H2NEW Hydrogen from Next-generation Electrolyzers of Water
U.S. DEPARTMENT OF ENERGY

H2NEW LTE: Durability and AST Development

Deputy Director : Rangachary (Mukund) Mukundan
Task Liaisons: Shaun Alia and Siddharth Komini Babu
Other Lab Leads: Debbie Myers and Haoran Yu

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DOE Hydrogen Program
2023 Annual Merit Review and Peer Evaluation Meeting

Project ID # 196a

NREL Transforming ENERGY · INL Idaho National Laboratory · Argonne National Laboratory · Berkeley Lab Bringing Science Solutions to the World · Lawrence Livermore National Laboratory · Los Alamos National Laboratory EST 1943 · National Energy Technology Laboratory · Oak Ridge National Laboratory · Pacific Northwest National Laboratory

Project Goals

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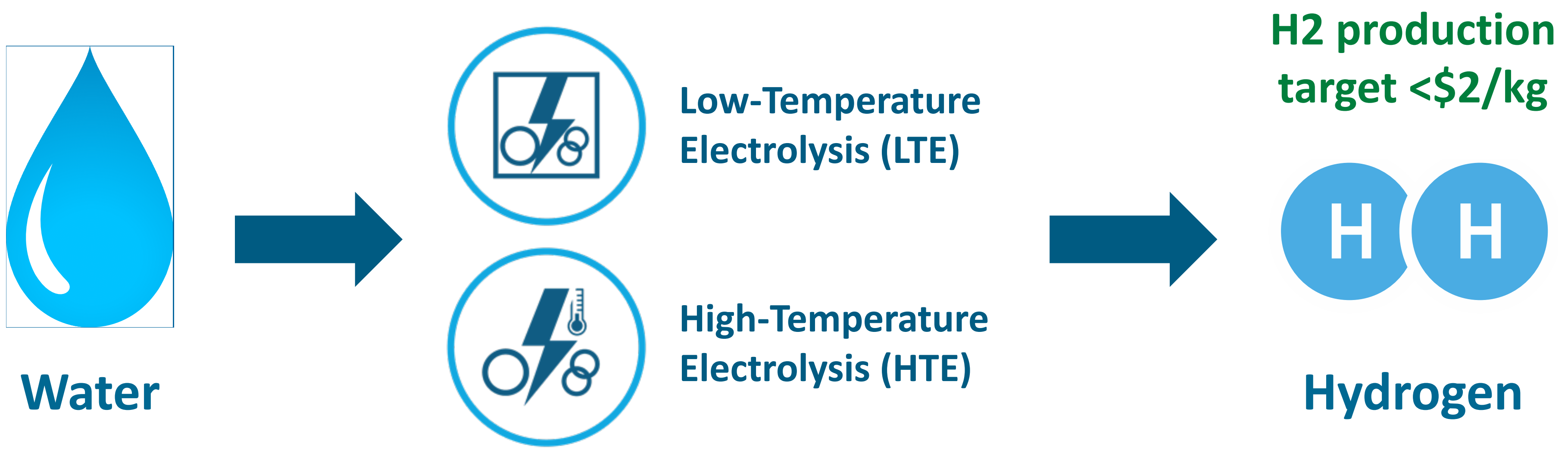
Goal: H2NEW will address components, materials integration, and manufacturing R&D to enable manufacturable electrolyzers that meet required cost, durability, and performance targets, simultaneously, in order to enable \$2/kg hydrogen.



H2NEW has a clear target of establishing and utilizing experimental, analytical, and modeling tools needed to provide the scientific understanding of electrolysis cell performance, cost, and durability tradeoffs of electrolysis systems under predicted future operating modes

Overview : H2NEW LTE Task 1: Durability and AST Development

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Timeline and Budget

- Start date (launch): October 1, 2020
- Awarded through September 30, 2025
- FY23 DOE funding: **$3.7M + 900K (overtarget)**
- Annual budget adjustments anticipated

Barriers/Targets

- Cost, Durability, Performance : Developing affordable, reliable, and efficient electrolyzers
- $2/kg green hydrogen production

Consortium Task Team

NREL NATIONAL RENEWABLE ENERGY LABORATORY · BERKELEY LAB · Los Alamos NATIONAL LABORATORY EST.1943 · Argonne NATIONAL LABORATORY · OAK RIDGE National Laboratory

Deputy Director:
Rangachary Mukundan (LBNL)

Task Liaisons:
Shaun Alia (NREL)
Siddharth Komini Babu (LANL)

Other lab leads:
Debbie Myers (ANL)
Haoran Yu (ORNL)

Partners:
Iryna Zenyuk (UCI)
Svitlana Pylypenko (Mines)
Shawn Litster (CMU)

Industrial partners as part of ASTWG
Nel Hydrogen, Plug Power, Cummins, De Nora, Electric Hydrogen, and Chemours

Relevance and Impact

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Technical Targets for PEM Electrolyzer Stacks and Systems [a,b]

CHARACTERISTIC	UNITS	2022 STATUS [C]	2026 TARGETS	ULTIMATE TARGETS
Stack				
Total Platinum Group Metal Content (both electrodes combined) [d]	mg/cm^2	3.0	0.5	0.125
	g/kW	0.8	0.1	0.03
Performance		2.0 A/cm2 @ 1.9 V/cell	3.0 A/cm2 @ 1.8 V/cell	3.0 A/cm2 @ 1.6 V/cell
Electrical Efficiency [e]	kWh/kg H_2 (% LHV)	51 (65%)	48 (69%)	43 (77%)
Average Degradation Rate [f]	mV/kh (%/1,000 h)	4.8 (0.25)	2.3 (0.13)	2.0 (0.13)
Lifetime [g]	Operation h	40,000	80,000	80,000
Capital Cost [h]	\$/kW	450	100	50
System				
Energy Efficiency	kWh/kg H_2 (% LHV)	55 (61%)	51 (65%)	46 (72%)
Uninstalled Capital Cost [h]	\$/kW	1,000	250	150
H_2 Production Cost [i]	\$/kg H_2	>3	2.00	1.00

Electrolyzer Stack Goals by 2026	
	LTE PEM
Total PGM content	**< 0.5 mg/cm^2**
Performance	**1.8 V/cell @ 3 A/cm^2**
Degradation Rate	**< 2.3 $\mu V/hr$**

- Task 1 durability activities specifically focus on the lifetime target
  - ✓ Primary focus of LTE efforts
  - ✓ Identification of stressors leading to degradation and subsequent accelerated stress test (AST) development
  - ✓ ***Ultimate goal is to mitigate degradation (<2.3 $\mu V/hr$) while simultaneously meeting efficiency (3.0 A/cm^2 @ 1.8V), lifetime (80,000 hours), and cost (Ir loading < 0.5 mg/cm^2) targets***

Approach : Durability and AST Development tasks

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Task 1: MEA Durability

Task 1a. Understanding and mitigating degradation

Subtask i. Cell aging studies (NREL, LANL, LBNL)

Subtask ii. Mitigation strategies (NREL, LANL, ANL)

Task 1b. Ex situ studies of components and interfaces

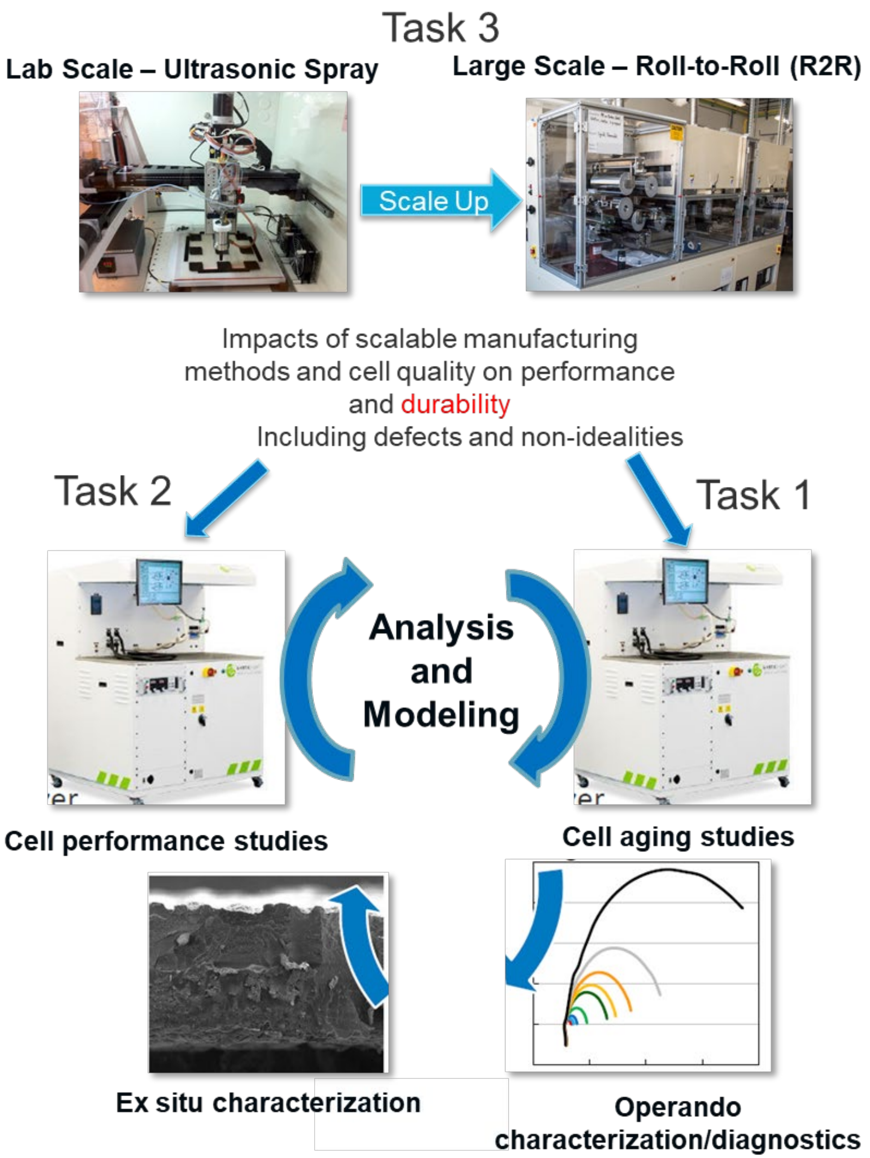
Subtask i. Anode electrocatalyst degradation (ANL, ORNL, NREL, LBNL)

Subtask ii. Membrane degradation (LBNL, NREL, LANL)

Subtask iii. Catalyst-ionomer interface degradation (LBNL)

Subtask iv. Bipolar Plates and Coatings (ANL)

Task 1c. AST development (LANL, NREL, LBNL)



Approach: FY23 Quarterly Progress Measures and Annual Milestone

Milestone Name/Description	Due Date	Type	Status
Conduct degradation test at NREL on rainbow stack assembled at NEL with at least 4 MEA variations. Two-dimensional map of the anode catalyst, PTL, and BPP atomic structure and oxidation state for select cells from rainbow stack. (NREL, ORNL, ANL)	6/30/23	QPM	On-going (See Slide 21)
Quantify performance losses from Na and Ca contamination for FuGeMEA cells and degree of recovery from DI water rinse and cell operation coordinated with modeling efforts. (LANL, LBNL, NREL, ANL)	6/30/23	QPM	Completed (see Slide #19)
Complete dissolution studies and identical location TEM study of Umicore IrO_2/TiO_2 Elyst IR75 0480 (core shell catalyst) or other catalyst studied in device level performance and durability sub-tasks (ANL, ORNL, LBNL)	6/30/23	QPM	On-going (See slide 7)
Complete durability testing under steady state operation and dynamic operation over 3 voltage windows. Validate the IrO2 dissolution model by comparing OER kinetic over potential increase observed in cell-level AST experiments to those predicted from dissolution-based models. Propose and validate at least one mitigation strategy to improve the durability of electrolysis cells under dynamic operation (NREL, LANL, ANL, LBNL).	9/30/23	Annual Milestone	On-going (See Slide 10, 11 14 - 17)

Time-resolved Ir dissolution from Alfa Aesar IrO_x: Effect of lower potential limit of cycling

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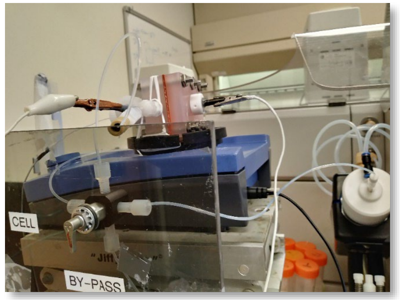
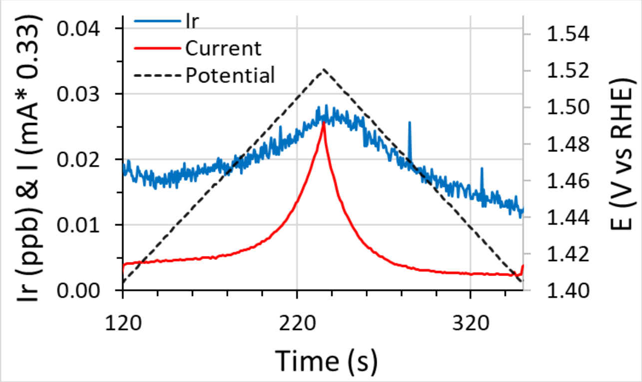
1.523 V Upper Potential Limit (equivalent to 2V iR-corrected in FuGeMEA); 1 mV/s

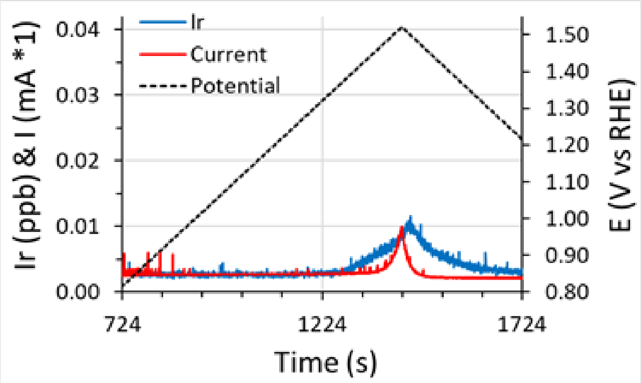
Electrochemical flow cell coupled with ICP-MS. 0.1 M $HClO_4$ electrolyte.



