Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Degradation Characterization and Modeling of a New Solid Oxide Electrolysis Cell Utilizing Accelerated Life Testing

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Project ID: P153

NREL BERKELEY LAB Sandia National Laboratories INL Idaho National Laboratory Lawrence Livermore National Laboratory SRNL

Project Overview

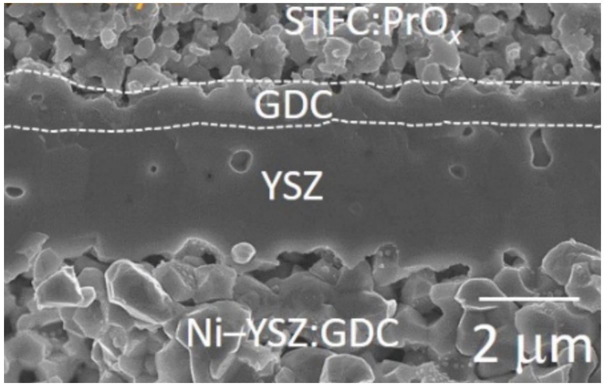
Project Partners

Scott A Barnett, PI, Northwestern Univ
Peter W Voorhees, co-PI, Northwestern Univ
Michael Tucker, co-PI, LBNL
Jim O'Brien & Dong Ding, co-PIs, INL

Award #	EE0008079
Start/End Date	09/01/2017 – 08/31/2020
Year 2 Funding*	$294,000

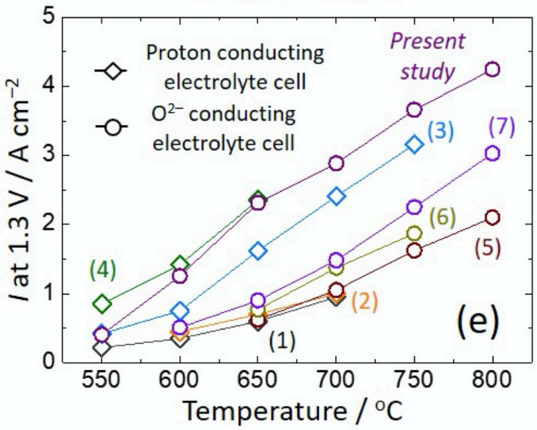
Project Vision

Degradation mechanisms in solid oxide electrolysis cells (SOECs), which are poorly understood at present, will be studied using accelerated testing at high current density, closely coupled with theory.



Project Impact

Developing accelerated testing protocols and a basic understanding of degradation mechanisms will have a broad impact on the field. A key outcome will be improved SOECs that allow long lifetime at higher current density, significantly improving economic viability.



Approach- Summary

Project Motivation

Barnett has been using accelerated testing combined with 3D tomography to develop quantitative Solid Oxide Fuel Cell degradation models for several years, and has worked with Voorhees in this area. It was natural to extend these ideas and methods to electrolysis cells.

Key Impact

Metric	State of the Art	Expected Advance
Current Density	*0.5 A/cm²*	*> 1.0 A/cm²*
Degradation Rate	*>10 mV/kh*	*< 4mV/kh*
Electrode Overpotential	> 0.2 V	< 0.2 V

Barriers

SOECs run at high current density typically exhibit fast degradation. Quantitative physically-based models of degradation mechanisms are needed. Models will be developed with input from extensive targeted experiments. Finding pathways to reduced degradation based on this understanding.

Partnerships

Michael Tucker at LBNL has long experience with solid oxide fuel cells, particularly metal-supported cells, which have not been tested in electrolysis mode previously.

Dong Ding at INL has extensive experience with solid oxide electrolyte cells, and have fabrication and testing facilities relevant to this project.

Approach - Innovation

Materials Innovation

- Cells were modified with ultra-thin bi-layer electrolyte, Ceria-infiltrated cathode, PrOx-infiltrated anode, and improved support porosity, yielding:
  - Outstanding cell performance
  - Low degradation rate at high current density
- Ni-YSZ cathode degradation mechanisms observed by microscopy
- SOEC theory correlates degradation with conditions that yield very low oxygen partial pressure at cathode
- Much improved stability of metal-supported electrolysis cells

Budget Period 2 Scope of Work

- Advanced solid oxide electrolysis cells are fabricated and electrochemical life testing carried out along with microstructural/chemical characterization
- Life test results are used to develop and refine cell degradation theory
- Ongoing work will extend the theory and improve cell stability in the following budget period
- Go/No-Go Decision Point based on promising SOEC durability and model predictive capability

