
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 long lifetime at high current density in order to improve economic viability.

Fiscal Year (FY) 2018 Objectives

- Develop model for electrolyte degradation in solid oxide cells.
- Carry out experimental life tests of SOECs designed to observe electrolyte degradation processes and thereby provide input for model development and vetting.
- Develop new solid oxide cells with capability for electrolysis at high current density with low degradation rates.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year

Research, Development, and Demonstration (MYRDD) Plan¹:

(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 cost. 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% lower heating value (44 kWh/kg)
- Stack energy efficiency: 77% lower heating value (43 kWh/kg).

FY 2018 Accomplishments

- Developed an electrolyte transport model that predicts the electrical and oxygen potential versus position and correctly predicts the conditions (oxygen electrode overpotential >0.2 V) where electrolyte failure occurs.
- Carried out life tests that show where failure occurs and successfully agree with the above theory. The results show that for high-quality oxygen electrodes, overpotential can become

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

large enough to cause failure only for operating temperatures $<650^{\circ}\text{C}$ or current densities $\gg 1$ A/cm^2 .

- Demonstrated high-performance SOECs that can readily meet program targets of >1 A/cm^2 at 1.3 V at operating temperature $>700^{\circ}\text{C}$.

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/cm²), at higher current densities desired for cost-effective hydrogen production, various degradation mechanisms are observed that can severely decrease cell lifetimes.

While each of the cell components may exhibit degradation at high current density, in the first year of this project the focus has been on the electrolyte. The degradation rate increases rapidly with increasing current density because the associated increase in overpotential η yields a more extreme oxygen partial pressure at the electrode/electrolyte interface. A model was developed and used with input values from our experimental cells and testing conditions in order to calculate the oxygen partial pressure in the electrolyte. These values were compared with the pressure required for fracture based on a simple fracture model. The critical pressure and corresponding overpotential agreed well with the experimental degradation observations for multiple data sets.

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 thickness 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 first year of this project, Northwestern University developed high-performance SOECs and carried out extensive life testing in parallel with development of a model for electrolyte degradation mechanisms. The full SOECs consist of a Ni-YSZ support, Ni-YSZ functional layer, (ZrO₂)_{0.92}(Y₂O₃)_{0.08} (YSZ) electrolyte, Gd_{0.1}Ce_{0.9}O_{1.95} (GDC) barrier layer, and Sr(Ti_{0.3}Fe_{0.63}Co_{0.07})O₃ (STFC) oxygen electrode. Performance met program targets of >1 A/cm² current density at an operating voltage of 1.3 V for temperature $>700^\circ\text{C}$. Life tests were carried out under practical cell operating conditions: DC current density of 1 A/cm² at 800°C in air and 50% H₂/50% H₂O. Although the cell voltage increased by >150 mV during the first ~ 300 h, it stabilized at a value of 1,340 mV. Electrochemical impedance spectroscopy data showed that the polarization resistance gradually increased with time, before stabilizing, while the ohmic resistance remained constant. Since the STFC electrodes do not show an increase in polarization resistance under these conditions, it is suggested based on literature data [1] that this arises from the Ni-YSZ fuel electrode (note that fuel electrode degradation is outside the scope of the Year 1 work, but it will be studied in detail in the upcoming years). Cross-sectional scanning electron microscopy (SEM) analysis of the cell after life testing (Figure 1) shows a structure that appears identical to that of the as-prepared cells. That is, there was no evidence of cell degradation. This is consistent with the electrochemical impedance spectroscopy data, indicating no significant change in ohmic resistance during the life test.

