H2NEW HTE: Cell Characterization

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National Renewable Energy Laboratory
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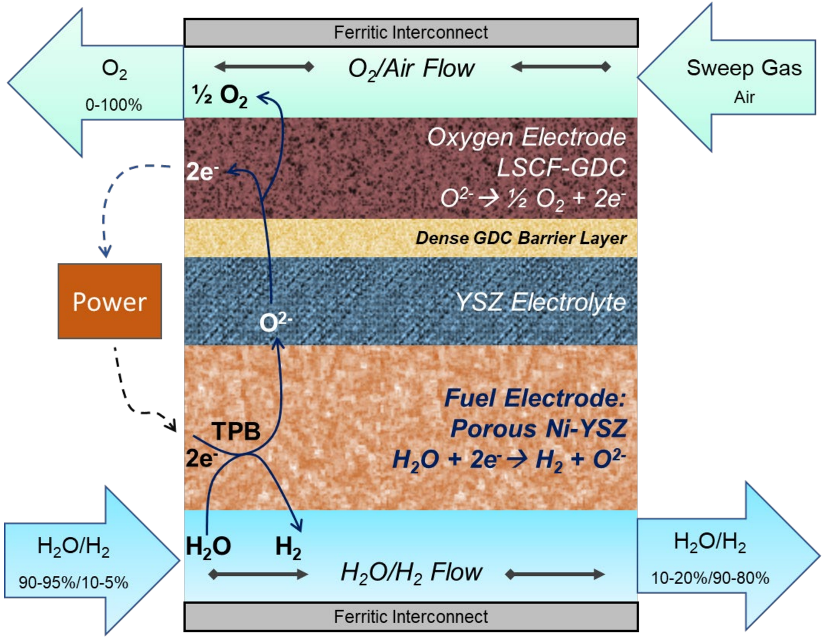
Introduction

The Problem: H2@Scale is reliant on efficient electrolysis; high temperature electrolysis (HTE) is the most efficient technology, but durability is main impediment



Schematic of a representative HTE solid oxide cell

Oxygen electrode: Perovskite decomposition results in cation migration & subsequent reaction, reducing conductivity.

Fuel electrode: Ni migration & coarsening results in decreased triple phase boundary and subsequent performance loss.

Understanding degradation mechanisms and their correlation to operating condition is critical for next-generation cell development.

Project goal

Develop and employ a ***multi-faceted characterization approach*** across multiple length scales (nm to micron) to elucidate failure mechanisms enabling next generation cell development.

- Characterize cells aged for varying lengths of time and under varying conditions to ***discover trends in degradation*** and evaluate accelerated testing protocols to ensure kinetics, and not thermodynamics, of cell aging are altered.
- ***Integrate characterization*** efforts with ***modeling*** efforts to understand the impact of observed cell degradation on performance.

Overview

Timeline

- Project start date: 12/2020 (FY21)

Budget

- FY21 & FY22 DOE funding:
  - AOP plan: $555K
  - Received: $439,064
- FY23 AOP plan
  - $1,325,000
- Total funds received to date (FY21-23)
  - $439,064

Barriers

- Limited number of cells characterized – low throughput
- Limited understanding of impact of observed degradation on performance
- Lack of effective accelerated stress testing protocols – increase kinetics of degradation without changing thermodynamics

Partners

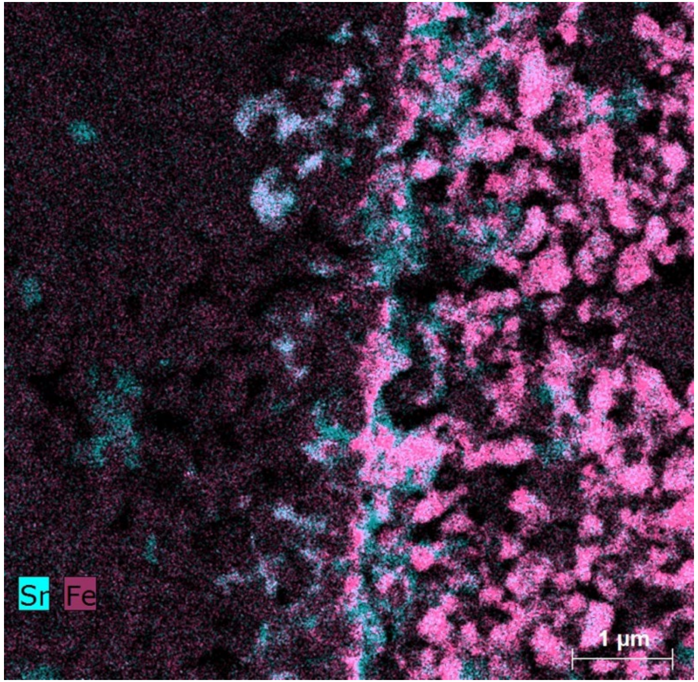
- SLAC National Accelerator Laboratory
- Colorado School of Mines

