

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

Date: 5/7/2024

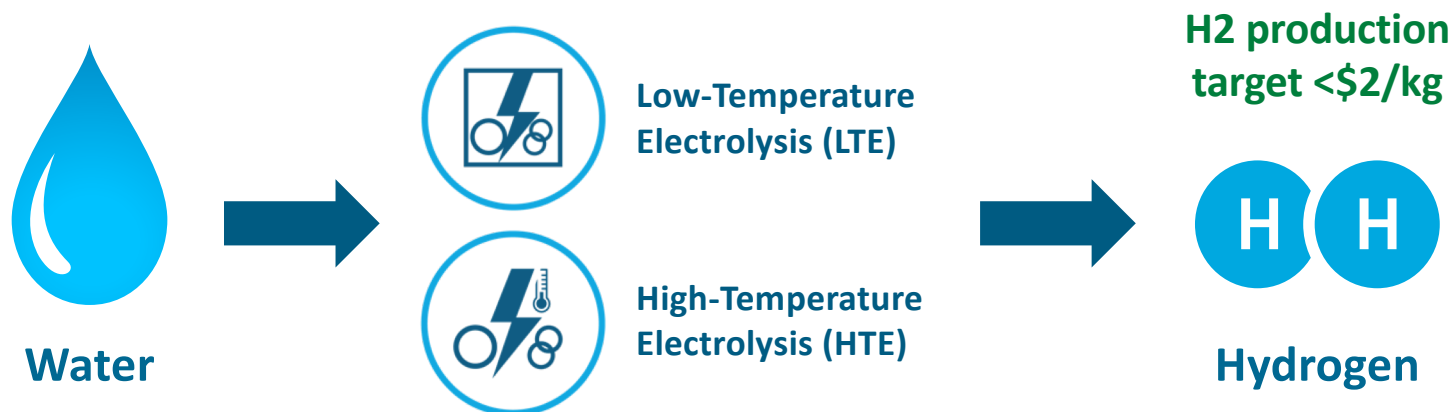
DOE Hydrogen Program

2024 Annual Merit Review and Peer Evaluation Meeting

Project ID # 196a

Project Goals

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

Timeline and Budget

- Start date (launch): October 1, 2020
- Awarded through September 30, 2025
- FY24 DOE Task 1 funding: **\$3.7M + 900K**
- FY24 Task 1 funding: **\$4.6M**

Barriers/Targets

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

Consortium Task Team



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)

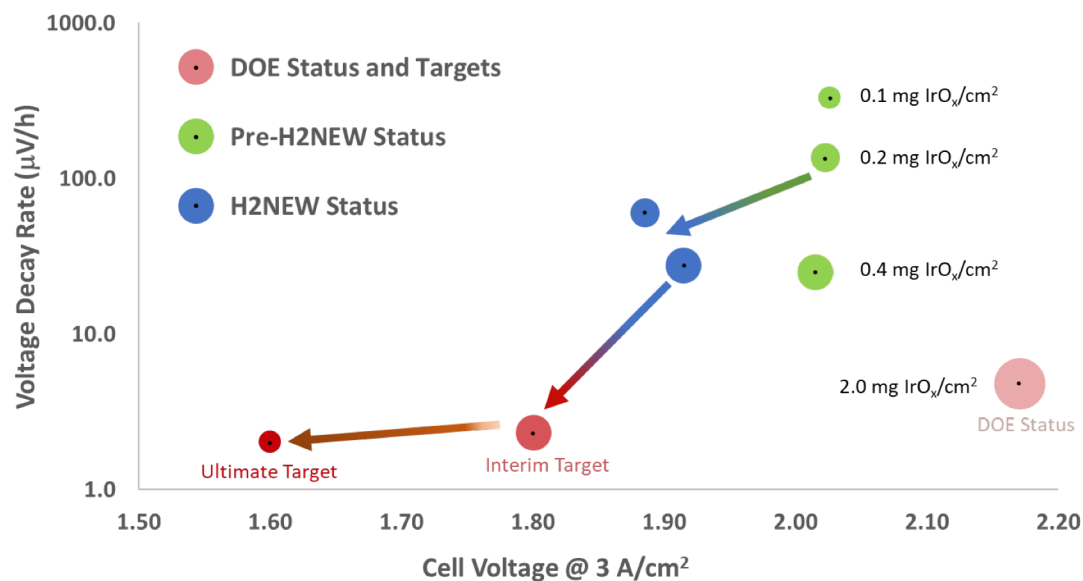
Shawn Litster (CMU)

Industrial partners as part of ASTWG

Nel Hydrogen, Plug Power, Cummins, De Nora, Electric Hydrogen, and Chemours

Relevance and Impact

Figure of Merit



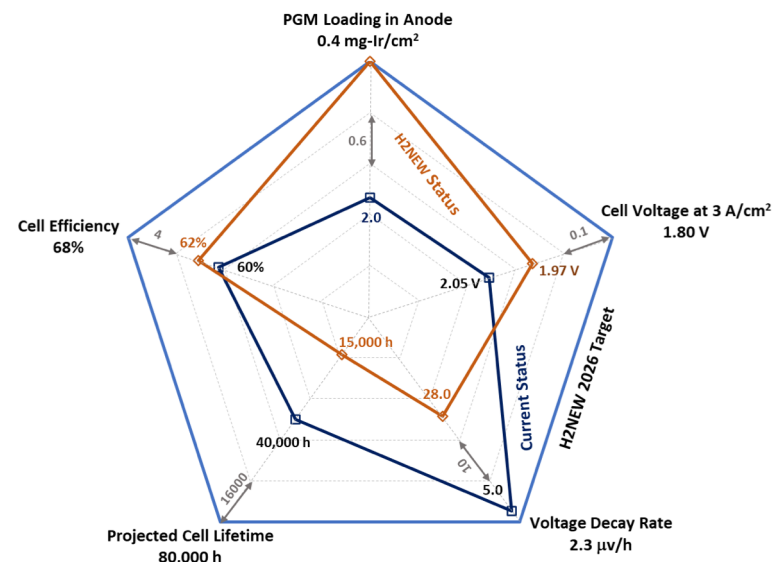
<i>Electrolyzer Stack Goals by 2026</i>	
	LTE PEM
<i>Total PGM content</i>	< 0.5 mg/cm²
<i>Performance</i>	1.8 V/cell @ 3 A/cm²
<i>Degradation Rate</i>	< 2.3 µV/hr

- Task 1 focused on lowering voltage decay rates at lowered Ir loadings
- Quantify effect of operating parameters on durability
- Address PFAS concerns and improve understanding of membrane durability

Relevance and Impact

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/cm ² @ 1.9 V/cell	3.0 A/cm ² @ 1.8 V/cell	3.0 A/cm ² @ 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



- 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 μV/hr) while simultaneously meeting efficiency (3.0 A/cm² @ 1.8V), lifetime (80,000 hours), and cost (Ir loading < 0.5 mg/cm²) targets**

Approach : Durability and AST Development tasks

Task 1: MEA Durability

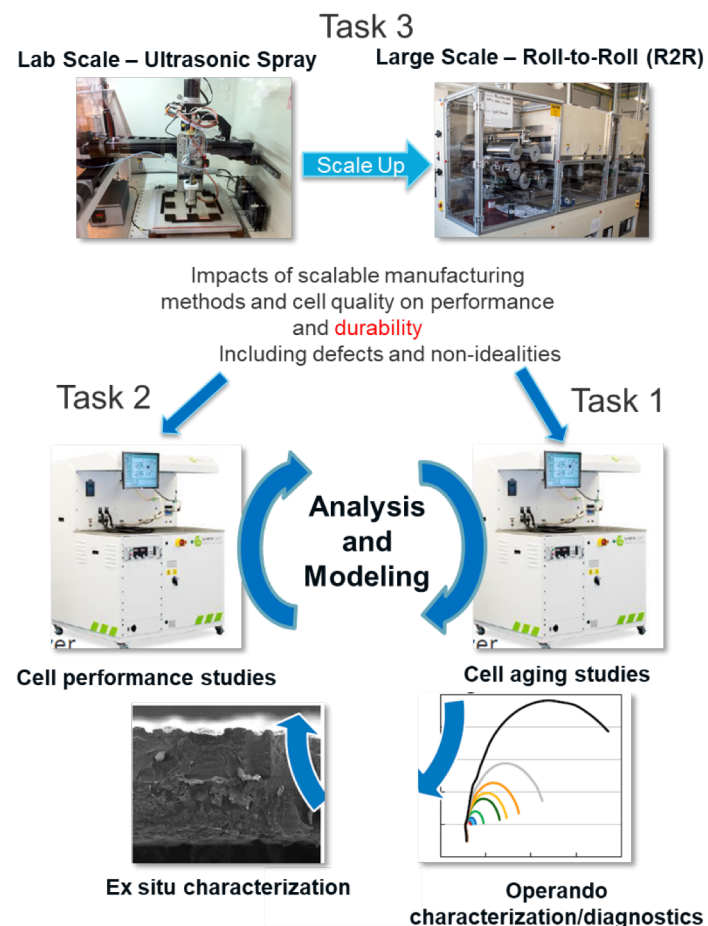
Task 1a. Understanding and mitigating degradation

- 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: FY24 Quarterly Progress Measures and Annual Milestone

Milestone Name/Description	Due Date	Type	Status
Quantify metal dissolution reactions from BPPs and coatings by measuring dissolution rates of metals under different potential profiles (start-stop, steady-state, and intermittent operation) using on-line ICP-MS. (ANL)	3/31/24	QPM	Complete (See Slide 11)
Quantify sources of voltage decay during long term (> 1000 hours) steady state durability test. Perform advanced diagnostics to quantify contributions from anode degradation, cation contamination, interface resistance changes, and electrode structure changes. (NREL, ORNL, and ANL)	6/30/24	QPM	Ongoing (see Slides 13,14)
Propose a validated catalyst AST and determine accelerating factor of the AST compared to steady-state current hold experiment. Evaluate the effect of operating conditions including temperature and potential cycling as accelerating factors for catalyst degradation. (NREL, LANL, LBNL, ANL)	9/30/24	QPM	On-going (See slides 15-21)
Quantify PFSA membrane fluoride and investigate methods for determining PFSA molecular fragment release rate as a function of temperature, voltage, presence of GRC. Evaluate the BOL performance of PEMWEs with commercial and developmental hydrocarbon membranes. (NREL, LANL, LBNL, ORNL, ANL)	9/30/24	Annual Milestone	On-going (See Slide 24)

Approach: Safety Planning and Culture

- See H2NEW Presentation File (Project ID # P196)

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, Ram Gawas, Ahmet Kusoglu, Rangachary Mukundan, Xiong Peng, and Adam Weber

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,

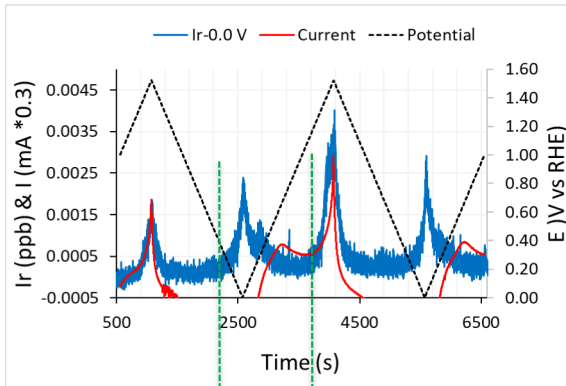
LANL: Kui Li, Jacob Spendelow, and Siddharth Komini Babu

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).