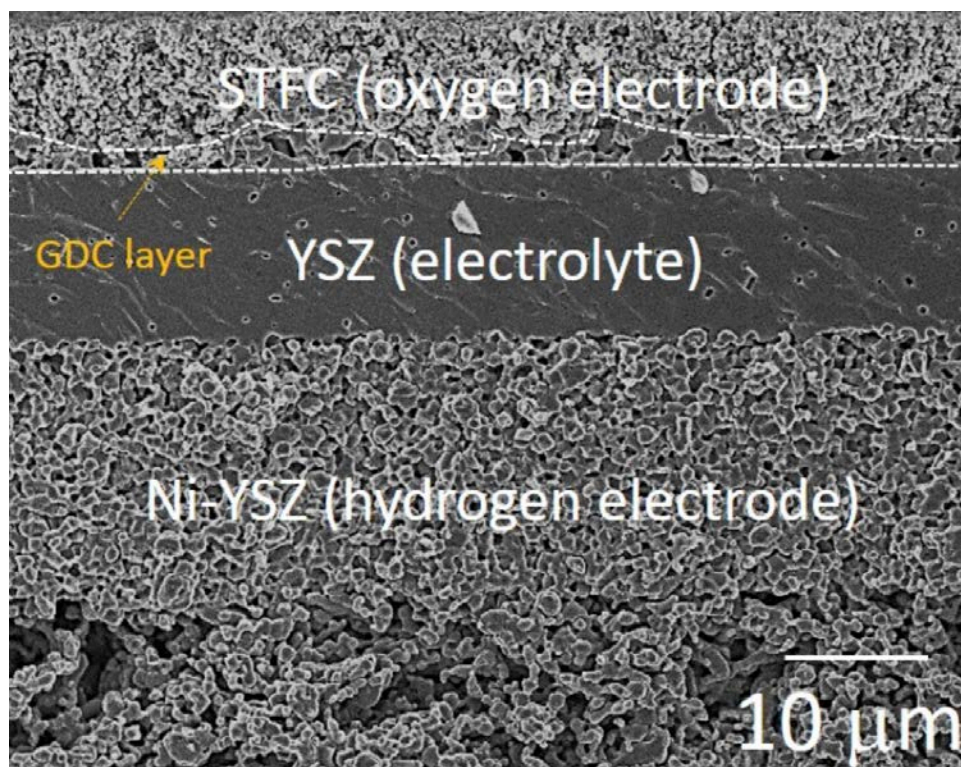


Figure 1. Cross-sectional SEM image of the SOEC after the life testing at 1 A/cm^2 and 800°C

Life-test experiments were designed based on our model that predicts deleteriously high oxygen pressures in the electrolyte when the oxygen electrode overpotential is too high; this occurs when the operating temperature is too low and/or the current density is too high. The cells had YSZ electrolytes with GDC barrier layers—oxygen electrodes were $\text{Sr}(\text{Ti}_{0.3}\text{Fe}_{0.7})\text{O}_3$ (STF) in most cases, but $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_3$ (LSCF) and STFC electrodes were also tested. Life tests were done with a DC electrolysis current density of $0.8\text{--}1.6 \text{ A/cm}^2$ at $600\text{--}800^\circ\text{C}$ in air. Impedance spectra were measured and used to obtain an ohmic resistance (R_Ω) and a polarization resistance (R_p). In order to estimate the electrode overpotential η , we used the measured R_p values together with an approximate form of the Butler-Volmer equation [2]. Different data sets were obtained by varying different aspects in the life tests:

1. Operating temperature variation to vary R_p and hence electrode overpotential
2. Varying the electrode material
3. Porous versus dense GDC barrier layer
4. Symmetric versus full cells.

Life tests were done at temperatures of 600° , 650° , 700° , and 800°C . The R_Ω and R_p values were generally quite stable at the higher temperatures during the $\sim 1,000 \text{ h}$ tests, but at 600°C the cell failed 144 h into the test. The dramatic decrease in cell life with decreasing temperature can be explained by a higher η , reaching 200 mV at 600°C . Cross-sectional SEM analysis showed no sign of fracture or delamination at the higher temperatures, but the cell tested at 600°C had an obvious fracture on the electrolysis-side electrode/electrolyte (STF/GDC) interface.

