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

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Subcontractor(s):
Los Alamos National Laboratory, Los Alamos, NM

Project Start Date: October 2017
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) 2019 Objectives

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

INTRODUCTION

While hydrogen is a large chemical commodity, low-temperature electrolysis is a relatively small contributor due to high hydrogen production costs. Low-temperature electrolyzers currently use high quantities of iridium (Ir) at the anode, both 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 will need to be coupled with low-cost power sources and reduced catalyst loadings to address the increased capital cost at lower capacity.

Reducing the iridium loading has previously 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.

- 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 Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- 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 2019 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.

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

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 to establish degradation modes and suggest methods for mitigating performance loss.

RESULTS [1]

Membrane electrode assembly durability was explored for polymer electrolyte membrane electrolyzers, focusing on catalyst (iridium) degradation at low loading and dynamic operation. Low catalyst loading and high cell potential were critical to observing durability losses over reasonably short experiments, regardless of test profile. These efforts build off experiments in FY 2018 and were expanded to include three catalyst loadings (0.1, 0.2, and 0.4 mg_{Ir} cm⁻²) and different load profiles, including steady-state operation and accelerated cycling (square wave, triangle wave). While small losses were seen during steady operation, cycling greatly accelerated performance decreases (Figure 1).

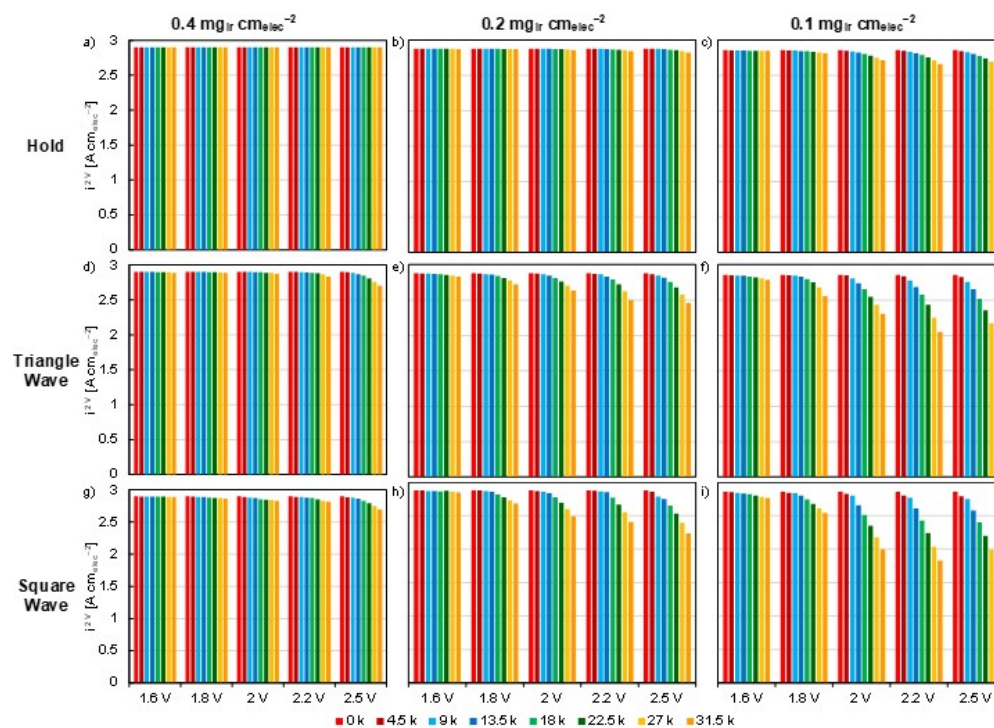


Figure 1. Steady-state potential holds of membrane electrode assemblies (MEAs) with Ir loadings of (a) 0.4, (b) 0.2, and (c) 0.1 mg_{Ir} cm⁻². Potential-based triangle waves of MEAs with Ir loadings of (d) 0.4, (e) 0.2, and (f) 0.1 mg_{Ir} cm⁻². Potential-based square waves of MEAs with Ir loadings of (g) 0.4, (h) 0.2, and (i) 0.1 mg_{Ir} cm⁻². Performance data were presented in terms of current density at 2 V initially and following 75, 150, 225, 300, 375, 450, and 525 hours, corresponding to 4.5, 9, 13.5, 18, 22.5, 27, and 31.5 thousand cycles (k) (triangle and square waves), respectively. Potential holds were completed at 1.6, 1.8, 2, 2.2, and 2.5 V. Triangle and square waves were completed at a lower potential of 1.45 V and an upper potential at 1.6, 1.8, 2, 2.2, and 2.5 V.