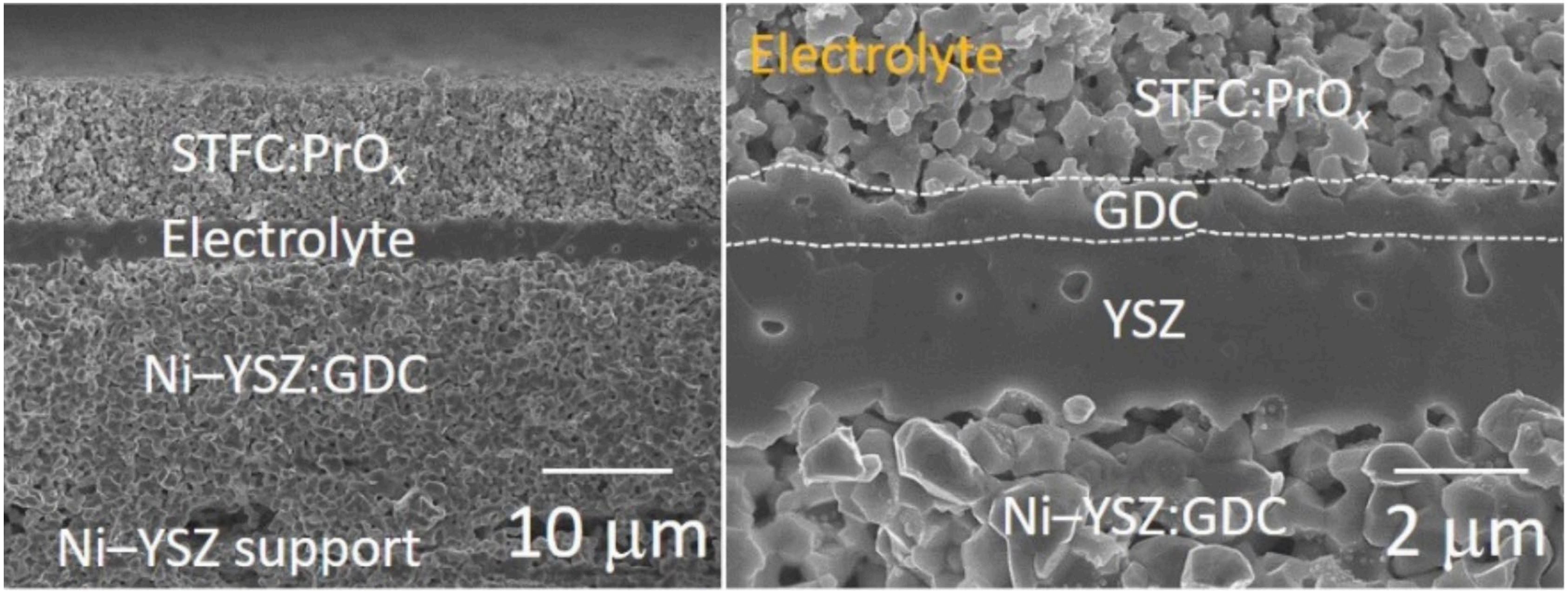
Relevance & Impact

- Solid oxide electrolysis cells have the potential to achieve the highest electricity-to-hydrogen conversion efficiency amongst electrolysis technologies. This project addresses the long-term stability of these cells at high current density, widely regarded as being a critical barrier for their commercial development
- Our project makes good use of the HydroGEN Consortium R&D model, enhancing our R&D with the input from two highly-regarded groups
- Enhancing the broader HydroGEN Consortium
  - Our node utilization helps to strengthen the capabilities at LBNL and INL in preparation, testing, and analysis of solid oxide cells
  - It could be valuable in the future if the HydroGEN Consortium had the capability to scale up small research cells to larger sizes for higher TRL development

Accomplishments - Milestones

- **Budget period 2 Go/No-Go milestones:**
  - Projected degradation rate of < 30 mV/kh at > 0.7 A cm^{-2}
  - Simulation models that can predict the experimentally observed degradation mechanisms at or near the fuel electrode
- **Significance of meeting these milestones:**
  - Demonstrated improved performance and stability, improving overall viability of SOECs
  - The theory developed can make quantitative predictions regarding the conditions that cause degradation. By matching the model to experimental data taken over a wide range of conditions, wide applicability is assured.
  - The theory will allow us to predict operating conditions that yield low degradation and design cells that allow higher current density without degradation.

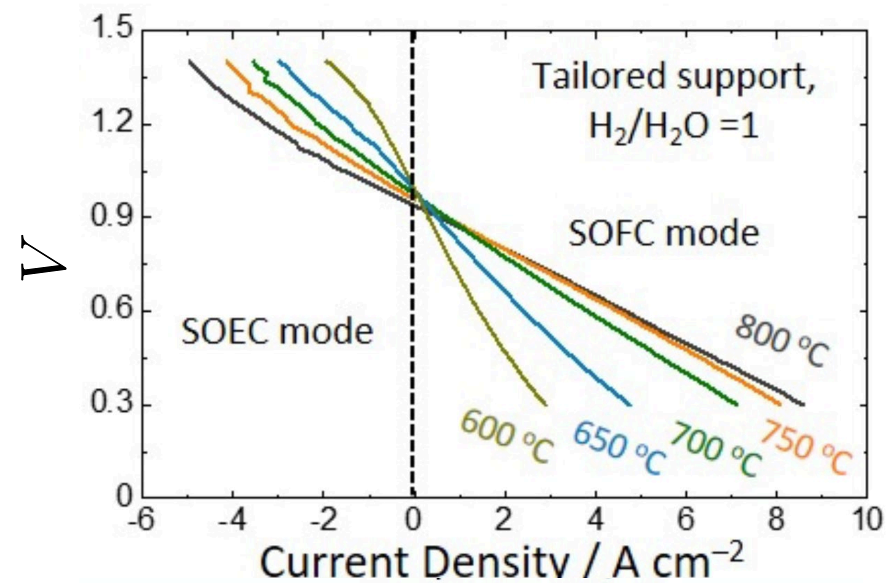
Accomplishments: Optimized Solid Oxide Electrolysis Cell

