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

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Overall Objectives

- Develop a fundamental understanding of degradation mechanisms in solid oxide electrolysis cells (SOECs) based on accelerated testing coupled with theory.
- Develop improved SOECs that provide a long lifetime at high current density in order to improve economic viability.

Fiscal Year (FY) 2019 Objectives

- Develop a model for fuel-electrode-related degradation in solid oxide cells.
- Carry out experimental life tests of solid oxide electrolysis cells designed to observe fuel-electrode degradation processes in order to develop means for decreasing degradation and provide input for model development.
- Develop new solid oxide cells with the capability for electrolysis at high current density with low degradation rates.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Generation by Water Electrolysis section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan[1]:

- (F) Capital Cost
- (G) System Efficiency and Electricity Cost.

Technical Targets

This project aims to study the operating characteristics and degradation mechanisms in state-of-the-art SOECs using accelerated life tests combined with modeling. SOECs are of interest because of their potential to achieve higher electricity-to-hydrogen efficiency, and thereby lower the hydrogen production electricity cost, as compared to other electrolysis technologies. The goal is to achieve an understanding that allows one to build SOECs that operate at high current density with good long-term stability and minimize the impact of stack cost on hydrogen production cost.
The project thereby addresses the following DOE 2020 electrolysis targets:

- Hydrogen levelized cost: $2.30/kg
- Electrolyzer system capital cost: $0.50/kg ($300/kW)
- System energy efficiency: 75% LHV (44 kWh/kg)
- Stack energy efficiency: 77% LHV (43 kWh/kg).

FY 2019 Accomplishments

- Successfully developed Ceria-infiltrated Ni-YSZ fuel electrodes and demonstrated that they provide reduced cell resistance and much-improved stability.
- Substantially improved SOEC performance and demonstrated full-cell degradation rate <20 mV/kh at a current density of 1.5 A/cm^2 at an operating temperature 700°C, easily meeting project targets.

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- Utilized an electrolyte transport model as the basis for explaining observed cell degradation related to the fuel electrode. The results strongly suggest that degradation arises because of the extremely low oxygen partial pressures that arise at or near the fuel electrode during the high-current-density electrolysis operation. A number of specific mechanisms have been proposed and tested. It has been shown that the fuel-electrode related degradation is worse for low steam content fuel, but that reducing fuel electrode overpotential mitigates degradation.

INTRODUCTION

SOECs have the potential to produce hydrogen at lower overpotential than other methods, thereby providing energy efficiency values much higher than those of existing technologies, exceeding 90%. Because the input electrical energy is a dominant cost of electrolytically-produced hydrogen, SOECs have great potential for reducing hydrogen cost. Although SOECs operate stably at relatively low current density (≤0.5 A/cm^2), at higher current density desired for cost-effective hydrogen production, various degradation mechanisms are typically observed that can severely decrease cell lifetime.

In the second year of this project, the focus has been on SOEC degradation related to the fuel electrode, following the first-year focus on electrolyte degradation associated with the oxygen electrode. The fuel electrode gas composition can vary over a fairly wide range, e.g., from 90% H_2O–10% H_2 to 10% H_2O–90% H_2 in different regions of a cell; thus, extensive studies are required to determine both the polarization resistance and characterize degradation processes that may vary significantly over this range. An initial survey study was carried out to sample the different results over this full range. The model previously developed for calculating the oxygen partial pressure in the electrolyte was used with input values from our experimental cells and testing conditions to help explain experimental results focused on low-steam conditions. These results show that the degradation rate increases rapidly with increasing current density but is strongly accelerated by low-steam (i.e., high steam utilization) conditions. Furthermore, improved SOECs were developed using the above understanding of degradation mechanisms. In particular, Ceria infiltration into the Ni-YSZ fuel electrode was utilized to reduce polarization resistance, greatly reducing degradation and enabling cells to exhibit promisingly low degradation rates.