Potential impact: Characterization of oxygen electrode and barrier layer

Degradation of the oxygen electrode is a major contributor to HTE performance loss:

- Secondary phase formation
- Cation migration and reaction
- Voids & delamination @ interfaces

Understanding oxygen electrode degradation mechanisms and the impacts on performance is key to mitigating performance loss and meeting DOE targets.



EDS map of Sr (blue) and Fe (maroon) – Sr migration into the GDC is evident

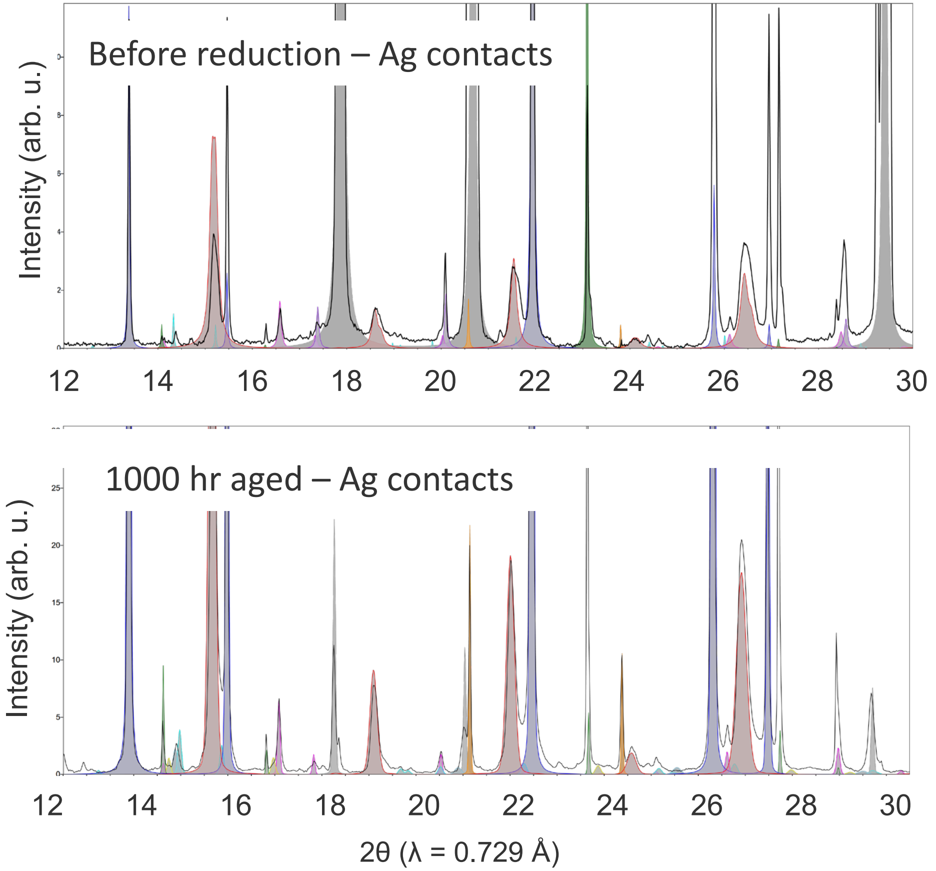
Approach: Characterization of oxygen electrode and barrier layer

Highly integrated synchrotron XRD and electron microscopy approach.

