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

Scott A Barnett
Northwestern University
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Project ID: P153

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Project Overview

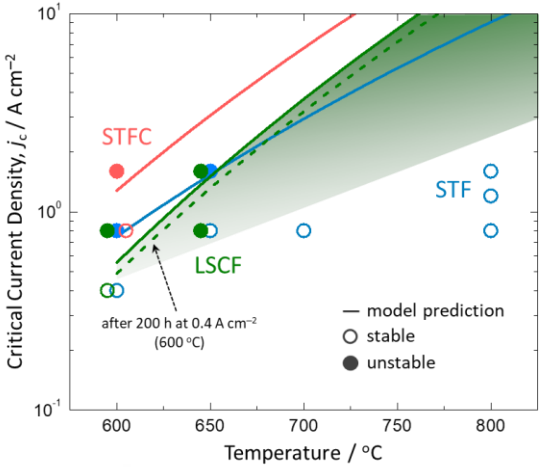
Project Partners

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 1 Funding* Year 2 Funding*	$277,860 $326,682

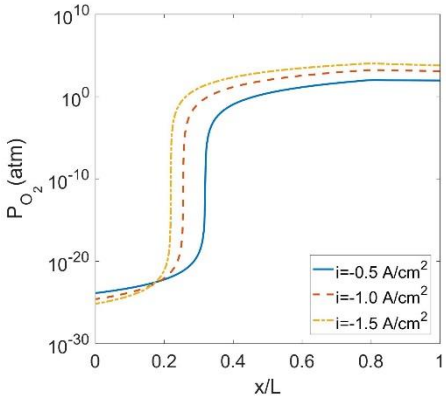
Project Vision

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.



**this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

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.

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.

Key Impact

Metric	State of the Art	Expected Advance
Current Density	*0.5 A/cm^2*	*> 1.0 A/cm^2*
Degradation Rate	*>10 mV/kh*	*< 4mV/kh*
Electrode Overpotential	> 0.2 V	< 0.2 V

Partners

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

Approach - Innovation

Materials Innovation

- Theory predicted oxygen partial pressure across the electrolyte compared with critical values for fracture or Zirconia reduction → failure criteria
- Solid oxide electrolysis cell (SOEC) life test results agree well with predicted oxygen electrode fracture condition
- Novel SOECs show promising performance and stability

Budget Period 1 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 electrolyte degradation theory
- Detailed plan developed for extending the theory and improving cell stability in the following budget period
- Go/No-Go Decision Point based on promising SOEC durability and model predictive capability (within 30% of cell degradation conditions)

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

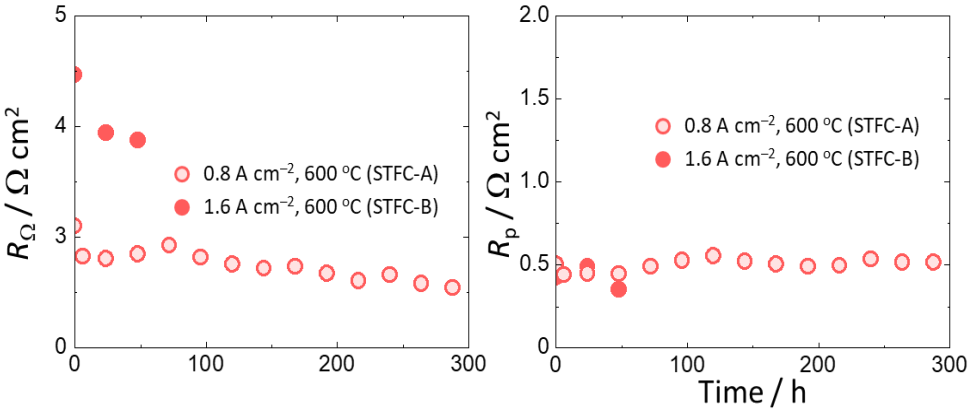
- **<u>Budget period 1 Go/No-Go milestone:</u>** Electrolyte degradation model predicts the experimentally-observed electrolyte resistance degradation caused by overpotential and current density to within 30% for multiple data sets.

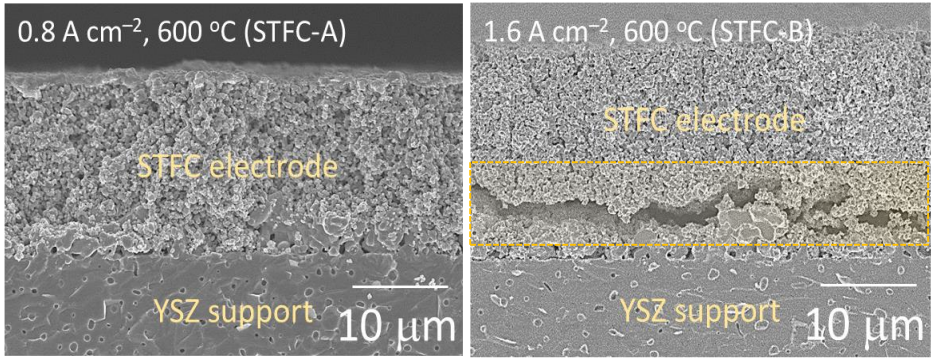
- **<u>Significance of meeting this milestone:</u>** This will mean that the theory developed can make quantitative predictions regarding the conditions that cause degradation. By matching the model to experimental data taken over a wide range of conditions, wide applicability is assured. The theory will allow us to predict operating conditions that yield low degradation and design cells that allow higher current density without degradation.