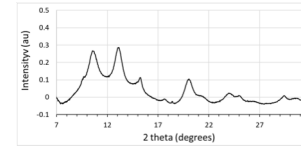
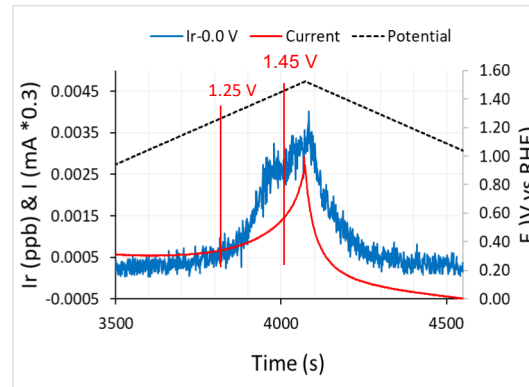


Time-resolved Ti dissolution from Umicore $\text{IrO}_x/\text{TiO}_2$

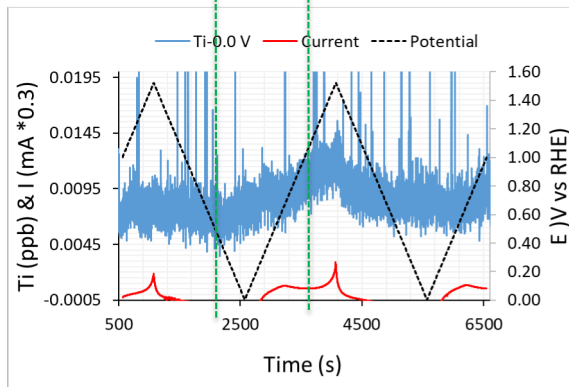
Ir dissolution



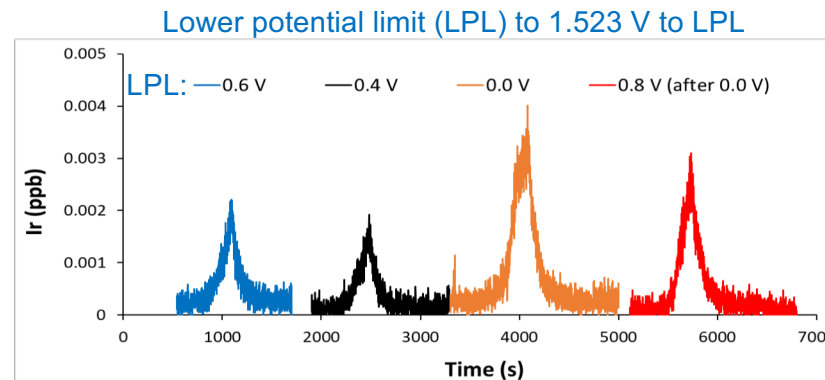
Ir dissolution



Ti dissolution



Ir dissolution



- Representative of rutile IrO_2 catalysts – lower Ir dissolution rates than AA IrO_x H2NEW baseline catalyst
- $\text{IrO}_2/\text{TiO}_2$ is stable against dissolution at potentials between 0.35 V and ~1.25 V
- Sharp increase in dissolution at >1.45 V coinciding with increase in OER current
- Increased Ir dissolution with lower potential limit of 0.0 V associated with dissolution between 0.2 and 0.0 V and with increased dissolution during oxide formation
- Ti dissolution corresponds with Ir Dissolution

Quantify metal dissolution reactions from BPPs and coatings using on-line ICP-MS

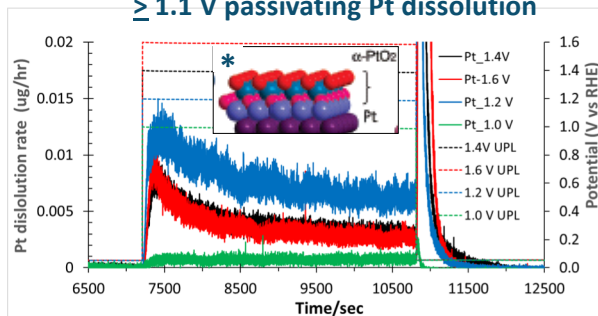
- Studied Pt and Ti dissolution rates from Pt-coated PTL as a function of time and potential profile using electrochemical flow cell coupled to ICP-MS
- Determined that the increase in anodic Ti dissolution at >0.9 V follows the same profile as Pt dissolution but decreases during cathodic scan
- Majority of Pt is dissolved during cathodic step and scan after exposure to >1.4 V
- Next Steps: Control the surfaces of PTL exposed to electrolyte by filling the pores in the PTL. Study dissolution of coatings and Ti for H2NEW collaborator PTLs.



Pt Coating Dissolution

- Anodic Pt dissolution rates:
1.0 V << 1.4 V ~ 1.6 V < 1.2 V

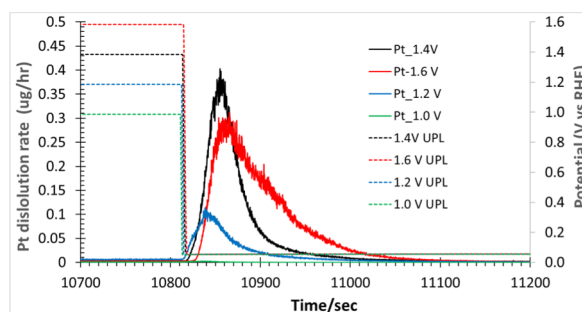
Formation of α -PtO₂ and β -PtO₂ at ≥ 1.1 V passivating Pt dissolution



*Figure from Imai et al., JACS, 121 (2009).

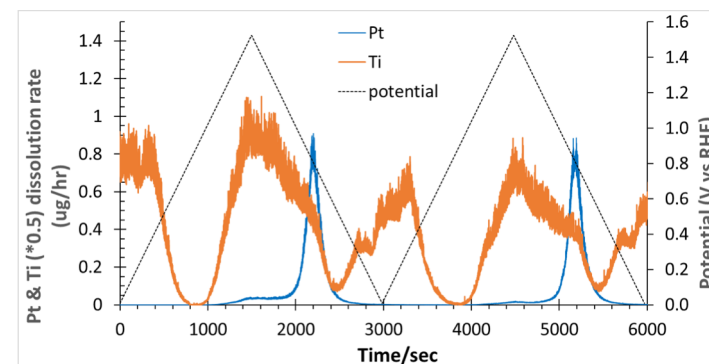
- Cathodic Pt dissolution rates after anodic holds at indicated potentials: 1.0 << 1.2 << 1.4 < 1.6 V

Reduction of α -PtO₂ and β -PtO₂ increasing Pt dissolution



Ti Dissolution

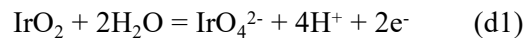
- Ti dissolution rate is > 40x higher than Pt dissolution
- Dissolution in two potential regimes:
> 0.9 V and < 0.6 V



MEA Catalyst utilization correlated with aqueous Ir dissolution

Aqueous Dissolution Rate

2-Species Dissolution Model



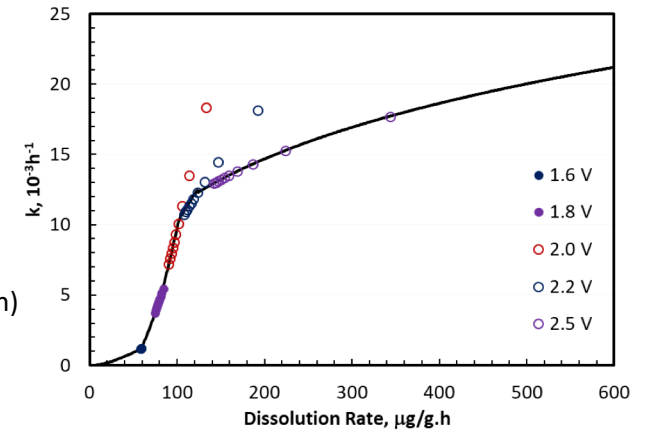
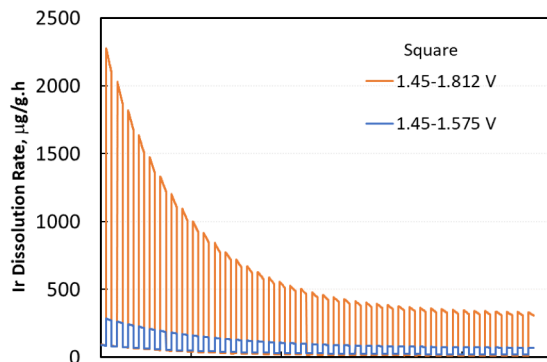
$$\frac{d\xi_a}{dt} = -k \xi_a$$

ξ_a = Catalyst utilization (Single parameter capturing degradation rate)

