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

H2NEW: Hydrogen (H2) from Next-generation Electrolyzers of Water LTE Task 9: Liquid alkaline

Meital Shviro NREL; Alexey Serov, ORNL; Xiong Peng, LBNL; Pietro Papa Lopes, ANL; Sandip Maurya, LANL;

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Project ID #P196h

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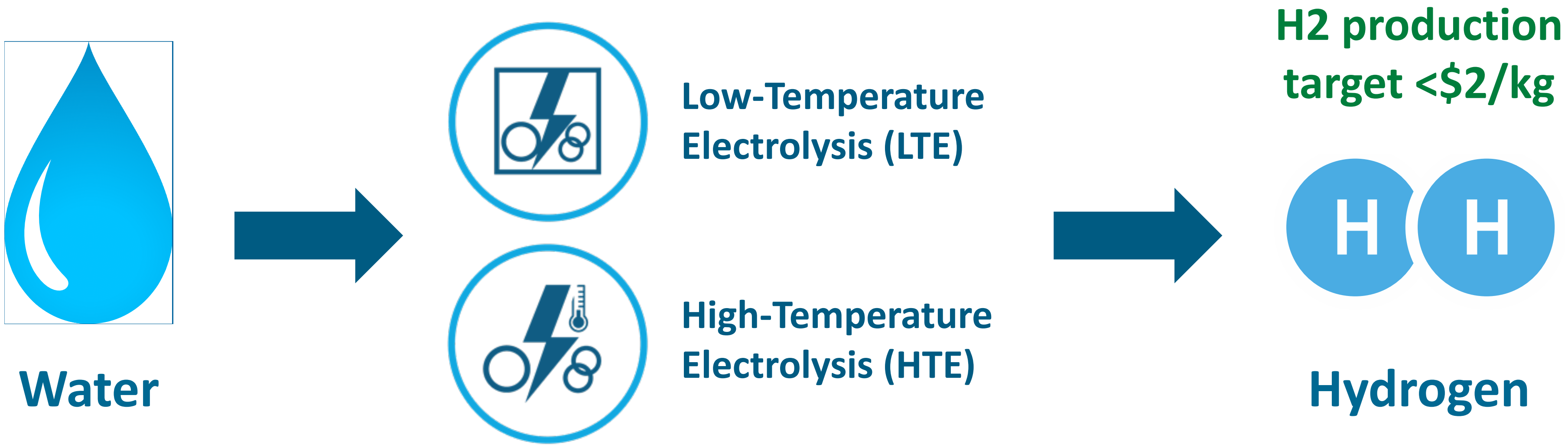
Project Goals

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.



Water

Low-Temperature Electrolysis (LTE)

High-Temperature Electrolysis (HTE)

H2 production target <\$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

Relevance: Liquid Alkaline Water Electrolysis

- Mature Technology?
  - Yes, but …
    - Designed for 24/7 steady-state operation
    - Dynamic operation challenges significant (needed for low-cost electrons/energy systems integration)
    - Power density low (turndown capability limited)
    - Degradation not understood, particularly under dynamic operation
- Research needs
  - Explore optimized operating strategies, quantify durability impacts
    - Maximum/minimum operating conditions (turndown capability limit key concern for economics)
    - Impact/ability to tolerate start-up/shut-down
  - Achieve higher operating current density (lower cell resistance, engineered separator)
  - Reduce minimum turndown (gas crossover reduction, engineered separator)
  - Improve efficiency (improved catalysis, engineered separator)
  - Improve durability (mitigation strategies)
  - Increased pressure operation (cell operating strategy, engineered separator)
  - Systems and Techno-economic Analysis (system design, operating strategy, hydrogen levelized costs)

Overview : H2NEW LTE Task 9:Liquid alkaline

Timeline and Budget

- Start date (launch): January 1, 2023
- Awarded through September 30, 2025
- FY24 DOE funding: ~$5M

Barriers/Targets

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

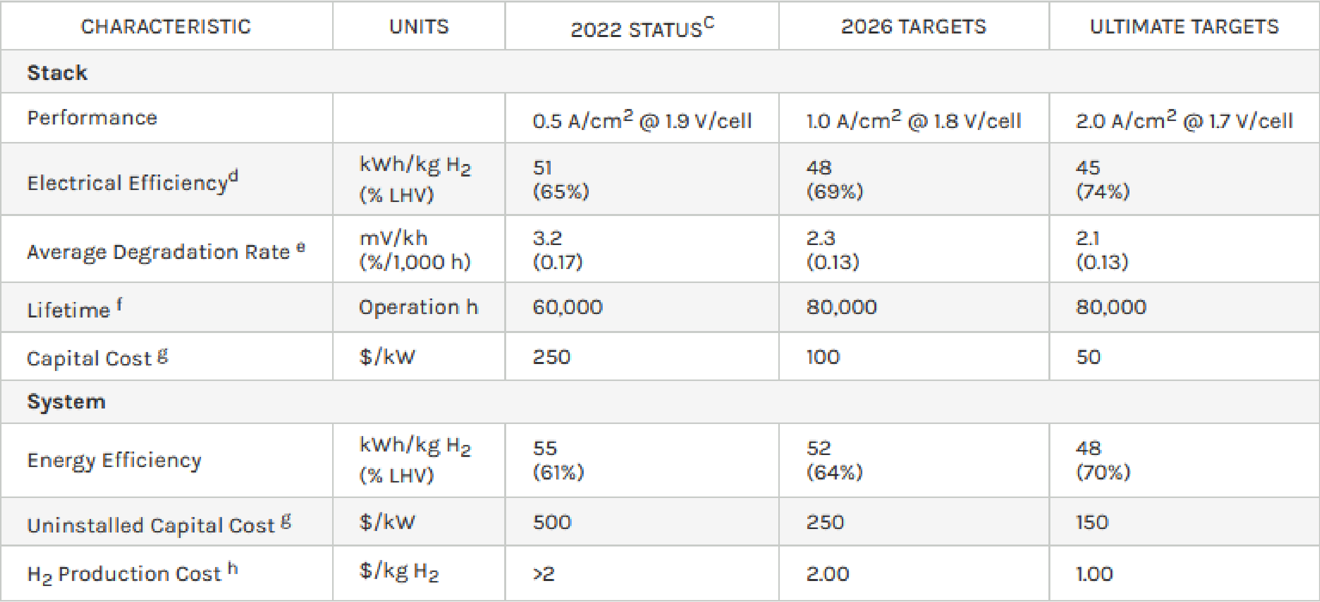
Consortium Task Team

Task Lead:
Bryan Pivovar (NREL)
Meital Shviro(NREL)

Other lab leads:
Xiong Peng (LBNL)
Sandip Maurya (LANL)
Pietro Papa Lopes (ANL)
Alexey Serov (ORNL)

Relevance and Impact

Technical Targets for Liquid Alkaline Electrolyzer Stacks and Systems



CHARACTERISTIC	UNITS	2022 STATUS[C]	2026 TARGETS	ULTIMATE TARGETS
Stack				
Performance		0.5 A/cm^2 @ 1.9 V/cell	1.0 A/cm^2 @ 1.8 V/cell	2.0 A/cm^2 @ 1.7 V/cell
Electrical Efficiency[d]	kWh/kg H_2 (% LHV)	51 (65%)	48 (69%)	45 (74%)
Average Degradation Rate [e]	mV/kh (%/1,000 h)	3.2 (0.17)	2.3 (0.13)	2.1 (0.13)
Lifetime [f]	Operation h	60,000	80,000	80,000
Capital Cost [g]	$/kW	250	100	50
System				
Energy Efficiency	kWh/kg H_2 (% LHV)	55 (61%)	52 (64%)	48 (70%)
Uninstalled Capital Cost [g]	$/kW	500	250	150
H_2 Production Cost [h]	$/kg H_2	>2	2.00	1.00

- Task 9 focuses on performance, components engineering, degradation and develop appropriate stack cost, performance, and durability targets.

https://www.energy.gov/eere/fuelcells/technical-targets-liquid-alkaline-electrolysis

Approach: Task 9 Work Breakdown

Task 9a: Degradation

i. Understanding and mitigation degradation
ii. Ex situ studies of components and interfaces
iii. AST developments
  - Determine key stressors
  - Development and validation of AST protocols

Task 9b: MEA Performance

i. Benchmarking, Validation
  - testing capability in liquid alkaline 7M ambient pressure,
  - Baseline study using state of the art components Standardized testing protocol
ii. Cell Performance
  - Model impact, develop understanding of structure and function, aid in design of new structures
iii. Cell level modeling

Task 9c: Scale-up-Integration Challenges

i. MEA fabrication, interface engineering
  - Different techniques for catalyst coating
  - Characterization of cell components
ii. Component engineering
  - Modification of Zirfon
  - Zirfon alternatives
iii. Systems/Technoeconomic analysis
  - System design, operating strategy, and performance tradeoffs
  - Identifying key differences in performance and cost between PEM and LAWE

Approach: Milestones

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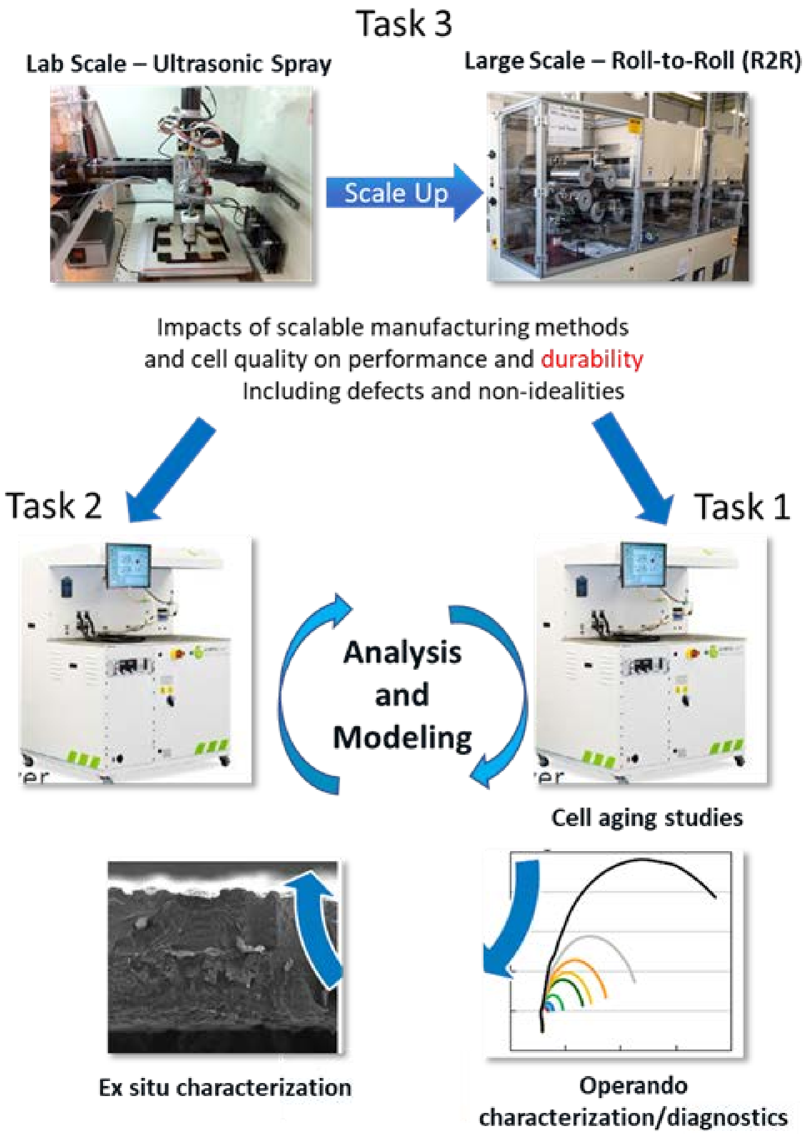
Milestone Name/Description	Due Date	Type	Status
Define the list of cell components to be established as the LAWE H2NEW baseline (including separator and electrodes)	12/31/23	QPM	Completed (Slide 11)
Perform screening tests on stainless steel (SS) and Ni for dissolution measurements under controlled potential by ICP-MS.	12/31/23	QPM	Completed (Slides 17-19)
Develop and validate a reference electrode system to be used as a probe for LAWE cell degradation.	3/31/24	QPM	Completed (Slide 20)
Incorporate multiphase flow physics into existing 1D and 3D cell models.	3/31/24	QPM	Completed (Slides 22-24)
Investigate activation protocol and establish a standard procedure with the baseline LAWE components based on reproducibility, break-in time, and initial stability.	6/30/24	QPM	In Progress (Slide 12)
Perform systematic studies of durability under multiple test conditions (potential/current hold, potential cycling) for comparison between standard operation and accelerated test conditions using the LAWE baseline cell.	6/30/24	QPM	In Progress (slide 16)
Perform and compare pre/post-mortem analysis for baseline cells with multiple characterization techniques to understand degradation mechanisms (SEM/EDS, XPS, XCT, FIB-SEM, electrochemical)	9/30/24	QPM	In progress
Demonstrate agreement in single-cell performance between H2NEW labs within +/- 50 mV at 1 A/cm2 at $V < 2.0V$ and operating temperature > 60 ^{o}C.	9/30/24	Annual	In progress