Accomplishments: Effect of current density on degradation

- Extensive life testing done versus current density, temperature, and electrode material
  - Materials studied: $(La,Sr)(Fe,Co)O_3$ (LSCF), $Sr(Ti,Fe)O_3$ (STF), $Sr(Ti,Fe,Co)O_3$ (STFC)
  - Example below shows effect of current density data for STFC
- Increasing current density from 0.8 to 1.6 A cm^{-2} causes fracture
  - Fracture is observed at interface between electrode and (porous) GDC electrolyte
  - Similar fracture for all materials at low temperature and high current

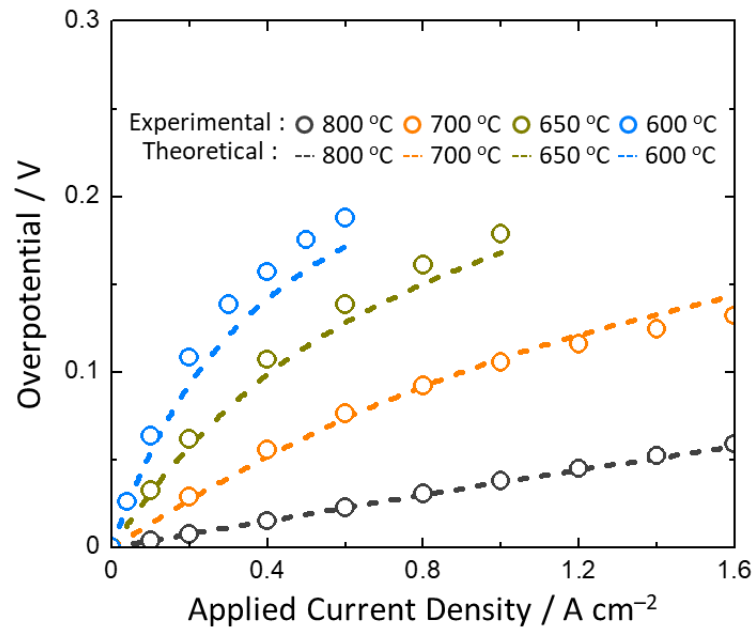
- *Milestone 2.1: electrochemical life testing*
- *Milestone 3.1: microstructural observations*



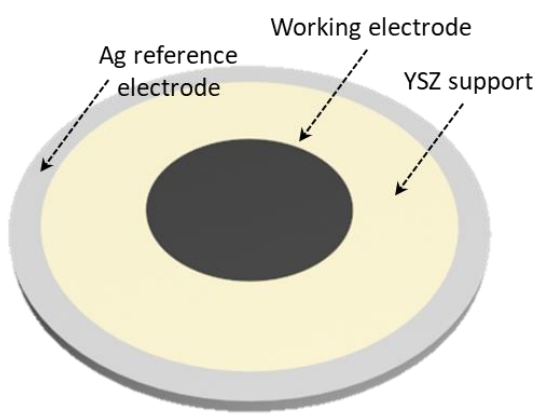


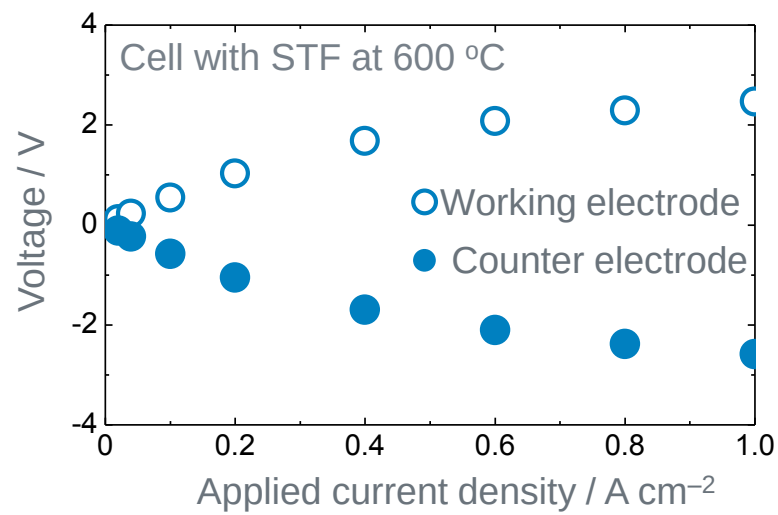
Accomplishments: Electrode Overpotential (η) Measurement

- Test theory that failure depends on η
- Polarization resistance R_P measured versus current density j by impedance spectroscopy
- Integrate to obtain $\eta(j) = \int R_P(j)dj$
- Agrees with approximate Butler-Volmer eqn: $\eta = \frac{2RT}{zF}\sinh^{-1}\left(\frac{j}{2j_0}\right)$; where $j_0 = \frac{RT}{zFR_P(j=0)}$
- Reference electrode measurement on symmetric cells → overpotentials in the two current directions are almost identical