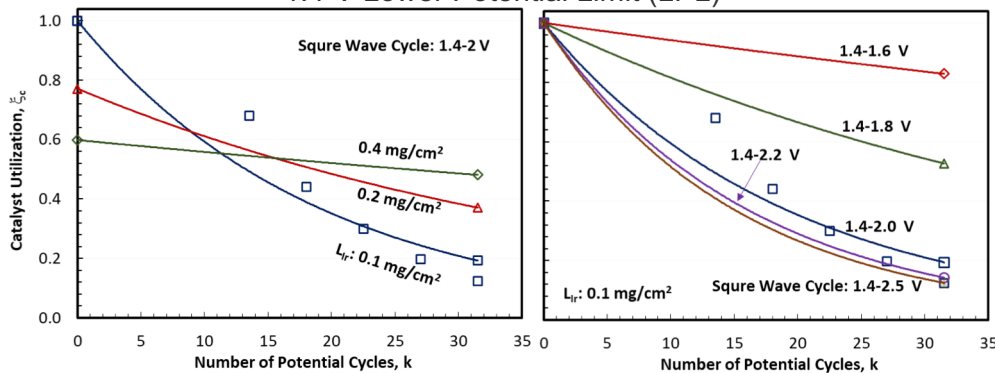
$k(\dot{r}_d, L_{Ir}/L_{Ir}^0)$ = Catalyst degradation rate constant (1/h)

$\dot{r}_d(E)$ = Aqueous Ir dissolution rate (mg/g.h)

$E = iR$ -corrected voltage



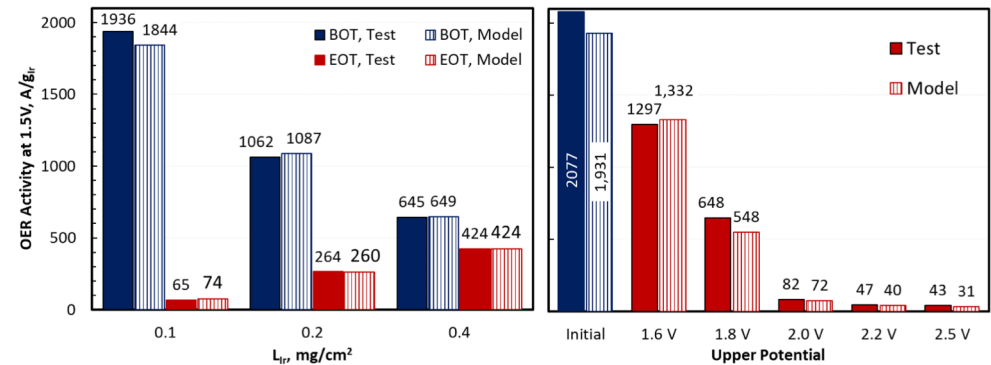
Degradation in Catalyst Utilization on Square Wave Potential 1.4-V Lower Potential Limit (LPL)



Variable Ir Loading, 2-V UPL

Variable UPL, 0.1 mg/cm² Ir Loading

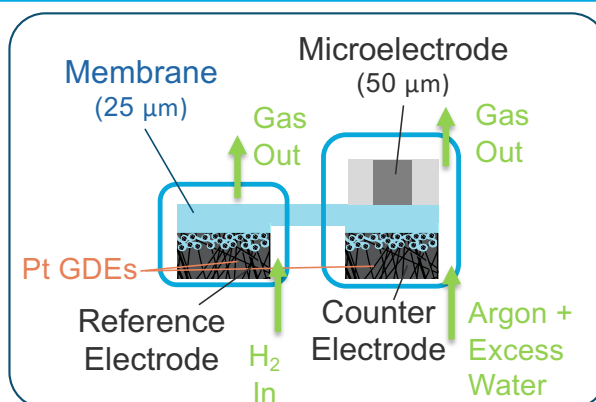
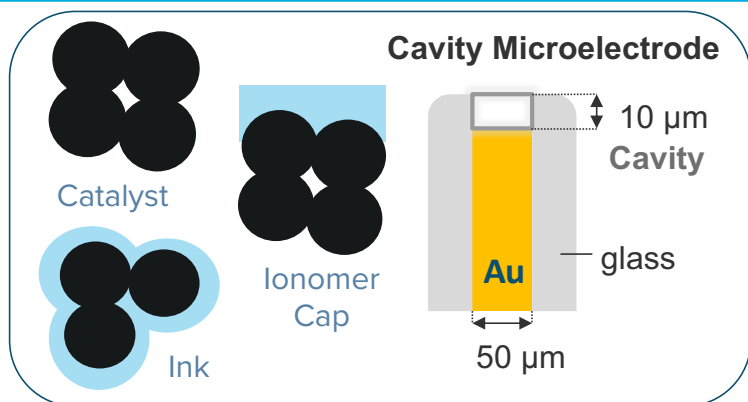
OER Activity Degradation on Square Wave Potential 1.4-V Lower Potential Limit (LPL)



Variable Ir Loading, 2-V UPL

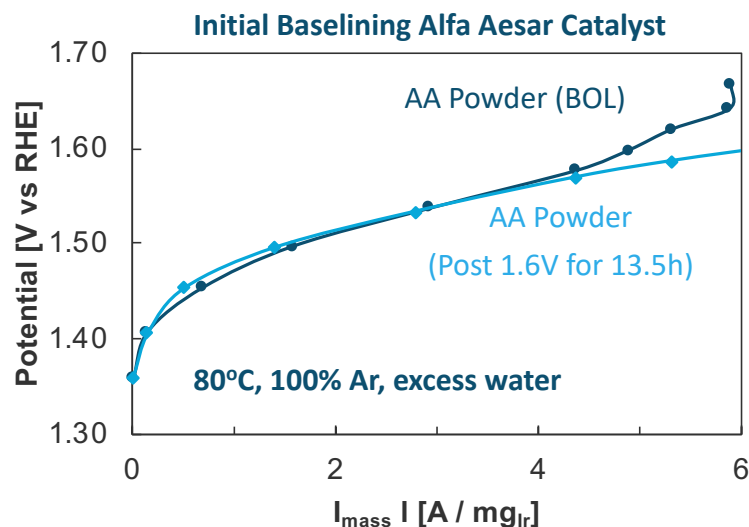
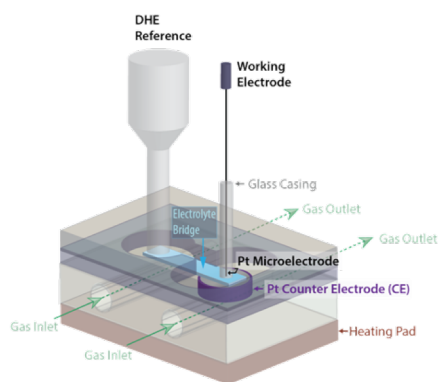
Variable UPL, 0.1 mg/cm² Ir Loading

Ex-Situ Analysis of Ionomer Impact on Catalyst Durability

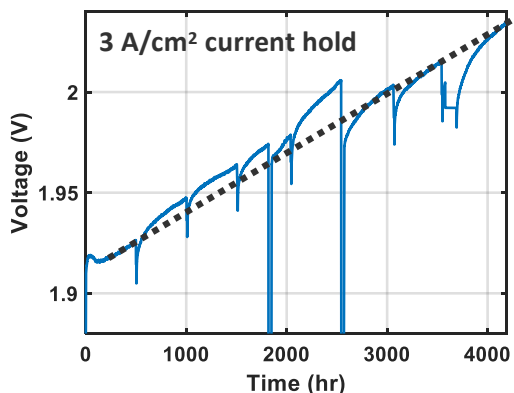


- Impact of ionomer on catalyst durability tested with ex-situ microelectrode measurements
- Oxygen evolution reaction (OER) performance and durability will be measured for:
 - Alfa Aesar IrOx
 - TKK 77110 IrOx
 - Umicore IrOx/Ti
- Ionomer impact probed through different ionomer configurations
 - Catalyst powder
 - Catalyst with ionomer layer
 - Catalyst ink
- Accelerated stress tests conducted at 80C (potential holds and potential cycling)
- Compare with long-term durability tests

3D Schematic

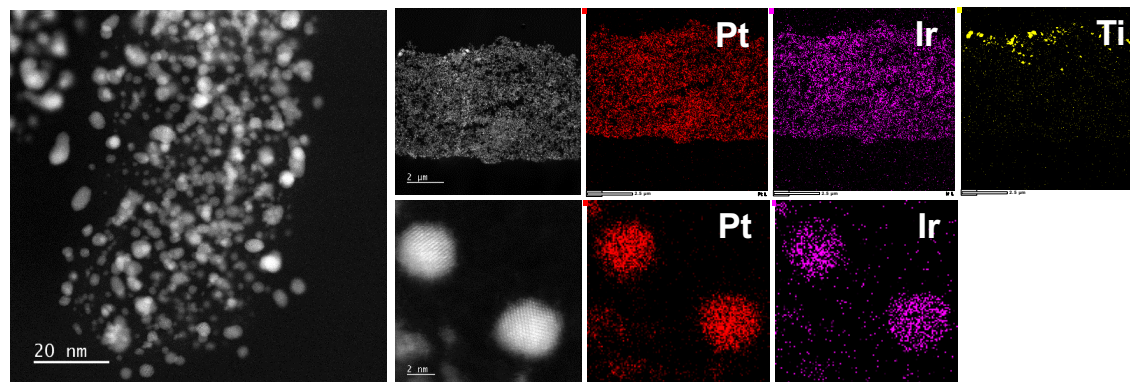


Post-mortem Characterization for 4000 hr Durability Test



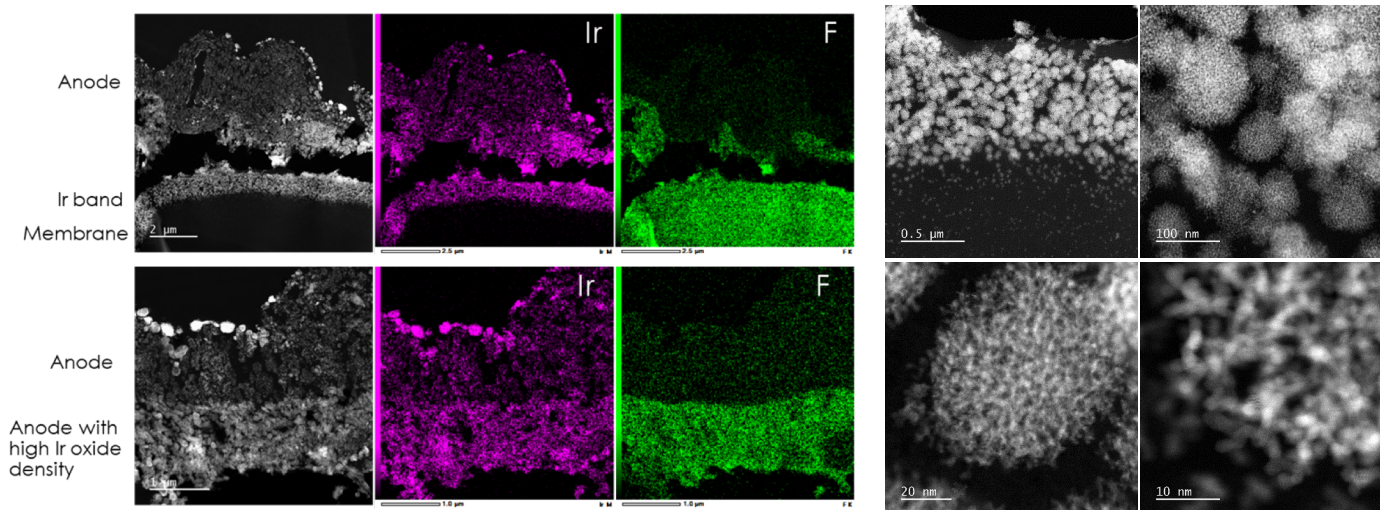
Cathode Degradation:

- No significant Pt coarsening
- Ir redeposition on Pt particles
- Ti redeposition near GDL interface

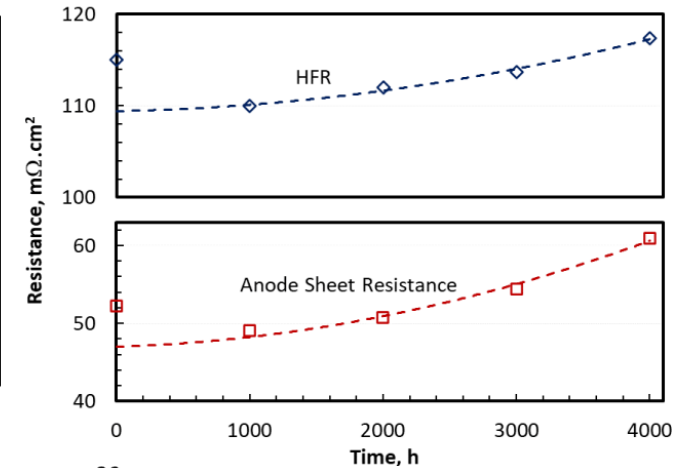
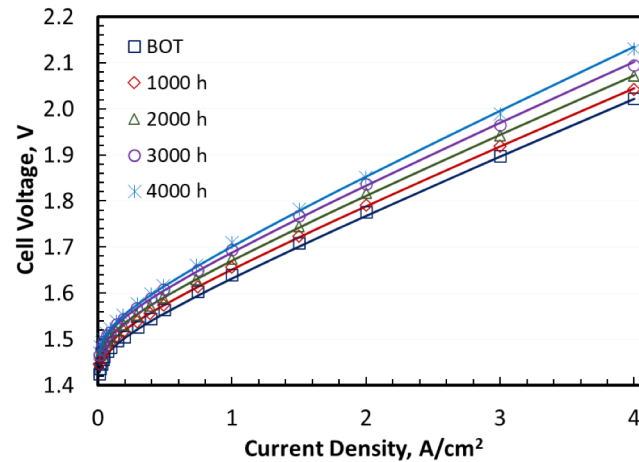
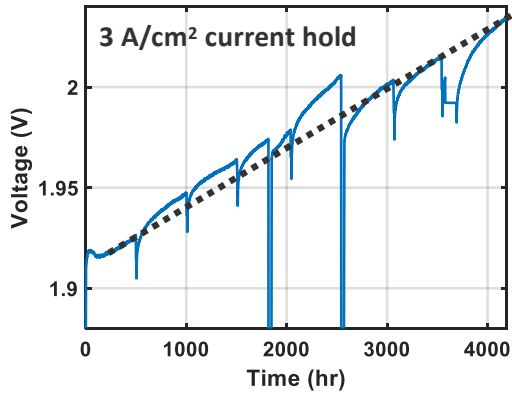


Anode Degradation:

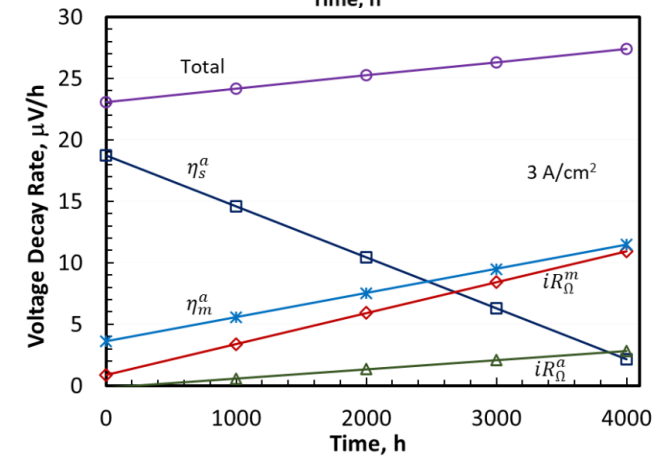
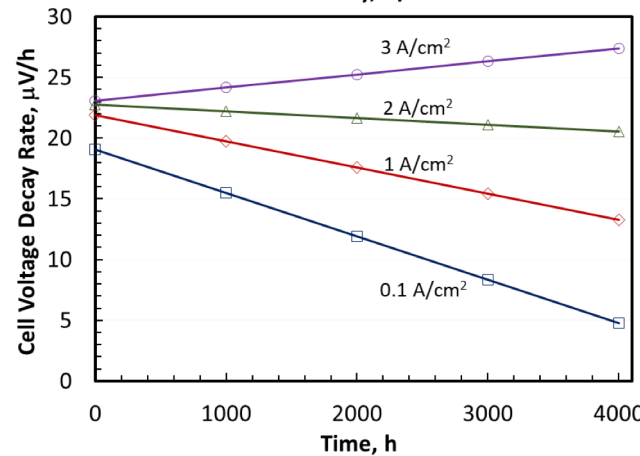
- Significant structural changes, compression of catalyst layer
- Ir dissolution and redeposition into membrane (Ir band) and possibly catalyst layer (dense regions)
- Unique morphology of redposited IrO₂ in membrane



Analysis of 4000 hr Durability Test for Lifetime Prediction



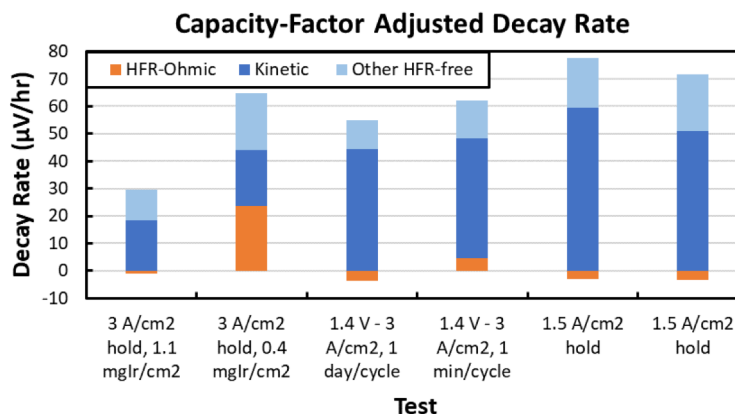
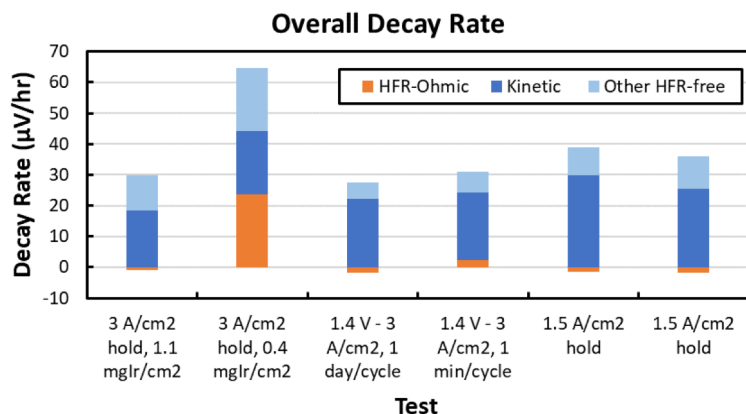
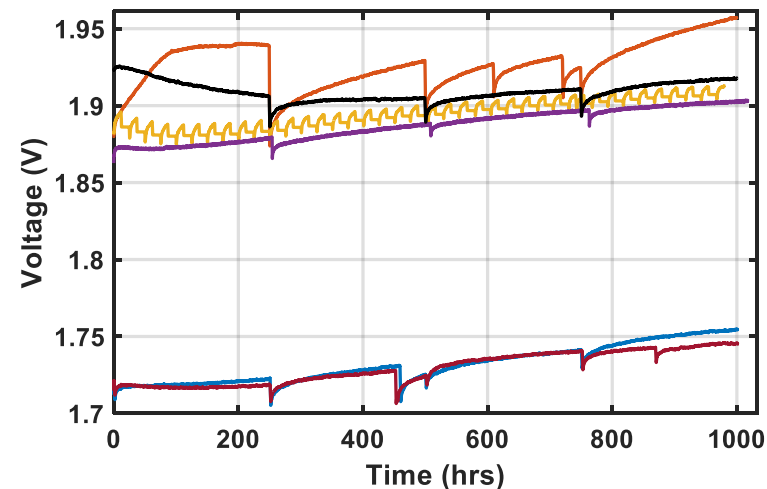
Analysis of decay rate trends over 4000 hr experiment to identify mechanisms of degradation, change in decay rate over time, and project lifetime.



Comparison of Decay Rates Under Varying Power Profiles

- Comparing degradation in 1000 hr experiments under different hold and cycle conditions.
- Clear decay rate impact from anode loading.
- Similar decay rates for different profiles on a per-hydrogen basis. Higher ohmic decay for 3 A/cm² indicates difference in mechanism.