STEM/EDX	Synchrotron XRD
Identifies frequently occurring cation correlations and locations at 1 nm-scale resolution. *XRD results inform TEM what phases are present	Identifies & quantifies all phases present at 1-µm resolution within minutes. *EDX results critical to differentiating between candidate phases w/ identical scattering patterns
Local phase concentrations	Bulk phase concentrations
Cation location within nm-resolution and migration pathways	Phase location with µm-resolution
Sub-nm resolution technique requiring significant sample prep	No sample prep/high throughput/µm-scale technique valuable for statistically relevant results & down selecting cells for further analysis

Results are integrated directly into the modeling effort.

Accomplishments and Progress: Characterization of oxygen electrode and barrier layer



- Secondary phases are present in cells prior to testing.
- Number and concentration of secondary phases increases with cell aging.
- Ag diffusion issues mitigated by replacing contacts with LSCF, but introduced undesired LSCF phases and decomposition products (e.g., B site spinels).

Phase Legend (compositions unrefined): LSCF, Gd-CeO_2, YSZ, Ni, $CeCoFeO_4$, Ag, SrO, $SrZrO_3$, $La_{0.8}Sr_{1.2}Co_{0.5}Fe_{0.5}O_{3.65}$

Accomplishments and Progress: Characterization of oxygen electrode and barrier layer

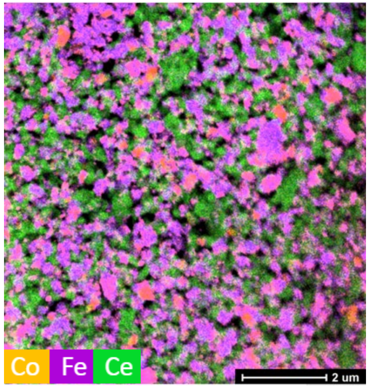
STEM-EDS – Pre Ni Reduction and Testing

- EDS of the oxygen electrode layer reveals initial cation exsolution (predominantly Sr) at the interface and in the barrier layer
- Formation of $CoFeO_x$, SrO, and other phases occur before testing

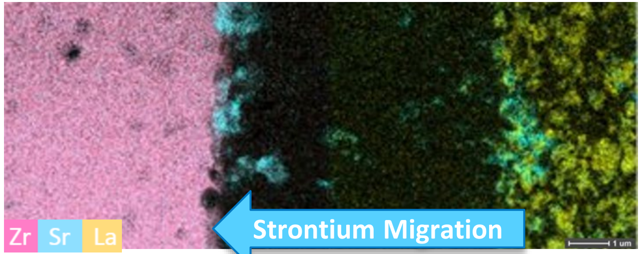
STEM-EDS – Tested for 1k hrs

- Sr migration through the GDC and accumulation at the YSZ interface occurs
- Increase in $CoFeO_x$ spinel concentration
- GDC breakdown resulting in Gd accumulation at the YSZ interface and Ce incorporation into $CeCoFeO_x$ spinel

The oxygen electrode has undesired phases present prior to any ageing; cation migration and degradation increase in severity with cell ageing



EDS map of Co, Fe, and Ce in the oxygen electrode where $CoFeO_x$ spinel appears pink