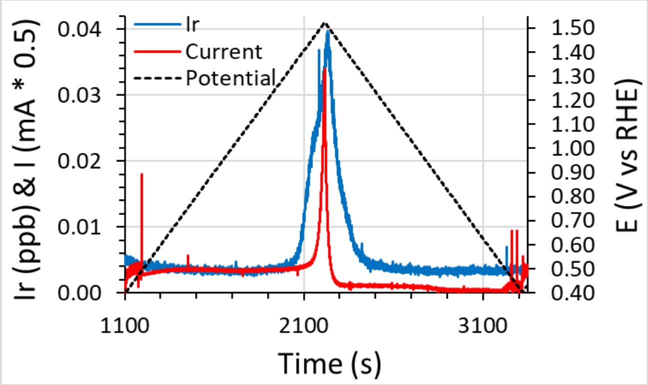
Lower Limit: 1.4 V

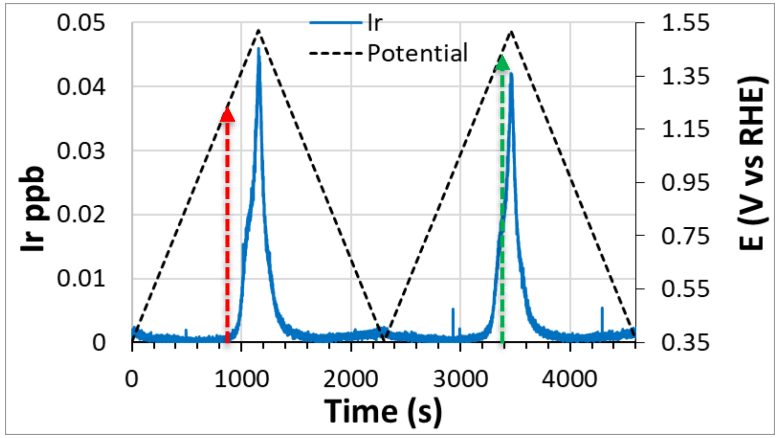


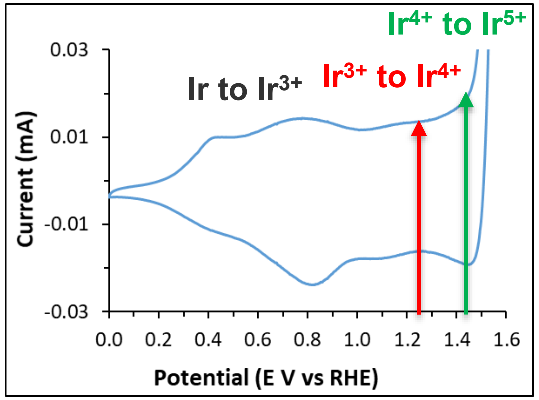
0.8 V



0.4 V

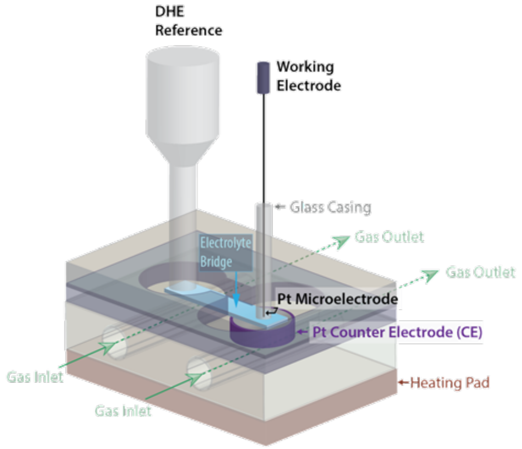


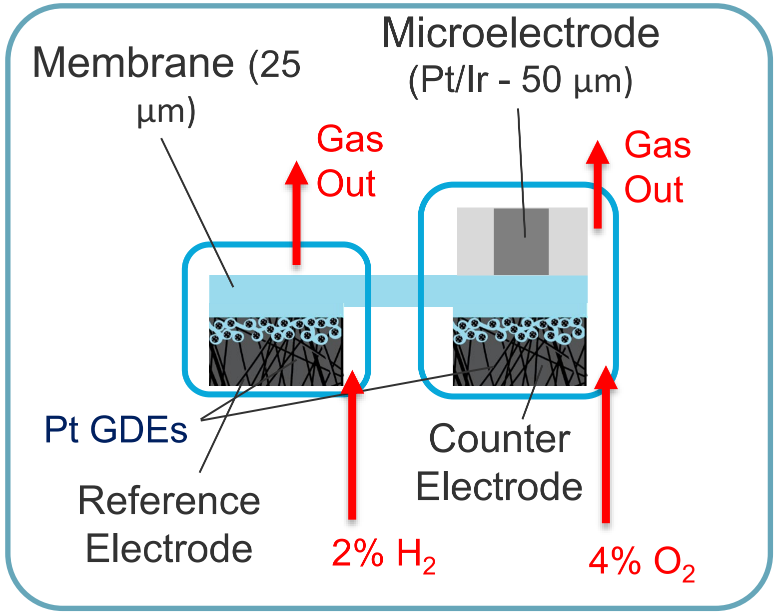




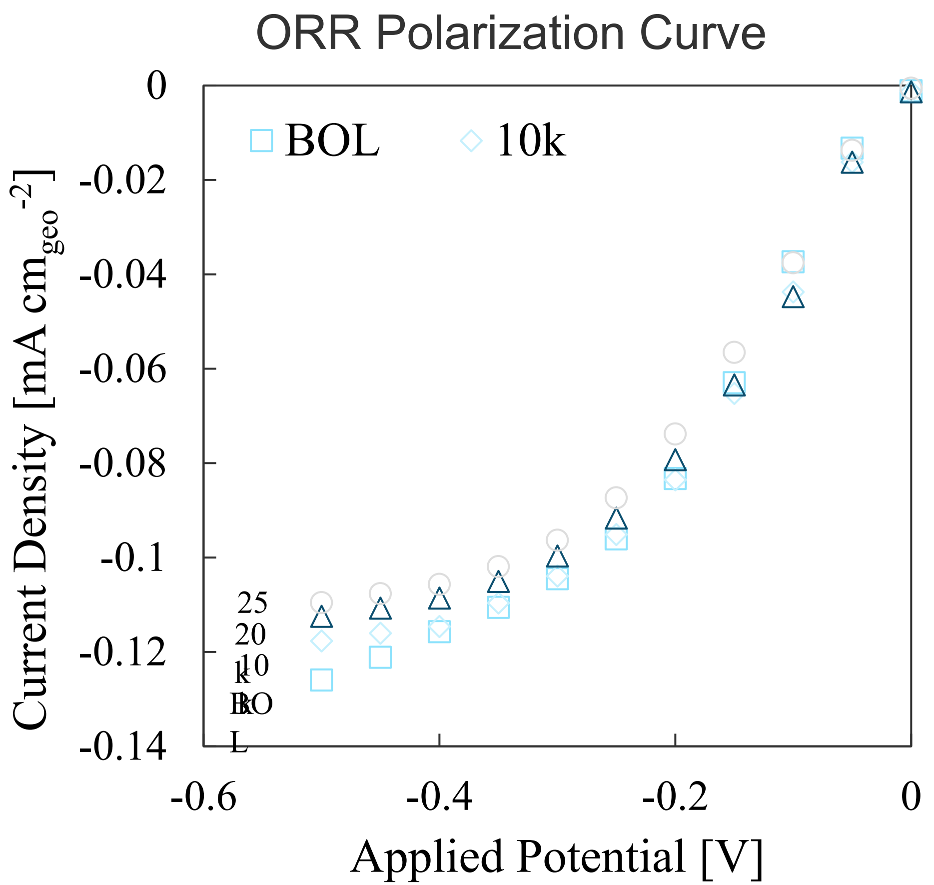
- Alfa Aesar IrO_x is stable at potentials between 0.35 V and ~1.25 V
- Onset of Ir dissolution is at 1.25 V, coinciding with oxidation of Ir^{3+} to Ir^{4+} (determined using in situ X-ray absorption spectroscopy)
- Sharp increase in dissolution at >1.45 V coinciding with onset of OER and oxidation of Ir^{4+} to Ir^{5+}
- Ir dissolution **during positive potential sweep** decreases with decreasing lower limit of sweep to 0.8 V and increases when lower limit is 0.4 V
- Indicates that increased degradation of Ir during start up-shut down cycling is not caused by dissolution of Ir metal, but by increased dissolution during Ir oxidation

Micro electrode durability studies



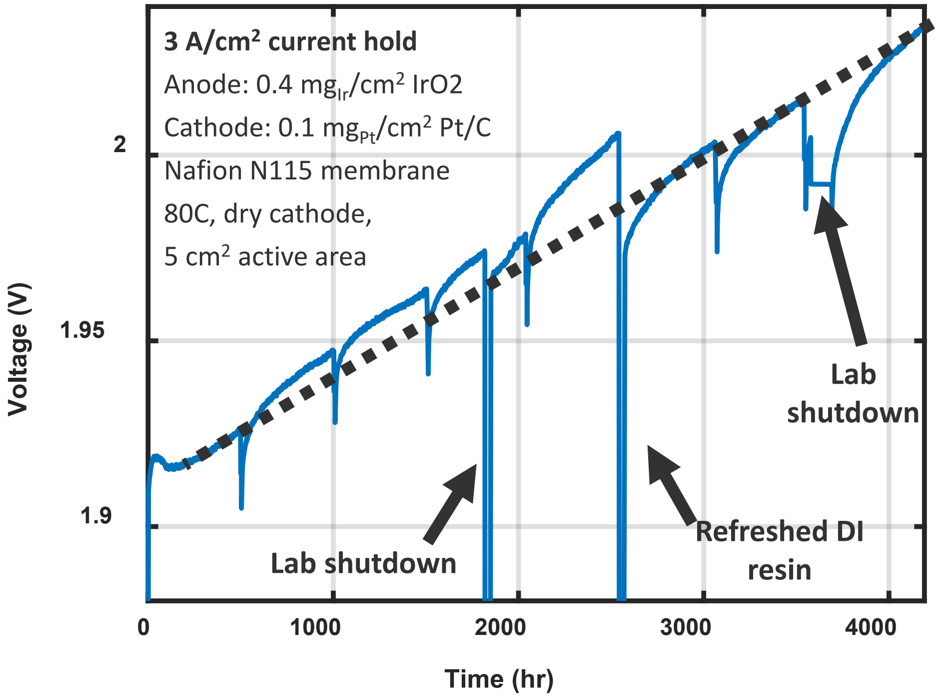


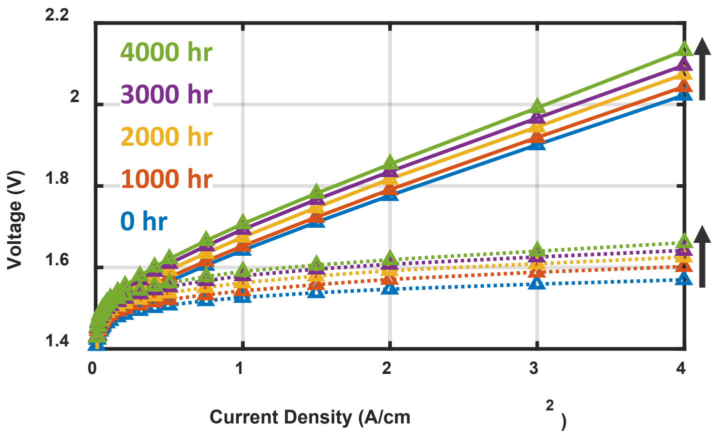
Grace Anderson



- Durability measurements initiated
- Pt microelectrode studied for ORR
- Slight decrease in kinetics observed with cycling but no change in ECSA as expected for the microelectrode
- Ir electrode studies initiated for OER. Changes in current correlate with bubble removal
- Extend to micro cavity electrodes