APPROACH

The project aims to develop mechanistic degradation models that realistically predict long-term SOEC durability, using input data from accelerated electrochemical life testing combined with quantitative microstructural and microchemical evaluation. A promising SOEC type is being further developed. The understanding achieved by combining experimental results and theory will be used to guide improvements in long-term SOEC durability and validate that this technology can reach DOE hydrogen production cost and durability targets. The approach includes (1) obtaining new experimental accelerated testing data on SOEC degradation at the oxygen electrode, fuel electrode, and electrolyte; (2) developing a predictive theory of degradation based on the accelerated test data; (3) developing and testing new electrode materials and processing methods that minimize degradation rate; (4) determining the impact of SOEC electrolyte and electrode composition and microstructure on performance and degradation; (5) determining the operating conditions where degradation is minimized; and (6) validation of degradation models for extrapolating accelerated test data to predict long-term durability.

RESULTS

In the second year of this project, Northwestern University developed much-improved SOECs and carried out extensive life testing in parallel with the development of a model for electrolyte degradation mechanisms. The full SOECs consist of a Ni–YSZ support and Ni-YSZ functional layer infiltrated with $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC), $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (YSZ) electrolyte, GDC barrier layer, and $Sr(Ti_{0.3}Fe_{0.63}Co_{0.07})O_3$ (STFC) oxygen electrode infiltrated with PrO_x. In addition to the GDC and PrO_x infiltration, the YSZ electrolyte thickness was reduced, and the support layer porosity was increased. Cell performance exceeds program targets, providing current density >1.5 A/cm^2 at an operating voltage of 1.2 V for a temperature of ~700°C. Life tests show promising stability. As illustrated in Figure 1, an SOEC operated at 1.5 A/cm^2 at 700°C in air, and 50% H_2/50 H_2O

showed a slight voltage increase over the first ~500 hours. Over the next 500 hours it stabilized with a degradation rate <20 mV/kh. Cross-sectional scanning electron microscopy (SEM) analysis of the cell after life testing shows no obvious structural or chemical changes compared to the pre-test cells. This is consistent with the electrochemical impedance spectroscopy data, indicating no significant change in ohmic resistance during the life test; the increase in voltage in the first part of the test was probably associated with the coarsening of the GDC and PrO_x catalysts.

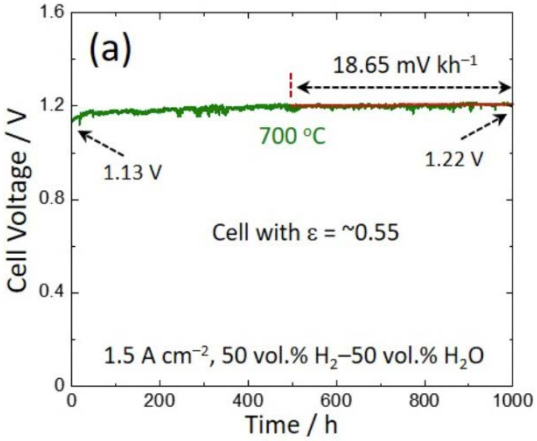

Figure 1. Cell voltage versus time for a fuel electrode supported SOEC operated at 1.5 A/cm², 700°C, in air and 50 vol % H_2O–50 vol % H_2.

Much of the improvement in cell performance and stability resulted from GDC infiltration into the Ni-YSZ fuel electrode, a measure that was extensively developed and studied this year. Figure 2 illustrates the dramatic reduction in electrode polarization resistance–by a factor of ~3 times for the optimal concentration–that results from the GDC infiltration.

