H_2@Scale: Experimental Characterization of Durability of Advanced Electrolyzer Concepts in Dynamic Loading

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May 1, 2019

DOE Hydrogen and Fuel Cells Program
2019 Annual Merit Review and Peer Evaluation Meeting

Project ID # ta022

Overview

Timeline and Budget

- Project start date: 10/1/2017
- FY17 DOE funding: $650k ($550k NREL, $100k LANL)
- Total DOE funds received to date: $650k
- Percent complete: 70%

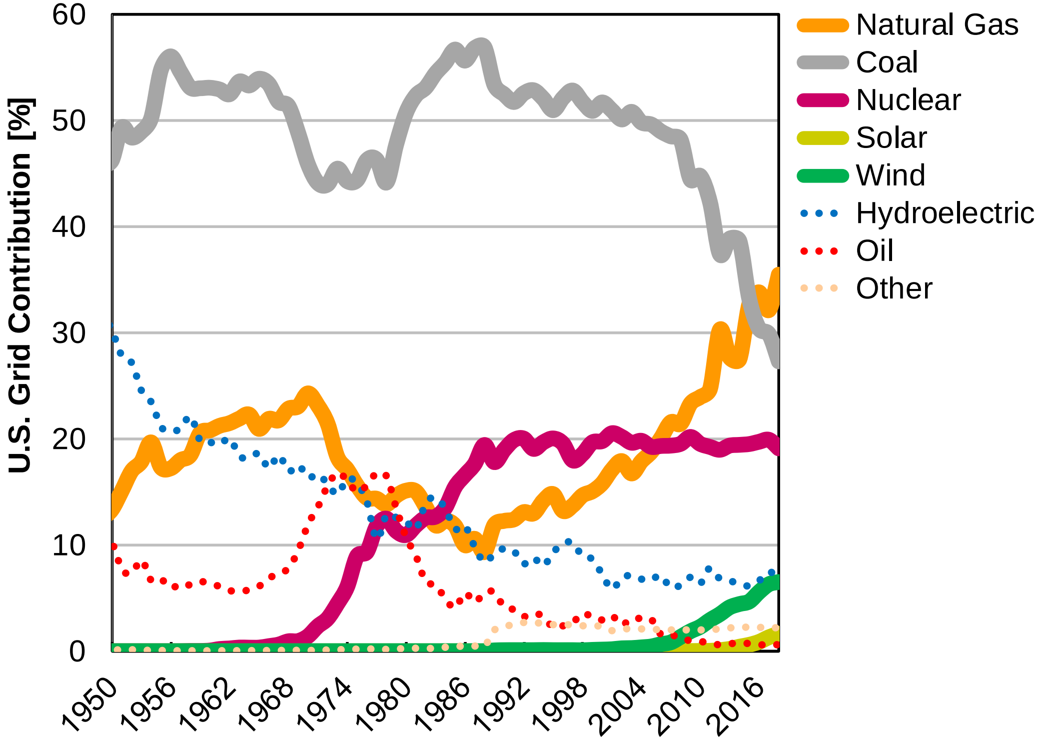
Partners

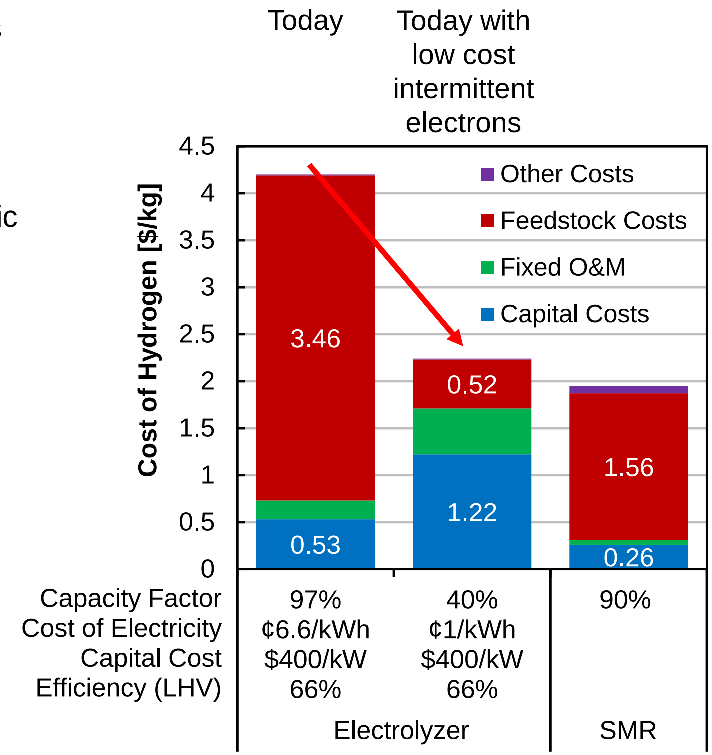
- Los Alamos National Laboratory – Rod Borup

Barriers

- Cost – Feedstock/capital cost reductions are needed to reduce the price of hydrogen by electrolysis.
- Durability – Durability losses have been observed with dynamic loading and intermittent input, and can have a significant impact on the price of hydrogen.

Relevance





- Need for electrolysis to become cost-competitive, to store/offload grid power.
- Objectives:
  – Establish baseline performance and durability as a guide to catalyst/electrode development.
  – Evaluate the influence of low loading, intermittency, and system controls on durability.

U.S. Grid Contribution adapted from – Electric Power Annual, U.S. Energy Information Administration, https://www.eia.gov/electricity/annual/
Hydrogen Production Cost adapted from – B. Pivovar, H_2 at Scale, NREL Workshop. U.S. Department of Energy, https://www.energy.gov/sites/prod/files/2016/12/f34/fcto_h2atscale_workshop_pivovar_2.pdf, 2016.

Relevance

Table 3.1.4 Technical Targets: Distributed Forecourt Water Electrolysis Hydrogen Production [a, b, c]				
Characteristics	**Units**	**2011 Status**	**2015 Target**	**2020 Target**
Hydrogen Levelized Cost [d] (Production Only)	$/kg	4.20 [d]	3.90 [d]	2.30 [d]
Electrolyzer System Capital Cost	$/kg $/kW	0.70 430 [e, f]	0.50 300 [f]	0.50 300 [f]
System Energy Efficiency [g]	% (LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency [h]	% (LHV)	74	76	77
	kWh/kg	45	44	43
Electricity Price	$/kWh	From AEO 2009 [i]	From AEO 2009 [i]	0.037 [j]

[a] The H2A Distributed Production Model 3.0 (www.hydrogen.energy.gov/h2a_production.html) used alkaline electrolysis parameters to generate the values in the table with the exceptions described in the notes below. Results are documented in the Current and Future H2A v3 case studies for Forecourt Hydrogen Production from Grid Electrolysis which can be found at http://www.hydrogen.energy.gov/h2a_prod_studies.html.

[b] The H2A Distributed Production Model 3.0 was used with the standard economic assumptions: All values are in 2007 dollars, 1.9% inflation rate, 10% After Tax Real Internal Rate of Return, 100% Equity Financing, 20-year analysis period, 38.9% overall tax rate, and 1% working capital (based on independent review input). A MACRS 7-year depreciation schedule was used. The plant design capacity is 1,500 kg/day of hydrogen. It is assumed that Design for Manufacture and Assembly (DFMA) would be employed and that production would have realized economies of scale.

[c] The plant production equipment availability is 98% including both planned and unplanned outages; four unplanned outages of 14h duration per year; 1 planned outage of 5 days duration per year. The plant usage factor (defined as the actual yearly production/equipment design production capacity) is 90% based on over sizing of the production equipment to accommodate a summer surge in demand of 10% above the yearly average demand.

[d] The levelized cost is equivalent to the minimum required selling price to achieve a 10% annual rate of return over the life of the plant.

[e] Electrolyzer uninstalled capital costs based on independent review panel results [DOE 2009, Current (2009)] State-of-the-Art Hydrogen Production Cost Estimate using Water Electrolysis, Independent Review, NREL/BK-6A1-46676, September 2009 (http://www.hydrogen.energy.gov/pdfs/46676.pdf). "Electrolyzer capital costs are expected to fall to $380/kW for forecourt production." Escalated to 2007 dollars = $430/kW (purchased equipment cost).

[f] Electrolyzer cells capital replacement = 25% of total purchased capital every 7 years (DOE, 2009).

[g] System energy efficiency is defined as the energy in the hydrogen produced by the system (on a LHV basis) divided by the sum of the feedstock energy (LHV) plus all other energy used in the process.

[h] Stack energy efficiency is defined as the energy in the hydrogen produced by the stack (on a LHV basis) divided by the electricity entering the stack. Additional electricity use for the balance of plant is not included in this calculation. Stack energy efficiency is a guideline and the targets do not need to be met as long as the system energy efficiency meets the targets.

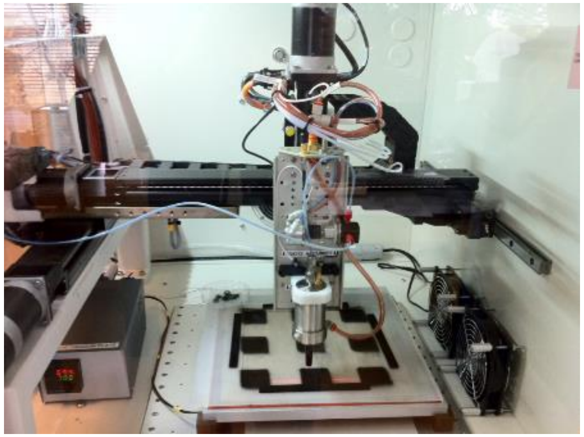
[i] Hydrogen cost is calculated assuming purchase of industrial grid electricity. Electricity prices are taken from the 2009 AEO Reference Case price projections to 2030. Prices beyond 2030 are not available in the 2009 AEO case so they are projected based on the PNNL MiniCAM model output http://www.globalchange.umd.edu/models/gcam/). The average electricity price is $0.063/kWh ($0.061/kWh effective) over the modeled life of the plant for the current (2011) case and $0.070/kWh ($0.069/kWh effective) for the 2015 case.

[j] Electricity cost is assumed to be 3.7¢/kWh throughout the analysis period to meet the $4.00/gge target for dispensed hydrogen.

[k] Costs for the forecourt station compression and storage are consistent with the status and targets in the Delivery MYRD&D section. Storage capacity for 1579 kg of hydrogen at the forecourt is included. It is assumed that the hydrogen refueling fill pressure is 5000 psi for 2010 and it assumed that in 2015 and 2020, the hydrogen refueling fill pressure is 10,000 psi.