Test Profile	Anode Loading
3 A/cm ² hold	1.1 mg _{Ir} /cm ²
3 A/cm ² hold	0.4 mg _{Ir} /cm ²
1.4 V - 3 A/cm ² , 1 day/cycle	0.4 mg _{Ir} /cm ²
1.4 V - 3 A/cm ² , 1 min/cycle	0.4 mg _{Ir} /cm ²
1.5 A/cm ² hold	0.4 mg _{Ir} /cm ²
1.5 A/cm ² hold	0.4 mg _{Ir} /cm ²

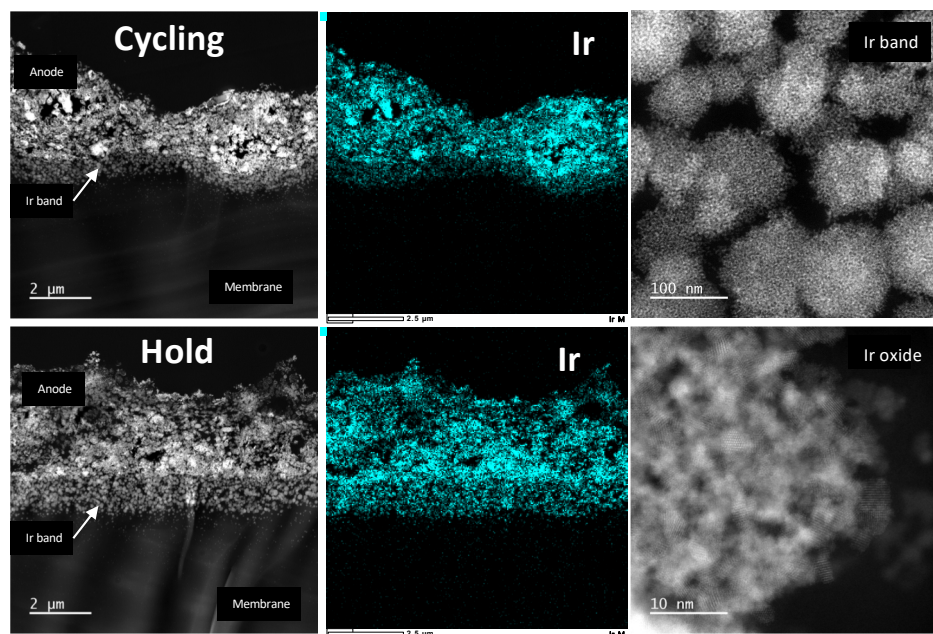


Capacity factor adjustment assuming 3 A/cm² “rated current” to show decay per hydrogen produced.

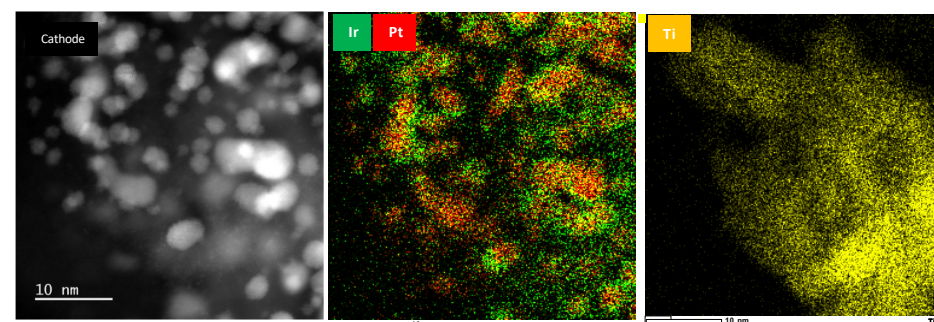
Durability test: 1000 hrs. current hold (3A/cm²) vs. cycling (1.4 V – 3A/cm²)

Ir loading mg/cm ²	Durability test (1000 hr)	Ir loss% in the Ir band	Cathode Pt/Ir atomic ratio	Ti in cathode
0.4	1 min cycle 1.4 V – 3 A/cm ²	10.0±3.0	No Ir	No
0.4	3 A/cm ² hold	19.5±2.0	73/17	Yes

Anode degradation



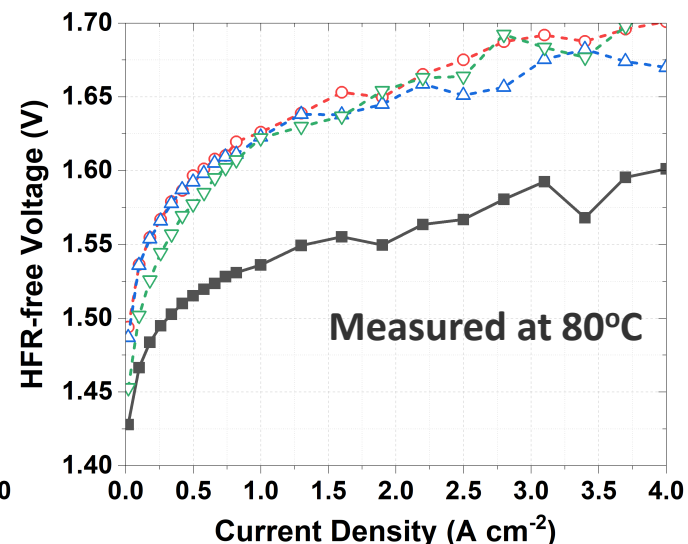
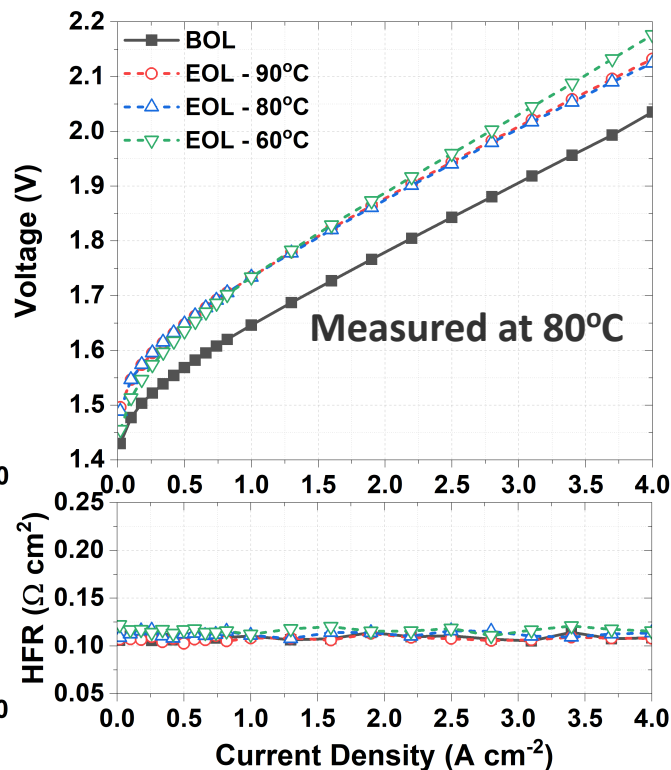
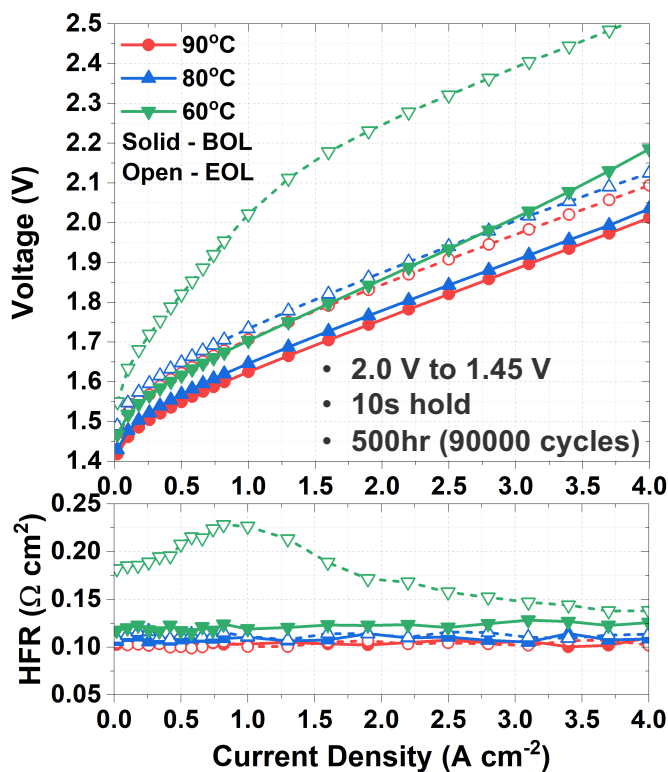
Current hold: Ir and Ti migration to cathode



Summary

- Highest loss% of Ir in the membrane observed for 3A/cm² hold at low Ir loading due to Ir dissolution and migration. The loss% of Ir can be reduced by decreasing hold current or increase Ir loading in the anode.
- Cycling shows less Ir loss% than current hold.
- All current hold tests show Ti oxide on the cathode. Cycling test did not.
- Ir migration and re-deposition in the cathode observed for high current hold (3A/cm²) test.
- General observations: Ir oxide remain in small crystalline size after test; the Ir band is composed of spherical agglomerates of Ir oxide crystals.

Effect of Temperature on Degradation Rate



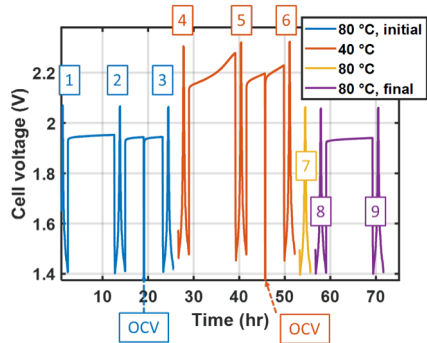
- Operating AST at higher temperature results in higher loss in kinetic activity.