Approach: Advanced Liquid Alkaline Electrolysis

Significant parallels to H2NEW approach for PEM

- Durability
  - Establish fundamental degradation mechanisms
  - Develop accelerated stress tests
  - Determine cost, performance, durability tradeoffs
  - Develop mitigation
- Performance
  - Benchmark performance
  - Novel diagnostic development and application
  - Cell level models and loss characterization
- Scale-up
  - Transition to mass manufacturing
  - Correlate processing with performance and durability
  - Guide efforts with systems and technoeconomic analysis



Task 3

Lab Scale – Ultrasonic Spray

Scale Up

Large Scale – Roll-to-Roll (R2R)

Impacts of scalable manufacturing methods and cell quality on performance and durability Including defects and non-idealities

Task 2

Analysis and Modeling

Task 1

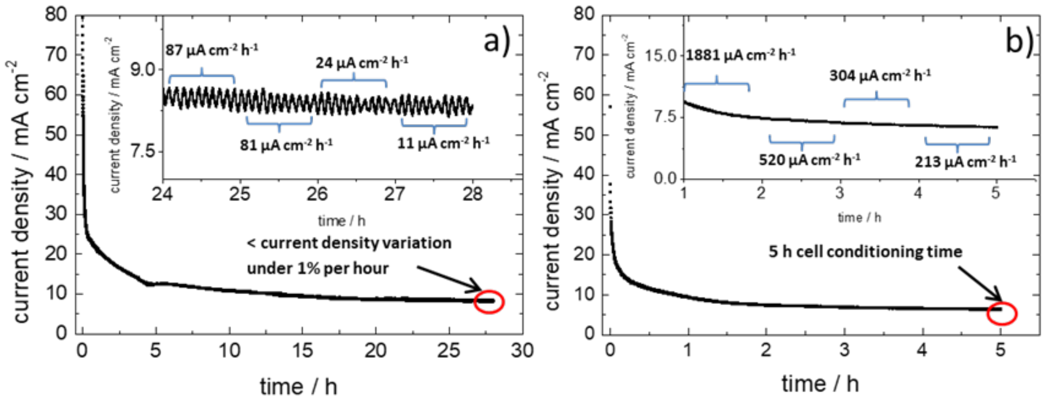
Cell aging studies

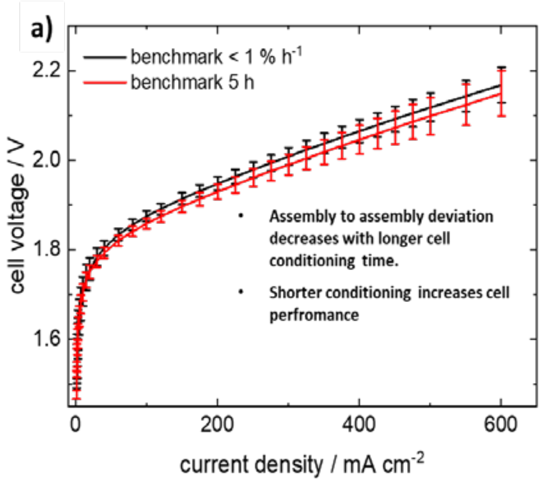
Ex situ characterization

Operando characterization/diagnostics

Accomplishments and Progress: Motivation for Baselining and Round Robin Testing

- **Similar motivation to PEM Benchmarking**: Comparison of literature data is difficult due to differences in setups and cell designs
- **Starting point:** 2022 Jülich paper “Challenges and important considerations when benchmarking single-cell alkaline electrolyzers”
- **Goal:** Development of harmonized testing protocols to improve comparability between research results



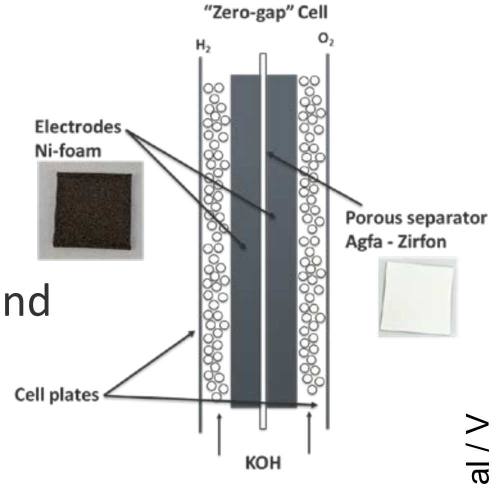


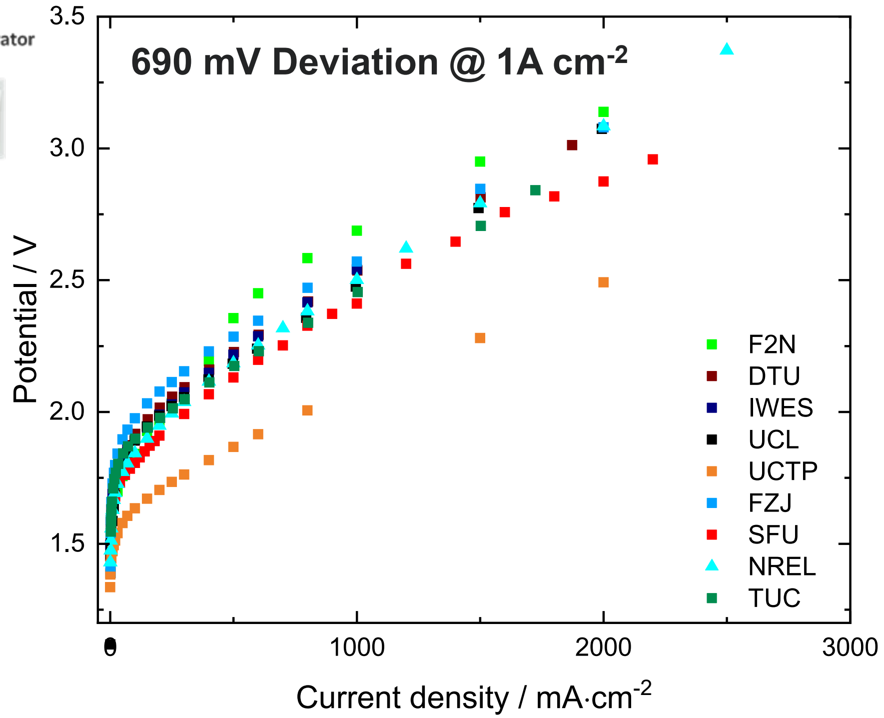
C. Karacan...M. Shviro et al., international journal of hydrogen energy 47 (2022) 4294

Accomplishments and Progress: Baselining and Round Robin test

iea International Energy Agency

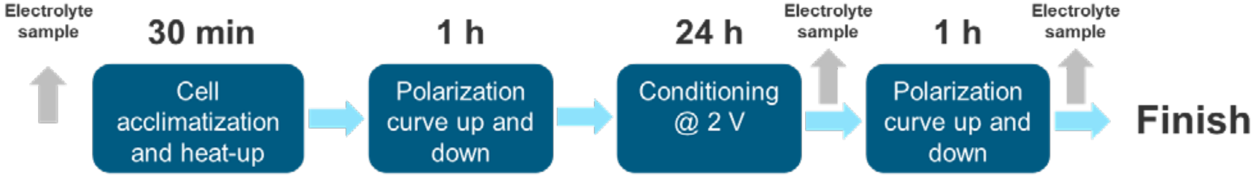
- Cell designed by FZ Jülich and fabricated by one contractor for all participants (9 groups)
- Industry standard separator Zirfon® Perl UTP 500 and Nickel foam from Alantum (thickness of 1.5mm)
- Large deviations are visible
  - Iron availability in electrolyte differs
  - Different heating methods
  - Deviations in flow and electrolyte concentration





Comparison of the polarization curve between participants

Next:
- ➢ Harmonization of iron content in the electrolyte
- ➢ Harmonization of temperature measurement and heating


Electrolyte sample

30 min: Cell acclimatization and heat-up

1 h: Polarization curve up and down

24 h: Conditioning @ 2 V

Electrolyte sample

1 h: Polarization curve up and down

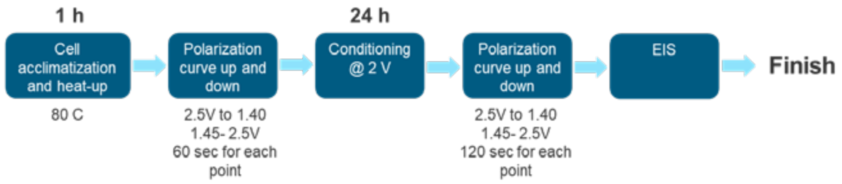
Electrolyte sample

Finish

Accomplishments and Progress: H2NEW Baselining

- Using same cell components :

  Electrodes: Ni foam 300 micron; Separator: Zirfon UTP 500
- Comparable results between LBNL and NREL, slight deviation at LANL
- Additional efforts to further align performance look at
  - Deviations in electrolyte concentration
  - Other Ohmic effects


1 h
Cell acclimatization and heat-up → Polarization curve up and down → Conditioning @ 2 V → Polarization curve up and down → EIS → Finish