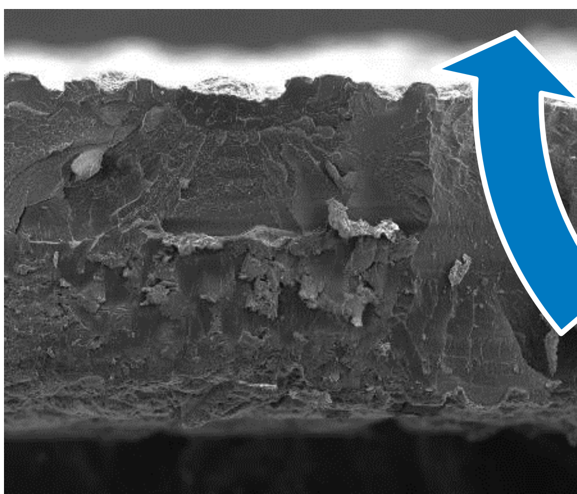
Multi-Year Research, Development, and Demonstration Plan – Fuel Cell Technologies Office, https://www.energy.gov/sites/prod/files/2015/06/f23/fcto_myrdd_production.pdf

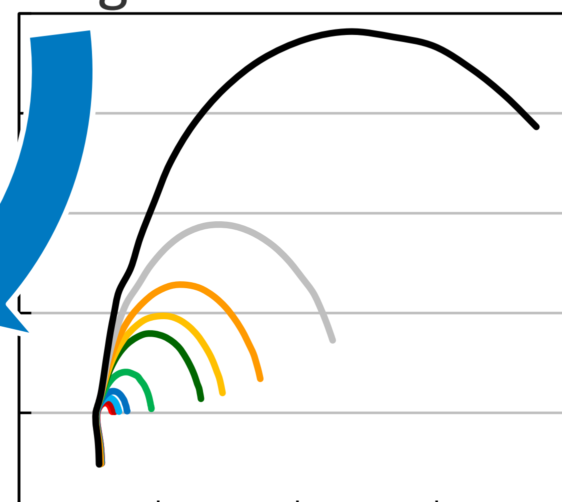
Approach



Electrode Fabrication

Electrolyzer Testing





Characterization

NREL: Cell Diagnostics, RDE

LANL: Microscopy

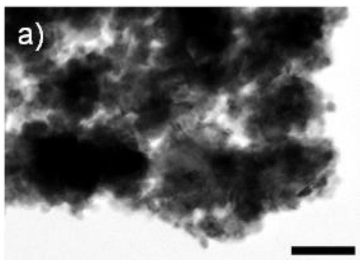
Electrolyzer Test Stand – Greenlight Innovation, http://www.greenlightinnovation.com/electrolyser/

Accomplishments and Progress

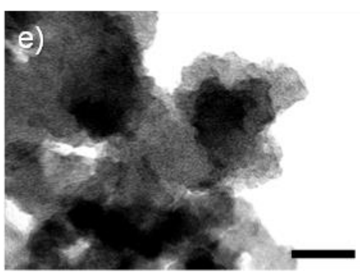
Differences in Performance and Durability, Iridium and Iridium Oxide

- Iridium oxide (rutile) used to evaluate electrolyzer durability and establish protocols.
- Electrolysis operation (time, potential, temperature) grows oxides, negates metal/hydroxide activity.

Iridium

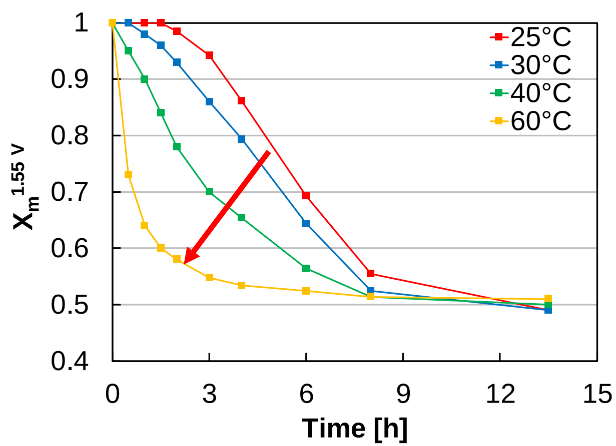


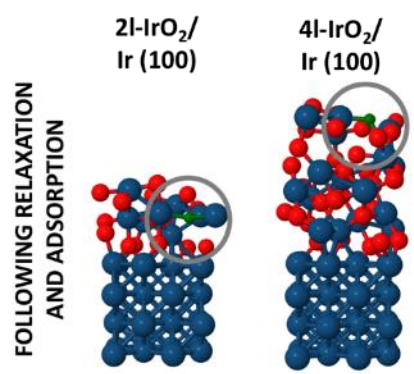
Iridium Oxide



Courtesy of Chilan Ngo, Svitlana Pylypenko, Colorado School of Mines

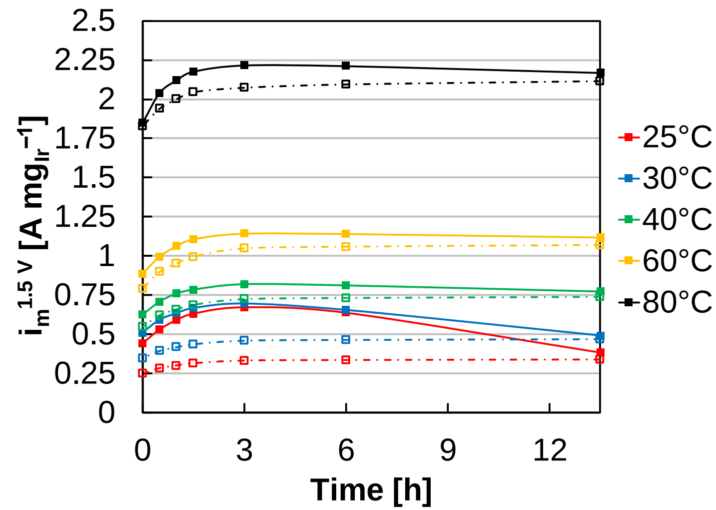
RDE Half-Cells

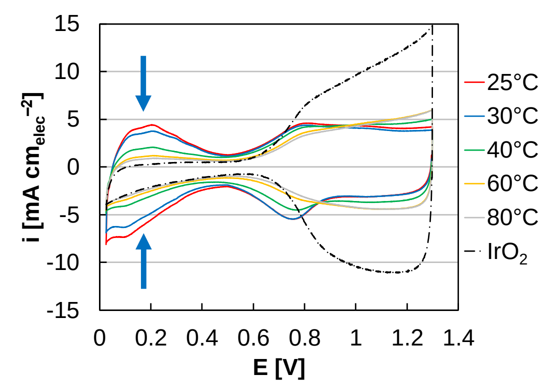




Courtesy of Mai-Anh Ha, Ross Larsen, NREL

MEA Single-Cells



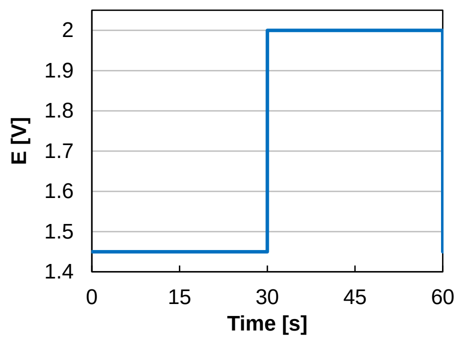


Microscopy – S.M. Alia, B. Rasimick, C. Ngo, K.C. Neyerlin, S.S. Kocha, S. Pylypenko, B.S. Pivovar, *J. Electrochem. Soc.*, **2016**, *163*(11), F3105-F3112. DOI:10.1149/2.0151611jes

Accomplishments and Progress

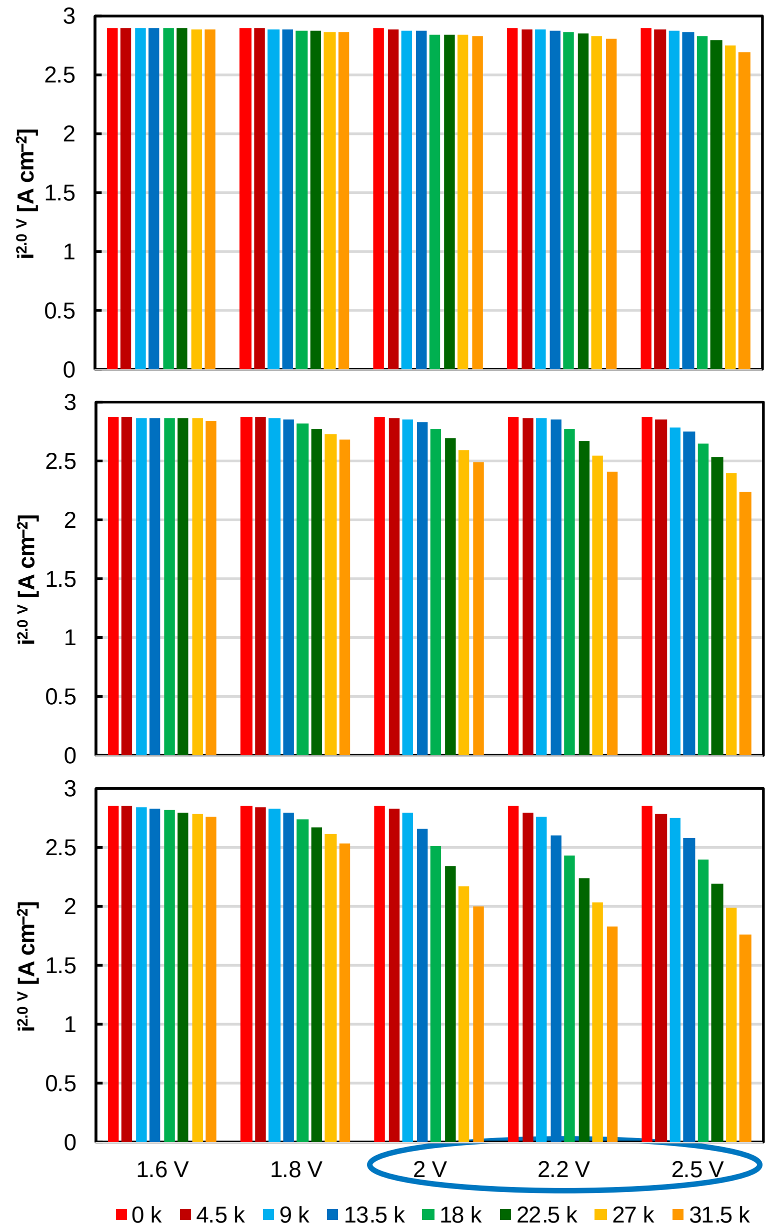
Impact of Loading and Upper Potential

Test Profile



- Focus on anode catalyst degradation by using:
  - Thick membranes to avoid crossover and plating
  - Thick PTLs to avoid coating corrosion and passivation

- Low loading ($\leq 0.1\ mg_{Ir}\ cm^{-2}$) and high potential ($\geq$ 2.0 V) necessary to observe loss over a reasonable timeframe.



