AEM Water Electrolyzer for Hydrogen Production from Offshore Wind

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Project ID # TA054

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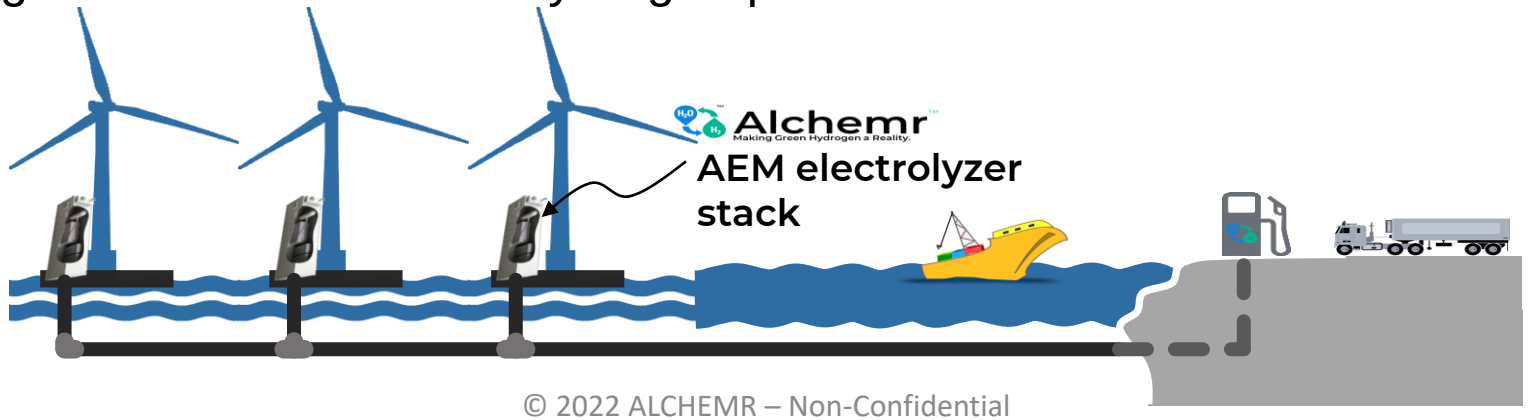
Project Goal

- Develop a low-cost anion exchange membrane water electrolyzer (AEMWE) for direct coupling to offshore wind farms, with the ability to operate using seawater. In general, seawater electrolysis has several advantages:
  - Produces high-pressure hydrogen to be transported back to shore through a pipeline in the seabed
  - Eliminates power conversion costs
  - Increases electrolyzer efficiency
  - Reduces transmission costs
  - Reduces hydrogen storage costs
- Develop high-performance oxygen evolution reaction (OER) selective electrodes and modify anode flowfield/current collector to improve the cell performance (0.3 A/cm^2) and cell durability (>1000 hr) in seawater environment at 5 cm^2 scale.
- Scale up and build a 3-cell single stack (active area of 250 cm^2 per cell) based on the architecture of the small single cell to increase the hydrogen production.



Overview

Timeline

- ❑ DOE SBIR Phase II
  - ❑ Project Start Date: 08/23/21
  - ❑ Project End Date: 08/22/23

Budget

- ➢ DOE SBIR Phase II
- ➢ Total project budget for Phase II: $1.15M
- ➢ Funds spent (as of 02/28/2022): $284,881.47

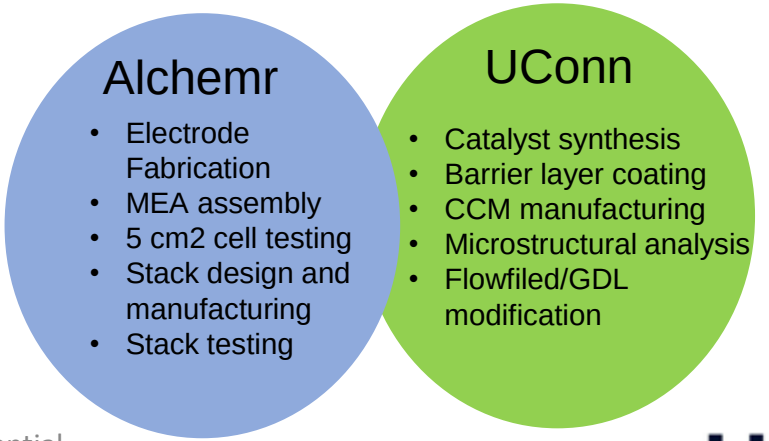
Barriers

Hydrogen Generation by Seawater Electrolysis

Barrier	Target
Capital Cost	< $2.00 $/kg$H_2$
System Performance	>1000 hr
Manufacturing	250 cm^2 (MEA)

Partners

- Project lead: Alchemr (PI, Dr. Gholamreza Mirshekari)
- Partner organization: University of Connecticut (Dr. Stoyan Bliznakov; Dr. Radenka Maric)



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Relevance

Overall objective:
The main goal of this SBIR Phase II proposal is to develop a low-cost anion exchange membrane water electrolyzer (AEMWE) for direct coupling to offshore wind farms, with the ability to operate using seawater.

Major accomplishments as of April 2022:

- Demonstrating the long-term operation of a seawater-fed 5 cm^2 cell for >1000 hr. **(100% accomplished)**
- Developing a high-performance and durable OER-selective anode electrode for the AEMWE cell operating with seawater. **(100% accomplished)**
- Developing a seawater stable flowfield/current collector. **(100% accomplished)**

Barriers	Impacts
Capital cost	Eliminates the high cost of the power electronics required for grid integration. Reduces hydrogen storage and transmission costs.
System efficiency and electricity cost	Development of high-performance AEM seawater electrolyzer cell. Improve and achieve the cell performance and durability of 1000 hours at 0.3 A/cm^2 and 60 ^oC.
Manufacturing	Scale-up manufacturing at 3-cell stack level (250 cm^2 active area per cell) fed with seawater.

Approach - Project Overview

Budget Period 1: Develop high performance seawater-fed AEMWE 5 cm² cell for 1000 hr (Year 1)

Budget Period 2: Scaling the AEMWE active area from 5 cm2 to 750 cm² through a 3-cell stack (Year 2)

Obj.#	Project Activity	Year 1				Year 2			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1.0	Developing a High-performance and Durable OER Anode Electrode for the AEMWE Cell Operating with Seawater								
2.0	Developing a Seawater Stable Flowfield/Current Collector								
3.0	Demonstrating the Stable Operation of a Seawater-fed 5 cm² Cell for 1,000 hr								
4.0	Scaling the AEMWE Active Area from 5 cm2 to 750 cm² Through Building a 3-Cell Stack								
5.0	Start/Stop Cycling of 5 cm² AEMWE Cell in Seawater								
6.0	Improving Our Techno-Economic Model for Future Commercial Implementation								

Deliverables

- ✓ **Scale-up MEA to 250 cm² and develop a 3-cell stack.**
- ✓ **Develop high performance OER anode catalyst.**
- ✓ **Durability of >1000 hours at 0.3 A/cm² and 60 °C for 5 cm² cell.**

Approach –Milestones

Tasks/Objectives Description	Due Date	%Complete
Fabricate the Anode CCS Using NiFe-LDH Catalyst	Q3 May 2022	100% completed
Developing a Seawater Stable Flowfield/Current Collector	Q3 May 2022	100% completed
Fabricate the Anode CCS Using Cl^- Blocking Overlayers	Q3 May 2022	100% completed
Demonstrating the Stable Operation of a Seawater-fed 5 cm^2 Cell for 1000 hours	Q4 Aug. 2022	100% completed
Fabricate the Anode CCS Using Mn-Based Oxide Catalysts (i.e. $(Mn_{1-x}Mo_x)O_{2+x}$ and $Mn_{1-x-y}Mo_xW_yO_{2+x+y}$) With Different Stoichiometry	Q4 Aug. 2022	50% completed
Fabricate CCMs by Using RSDT	Q4 Aug. 2022	10% completed

* Each quarter (Q) represents 3 months of the 2-year project.

