H2@Scale: Experimental Characterization of Durability of Advanced Electrolyzer Concepts in Dynamic Loading

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Project End Date: Project continuation and
direction determined annually by DOE

Overall Objectives

- Evaluate and quantify the impact of catalyst loss mechanisms—including constant, intermittent, and start-stop operation—on low-temperature electrolysis.

- Evaluate mitigation strategies, including materials and system controls, to minimize durability losses at low loading and under intermittent operation.

Fiscal Year (FY) 2018 Objectives

- Demonstrate low-temperature electrolysis in situ testing and durability capabilities.

- Quantify the impact of low loading and intermittent operation on low-temperature electrolysis durability.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Reducing the cost of hydrogen production by electrochemical water splitting

- Durability losses at low cost and the impact on the price of hydrogen production.

FY 2018 Accomplishments

- Demonstrated more than 15,000 hours of durability testing in low-temperature electrolysis.

- Established baseline performance and durability in ex situ and in situ testing to guide catalyst and electrode development efforts.

- Evaluated the impact of low loading, intermittent operation, water quality, and catalyst choices on single-cell durability and catalyst layer degradation.

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

INTRODUCTION

While hydrogen is a significant chemical commodity, low-temperature electrolysis is a relatively small contributor due to high hydrogen production cost. Low-temperature electrolyzers currently use high quantities of iridium at the anode, to avoid performance loss with extended operation and because the hydrogen cost is driven by the power-input cost. To meet electrolysis cost targets, however, electrolysis must be coupled with low-cost power sources and reduce catalyst loadings to address the increased capital cost at lower capacity.

Reducing the iridium loading previously has been found to accelerate the observation of durability losses. During FY 2018, work was completed to quantify the impact of operation profiles (constant, intermittent operation) on electrolysis durability and catalyst layer degradation to assess how renewable electrolysis affects catalyst/electrode development efforts and hydrogen production cost targets.

APPROACH

The National Renewable Energy Laboratory (NREL) has developed standard testing and durability protocols to establish:

- Reasonable metrics for ex situ and in situ testing performance and durability

- How catalyst loading impacts the onset of durability loss observations

- The relative impact of input profiles, including constant (current, steady input), square-wave (wind input), and triangle-wave (solar input) on electrolysis durability.

Approach development included setting conditioning and test procedures to establish initial performance baselines for catalyst and electrode development projects. Durability testing was used while varying singular parameters (loading, water quality, input profile) to evaluate their relative impact on long-term operation. Various techniques including cell performance, diagnostics, and microscopy were used establish degradation modes and suggest methods for mitigating performance loss.

RESULTS

As baseline materials, NREL evaluated iridium black (metal/hydroxide) and oxide (thermally oxidized) in ex situ and in situ testing (Figure 1). Although iridium produced high oxygen evolution activity in rotating disk electrode half-cells, the performance benefit generally was not observed in membrane electrode assemblies due to surface and near-surface oxidation during single-cell conditioning. Iridium oxidation was observed in half-cell tests, where activity and metallic features (hydrogen underpotential deposition) were lost at moderate potential (1.6 V). These losses, however, were not related to dissolution and were recoverable after extended operation at reducing conditions. Unrecoverable iridium losses were higher than oxides in half- and single-cells due to the relatively higher dissolution rate of metal/hydroxide as compared to oxide. Although iridium metal/hydroxide–based materials often are a focus of catalyst development efforts, thermal oxides might be better suited for low-temperature electrolysis due to the lower durability losses.