$0.4\ mg_{Ir}\ cm^{-2}$

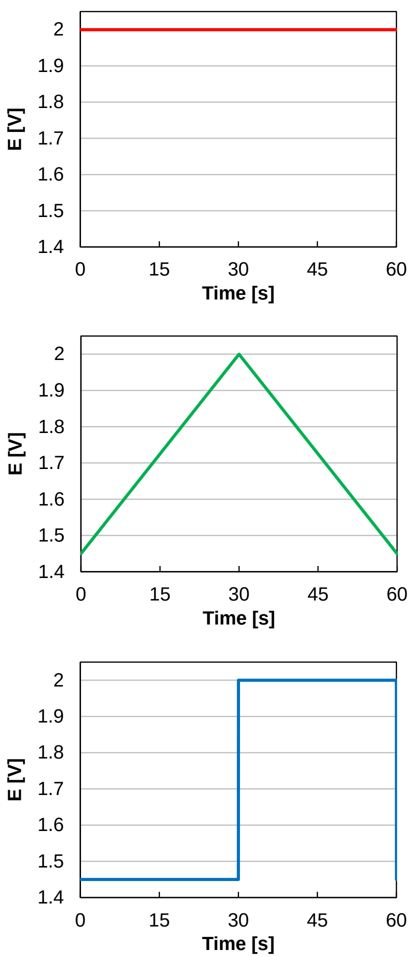
$0.2\ mg_{Ir}\ cm^{-2}$

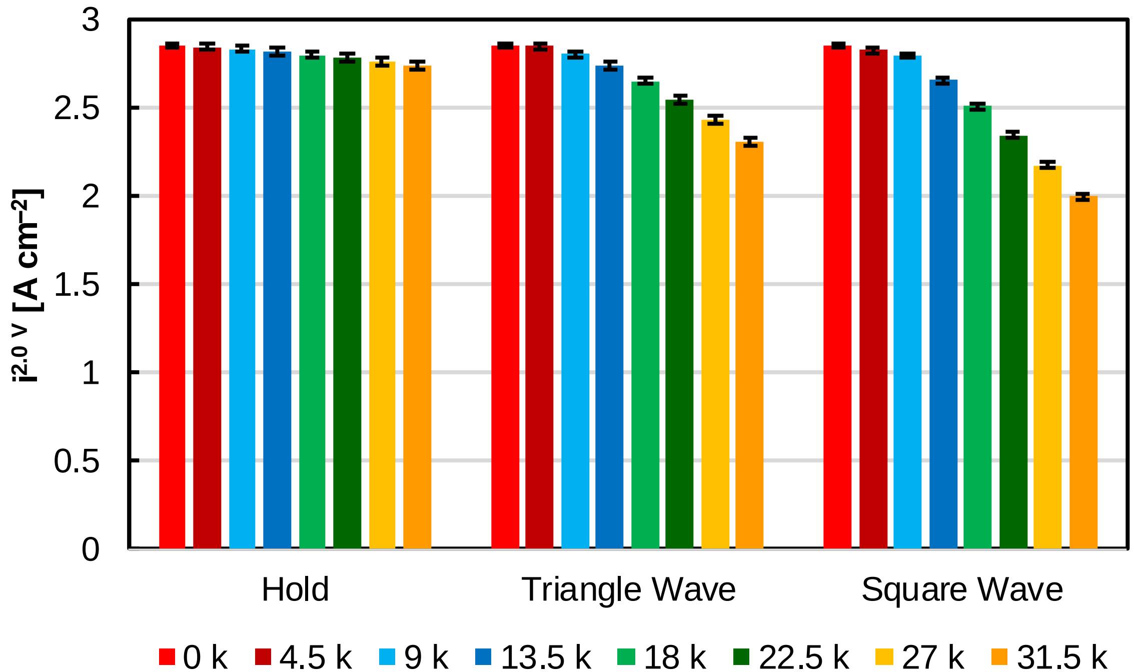
$0.1\ mg_{Ir}\ cm^{-2}$

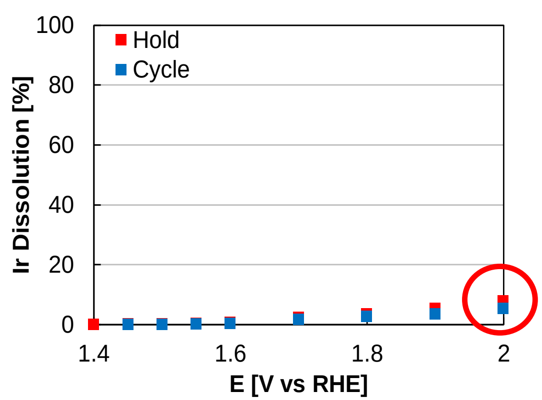
Accomplishments and Progress

Comparison of Load Profiles

Test Profiles







- Varying input/load dominated loss.
- Differences in load increase may affect potential distribution and dissolution in the catalyst layer (FY18).

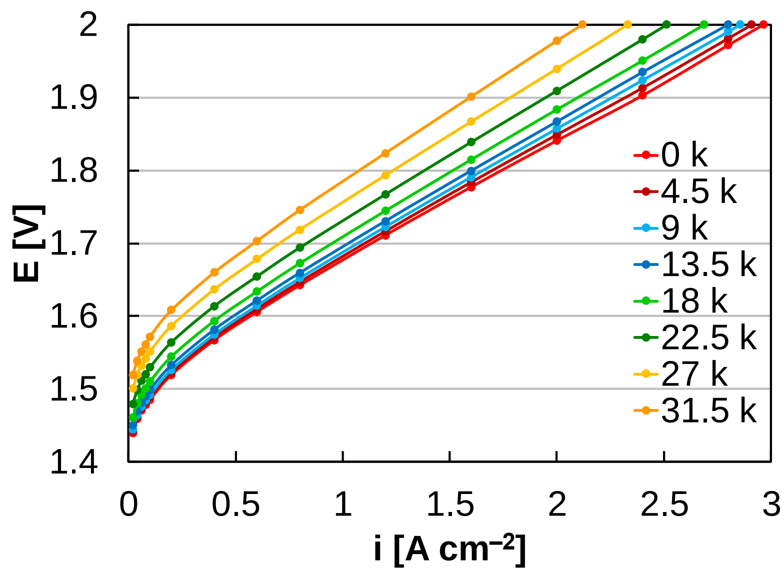
Ex-situ data – S.M. Alia, G.C. Anderson, *J. Electrochem. Soc.*, **2019**, *166*(4), F282-F294. DOI:10.1149/2.0731904jes

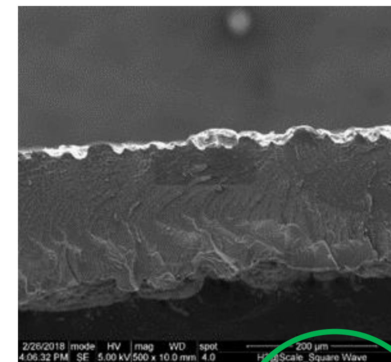
Accomplishments and Progress

Evaluating Loss, Mechanism

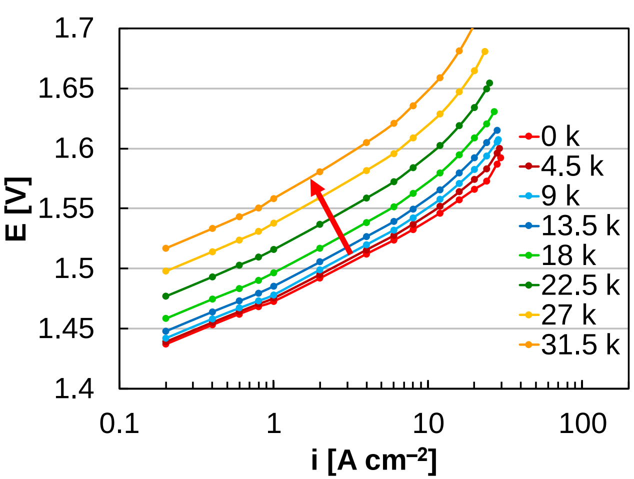
- Cell Diagnostics:
  - Kinetic loss was significant but did not account for all performance loss.
  - Incremental loss in cyclic voltammograms, not proportional to kinetic loss.
  - Increased resistance, not related to HFR.

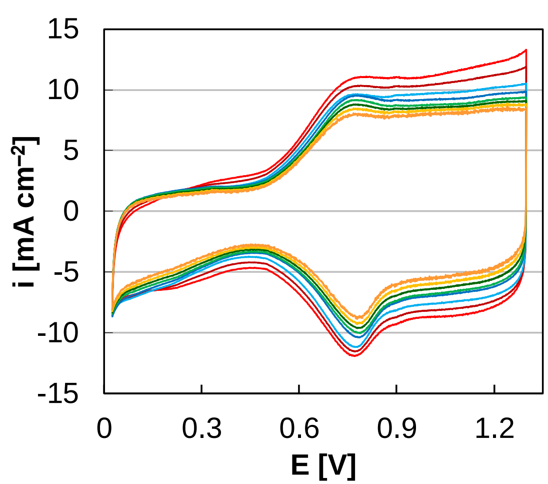
- Characterization revealed thinner catalyst layers and decreasing pore diameter (FY18).