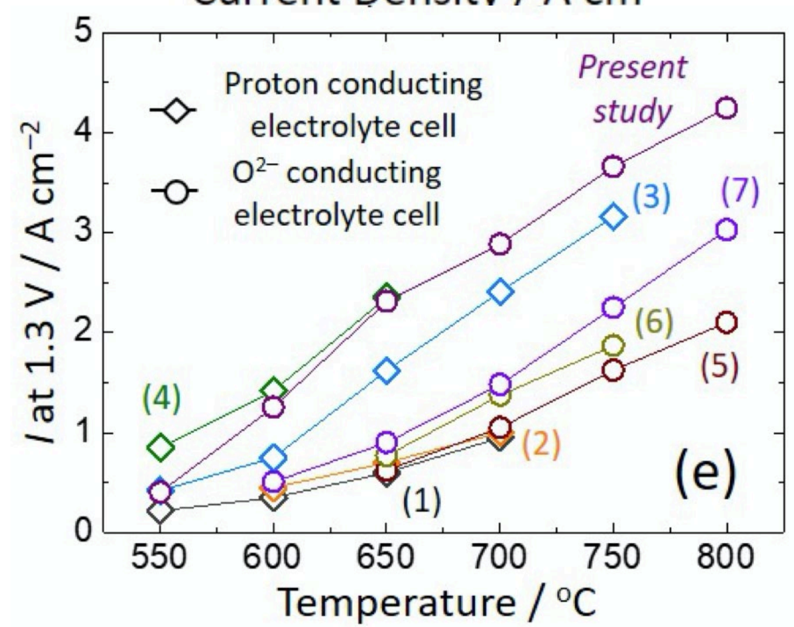


- Improvements made to each cell component:
  - Reduced-thickness YSZ/GDC electrolyte
  - GDC-infiltrated Ni-YSZ fuel electrode
  - PrO_x-infiltration STFC oxygen electrode
  - Increased porosity Ni-YSZ support
- **Milestone 5.1: Fabrication of SOECs with < 20 µm thick, dense (>90%) electrolyte**

Accomplishments: Optimized Cell Performance

- Current density at 1.3 V is 1 to 4 A/cm² (600 to 800 °C)
- Compares favorably with best reported electrolysis cells
- Fuel cell maximum power density ~ 3 W/cm² at 750 °C