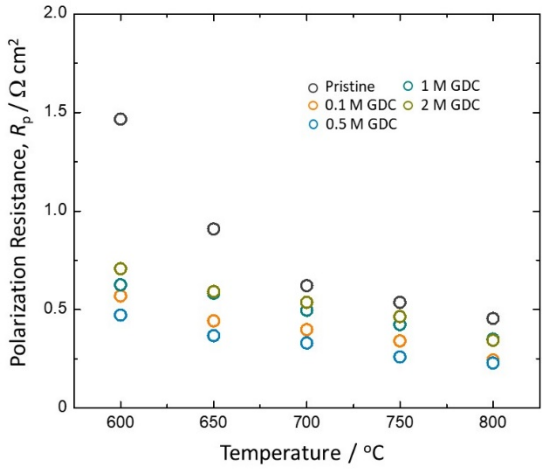

Figure 2. Temperature dependences of the polarization resistance (R_p) for the Ni–YSZ-supported symmetric cells with different concentrations of GDC solutions infiltrated.

Besides improving cell performance characteristics, the reduction in polarization resistance also reduces fuel electrode overpotential at a given current density; based on our model results, this should also help to limit cell degradation. This is demonstrated in Figure 3, which shows the results of an initial survey life test carried out at a range of fuel compositions, starting at 90% H_2O–10% H_2 and decreasing by 20% every 200 hours, ending at 10% H_2O–90% H_2. For the electrodes without GDC (pristine), the ohmic resistance increases slowly at higher steam contents but then shows a larger increase at 10% steam. This increase may be related to the electrolyte damage that can result in the most highly-reducing conditions, as discussed below. The polarization

resistance for the pristine electrodes shows an apparently continuous increase with decreasing steam content. This is due in part to the known tendency for R_P to increase with decreasing steam content. However, there does also appear to be some degradation occurring within the constant steam periods. On the other hand, for the GDC infiltrated Ni-YSZ cell, the Ohmic resistance remains fairly constant, although gradually increasing with time. For the GDC-infiltrated Ni-YSZ cell, R_P increases during the first 200 hours, but then remains essentially constant during each constant steam-content segment, but increases in steps with each steam content decrease. This change is not degradation but the expected change in R_P with fuel composition. These results confirm the much-improved performance of cells with GDC-infiltrated Ni-YSZ electrodes over a wide range of fuel compositions and also illustrate the associated improvement in cell stability.

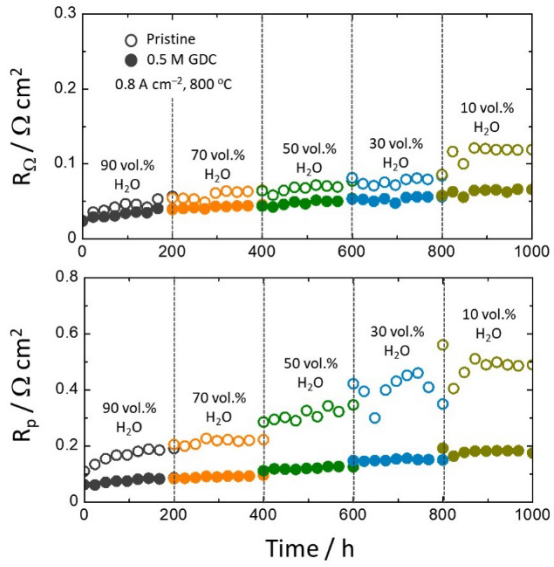

Figure 3. Evolution of ohmic ($R_\square$) and polarization (R_p) resistances for the Ni-YSZ and 0.5 M GDC-infiltrated Ni-YSZ-supported symmetric cells during the life tests performed in a range of H_2O–H_2 mixtures at 800°C under the dc current application of 0.8 A/cm².

On the theory side, the model developed in the prior year has been applied with an emphasis on predicting the oxygen partial pressure on the fuel side and thereby explain some of the reported fuel-side degradation mechanisms. In particular, increases in ohmic resistance during life tests in 97% H_2 /3% H_2O at current density ≥0.6 A/cm² were explained by the growth of electrolyte voids leading, in the most extreme case, to extended separations in the electrolyte. The formation of grain-boundary voids in YSZ and nanoparticles in Ni-YSZ have also observed afterlife tests under 3% H_2O and high current density conditions.

