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

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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.

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.
**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. Understanding will show pathways to reduced degradation rates.

**Key Impact**

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Expected Advance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Density</td>
<td>0.5 A/cm²</td>
<td>&gt; 1.0 A/cm²</td>
</tr>
<tr>
<td>Degradation Rate</td>
<td>&gt;10 mV/kh</td>
<td>&lt; 4 mV/kh</td>
</tr>
<tr>
<td>Electrode Overpotential</td>
<td>&gt; 0.2 V</td>
<td>&lt; 0.2 V</td>
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</tbody>
</table>

**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. Jim O’Brien at INL has worked on solid oxide electrolyte cell technology for many years, and has extensive knowledge and testing facilities relevant to this project.
Budget Period 1 Scope of Work

• Baseline SOECs are fabricated and accelerated electrochemical life testing carried out along with microstructural/chemical characterization.

• The results are used to guide development of a theory for electrolyte degradation during electrolysis.

• Based on the results, a detailed plan will be developed for extending the theory and improving cell stability in the following budget period.

• Go/No-Go Decision Point based on successful prediction (within 30% of cell resistance change) of degradation rate
Approach- Materials Innovation

• A model has been developed that predicts the oxygen potential across the electrolyte in a solid oxide electrolysis cell
  – When compared with models that predict the effective oxygen pressures that causes electrolyte degradation, we can predict the materials and operating conditions causing degradation
  – The model is broadly applicable to different materials & conditions

• Solid oxide electrolysis cells have been fabricated and preliminary tests indicate very good performance
  – Basic cell design is similar to most SOECs under current development; thus, test results are broadly applicable
  – A new oxygen electrode material shows excellent performance and low degradation rate at high current density
  – Reduced-temperature co-firing of YSZ electrolyte, GDC barrier, and fuel electrode yields low polarization resistance

• First-ever results on metal-supported solid oxide electrolysis cells
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

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

• **Significance of meeting this milestone:** 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.
Milestones

1.1: Successful fabrication of baseline cells with <20 \( \mu \text{m} \) thick, >90% dense electrolyte operating at < 1.3 V at 1.0 A/cm\(^2\)
   - Originally 12/31/17, moved to 2/28/18
   - 90% complete

2.1: Successful cell life testing over a wide range of operating conditions. Assessment of this data to develop an experimental plan for Budget Period 2
   - Originally 3/31/18, moved to 5/31/18
   - 50% complete

3.1: Successful observation of changes in baseline cell structure and chemistry after life testing
   - Originally 6/31/18, moved to 8/30/18
   - 20% complete

4.1: Successful development of a model for electrolyte degradation during electrolysis, based on the observations from Tasks 2 and 3
   - Originally 9/30/18, moved to 11/30/18
   - 50% complete
Milestone 4.1 Successful development of a model for electrolyte degradation during electrolysis, based on the experimental observations.

**Determine Oxygen partial pressure via electron concentration:**

\[
\pi - \phi = (\pi - \phi)_{\text{O}} - \frac{RT}{F} \ln \left( \frac{c_e}{c_e^0} \right)
\]

\[
\pi - \phi = (\pi - \phi)_{\text{O}} + \frac{RT}{4F} \ln \left( \frac{P_{O_2}}{P_{O_2}^0} \right)
\]

**Boundary conditions:**

\[
(\pi - \phi)_H = (\pi - \phi)_{OCV}^H + \eta_H
\]

\[
(\pi - \phi)_O = (\pi - \phi)_{OCV}^O - \eta_O
\]

\[
\eta_{H,O} = \frac{RT}{F} \sinh^{-1} \left( \frac{i_{P_{H,O}}}{RT} \right)
\]
Accomplishments: Effect of Oxygen Electrode Polarization Resistance

- Critical oxygen pressure for YSZ electrolyte fracture:
  \[ P_{cr} = \frac{1}{2} \sqrt{\frac{\pi}{(1 - v^2)c}} K_{IC} \]

- \( c \) is a crack radius, \( v \) is the Poisson ratio and \( K_{IC} \) the fracture toughness of the material

- Higher oxygen electrode resistance yields higher overpotential. Beyond a critical value this yields fracture near the oxygen electrode

\[ R_p^H = 0.1 \, \Omega \, cm^2 \]
\[ i = -1.5 \, A/cm^2 \]
\[ T = 800^\circ C \]
\[ t_{YSZ} = 20 \mu m \]
Accomplishments: Effect of Current Density