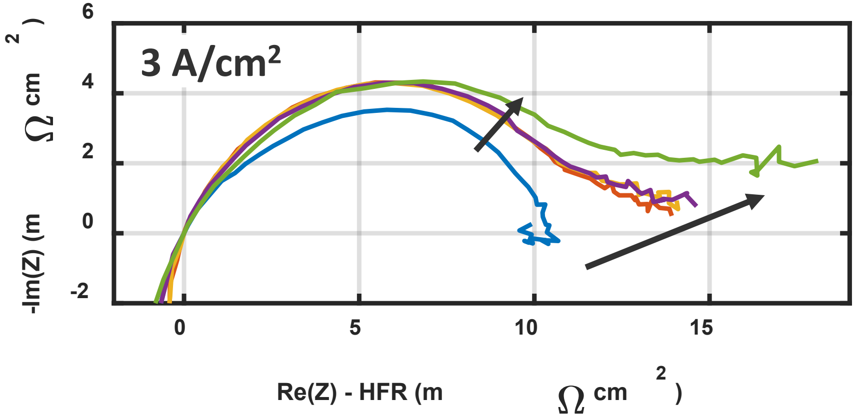
Long term Durability Test (4000 hour current hold)

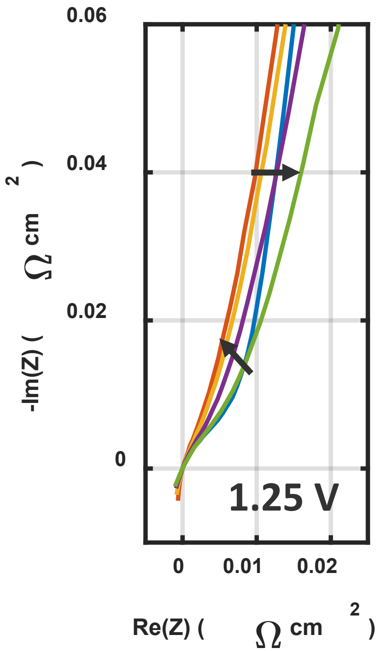




Completed 4,000 hr durability test of FuGeMEA cell:

- Benchmarking decay rates:
  - ~28 µV / hr at 3 A/cm²
    - ~ 7 µV / hr ohmic, 21 $\mu V_{HFR\text{-}free}$ / hr
    - Slower decay of ~ 11 $\mu V_{HFR\text{-}free}$ / hr at 0.1 A/cm²
- Understanding mechanisms of steady-state degradation:
  - Catalyst activity or surface area loss
  - Increasing catalyst layer resistance
  - Possible cation contamination

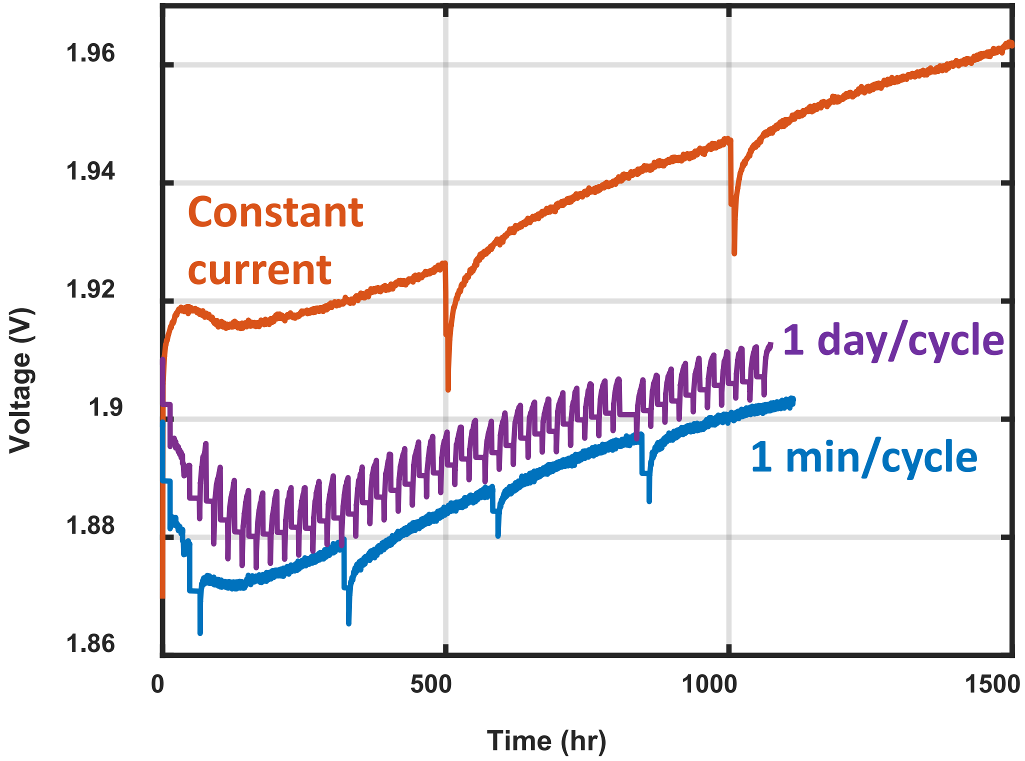




Post-mortem characterization underway to inform mechanistic understanding.

Ongoing Long-term Durability Testing to Inform TEA and ASTs

Long-term (1000+ hr) durability testing is ongoing focused on comparing decay rates and degradation mechanisms for different field-relevant and AST conditions to inform TEA and AST development. (See slide 10 P196d)



Completed and ongoing tests:

- Constant 3 A/cm^2 current hold
- 1 min/cycle, 1.4 V – 3 A/cm2
  - Representative AST cycle
- 1 day/cycle, 1.4 V – 3 A/cm2
  - Simplified renewable on/idle profile

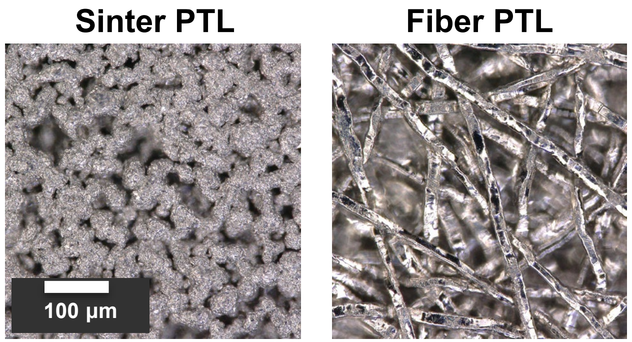
Planned future tests:

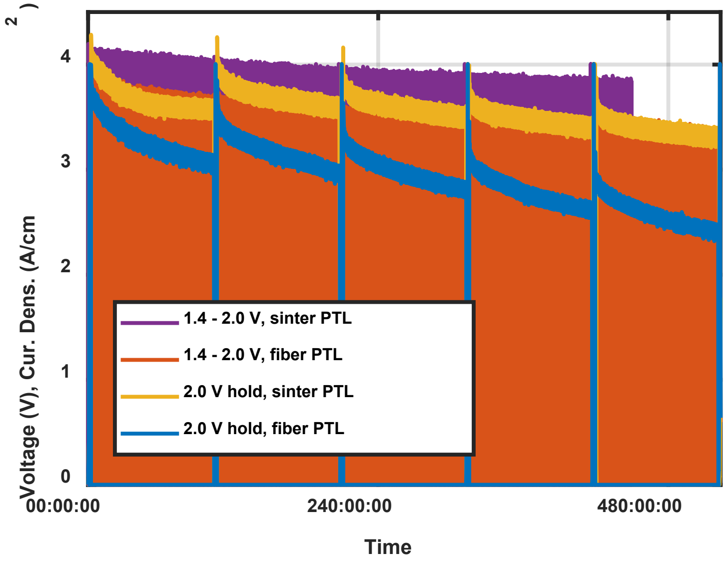
- Ramping at field-relevant rates (e.g. 1-4 hr ramp for 1 day/cycle)
- Start/Stop cycling incorporating relevant stressors.

Voltage Window Durability Testing and PTL/CL Interactions

Testing of anode durability for voltage cycling in different windows is ongoing for FY23 Q4 Milestone.

Results will inform fundamental degradation mechanisms and durability impacts of turndown ratio for dynamic operation.

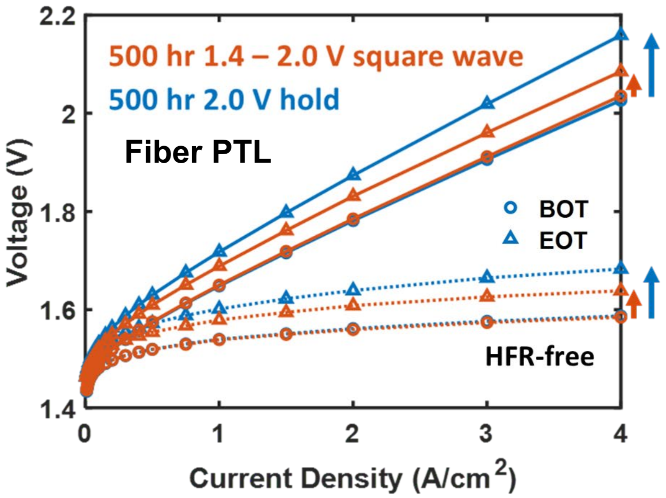


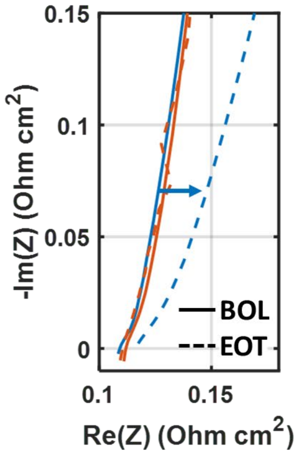


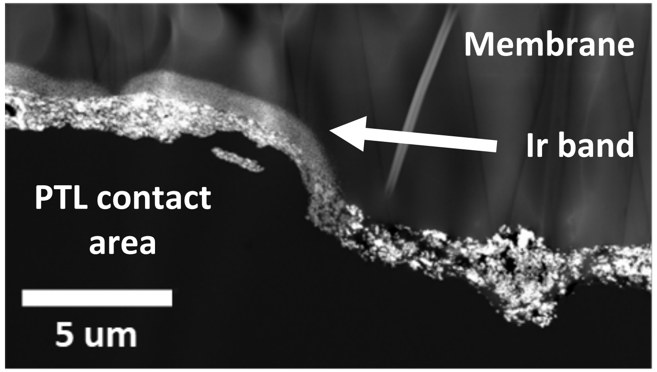
Surprising interaction with anode PTL observed:

- Fast degradation with fiber PTL under voltage hold conditions.
- Faster degradation for fiber PTL under constant voltage than voltage cycle, with growing anode catalyst layer resistance.
- Sinter PTL appears more stable under voltage hold conditions.

May be related to in-plane catalyst layer conduction effects found previously.







