cost reductions.

RESULTS

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. As such, the project has focused on three main tasks: (1) the synthesis and stabilization of phase pure nickelate and ceria compositions, (2) the fundamental analysis of these materials in terms of potential for electrochemical performance and compatibility with co-sintering within an all-ceramic stack, and (3) the production and testing of button cells in SOEC mode.

Synthesis and stabilization

Three cations were investigated in this study: La, Nd, Sm for incorporation into the nickelate and ceria materials. It was found that phase pure compositions could be synthesized by mixed oxide calcination of both

the La and Nd families but not the Sm family. Neodymium is shown as an example case with the phase purity and the resulting lattice parameter shift is shown in Figure 1. A critical point from this work is to note that up to 50% Nd can be incorporated into the ceria lattice while maintaining the fluorite structure. As such, the 50% Nd-doped ceria (designated 50NDC) was used during the stabilization testing.

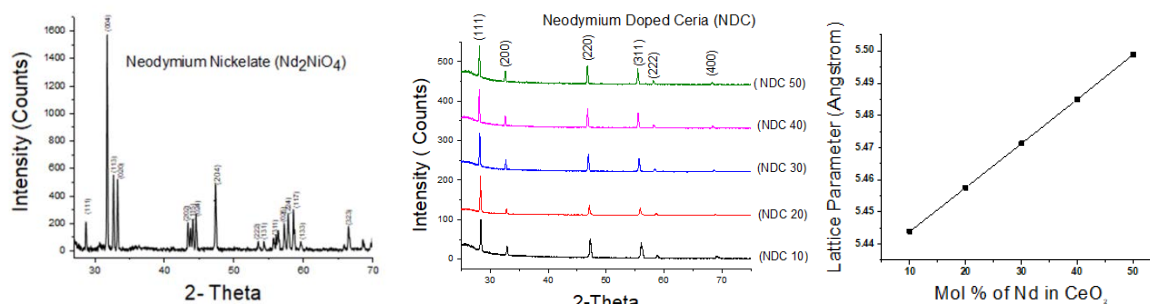


Figure 1. Phase purity of synthesized (left) neodymium nickelate, (center) neodymium-doped ceria, and (right) the change in lattice parameter for ceria as a function dopant level.

To minimize the potential for interaction with the corresponding nickelate, researchers used 50 mol % ceria as the high dopant level in mixed powder experiments. Figure 2 shows the effect of calcining neodymium nickelate with both (a) 20 mol % doped ceria and (b) 50 mol % doped ceria. When ceria with a low neodymium content was mixed and then calcined with NNO, the nickelate phase was consumed by the ceria, as evidenced by the lack of NNO peaks at $45^\circ 2\theta$ in the XRD trace taken after calcination. In contrast, Figure 2b shows that 50 mol % Nd in ceria is enough to prevent decomposition of the NNO phase. This result confirms the hypothesis of the project and allows the creation of both a mixed NNO/NDC air electrode and the use of an NDC barrier layer between the air electrode and the electrolyte. These results were duplicated in the lanthanum nickelate/lanthanum doped ceria system.

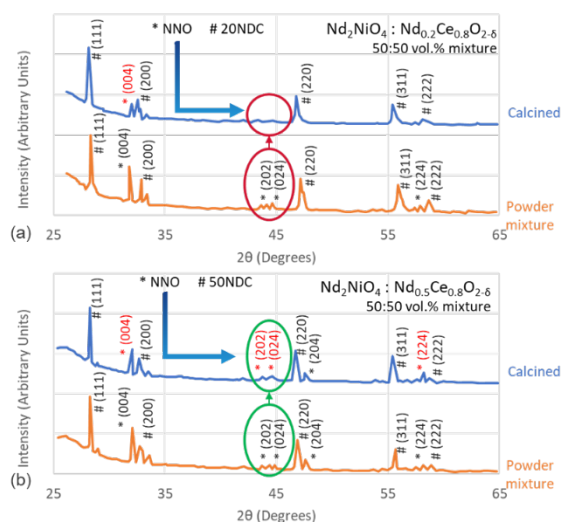


Figure 2. Effect of dopant concentration in ceria on the ability to maintain NNO phase.