Approach –Milestones

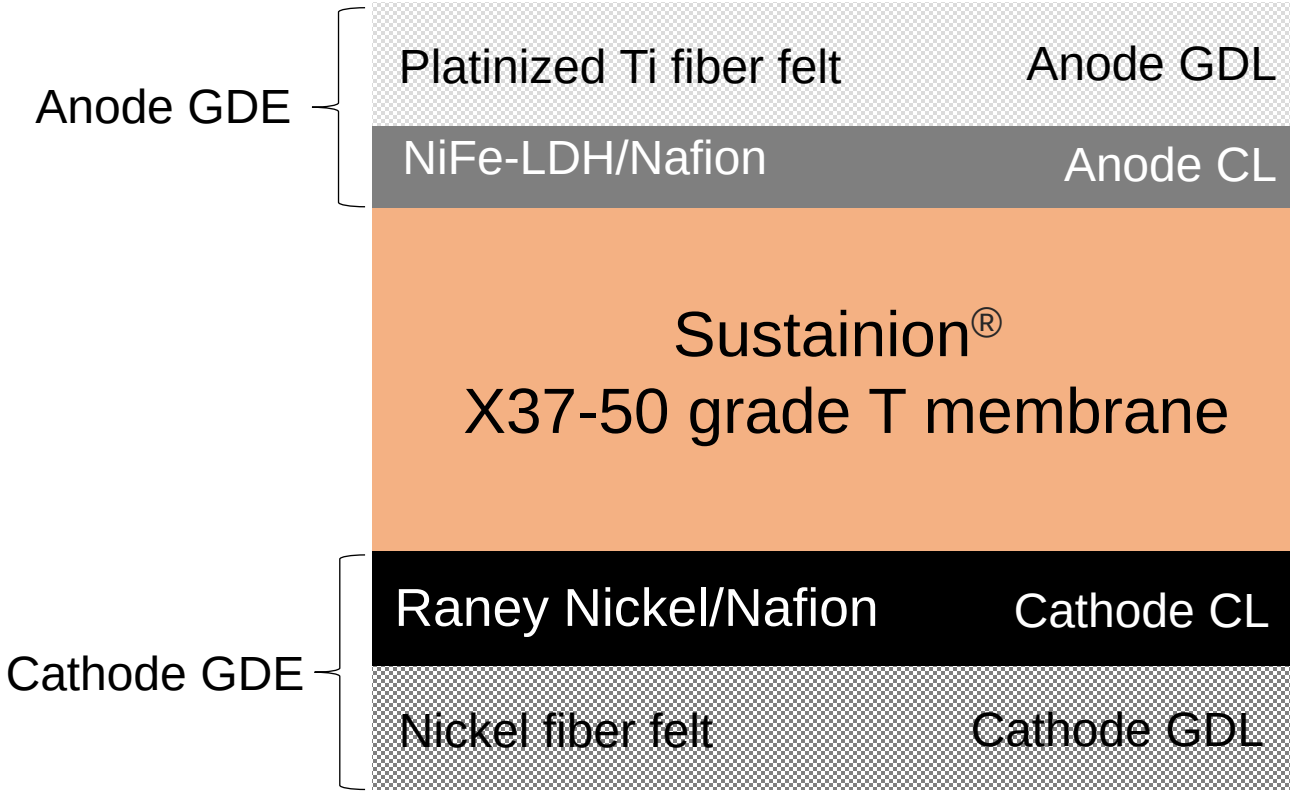
Tasks/Objectives Description	Due Date	%Complete
Design the Safety System and Stack Assembly	Q6 Feb. 2023	20% completed
Design and Build the 3-Cell Stack	Q6 Feb. 2023	10% completed
Start/Stop Cycling of 5 cm^2 AEMWE Cell in Seawater	Q6 Feb. 2023	0% completed
Operate the Stack Assembly	Q8 Aug. 2023	0% completed
Improving Our Techno-Economic Model for Future Commercial Implementation	Q8 Aug. 2023	0% completed

* Each quarter (Q) represents 3 months of the 2-year project.

End of project goal:

Developing a low-cost anion exchange membrane water electrolyzer (AEMWE) stack for direct coupling to offshore wind farms, with the ability to operate using seawater.

Schematic of the Fabricated MEA



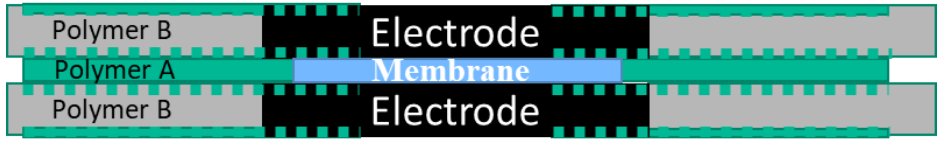
* Drawing not to scale

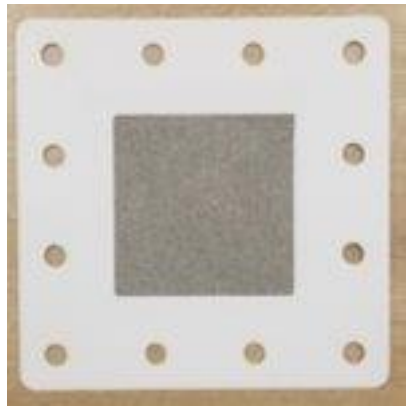
MEA fabrication steps:

Step 1: Deposition of anode catalyst layer (CL) on the anode gas diffusion layer (GDL) (loading: 2 mg/cm^2).

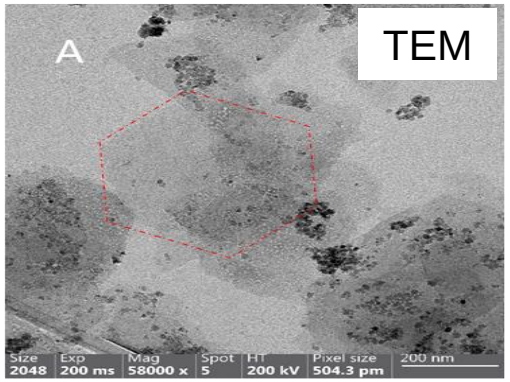
Step 2: Deposition of cathode CL on the cathode GDL (loading: 2 mg/cm^2).

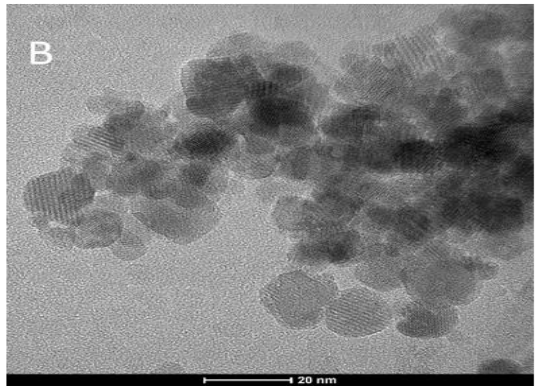
Step 3: Sandwich membrane between the anode and cathode gas diffusion electrodes (GDEs), and Teflon gaskets.

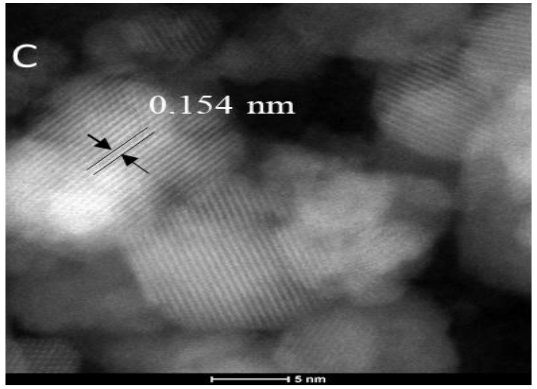


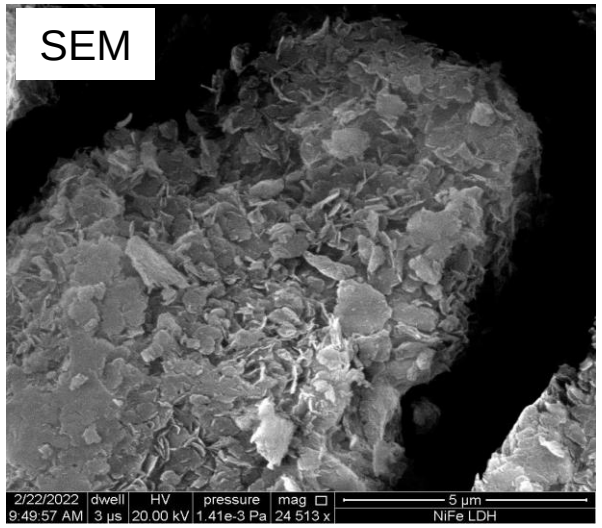


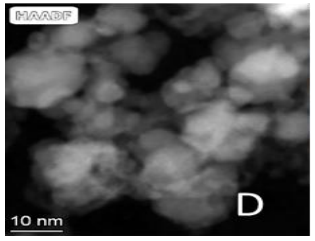
Characterization of the Anode Catalyst and GDE