Mechanistically, Ir dissolution drove performance loss, thinning the anode catalyst layer and resulting in increasing kinetic losses during extended operation (Figure 2). While morphological changes to the catalyst layer were previously found, increasing polarization resistance suggested that degradation at the catalyst/ionomer/membrane interface may also contribute. Transport losses also began to appear following extended operation. Deterioration of the transport layers, however, did not occur, and increasing transport loss may support catalyst loss creating interfacial issues. Under more aggressive test protocols, the high-frequency resistance (HFR) slightly increased and may indicate that pitting in the catalyst layer occurred; these losses were also consistent with patterned electrodes and suggested loss of the membrane/interface contact.

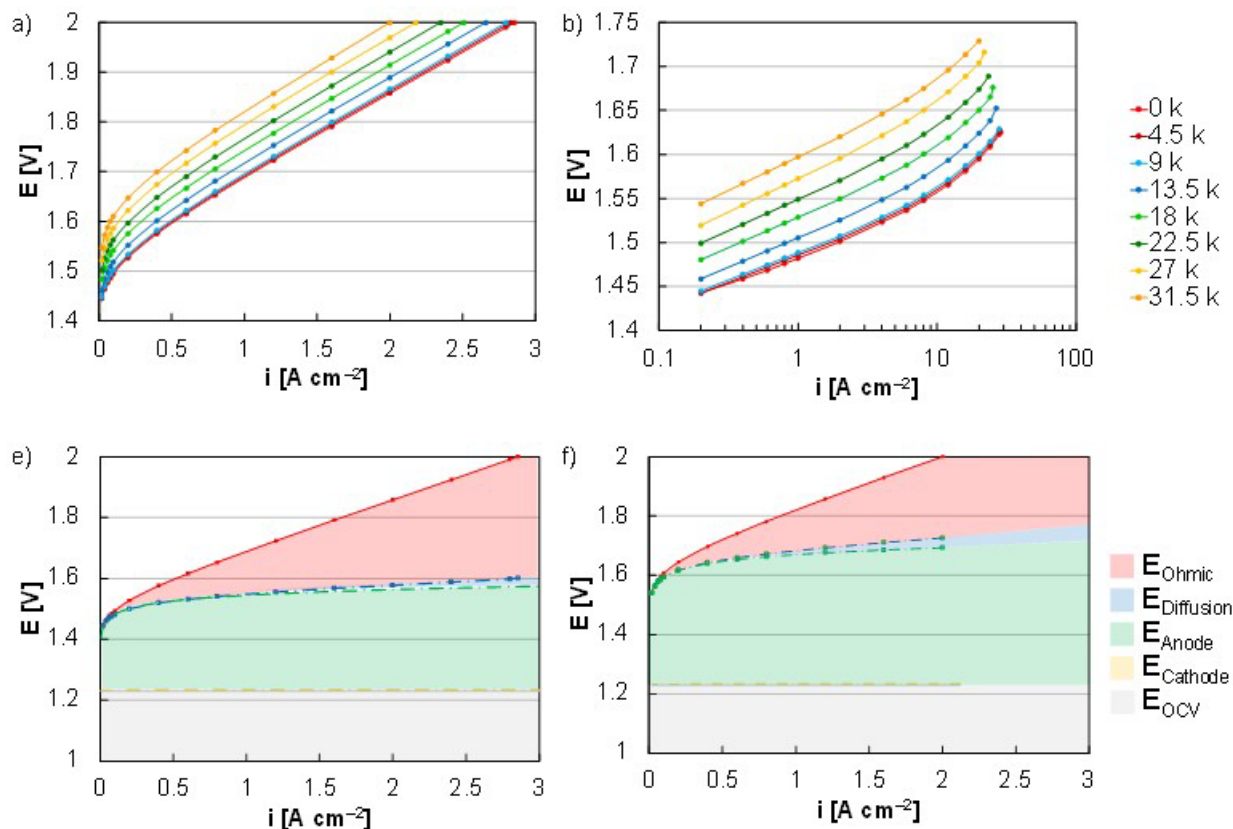


Figure 2. Polarization curves of MEA durability (square wave, 1.45–2 V) at an Ir anode loading of $0.1 \text{ mg}_r \text{ cm}^{-2}$ with a focus on (a) overall performance (not corrected for resistance, HFR) and (b) kinetic performance (corrected for resistance, HFR). MEA performance at (c) beginning of life (0 k) and (d) after 31.5 k cycles (square wave, 1.45–2 V).