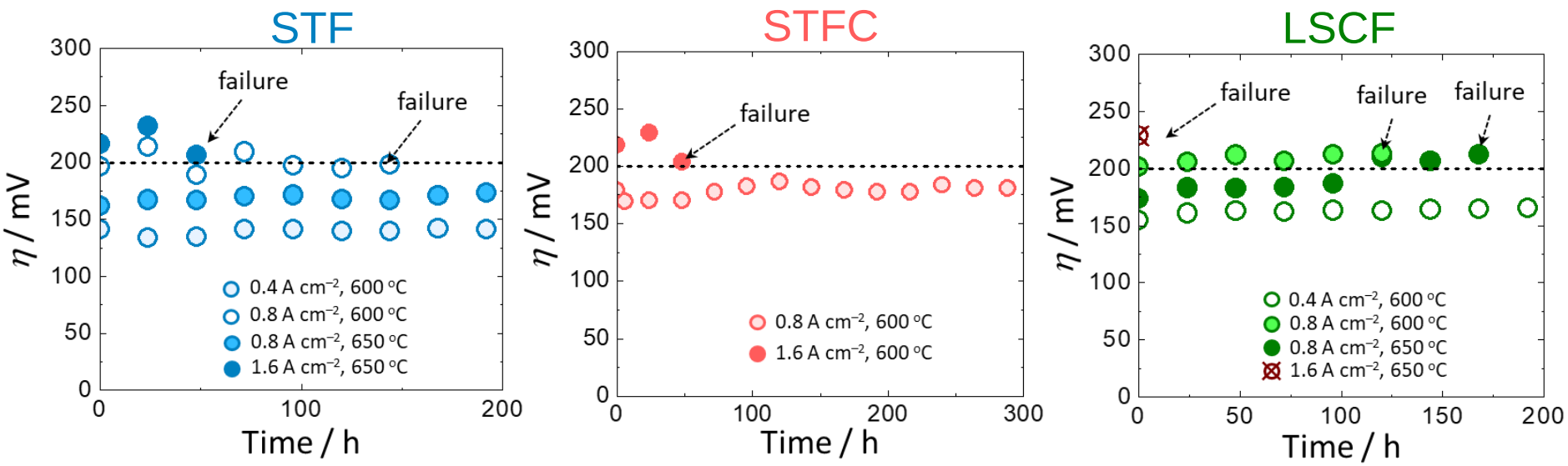
Symmetric cell with reference electrode





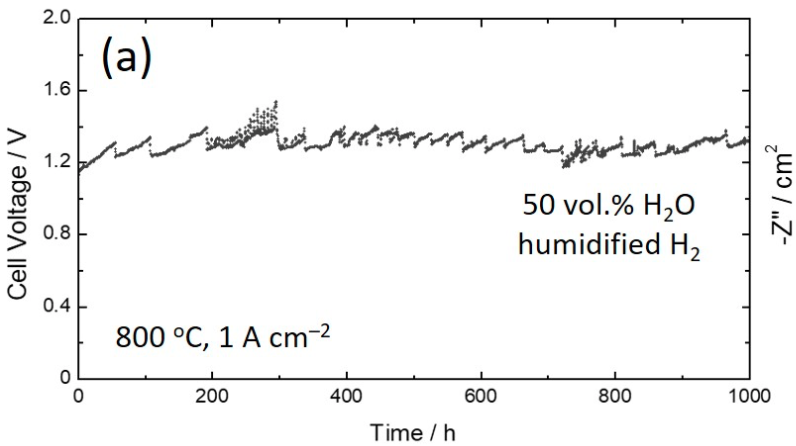
Accomplishments: Overpotential Criterion

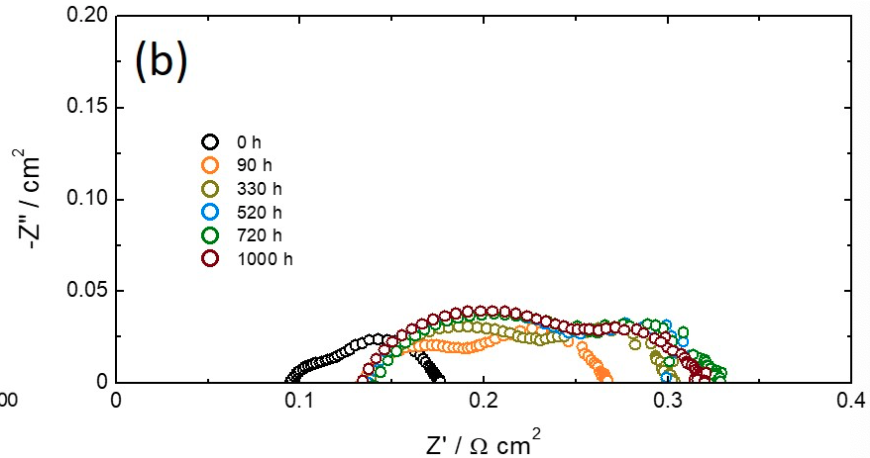
- Electrode materials and operating conditions yielding electrode overpotential (η) values > 190 mV led to cell failure
- STF and STFC provided fairly stable R_P and hence stable η
- LSCF degraded slowly during tests due to Sr segregation
  - For 0.8 A cm^{-2} and 650 °C, η for LSCF gradually increased, causing cell failure after exceeding 190 mV
- *Milestone 2.1: successful electrochemical life testing*