Diagnostics for Cell Depolarization Mechanisms and Start/Stop Durability

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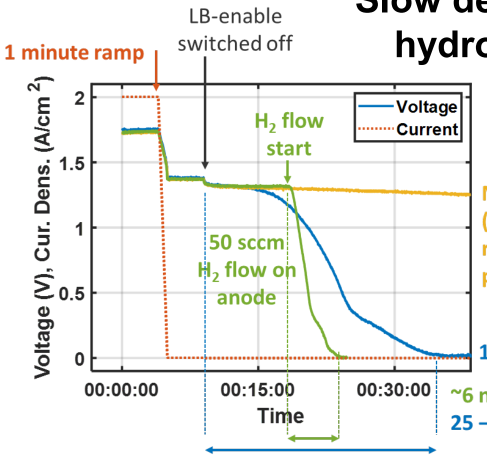
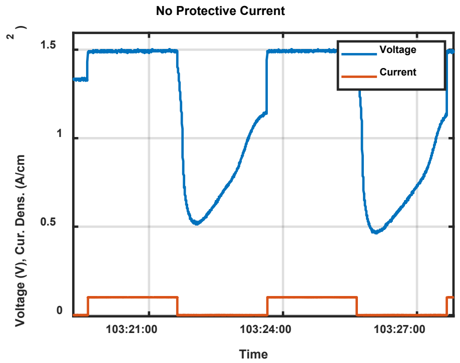
Different Depolarization Behavior Depending on Shutdown Conditions

Slow depolarization (minutes) caused by hydrogen interaction with the anode



Important shutdown stressor from crossover with cathode backpressure

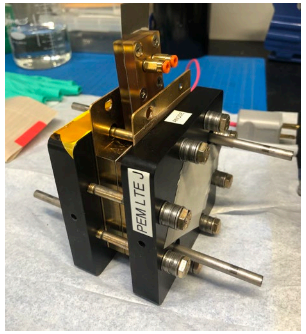
Fast depolarization (seconds) caused by rapid current stepping (possible capacitive effect)

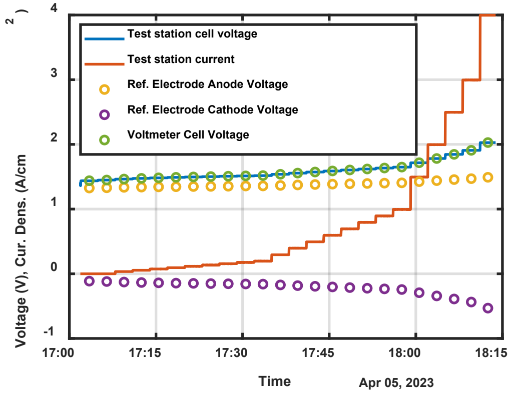


Mechanisms must be understood and controlled to design ASTs and mitigation strategies.

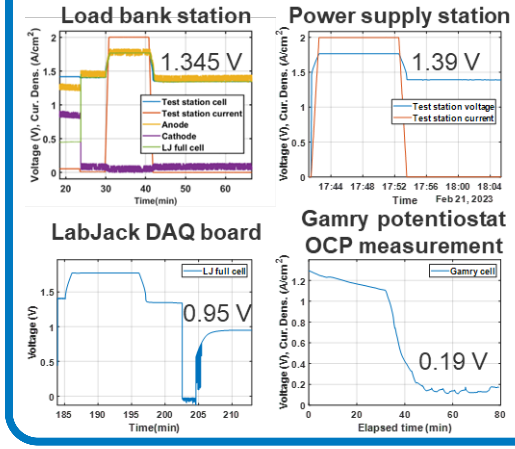
Cell voltage change in shutdown can come from anode or cathode independently

Monitoring anode and cathode states with reference electrode





Measurement of anode and cathode potentials to identify depolarization mechanism and stressors during shutdown.



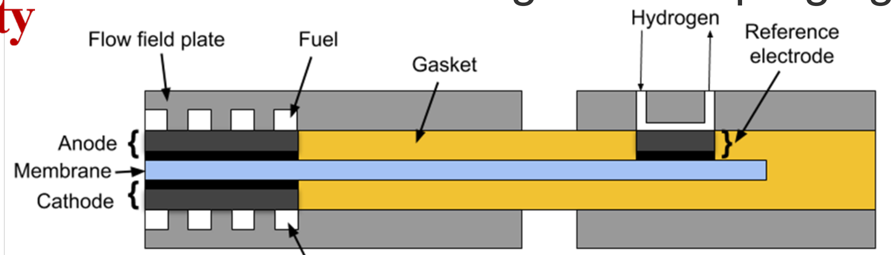
Experimental Challenge Identified:
Stray currents from test station, potentiostat, or voltage measurement devices can influence shutdown conditions and reference electrode measurements.

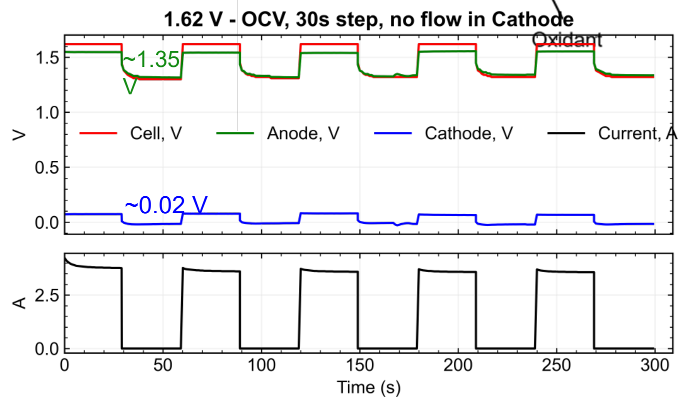
Effort ongoing to identify accurate, reproducible techniques for shutdown diagnostics and start/stop durability testing.

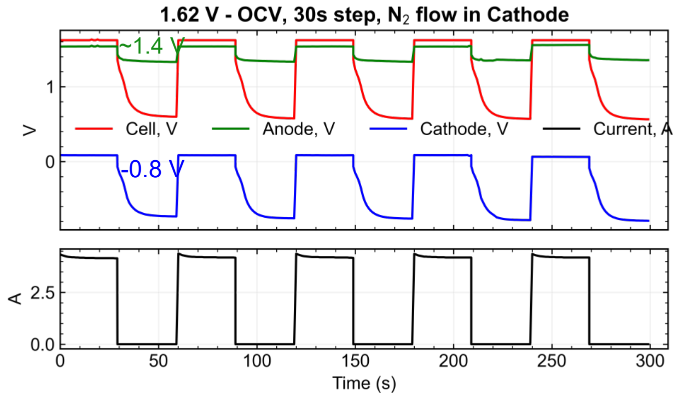
Diagnostics for Cell Depolarization Mechanisms and Start/Stop Durability

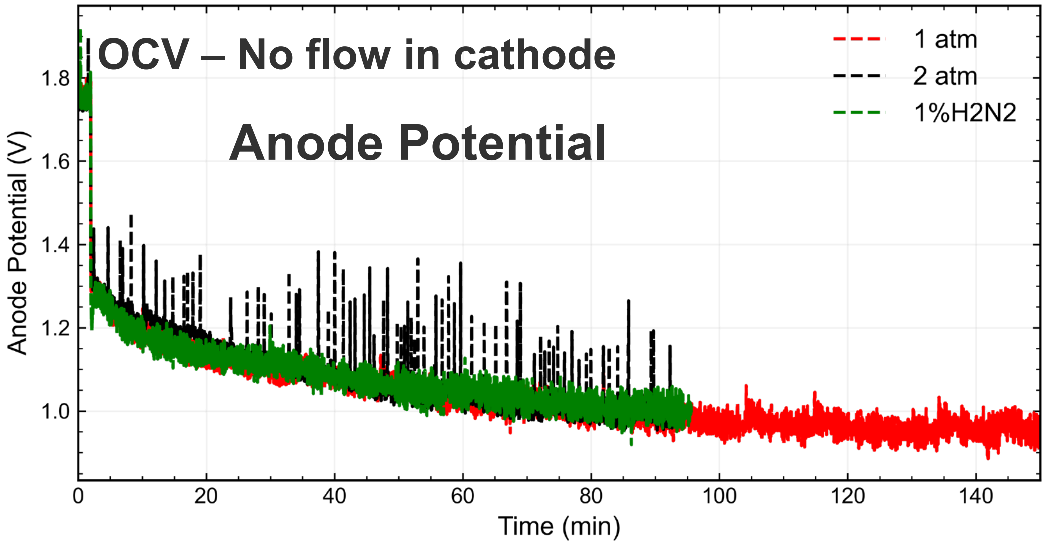
Carnegie Mellon University

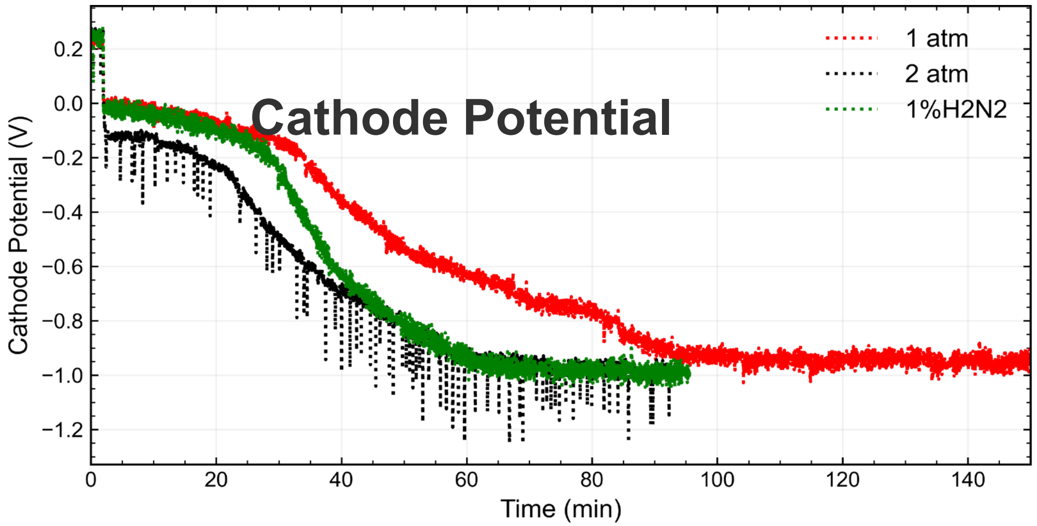
Reference electrode for cathode potential measurement during cathode purging [1]







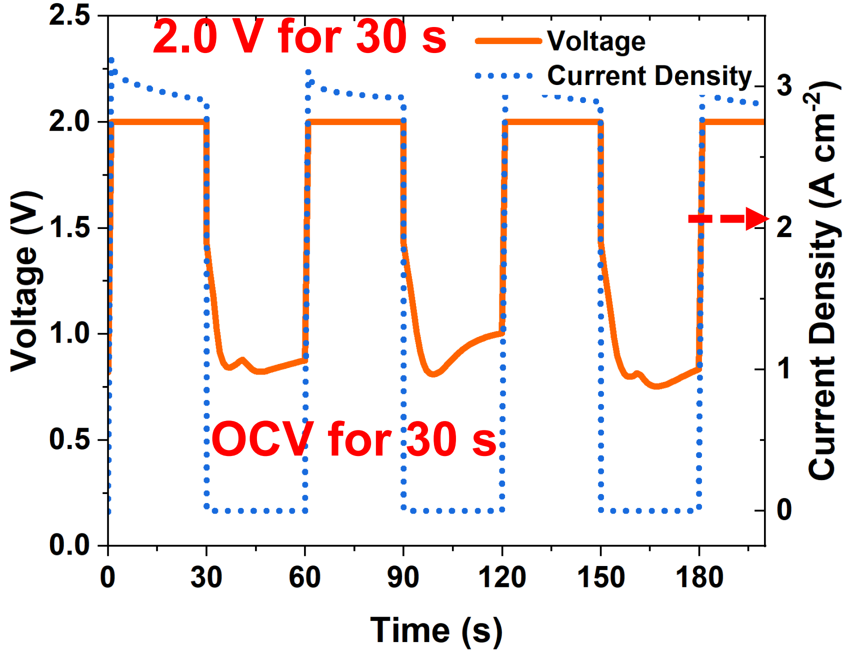


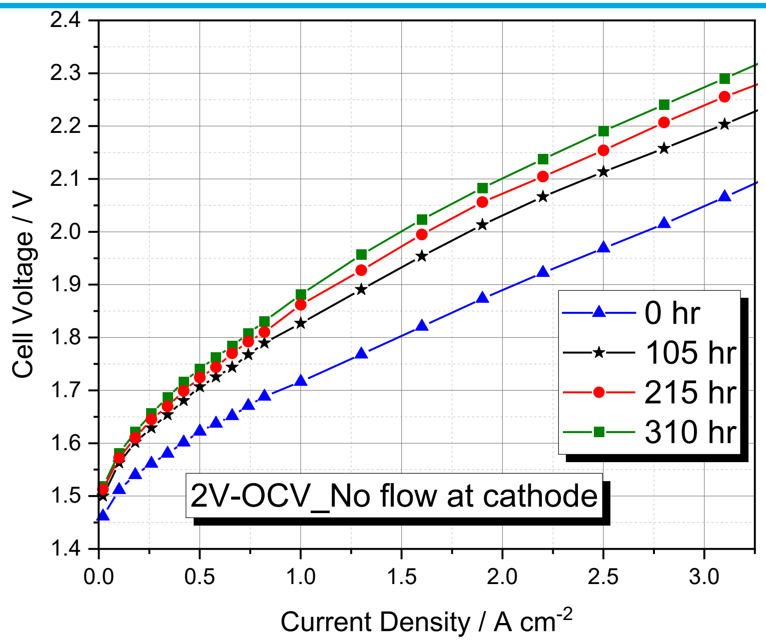


- N_2 purging the cathode increases cell durability by increasing the anode potential and decreasing the cathode potential enabling a more stable environment for both electrodes' catalysts.