- Higher electrolysis current density yields higher oxygen pressure at the oxygen electrode
  - Can lead to fracture when critical value is exceeded
- Higher electrolysis current density yields lower oxygen pressure at the fuel electrode
  - Can yield fuel electrode degradation by, e.g., formation of Ni-Zr alloy formation at Ni-ZrO₂ interface.

\[ R_P^o = 0.9 \, \Omega \, \text{cm}^2 \]
\[ R_P^H = 0.1 \, \Omega \, \text{cm}^2 \]
\[ T = 800^\circ C \]
\[ t_{YSZ} = 20 \, \mu \text{m} \]
Accomplishments: Solid Oxide Electrolysis Cell Fabrication

- SOECs have been fabricated using a combination of tape casting and screen printing
- The cell structure and performance has been optimized and fabrication of a large set of cells is underway
- This meets Milestone 1.1
  - Successful fabrication of at least 20 baseline cells with porous electrode structures allowing for high electrochemical activity and a <20 µm thick, dense (>90%) electrolyte

※ STFC: Sr(Ti\textsubscript{0.3}Fe\textsubscript{0.63}Co\textsubscript{0.07})O\textsubscript{3}
GDC: Gd\textsubscript{0.1}Ce\textsubscript{0.9}O\textsubscript{2}
YSZ: 1 mol.% Fe\textsubscript{2}O\textsubscript{3}-doped 8YSZ
8YSZ: 8 mol.% Y\textsubscript{2}O\textsubscript{3}-stabilized ZrO\textsubscript{2}
Accomplishments: Solid Oxide Electrolysis Cell Performance

- Cell performance has been fully characterized
- Cell current density at expected electrolysis voltage, and cell resistance, are as desired
- The performance results meet the second part of Milestone 1.1:
  - < 1.3 V at 1.0 A/cm² (800 °C, in air and humidified hydrogen)

The SOEC indicates the cell voltage of ~1.15 V at 1 A cm⁻² (800 °C).
Accomplishments: Life tests of SrTi$_{0.3}$Fe$_{0.7}$O$_3$ air electrode

- EIS data collected from cells with STF electrodes tested at various current densities (800 °C)
  - Ohmic and polarization resistance components are extracted by fitting the EIS spectra
- Results show initial changes in cell performance followed by stabilization
  - Electrodes appear stable even at high current density
- Meets Milestone 2.1: Successful life testing (~1000 hr) of the baseline cell type showing different degradation rates and mechanisms over a wide range of operating conditions
Accomplishments: Metal-Supported Solid Oxide Electrolysis Cells (LBNL)

- **Symmetric Structure Metal-Supported Solid Oxide Electrolysis Cells (MS-SOECs)**

 Advantages include low cost, high strength, thermal cycling capability
- First MS-SOEC results
- Initial performance excellent
- Fast degradation

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Accomplishments: Stability of MS-SOECs (LBNL)

- Fast initial degradation, probably due to nanoparticle coarsening
- Stability is improved by pre-oxidizing the cell before infiltration
- Further testing to longer times will show if performance stabilizes
Accomplishments: Alternative cells and testing (INL)

- Developed anode supported solid oxide electrolysis cells
  - Provide additional electrochemical life test data from cells that are different from those made at Northwestern, providing a broader range of data on which to base theory development
- Electrochemical testing of both INL and Northwestern SOECs
Accomplishments Summary

• Full cell development is complete, allowing us to prepare the required number of cells for testing in the remaining budget period.
• Theory of oxygen potential versus position in electrolyte is complete. Models for electrolyte degradation versus oxygen potential are nearly complete. The combination will allow us to make direct comparisons of degradation with experiment in the remaining budget period.
• Life testing is partially completed, and we expect to be able to complete in the remaining budget period.
• 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. < 20 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

• A model has been developed that predicts the oxygen potential across the electrolyte in a solid oxide electrolysis cell. When compared with model that predicts the effective oxygen pressure that causes oxygen bubble nucleation, conditions where cell degradation occur are predicted
  – Predicted effects of electrode resistance, current density, and operating temperature in basic agreement with experimental observations

• Solid oxide electrolysis cells have been fabricated
  – Preliminary tests indicate very good performance – these will be used in ongoing testing
  – Results to date show that a new oxygen electrode material exhibits excellent performance and low degradation rate at high current density

• First-ever results on metal-supported solid oxide electrolysis cells from LBNL show promising initial performance, but fast degradation

• On track to project goals – obtain quantitative electrolyte degradation theory and high-performance cells with low degradation rate