- Higher degradation observed at 60°C but recovered when cell temperature increased to 80°C
- Anode gas bubble coverage and transport differs at 60°C compared to 80°C and 90°C

• Anode: catalyst loading, 0.12 mg_{Ir}/cm² Alfa Aesar IrO₂; Pt-coated 2GDL10-0.25. Cathode: catalyst loading, 0.1 mg_{Pt}/cm² TEC10V50E; MGL370; Active area: 5 cm²

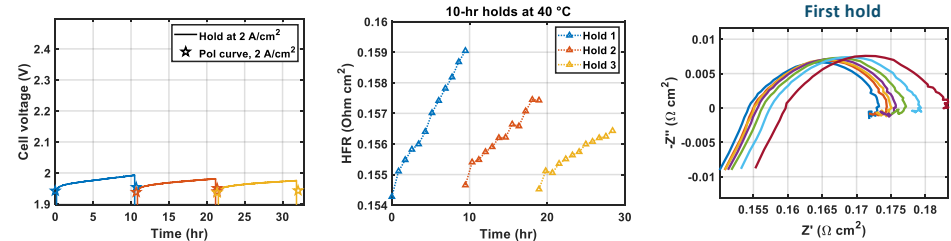
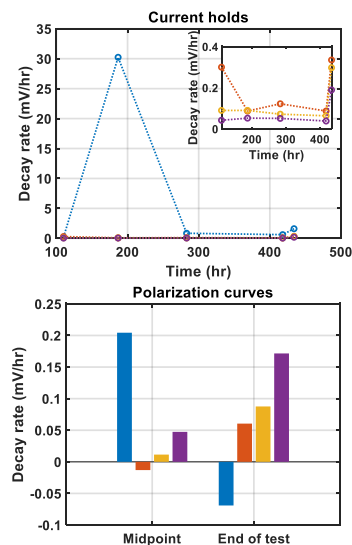
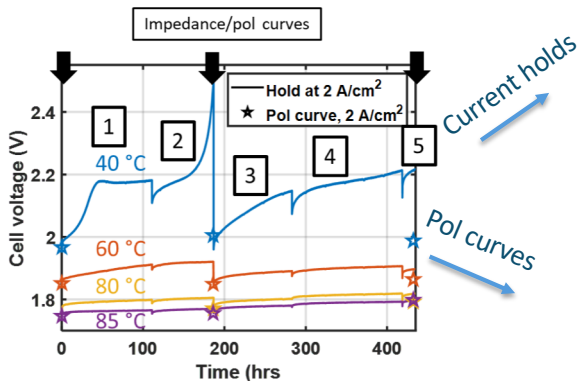
Losses resulting from low-temperature operation show reversibility

Objective : Understand reversibility of anode degradation mechanisms under a variety of operating conditions

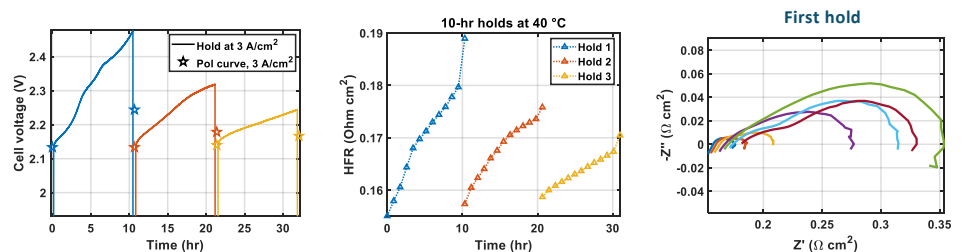


- “Runaway” cell voltage observed during 3 A/cm² holds at low temperature
 - Interruption of current hold with impedance/pol curves partially recovers performance
- Returning to 80 °C almost entirely recovers BOT cell performance

Polarization curve measurements not reflective of anode state during current holds



Low temperature operation at 2 A/cm² does not result in runaway condition over short timescales, although impedance shows beginnings of additional feature. Changes in HFR are largely reversible

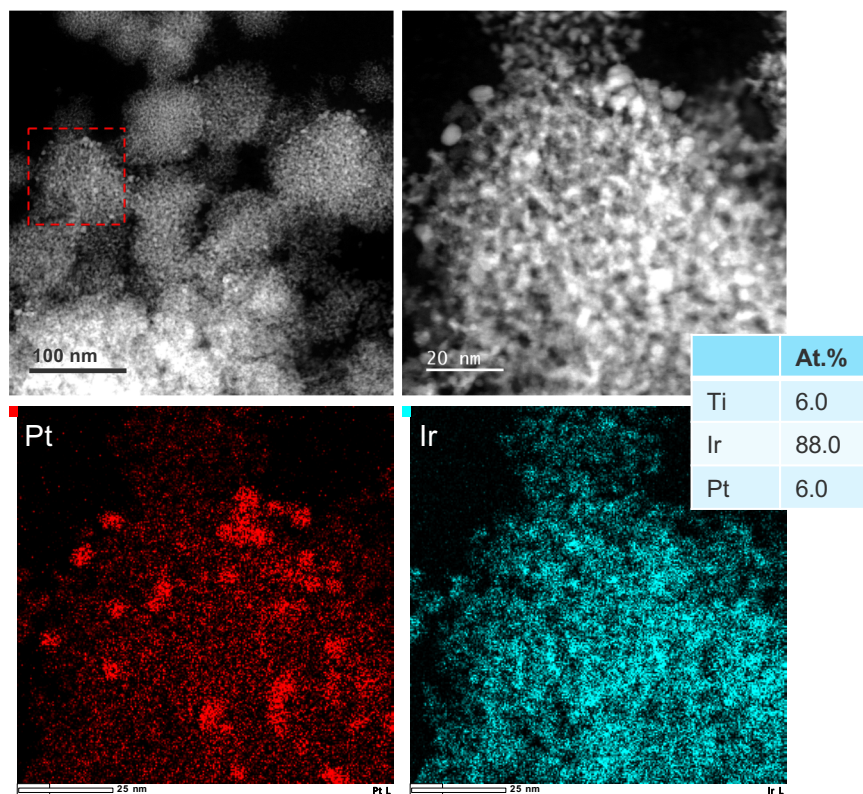


Low temperature operation at 3 A/cm² results in runaway condition over short timescales, and impedance shows clear shape differences that correspond to accelerations in voltage increases

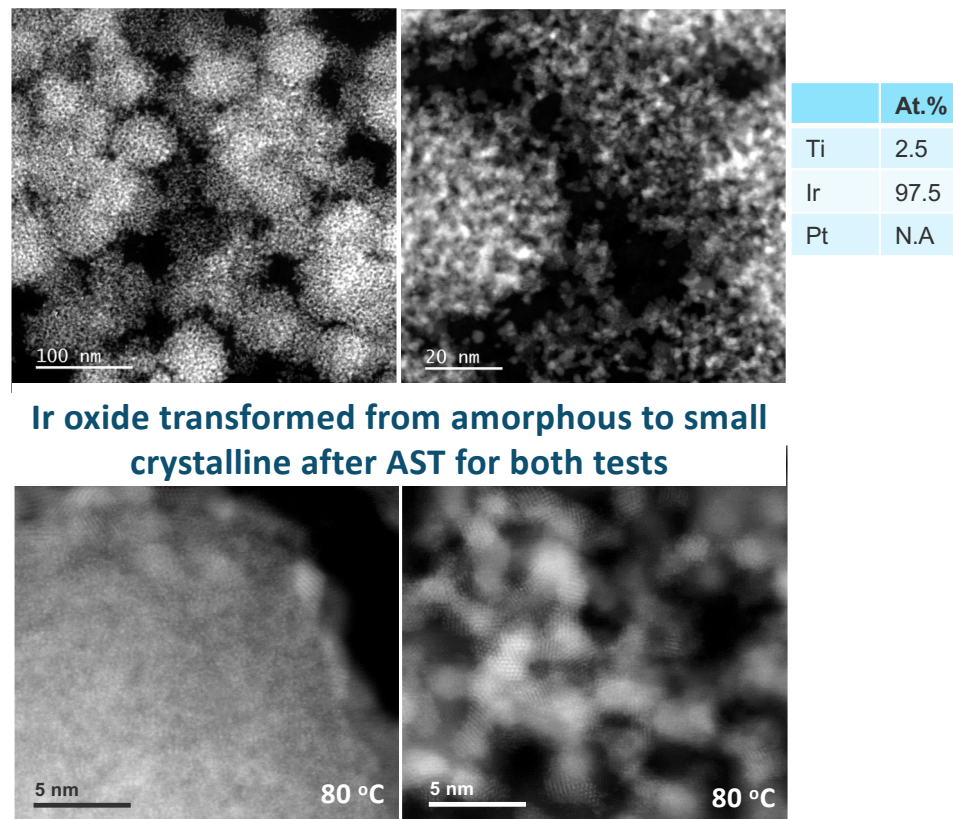
- *In situ* characterization is necessary to understand anode degradation mechanisms
- Low-temperature operation could be a candidate for an AST that stresses the anode

AST temperatures @ 90 °C vs. 80 °C

AST @ 90 °C shows Pt (nanoparticles) and Ti in the Ir band, implying PTL degradation



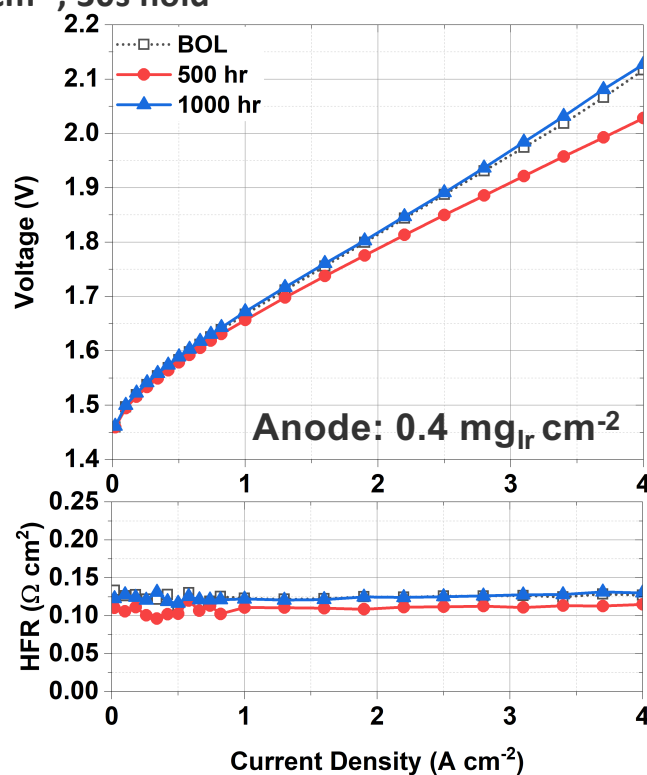
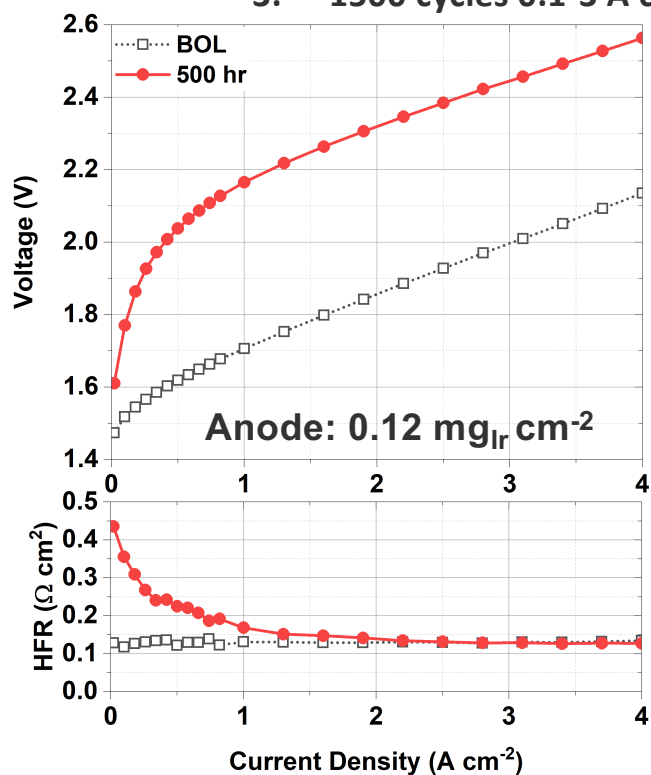
AST @ 80 °C shows no Pt and negligible Ti content in the Ir band