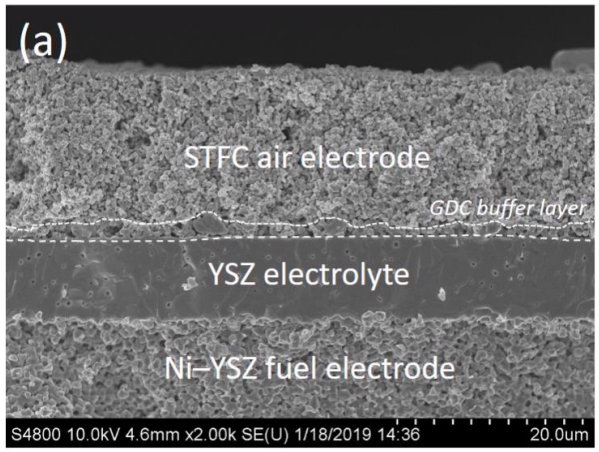


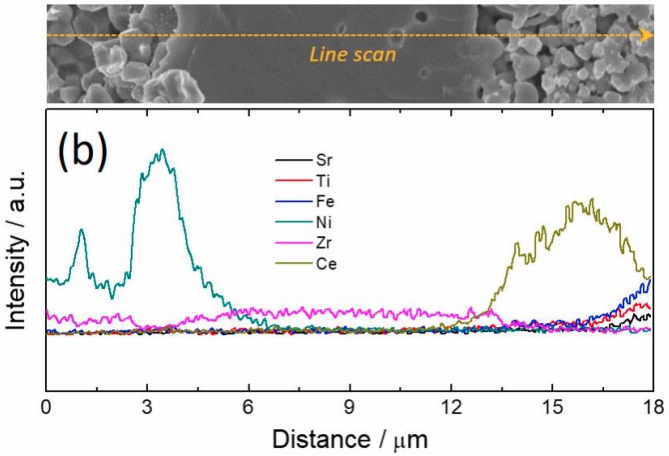
Accomplishments: Full Cell Life Test

- Stable operation achieved by using low-R_p STFC electrode and 800 °C
- Small fluctuations due to variability in test setup
- *Milestone 1.1: cell fabrication; 2.1 life testing; 3.1 microstructural observations*



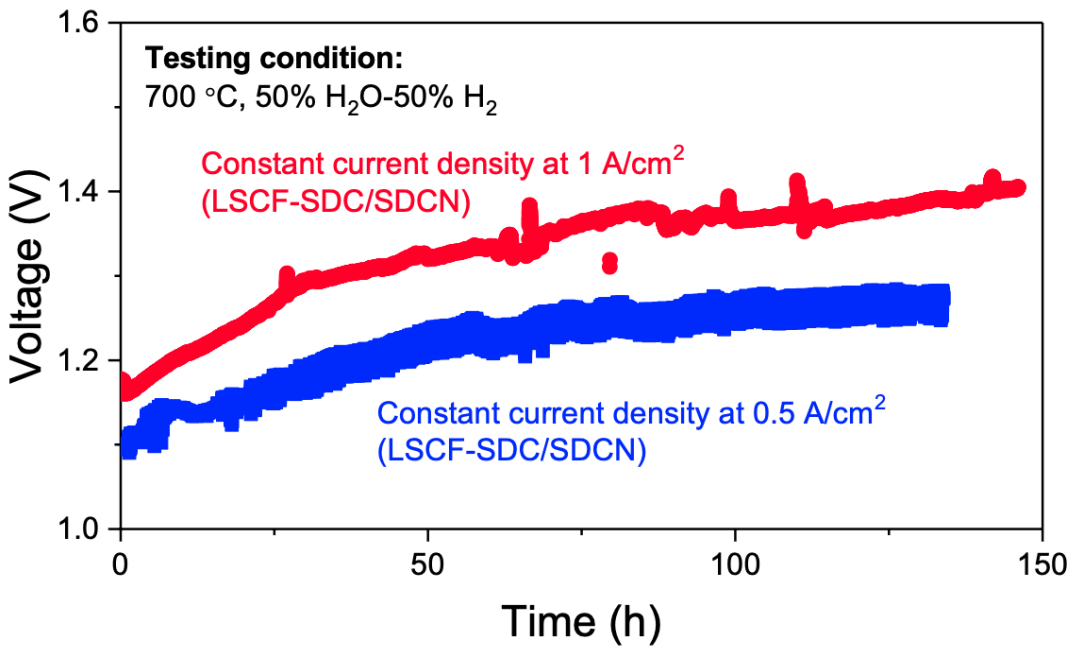






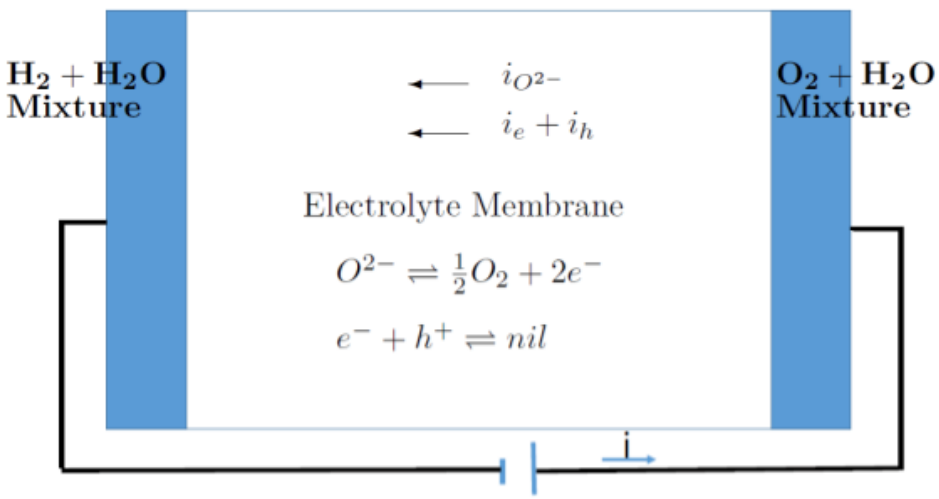
Accomplishments: Metal-Supported Electrolysis Cells