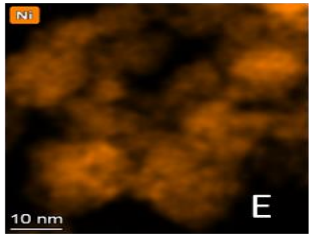


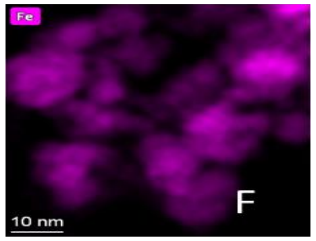


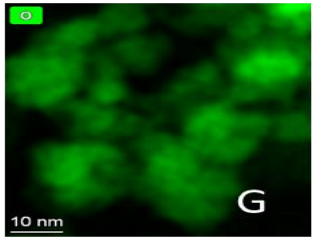


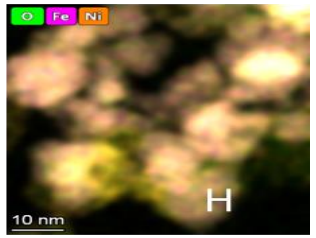


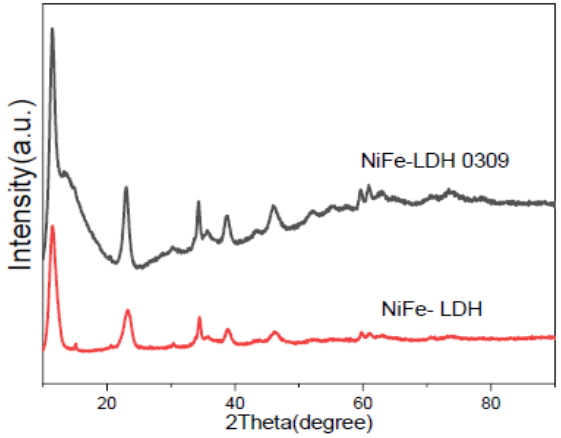




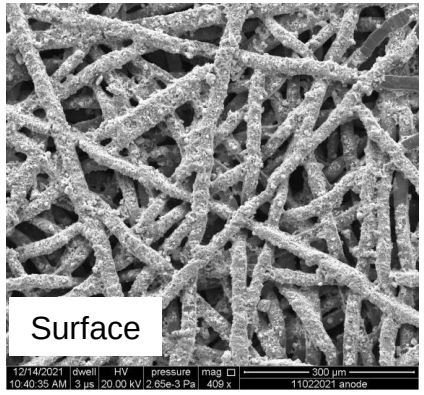


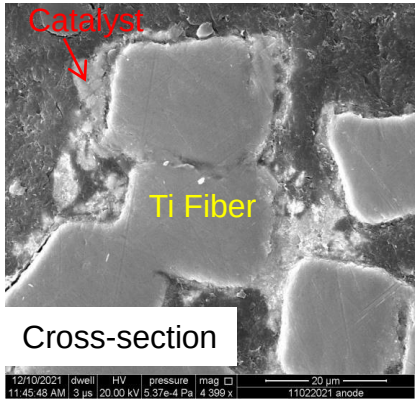






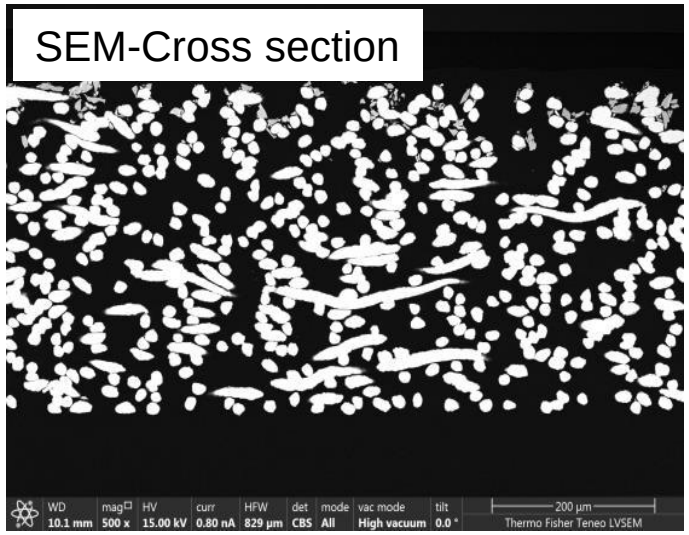
The XRD patterns for two batches of synthesized NiFe-LDH catalyst.

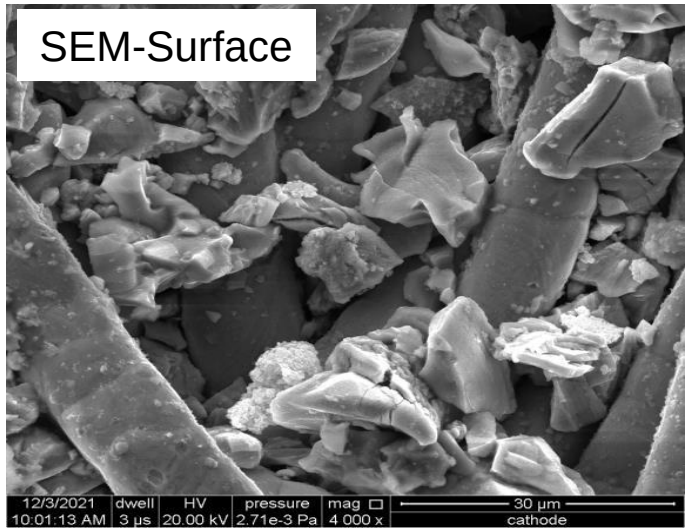


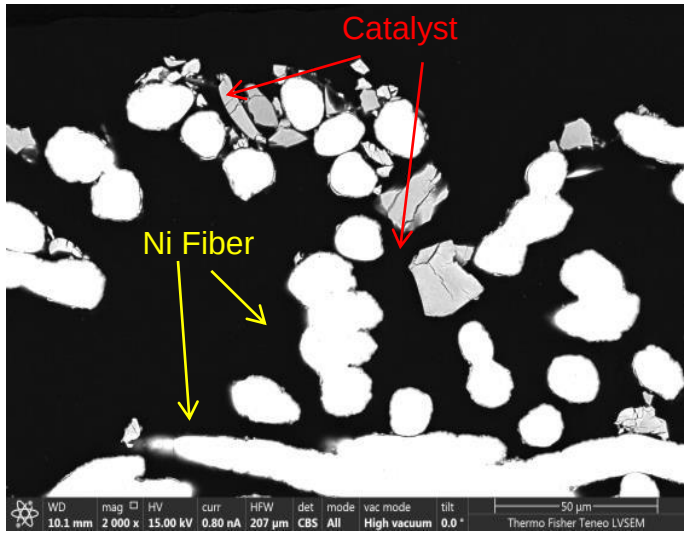


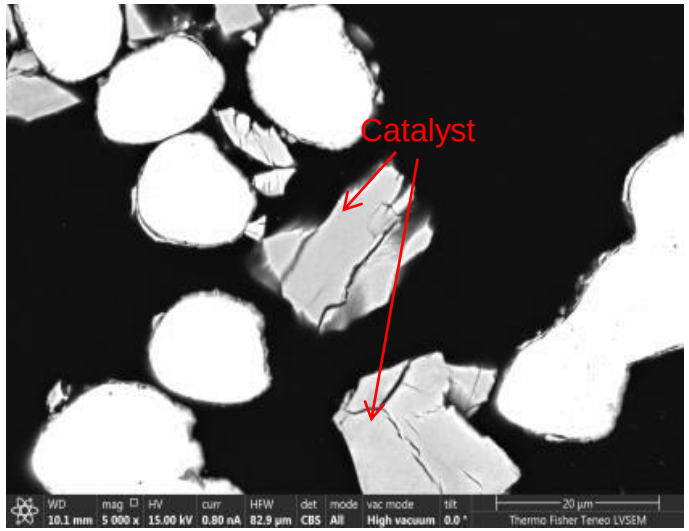
- The hexagonal shape of the synthesized NiFe layered double hydroxide (NiFe-LDH) nanoplatelets is clearly seen from the TEM image.
- From the SEM image, the layered structure of NiFe-LDH is clearly seen.
- Average particles size of the synthesized NiFe-LDH is 10 nm.
- EDS maps confirm that the catalyst is consisting of Ni(E), Fe(F) and O(G).
- The catalyst has well covered the GDL fibers at the surface.

Characterization of the Cathode GDE







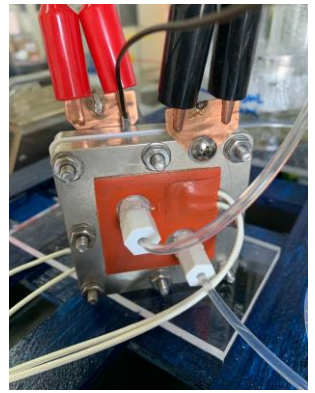


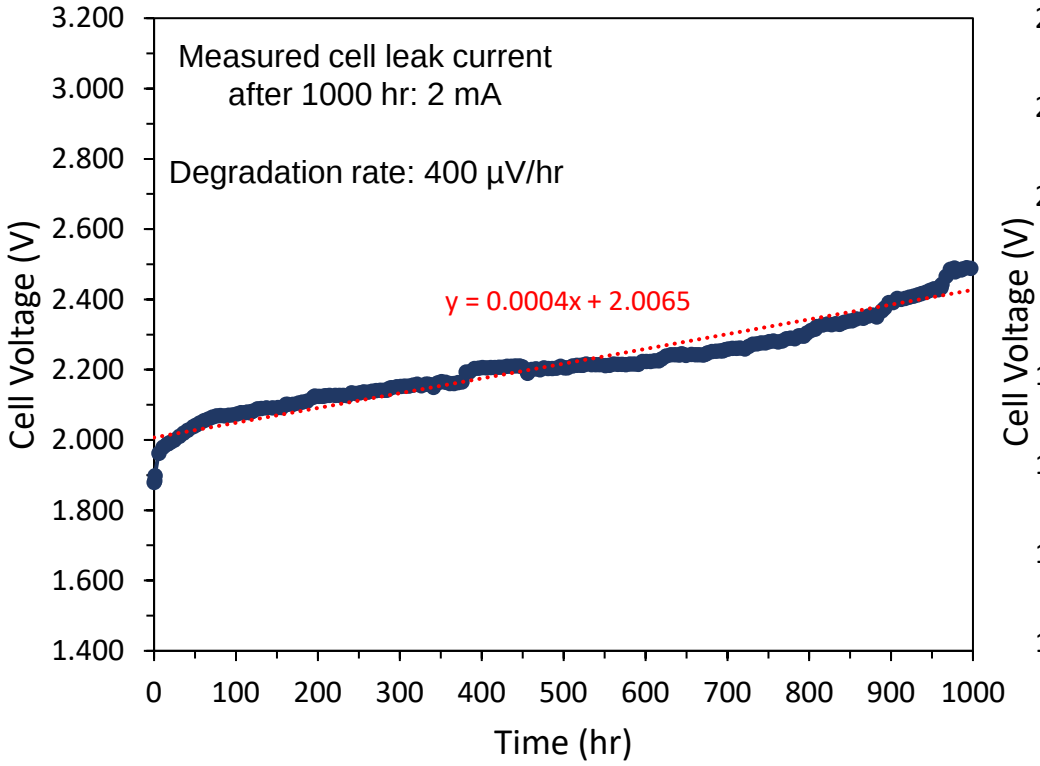
- The Raney nickel catalyst was coated on the Ni fiber felt.
- The catalyst has not entirely covered the GDL fibers at the surface.
- The Raney nickel catalyst particle size is <20 um.