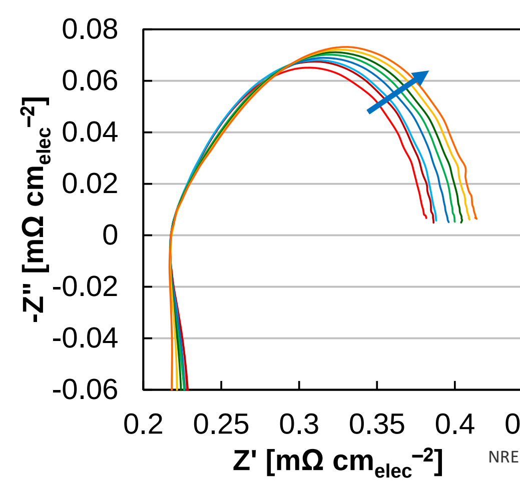




	Initial	Hold	Square Wave	Triangle Wave
[µm]	1.07	1	0.77	0.75



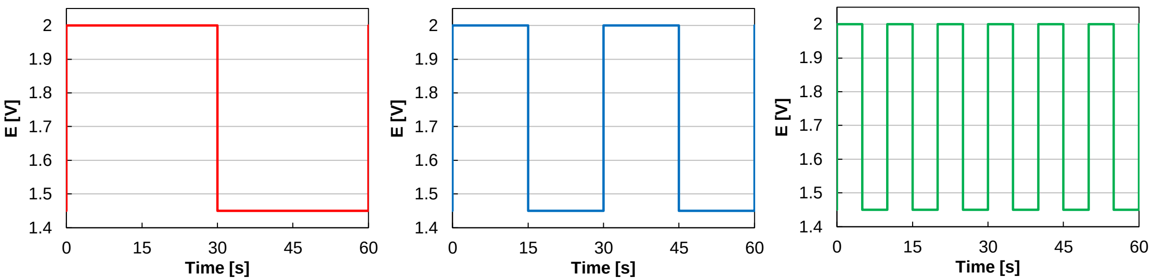


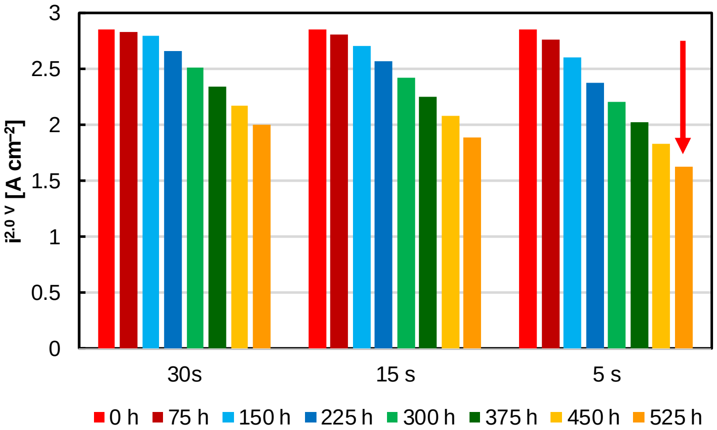


Accomplishments and Progress

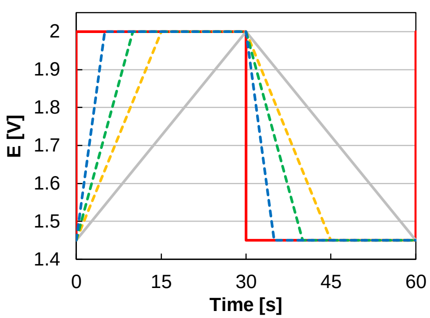
Effect of Period, Strategies for Mitigating Loss

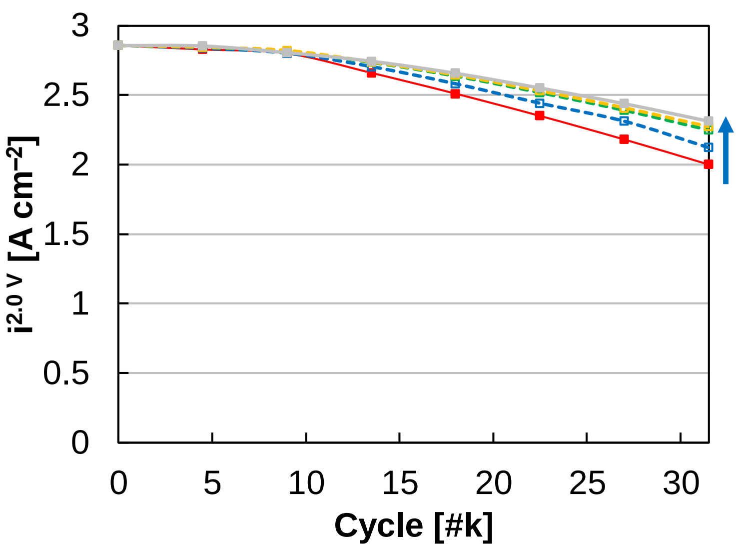
Test Profiles





Test Profile

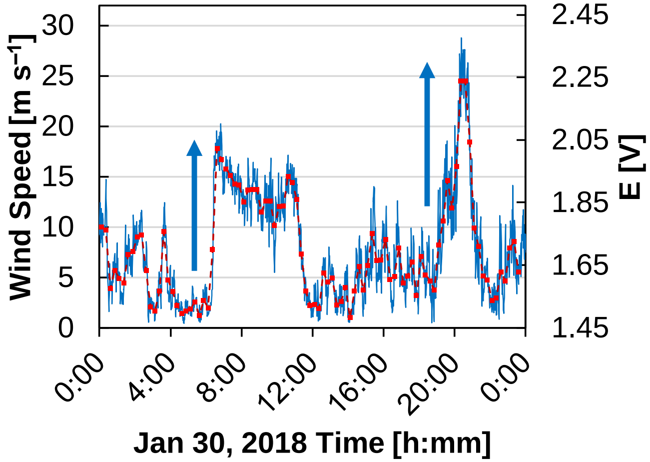


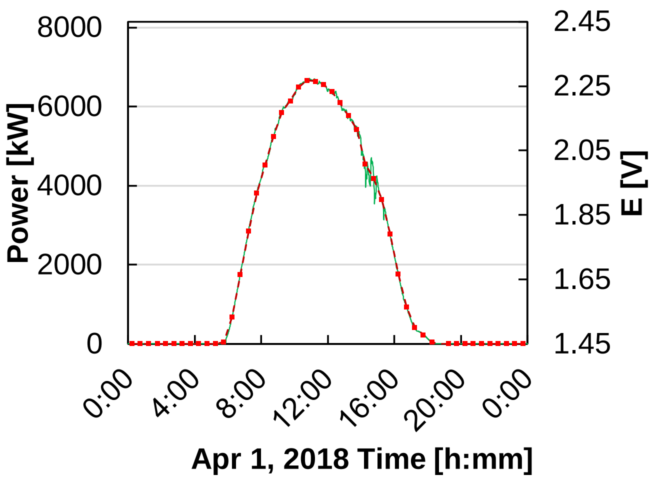


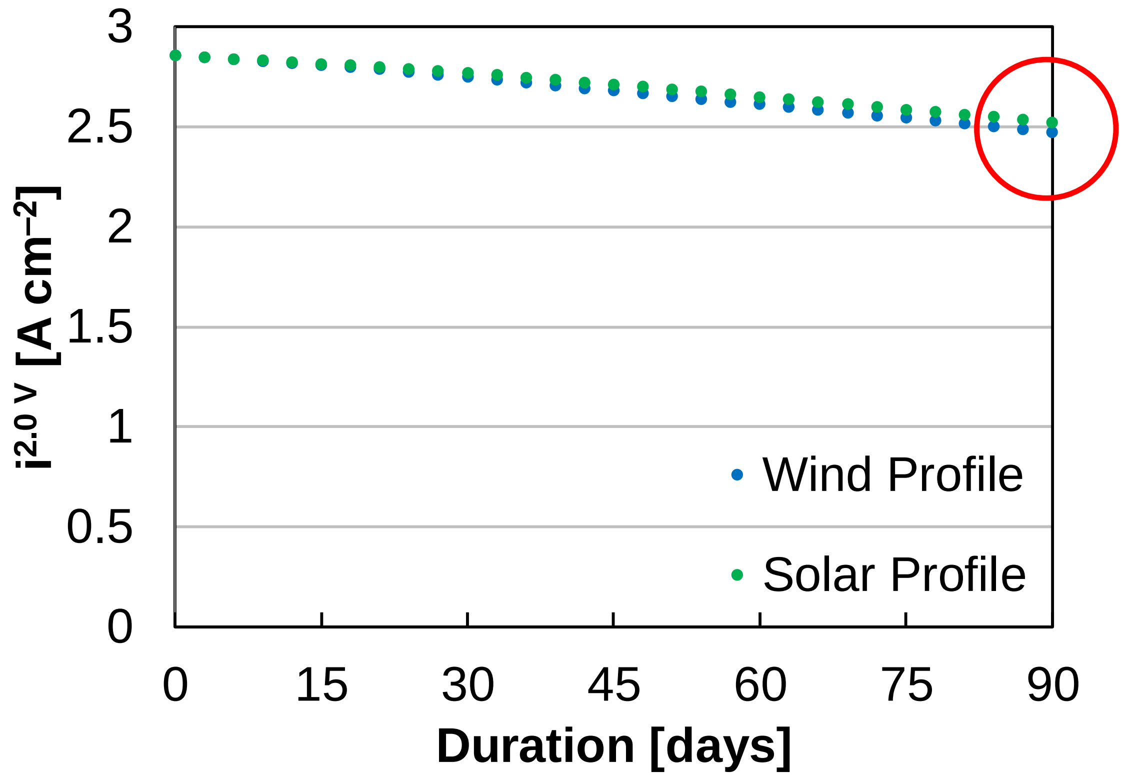
- Higher cycle frequency increased loss, although the increase was not proportional.
- Varying input/load dominated loss. Ramping input slightly improved durability.