- Data from LBNL under Energy Materials Network support
- First example of metal-supported solid oxide cells tested as electrolyzers
- Recent results show potential for good stability in electrolysis mode
- Results suggest faster voltage degradation for higher current density
  - Similar to observations on conventional solid oxide cells
- *Milestone 1.1: Successful cell fabrication; 2.1 Successful life testing*



Accomplishments: Calculating oxygen potential in the electrolyte

- *Milestone 4.1 Successful development of a model for electrolyte degradation during electrolysis, based on the experimental observations*



$$i = i_{O^{2-}} + i_e + i_h$$

Calculate electron, hole, and vacancy currents due to drift and diffusion, assuming local reaction equilibrium and electroneutrality

Determine Oxygen partial pressure via electron concentration:

$$E = E^{\varnothing} - \frac{RT}{F}\ln\left(\frac{c_e}{c_e^{\varnothing}}\right)$$

$$E = E^{\varnothing} + \frac{RT}{4F}\ln\left(\frac{P_{O_2}}{P_{O_2}^{\varnothing}}\right) + \frac{RT}{2F}\ln\left(\frac{C_V}{C_V^{\varnothing}}\right)$$

$$P_{O_2} = P_{O_2}^{\varnothing}\left(\frac{C_e}{C_e^{\varnothing}}\right)^{-4}\left(\frac{C_V}{C_V^{\varnothing}}\right)^{-2}$$

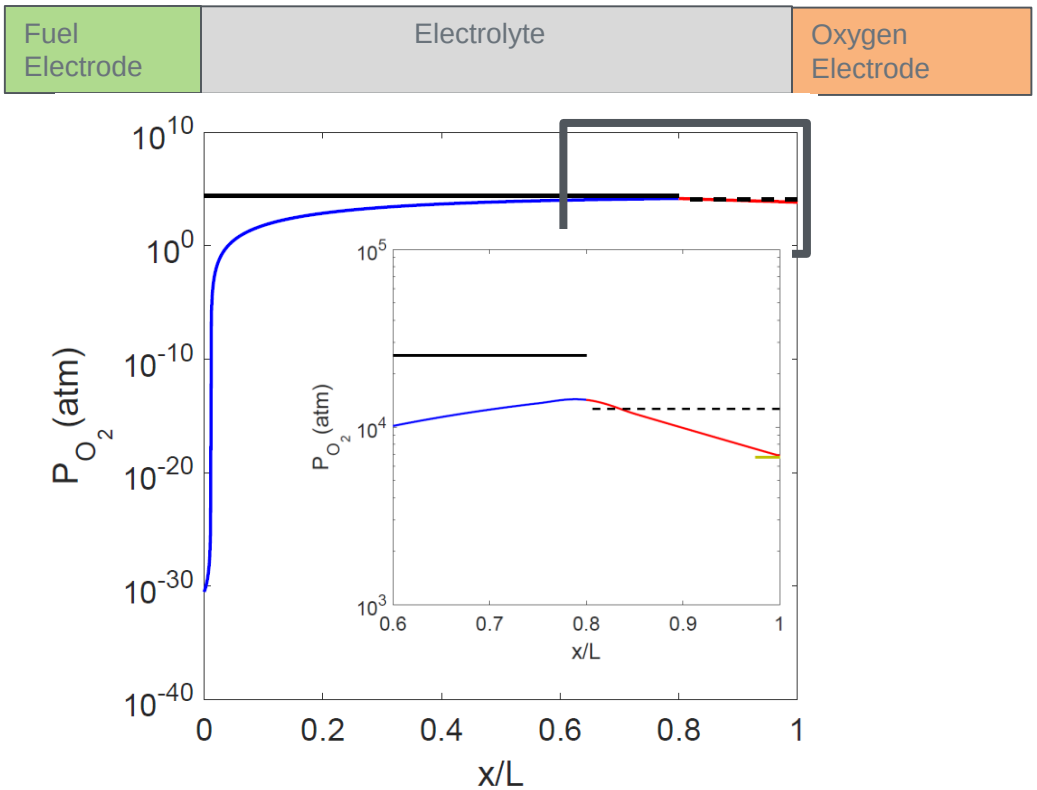
Boundary conditions:

$$E_H = E_H^{OCV} + \eta_H$$

$$E_O = E_O^{OCV} - \eta_O$$

Accomplishments: Numerical Prediction vs. Experiment

- Oxygen pressure exceeds fracture toughness of perovskite at interface
- Peak pressure at YSZ/GDC interface suggest possible failure at this interface