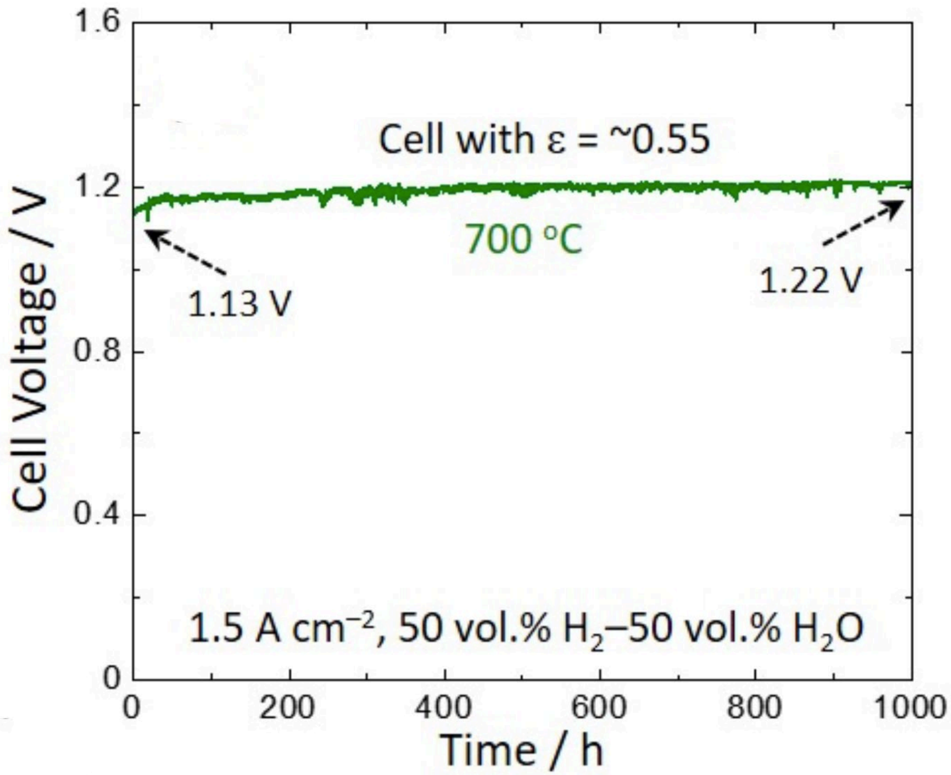




- **Milestone 5.1 easily met:**
  - **1.0 A/cm² at < 1.3 V (800 °C)**

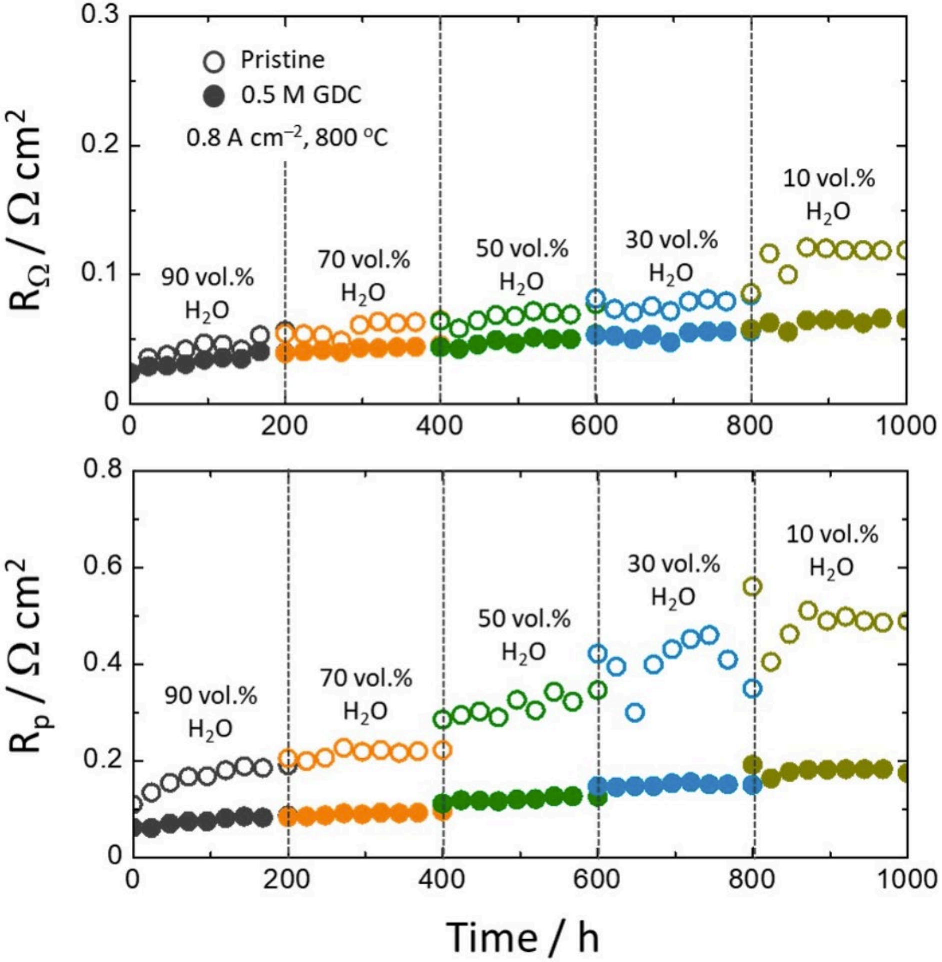
Accomplishments: High Current Density Life Test

- Optimized cell at 1.5 A/cm^2, 700 °C, 50 % steam
- Initial fast degradation due to cell break-in over first ~ 500 h
- Degradation slows to ~ 20 mV/kh over final 500 h
- **Milestone 6.1: Life testing (~1000 hr) of symmetric and full cells**
- **Go/no-go: projected degradation rate of < 30 mV/kh at > 0.7 Acm^{-2}**

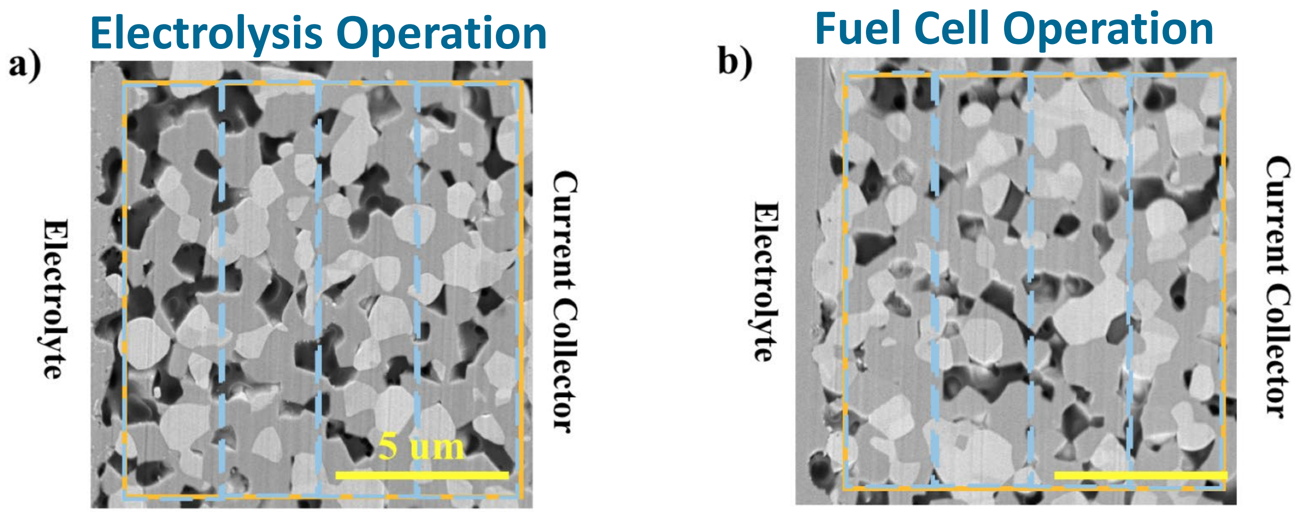


Accomplishments: Effect of GDC Infiltration on Ni-YSZ Degradation

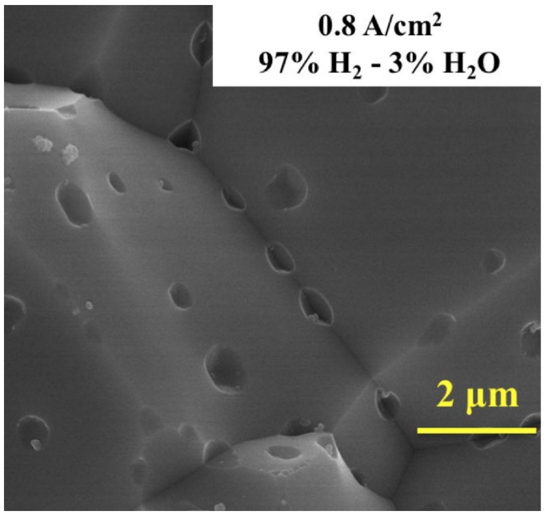
- Life test with varying H_2O content
- Ni-YSZ / YSZ / Ni-YSZ cell with and without GDC infiltration
- Much improved stability with GDC
- Polarization resistance increases with decreasing H_2O content
  - Serious degradation for Ni-YSZ
  - Ni-YSZ:GDC is much more stable
- Ohmic resistance increases with time
  - Some degradation for Ni-YSZ fuel electrode
  - Increase for Ni-YSZ:GDC may be mostly just early stage break-in