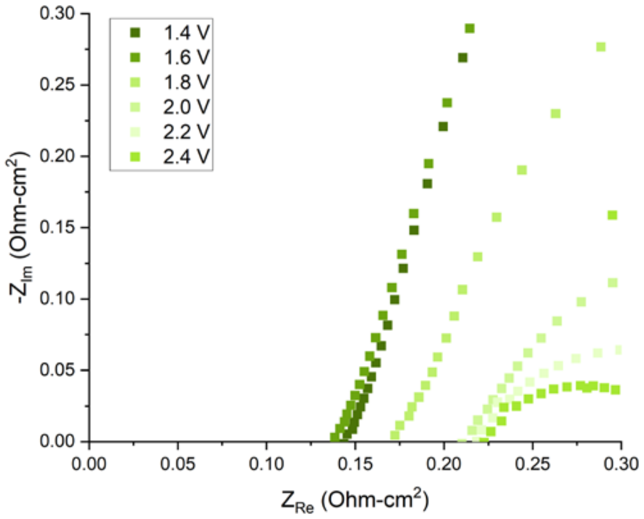
80 C

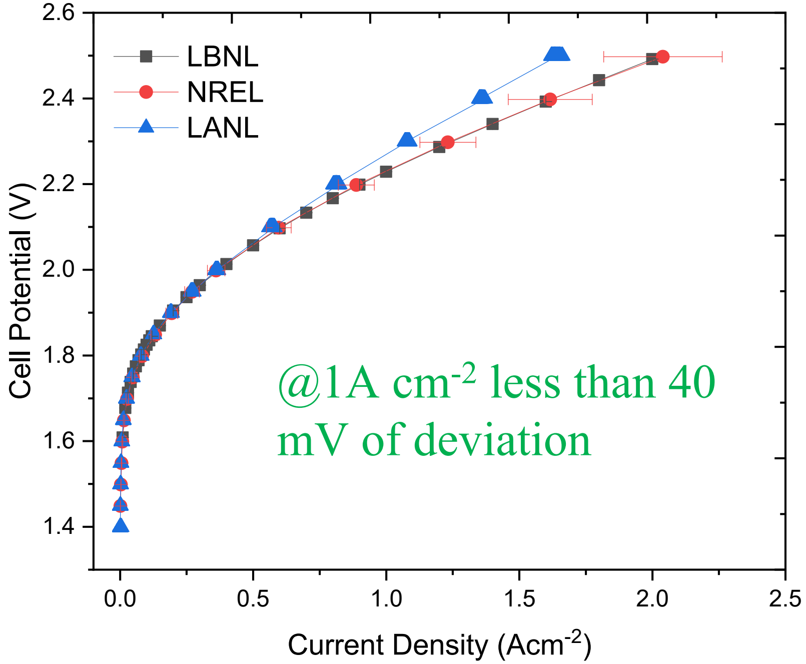
2.5V to 1.40
1.45- 2.5V
60 sec for each point

24 h

2.5V to 1.40
1.45- 2.5V
120 sec for each point

HFR increases with voltage & current density Due to bubble accumulating on the surface.





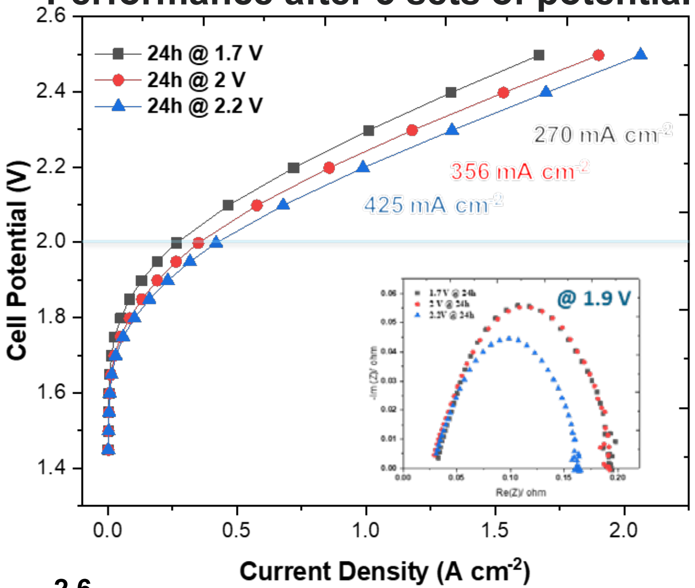
@1A cm^{-2} less than 40 mV of deviation

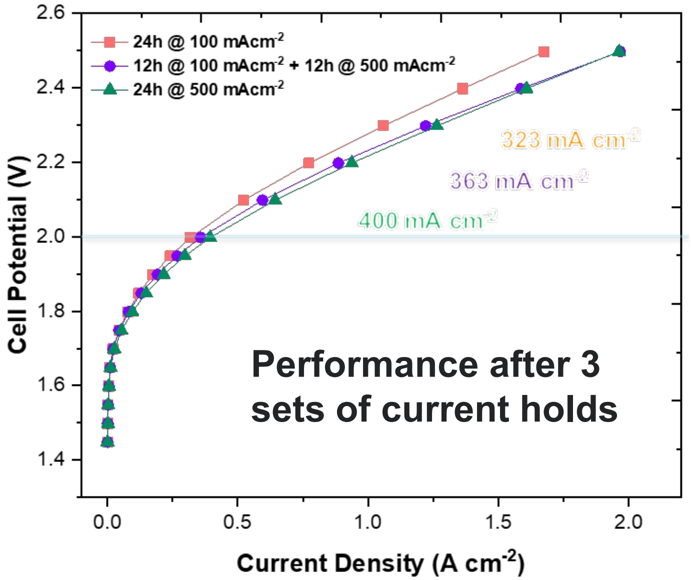
Comparison of the polarization curve between NREL, LBNL and LANL

Accomplishments and Progress: Development of activation protocol

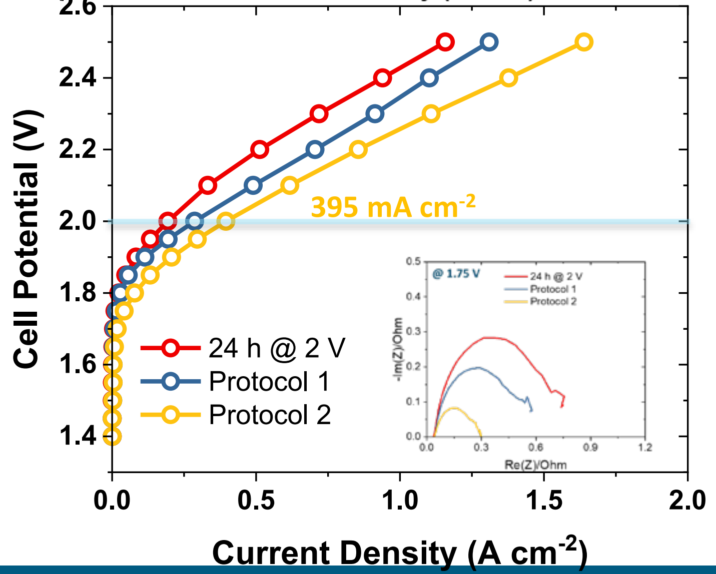
- ➢ The mechanism and impact of the activation process for liquid alkaline water electrolysis (LAWE) are not well understood. To achieve competitive performance levels in LA, a clear understanding of the activation protocol is necessary.
- ➢ An improved activation protocol enables the development of more efficient and durable systems, leading to increased hydrogen production rates and reduced energy consumption.
- ➢ Several activation protocol were study
- ➢ Next: Correlation between the electrochemical performance with the surface composition, and morphology.

Performance after 3 sets of potential holds





Performance after 3 sets of current holds



Protocol 1:

20 cycles between 2 V – 0.8 V

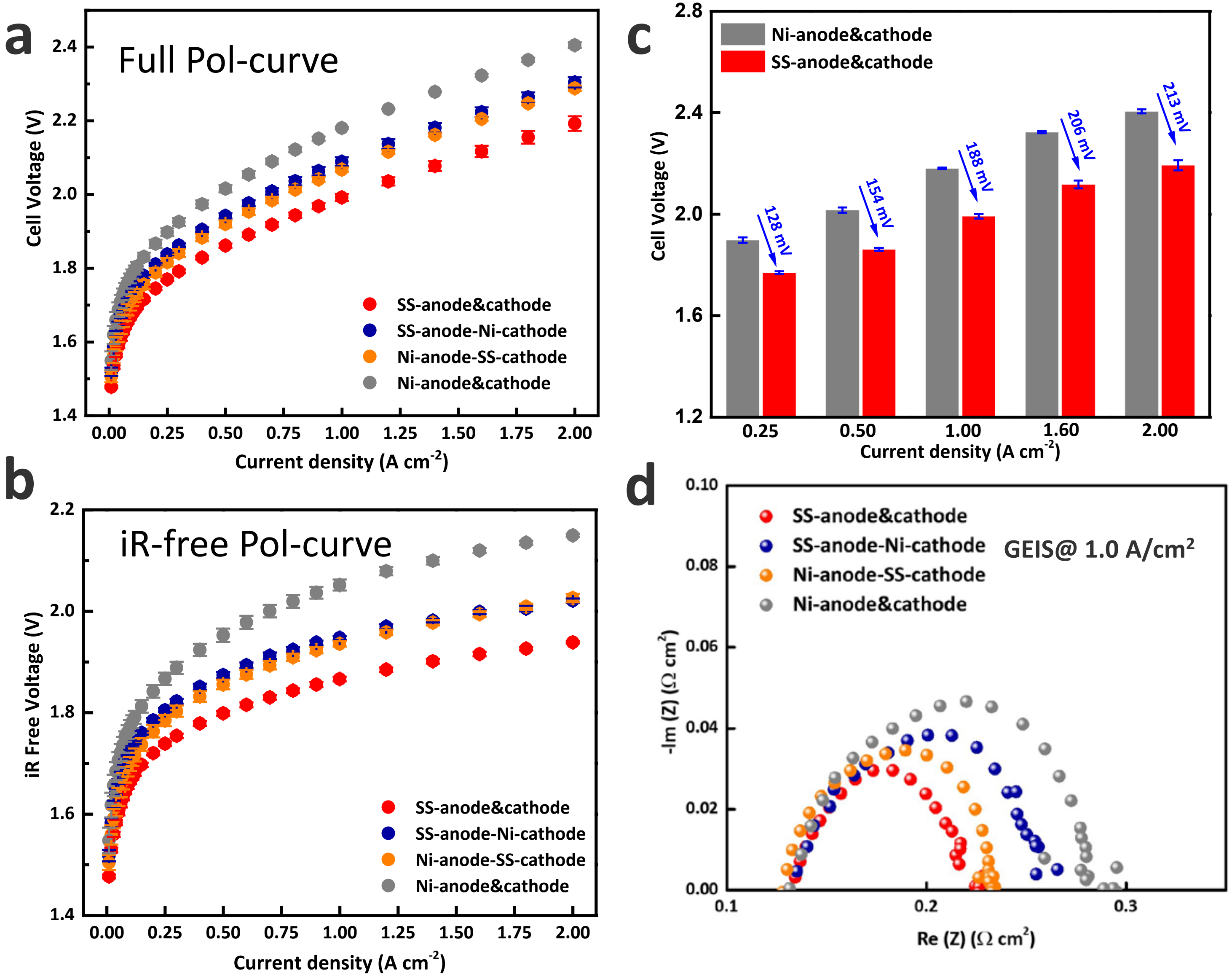
2 V: 60 s – 0.8 V 60 s

Protocol 2:

20 cycles between 2 V – 0.2 V

2 V: 60 s – 0.2 V 60 s

Accomplishments and Progress: Stainless Steel as high performing electrode

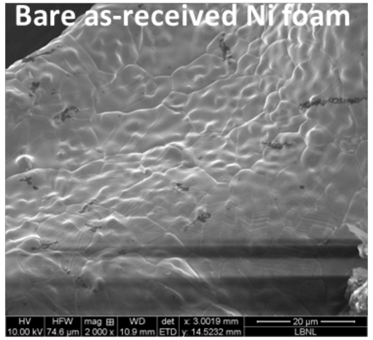


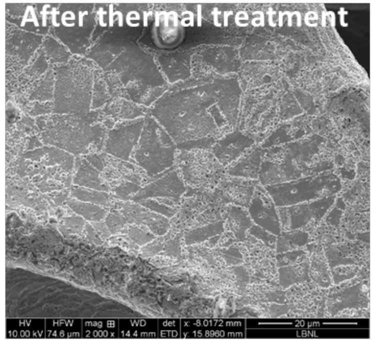
- Both anode and cathode electrodes can impact LAWE performance dramatically.
- SS electrode is more active for both OER and HER than Ni electrode and enhance the LAWE performance as both anode and cathode, due to presence of NiFe, NiCr, and NiMo active species for OER and HER.
- Voltage reduction of 213 mV @2.0 A cm^{-2} using SS as electrodes for LAWE

Accomplishment: Ni Electrode Surface Area Enhancement

- ➢ Enhance Ni ECSA with thermal treatment
- ➢ Enhance Ni ECSA with infiltrated catalyst washcoat

Thermal treatment to roughen Ni surface

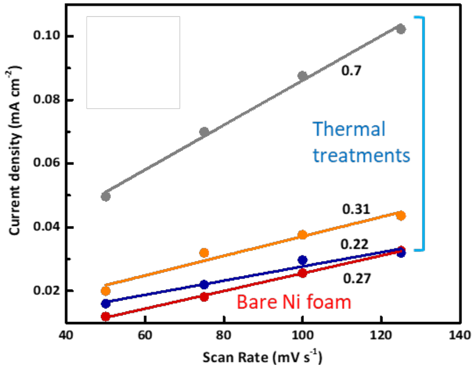




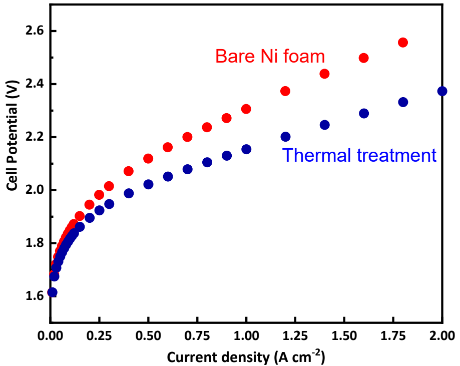
- ➢ Optimized treatment time, temperature, atmosphere

Significantly improved performance

Increased cyclic voltammetry current

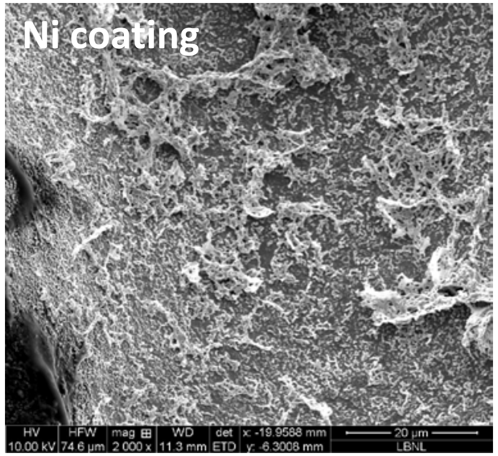


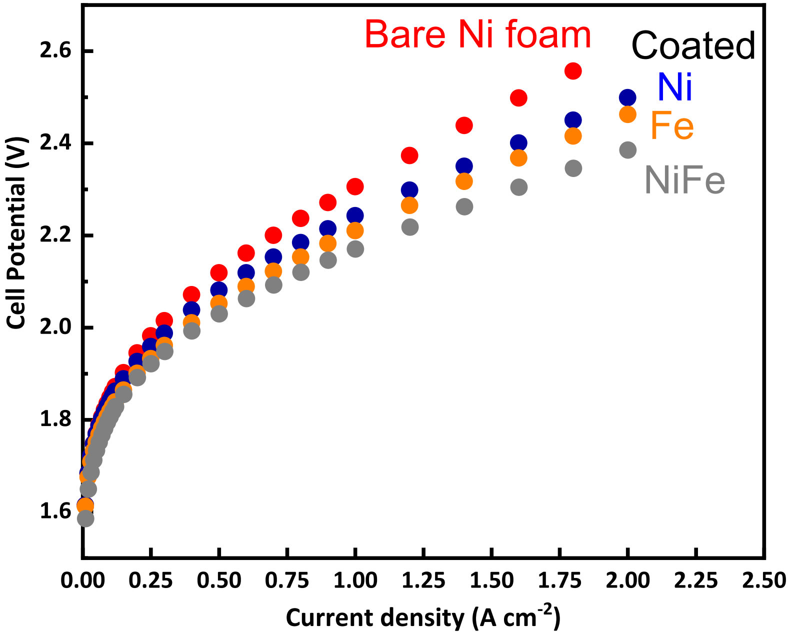
Improved performance



- ➢ Infiltration of Ni, Fe, or NiFe washcoat catalyst
- ➢ Optimized loading, composition, sintering temperature

Significantly improved performance

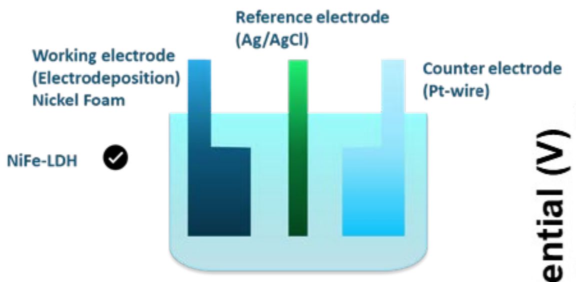




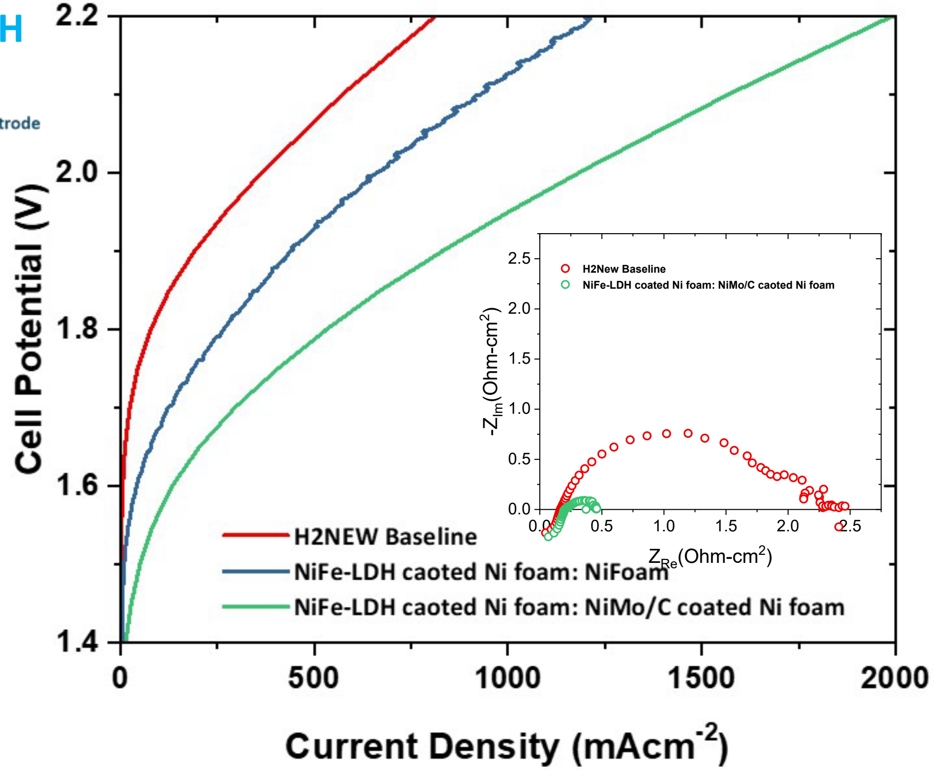
Accomplishments and Progress: NiFe-LDH and NiMo/C for enhancing the performance of LAWE

- NiFe layered double hydroxides (LDH) are widely known as highly active OER catalysts in alkaline conditions.
- Electrodeposition method was used to coat the NiFe-LDH on the Ni foam. The method is readily scalable for the modification of large-scale electrode surfaces and as such can be rapidly incorporated into LAWE stacks.
- NiFe LDH anode electrodes combined with a NiMo/C cathode, result in a 3-fold increase in current density at 2.0 V.