Accomplishments and Progress

Correlating to Renewable Profiles, Anticipated Use



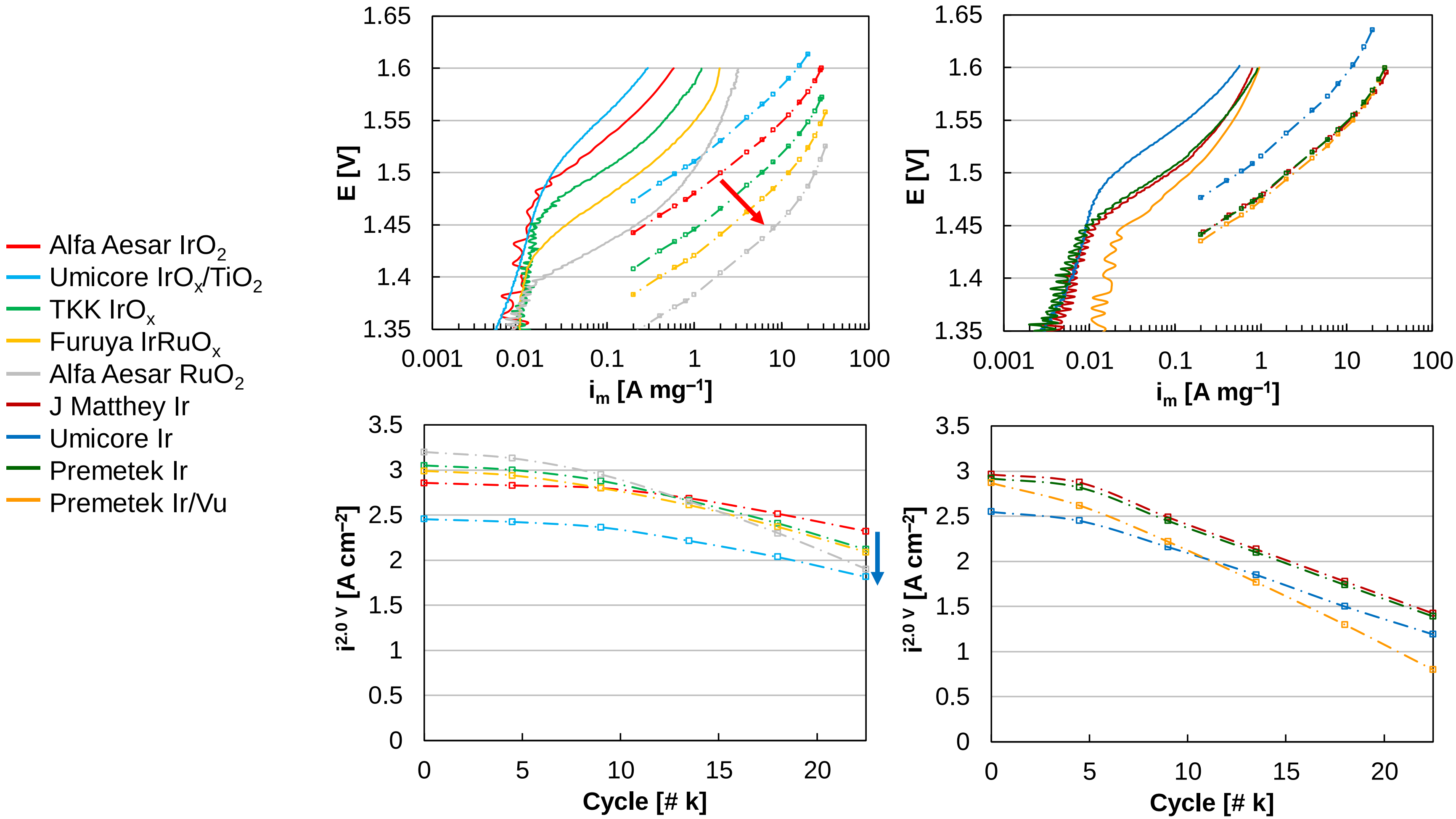




- Square- and triangle-wave profiles accelerated loss.
- Similar loss rates for wind and solar profiles.
  - Varying input/load dominates loss
  - Slight differences may be due to sudden/multiple load increases

Accomplishments and Progress

Incorporation of Different Catalyst Types

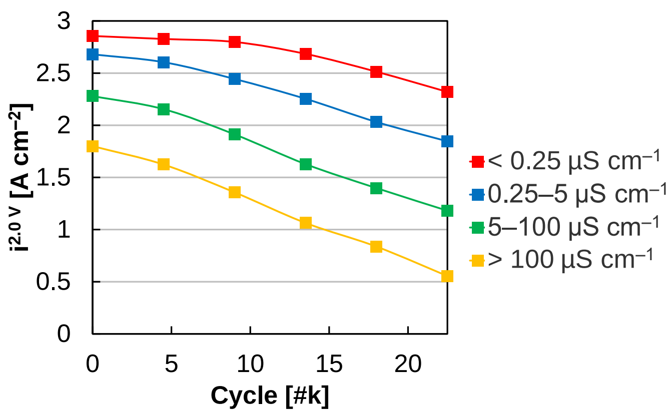


- Testing expanded to different catalyst types (commercial) – surfaces, components, morphology (surface area), and supports.
- Catalysts evaluated showed kinetic improvements, higher durability losses.

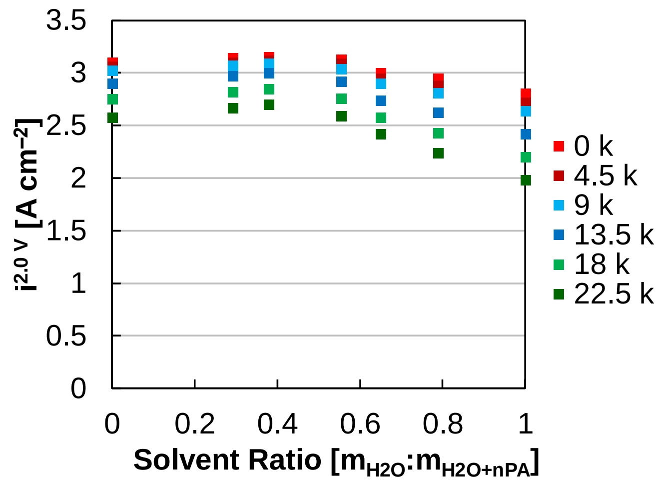
Accomplishments and Progress

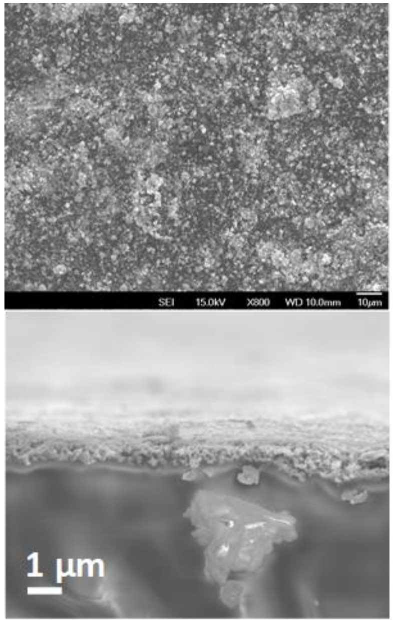
Impact of Spray Parameters

Water Quality (FY18)

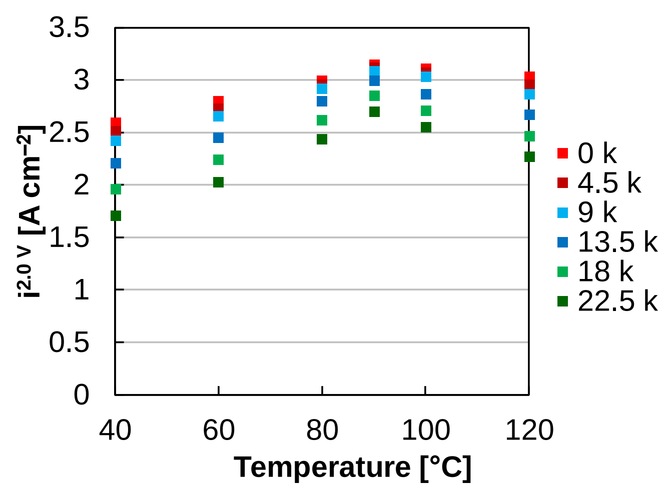


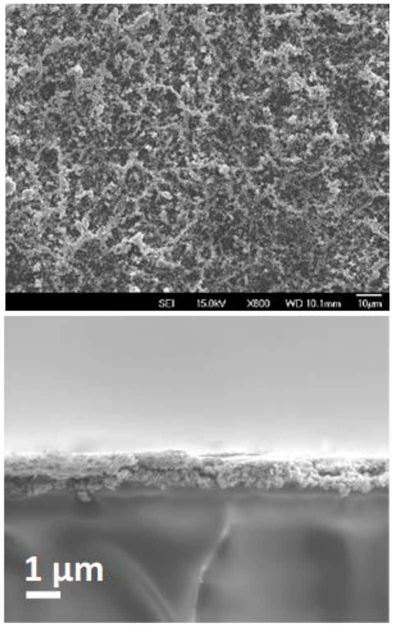
Solvent





Drying Temperature



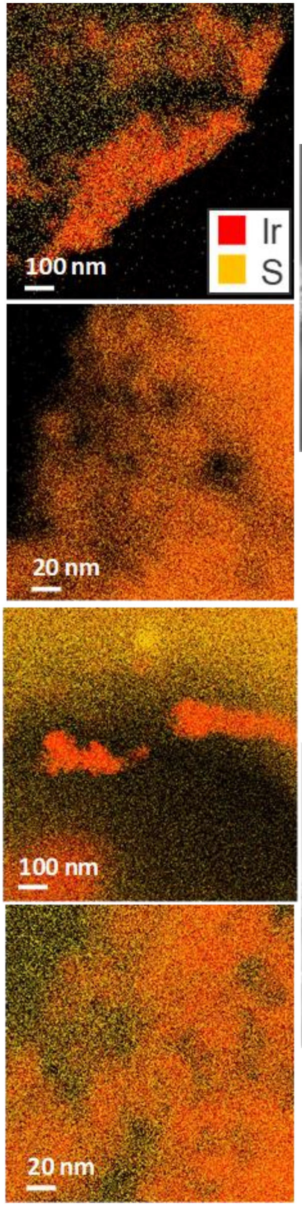


- Factors examined for an effect of durability – ink concentration, solvent, pump rate, drying temperature, and ionomer content.
- Particle aggregates, coating uniformity, and layer density (porosity) may influence performance and durability.

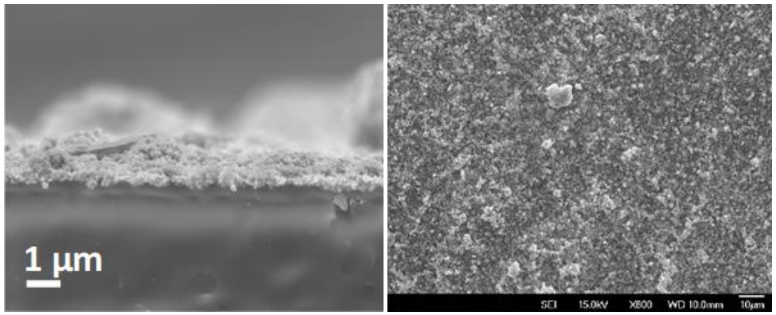
Microscopy Courtesy of Sarah Zaccarine, Svitlana Pylypenko, Colorado School of Mines