Model calculations suggest that the microstructural changes are driven by the strong electric potential and the very low oxygen pressure that develops across the electrolyte during electrolysis. Electrolysis operation under low-steam conditions was found to strongly accelerate degradation compared to the high steam electrolysis life test, where no degradation was observed. While this can be useful for accelerated testing, it also illustrates the importance of avoiding high steam utilization in practical SOECs. These results corroborate prior literature data [1], showing that high current density electrolysis can lead to degradation due to the reduction of ZrO_2, resulting in the formation of Ni-Zr alloys or compounds. Figure 4 shows the predicted oxygen pressure versus position across the electrolyte during the SOEC operation. Electrolysis operation drives P_{O_2} to lower values on the SOEC side with increasing j, due to higher overpotentials. Shifting from 3% to 50% H_2O moderates the P_{O_2} value, both because of the higher effective P_{O_2} value in the gas phase and reduced electrode overpotentials. Figure 4 also indicates the critical P_{O_2} where zirconia reduction to form Ni-Zr phases is expected[1,2]; this is shown as a range of values due to the uncertainty in the thermodynamic data. Nonetheless, it can be qualitatively seen that increasing j or decreasing the H_2O content can decrease P_{O_2} into the range where zirconia reduction can be expected.

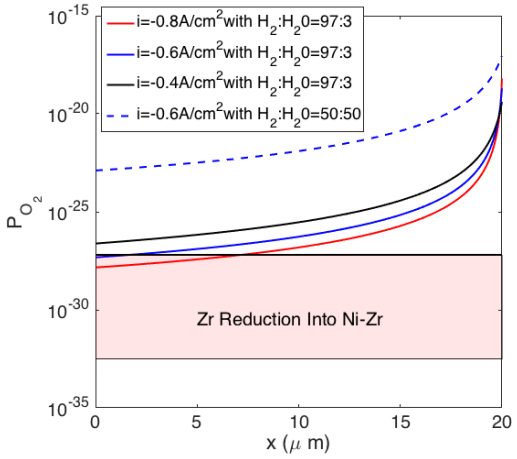

Figure 4. P_{O_2} versus position across the YSZ electrolyte from the SOEC side (left) to the SOFC side (right), for various current densities and gas compositions. The red band indicates the range where ZrO_2 reduction to form a Ni-Zr compound is expected.

Lawrence Berkeley National Laboratory (LBNL) has adapted its metal-supported solid oxide cells, which had previously only been utilized as fuel cells, for application as SOECs. In work on metal-supported cells at LBNL, the electrodes have been engineered to improve stability, tests at constant current and constant voltage have been compared, and initial results show that increasing current density increases degradation rate, in agreement with the Northwestern results. The effect of the H2/H2O ratio was investigated for metal-supported SOECs. Lower H2/H2O ratio decreased the extent of degradation in the long-term, and resulted in good durability. A long-term (>1000 h) electrolysis durability test was conducted on a metal-supported cell, yielding a degradation rate of 16%/1000 h, arguably the best ever reported for such a cell.

Idaho National Laboratory has applied its extensive SOEC testing capabilities and expertise in this project. Specifically, they have contributed additional cell testing and data interpretation to expand the scope of the project, carrying out SOEC testing over a range of H_2/H_2O ratios.

CONCLUSIONS AND UPCOMING ACTIVITIES

The present experimental and theoretical results show very promising results regarding SOEC performance and durability. The importance of modifying the Ni-YSZ fuel electrode with Ceria infiltration, both for improving cell performance and minimizing degradation, has been established. Degradation effect occurring under low-steam, high current conditions have been explained using the SOEC electrolyte transport theory as being due to extremely low effective oxygen partial pressures.