Material Characterization

Another goal of this project is to characterize various nickelate compositions in order to predict their performance in button cell testing. It is hypothesized that the degree of oxygen hyperstoichiometry in the nickelate phase will be proportional to both the performance and durability of the cell. This is due to the ability of the material to quickly move oxygen ions from the electrolyte out to the electrocatalytic surfaces within the three-dimensional network of the porous electrode. In addition, the oxygen exchange coefficient for the

materials is to be measured as another indication of potential electrolysis performance. Figure 3 shows examples of (a) electrical conductivity relaxation and (b) oxygen uptake for NNO and LNO. Characterization of LNO and NNO bar samples using electrical conductivity relaxation is currently ongoing. Figure 3a shows the normalized conductivity transient of an NNO bar when the gas composition is changed from air (21% O₂, balance N₂) to 5% O₂, balance N₂ gas and vice versa. Note that normalized electrical conductivity is defined as $(\sigma_t - \sigma_0) / (\sigma_\infty - \sigma_0)$ where the subscripts t, 0, and ∞ refer to conductivities at time t, initial conductivity, and time after conductivity stabilization. In this experiment, the sample is equilibrated at an initial gas composition (say air) and suddenly changed at time t = 0 to a different composition (5% O₂, balance N₂) and the electrical conductivity is tracked as a function of time, and plotted as normalized conductivity. As can be seen from NNO, the transient in an oxidizing direction (relevant to the oxygen electrode functioning as an anode) is more rapid than the transient in the reducing direction (relevant to the oxygen electrode functioning as a cathode). Work is continuing in the analysis many such transients to obtain fits to the oxygen exchange coefficient in oxidizing and reducing directions. These will later be correlated with cell test results.

With the base stoichiometry identified after pre-reduction, the change in stoichiometry with pO₂ can be calculated from the weight loss. Figure 3b shows the oxygen stoichiometry map for both LNO and NNO at 800°C, after initial pre-reduction. Specimens were pre-reduced (5% H₂) to a stoichiometric starting point, then exposed to increasing p(O₂) for 30 minutes each. Oxidation was done in an O₂ + Ar mixture where UHP Ar was passed through a getter furnace upstream of TGA. There is a large, fast uptake of oxygen going from 0 Torr O₂ to 6.3 Torr O₂. After this point, there is a gradual change with no discernible change steps between 6.3 Torr O₂ and 598.5 Torr O₂. When the pO₂ is dropped again to 0 Torr, there is a rapid ejection of some of the gained oxygen. The respective stoichiometry of the nickelates at different points are indicated in the figure. This data indicates that both LNO and NNO are stable up to 598 Torr (0.79 atm). Although the exact range of oxygen over-pressure at the electrode-electrolyte interface is not known, both NNO and LNO show significant improvement over LSM and are good potential replacements, pending further investigation. In either case, a prudent strategy would be to improve oxygen removal rates from the air side. This initial information suggests that NNO will outperform LNO during button cell operation.

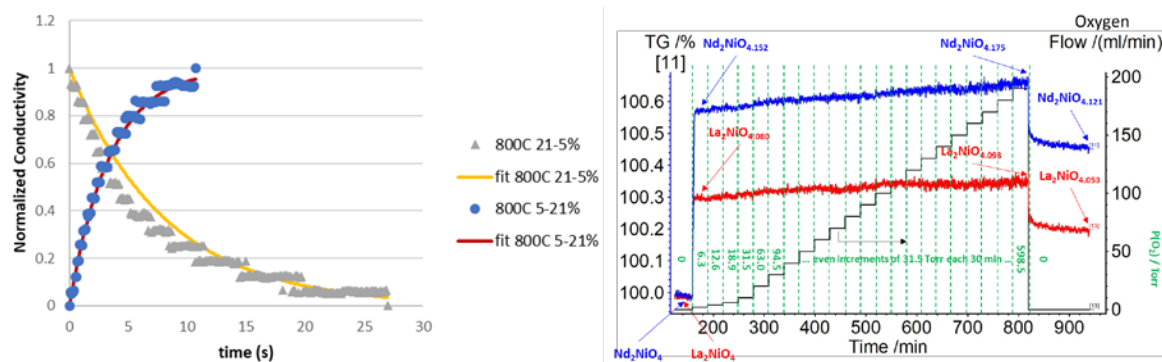


Figure 3. (left) electrical conductivity relaxation results for NNO in oxidizing and reducing directions, (right) increase in weight as a function of PO₂ for NNO and LNO.