Accomplishments and Progress

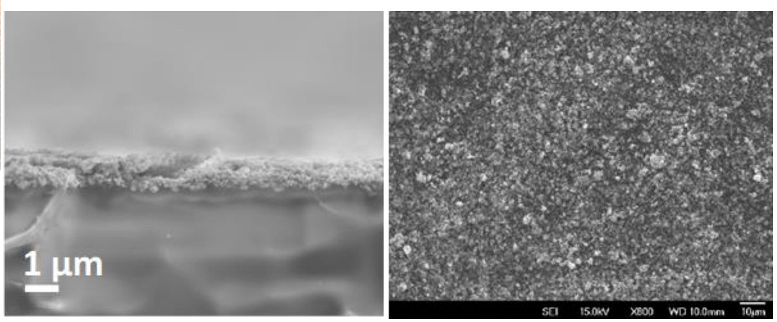
Impact of Ionomer Content

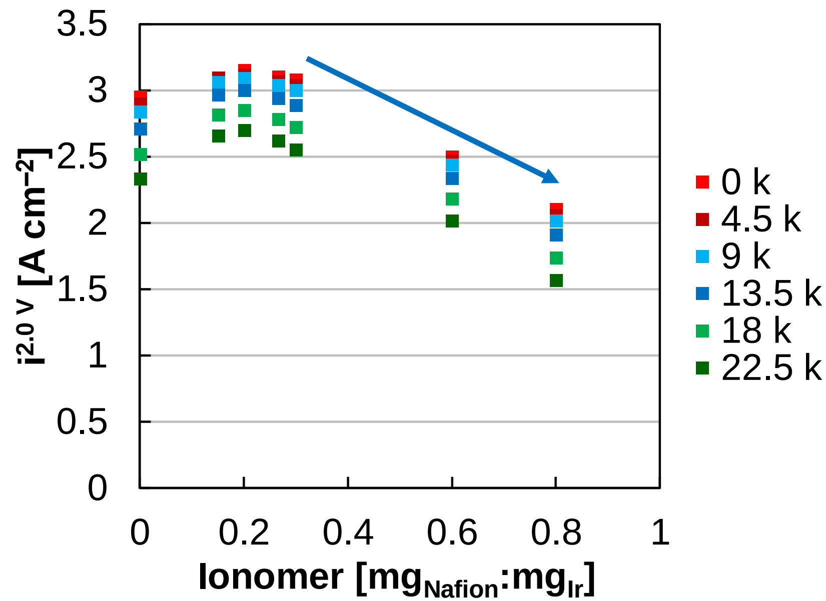


Standard



Increased Nafion





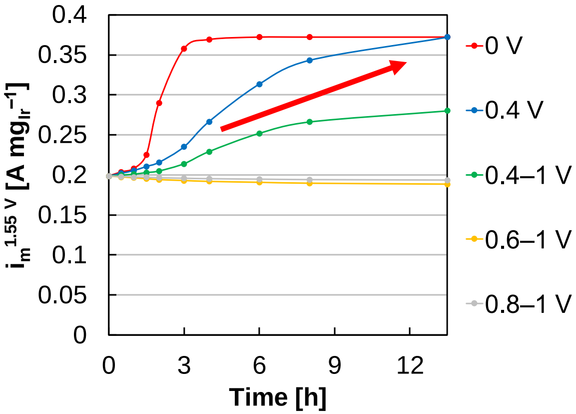
- Sulfur signal tracked closely to iridium. Excess Nafion in catalyst layer linked to performance/durability decreases.
- Ionomer balance needed:
  - For interface and ink dispersion
  - To avoid catalyst isolation and contaminant effects

Microscopy Courtesy of Sarah Zaccarine, Svitlana Pylypenko, Colorado School of Mines

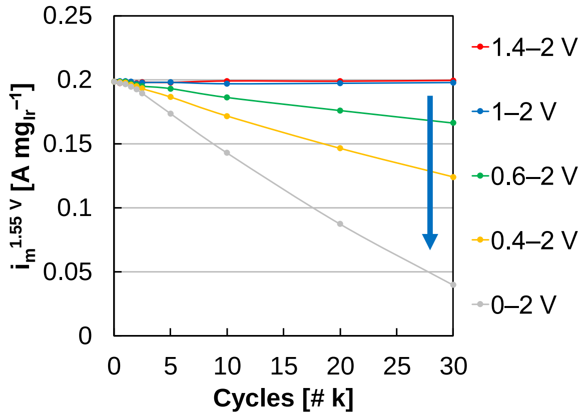
Accomplishments and Progress

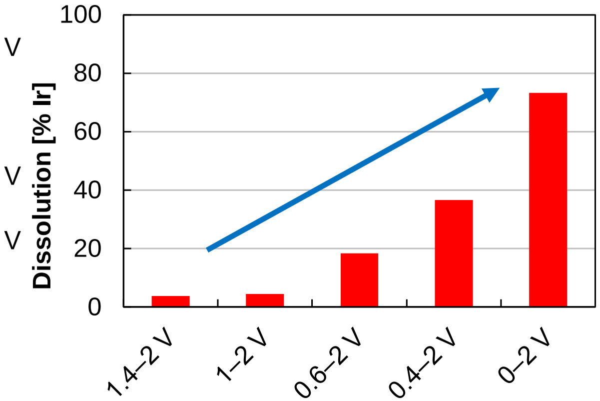
Effect of Start-Stop Operation

Reduction, Agglomeration

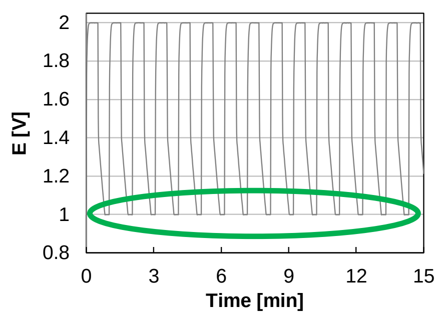


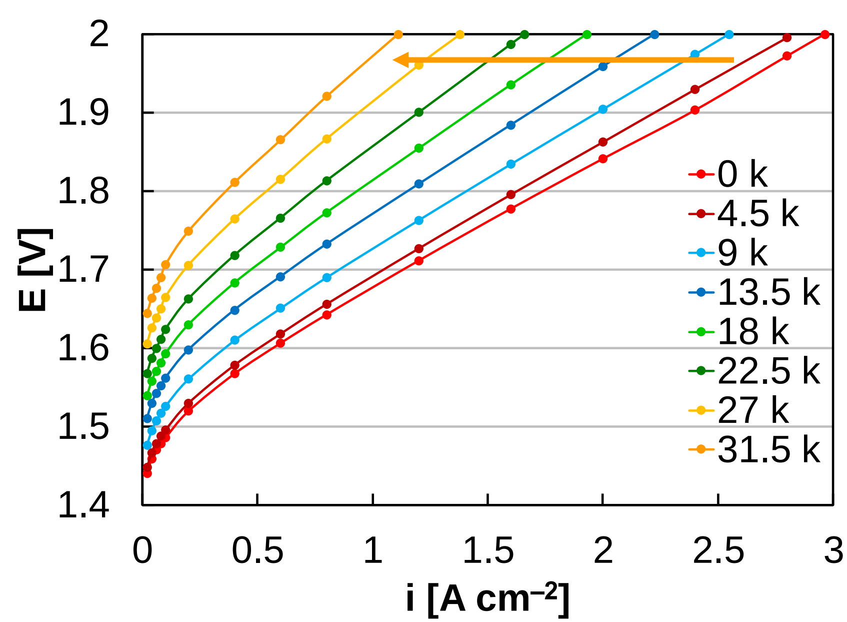
Reduction, Dissolution





- Competing processes of near-surface reduction/oxidation, aggregation, and dissolution.
- Combined reduction/dissolution dramatically increased dissolution and activity loss.
- Difficult to rely on crossover to quickly accelerate loss. Have used thinner membranes, backpressure, and dictated potential to accelerate loss at the cell level.





Responses to Previous Year Reviewers' Comments

- Reviewer Comment: The project team should ensure that an increased amount of effort is spent on communicating results to both the academic and commercial communities.
- Response: We have increased efforts to disseminate data, through publications (in print, several submitted) and presentations, and community interactions through H_2@Scale and HydroGEN EMN projects and the IEA.

- Reviewer Comment: The project's scope is limited. While it is hoped that results will inform electrolyzer design, materials selection, and operation, the project will likely contribute to cost competitive hydrogen production only when combined with other, more robust development and testing projects. A critical assessment should be done to determine the probability that results achieved will contribute substantively to FCTO's goals of improving hydrogen production performance and lowering costs.
- Response: In its first year, the project scope was limited to catalyst choices and preliminary tests assessing low loading and variable input. This year, the scope expanded to include: a full study of these parameters; correlating accelerated tests to renewable profiles; mitigating loss through system controls and catalyst type; and evaluating parameters that affect electrode structure. Continuing efforts include rainbow- and short-stack testing to further expand the work scope and link cell- and system-level durability. We have worked to disseminate data to interested parties through papers and publications. We have also engaged our collaborators to share these results and provide input for catalyst development and device-level projects addressing hydrogen production cost and durability.

- Reviewer Comment: There has been outstanding progress in achieving project objectives. To date, the iridium and iridium oxide catalyst materials have been tested. No conclusions regarding bigger picture issues can be drawn yet in regard to the implications of results so far for overall electrolyzer performance and cost.
- Response: We have expanded durability testing this year and found that intermittent load and thin catalyst layers significantly accelerate loss observations. We have also added mitigation strategies based on system controls and catalyst type, finding that higher catalysts loadings, lower operating potentials, and ramping sudden load increases reduce loss. These results indicate that while catalyst loading reductions are needed to minimize hydrogen cost at lower capacity, durability tradeoffs are a critical concern and may limit loading reductions. While catalyst development efforts are critical to improve performance and lower operating potential (dissolution, durability), aspects of system controls will be necessary to minimize loss during extended operation.

Collaboration and Coordination

Institutions	Role
National Renewable Energy Laboratory (NREL): Shaun Alia (PI), Grace Anderson, Shraboni Ghoshal, Guido Bender, Bryan Pivovar	Prime, oversees the project; lead electrode fabrication, electrolyzer testing, and diagnostics
Los Alamos National Laboratory (LANL): Rod Borup, Sarah Stariha	Sub; materials characterization using microscopy

Mai-Anh Ha, Ross Larsen (NREL)
Svitlana Pylypenko, Sarah Zaccarine, Chilan Ngo (Colorado School of Mines)

Remaining Challenges and Future Work

- Continue to evaluate the effect of dynamic loading on durability.
  - Incorporate rainbow- and short-stack testing for durability statistics, to expand test parameters, and to link to system-level durability
  - Assess losses from start-stop operation
  - Continue correlating loss to anticipated power inputs
- Evaluate the effect of transport layer and membrane changes on catalyst degradation and combined loss mechanisms on electrolyzer loss.
- Use current-based operation to assess the ability of performance improvements to mitigate durability loss.
- Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

- This project is focused on assessing electrolysis durability with dynamic operation and reduced catalyst loadings, and has not explicitly generated IP.

- We have worked to disseminate data through publications, presentations, and community interactions to share these results and provide input for electrolysis-related projects addressing hydrogen production cost and durability.

Summary

- Relevance: The project evaluates electrolyzer durability with dynamic loading and assesses the ability of water splitting-based hydrogen production to reduce cost (intermittent input, loading) while maintaining performance with extended operation.

- Approach: The project establishes baseline performance and durability as a guide to catalyst/electrode development. Additionally, the influence of low loading, intermittency, and system controls on durability are evaluated.

- Accomplishments and Progress: Low loading, high potential, and intermittency were found to accelerate loss, attributed to thinning the catalyst layer, decreasing kinetics, and increasing resistance. Performance decrease could be mitigated by increasing loading, minimizing potential, and ramping sudden input increases. Square- and triangle-wave profiles were found to accelerate loss compared to anticipated wind and solar inputs, likely due to the increased frequency. Testing was expanded to commercial catalysts with different surfaces (metal, hydroxide, rutile), morphologies (surface area), supports, and components (ruthenium); although performance increases were found, loss under the same potential profiles tended to be larger. Fabrication parameters, including ionomer content, ink formulation, and temperature were further found to have an effect on beginning of life performance and durability.