Electrochemical Performance of the Fabricated MEA

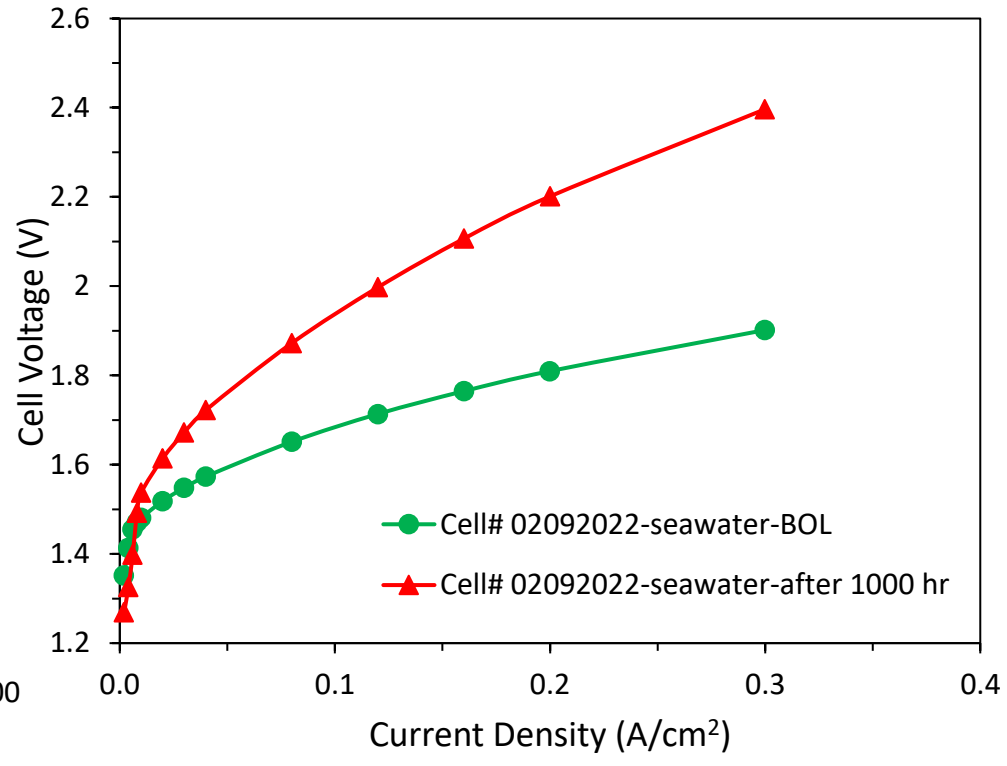
Milestone for 5 cm^2 cell durability of 1000 hr reached!

Cathode GDE: Activated Raney Ni catalyst, Loading of 2 mg cm^{-2}, 5 wt% Nafion ionomer, Ni fiber felt GDL; Anode GDE: NiFe-LDH catalyst, Loading of 2 mg cm^{-2}, 5 wt% Nafion ionomer, Platinized Ti fiber felt GDL; membrane: Sustainion® X37-50 grade T; 60 ˚C; Active area: 5 cm^2; Electrolyte: 1M KOH seawater





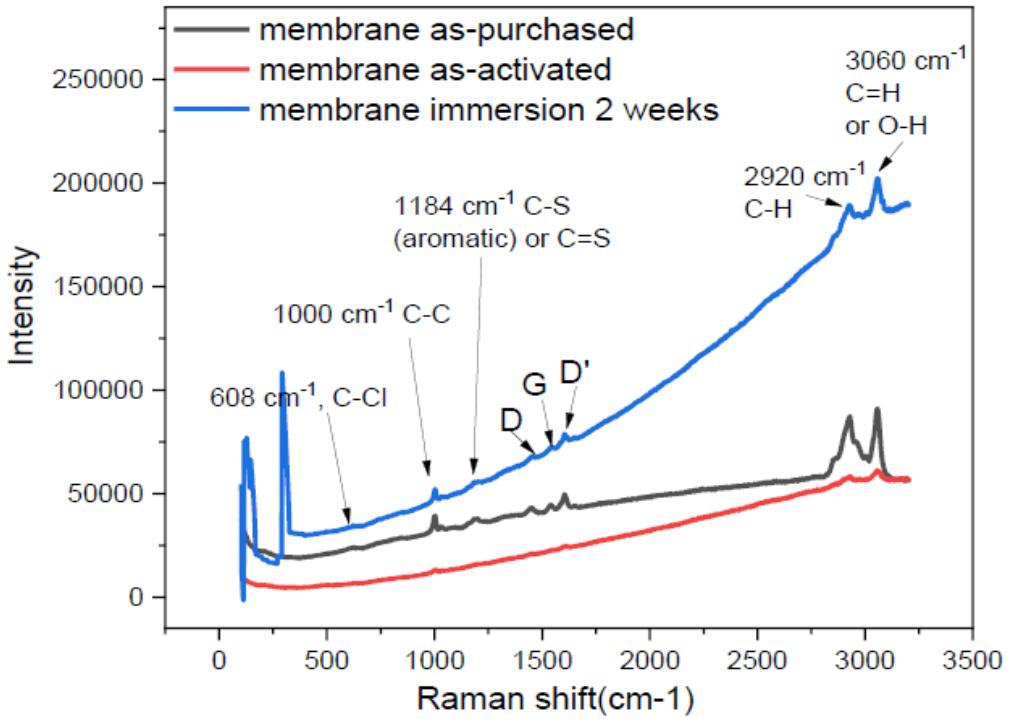
Cell voltage transients at constant current of 300 mA/cm^2 in 1M KOH seawater.

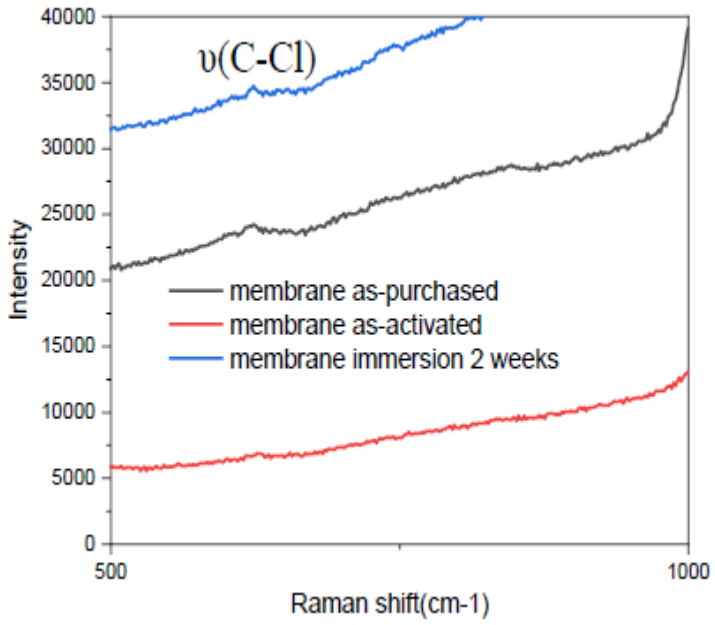


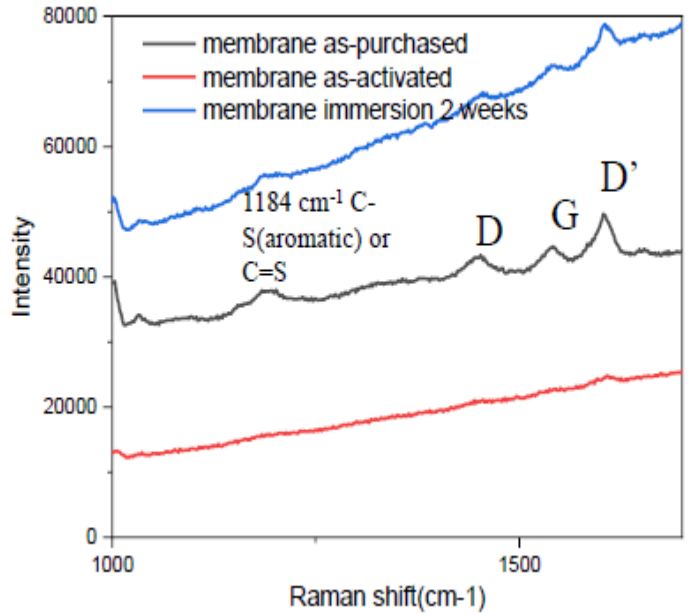
Polarization curves measured at BOL and after 1000 hr of cell operation in 1M KOH seawater.

- The 5 cm^2 single cell operated for 1000 hours (target 1000 hours) in seawater environment.
- The polarization curves show considerable ohmic loss after 1000 hours compared to BOL after the MEA voltage became stable (after ~1 hr).
- The increase in ohmic loss could be due to reduction in membrane ionic conductivity (see the next slide) and oxidation of the anodic components (decrease in electrical conductivity). The latter will be studied by Post-test analyses on cell/MEA.
- **The 1000 hr milestone has been met.**