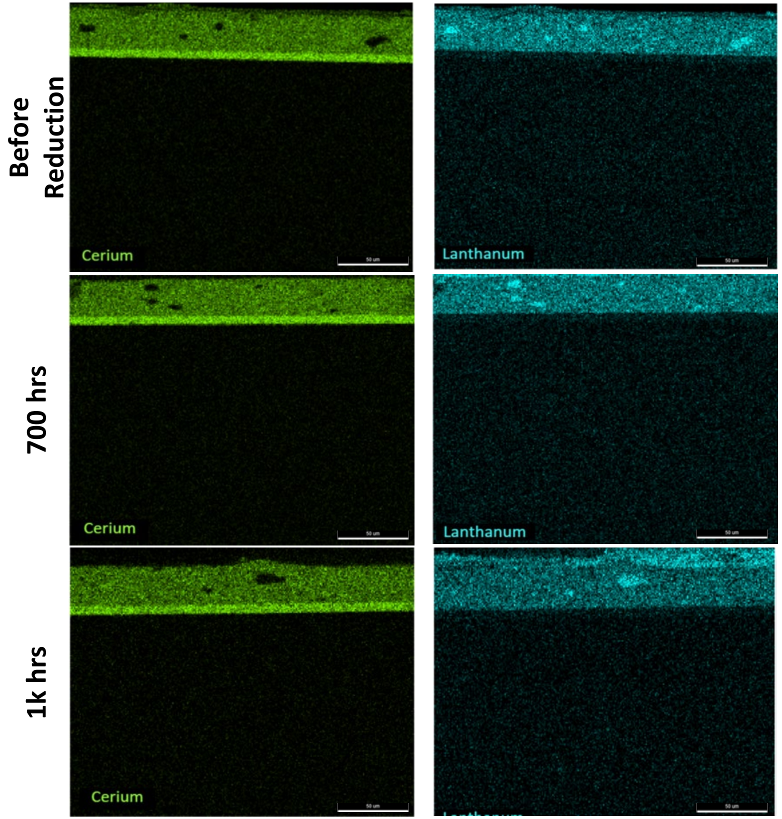


Zr, Sr, and La EDS map of the electrolyte, barrier layer, and oxygen electrode illustrating the migration of Sr

Accomplishments and Progress: Characterization of oxygen electrode and barrier layer

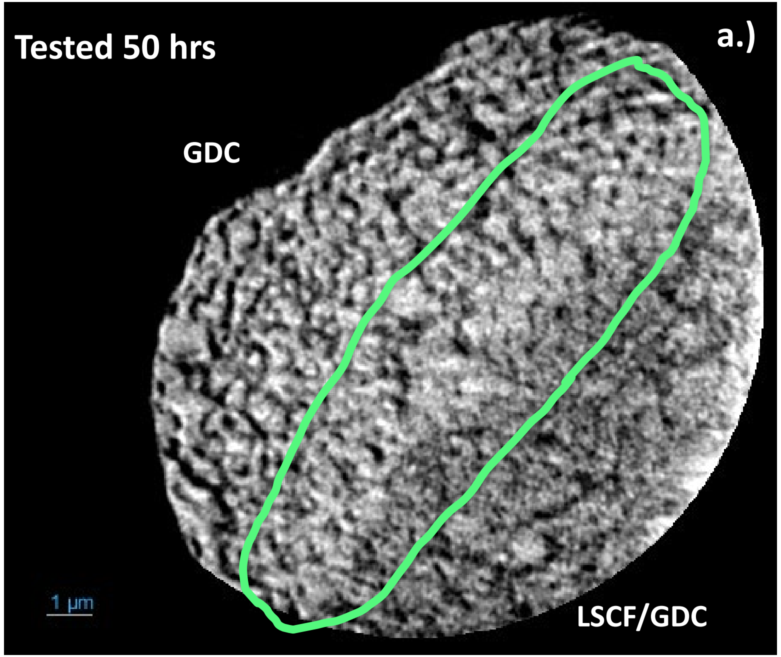
- SEM EDS maps indicates ***macro-scale inhomogeneities*** consistent through the entire production set (observed in unaged and aged cells)
- Ce maps show ***depleted regions*** that correlate to higher concentrations of LSCF (shown in La maps)

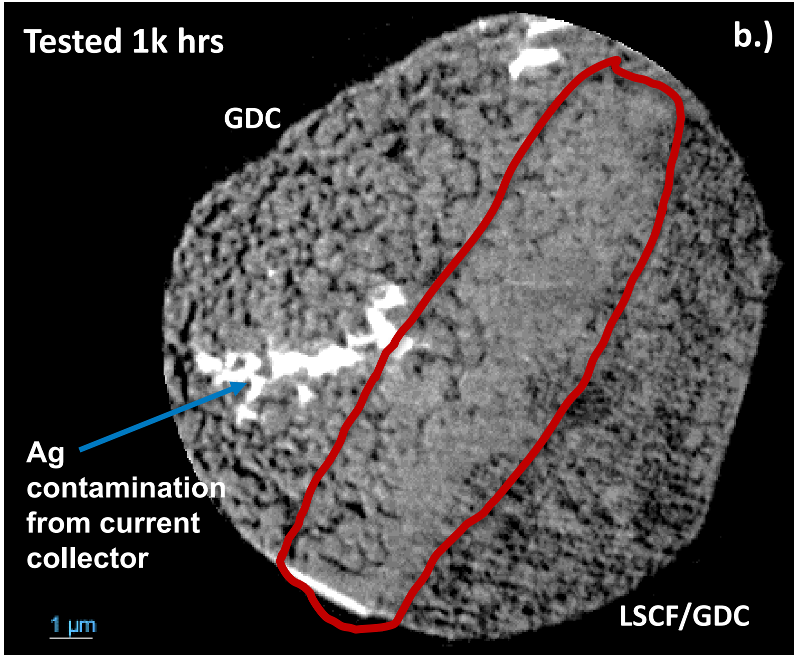
Macro-scale heterogeneities in the form of dense LSCF, GDC depleted regions are consistently present in both unaged and aged cells



