22\textsuperscript{nd} Annual Project Review Meeting

DE-FE0031972

Reversible SOFC-SOEC Stacks Based on Stable Rare-Earth Nickelate Oxygen Electrodes

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MAKING THE WORLD A BETTER HOME

SAINT-GOBAIN
DE-FE0031972: TECHNICAL STRENGTHS AND BACKGROUND
SAINT-GOBAIN & SOFC PROJECT SUMMARY

Worldwide Footprint
- 2020 Turnover: €38bn
- Operations in 67 COUNTRIES
- Over 170,000 EMPLOYEES

Innovative & Reliable Stack Technology
- All-ceramic stack
  - 10+ year lifetime
- Operational simplicity
  - Modular design
- Recognized Supplier
  - Industrialization

Culture of Innovation: 350 Years of Growth

History of Collaboration

One of the world’s 100 most innovative companies*
*Source: Thomson Reuters

SGR NORTH AMERICA • CRL • CERAMIC PROCESSING
**SOEC BACKGROUND: SUCCESSFUL EERE FUNDED SEEDLING PROJECT**
DE-EE0008377: DEVELOPMENT OF DURABLE MATERIALS FOR COST EFFECTIVE ADVANCED WATER SPLITTING

**Leverage Strengths**

**Core Competencies**

Businesses built around tailoring powder properties and scaling to production at industrial quantities

**High Potential Material Set**

**Performance Potential of Nickelates** \((\text{Ln}_2\text{NiO}_4)\)

- Open alternating crystal structure provides a large number of oxygen interstitial sites
- Oxygen exchange and transport is greater than state-of-the-art perovskite oxides
- Potential to avoid degradation due to voids and cracks which typically form during operation

**Issue To Be Solved**

**Material Decomposition**

- Decomposition of nickelate phase when in contact with Ceria

\[
\text{La}_2\text{NiO}_4 \rightarrow x \text{La}_0.15 + 0.5x \text{NiO}
\]

Resulting Ceria Phase: \(\text{La}_{3}\text{Sm}_{0.25}\text{Ce}_{0.75}\text{O}_{2+\frac{4}{2}}\)

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Stabilization Achieved

Stabilized LNO in presence of Ceria

La$_2$NiO$_4$ retention

Co-Sintering Developed

Incorporated nickleate within co-sintered cells

SOFC structure
- LSM O$_2$ Electrode
- LSM O$_2$ Functional Layer
- 8YSZ Electrolyte
- Ni-YSZ Fuel Functional Layer
- Ni-YSZ Fuel Electrode

SOEC structure
- LSM O$_2$ Electrode
- LNO-LDC O$_2$ Functional Layer
- 8YSZ Electrolyte
- Ni-YSZ Fuel Functional Layer
- Ni-YSZ Fuel Electrode

Microstructure achieved

Functional Layer

Barrier Layer

Electrolyte

SOEC Performance Enhancement

Performance Improvement

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

SOEC

SDFC

Current Density (A/cm$^2$)

Voltage (V)
Stack designs can be grouped by the thickest layer of an individual cell and how they are connected into a stack.

Commonalities to be studied:
- Utilize the novel air electrode
- High humidity at fuel electrode
- Interconnect Metal or Ceramic

Stack Supported
- Air Electrode
- Electrolyte
- Fuel Electrode
- Ceramic Interconnect

Anode Supported
- Air Electrode
- Electrolyte
- Fuel Electrode
- Metal Interconnect

Electrolyte Supported
- Air Electrode
- Electrolyte
- Fuel Electrode

Metal Supported
- Air Electrode
- Electrolyte
- Fuel Electrode
- Metal
- Integrated Interconnect
Cell Level Developmental Work
Stack Agnostic Solutions for Mode Switching on the Air Electrode

- Operational mode switching between SOFC/SOEC
- Dopant type/concentration in barrier layer and active layers
- Microstructural/compositional changes due to chemical and electrochemical driven processes

Investigate Composition-Performance-Stability relationship

- Oxygen Electrode Investigations (Nickelates)
- Fuel Electrode Investigations (Nickel migration)

Stack Supported
Anode Supported

Fuel Electrode
Electrolyte
Fuel Electrode
Electrolyte

Cell Level

Quantify Electrode Performance
- Stochiometry Substitutions
  - A-site
  - B-site

Baseline:
- Barrier SDC20
- Air electrode NNO/ND50
- Directly out of Seeding

Switch to better performing barrier layer from Seeding

Quantify Cell Performance
- Button cells
  - Barrier SDC20
  - Pant down air electrodes

- Performance:
  - DRT, IMP
  - IV curves
  - Operational conditions

Microstructural:
- Physical porosity, etc
- Compositional EDS, TEM, XRD

- Effect of Impurities
  - Experimental at WVU

Y. Zhang (v) Dopant S. Saunders (v) Dopant

Calculated: Calphad (WPI)
- Stability calculations
- Conductivity (defect chemistry + mobility)
- TGA/conductivity

Measured: Powder, Bars, Symmetric cells
- XRD
- DRT, IMP
- Microstructure
- Ionic conductivity bars
- EC Relaxation

Current Density (mAcm⁻²)
1000
12 h
12 h
12 h
1000

½ La₂O₃

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Mitigation of Ni migration

- Focus solutions on MIEC anode side infiltration
- Dynamic SOFC-SOEC mode switching
- A range of simulated fuel compositions & temperatures
- Microstructure and compositional evolution probed through SEM, TEM and SEM-FIB analysis
- Studies to be guided by CALPHAD
INVESTIGATING EFFECT OF BOTH METALLIC AND CERAMIC BASED INTERCONNECTS