Accomplishments: Electrolysis Degradation Observations

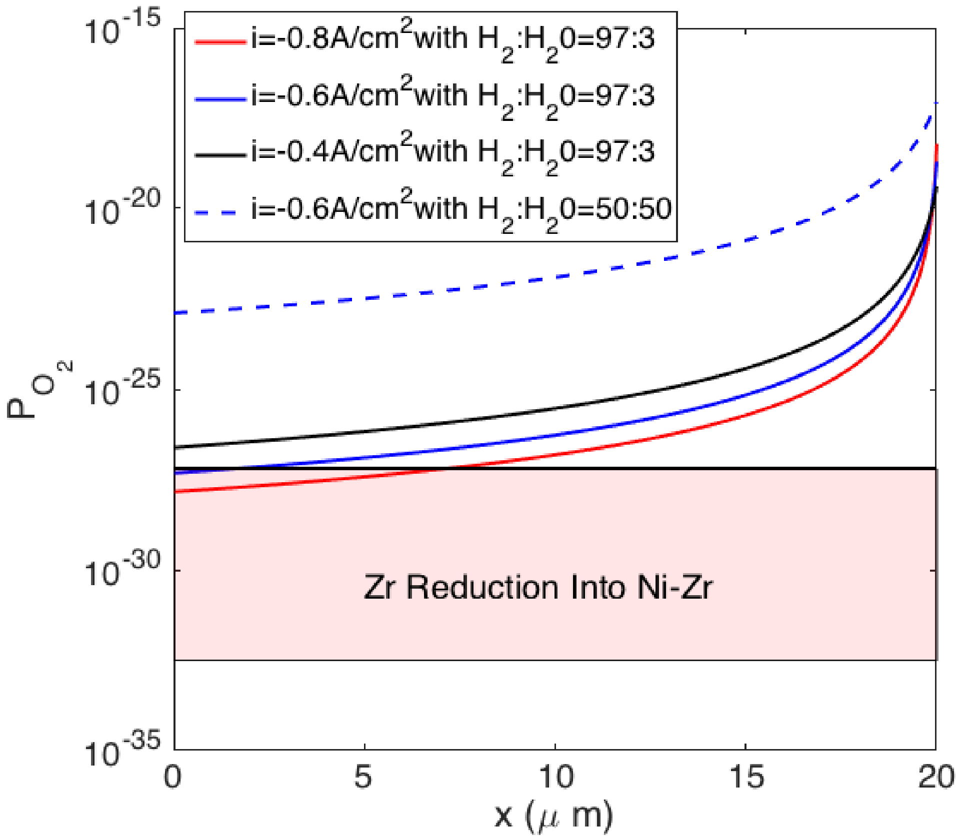


- Life tests show that ohmic resistance degradation is exacerbated by low (3%) steam, high current density
- Cells shown tested for 1000 h at 800C and 0.8 A cm^{-2}
- Electrolysis operation yielded apparent depletion of Ni from regions within ~ 5 µm of electrolyte
- Electrolyte grain boundaries decorated with pores
- Similar to literature observations
  - New here: observed effect of operating conditions



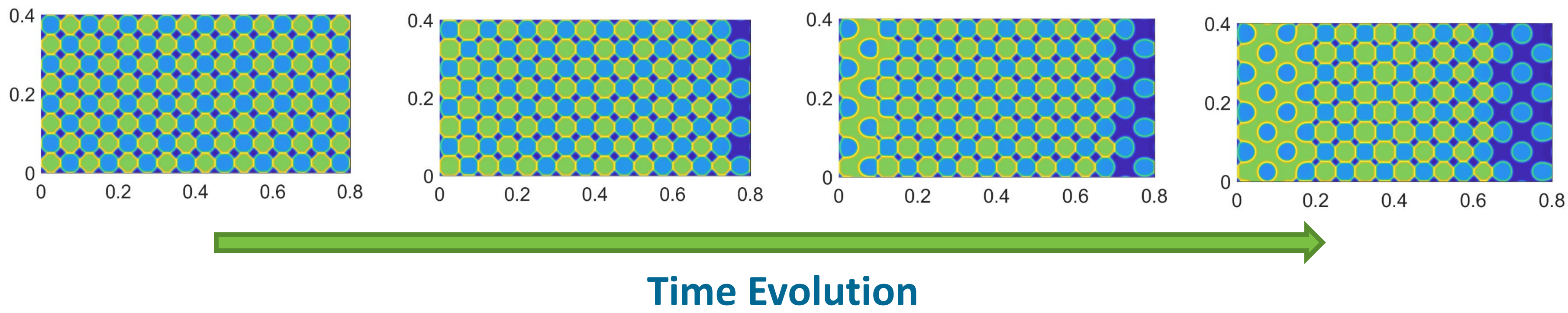
Accomplishments: Oxygen partial pressure distribution in the electrolyte