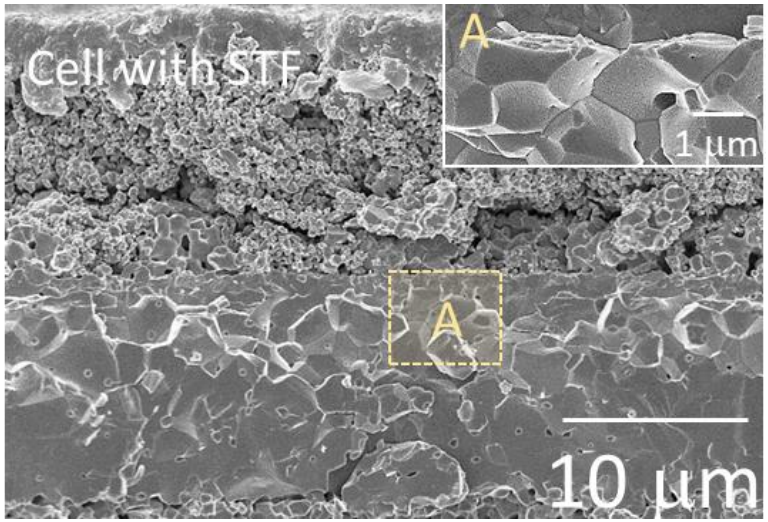


Cell: Ni-YSZ/ YSZ (10 µm) / GDC (2.5 µm) /STF
Test conditions: 600 C, -0.8 A cm^{-2}

$$P_{cr} = \sqrt{\frac{\pi \gamma E_Y}{2(1-v^2)c}} = \frac{1}{2}\sqrt{\frac{\pi}{(1-v^2)c}} K_{IC}$$

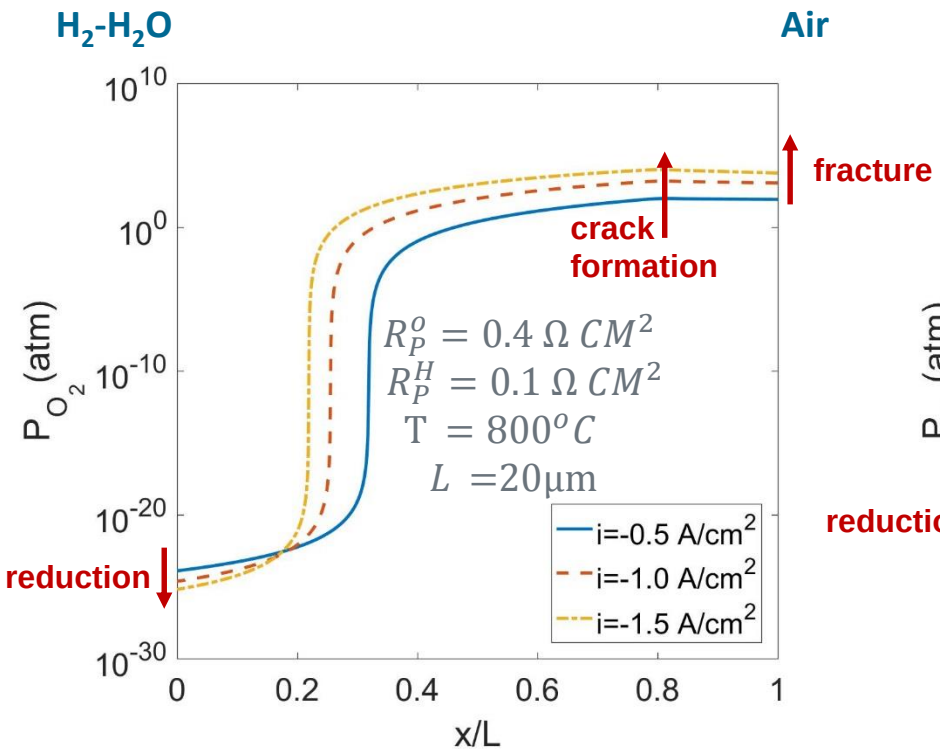
Here, v is the Poisson ratio of the solid material and c is a crack radius, K_{IC} is the fracture toughness of the corresponding material.

YSZ fracture P_{O2} : 2x10^4 atm
GDC fracture P_{O2} : 1x10^4 atm
Perovskite fracture P_{O2} : 0.7x10^4 atm

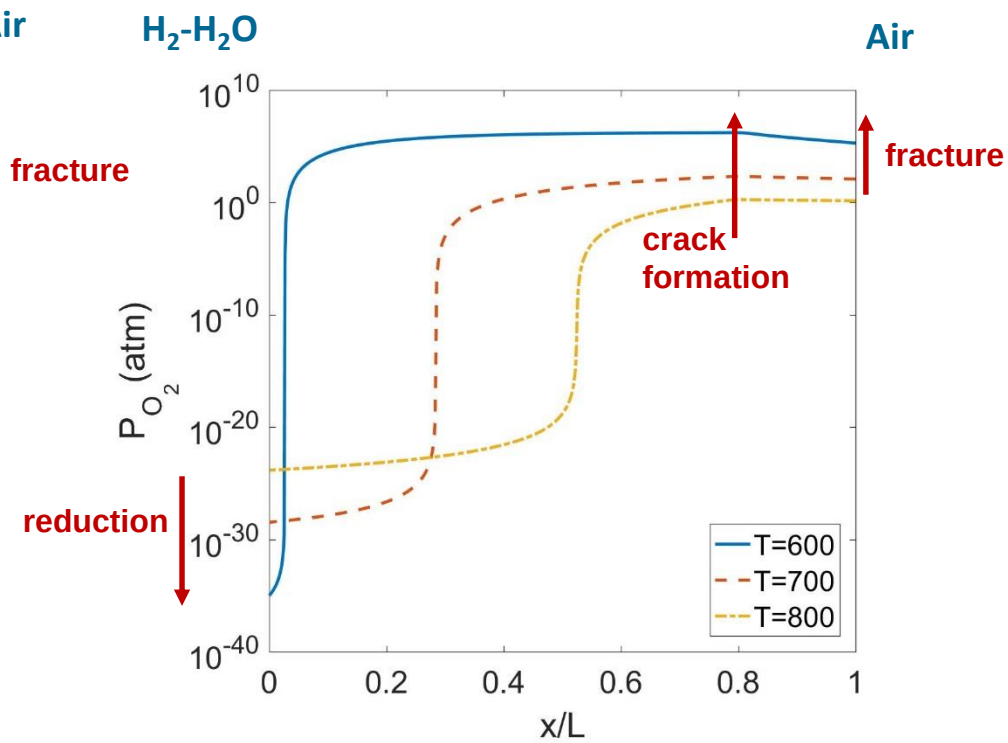


Accomplishments: Effect of Operating Conditions

- Current density (left) or temperature (right) can lead to high overpotentials
- Leading to extreme oxygen pressures near electrode/electrolyte interfaces
- *Milestone 4.1 Successful development of a model for electrolyte degradation*