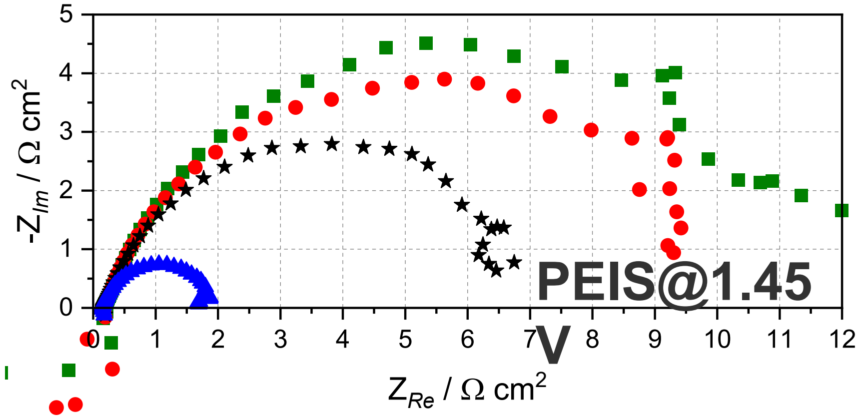
[1] Abdelrahman, M. E. et al. Electrochimica Acta 416 (2022): 140262.

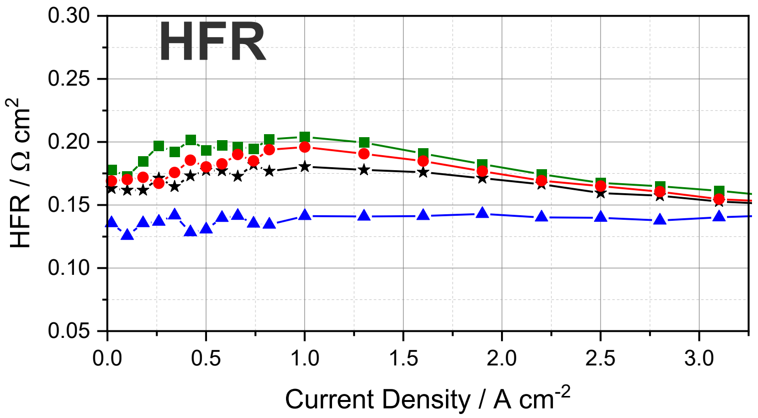
Degradation behavior during ON (2V) off (OCV) cycle





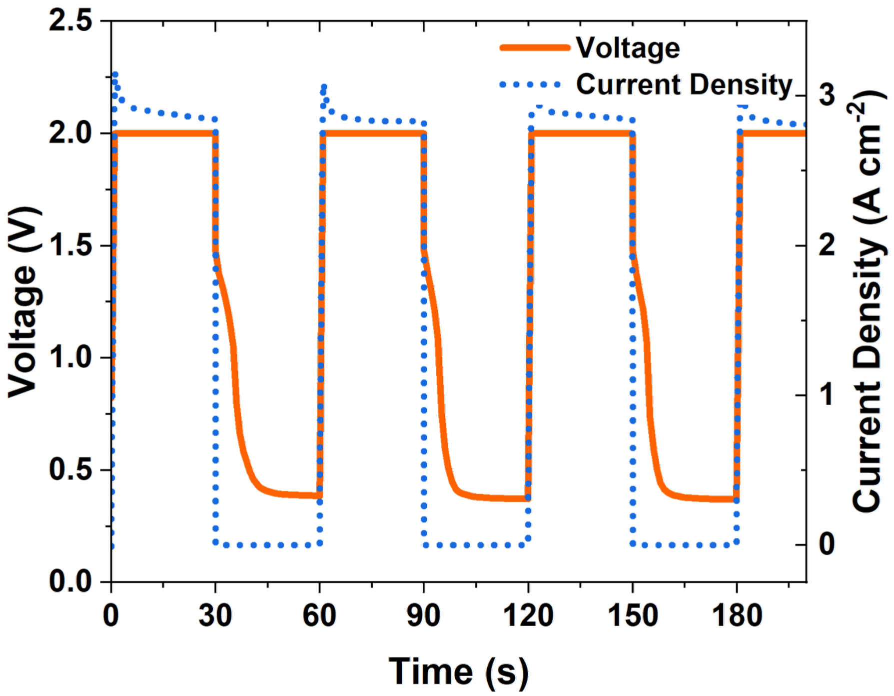
- Performance loss after 300-hr
  - Catalytic activity
  - HFR



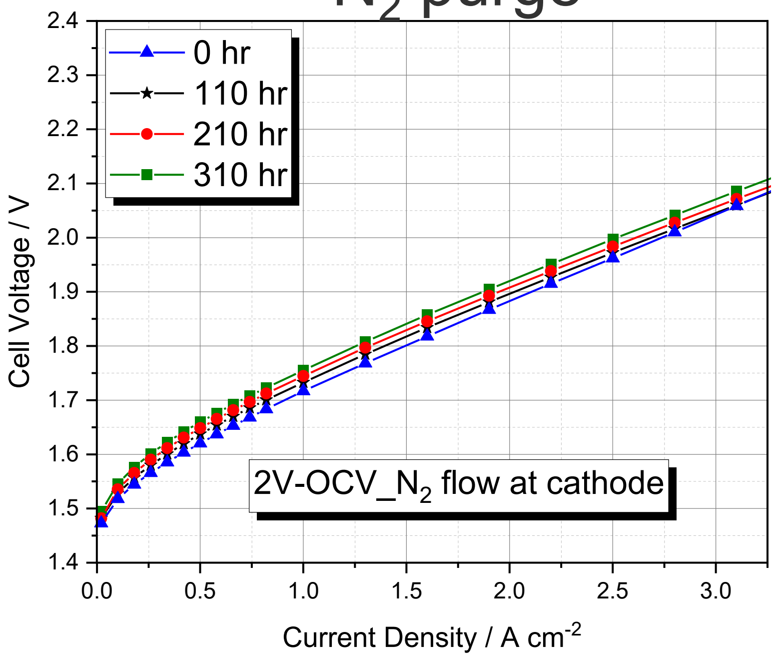


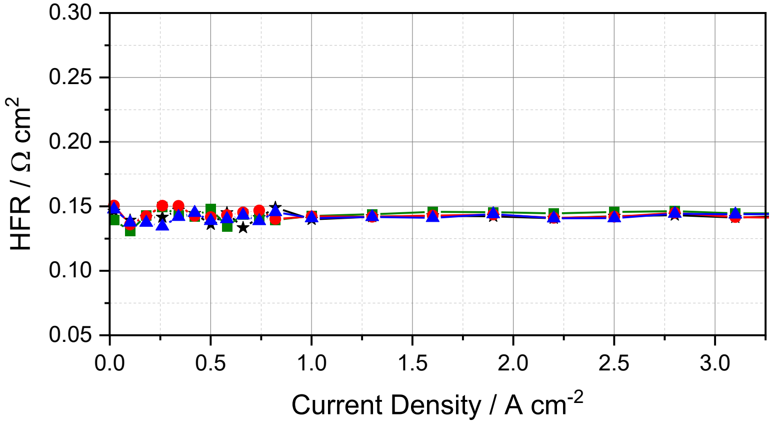
Cell Temperature: 80 °C; Flow rate: 50 ml min^{-1}; Active area: 25 cm^2; Anode: 0.1 mg cm^{-2} IrO_2 (Alfa Aesar) ; Cathode: 0.1 mg cm^{-2} Pt/C; PTL: 2GDL10