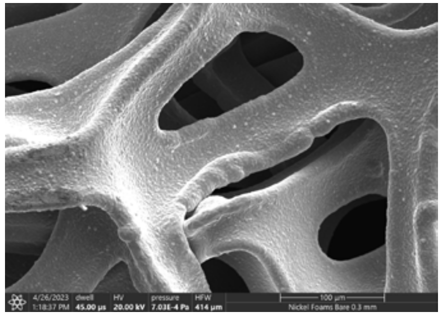
Electrodeposition of NiFe-LDH



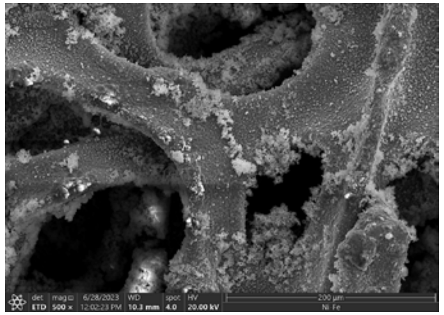
Applied DC voltage -1 V



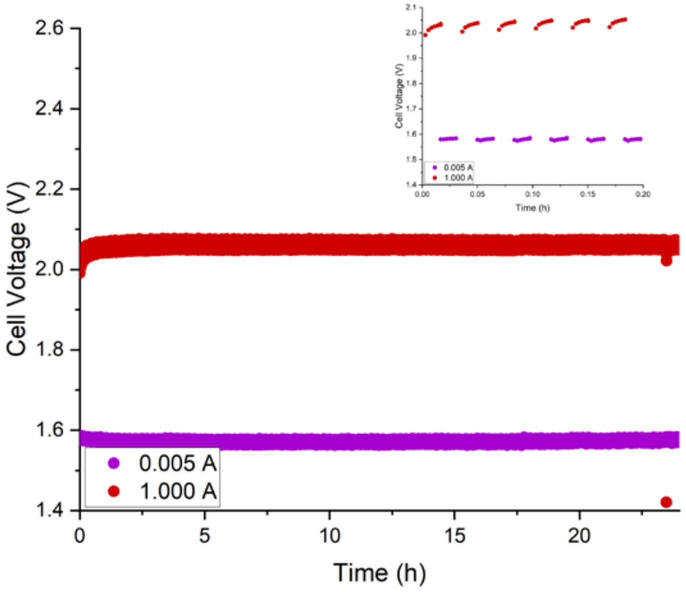
Ni foam

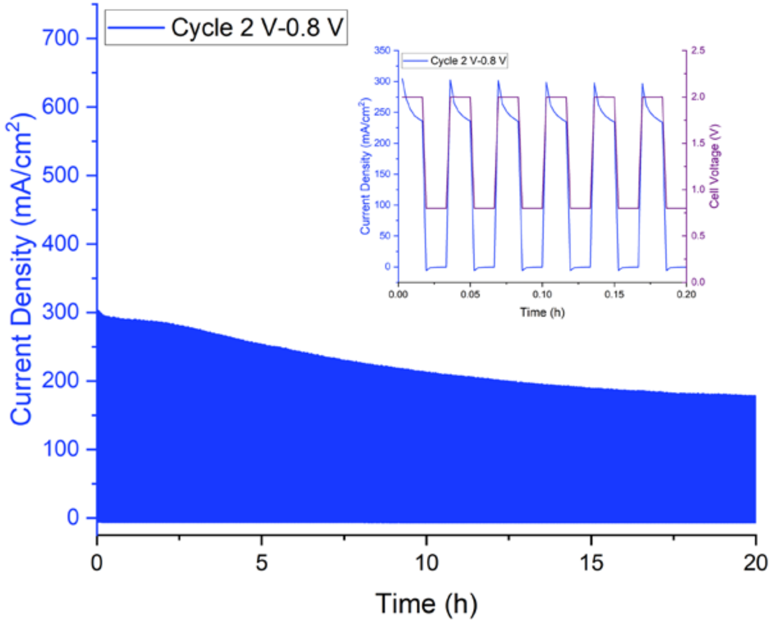


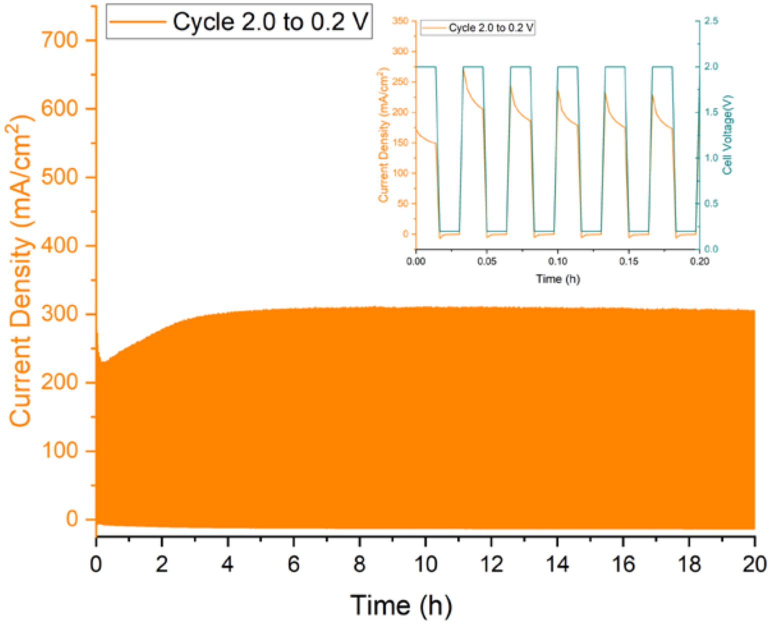
NiFe-LDH on Ni foam



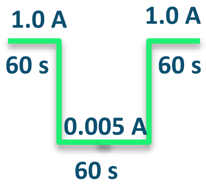
Accomplishments: AST Development

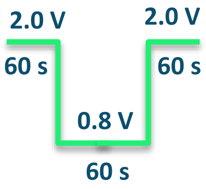


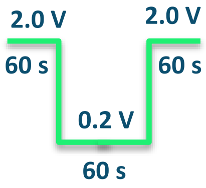




- **Cycling is expected to be detrimental to LAWE cells.**
- **Subjected the Benchmark cell to 3 different cycling protocols.**







Protocol 1: 99.95% Turndown

24 h between 1.0 A – 0.005 A

Protocol 2:

20 h between 2 V – 0.8 V

Protocol 3:

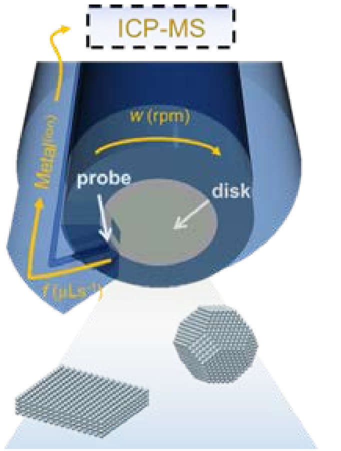
20 h between 2 V – 0.2 V

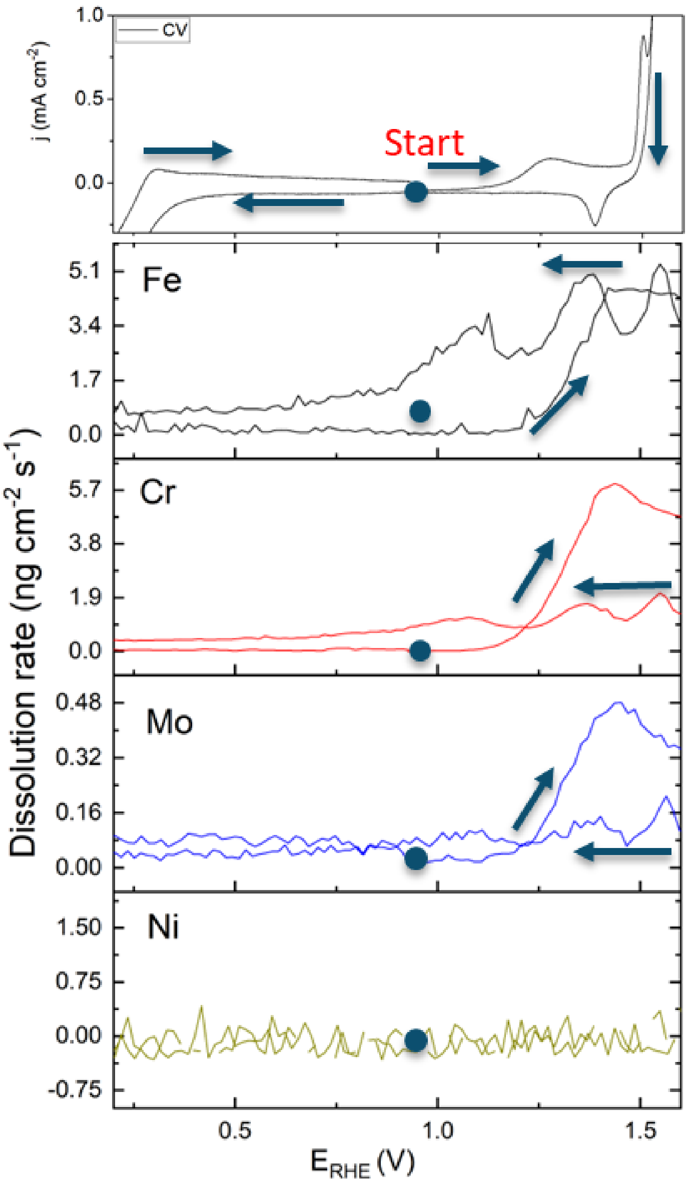
Accomplishments and Progress :In Situ Dissolution Studies for Liquid Alkaline Water Electrolyzer Materials

Frederick Agyapong-Fordjour, Ronnie Emmons, Pietro Papa Lopes (ANL)

Advanced degradation studies required for understanding durability constraints during dynamic operation