Membrane electrode assembly evaluations focused on iridium oxide due to the slower dissolution kinetics. Electrode spraying method and ink composition influenced catalyst layer uniformity and the resulting performance and durability of single-cell tests. In general, a balance was needed in ionomer content to ensure ink uniformity while minimizing contaminant effects; a balance also was required in spray rate and temperature to produce evenly coated catalyst layers. Ensuring uniform coating appeared critical in obtaining reproducible durability experiments, because membrane electrode assemblies with undercoated or weak points in the catalyst layer might have accelerated degradation and performance decline.
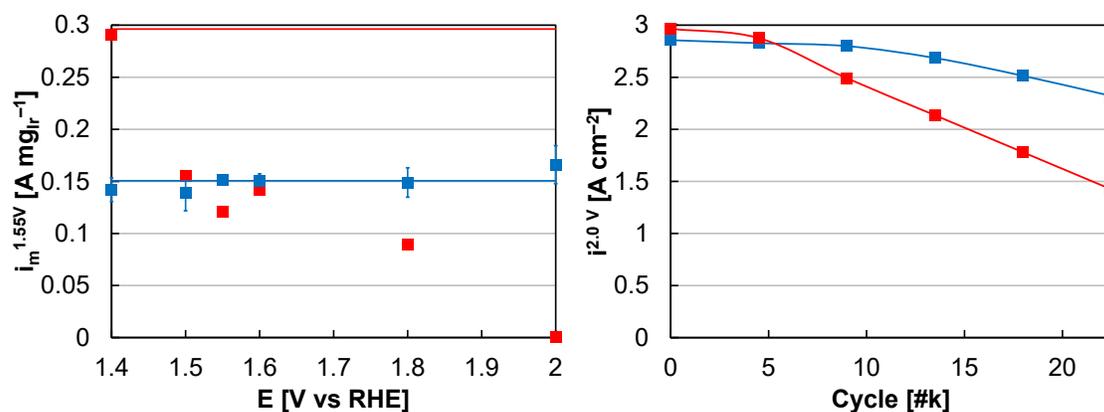
Figure 1. Durability losses of iridium (red) and iridium oxide (blue) nanoparticles in (a) rotating disk electrodes and (b) membrane electrode assemblies

Catalyst loading and operating potential were found to significantly impact membrane electrode assembly durability (Figure 2). Although iridium dissolution and loss occurred at higher loading (0.4 mg cm^{-2}), thicker catalyst layers masked loss observations and lower loading (0.1 mg cm^{-2}) was needed to observe durability losses during a reasonable amount of time. Reaching operating potentials of 2 V and greater was also necessary to accelerate iridium dissolution, and lower potential appeared to minimize loss or delay the impact of iridium degradation on cell performance.
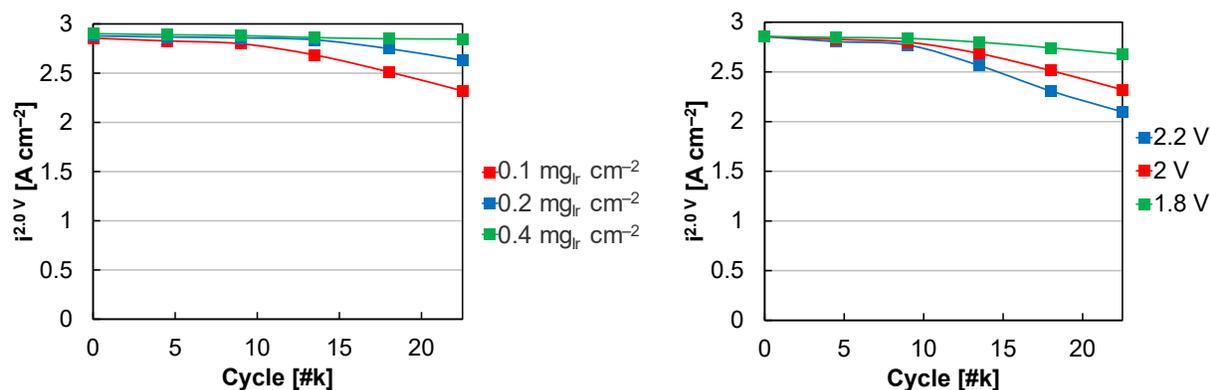
Figure 2. The impact of (a) loading and (b) upper potential on membrane electrode assembly durability. Durability tests were completed using square-waves, between 1.45 V and (a) 2.0 V or (b) as specified in the figure legend.