Ir oxide transformed from amorphous to small crystalline after AST for both tests

Dynamic Cycling: Effect of Anode Loading

- Dynamic cycle: 1. 24hr hold at 0.1 A cm⁻²
 2. 24hr hold at 3 A cm⁻²
 3. 1500 cycles 0.1-3 A cm⁻²; 30s hold

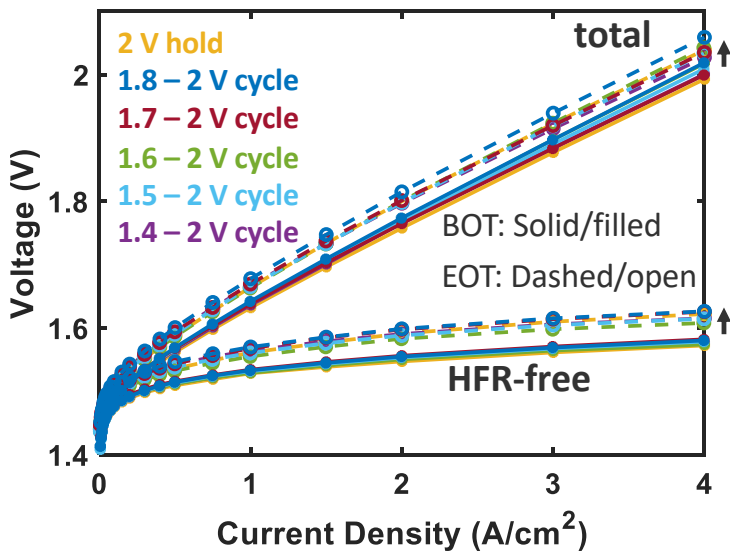


- Lower loading shows faster degradation rate due to higher loss in surface area
- Performance improvement after 500hr with 0.4 mg_{Ir} cm⁻² loading due to decreased HFR and lower loss in IrO₂ surface area compared to 0.1 mg_{Ir} cm⁻²
 - At 500hr, the presence of the metallic Ir on the surface observed in CV with 0.4 mg_{Ir} cm⁻²
- Minimal loss in performance is observed after 1000 hr for 0.4 mg_{Ir} cm⁻².

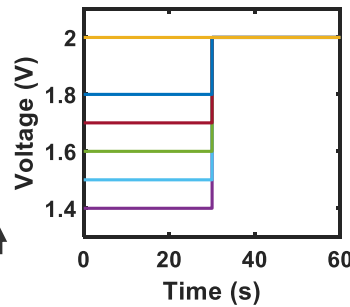
- **Cathode:** catalyst loading, 0.1 mg_{Pt}/cm² TEC10V50E; MGL370; **Active area:** 25 cm²; **Membrane:** N115

Durability with Different Voltage Turndown Levels

Comparing durability with voltage turndown to different lower voltage limits

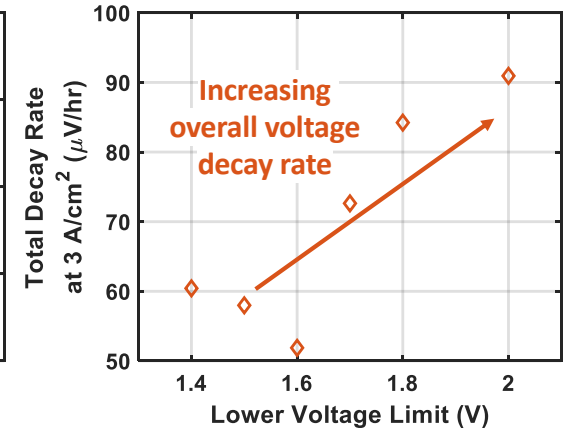
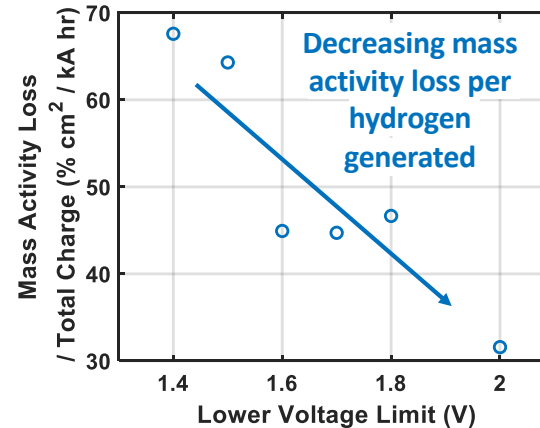


Comparing different voltage cycles and hold to test Ir dissolution predictions, informing TEA and AST development.



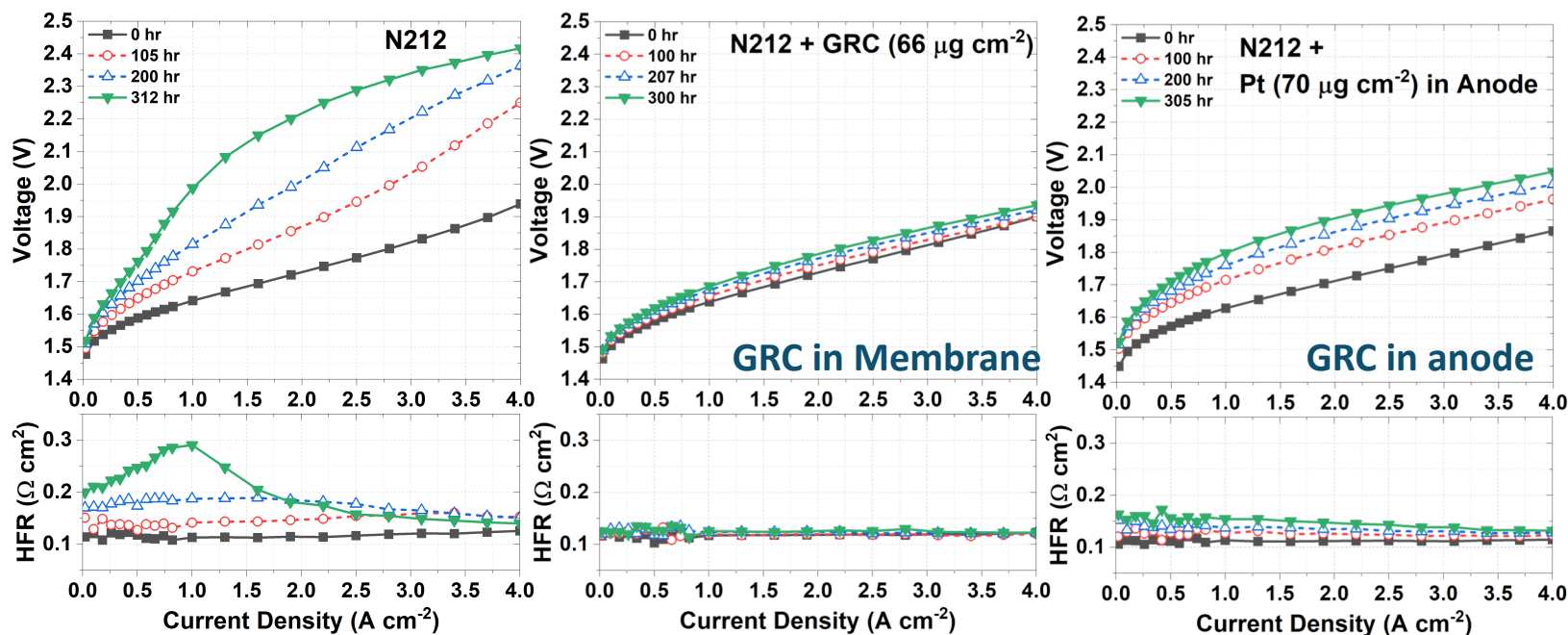
Key result: different degradation mechanisms for different levels of voltage turndown.

Anode: 0.2 mg_{Ir}/cm² AA IrO₂, Pt/Ti Sinter PTL
Cathode: 0.1mg_{Pt}/cm² Pt/HSC, MGL280, 20% compression
Membrane: Nafion N115, no pretreatment.
Test: 500 hrs, 80°C, anode/cathode (50 mL/min, ambient / 0 mL/min, ambient). 1 min/cycle for square wave cycle tests.