- Collaborations: This project is a collaboration between NREL and LANL.

- Proposed Future Research: Future research plans include incorporating rainbow- and short-stack testing for durability statistics and to link cell- and system-level durability. Additional degradation mechanisms will be explored and current-based testing will be used to assess the ability of performance improvements to mitigate durability loss.

Thank You

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This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL
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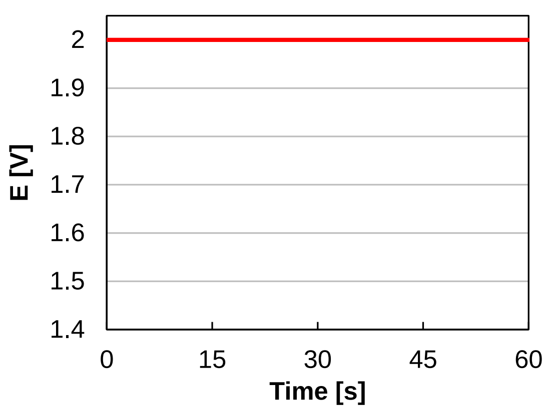
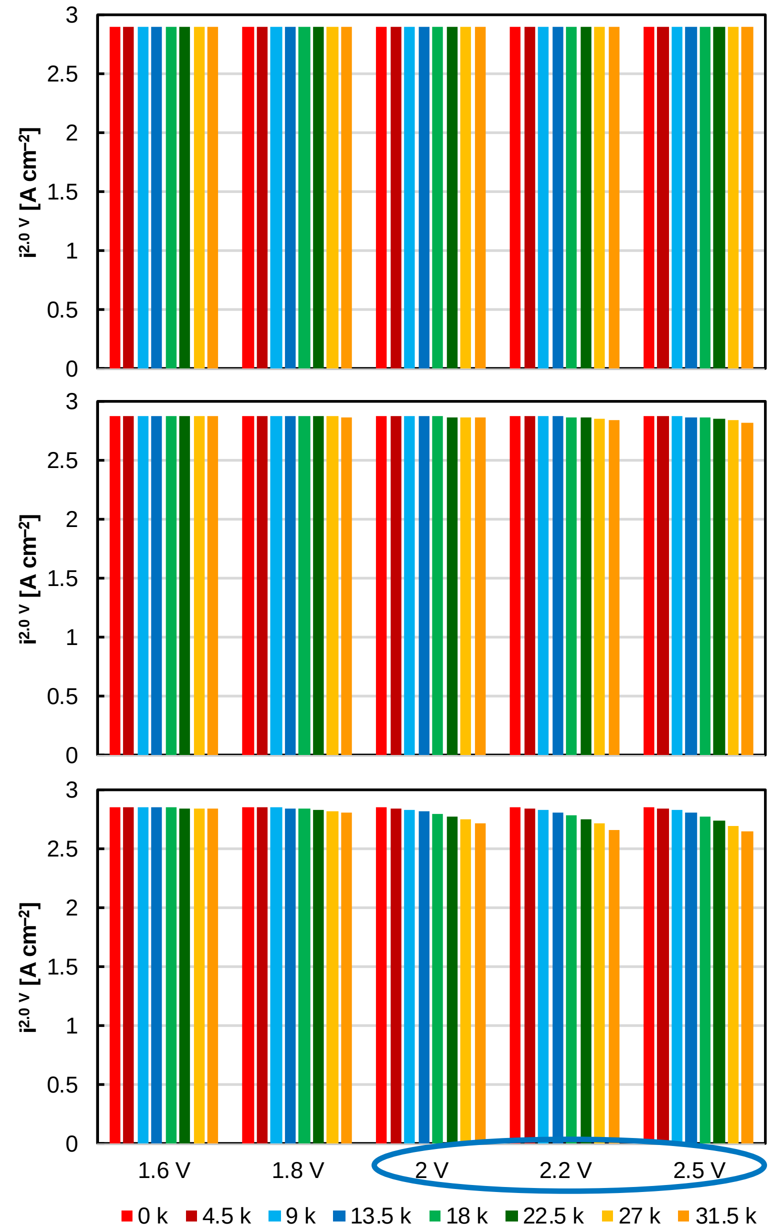
Technical Back-Up Slides

Accomplishments and Progress

Constant Input

Test Profile





0.4 mg_{Ir} cm^{-2}

0.2 mg_{Ir} cm^{-2}

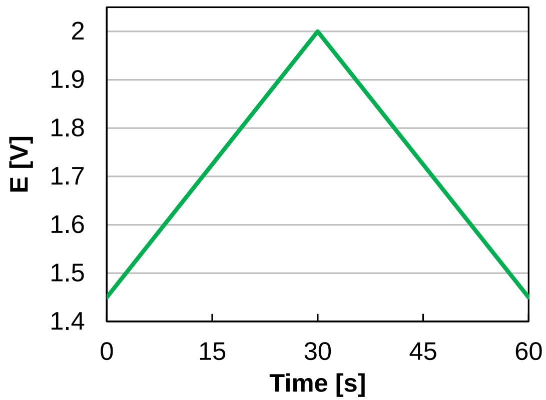
0.1 mg_{Ir} cm^{-2}

Low loading ($\leq$ 0.1 mg_{Ir} cm^{-2}) and high potential ($\geq$ 2.0 V) necessary to observe loss over a reasonable timeframe

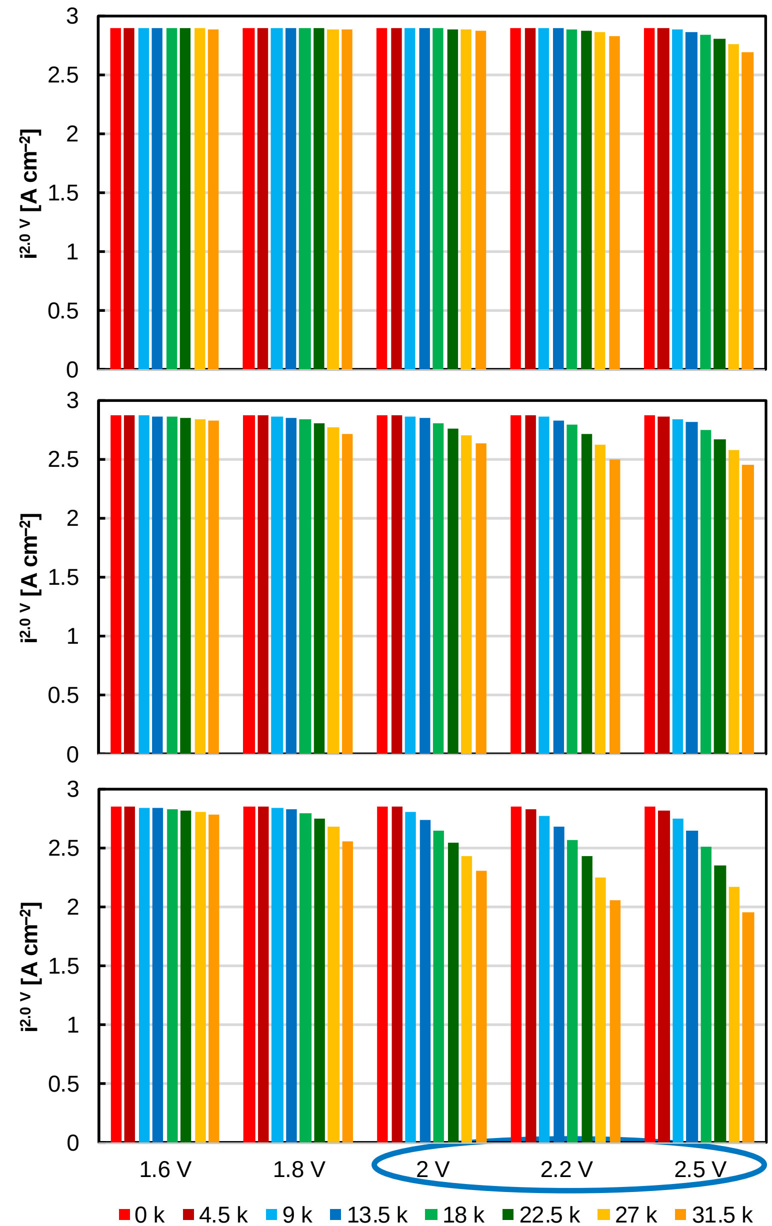
Accomplishments and Progress

Triangle Wave Input

Test Profile



Low loading (≤ 0.1 mg_{Ir} cm^{-2}) and high potential (≥ 2.0 V) necessary to observe loss over a reasonable timeframe



0.4 mg_{Ir} cm^{-2}

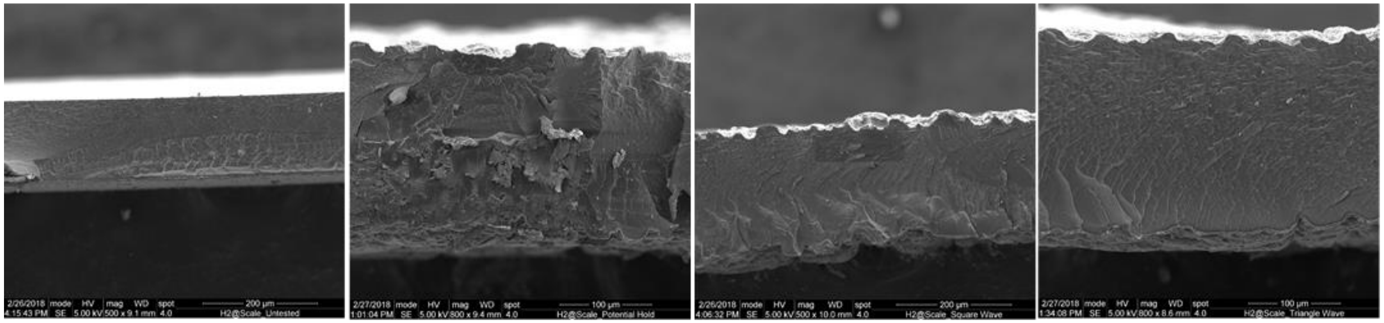
0.2 mg_{Ir} cm^{-2}

0.1 mg_{Ir} cm^{-2}

Accomplishments and Progress

Catalyst Layer Thickness, Single-Cell Tests (FY18)