SEM-EDS maps of Ce and La for a cell before reduction and testing, aged 700 hrs, and aged for 1k hrs are shown

Accomplishments and Progress: Characterization of oxygen electrode and barrier layer





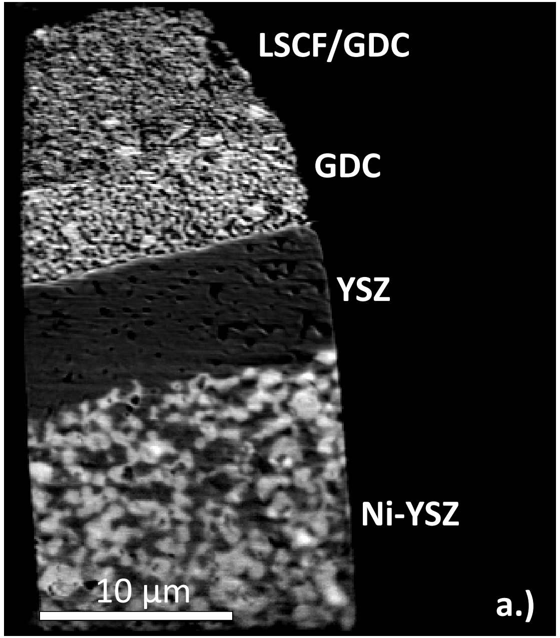
2D Nano-CT projections capturing the oxygen electrode and barrier layer interface in cells tested for a.) 50 and b.) 1k hours

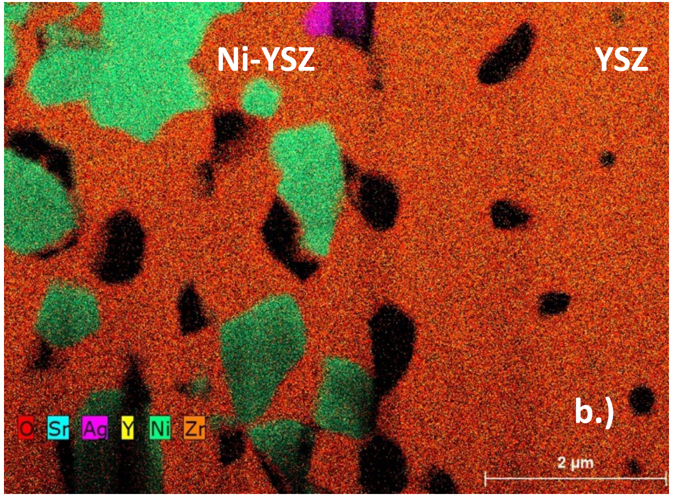
Nano-CT images reveal interface densification occurring after extended cell operation, which may result in performance loss due to restricted mass and ionic transport

Potential impact: Characterization of fuel electrode

It is consistently found across the literature that the *fuel electrode is the greatest contributor to cell resistance increases* in single cell performance studies due to nickel migration and coarsening, which reduces the amount of accessible TPB decreasing H_2 production.

Correlating changes in the Ni microstructure with sintering conditions and operating conditions is critical to mitigating TPB loss.