Gas Recombination Catalyst in Anode vs. Membrane

Startup/Shutdown Cycle: ON (1.8 V) – OFF (OCV); 30s step;



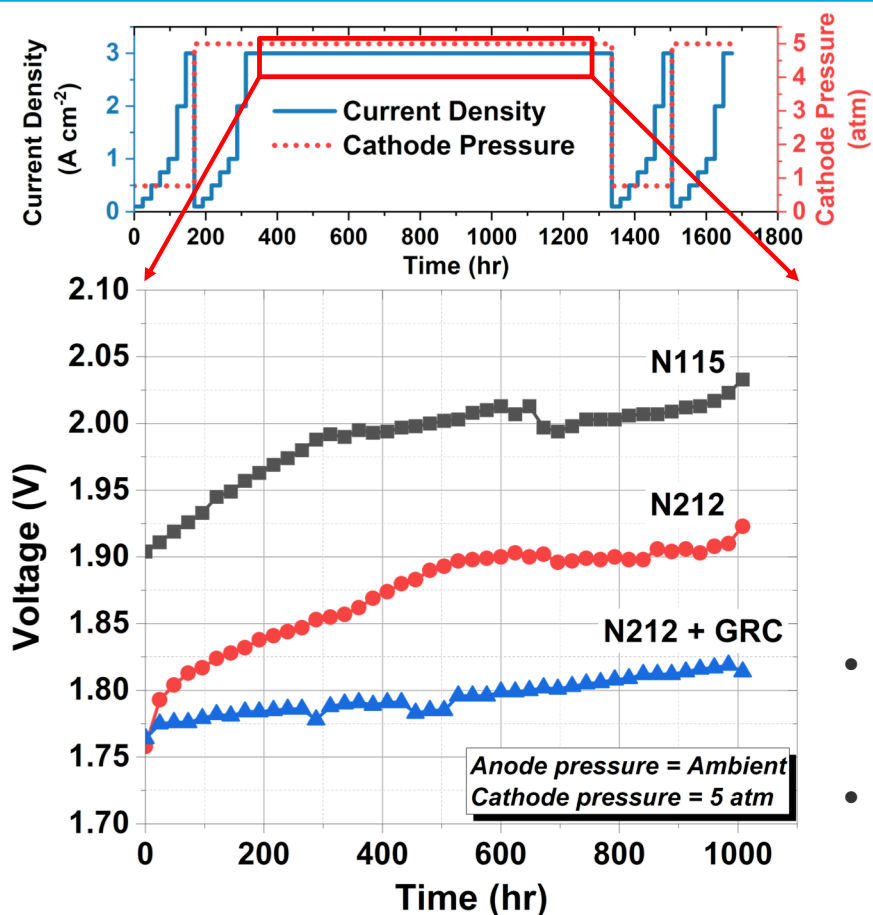
The role of Pt in the catalyst layer needs further characterization to understand

- Effect of potential on Pt for recombination (PtO vs. Pt)
- Dissolution of Pt

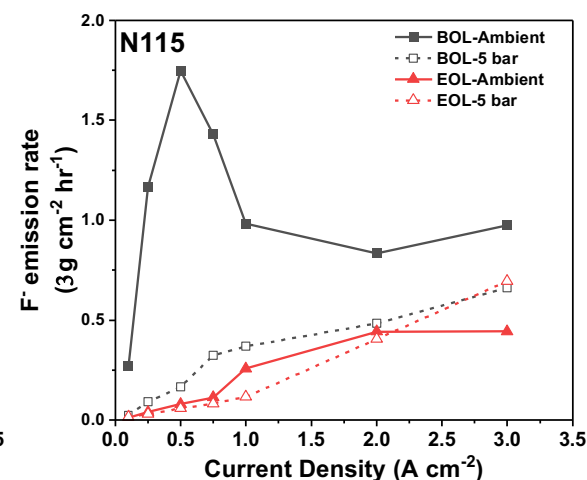
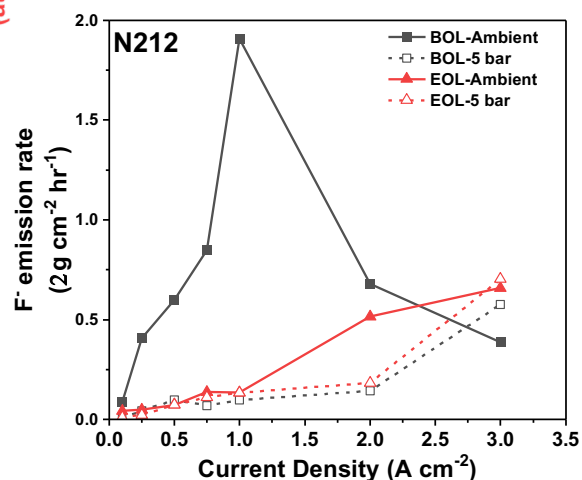
- GRC in the membrane shows high durability compared to pristine N212 and GRC in anode

• **Anode:** catalyst loading, 0.12 mg_{Ir}/cm² Alfa Aesar IrO₂; Pt-coated 2GDL10-0.25. **Cathode:** catalyst loading, 0.1 mg_{Pt}/cm² TEC10V50E; MGL370.

Membrane Degradation During Long Term Hold



FER at BOL and EOL at different Cathode Pressures



- N212 with GRC (66 μg_{Pt} cm⁻²) shows low degradation rate compared to membranes without GRC
- F⁻ emission measured at different current density and differential pressure

Anode: catalyst loading, 0.4 mg_{Ir}/cm² Alfa Aesar IrO₂; Pt-coated 2GDL10-0.25. Cathode: catalyst loading, 0.1 mg_{Pt}/cm² TEC10V50E; MGL370;

Ex-situ Membrane Durability: Mechanical Characterization

Mechanical response of cell components

- To assess in-situ mechanical response of cell components during assembly, electrolyzers components were mechanical tested in-situ under uniaxial compression at 25 and 80C.
- Effect of temperature and hydration (for Nafion) on mechanical properties and thickness contraction are analyzed

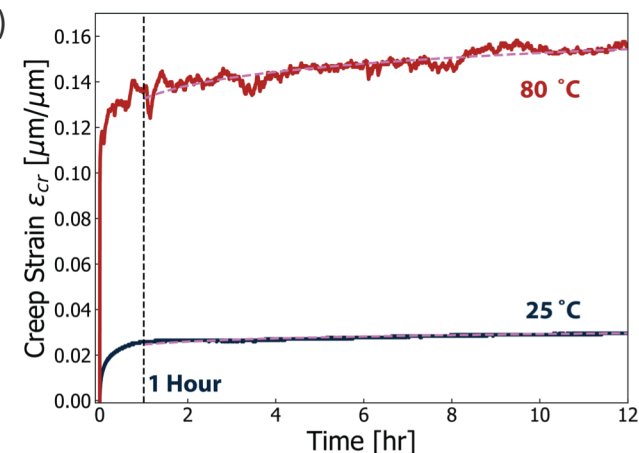
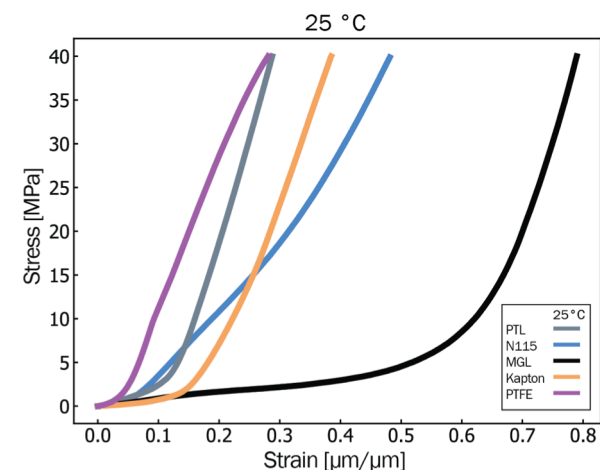
Membrane creep response

- Conducted 12- to 24-hour creep experiments of hydrated N115 and N117 at three temperatures, by applying & holding 35MPa pressure on the wet membrane to monitor its thickness change over time. Membrane exhibits a nonlinear creep strain which increases at higher temperature. This ex-situ characterization confirms and quantifies the creep-induced thickness change in membranes

Compressive stress-strain response of electrolyzers components measured at 25C. Data for Nafion was collected in hydrated state.

The mechanical response vary widely from solid polymer response (Nafion, gaskets) to more brittle porous metal (PTL) and softer, porous carbon (GDL)

Creep measurement of Nafion in hydrated state under compression at 3 temperatures showing the increase creep (reduced thickness) over time.



Proposed Future Work

- **Subtask 1a.i: LTE Aging Studies**

- ✓ Utilize EIS, Voltage loss breakdown and cell modeling to attribute voltage losses to specific degradation mechanisms
- ✓ Quantify the impact of cross-over hydrogen on degradation rates
- ✓ Expand durability studies to other catalysts including supported catalysts
- ✓ Examine the impact of ionomer in the electrode and electrode structure on durability
- ✓ Continue to co-ordinate with TEA and modeling to quantify cost, durability and performance trade offs

- **Subtask 1a.ii : Mitigation Strategies**

- ✓ Continue to quantify the impact of GRC on cross-over hydrogen and anode degradation rates
- ✓ Outline operating conditions that enhance catalyst and membrane durability

- **Subtask 1bi: Ex-situ: Anode Catalyst Degradation**

- ✓ Continue micro-cavity electrode measurements to relate MEA degradation rates to RDE degradation rates
- ✓ *Continue In situ* X-ray absorption spectroscopy and X-ray photoelectron spectroscopy to quantify catalyst oxidation state and degradation rates as a function of potential
- ✓ Continue ICP-MS studies of advanced catalysts including supported catalysts

Proposed Future Work

- **Subtask 1bii: Ex-situ: Membrane Degradation**
 - ✓ Relate ex-situ creep measurements to membrane behavior under operating conditions
 - ✓ Continue to quantify effect of pressure cycling (shut-down/start-up) on membrane durability
 - ✓ Quantify membrane chemical degradation rates through effluent analysis
- **Subtask 1biii: Ex-situ: Catalyst-ionomer Interface Degradation**
 - ✓ Continue visualization of membrane/PTL and MEA/PTL interfaces
 - ✓ Expand microcavity electrodes to track influence of differing ionomer/catalyst interfaces on durability
- **Subtask 1biv: Bi-polar plates and coatings**
 - ✓ Continue ICPMS measurements to quantify material dissolution rates from bipolar plates and PTLs
 - ✓ Quantify the effect of PTL coatings on Ti dissolution in MEAs and correlate to voltage loss in durability testing
- **Subtask 1c: Accelerated Stress Test Development**
 - ✓ Publish and disseminate two anode catalyst AST protocols related to regular and start-up/shut-down operations
 - ✓ Continue development of membrane chemical and mechanical degradation protocols
 - ✓ Continue to engage Industry stakeholders through the ASTWG and SAB

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 and GRC from Task 3 are currently used for Task 1 efforts
 - Durability results from Task 1 are being utilized in TEA
- Task 1 efforts focused on understanding various sources of voltage losses and attributing them to specific degradation mechanisms to aid AST development
- **Key findings from last year include:**
 - Ir dissolution rates from ICP-MS can be utilized to model degradation rates in MEA
 - Voltage degradation rates highly influenced by Ir loading and operating conditions like temperature and load profile
 - Reversible degradation observed at low temperature (60 °C)
 - Irreversible degradation increases with temperature
 - Both PTL (Pt, Ti) and Catalyst (Ir) dissolution and reprecipitation observed with PTL degradation increasing with temperature and high current long-term holds
 - Start/stop testing results in increased degradation rates that can be mitigated by using a GRC
 - FER of water from electrolysis experiments utilized to quantify membrane degradation rates: High degradation rates observed at BOL with degradation rates increasing with current density and almost independent of pressure
 - Recovery mechanisms depend on the contaminant ion and include high current operation (Ca⁺, Na⁺) or acid etching (Pt)