In order to prove that this effect is universal, and not just specific to STF electrodes, otherwise identical cells with LSCF and STFC electrodes were tested using the same DC current density of 0.8 A/cm^2 at 600°C . Figure 2a indicates the R_Ω , R_p , and η values determined from the impedance data periodically collected with time for the cells with the LSCF and the STFC electrodes. These results show that LSCF, the widely used SOEC

electrode, has a higher R_p and η than STF, whereas STFC had a lower R_p and η than STF. The η values of the cell with LSCF exceeded 200 mV, and the cell failed in <200 h. The SEM image in Figure 2b shows a clear fracture at the LSCF/GDC interface. For STFC, η <200 mV, and the cell remained stable throughout the entire test. No evidence of fracture can be seen in the post-test SEM image (Figure 2c). These results suggest a critical value for fracture of \sim 200 mV.

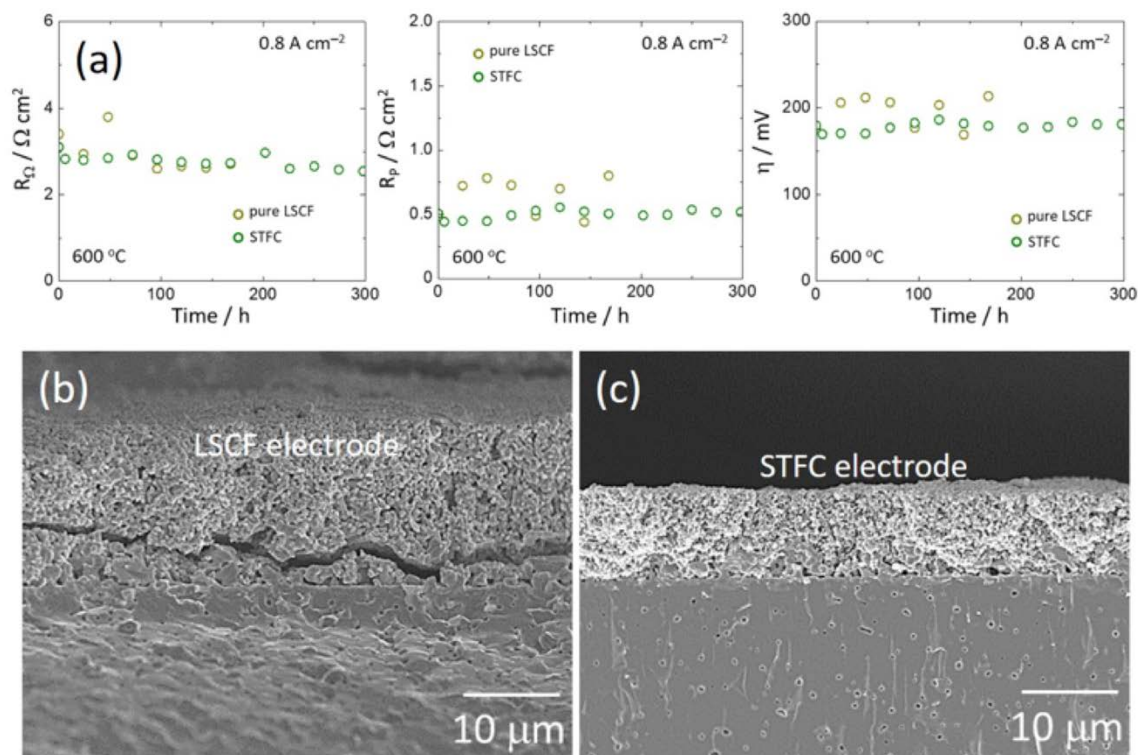


Figure 2. (a) Evolution of R_{ohm} , R_p , and η with time for the symmetric cells with the LSCF and the STFC electrodes tested at 600°C. Cross-sectional SEM images of the cells with (b) the LSCF and (c) the STFC after the life tests.

Life tests were also done on full cells—Ni-YSZ-supported SOECs with STF oxygen electrode—with the life tests carried out at 600°C and 800°C with a DC current density of 0.8 A/cm² in air and 50% H₂/50% H₂O. The cell tested at the higher temperature eventually stabilized as discussed above, whereas the cell tested at the lower temperature failed after <50 h. Cross-sectional SEM analysis showed that the higher-temperature cell had no evidence of damage whereas the 600°C-tested cell showed clear fracture at the electrode/electrolyte interface, similar to that shown in Figure 2b.