Electrolyzer operation with model wind and solar profiles results in less severe performance losses compared to triangle- and square-wave potential cycling tests due to the lower cycling frequency of the model profiles (Figure 3). However, in both cases the kinetics dominated the loss with increased polarization resistances, indicating that higher cycling rates accelerate loss and can be used to project the impact of intermittency on device lifetime. These results suggest that performance losses impact electrolyzers' abilities to operate with low catalyst loading and intermittent inputs, and that a combination of component development and system controls are needed to limit potential and performance loss.

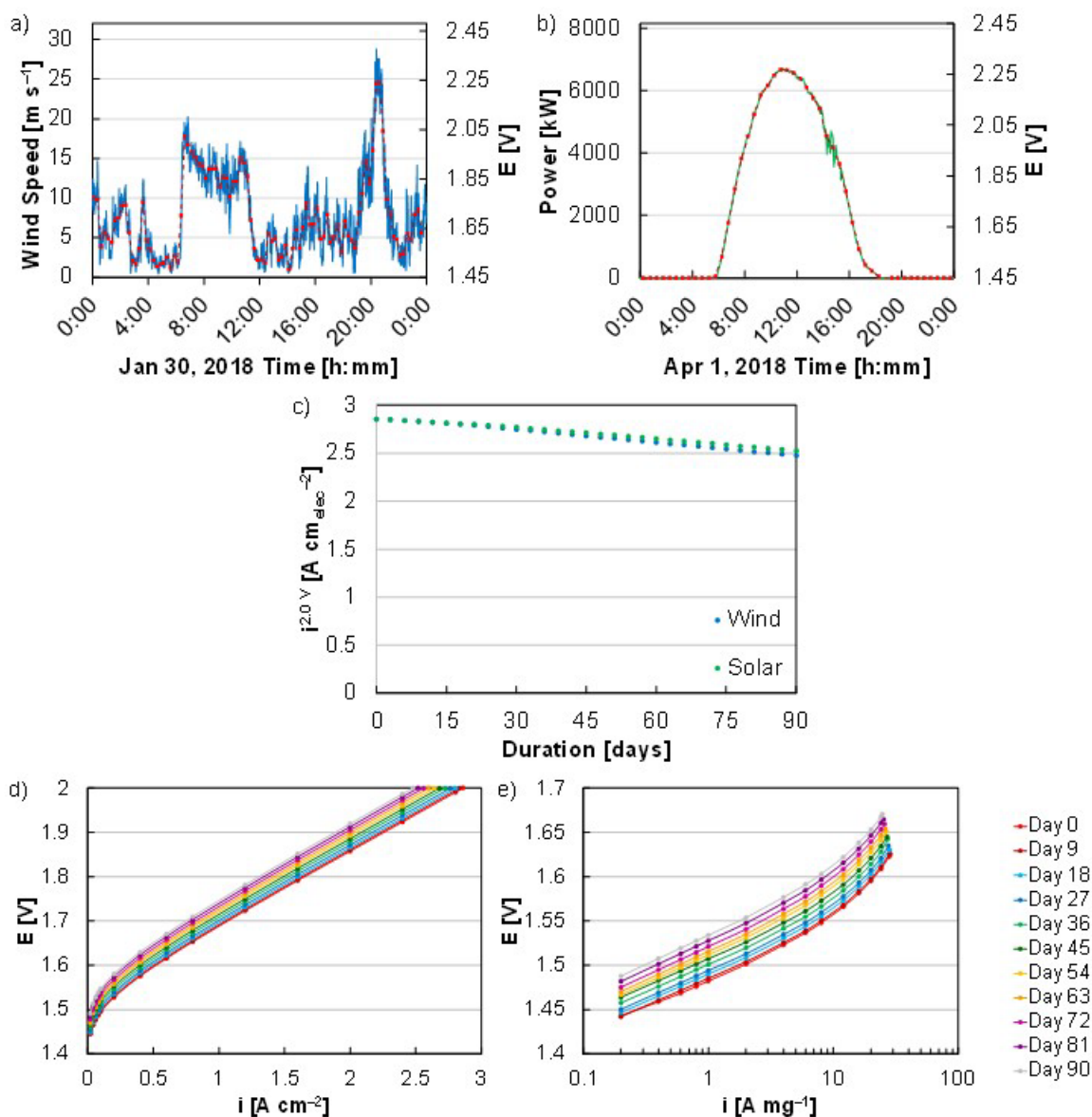


Figure 3. (a) Model wind profile from the National Wind Technology Center M2 Tower at 50 m on January 30, 2018 with corresponding potential applied during extended MEA operation. (b) Model solar profile from the NREL PVDAQ Site 51 on April 1, 2018 with corresponding potential applied during extended MEA operation. Applied potentials were calculated to maintain the same range (1.45–2.25 V) and average (1.70 V). (c) Comparison of MEA performance at 2 V with wind (blue) and solar (green) profiles. MEA polarization curves and Tafel plots during extended operation with (d–e) wind input profiles.

Additionally, we have begun to evaluate how catalyst layer structure and coating parameters can affect cell performance and durability (Figure 4). Most MEAs in this project were coated using ultrasonic spraying. Ink composition, including ionomer content, solids concentrations, and solvent ratios (alcohol, water) each had an effect on performance during extended operation. Specifically, low amounts of ionomer resulted in lower performance, likely due to poor catalyst layer/membrane contact; conversely, high ionomer amounts also resulted in lower performance due to contaminant effects and lower access to iridium sites. Spray parameters, including temperature and pump rate were also evaluated and were used to incrementally improve single-cell performance and durability. Lessons learned from ultrasonic spray optimization are being applied to manufacturing-appropriate processes and improving performance for MEAs formed with roll-to-roll (R2R) coating.