SPRDE ICP-MS



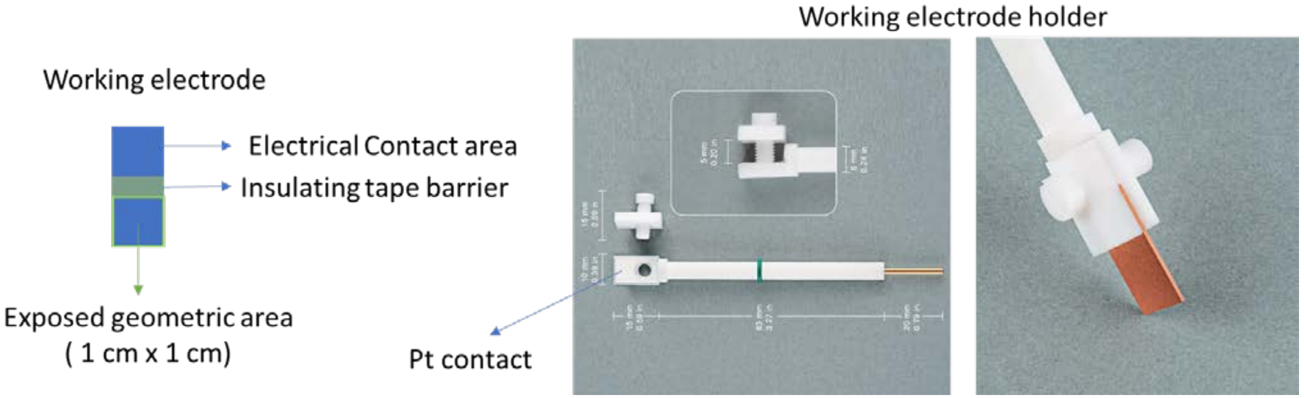


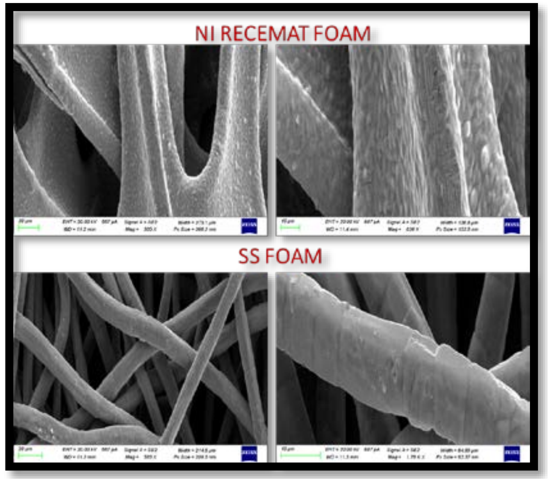
WE: SS316
1.0 M KOH
10 mV/s
T= 22ºC

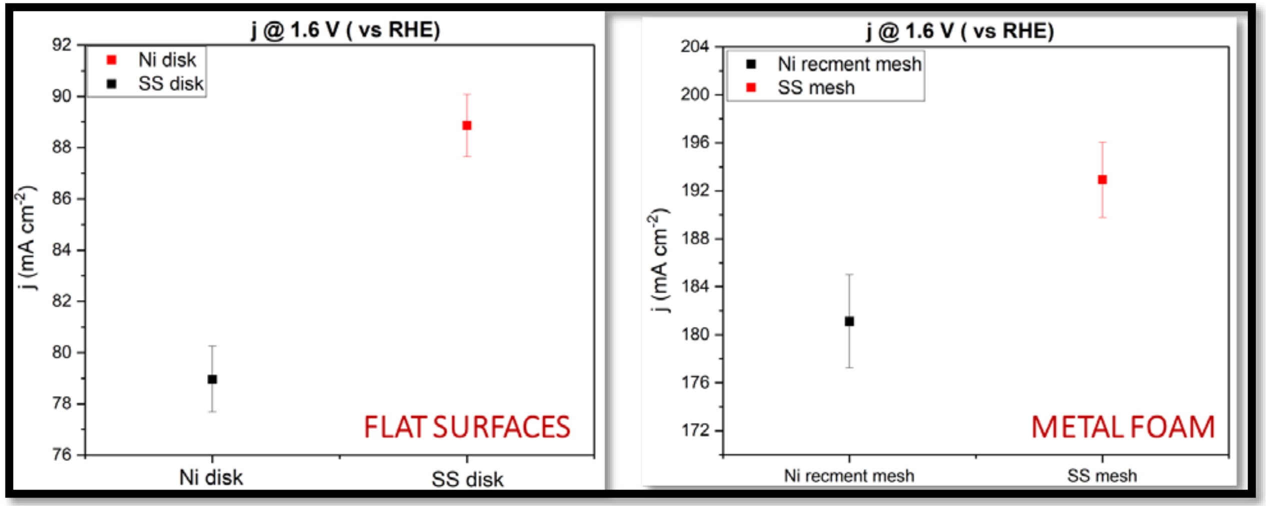
In situ ICP-MS method applied practical KOH concentrations (>1 M) is well-suited for resolving dissolution rates of multi components materials as a function of potential and temperature

Accomplishments and Progress: OER performance and metal dissolution rates – Foam/Mesh electrodes

- Foam wire thickness for Ni Recemat is larger than observed on SS foam, Ni foam shows a far more textured surface.
- Stainless steel shows higher OER activity than Ni in both foam and flat surfaces.
- Current densities at 1.6 V (vs RHE) from foam samples are about triple that of the flat electrodes.

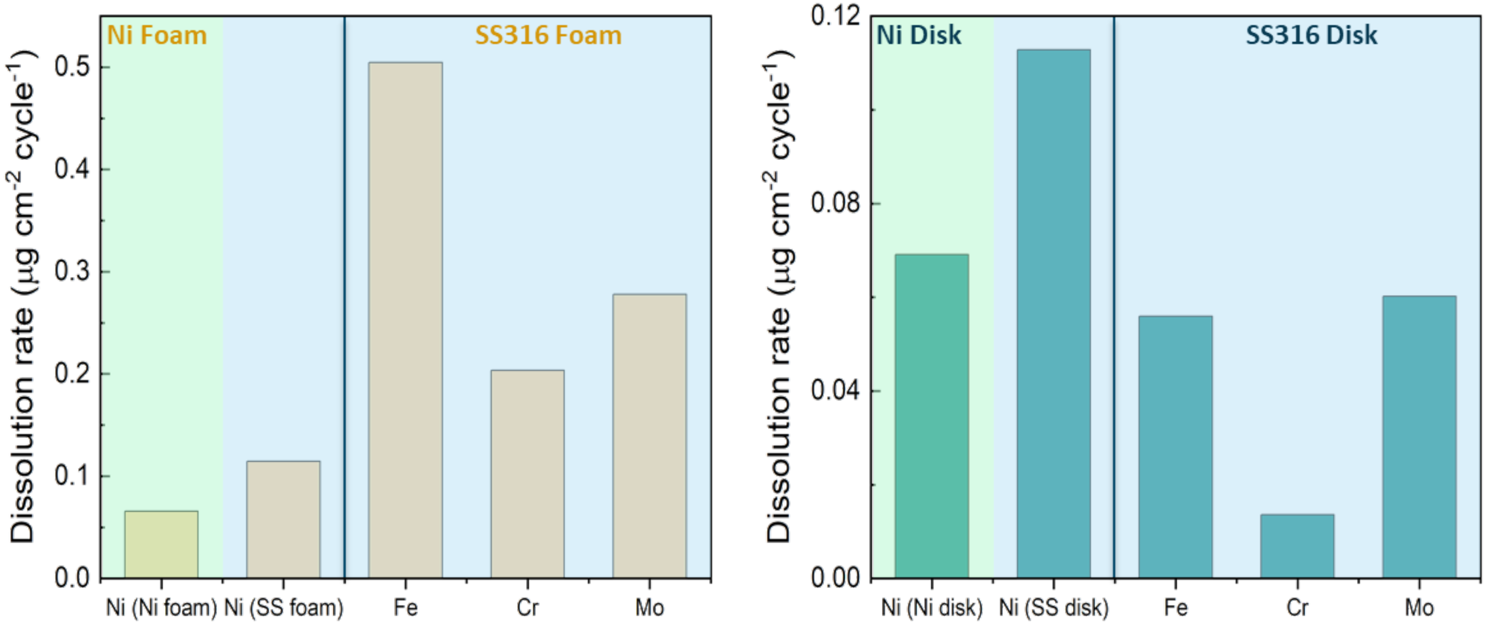






Accomplishments and Progress: ICP-MS Analysis (Ex-situ) – Metal foam vs flat disks

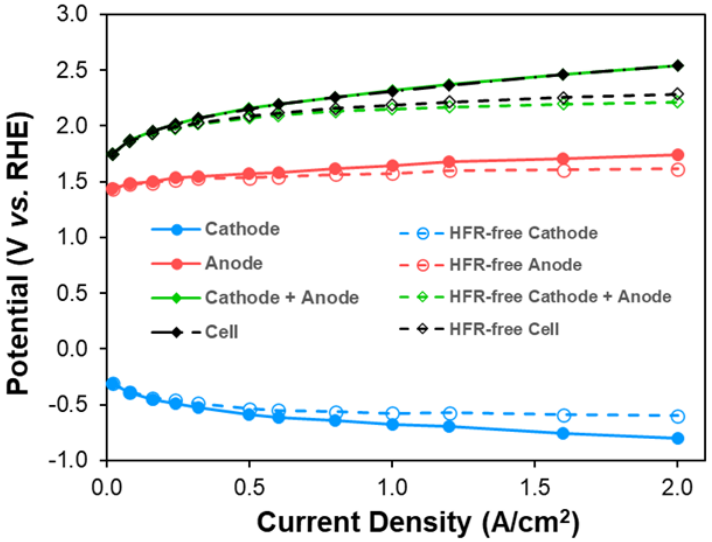
- ICP-MS analysis reveals the extent of dissolution from Ni and SS alloy components.
- Ni dissolution from SS316 higher than pure Ni.
- Dissolution of SS alloy components (Fe, Cr, Mo) is far greater on foam electrode, 3-5 times more for Mo and about 10 times more Fe dissolution
- Ni dissolution from foam or disk equivalent.
- Purification of KOH to remove background trace of Ni and Fe are required for precise quantification of dissolution at onset potentials.



Element	KOH background concentration (ppm)
Ni	0.01
Fe	0.006
Cr	0.003
Mo	0.03

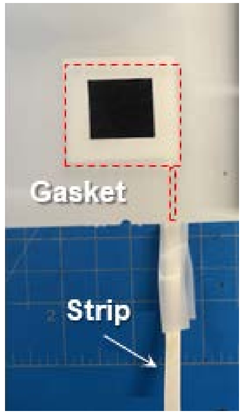
Accomplishments and Progress: Reference Electrode Integrated Liquid Alkaline Cell

- Reference electrode technique has several motivations that contribute to advancements in the liquid alkaline water electrolysis field. These include improving efficiency, enhancing durability, and understanding the electrochemical kinetics at the electrode-electrolyte interface.
- Investigating and understanding the behavior of different types of electrodes and catalyst coating can lead to the development of more efficient processes and together with that a more durable electrode materials and thereby extending the operational lifespan of the LA system.



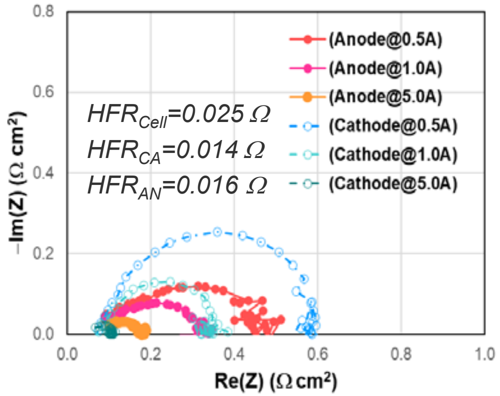
Feasibility test of reference integrated LA cell:

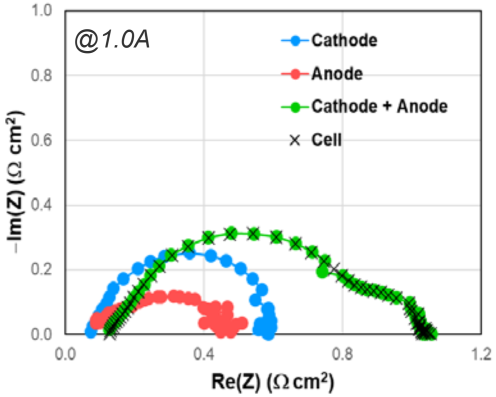
- Independent potential reading of cathode and anode
- Well-matched Pol-curve w/ and w/o iR-compensation
- Constant HFR_{CA} and HFR_{AN} regardless of the applied current
- Well-matched Nyquist plot b/w the sum and the entire cell profile



Experimental parameters

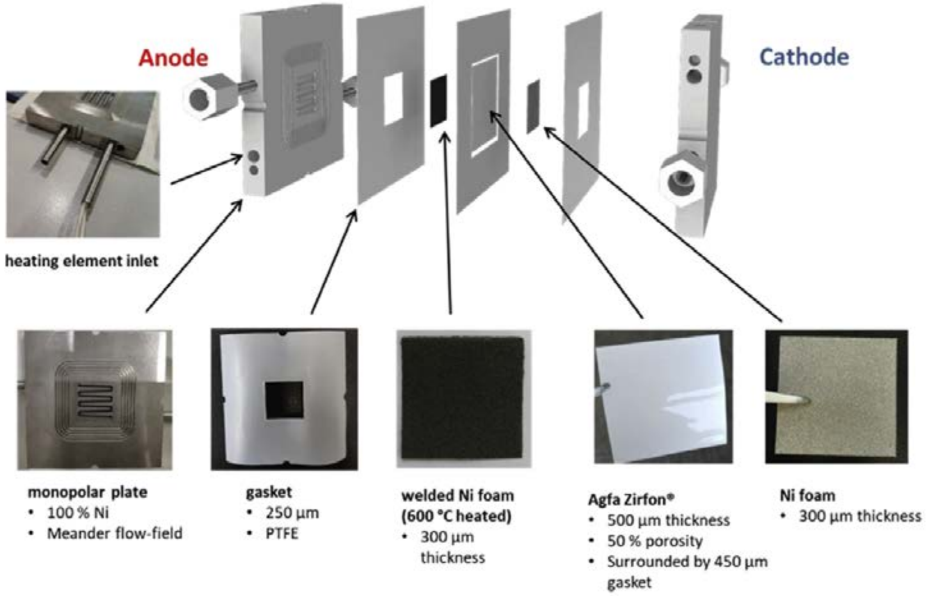
- Ni foam (5cm^2, ~300μm) for the cathode and anode
- 30% wt.% KOH, T = 80 ^{0}C, 50 ml min^{-1}
- Calibration: +0.86V (Thermodynamic)
- No activation before the test
- Amp: 5% of the DC current, 0.2 Hz – 10,000 Hz