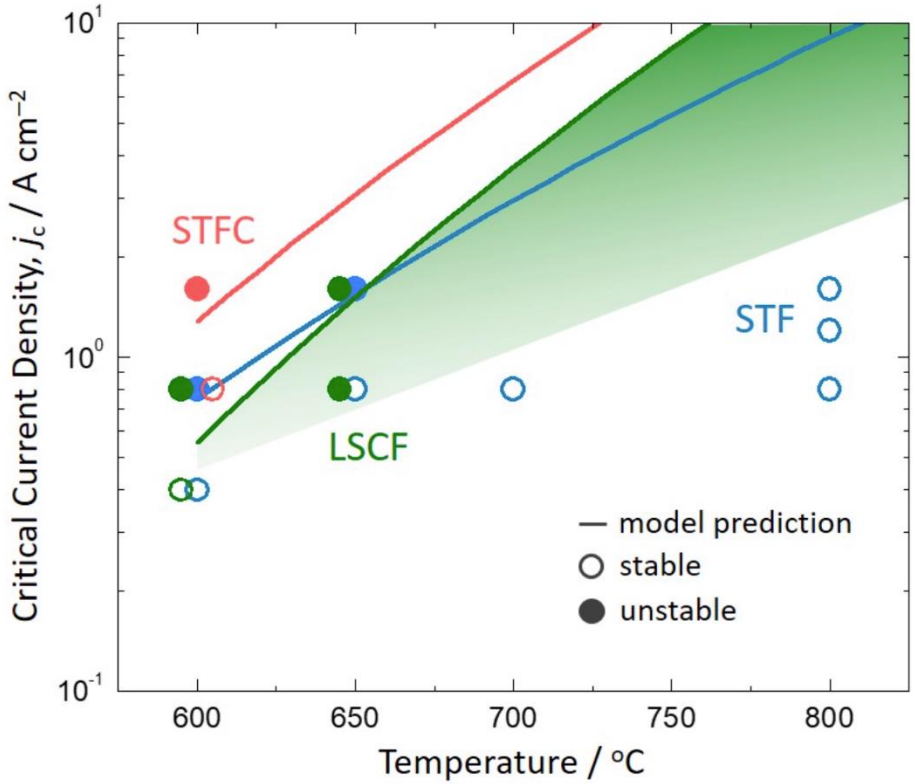
Increasing Current Density



Decreasing Temperature

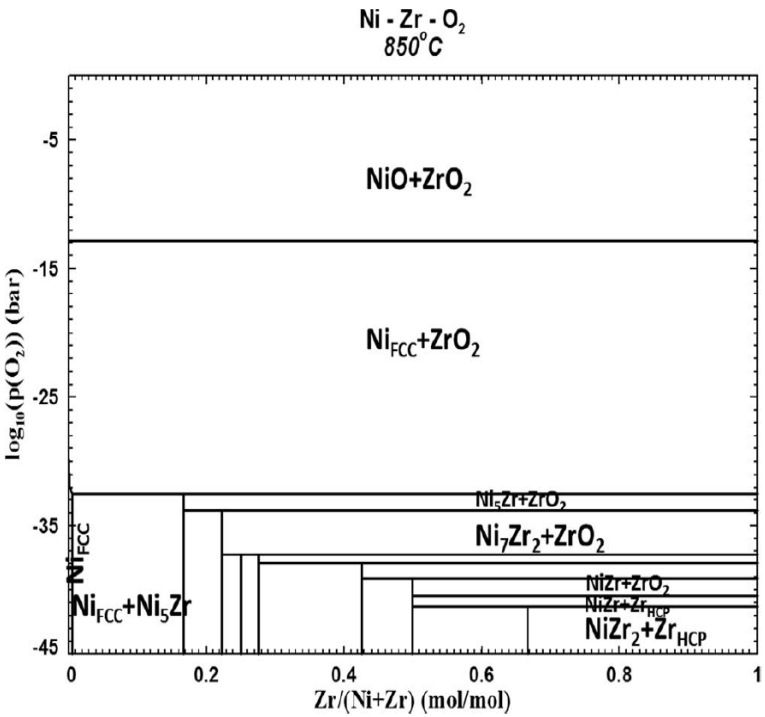
Accomplishments: Theory Vs Experiment Comparison