In the experiments described above, delamination was found at the SOEC side at temperature 600°C with current density 0.8 A/cm² for the cell tested in air, but not at 650°C and above. Figure 3 shows the oxygen partial pressure distribution in the electrolyte with different temperatures (600°C, 700°C, 800°C) obtained using a numerical simulation. Parameters used, including the electrolyte YSZ and GDC layer thicknesses and the electrode polarization resistances, are taken from measurements of the experimental cells. The figure shows that p_{O_2} is low at the fuel cell side of the cell but increases rapidly to values well above 1 atm and increases very slightly throughout the electrolyte with peak values at the electrolysis side of the cell. The maximum p_{O_2} value increases with decreasing temperature, reaching $\sim 10^4$ atm at 600°C.

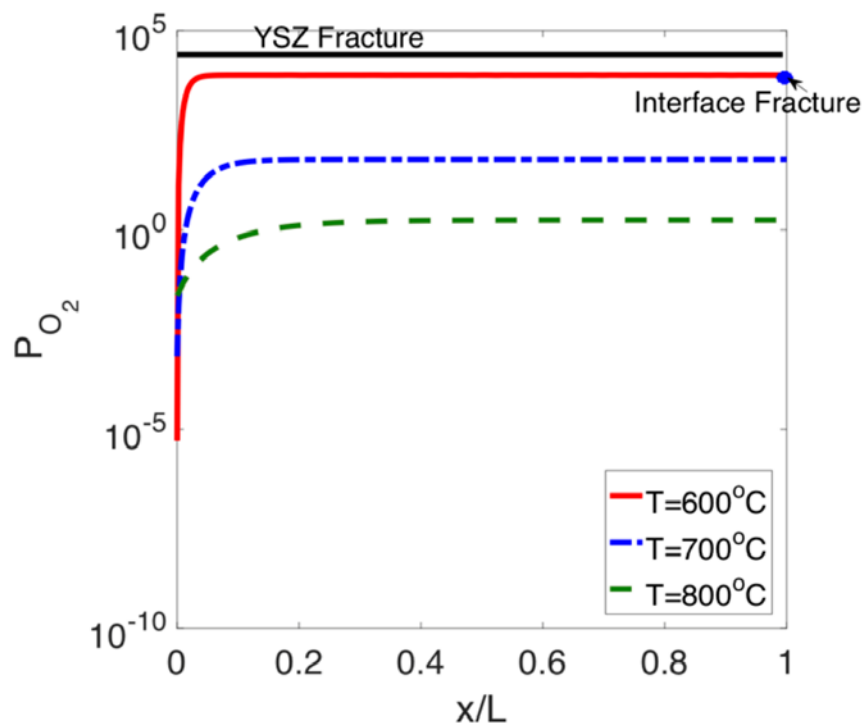


Figure 3. Distribution of oxygen partial pressure versus normalized position in a YSZ electrolyte with thickness $L = 400 \mu\text{m}$ and thin GDC barrier layers on both sides, using polarization resistance values as measured for STF electrodes in air, for different temperatures at 0.8 A/cm^2 . Also shown for comparison (in black) are calculated pressures required for YSZ fracture and for fracture of the YSZ/electrode interface. The interface fracture criterion, represented by the blue dot, is given by the fracture toughness of the perovskite.