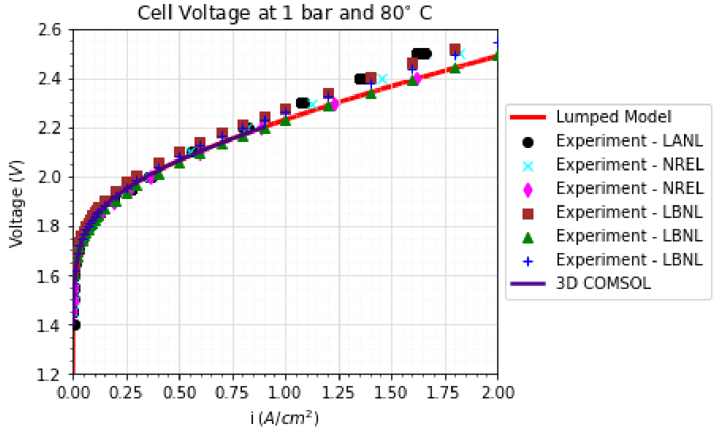


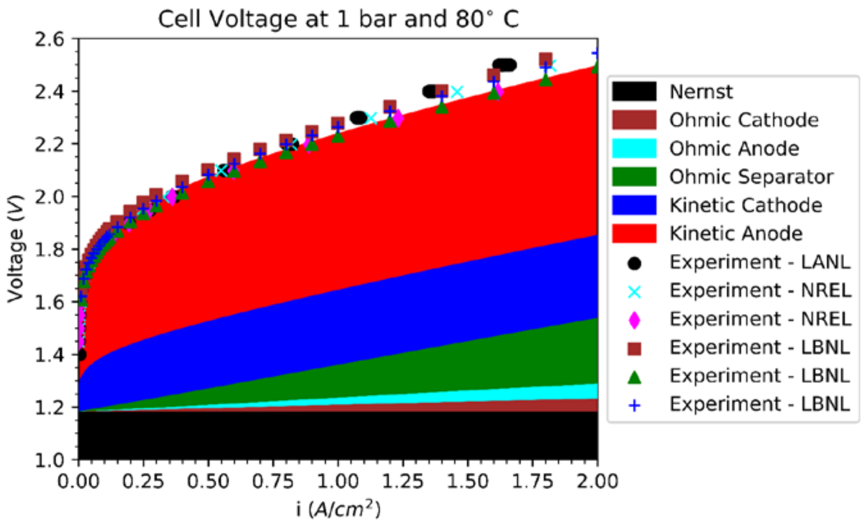


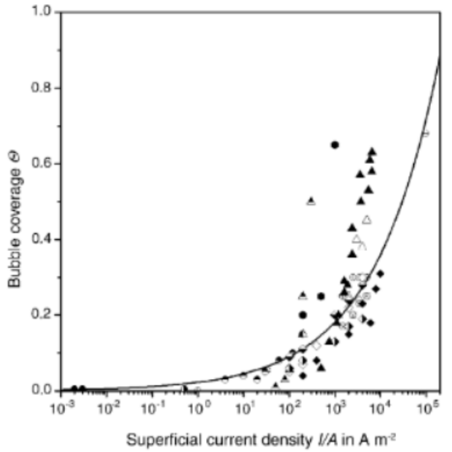
Accomplishments and Progress: 1D Model with Overpotential Breakdown

- 1D/Lumped model developed to predict cell pol curves:
  - Effect of electrolyte KOH concentration, temperature, and H_2 physical and transport properties
  - Effect of electrode and separator structure on ohmic drops
  - Effect of anode and cathode material on activation overpotentials
  - Bubble coverage reduction of active area
  - Hydrogen crossover (preliminary)
  - Input to system modeling









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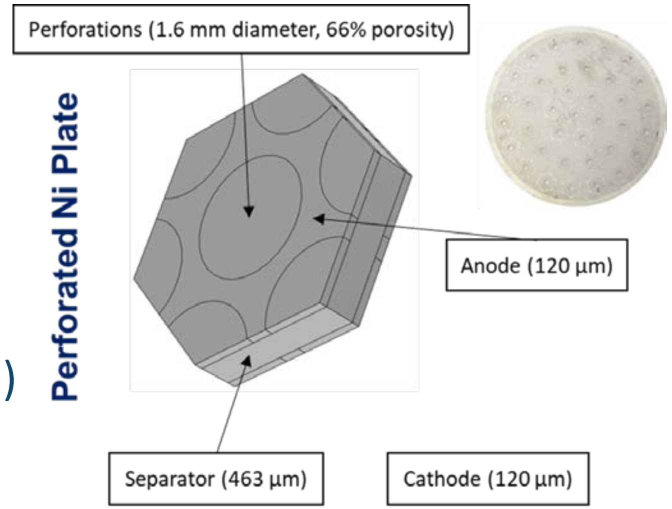
Accomplishments and Progress: 3D Multiphase Flow in a Perforated Plate

- 3D Electrochemistry/Multiphase flow coupled setup:
  - Objective is to provide insight into the feasibility of VOF-based modeling (Euler-Euler interface)
  - Electrochemistry model predicts bubble generation (through current density)
  - Multiphase flow model predicts bubble coverage (coupled back to active area)



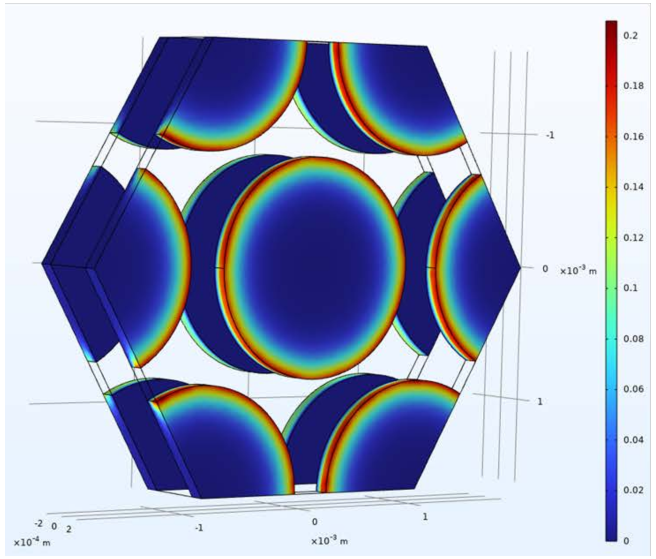
Perforations (1.6 mm diameter, 66% porosity)

Anode (120 µm)

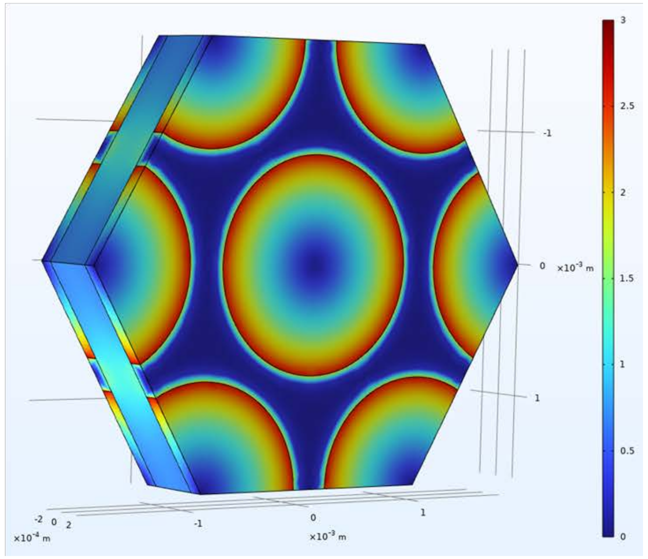
Separator (463 µm)

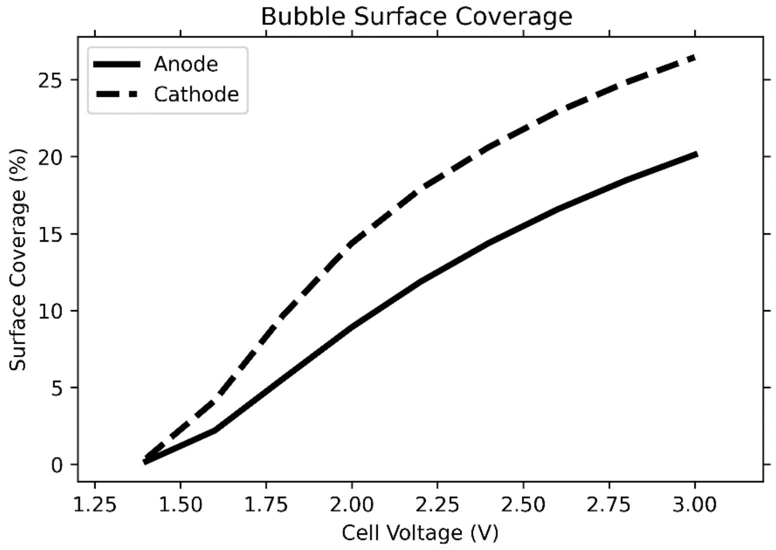
Cathode (120 µm)