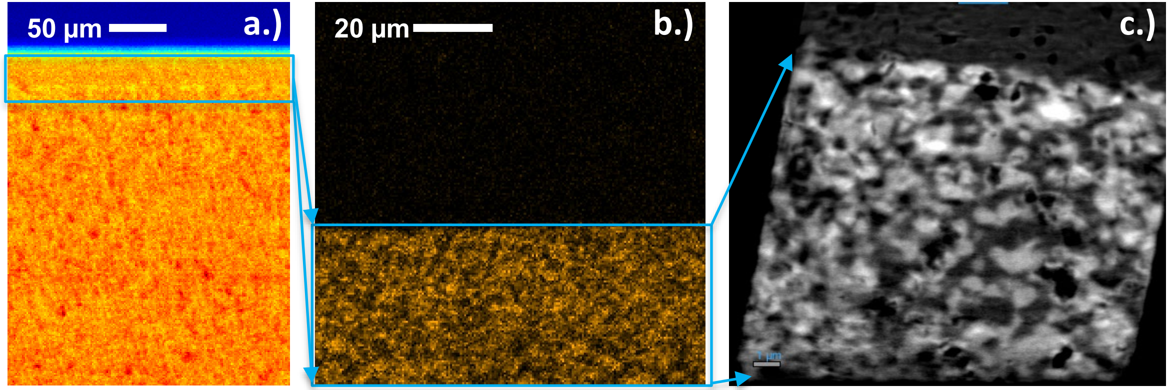


a.) Nano-CT 2D projection of the layers of interest and b.) STEM-EDS image of the Ni-YSZ/YSZ interface

Approach: Characterization of fuel electrode

Ni microstructure is characterized by a multi-technique, multi-scale approach:

- Micro-XAS: large scale Ni and YSZ distribution, Ni and Zr oxidation state
- SEM-EDS: finer scale Ni distribution and Ni-YSZ morphology
- Nano-CT: high resolution, 3D Ni distribution leading to quantification of changes in Ni-YSZ microstructure



a.) Ni-specific X-ray fluorescence map of both the fuel electrode and the supporting Ni-YSZ, b.) Ni-specific EDS map of the fuel electrode, and c.) 2D slice of a Nano-CT reconstruction of the Ni-YSZ fuel electrode

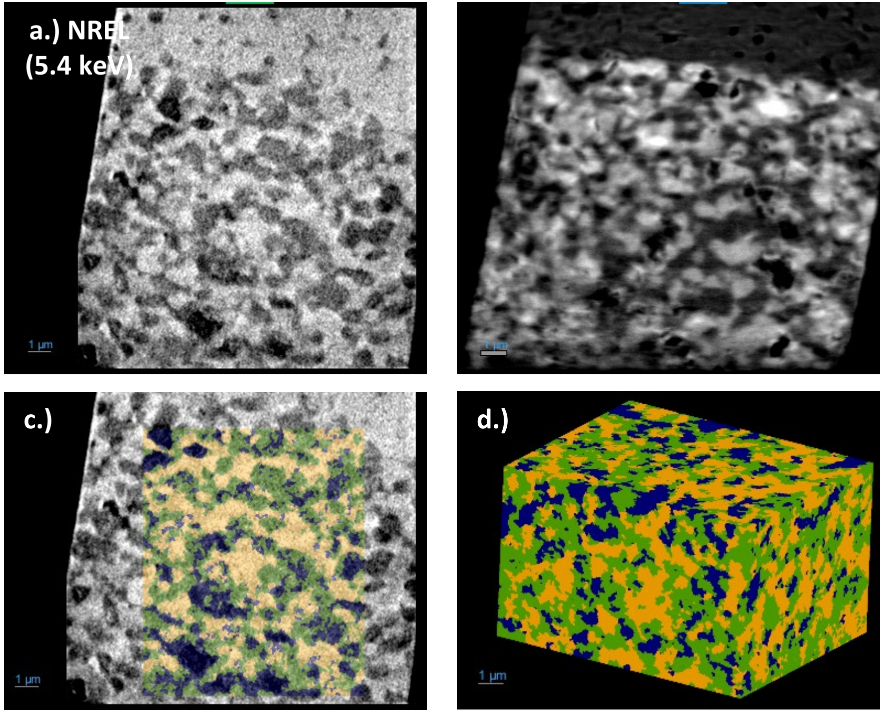
Multi-scale, multi-technique approach to characterization of the Ni-YSZ microstructure is applied to identify changes in the Ni-YSZ microstructure upon ageing