The critical oxygen partial pressure for fracture was calculated using the expression by Virkar [3] based on the balance among surface energy at a crack surface in YSZ, strain in YSZ, and the oxygen pressure introduced electrochemically. Using the Virkar model with an initial crack radius of $\sim 1.0 \mu\text{m}$ based on the observed YSZ pore size and a YSZ fracture toughness of $3.0 \text{ MPa m}^{1/2}$ yields a critical pressure of $\sim 5 \times 10^4 \text{ atm}$. The overpotential η required to reach this pressure is 221 mV . Note that the values predicted by the electrolyte model, shown in Figure 3, are less than this value even at 600°C , indicating that fracture within the YSZ electrolyte is not expected. This prediction is correct because fracture does not occur within the electrolyte but rather at the electrolyte/electrode interface (see Figure 1). This can be explained by the lower fracture toughness of the GDC and perovskite electrode. An estimate of the fracture toughness of the perovskite electrode materials (e.g., STFC, LSCF) is $0.8 \text{ MPa m}^{1/2}$ [4], lower than that of GDC ($\sim 1.5 \text{ MPa m}^{1/2}$). Using the lower value gives rise to a critical pressure $\sim 1 \times 10^4 \text{ atm}$ achieved for $\eta = 196 \text{ mV}$ at 600°C . As shown in Figure 3, at 600°C the p_{O_2} induced by the overpotential exceeds this value, predicting the observed interfacial fracture for this condition. In addition, the calculation was carried out for full cells and compared with experimental data. Again, the predicted condition for fracture agreed well with the experimental observation.

Lawrence Berkeley National Laboratory (LBNL) adapted their metal-supported solid oxide cells, which had previously only been utilized as fuel cells, for application as SOECs. By optimizing the catalyst materials and catalyst infiltration processes, an excellent SOEC performance was obtained (i.e., current densities of -5.31 , -4.09 , -2.64 , and -1.62 A/cm^2 at 800°C , 750°C , 700°C , and 650°C , respectively, at 1.3 V and $50 \text{ vol}\%$ steam content). To the best of our knowledge, this is the highest SOEC performance for oxygen-conducting type cells. However, rapid performance degradation is observed. This has been a key challenge addressed in the first year. LBNL has carried out systematic studies to determine primary degradation modes and mechanisms. Examples include using symmetric cells operated with air on both sides to isolate the effects of oxygen ion current and

oxygen pressure, and post-life-test analysis of the cells. Results to date show promising improvements in cell stability.

Idaho National Laboratory (INL) has applied their 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 H₂/H₂O ratios.

CONCLUSIONS AND UPCOMING ACTIVITIES

The present experimental and theoretical results show stable cell operation until a specific critical value of the oxygen electrode overpotential η is exceeded, whereupon rapid electrolyte degradation and eventual cell failure results. Specifically, our experimental results indicate that fracture occurs when $\eta_{\text{exp}} > 0.19 \pm 0.015$ V. This has been shown to be valid for a few different electrode materials and both full and symmetric cells. The result applies to the YSZ electrolyte with a thin doped ceria barrier layer used in our experiments; the result has broad applicability because this design is widely used by SOEC developers. By comparison the model predicts that the overpotential at the point where fracture occurs is at $\eta_{\text{calc}} = 0.196$ V. There are no adjustable parameters used in the prediction of simulation, and thus the agreement with experiment is very good.

In the coming year, the model will be further developed to help explain degradation effects observed at the oxygen electrode and H₂/H₂O electrode. 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 hydrogen production efficiency and cost targets.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. S.A. Barnett, “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., June 2018.
2. S.A. Barnett, “Degradation Characterization and Modeling of a New Solid Oxide Electrolysis Cell Utilizing Accelerated Life Testing,” Presentation at the Hydrogen Production Technical Team review of the HydroGEN High Temperature Electrolysis projects, Idaho Falls, Idaho, September 2018.

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2. J.G. Railsback, H. Wang, Q. Liu, M.Y. Lu and S.A. Barnett, “Degradation of La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3- δ} Oxygen Electrodes on Ce_{0.9}Gd_{0.1}O_{3- δ} Electrolytes during Reversing Current Operation,” *Journal of The Electrochemical Society* 164 (2017): F3083–F3090.
3. A.V. Virkar, “Failure of Ion-Conducting Materials by Internal Precipitation Under Electrolytic Conditions,” in *Engineered Ceramics* (John Wiley & Sons, Inc., 2016).
4. M.D. Thouless, E. Olsson, and A. Gupta, “Cracking of Brittle Films on Elastic Substrates,” *Acta Metall. Mater.* 40 (1992): 1287–1292.