In an effort to minimize the length of single-cell durability tests (16 days), membrane electrode assemblies were used with low loadings (0.1 mg cm^{-2}) and with an upper potential of 2.0 V. A variety of power input profiles were evaluated to quantify their impact on device durability, and loss increased in the following order: constant/hold, triangle-wave, and square-wave (Figure 3). These findings were different from half-cells. In rotating disk electrodes, high potential accelerated loss due to an increased dissolution rate. Potential cycles, however, did not accelerate loss because the potential range of interest did not include a redox transition, and resulted in lower loss rates because less time was spent at elevated potential. In single-cell tests, the higher loss rate likely was due to differences between the potential applied to the catalyst layer and observed at the current collectors. Cycling potential likely resulted in nonuniform potentials at catalyst sites and accelerated loss due to potential spikes increasing the dissolution rate. Potential cycling further resulted in thinner catalyst layers and decreases in the iridium oxide equivalent pore diameter.

	Initial	Hold	Square Wave	Triangle Wave
[μm]	1.07	1	0.77	0.75
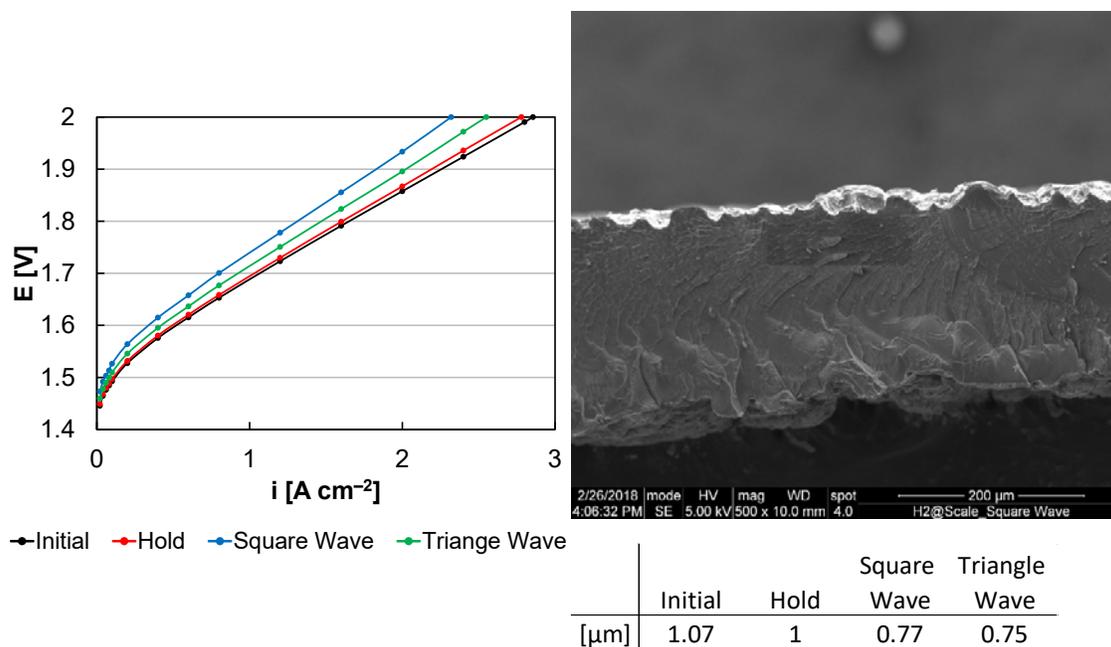
Figure 3. (a) Membrane electrode assembly performance, initially and following durability, and (b) microscopy of a cross-sectioned membrane electrode assembly following a square-wave durability testing; anode (iridium oxide) catalyst layer thicknesses initially and following durability