In the coming year, the model will be further developed to help explain the degradation effects observed at the H_2/H_2O electrode. In particular, the degradation effects occurring at different fuel steam contents of interest in practical SOEC stacks will be fully explored. Full cell development will continue, and more extensive life testing will be carried out, providing additional input to the model development. Work done at LBNL and INL will continue to provide important results, augmenting the Northwestern work with life testing of novel metal-supported cells and supporting a broader range of testing conditions. Overall, this work should lead to improved long-term stable SOECs as needed to meet H_2 production efficiency and cost targets.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. B.K. Park, Q. Zhang, P.W. Voorhees, S.A. Barnett, "Conditions for Stable Operation of Solid Oxide Electrolysis Cells: Oxygen Electrode Effects," DOI: 10.1039/C9EE01664C *Energy Environ. Sci.*, **12** (2019): 3053-3062.

2. Q. Liu, Q. Zhang, P.W. Voorhees, S.A. Barnett, "Effect of Direct-Current Operation on The Electrochemical Performance and Structural Evolution of Ni-YSZ Electrodes," Journal of Physics – Energy, in review.
3. B.K. Park, Q. Zhang, P. Voorhees, S.A. Barnett, "The Role of the Oxygen Electrode Overpotential on the Solid Oxide Electrolysis Cell Degradation," 16th Inter. Conf. On Advanced Ceramics and Composites, Daytona Beach, January 30, 2019
4. Q. Zhang, B.K. Park, S. Barnett, P. Voorhees, "Influence of Distribution of Oxygen Partial Pressure on the Electrolyte Degradation of Solid Oxide Electrolyser Cells," 16th Inter. Conf. On Advanced Ceramics and Composites, Daytona Beach, January 30, 2019
5. S.A. Barnett, P. Voorhees, B.K. Park, Q. Zhang "Degradation Characterization and Modeling of a New Solid Oxide Electrolysis Cell Utilizing Accelerated Life Testing," Presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, D.C., April 2019.
6. S.A. Barnett, "Electrochemical and Microstructural Studies of Degradation Mechanisms in Solid Oxide Cells," 235th Electrochemical Society meeting, Dallas, TX, May 26-30, 2019.
7. S.A. Barnett, Q. Liu, Q. Zhang, B.K. Park, P. Voorhees, "Degradation Phenomena in Solid Oxide Electrolysis Cell Fuel Electrodes," 2nd International Conference on Electrolysis, Loen Norway, 9-13 June 2019
8. S.A. Barnett, B.K. Park, Q. Zhang, P. Voorhees, "Degradation Phenomena in Solid Oxide Electrolysis Cell Oxygen Electrodes," 2nd International Conference on Electrolysis, Loen Norway, 9-13 June 2019
9. S.A. Barnett, B.K. Park, R. Scipioni, "Effect of Infiltration on Performance of Ni-YSZ Fuel Electrodes," Solid Oxide Fuel Cells 16 (SOFC-XVI), Kyoto. Japan, 9-13 September 2019
10. S.A. Barnett, P. Voorhees, B.K. Park, Q. Zhang "Degradation Characterization and Modeling of a New Solid Oxide Electrolysis Cell Utilizing Accelerated Life Testing," Presentation at the Hydrogen Production Technical Team (HPTT) review of the HydroGEN High Temperature Electrolysis projects, Boston MA, September 2019.
11. 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.
12. 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.

REFERENCES

1. M. Chen, Y.L. Liu, J.J. Bentzen, W. Zhang, X. Sun, A. Hauch, Y. Tao, J.R. Bowen and P.V. Hendriksen, "Microstructural Degradation of Ni/YSZ Electrodes in Solid Oxide Electrolysis Cells under High Current," *Journal of the Electrochemical Society* **160** (2013) F883-F891
2. Q. Liu, Q. Zhang, P.W. Voorhees and S.A. Barnett, "Effect of direct-current operation on the electrochemical performance and structural evolution of Ni-YSZ electrodes," *Journal of Physics: Energy* **2** (2019).