- Theory focus in Year 2 shifted from air electrode side to fuel electrode
- Electrolysis operation drives p(O_2) to lower values at the fuel electrode with increasing current density j
- Shifting from 3 % to 50 % H_2O moderates p(O_2)
- Calculation shows deleteriously low pO_2 values under the conditions where Ni depletion and grain boundary void formation are observed
- Mechanisms:
  - Pore formation: several possibilities have been explored
  - Ni depletion: being simulated



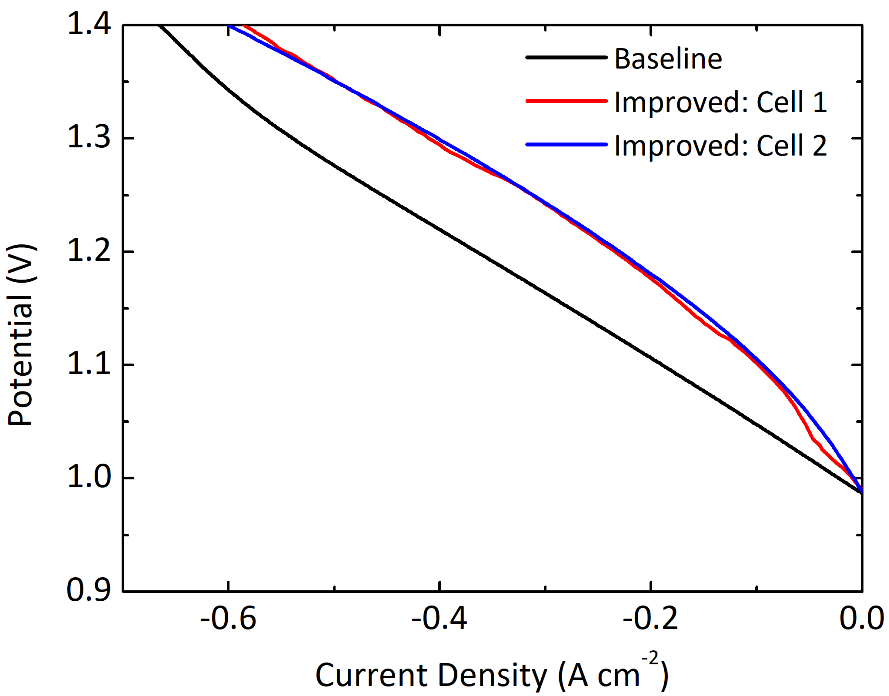
MILESTONE 8.1: Develop initial electrode degradation models based on experimental observations
GO/NO-GO CRITERION: Simulation models that can predict the experimentally observed degradation mechanisms at or near the fuel electrode

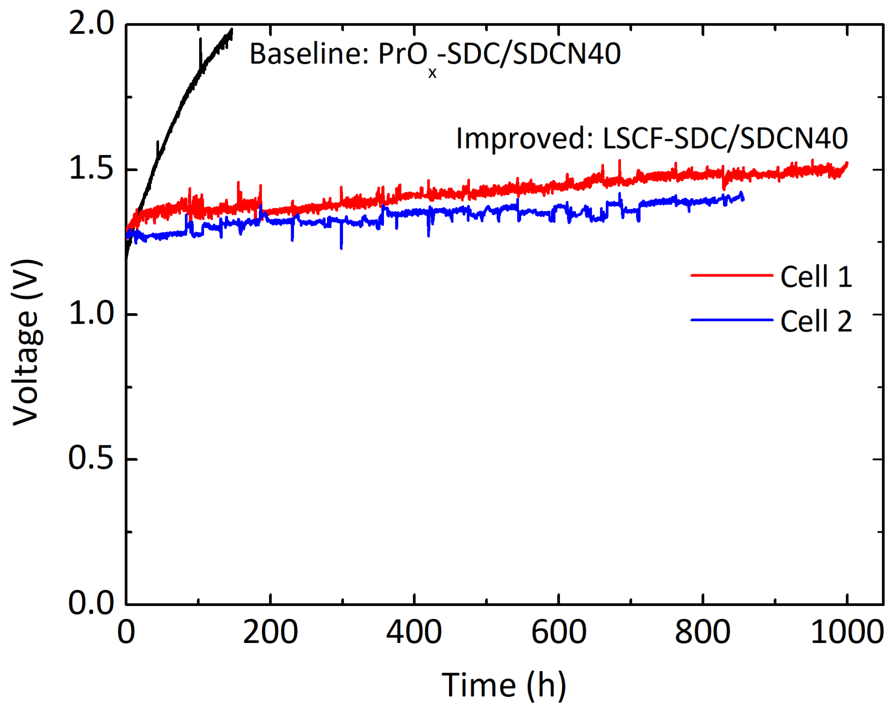
Accomplishments: Numerical simulation results



- Simple two-dimensional phase field model developed
  - Includes Ni (green), YSZ (blue), and pore (purple)
  - Left image shows initial ideal structure
- Model includes Ni-YSZ contact angle gradient with position
  - Derives from change in surface energies with local electric field and/or H_2O/H_2 concentration gradients
- Initial results show a clear depletion of Ni from higher contact angle side, i.e., near the electrolyte interface
  - Agrees with experiments
- Future 3D model can be compared directly with experiment
- **MILESTONE 8.1: Develop initial electrode degradation models based on experimental observations**