Membrane Degradation in Seawater Electrolyte

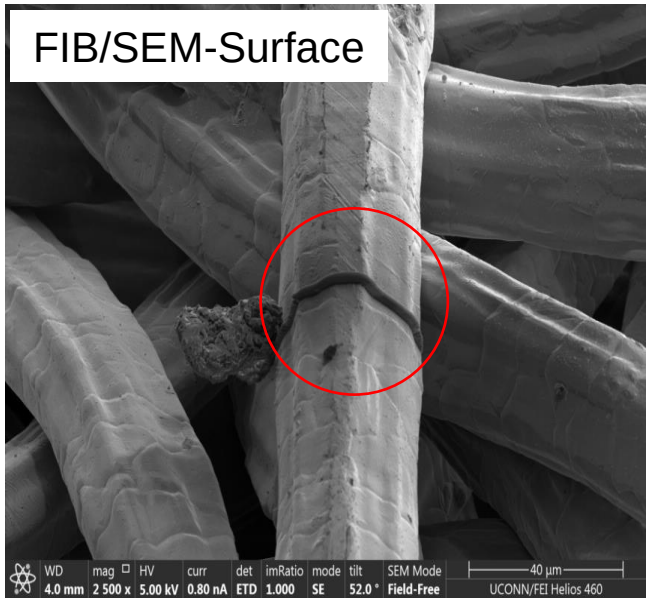


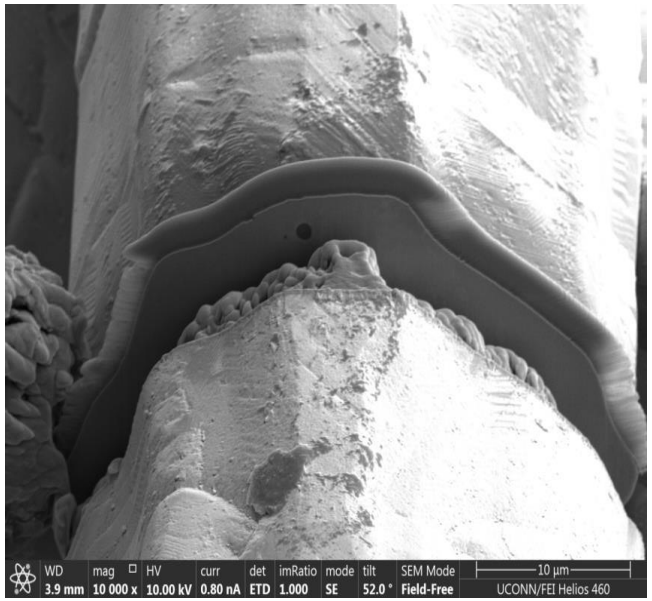


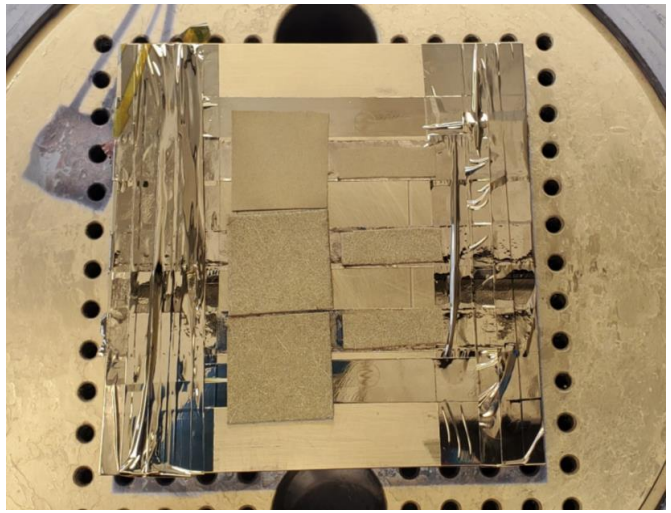


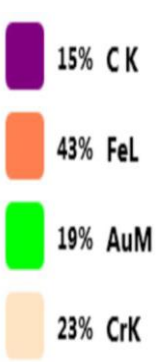
- Raman spectroscopy was conducted on three membrane samples: 1) as-purchased membrane, 2) as-activated membrane (soaked in 1 MKOH overnight to convert from Cl^- form to OH^- form), and 3) activated membrane which was then immersed in seawater electrolyte for 2 weeks.
- The low frequency peaks around 120 cm^{-1} and 300 cm^{-1} are likely from cosmic ray as they don't correspond to any reference vibrations.
- For the as-activated sample, the vibration of C-Cl is not clearly seen which could be associate with the fact that the Cl is replaced by OH as a result of the activation.
- For the immersed sample, the vibration of C-Cl is intensified which could be associate with the fact that the OH is replaced by Cl in seawater, decreasing the membrane conductivity over time.

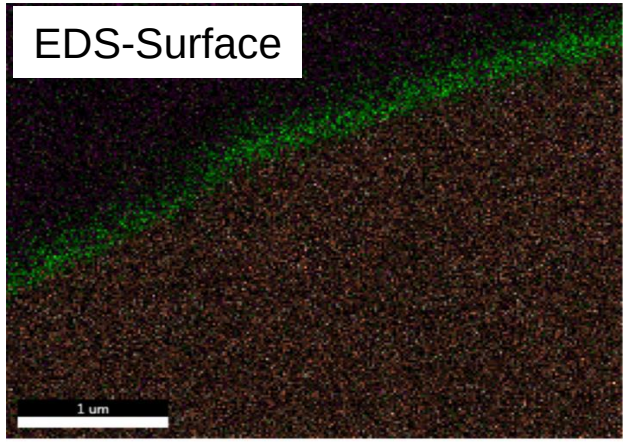
PVD Gold Deposition onto Stainless Steel, Nickel, and Titanium GDLs

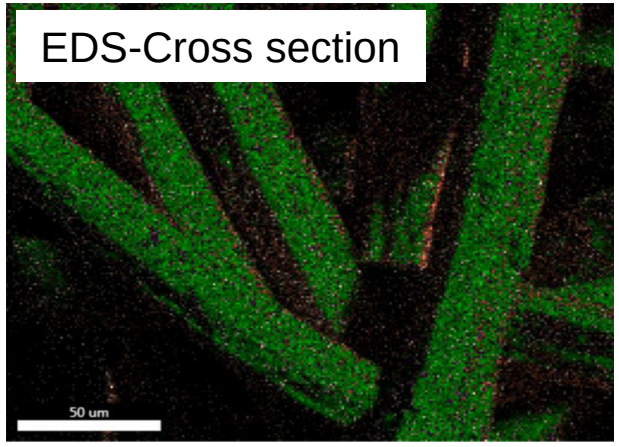






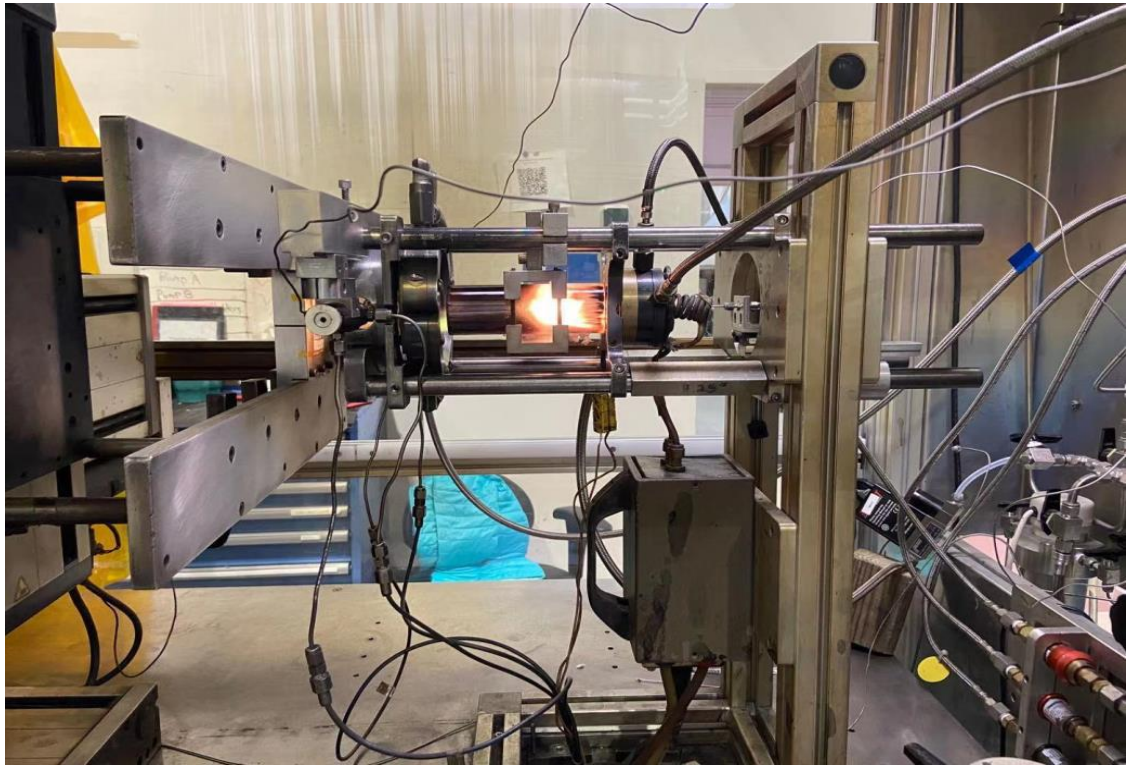


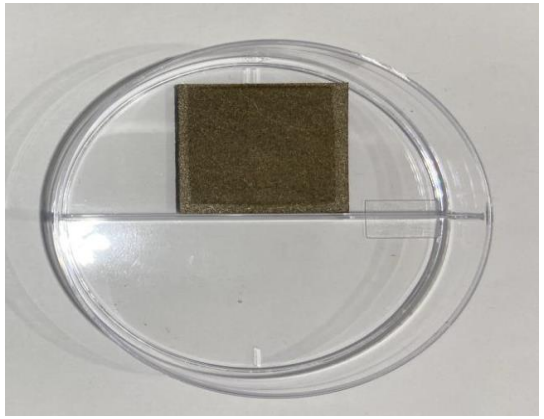


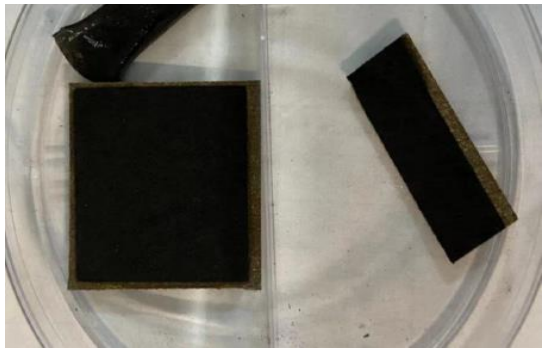


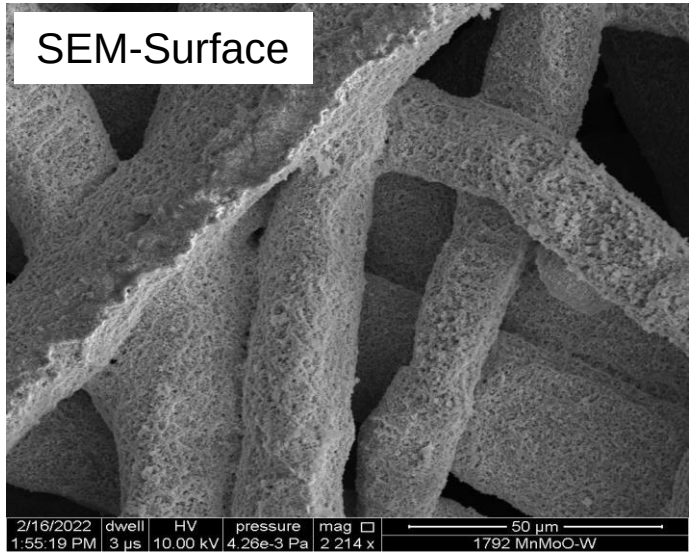
- Three GDL samples were loaded for Au deposition:
  1) Titanium Fiber Felt
  2) Stainless Steel Fiber Felt
  3) Nickel Fiber Felt
- The target thickness was 120 nm (1.2 KÅ). The
- Measured thickness was in the range of 110-120 nm.
- Total deposition time was for 9 minutes and 19 seconds.
- FIB/SEM was used to cut the width of a fiber and to take cross section measurements.
- The results verify that the surface of the GDLs is uniformly covered by Au.
- Further cross-sectional analysis is required to verify the coating's uniformity within the GDL's structure.