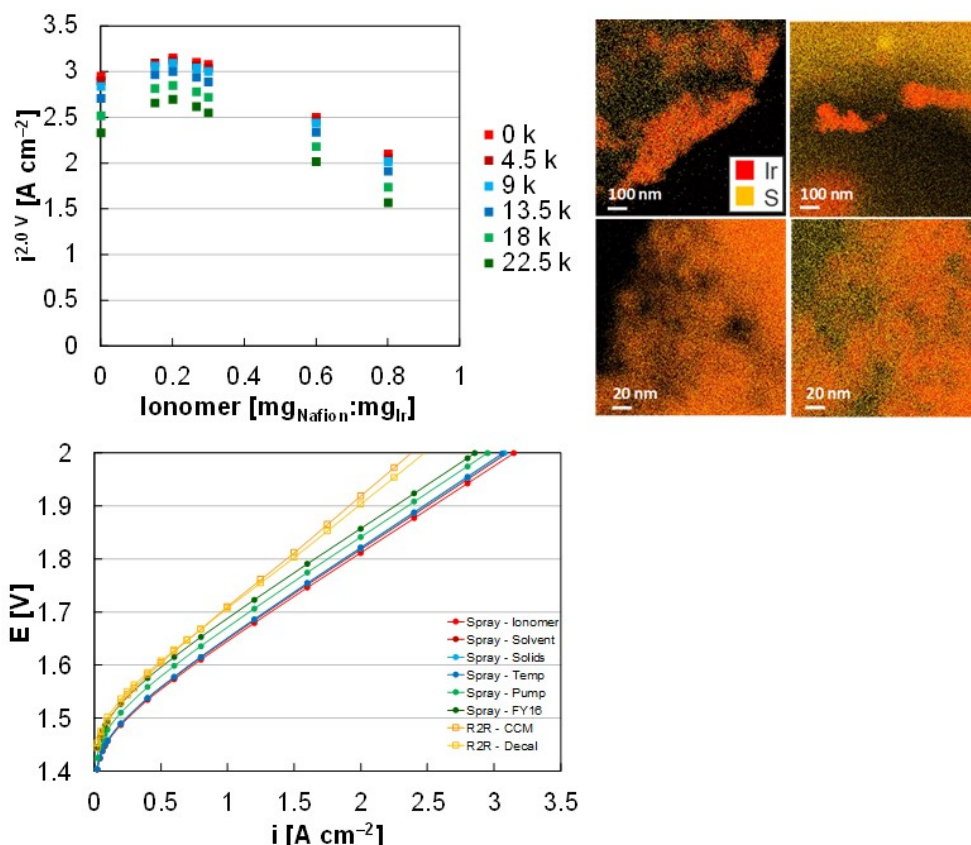


Figure 4. (top left) Cell performance with extended operation (square-wave cycling, 1.45–2 V) as a function of ionomer to catalyst ratio in the anode catalyst layer. (top right) Microscopy of iridium catalyst layer with (left) optimal and (right) high amounts of Nafion ionomer with tracked sulfur used to identify ionomer location. (bottom left) Optimization of spray parameters (denoted spray), compared to current performance from R2R processes.

CONCLUSIONS AND UPCOMING ACTIVITIES

Project findings have indicated that significant durability losses are observed at low loading when adding intermittent power inputs. Mitigation strategies, including catalyst improvements to lower 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 include operating a rainbow stack to increase the rate of data acquisition and gain improved statistics of these degradation process. In terms of mitigation strategies, operation in current control mode is underway to assess the ability of membrane and catalyst developments to improve durability under extended operation. Scaling of stack load and potential limits are also being explored to mitigate losses. Additionally, lessons learned during ultrasonic spray optimization are also being applied to R2R coating in an effort to translate performance/durability improvements to manufacturing-appropriate processes.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. S.M. Alia and G.C. Anderson, “Iridium Oxygen Evolution Activity and Durability Baselines in Rotating Disk Electrode Half-Cells.” *J. Electrochem. Soc.* 166, no. 4 (2019): F282–F294, <http://doi.org/10.1149/2.0731904jes>.