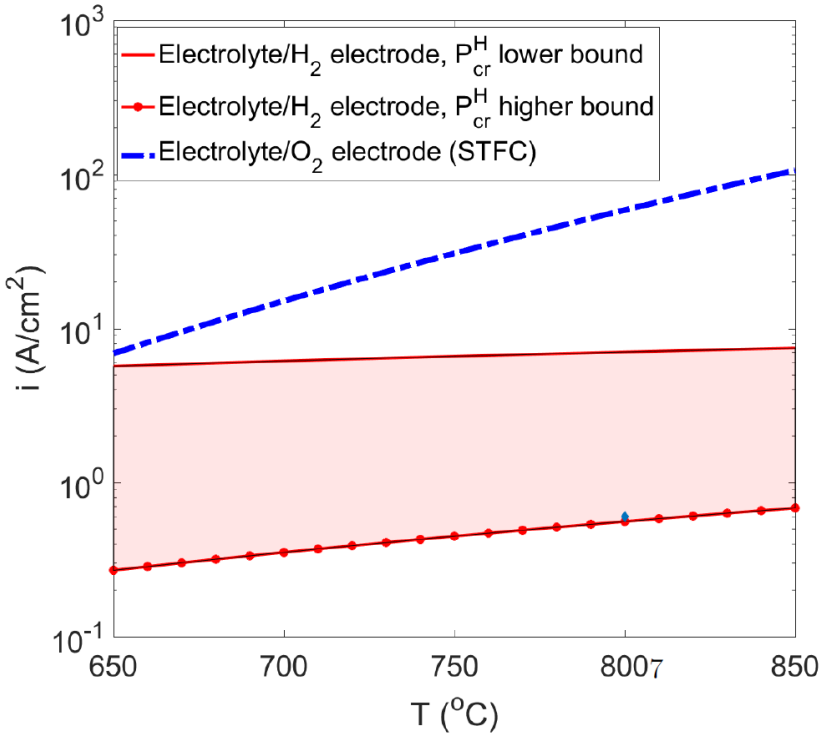
- Predicted critical current density for fracture versus temperature for three different electrode materials
  - Compared with experimental fracture observations
- Excellent agreement for STF and STFC electrodes – STFC shows best stability
- LSCF electrode failure criterion varies with time (shaded region)
  - Critical current density decreases with time as R_P and η increase
- *Milestone 4.1 Successful development of a model for electrolyte degradation*



Accomplishments: Fuel Electrode Degradation

- Altered layer observed at electrode/electrolyte (Ni-YSZ/YSZ) interface at high current density
  - *Liu et al. J Elec Soc 165 (2018) F870; Chen et al., J Elec Soc 160 (2013) F883*
- Explained by reduction of zirconia to form Ni-Zr alloy or compound
  - Estimated phase diagram by extrapolation from higher T data → P_{cr} ~ 10^{-27} – 10^{-33} bar
- Model prediction of critical current density for degradation of typical Ni-YSZ electrode
  - Wide range reflects uncertainty in P_{cr} value
  - Higher critical current for lower electrode R_P, higher H_2O / H_2 ratio





Accomplishments - Outlook

- Theory of oxygen pressure versus position in electrolyte developed that accurately predictions conditions for fracture at the air-electrode / electrolyte interface
  - Model will be further developed to include additional effects such as YSZ/GDC interdiffusion
  - Model will be applied to provide predictions of other degradation mechanisms, including fuel-electrode/electrolyte interface degradation and grain boundary cavitation within the electrolyte
- Further symmetric cell and full cell life testing will provide data that will inform the models and provide new insights into accelerated stress testing methods
- Full cells have been developed that show good stability in 1000-h life tests
  - Future work will include improvements in the life test setup, improvements in cells to provide stable lower-temperature performance, to reach the Go/no-go milestone
- We fully expect that we will be able to make good quantitative comparisons between model and experiment, and thereby vet the model as needed for the Go/No-Go milestone.
- The major impact of this milestone to the broader water-splitting research community will be in providing a better understanding of degradation mechanisms. This will in turn allow development of improved electrolysis cells with low degradation at high current density

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 2* ($326k):
  - Advanced versions of the solid oxide electrolysis cells (SOECs) will be life tested using electrochemical and microstructural characterization
  - Refine electrolyte degradation theory, and develop electrode degradation models
  - Achieve promising SOEC durability (e.g. < 40 mV/kh)
  - Define the optimized SOEC design for the next project period
  - HydroGEN EMN nodes (LBNL and INL) will continue to enhance the project with alternative cell designs and testing methods
- Budget period 3* ($336k):
  - Optimized SOECs will be fabricated and life tested
  - Longer life tests will be used to help refine and validate the electrolyte and electrode degradation theories
  - End of project goals include well-developed predictive degradation models and SOECs that meet program durability targets
  - HydroGEN EMN nodes (LBNL and INL) will continue to enhance the project with input on alternative cell designs and testing methods

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

Project Summary

- Full cells have been developed that show good stability in 1000-h life tests
- A quantitative theory has been developed that predicts the oxygen potential across the electrolyte in a solid oxide electrolysis cell
  - Degradation when the oxygen pressure exceeds the fracture threshold
    - No fitting parameters in either model
- Comparison with experimentally-observed degradation:
  - Correctly predicts experimentally observed degradation of symmetric and full cells by fracture at electrode/electrolyte interface
  - Predicts critical overpotential value of ~ 200 mV (pO_2 ~ 10^4 atm) across various electrode materials
  - Experimental: 190 ± 15 mV
- LBNL metal supported cells provide an alternative system to validate our understanding of degradation; technological alternative
  - First-ever results on metal-supported solid oxide electrolysis
- INL testing expertise and capabilities substantially extend those at Northwestern
- On track to project goals – obtain quantitative electrolyte degradation theory and high-performance cells with low degradation rate