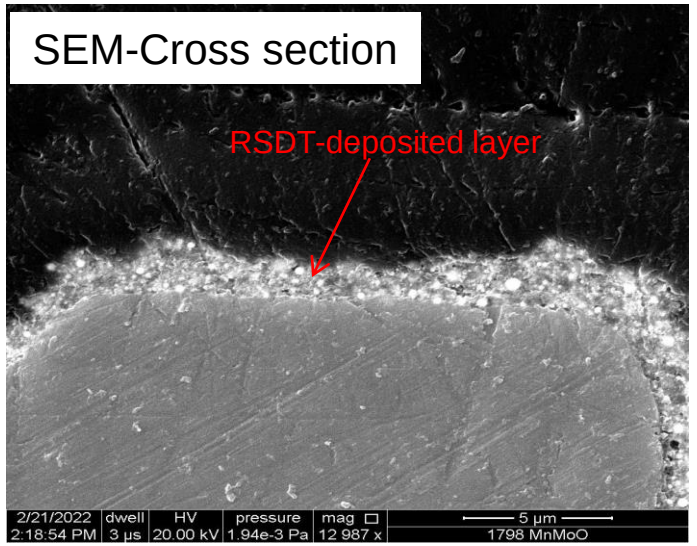
Initial RSDT Fabrication of Mn-Based Oxide Catalysts and Cl^- Barrier Layers





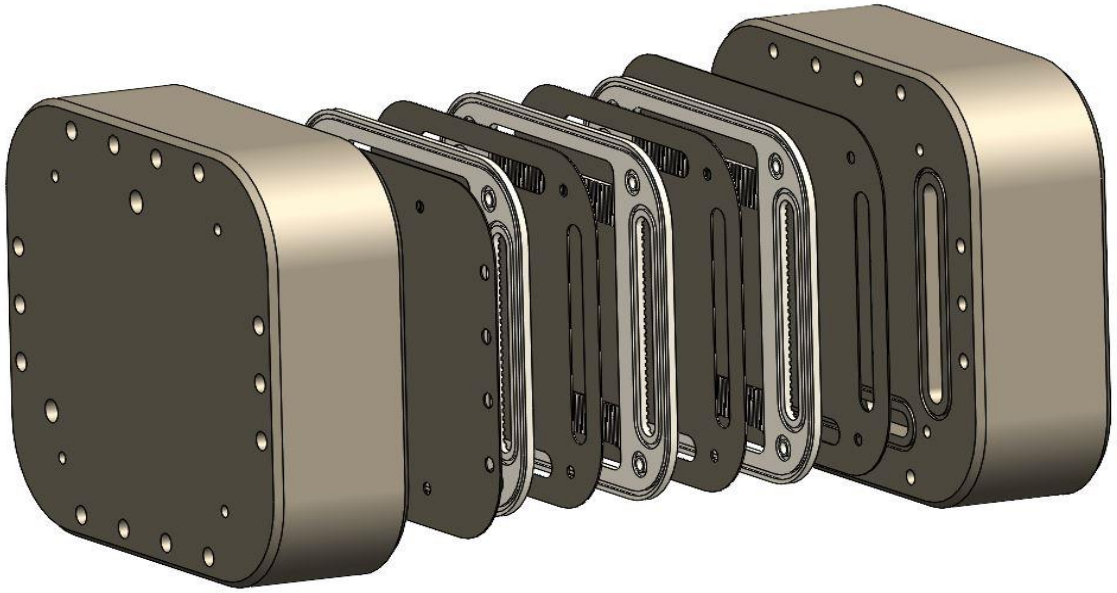


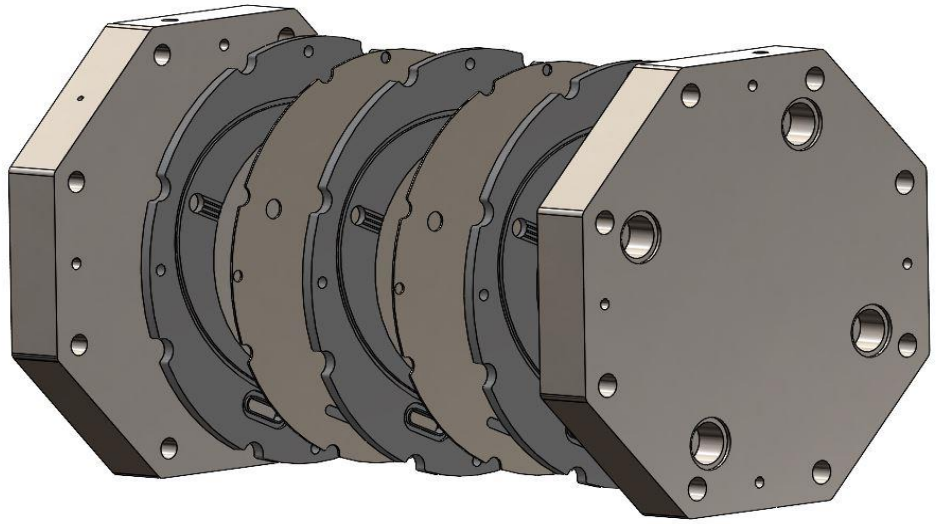




- Reactive Spray Deposition Technology (RSDT) has been used to deposit a uniform Mn-based oxide catalyst layers (i.e. $(Mn_{1-x}Mo_x)O_{2+x}$ and $Mn_{1-x-y}Mo_xW_yO_{2+x+y}$) and/or Cl^- barrier layers (i.e. MnO_2 and CeO_2) on the anode GDL.
- RSDT has been modified to deposit layers with desired loading and thickness.
- UConn is working on modifying RSDT parameters to deposit layers with desired chemical composition and electrical conductivity.

3-cell Stack Design (250 cm^2 Active Area Per Cell)





- SolidWorks 3D modelling software was used to generate two 3-cell stack designs: circular and rectangular.
- The circular design provides more uniform compression because the bolts are equally spaced from the center of the end plate.
- The rectangular design provides less material waste in MEA manufacturing and more confidence in flow field uniformity.
- End plate dimensions were optimized using Finite Element Analysis and the “design study” feature in the SolidWorks Simulation Add-in.
- Further discussion is required to determine which design will be used going forward.

Responses to Previous Year Reviewers' Comments

This project was not reviewed at the 2021 AMR

Collaboration and Coordination

Partners	Project Roles	Collaborative Relationship
Alchemr (Industry)	Project lead Management and coordination; MEA design; Electrode fabrication; Cell/stack testing and performance evaluation; Stack design and manufacturing	• Bi-weekly conference meetings • Technical progress reports discussions • Planning research activities • Quarterly reports, discussions and coordination • Site visits if required to address development needs
UCONN (University)	Sub Catalysts development; Catalyst and barrier layer coatings by RSDT; direct CCMs fabrication, materials analysis and characterization	

Remaining Challenges and Barriers

- Variability of wind power as well as cost of hydrogen production and transport to shore.
- Scale up the manufacturing process and demonstrate capabilities for fabrication of large (250 cm^2) MEAs with industrial significance.
  - Demonstrate functionality (V-t and I-V polarizations) of MEAs for a 3-cell stack with 250 cm^2 active area per cell.
  - Demonstrate stable performance for the 3-cell stack.
- Modify the anodic flowfield/current collector design and coating to avoid oxidation and improve cell durability.
- Synthesize and test Mn-base oxide catalyst with desired chemical composition and electrical conductivity.

Proposed Future Work

- Scale-up the MEAs fabrication size from 5 to 250 cm^2, with catalysts loading of 2 mg/cm^2 for both cathode and anode electrodes.
- Finalize the 3-cell stack design, build the stack, and modify safety system and balance of plant.
- Test the 3-cell stack (750 cm^2 active area) at 0.3 A/cm^2 in seawater environment and demonstrate identical or better performance with the 5 cm^2 MEA.
- Perform post-test analyses of the 5 cm^2 cell/MEA operated for 1000 hours in seawater environment by different techniques such as EIS, HRTEM, STEM, XRD, EDS, SEM, ICP, XPS, and XCT and identify the potential degradation mechanisms.
- Determine the optimal chemical composition of the Mn-based oxide catalysts fabricated by RSDT or any other alternative synthesis methods.
- Verify the uniformity of PVD gold coated GDLs with SEM and TEM.
- Fabricate catalyst-coated membrane (CCM) using RSDT.
- Perform start/stop cycling test on 5 cm^2 cell for AEM seawater electrolysis.
- Improve our techno-economic model for future commercial implementation.

Summary

Objective:

Demonstrate a low-cost anion exchange membrane water electrolyzer (AEMWE) for direct coupling to offshore wind farms, with the ability to operate using seawater.

Accomplishments (August 2021 – April 2022):

- ✓ Developed a non-PGM OER-selective NiFe-LDH anode catalyst for seawater electrolysis.
- ✓ Developed anode flowfield/current collector/GDL for seawater electrolysis.
- ✓ Demonstrated long-term performance of 5 cm^2 AEM seawater electrolyzer cell with non-PGM anode and cathode catalysts at 0.3 A/cm^2, 60 ^oC.
- ✓ Demonstrated durability of the MEA for 1000 hours with 400 microvolts/hour degradation rate for seawater electrolysis.
- ✓ Tested different RSDT-fabricated Cl^- barrier layers.