Effect of purging the cathode during ON (2V) off (OCV) cycle

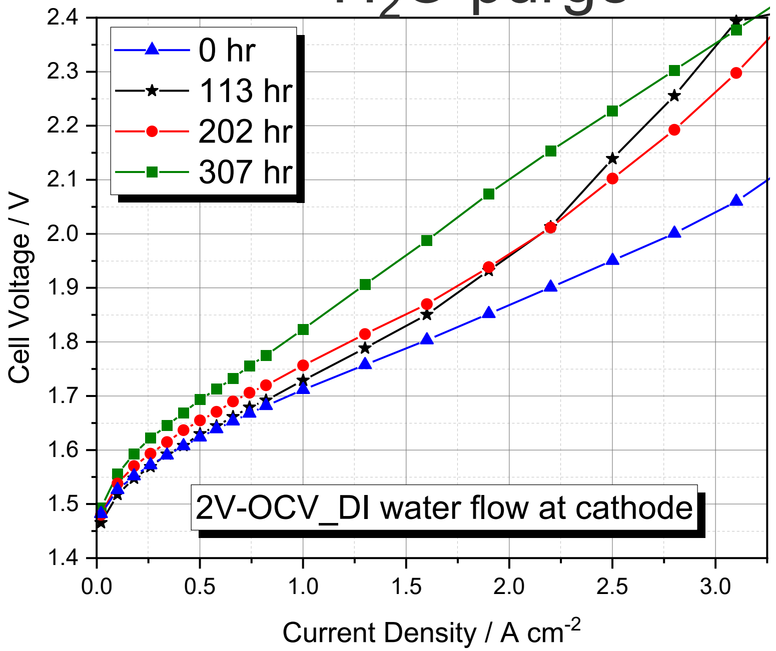


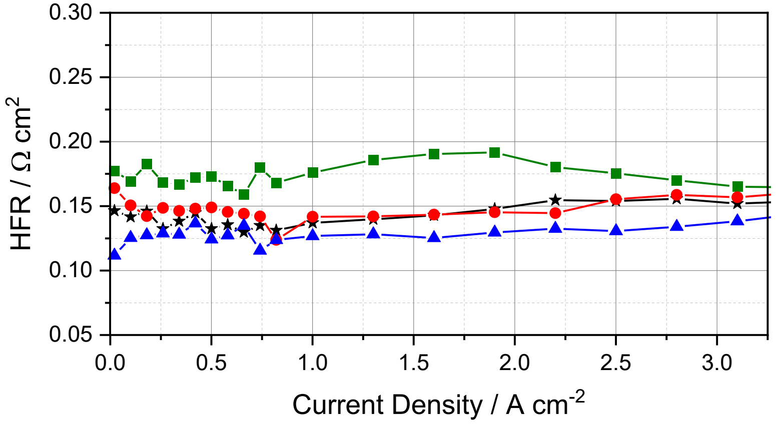
N_2 purge





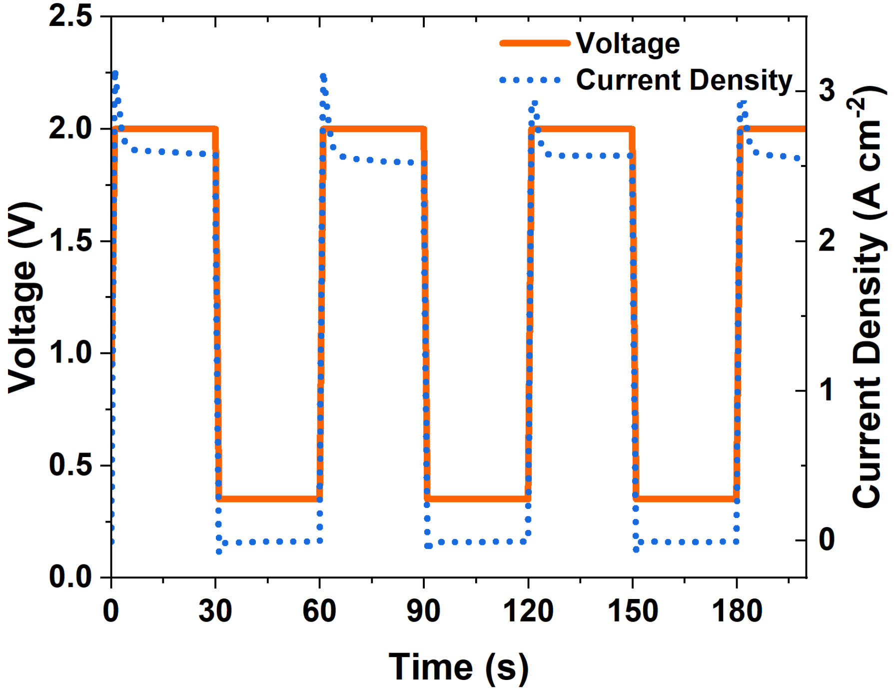
H_2O purge

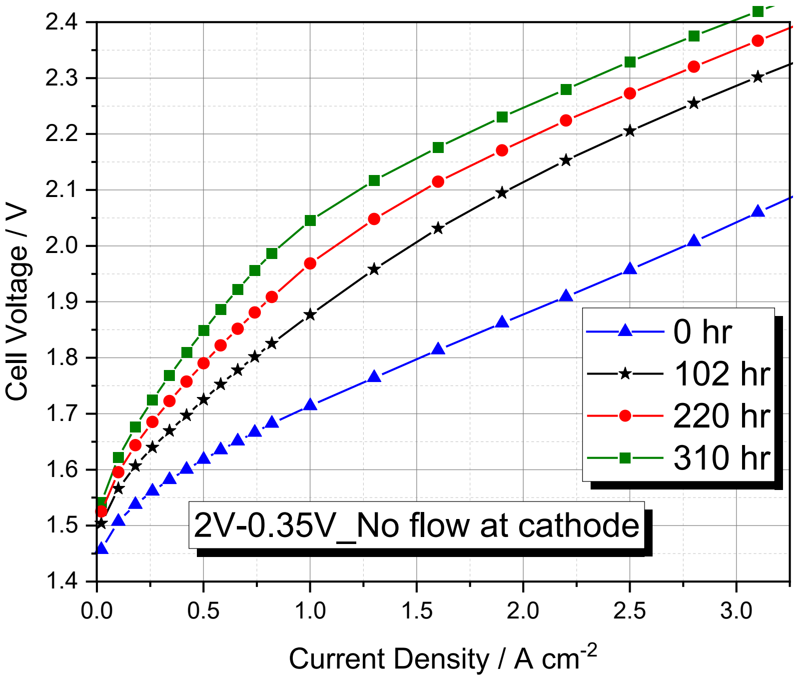


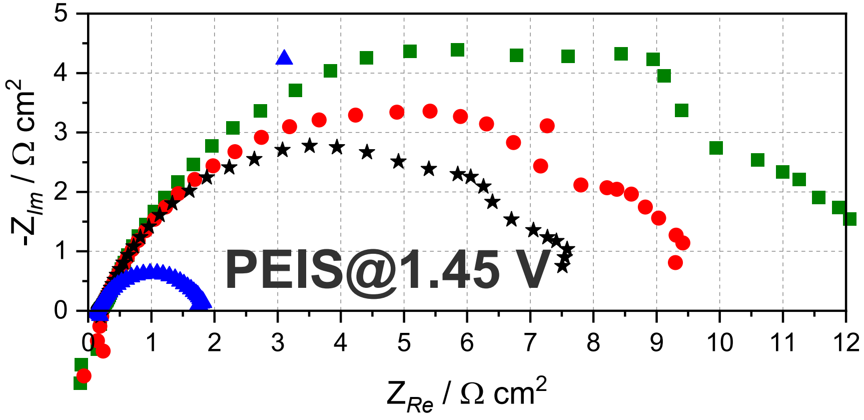


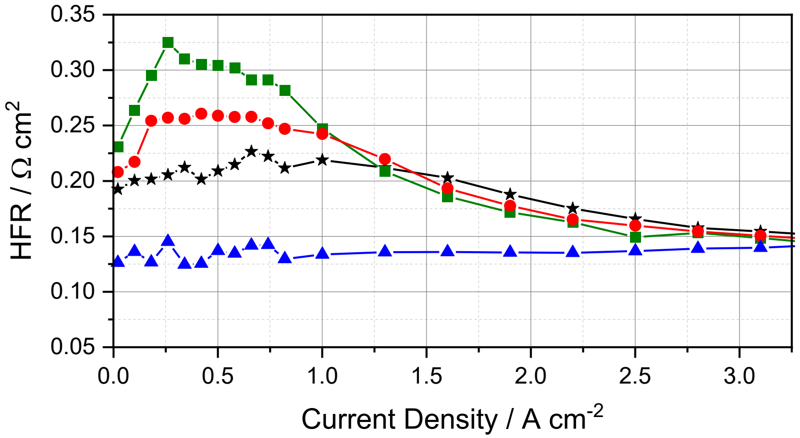
Cell Temperature: 80 °C; Flow rate: 50 ml min^{-1}; Active area: 25 cm^2; Anode: 0.1 mg cm^{-2} IrO_2 (Alfa Aesar) ; Cathode: 0.1 mg cm^{-2} Pt/C; PTL: 2GDL10

Forcing the anode potential below Ir redox potential









- Significant loss in performance and dual slope in polarization curve observed.

Cell Temperature: 80 °C; Flow rate: 50 ml min^{-1}; Active area: 25 cm^2; Anode: 0.1 mg cm^{-2} IrO_2 (Alfa Aesar) ; Cathode: 0.1 mg cm^{-2} Pt/C; PTL: 2GDL10

Performance recovery by acid washing

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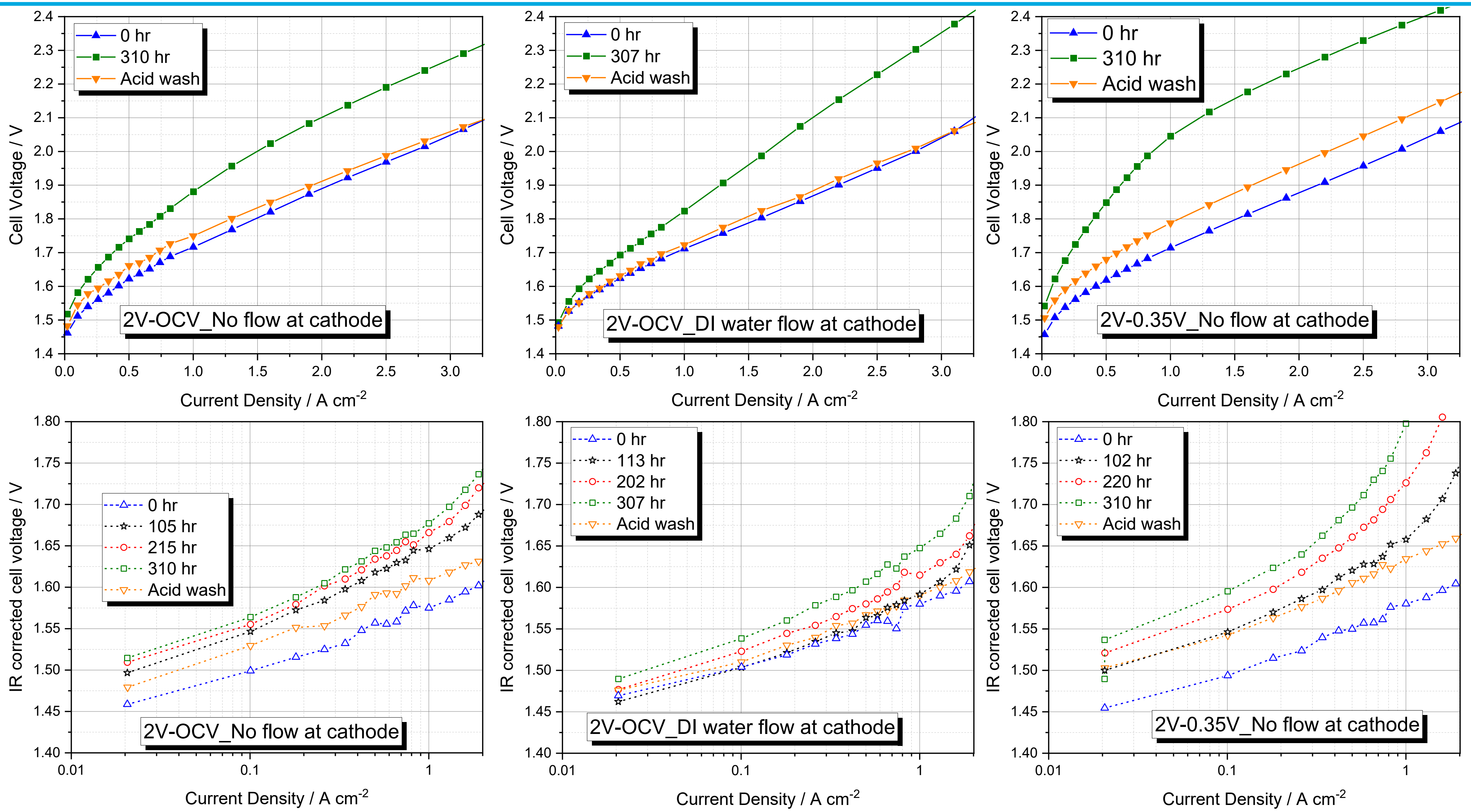
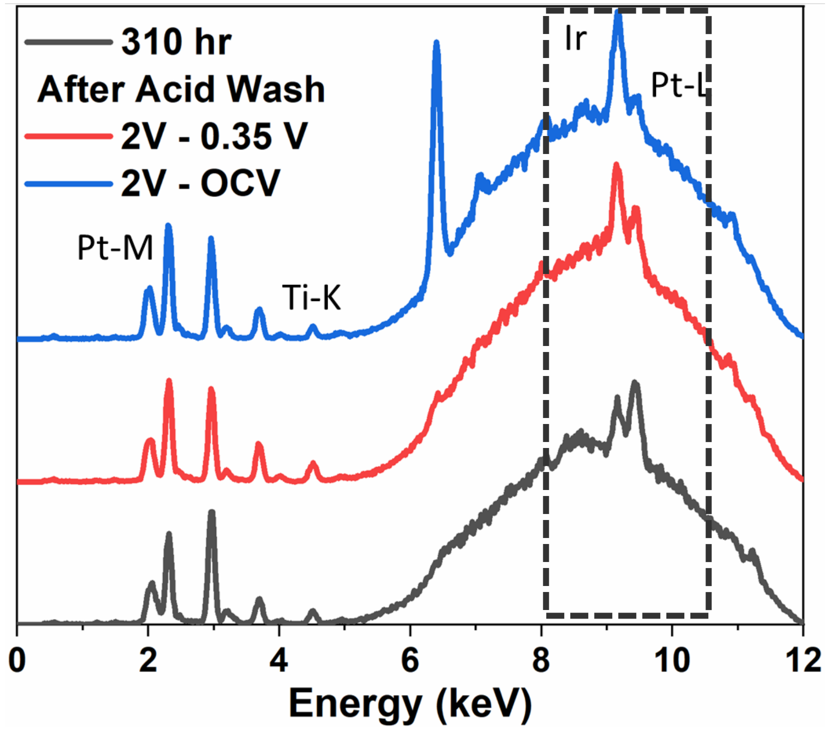


- Acid washing: soaking the MEA in 0.5 M H_2SO_4 overnight
- Performance recoverability after acid washing :
  - Larger unrecoverable performance loss found in the no flow MEA
- What is the unrecoverable performance loss?

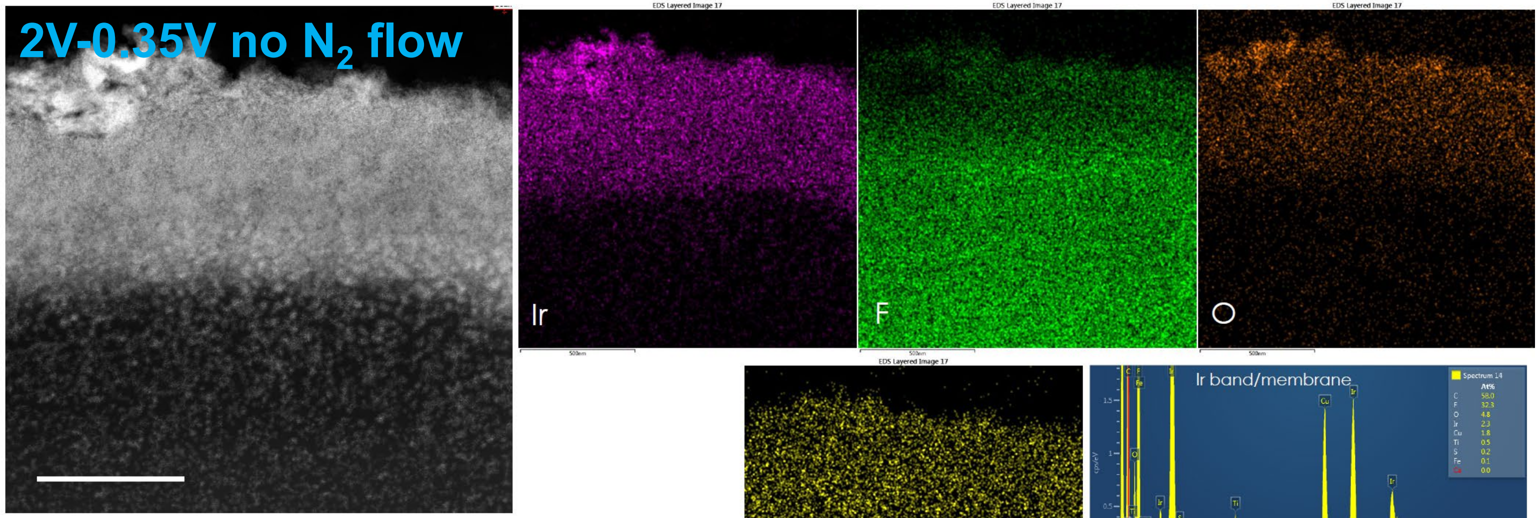
Cell Temperature: 80 °C; Flow rate: 50 ccm; Active area: 25 cm^2; Anode: 0.1 mg cm^{-2} IrO_2 (Alfa Aesar) ; Cathode: 0.1 mg cm^{-2} Pt/C; PTL: 2GDL10

Recoverable and Unrecoverable Losses

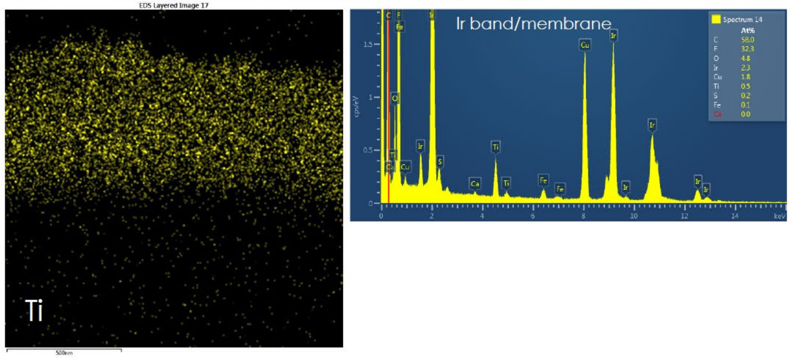
XRF on tested MEAs



Anode EDS analysis: More degradation



Ti observed in Ir band and membrane.