Accomplishments (LBNL): Enhanced durability in long term MS-SOEC test





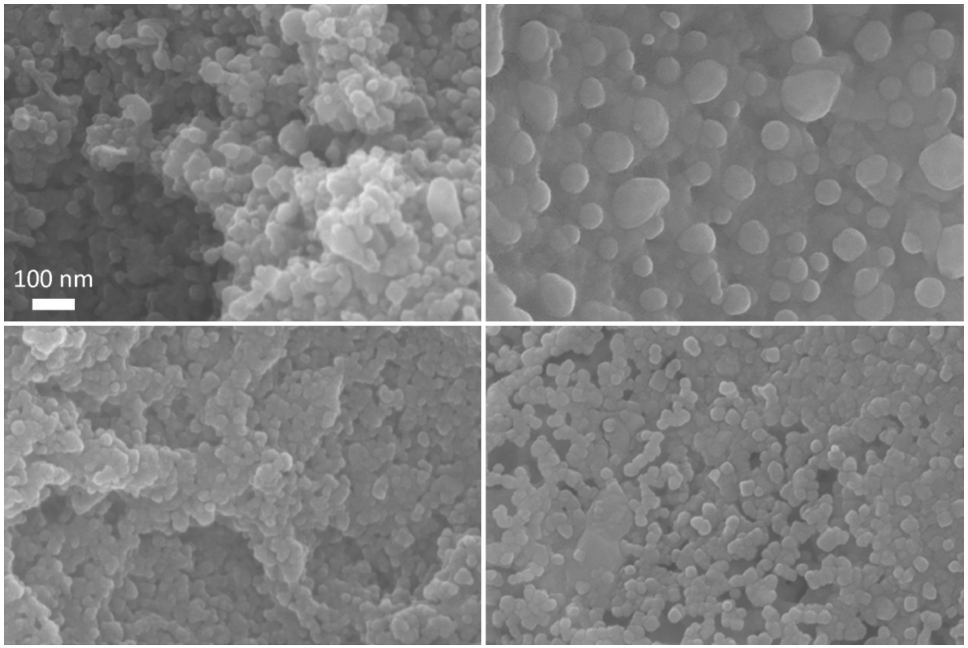
- Few reports of life testing of metal-supported solid oxide electrolysis cell (MS-SOECs)
- Cell with LSCF-SDC air electrode achieves good durability
  - Better than PrOx-SDC air electrode
  - Degradation rate at -0.4 A cm^{-2} is ~ 100 mV/kh

Accomplishments (LBNL): Major degradation modes for MS-SOEC

0 h | 1000 h

Fuel electrode

Air electrode

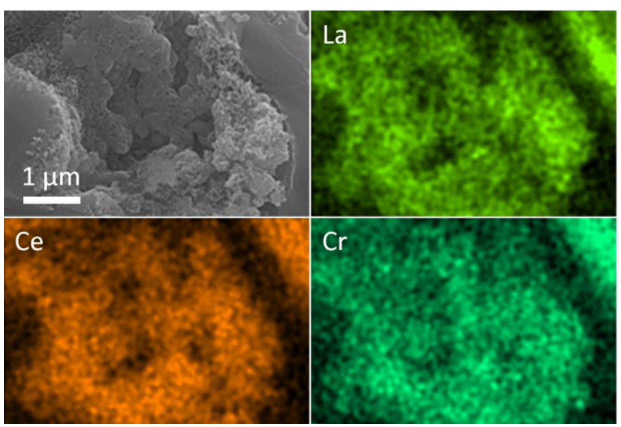


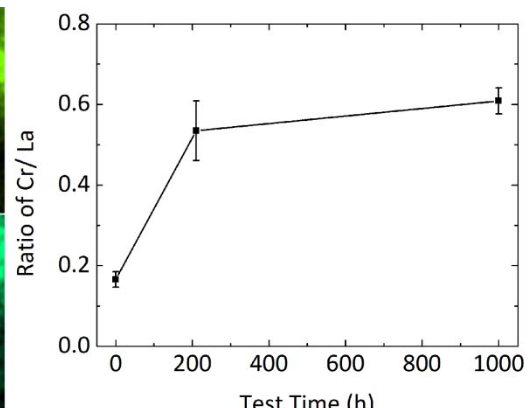
Fuel electrode:

catalyst coarsening observed

Oxygen electrode:

no coarsening





Cr poisoning on air electrode catalyst

Cr distribution overlaps with catalyst

Cr loading increases with time

Accomplishments - Outlook

- SOECs developed in past year show outstanding performance and stability, and similarity to commercial cells makes planned studies of broad interest
  - Cells of this type will be used to map out SOEC performance and degradation
  - Above data will inform the theory, provide new insights into accelerated stress testing methods, and map out viable SOEC operating range
  - Reaching final milestone: < 4 mV/kg degradation rate at 1 A cm^2 appears feasible
- SOEC theory is being expanded beyond oxygen electrode to help explain degradation in electrolyte and fuel electrode
  - User friendly version of oxygen-electrode delamination theory being developed for posting on HydroGEN Data Hub
  - Phase-field theory development will continue to provide mechanistic modeling of Ni-depletion from Ni-YSZ electrode
  - Work will also continue to explain observed fuel-electrode/electrolyte interface degradation and grain boundary cavitation within the electrolyte
- Continued metal-supported SOEC development/testing may provide a viable alternative design along with additional data for modeling