Initial | **Hold** | **Square Wave** | **Triangle Wave**

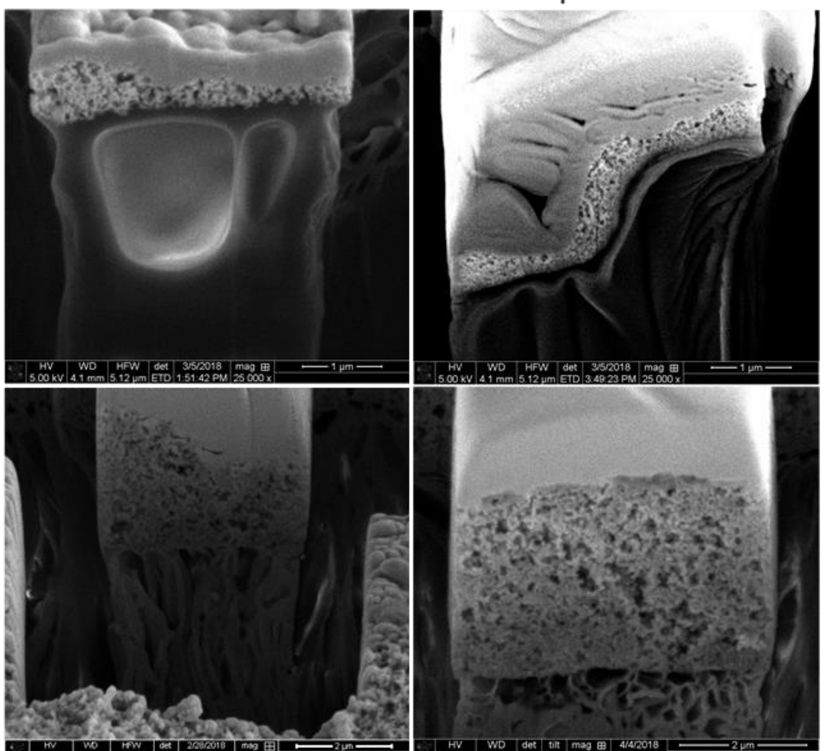


	Initial	Hold	Square Wave	Triangle Wave
[µm]	1.07	1	0.77	0.75

Initial | Square Wave

Iridium

Platinum

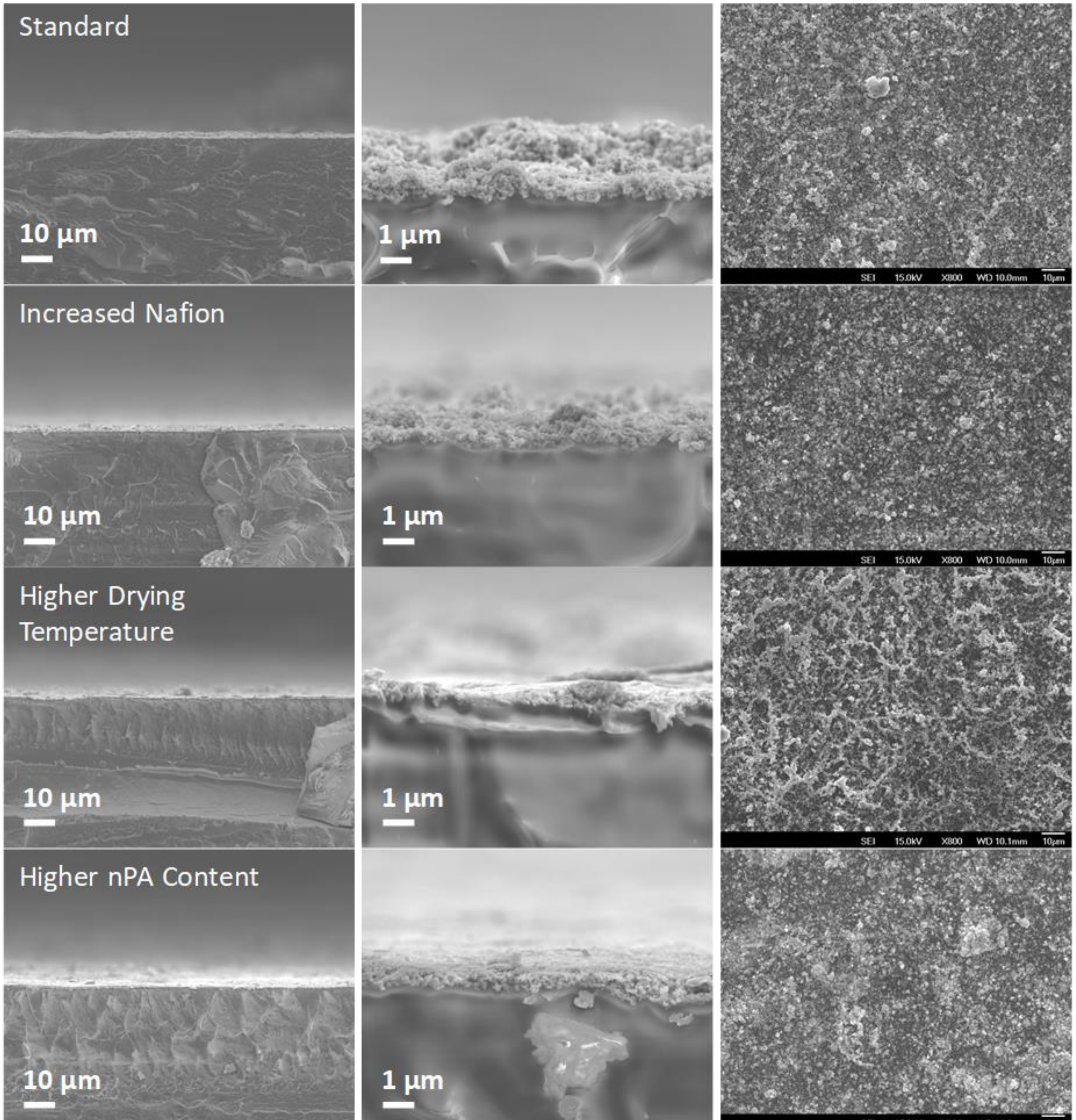


	Initial	Square Wave
IrO_2 Thickness [µm]	1	0.77
IrO_2 Porosity [%]	38.8	33
IrO_2 Ave Pore Area [µm^2]	0.004	0.002
IrO_2 Equ. Dia. [nm]	52.9	35.9
Pt/HSC Thickness [µm]	4.1	2.51
Pt/HSC Porosity [%]	44.1	45.9
Pt/HSC Ave Pore Area [µm^2]	0.019	0.01
Pt/HSC Equ. Dia. [nm]	126.8	77

- Found catalyst layer thinning was more prominent in the square and triangle wave tests.
- Although the porosity didn't change significantly, the equivalent diameter (Equ. Dia.) of the pores decreased.

Accomplishments and Progress

Impact of Ionomer Content, Spray Parameters

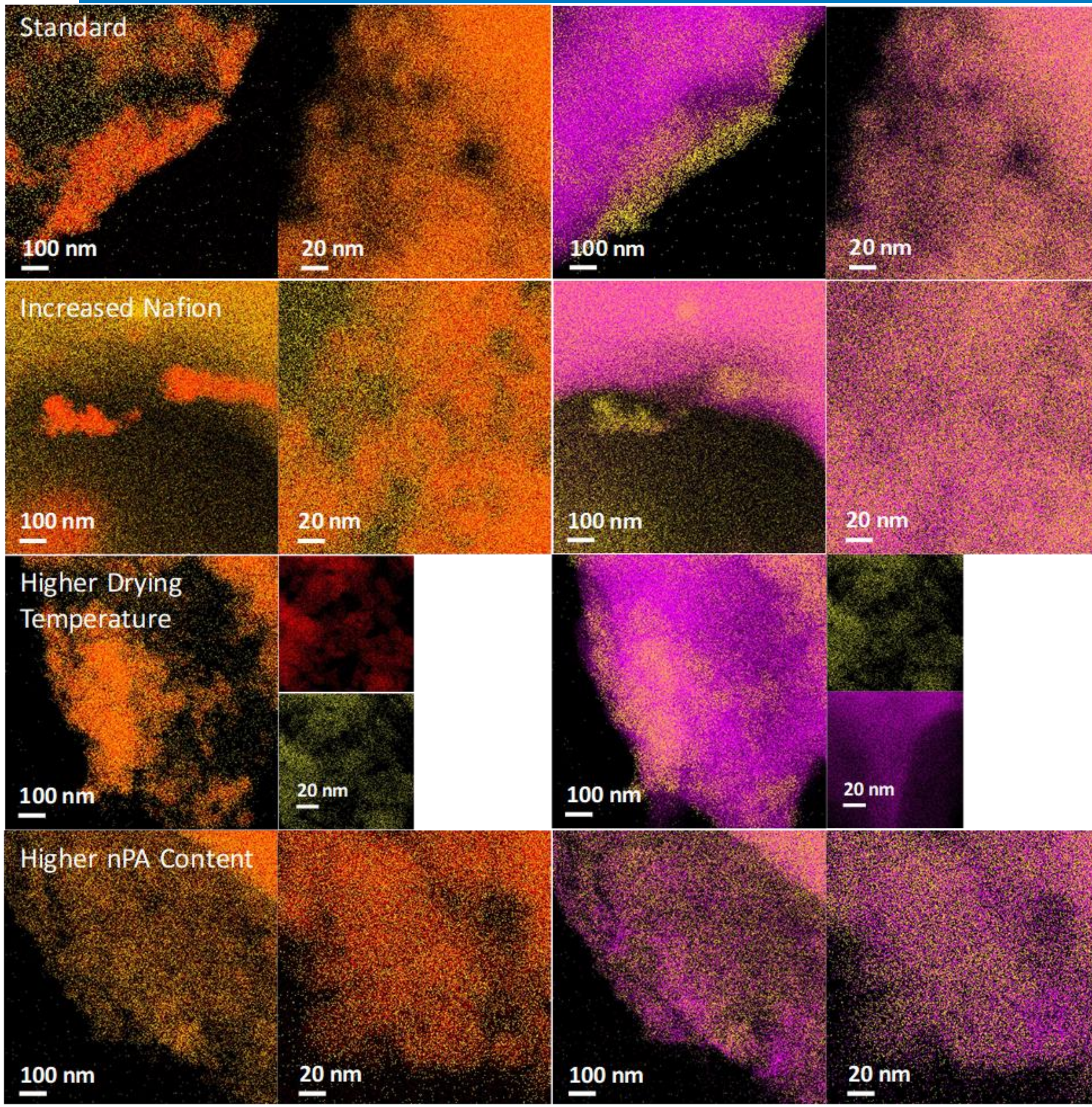


- All layers relatively thin and heterogeneous
- Increased Nafion appeared slightly more homogeneous
- Higher drying temperature appeared slightly thinner

Courtesy of Sarah Zaccarine, Svitlana Pylypenko, Colorado School of Mines

Accomplishments and Progress

Impact of Ionomer Content, Spray Parameters



- Energy dispersive X-ray spectroscopy tracked iridium, sulfur, fluorine
- Sulfur closely tracked iridium, fluorine relatively homogenous

Courtesy of Sarah Zaccarine, Svitlana Pylypenko, Colorado School of Mines