Accomplishments and Progress: Characterization of fuel electrode

Nano-CT data has been collected at NREL (Zeiss Xradia 810) and SLAC (Synchrotron)

- NREL Nano-CT offers higher throughput and improved edge contrast
- SLAC Nano-CT offers shorter measurement time and better phase contrast
- 3-phase segmentation of pore space, Ni, and YSZ has been demonstrated

3D analysis of Ni-YSZ microstructure has been conducted at NREL and SLAC, 3-phase segmentation ongoing to support modelling and quantify microstructure



a.) Nano-CT image of the Ni-YSZ collected at NREL, b.) Nano-CT data collected at SLAC, c.) Transparent 3-phase segmentation is overlaid on raw nano-CT data, and d.) resulting segmented 3D volume with Pores, Ni, and YSZ differentiated by color

Collaboration and Coordination

Success of H2NEW cell characterization is contingent on a highly collaborative approach that leverages expertise from each of the participating national labs.

This project is a collaboration between Pacific Northwest National Laboratory (PNNL), Idaho National Laboratory (INL), Lawrence Livermore National Laboratory, the National Energy Technology Laboratory (NETL), and the National Renewable Energy Laboratory (NREL).

All cells characterized by NREL are synthesized at PNNL and aged and INL or LBNL.

Chemical and structural changed with cycling are correlated to operating conditions and electrochemical data collected at INL and LBNL.

Characterization results (tomography and secondary phase information) are provided and used by the modeling teams.

Remaining Challenges & Barriers

Oxygen Electrode

- LSCF has undesired phases present prior to any processing or testing; unable to conclude whether the initial presence of undesired phases accelerates aging relative to the intended phases.

Fuel Electrode

- Uncertainty about homogeneity of the Ni-YSZ functional layer is present within the field, initial nano-CT data must be proven to be representative.
  - Conducting triplicate series of data on regions pulled from the same cell
- Sample-prep obstacles limits Nano-CT data acquisition throughput
  - New prep method featuring laser-laithe and subsequent FIB thinning in development.

Future Work

Design and fabrication of an *operando* XRD sample stage

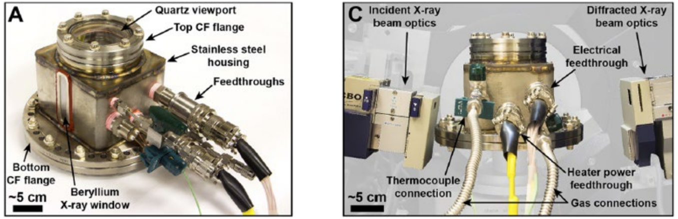
- Synchrotron X-rays are one of the only structural probes capable of *operando* HTE measurements -requires 1) high energies and brilliance, 2) small beam size, 3) fast acquisition, and 4) depth resolution

Advantages of *operando* XRD characterization:

- Observations directly related to performance
- Eliminates "artifacts" caused by decommissioning cells (e.g., inadvertent oxidation of Ni-YSZ electrode)
- Identify early-stage structural and compositional changes that gradually lead to late-stage cell failure (***saves time and cost associated with long term aging processes and extends lifetimes of cells***)
- Validate accelerated aging processes

Successfully achieving the project goals will require involvement of multiple H2NEW laboratories

Sample cell design templated by Benck et al. *Rev. Sci. Instrum.* **2019**



Operation strategy:

1. Stationary operation in SSRL laboratories
2. Periodic transition to beamline with uninterruptible modular setup (automated alignment + depth resolved data acquisition)
3. Returned to laboratory for stationary operation

Summary

A ***multi-faceted characterization approach*** across multiple length scales (nm to micron) to elucidate failure mechanisms in SOECs has been developed

- Characterization has been highly integrated with the modeling efforts

Advanced characterization methods have been developed:

- Depth profiling of in-tact button cells using synchrotron XRD
- High throughput synchrotron XRD for in-tact button cells

Results have identified:

- Unintended secondary phases from cell fabrication
- Inhomogeneities in the oxygen electrode structure
- Increase in secondary phases as a function of cell aging
- Cation migration and subsequent reaction at interfaces as a function of cell aging