Collaboration: Effectiveness

- With the EMN node at LBNL: their metal-supported SOECs provide additional data for comparison with theory, and an alternative pathway to robust low-degradation cells
- The EMN node at INL is utilizing alternative electrolysis cells and testing methods, complementing results at NU
- We have communicated with and provided feedback to the “2B Benchmarking/Protocols” team – this is especially important for SOECs, for which benchmarks/protocols are mostly not defined
- We have begun sharing data with LBNL using the data hub. If we can use the hub to obtain SOEC data from the broader HydroGEN program, this will aid theory development

Proposed Future Work

- Budget period 3* ($302k)
- End of project goals include well-developed predictive degradation models and SOECs that meet program durability targets
- Extensive life testing of optimized cells with good performance and stability
  - Study fuel-electrode related degradation over full range of fuel compositions expected in stacks; also temperature and current density
  - Find parameters for accelerated study of Ni depletion from Ni-YSZ
  - Determine whether degradation mechanisms observed at very low steam (3%) are present at more practical stack conditions (> 20% steam)
  - Will attempt to parlay results into models that can use accelerated stress test data to predict long-term stability
- HydroGEN EMN nodes (LBNL and INL) will continue to contribute with input on alternative cell designs and testing methods

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

Project Summary

- SOECs have been developed that show outstanding performance
  - Lower degradation rate than year-2 goal
- Year 2 studies focused on degradation in the fuel electrode and the fuel-electrode side of the electrolyte
  - Ni depletion near electrolyte and grain boundary voids within the electrolyte
  - Theory correlates these issues with extremely low oxygen partial pressure during electrolysis
  - Initial phase-field model correctly predicts Ni depletion
- LBNL metal supported cells provide an alternative system to validate our understanding of degradation; technological alternative
  - Best-ever stability for metal-supported solid oxide electrolysis
- INL testing expertise and capabilities extend those at Northwestern
- On track to project goals – obtain quantitative electrolyte degradation theory and high-performance cells with low degradation rate

Publications and Presentations

- Beom-Kyeong Park, Qian Zhang, Peter Voorhees, and Scott Barnett, “Conditions for Stable Operation of Solid Oxide Electrolysis Cells: Oxygen Electrode Effects,” Energy & Environmental Science, 12 (2019) 3053-3062, DOI: 10.1039/C9EE01664C.
- B.-K. Park, R. Scipioni, D. Cox and S.A. Barnett, "Enhancement of Ni–(Y2O3)0.08(ZrO2)0.92 fuel electrode performance by infiltration of Ce0.8Gd0.2O2−δ nanoparticles," Journal of Materials Chemistry A 8 (2020) 4099-4106
- Qinyuan Liu, Qian Zhang, Peter W. Voorhees, Scott A. Barnett, “Effect of Direct-Current Operation On The Electrochemical Performance and Structure Evolution of Ni-YSZ Electrodes” Journal of Physics: Energy 2 (2019) 014006.
- Qian Zhang, Qin-Yuan Liu, Scott Barnett and Peter Voorhees, “Influence of distribution of oxygen partial pressure and oxygen vacancy concentration on the electrolyte degradation of solid oxide electrolysis cells,” submitted to Acta Materiala.
- Qian Zhang, Beom-Kyeong Park, Scott Barnett and Peter Voorhees, “A new model of distribution of oxygen partial pressure for multi-layer electrolyte of solid oxide electrolyzer cells,” submitted to Applied Physics Letters.
- Scott Barnett, “High-Efficiency Electrical Energy Storage Using Reversible Solid Oxide Cells,” Lecture presented at University of Louisiana – Lafayette, February 17, 2020.
- Scott Barnett, “Degradation Studies of Reversible Solid Oxide Cells Used For Electrical Energy Storage,” Lecture presented at CSIRO, Clayton, Australia, February 3, 2020.
- Q. Zhang, B. K. Park, S. A. Barnett, and P. W. Voorhees, “Distribution of Oxygen Partial Pressure in Multilayer Electrolytes: Explaining Degradation of Solid Oxide Electrolyzer Cells,” 236th Electrochemical Society meeting, Atlanta GA, October 12-17, 2019.
- B. K. Park, Q. Zhang, Q. Liu, P. W. Voorhees, and S. A. Barnett, “Understanding of Solid Oxide Electrolysis Cell Degradation: The Role of the Electrode Overpotential,” 236th Electrochemical Society meeting, Atlanta GA, October 12-17, 2019.
- Fengyu Shen, Emir Dogdibegovic, Ruofang Wang, Grace Lau, and Michael C. Tucker, “Performance and degradation of metal-supported solid oxide electrolysis cells with infiltrated catalysts”, ACS Fall 2019 meeting, Aug 25-29, 2019
- Emir Dogdibegovic, Fengyu Shen, Ruofan Wang, Ian Robinson, Grace Lau, Michael C Tucker, “Performance and degradation of metal-supported solid oxide electrolysis cells with infiltrated catalysts”, SOFC-XVI, Sept 10, 2019
- Scott A Barnett, Qinyuan Liu, Qian Zhang, Beom-Kyeong Park, and Peter Voorhees, “Degradation Phenomena in Solid Oxide Electrolysis Cell Fuel Electrodes,” 2nd International Conference on Electrolysis, Loen Norway, 9-13 June 2019
- Scott A Barnett, Beom-Kyeong Park, Qian Zhang, and Peter Voorhees, “Degradation Phenomena in Solid Oxide Electrolysis Cell Oxygen Electrodes,” 2nd International Conference on Electrolysis, Loen Norway, 9-13 June 2019