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- ➢Loss in Pt observed in PTL after 310-hr AST.
- ➢Acid wash removes Pt/Ir in the membrane, which caused the recoverable performance loss.
- ➢The Pt in the anode catalyst layer comes from the PTL, resulting in the unrecoverable performance loss.

Performance Losses and Recovery from Cation Contaminants

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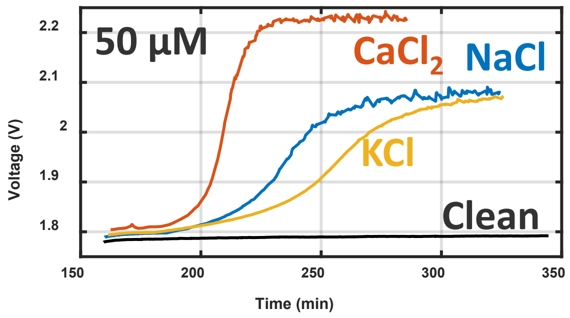
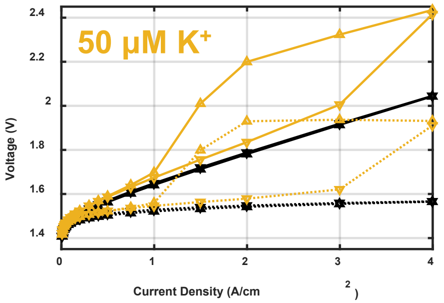
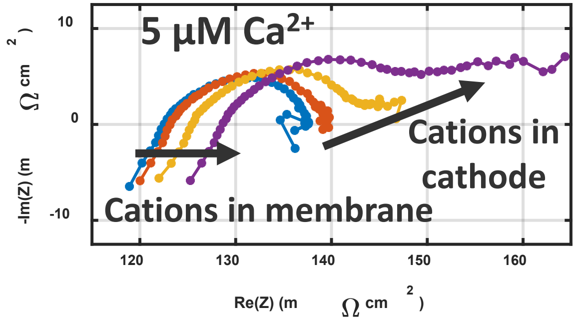
FY23 Q3 Milestone: Completed comparison of performance impacts from Na, Ca, and K cation contaminants in water feed at concentrations from ASTM Type II to tap water.

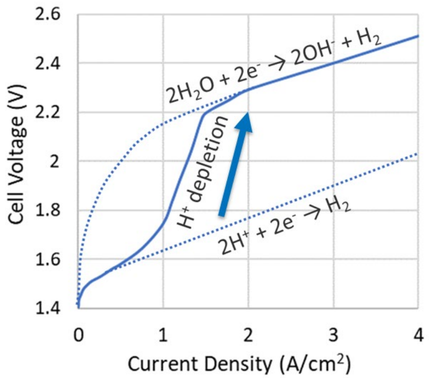
Performance losses and mechanisms

Identified diagnostic signatures and voltage loss mechanisms





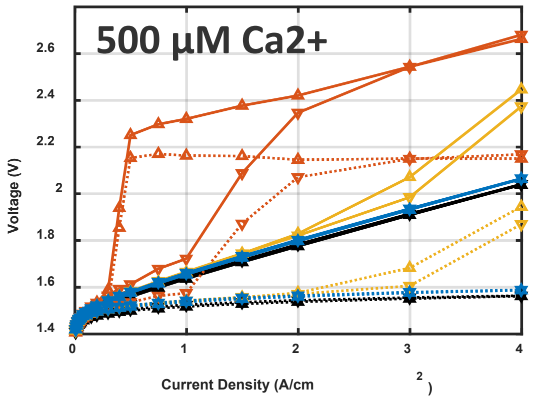


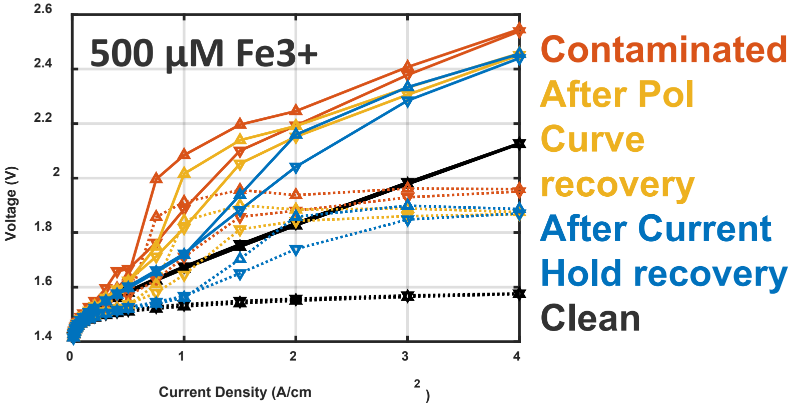


Cell recovery after contamination

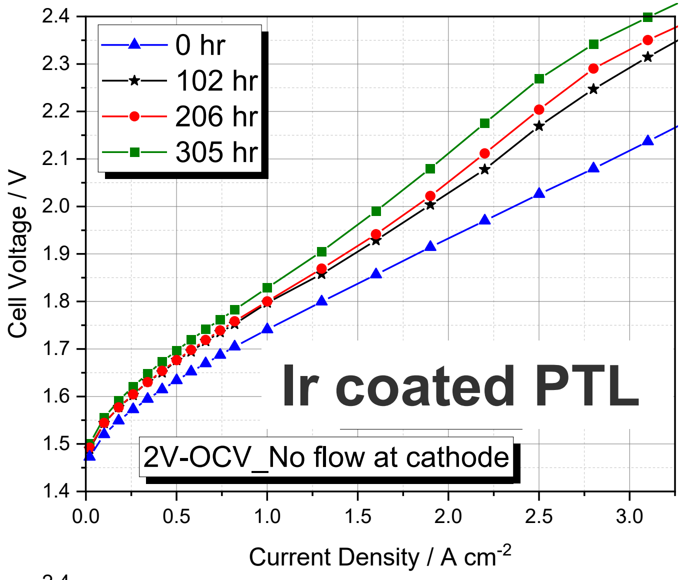
Demonstrated high-current recovery mechanism that is effective for Na and Ca, but less effective for Fe.

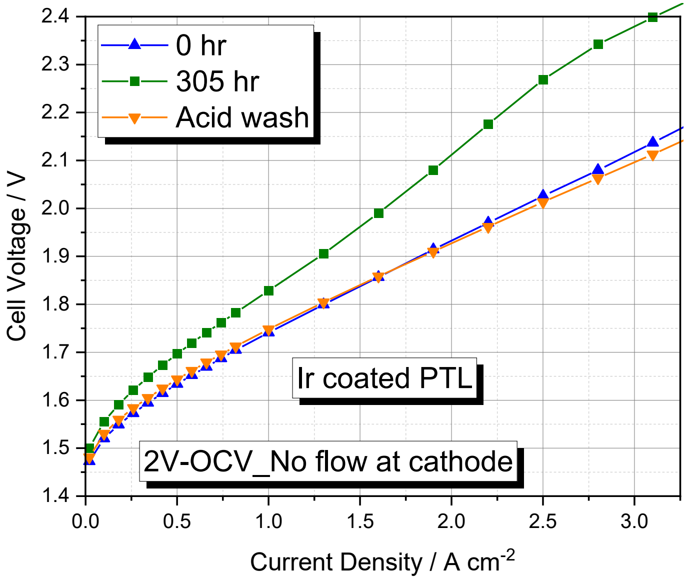
Coordinating with modelling efforts to understand contaminant dynamics and recovery.