**CHALLENGES OF CELL TO CELL CONNECTIONS WITHIN A STACK**

**Cell Level**
- Oxygen Electrode (Nickelates)
- Air Electrode
- Electrolyte
- Fuel Electrode

**Stack Level**
- Stack Supported
- Anode Supported

**Nickelate – Cr interconnect interactions**
- Air Electrode
- Electrolyte
- Fuel Electrode
- Ceramic IC

**Ceramic IC humidity interactions**

**Reaction paths and kinetics of Chromium poisoning**
- Electrochemical deposition identified in general but not well studied in nickelate systems
  \[2CrO_2(g) + 6e^- \rightarrow Cr_2O_3(s) + 3O^2^-\]
  \[2CrO_2(OH)(g) + 6e^- \rightarrow Cr_2O_3(s) + 2H_2O + 3O^2^-\]
- Determination of dominant reaction path as a function of operational state: SOFC, OCV, SOEC
- Utilization of EIS and microstructural observations along with Calphad simulation

**Library of Cr Poisoning**
- Button cells from 60
- Air side compositions from OEL

**Evaluation**
- EIS
- TEM
- SEM

**Feedback to Task 2**
- Cr poisoning to LMO performance
- So poisoning from point
- check experimentally if continues

**Button connecting to quantity deposition**
- SoPBC
- Button back

**LNO modeling**
- Cr poisoning to LMO performance
In investigating effect of both metallic and ceramic based interconnects, challenges of cell to cell connections within a stack are highlighted. The diagram illustrates cell level and stack level interactions:

- **Cell Level**
  - Oxygen Electrode (Nickelates)
  - Fuel Electrode (Nickel migration)
  - Stack Supported
  - Anode Supported

- **Stack Level**
  - Nickelate – Cr interconnect interactions
  - Ceramic IC humidity interactions
  - Stack Supported
  - Anode Supported

**Performance of Ceramic Interconnect**
- Chemical stability and electrical conductivity: Upon change of $P_{O_2}$, reaction with $H_2$ or steam
- Chemical expansion: Change of $P_{O_2}$
- Cation diffusion under high current density: Induced cation/anion diffusion
- Mechanical stability in high steam concentration
- Conductivity experiments
- Microstructural and phase analysis

Fuel electrode//interconnector//oxygen electrode

$H_2, H_2O \rightarrow O_2, N_2$
ENABLING STACK AGNOSTIC VOLUME PRODUCTION
LOW COST, HIGH VOLUME POWDER PRODUCTION CRITICAL FOR SOEC/SOFC ADOPTION

Cell and Stack Production at Saint-Gobain
- Existing process was developed for the production of all-ceramic SOFC
- New materials will be incorporated into the existing process
- Co-sintering process to be optimized for new powders

Powder Production
- Saint-Gobain Grains and Powders is a leading manufacturer of ceramic materials, ex. zirconia
  - Production plants include chemical and fusion based processes
  - Research equipment includes box, tube and rotary furnaces as well as extensive powder characterization tools

Scale Up

Solution integration and stack testing

Techno-economic analysis

Incoming Powder
- Powders are formed processed to desired characteristics

Sheet/Tape Casting
- Powders are dispersed with binders and cast into sheets

Assembly/Firing
- Components are combined and sintered into cells/stacks

Finishing/Sealing
- Final dimensions are achieved and glass seal to applied
MULTI-LEVEL MODELING SUPPORTING THE PROGRAM
THERMODYNAMIC AND SYSTEM MODELING

Thermodynamic Calculations

CALPHADPLUS Approach

System Modeling

Gaia Energy Research Institute LLC (Gaia)
Energy, Environmental, and Engineering Research

SOE System Cost Drivers
- Stack power density
- System capital costs
- Electricity consumed per unit hydrogen produced
- Recovered heat

Solution integration and stack testing

Techno-economic analysis
AMBITIOUS PROGRAM FOCUSED ON SCALING AND REVERSIBLE OPERATION
SOLUTIONS AT EACH LEVEL DESIGNED TO BE PORTABLE TO MANY SYSTEM CONFIGURATIONS

Cell Level
- Oxygen Electrode (Nickelates)
- Air Electrode
- Electrolyte
- Fuel Electrode
- Stack Supported
- Anode Supported
- Fuel Electrode (Nickel migration)

Stack Level
- Nickelate – Cr interconnect interactions
- Air Electrode
- Electrolyte
- Fuel Electrode
- Ceramic IC
- Stack Supported
- Anode Supported
- Ceramic IC humidity interactions

Scale Up
Solution integration and stack testing
- Air Electrode
- Electrolyte
- Fuel Electrode
- Ceramic IC
- Anode Supported

Techno-economic analysis
- Metal IC
- Air Electrode
- Electrolyte
- Fuel Electrode
- Stack Supported

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Objectives to be reached during this project

1. Establish state-of-the-art oxygen electrode materials
2. Stabilize Ni-YSZ hydrogen electrode against Ni migration
3. Quantify the effect of cell & stack design on durability – then improve it
4. Develop and quantify cost-effective and scalable manufacturing

Program started in H2 2021

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<th>Budget Non-Federal</th>
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Diverse and experienced team assembled

Acknowledgement