Approach:

- ✓ Optimize RSDT parameters for fabrication of Mn-based oxide anode catalysts.
- ✓ Finalize the 3-cell stack design and build the stack for more hydrogen production.
- ✓ Evaluate the 3-cell stack performance at 0.3 A/cm^2, 60 ^oC.
- ✓ Examine the MEA degradation modes after 1000 hours of operation in seawater environment.
- ✓ Develop a high-performance CCM by RSDT for seawater electrolysis.
- ✓ Evaluate stability of the MEA under cycling condition (start/stop) in seawater environment.

Technical Backup and Additional Information

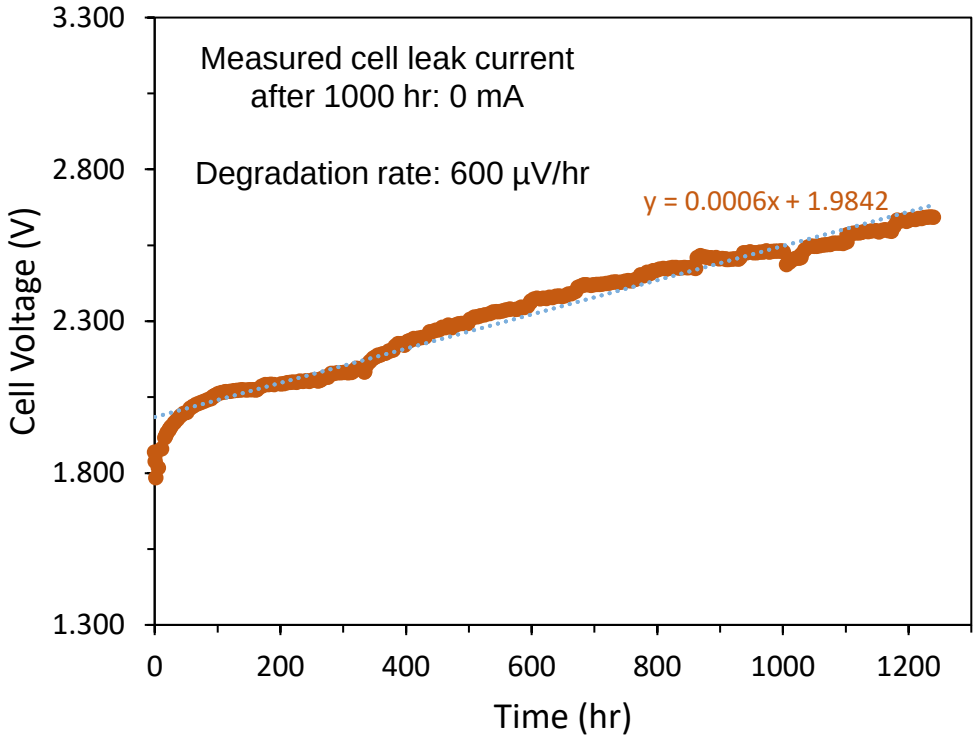
Technology Transfer Activities

Alchemr and UConn have an Intellectual Property Agreement which provides Alchemr with an option to an exclusive license in its field to any Project IP or UConn Background IP that may be necessary for the commercialization of its seawater electrolyzers.

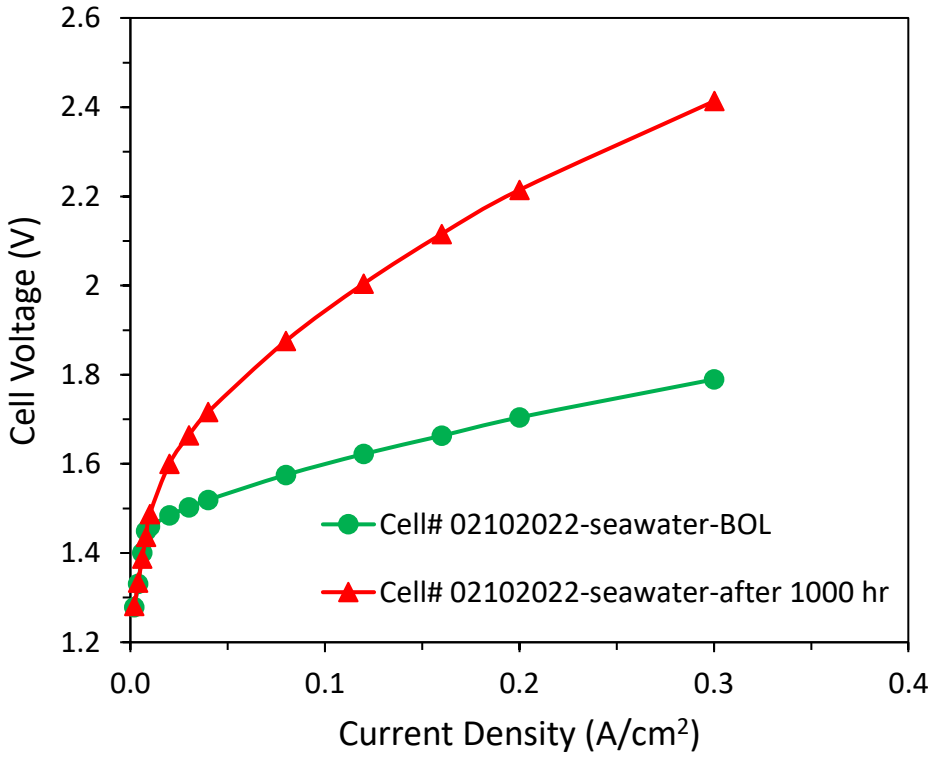
Electrochemical Performance of the Fabricated MEA (2nd cell)

Milestone for 5 cm^2 cell durability of 1000 hr reached! The result was repeatable.

Cathode GDE: Activated Raney Ni catalyst, Loading of 5 mg cm^{-2}, 5 wt% Nafion ionomer, Ni fiber felt GDL; Anode GDE: NiFe-LDH catalyst, Loading of 2 mg cm^{-2}, 5 wt% Nafion ionomer, Platinized Ti fiber felt GDL; membrane: Sustainion® X37-50 grade T; 60 ˚C; Active area: 5 cm^2; Electrolyte: 1M KOH seawater



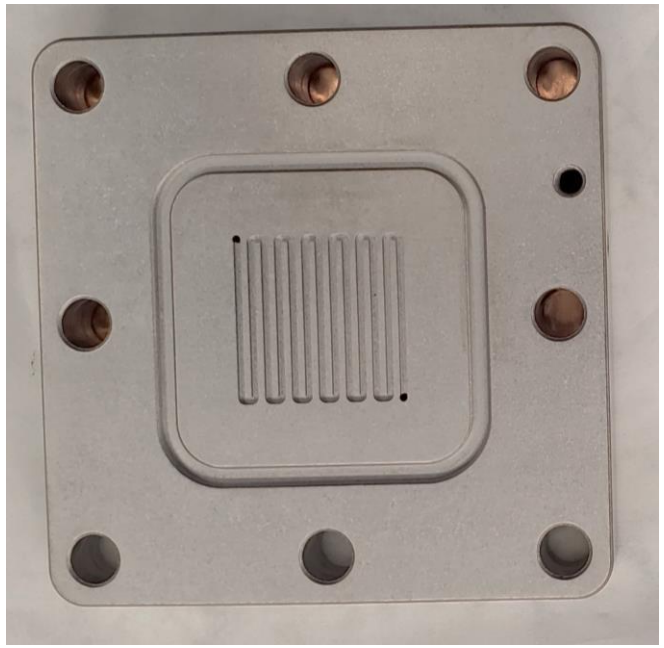
Cell voltage transients at constant current of 300 mA/cm^2 in 1M KOH seawater.



Polarization curves measured at BOL and after 1000 hr of cell operation in 1M KOH seawater.

- As of April 15th, 2022, the 2nd 5 cm2 single cell has also been operating for over 1200 hours in seawater environment (target 1000 hours).
- The polarization curves show considerable ohmic loss after 1000 hours compared to BOL after the MEA voltage became stable (after ~1 hr).