In addition to these measurements, the candidate material sets are in the process of being evaluated for:

- Chemical expansion tests on bar samples
- Decomposition conditions and products
- Thermal and chemical expansion
- Sintering rate.

Button Cell Testing

Button cells were prepared using both the baseline electrode material, LSM, and the newly developed nickelate/ceria electrode. The new materials required optimization of the tape casting procedure as the surface

characteristics, and thus the disposability was different than the baseline LSM materials. Solutions to the dispersion issue were developed, and adequate tapes were cast of both ceria and nickelate/ceria mixtures. These tapes were co-sintered under similar conditions as the baseline LSM cells, and the microstructure was evaluated. Microstructural analysis showed there were no cracks or delamination caused by replacing the baseline electrode with the new electrode. This finding indicates a good match of both sintering rates and thermal expansion. There were undesirable agglomerates present in the new material sets, so these were not initially electrochemically evaluated. Further optimization of the microstructure is under development, which will be followed by electrochemical evaluation.

Electrochemical testing rigs for the button cells were established in three laboratories (Boston University [BU], Saint-Gobain [SG], and Pacific Northwest National Laboratory [PNNL]). Set-up and testing protocols were discussed and standardized before conducting a round-robin testing on SGs baseline co-sintered (LSM oxygen electrode) button cells. The results of the electrochemical testing are given in Figure 4. Similar behavior trends were observed at the three laboratories. At 1.1 V, the cells tested at SG and PNNL have a current density of 0.53 A/cm² and 0.47 A/cm², whereas the cell tested at BU shows lower performance at 0.32 A/cm². The open cell voltages for the cells match well, and the differences between behavior are probably due to slight differences in the test setups. Work is underway to narrow these differences further. However, this data sufficiently establishes the performance of SG baseline cells in SOEC mode. The next steps will include performance and long term testing of the newly developed material sets.

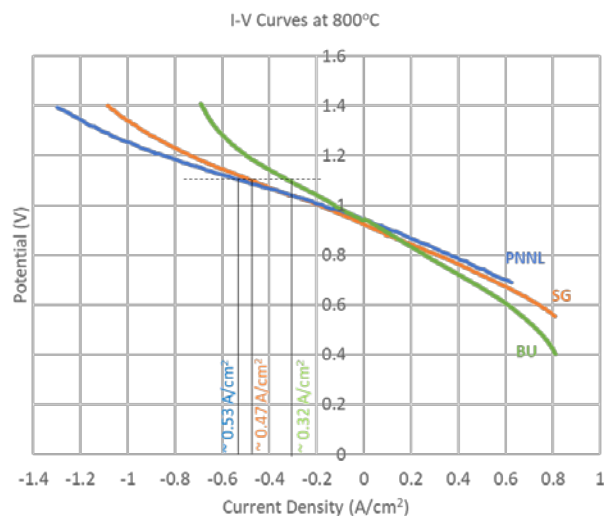


Figure 4. Electrochemical testing results of identical button cells performed at SG, BU, and PNNL.

Interaction with Nodes

The team functioned well by incorporating expertise at various nodes (Idaho National Laboratory [INL], PNNL, and Sandia National Laboratory [SNL]). These interactions took place during the analysis of results and planning for the next steps throughout the year, and the node representatives were incorporated as full team members. The only shortcoming was the lack of electrochemical testing availability at PNNL due to issues in recommissioning the testing lab. This process took the better part of the year due to the nature of the incident and additional safety precautions implemented. The team was able to respond by setting up a test stand at SG to be used until the work was completed at PNNL. A short summary of node analysis follows:

- INL: coefficient of thermal expansion of sintered bars
- INL: chemical expansion on sintered bars
- INL: button cell microstructure evaluation through CT scan

- SNL: thermogravimetric analysis and differential scanning calorimetry measurements on powder as a function of PO₂
- PNNL: button cell testing in solid oxide fuel cell and SOEC modes, both short term and long term.

CONCLUSIONS AND UPCOMING ACTIVITIES

The work in this period focused on the first two major barriers within the project, (1) phase stability of nickelates/ceria mixtures and (2) co-sintering of newly developed materials. If funded, the next budget period will focus on:

- Button cell fabrication and testing of top candidates identified in BP1
- Engage with additional Nodes for modeling support
- Additional focus on potential interfacial reactions
- 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.