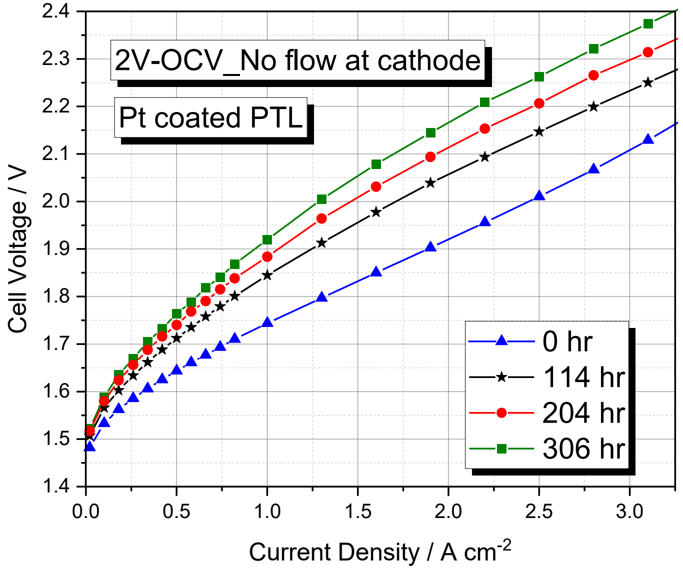


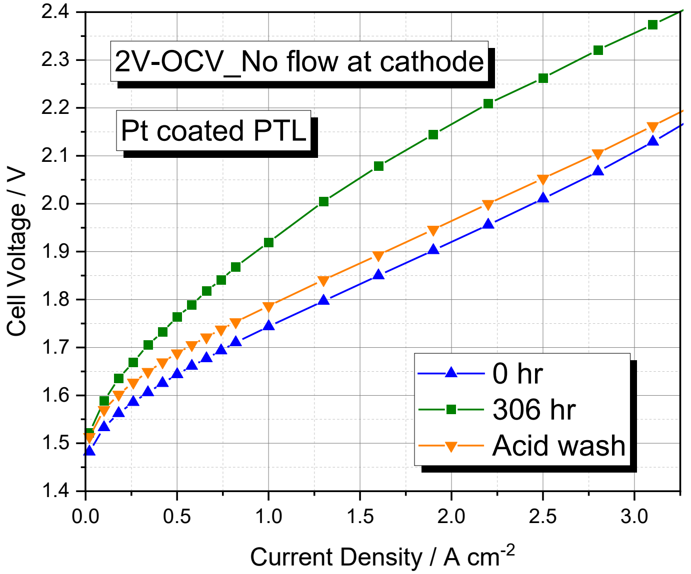


Mitigation Strategies : Effect of PGM coating on the PTLs



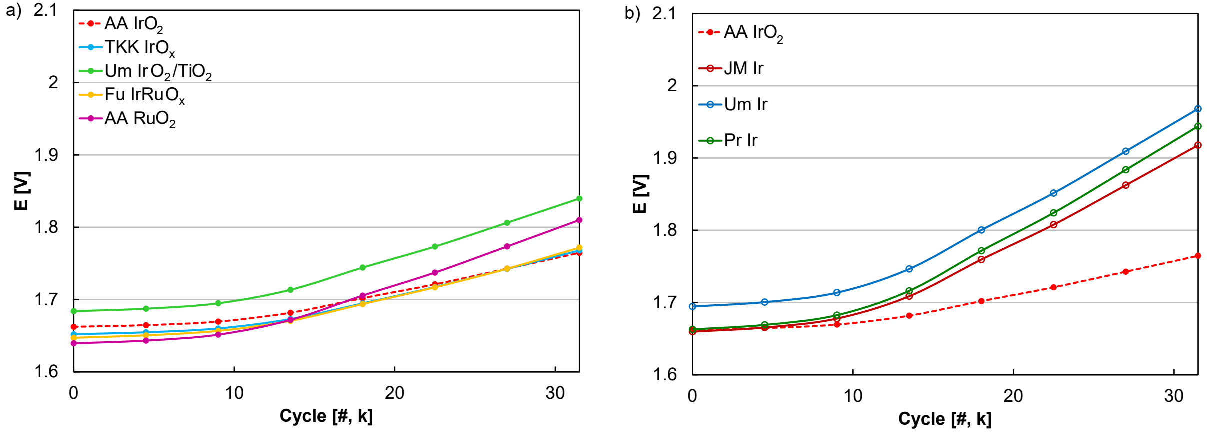


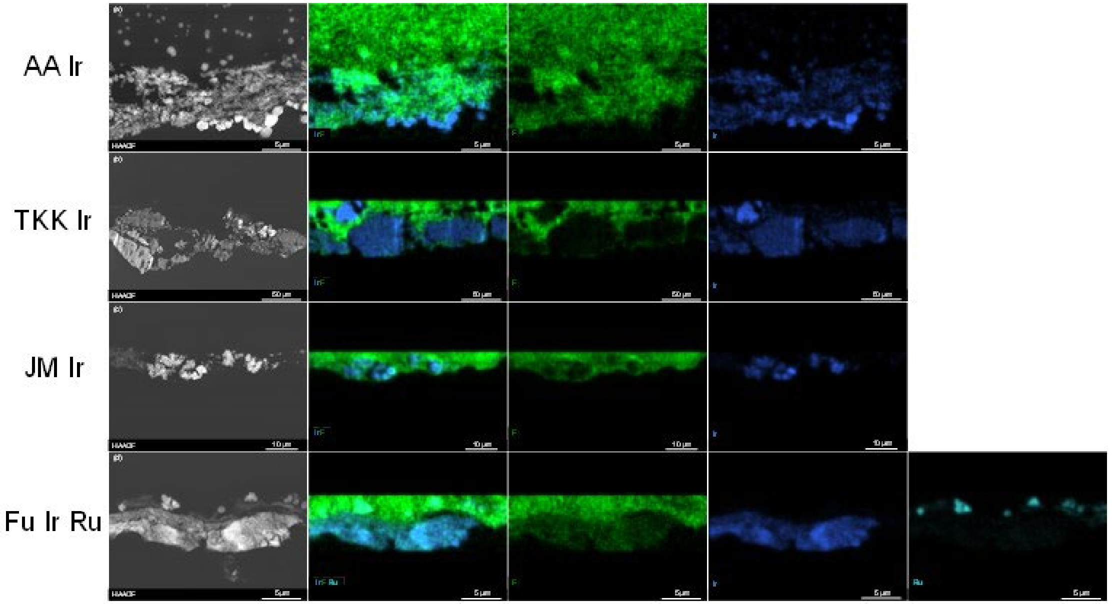




- The comparison of the HFR-free performance shows the MEA with Ir-PTL has less catalytic activity loss than the MEA with Pt-PTL;
- HFR increasing for both MEAs

Loss Mitigation through Materials and Catalyst Layer Integration





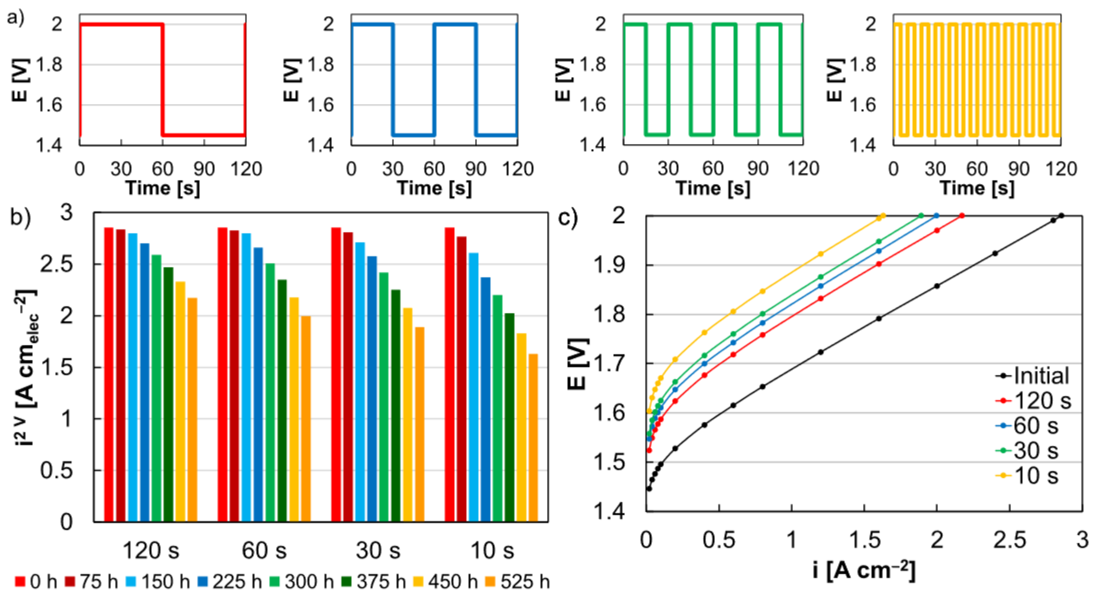
- Commercial catalysts containing Ir, Ru
  - Higher loss rates for with high metal, Ru content
  - Correspond to larger catalyst layer changes: catalyst mobility and catalyst/ionomer segregation
- Additives
  - Site-access improvement through pore formers, higher performance initially and following durability testing
  - Catalyst layer conductivity/stability challenges in supports
- Future work: stack testing increasing throughput and capability bandwidth

Side view of the short stack testing platform at NREL. This highly automated system can monitor BoP and stack performance during stack durability testing.

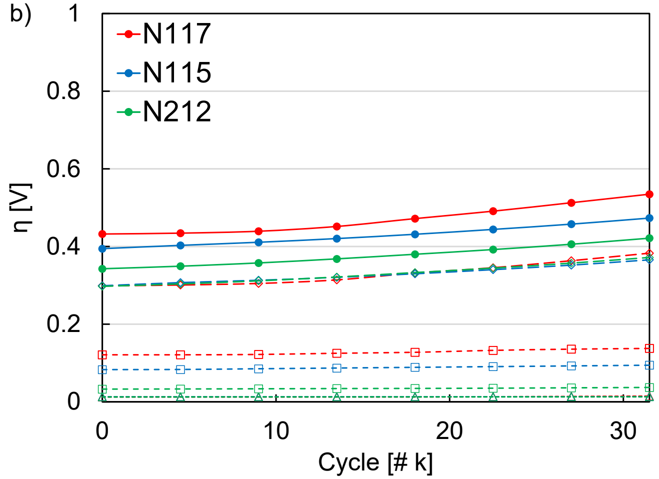
AST Development

- Higher cycling frequency
  - Relevant to increasing loss rate, consistency in mechanism
  - Concerns at cycle time below 20 s with load stabilization, reproducibility
- Membrane thickness has small impact on catalyst durability through load cycling, losses consistency with anode catalyst layer potential (HFR-free)
- Set of options evaluated for catalyst layer ASTs:
  - HFR-free potential is optimal, capabilities limit implementation
  - Potential based cycling less severe, requires setting other components
  - Current based may be more field test relevant, heavily affected by manufacturing and catalyst layer properties

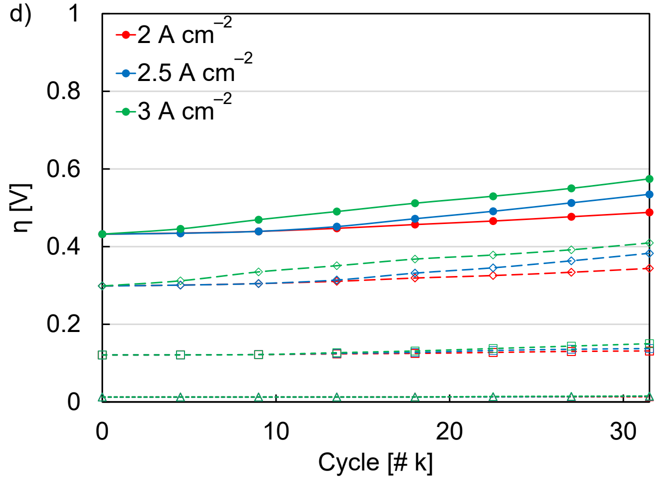
Increasing Cycling Frequency



Impact of Membrane Thickness on Current-Based Load Cycling



Current-Based Load Cycling, Stressor Options



Collaboration and Coordination

NREL Team Members: Shaun Alia, Elliot Padgett, Meital Shviro, Ai-Lin Chan, Sarah Blair, and Samantha Medina

LBNL Team Members: Grace Anderson, Claire Arthurs, Arthur Dizon, Ahmet Kusoglu, Xiong Peng, Adam Weber and Rangachary Mukundan

ANL Team Members: Rajesh Ahluwalia, Luke Johnson, Nancy N. Kariuki, Samuel J. Kazmouz, A. Jeremy Kropf, Debbie Myers, Jaehyung Park, Jui-Kun (Michael) Peng, and Xiaohua Wang

ORNL Team Members: Dave Cullen, Haoran Yu,

LANL: Kui Li, Abdurrahman Yilmaz, Jacob Spendelow, and Siddharth Komini Babu

ASTWG Collaborators: Svitlana Pylypenko (CSM), Shawn Litster (CMU), Iryna Zenyuk (UCI), Kathy Ayers (Nel Hydrogen), Corky Mittelsteadt (Plug Power), Andrew Smeltz (De Nora) Nemanja Danilovic (Electric Hydrogen), Udit Shrivastava (Cummins), and Andrew Park (Chemours).

Proposed Future Work

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- **Subtask 1a.i: LTE Aging Studies**
  - ✓ Continue to quantify degradation rates under steady state, current/potential cycling and shut-down/start-up operations
  - ✓ Study effect of Ir-loading, and cathode back pressure on degradation rates
  - ✓ Expand stack testing to increase testing throughput
  - ✓ Co-ordinate with TEA and modeling to quantify cost, durability and performance trade offs

- **Subtask 1a.ii : Mitigation Strategies**
  - ✓ Investigate effect of GRC on cross-over hydrogen and anode degradation rates
  - ✓ Quantify impact of shut-down strategies on degradation rates
  - ✓ Quantify impact of PTL and PTL coating on Anode catalyst degradation

- **Subtask 1bi: Ex-situ: Anode Catalyst Degradation**
  - ✓ Develop micro-cavity electrode measurements to quantify the effect of ionomer on Ir degradation rates
  - ✓ *Continue In situ* X-ray absorption spectroscopy to quantify catalyst oxidation state and degradation rates as a function of potential
  - ✓ Extend ICP-MS studies to advanced catalysts including supported catalysts

Any proposed future work is subject to change based on funding levels

Proposed Future Work

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- **Subtask 1bii: Ex-situ: Membrane Degradation**
  - ✓ Quantify effect of membrane intrusion into PTL and correlate to membrane durability (differential pressure)
  - ✓ Quantify effect of pressure cycling (shut-down/start-up) on membrane durability
  - ✓ Quantify effect of contaminants on membrane durability

- **Subtask 1biii: Ex-situ: Catalyst-ionomer Interface Degradation**
  - ✓Continue visualization of membrane/PTL and MEA/PTL interfaces
  - ✓Use microcavity electrodes to track ionomer/catalyst interface as a function of durability testing

- **Subtask 1biv: Bi-polar plates and coatings**
  - ✓Continue ICPMS measurements to quantify bipolar plate material dissolution rates as a function of operating conditions
  - ✓Evaluate the effect of PTL coatings on PEMWE durability

- **Subtask 1c: Accelerated Stress Test Development**
  - ✓ Publish and disseminate anode catalyst AST protocol
  - ✓ Develop membrane and PTL AST protocols
  - ✓ Continue to engage Industry stakeholders through the ASTWG and SAB

Any proposed future work is subject to change based on funding levels

Summary : Task 1 – Durability and AST development

- Task 1 effort last year focused on a better understanding of anode durability and AST development
  - Efforts are highly integrated with Task 2 performance, Task 3 Scale up Manufacturing and TEA
  - FUGEMEA from Task 2 is currently the benchmark for Task 1 efforts
  - Durability results from Task 1 are being utilized in TEA
- Task 1 efforts will focus on GRC, membrane durability, and differential pressure operation over the next year
- Two catalyst AST currently being finalized with future work on membrane and PTL ASTs
- **Key findings to date include:**
  - Ir dissolution rate is a function of potential cycling and peaks under anodic cycling
  - Ir dissolution rate increases if Ir is cycled from lower potentials (≈ 0.4V) where the surface is reduced
  - Fast degradation observed in fiber PTLs under voltage hold measurements
  - Voltage cycling results in significant Ir dissolution and migration into membrane and accompanied loss in performance
  - Voltage loss during shut-down/start-up can be mitigated by removing the H_2 from the cathode side
  - Contaminants (both external Na+, Ca+, Fe and internal Pt) can reduce electrolzyer performance
  - Recovery mechanisms depend on the contaminant ion and include high current operation (Ca+, Na+) or acid etching (Pt)