Although potential cycling resulted in higher durability losses than potential holds, the square-wave profile also produced greater losses than the triangle wave. Sawtooth profiles were used to identify the source of increased loss—whether due to the sudden increase or decrease in applied current (Figure 4). The hard-up profile (sudden increase to 2.0 V, gradual decrease to 1.45 V) produced loss similar to the square wave. Conversely, the hard-down profile (sudden decrease to 1.45 V, gradual increase to 2.0 V) produced loss similar to the triangle wave. Although adding intermittency increased the rate of performance loss, the sudden increase in power input appeared to be more detrimental with continued operation. The sudden increase may have resulted in greater variation of potentials within the catalyst layer, accelerating catalyst dissolution and performance loss.
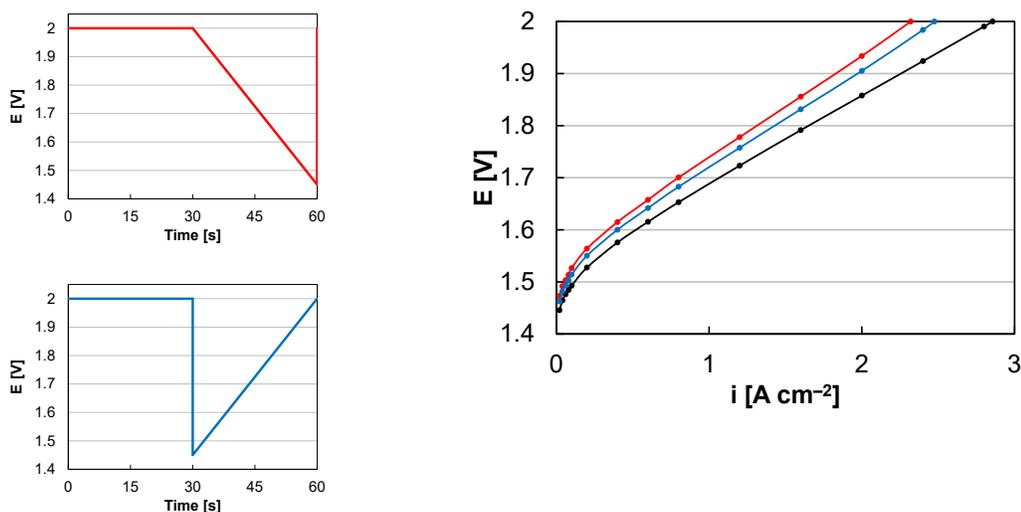
Figure 4. (a) Sawtooth test profiles and (b) membrane electrode assembly performance, initially and following durability

Water quality also was studied as a test concern, to evaluate how contaminants affect the measured performance and durability of membrane electrode assemblies. When the conductivity of the water increased, several observations were made: a hysteresis was found between anodic and cathodic polarization curves; initial membrane electrode assembly performance decreased; and durability losses increased under the same input profiles.

Nickel was found to be the primary contaminant source in these studies, and different effects may be observed with other contaminants. An expanded contaminant effort is underway in half- and single-cells to better understand the effect of likely system contaminants on cell performance and durability.

CONCLUSIONS AND UPCOMING ACTIVITIES

Project findings indicate that significant durability losses are observed at low loading when adding intermittent power inputs. Mitigation strategies, including catalyst improvements to reduce the upper operating potential, moderate loading, or system control to limit the upper operating potential will be critical in extending device lifetime when adjusting electrolysis operation for lower hydrogen production cost.

Continuing efforts have expanded upon constant and intermittent operation to include potential excursions and controlled or uncontrolled stops. These situations are being evaluated to assess the relative durability impact of iridium redox on cell durability, and how combined processes (hydrogen crossover, iridium reduction, increasing dissolution rates) influence electrolysis durability. NREL is developing a rainbow stack testing capability to increase the rate of data acquisition and gain improved statistics of these degradation process. Simulated wind and solar profiles also are being added to assess how square- and triangle-wave durability compares to more realistic models of power inputs.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Shaun M. Alia. "H2@Scale: Experimental Characterization of Durability of Advanced Electrolyzer Concepts in Dynamic Loading." Poster at the DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, D.C. (June 2018).

2. Shaun M. Alia and Grace C. Anderson. "Iridium Oxygen Evolution Activity and Durability Baselines in Rotating Disk Electrode Half-Cells." *Journal of the Electrochemical Society* (submitted 2018).

3. Shaun M. Alia, Sarah Stariha, Rod L. Borup, and Bryan S. Pivovar. "H2@ Scale: The Effect of Loading, Test Parameters, and Oxides on Electrolyzer-Catalyst Durability." In *Meeting Abstracts*, no. 46, 1604–1604. The Electrochemical Society (2018).

4. Shaun M. Alia and Bryan S. Pivovar. "The Effect of Loading, Test Parameters, and Oxides on Electrolyzer-Catalyst Durability." AIChE Annual Meeting 2018. In *Meeting Abstracts*, no. 46, 1604–1604. The Electrochemical Society (2018) 83a.