2. S.M. Alia, S. Stariha, and R.L. Borup, “Electrolyzer Durability at Low Catalyst Loading and with Dynamic Operation.” *J. Electrochem. Soc.* 166, no. 15 (2019): F1164–F1172, <http://dx.doi.org/10.1149/2.0231915jes>.

3. S.M. Alia, S. Stariha, R.L. Borup, and B.S. Pivovar, “H₂@Scale: The Effect of Loading, Test Parameters, and Oxides on Electrolyzer-Catalyst Durability.” Presented at AiMES 2018, Cancun, Mexico, October 2, 2018.
4. S.M. Alia and B.S. Pivovar, “The Effect of Loading, Test Parameters, and Oxides on Electrolyzer-Catalyst Durability.” Presented at the 2018 AIChE Annual Meeting, Pittsburgh, PA, October 29–30, 2018.
5. S. Alia, S. Ghoshal, G. Anderson, M.-A. Ha, R. Larsen, S. Stariha, R. Borup, S. Zaccarine, C. Ngo, and S. Pylypenko, “Electrolysis Efforts at NREL, Catalysis.” Presented at the 3M Seminar, St. Paul, MN, November 2018.
6. S.M. Alia, M.-A. Ha, G.C. Anderson, C. Ngo, S. Pylypenko, and R. Larsen, “Effects of Low Loading and Intermittency on Low Temperature Electrolysis from a Catalyst Perspective.” Presented at 2019 MRS Spring Meeting, Phoenix, AZ, April 25, 2019.
7. S.M. Alia, M.-A. Ha, G.C. Anderson, C. Ngo, S. Pylypenko, and R. Larsen, “Iridium and Iridium Oxide Performance in Electrolysis and Resolving Half- and Single-Cell Test Differences.” Presented at the 235th ECS Meeting, Dallas, TX, May 29, 2019.
8. S.M. Alia, G.C. Anderson, S. Ghoshal, S.F. Zaccarine, and S. Pylypenko, “Durability Loss Mechanisms and Sources in Proton Exchange Membrane-Based Electrolysis.” Presented at the 236th ECS Meeting, Atlanta, GA, October 15, 2019.

REFERENCES

1. Alia, Shaun M. “H₂@Scale: Experimental Characterization of Durability of Advanced Electrolyzer Concepts in Dynamic Loading,” Oral Presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review, Crystal City, VA, June 2019.