PVD Gold Deposition onto Ti Flowfield/Current Collector

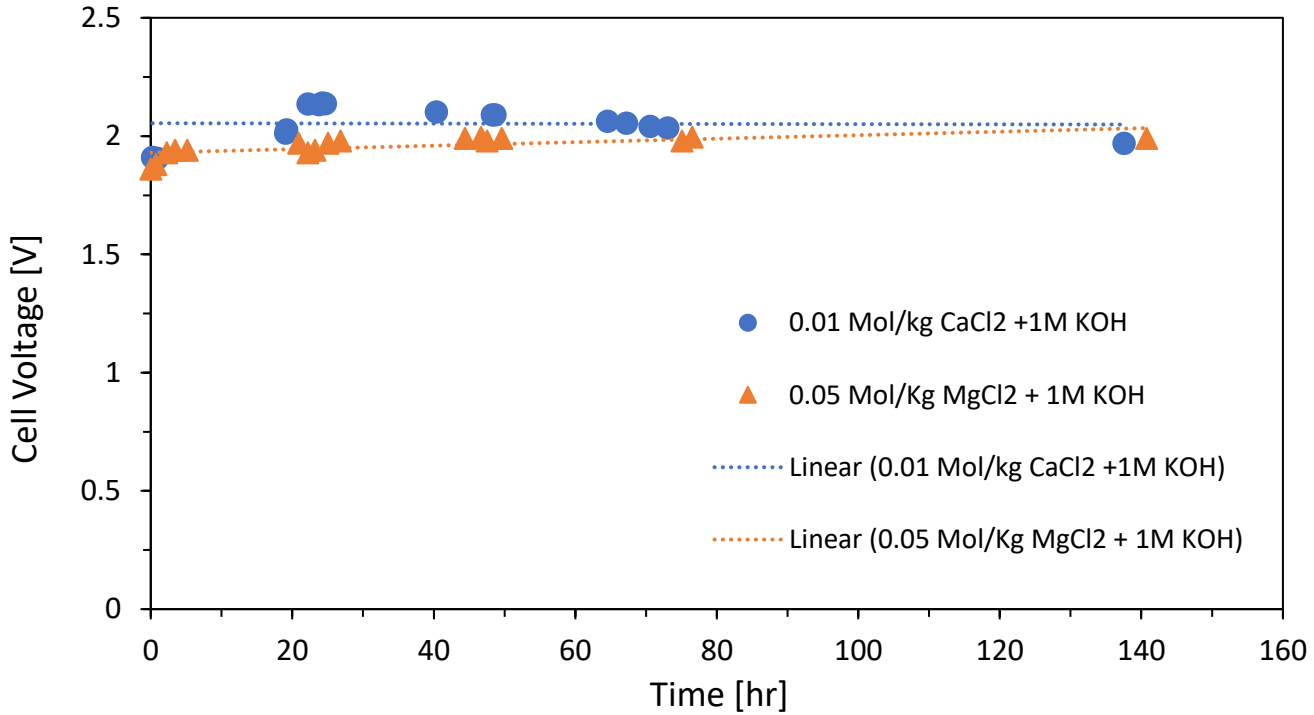


After removing the surface oxides

After PVD deposition of ~100 nm thin film Au

- A Ti flowfield/current collector used in 5 cm2 cell was PVD coated using gold.
- The very thin layer of gold coating is to protect the Ti surface from oxidation during long-term cell operation in seawater environment.
- The gold coated Ti flowfield/current collector will be tested in the cell.

5 cm^2 AEMWE Cell Tested with $MgCl_2$- and $CaCl_2$-Containing Feedstock



- This figure shows our cell stability in the presence of calcium and magnesium salts.
- For this test, Alchemr 5 cm^2 cell was assembled using Sustainion® X37-50 grade RT membrane, cathode electrode was made out of Raney nickel catalyst coated on nickel fiber paper and anode electrode was made out of $NiFeO_x$ based catalyst coated on stainless steel fiber paper. $MgCl_2$ and $CaCl_2$ were used to prepare electrolyte with 0.05 mol/kg of $MgCl_2$ (cell 1) and 0.01 mol/kg $CaCl_2$ (cell 2). These electrolyte concentrations were designed to match the Ca^{2+} and Mg^{2+} concentrations in seawater.
- The results indicate no major cell voltage loss over 120 hours.

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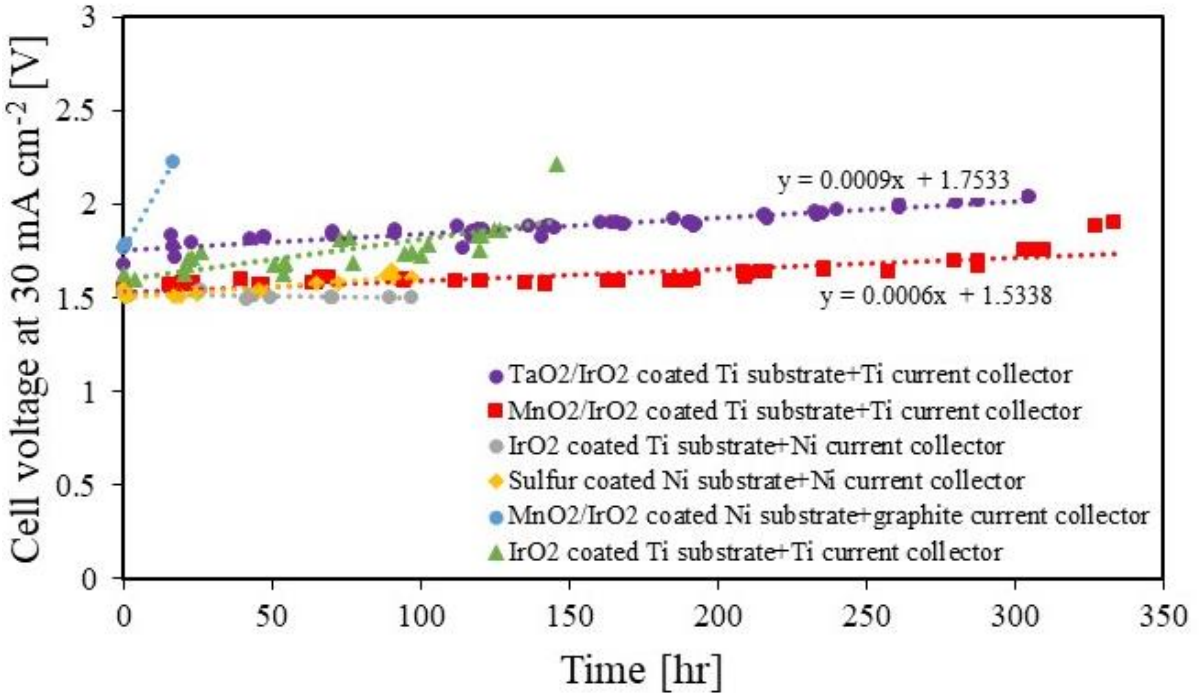
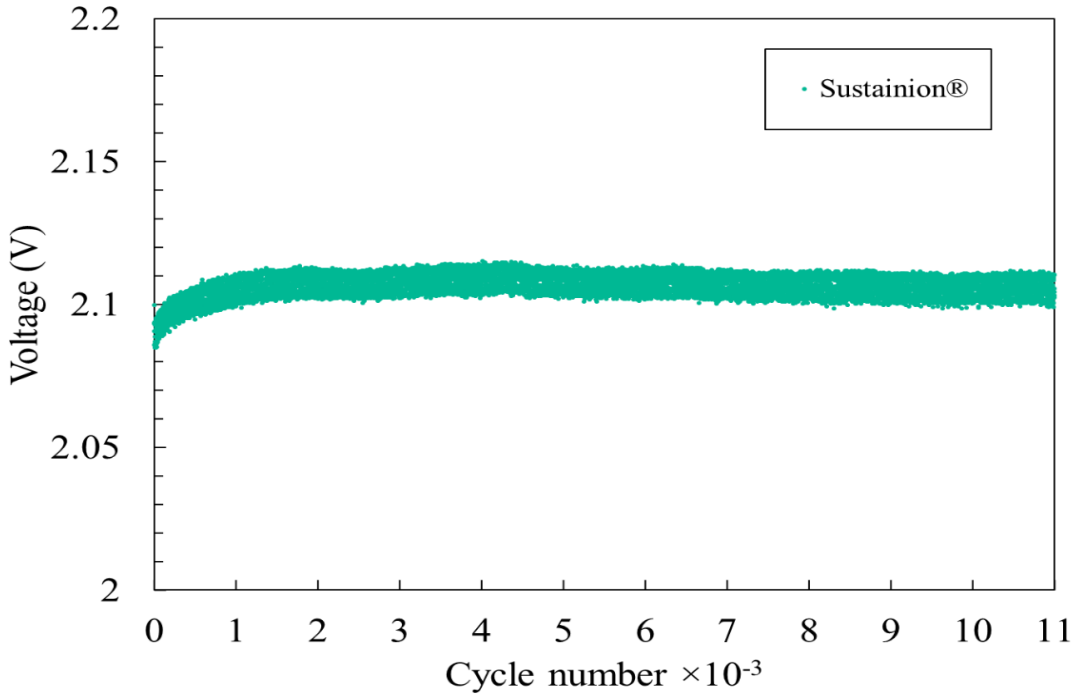
Different Cell Configurations tested in Phase I for AEM Seawater Electrolysis



- This figure shows the different cell performances at 30 mA/cm^2 , 60 °C in 1M KOH seawater electrolyte.
- The results indicate that anode electrode configurations of TaO_2/IrO_2 catalyst coated Ti substrate and MnO_2/IrO_2 catalyst coated Ti substrate show low degradation of 0.9 and 0.6 mV/hr, respectively. No corrosion on the electrode or titanium flowfield/current collector was observed during the 300 hours of operation.
- In Phase II, we improved the cell performance (current density increased by a factor of 10, up to 300 mA/cm^2) and durability (>1000 hr) using non-PGM anode catalyst.

Voltage Shock/Cycling Test in 1 M KOH electrolyte, 60 °C



- Cycling current or voltage has been used as a fast and informative durability test of MEAs for various electrochemical applications. Alchemr tested the durability of our 5 cm^2 AEMWE using the following components: Sustainion® membrane; Raney nickel-based catalyst coated onto nickel fiber paper (cathode); $NiFeO_x$ catalyst coated on stainless steel fiber paper (anode).
- The cell was cycled between 100 mA and 12,000 mA for 11,000 cycles to simulate abusive conditions through rapid voltage spikes.
- The rate of voltage increase per cycle is 0.15 µV/cycle for the virgin membrane. The degradation rate is very low, indicating that the membrane is stable under these abusive conditions.

Publications and Presentations

- Behrooz Motealleh, Zengcai Liu, Rich I. Masel, Julian P. Sculley, Zheng Richard Ni, and Laureen Meroueh. "Next-generation Anion Exchange Membrane Water Electrolyzers Operating for Commercially Relevant Lifetimes" International Journal of Hydrogen Energy 46, no. 5 (2021): 3379-3386.

- Jiale Xing, Zhiqiao Zeng, Arkid Koni, Stoyan Bliznakov, Gholamreza Mirshekari, Wesley Best, Lauren Sammmes, Leonard Bonville, Radenka Maric. “One-step Synthesis of Selective NiFe-Layered Double Hydroxide Anode Catalyst for Highly Efficient and Stable Anion Exchange Membrane Water Electrolyzers, Operating with Seawater” 242nd ECS meeting, Atlanta, GA (2022).