Bubble volume fraction at 2V



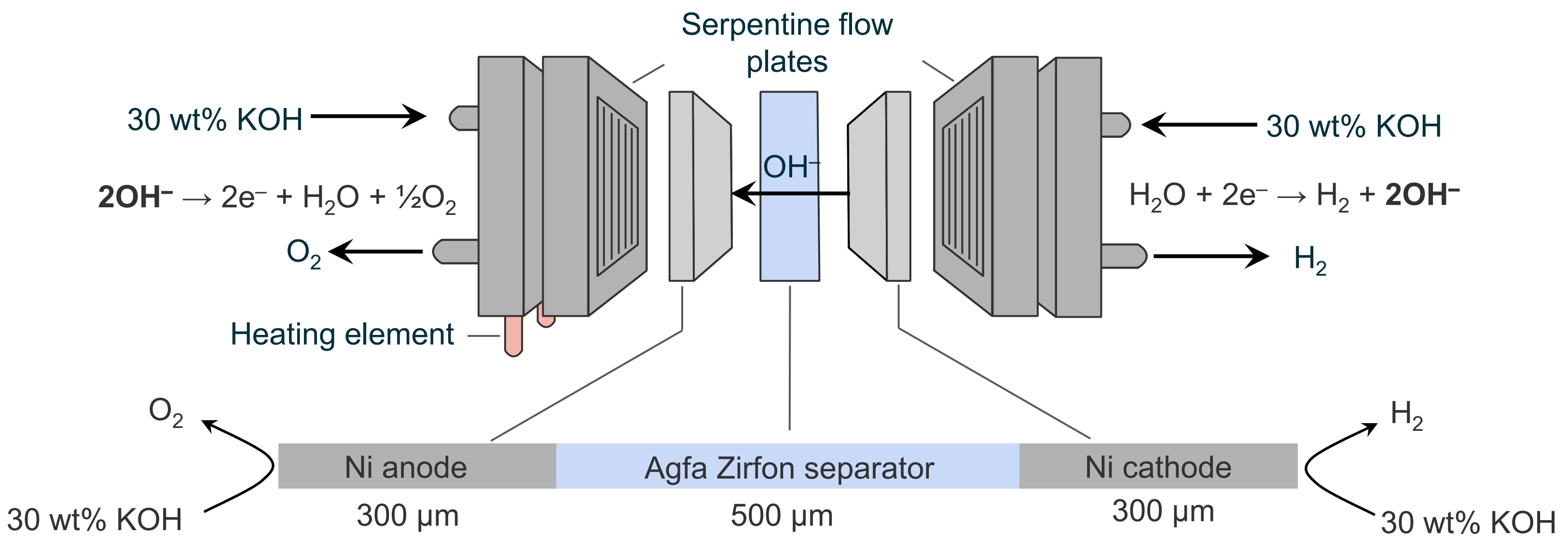
Current Density (A/cm^2) at 2V





Accomplishments and Progress: 1D Continuum Modeling Overview

- Continuum model developed that elucidates the effect of changes in local species activity and gas/liquid saturation on electrolyzer performance
- Impact of electrode geometry on polarization behavior and high frequency resistance (Ohmic drop) was investigated
- Effects of multiphase flow on the 1D simulation are the focus of current work



Conservation equations

$$\nabla \cdot n_i = \varepsilon_I \sum_i R_{k,i}$$

$$n_i = -D_i^{\mathrm{eff}} \nabla c_i + z_i \frac{F}{RT} D_i^{\mathrm{eff}} c_i \nabla \phi_I$$

$$\sum_i z_i c_i = 0$$

$$\nabla \cdot \mathrm{i}_s = -\nabla \cdot (\sigma_{\mathrm{eff}} \phi_s)$$

Charge-transfer reactions

$$R_{CT,\mathrm{i}} = -M_i \frac{a_v s_{i,k} i_k}{n_k F}$$

$$i_{\mathrm{HER,base}} = -i_{0,\mathrm{HER,base}}\ exp\left(-\frac{\alpha_{c,\mathrm{HER}} F}{RT} \eta_{\mathrm{HER}}\right)$$

$$i_{\mathrm{OER,base}} = i_{0,\mathrm{OER,base}} \left(\frac{c_{\mathrm{OH^-}} \gamma_{\mathrm{OH^-}}}{1\ [\mathrm{M}]}\right) exp\left(\frac{\alpha_{a,\mathrm{OER}} F}{RT} \eta_{\mathrm{OER}}\right)$$

$$\eta_k = \phi_s - \phi_l - \left(U_k^0 - \frac{2.303RT}{F} \mathrm{pH}\right)$$

$$\mathrm{pH} = -\log K_W - \log \frac{a_W}{\gamma_{\mathrm{OH^-}} m}$$

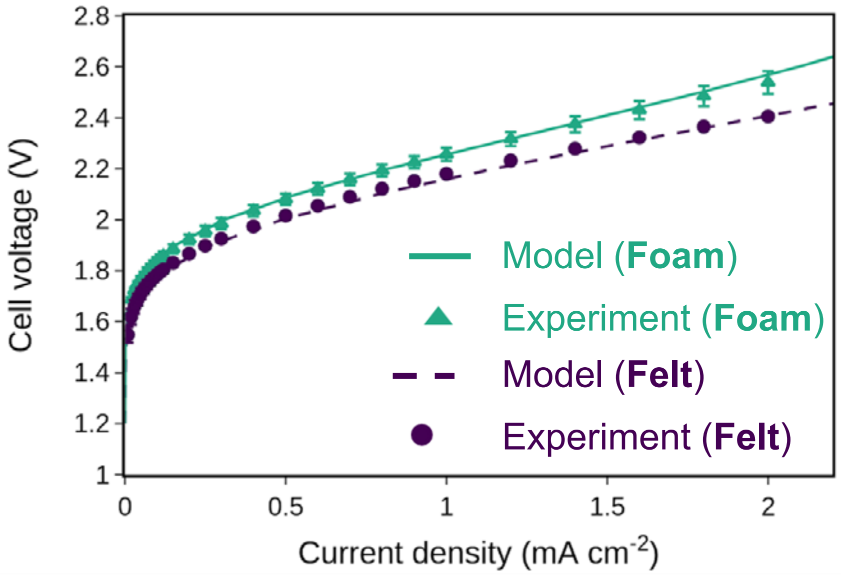
Buffer kinetics

$H^+ + OH^- \rightleftharpoons H_2O$

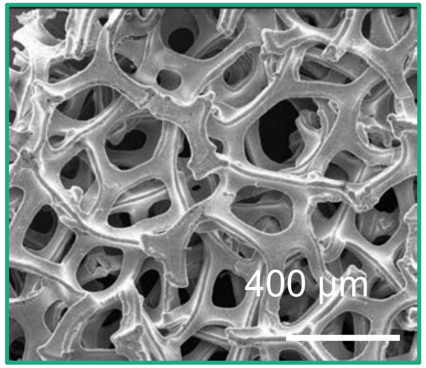
$$R_{B,i} = M_i \sum_i s_{i,n} (k_n \prod_{s_{i,n} < 0} c_i^{-s_{i,n}} - \frac{k_n}{K_n} \prod_{s_{i,n} > 0} c_i^{s_{i,n}})$$

Accomplishments and Progress: 1D Continuum Modeling Validation

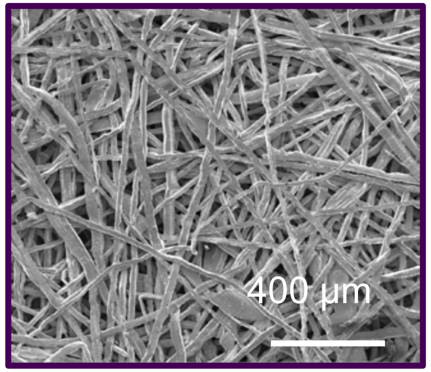
- The model predicts the polarization curve of the nickel foam and felt electrodes with the same kinetic parameters
- Conductivity values (diffusion coefficients) used to simulate transport through Zirfon match area resistance measurements
- High frequency resistance (HFR) measurements of Ohmic drop agree with the simulation results

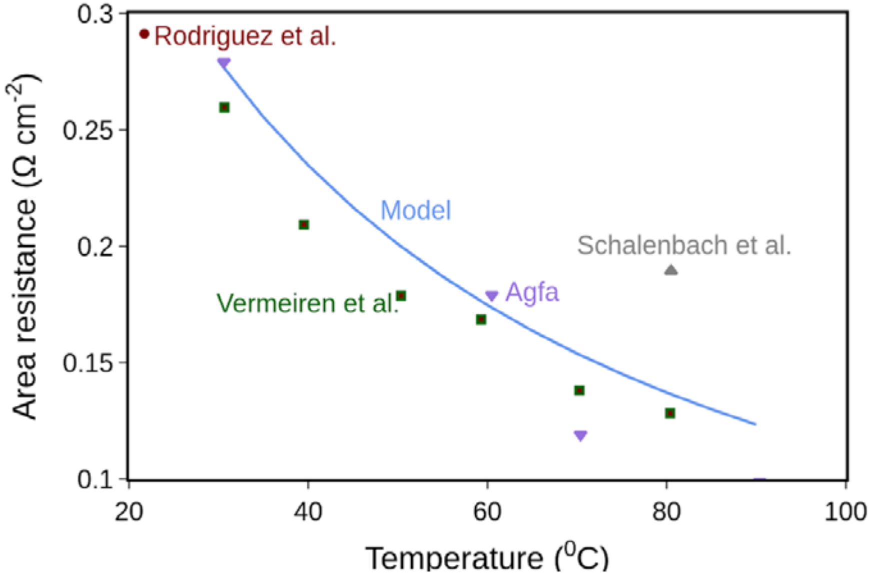


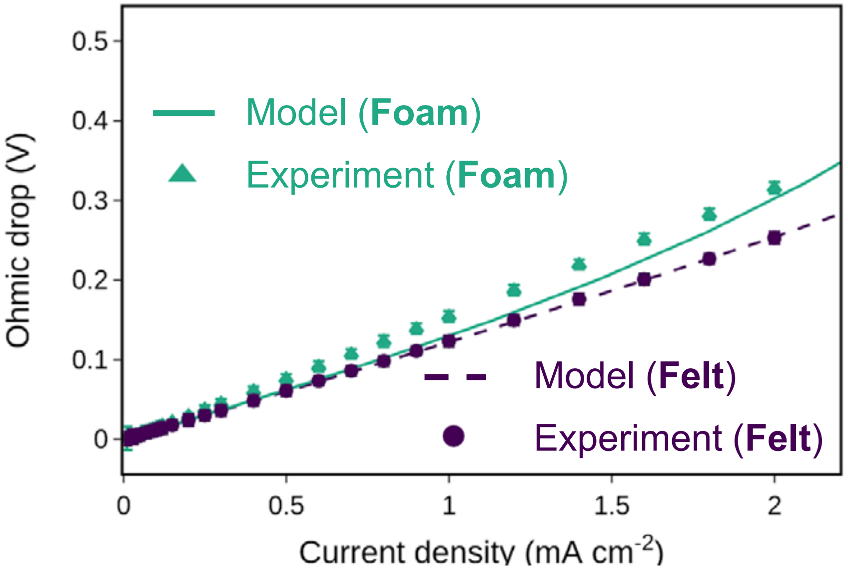
Foam



Felt







Collaboration and Coordination

NREL Team Members: Meital Shviro, Woo Yeong Noh, Bryan Pivovar [Electrode coating, In situ testing, Reference electrode development and validation]

LBNL Team Members: Xiong Peng, Rangachary (Mukund) Mukundan, Eric Lees, Mike Tucker, Guanzhi Wang (Electrode coating, In situ testing, Reference electrode development and validation, 1D modeling)

ANL Team Members: Pietro Papa Lopes, Debbie Myers, Rajesh Ahluwalia, Samuel Kazmouz, Frederick Agyapong-Fordjour, Ronnie Emmons, [Dissolution study, 1D and 3D modeling]

ORNL Team Members: Alexey Serov, Flavio Dal Forno ChuahyDave Cullen, Haoran Yu, [Electrode development, Electron microscopy 1D and 3D modeling]

LANL: Sandip Maurya, Daniel Leonard, Yu Seung Kim [Electrode coating, In situ testing, Reference electrode development and validation]

University Collaborators: Svitlana Pylypenko, Jayson Foster (Mines) [Electron microscopy and XPS]; Shawn Litster, Kara Ferner (CMU) [Tomography]; Jack Lang, Iryna Zenyuk (UCI) [Tomography]

Remaining Challenges and Barriers

- Relate activation protocol to performance and durability
- Catalyst and electrode improvements for performance enhancement and durability
- Optimize the interfaces between electrode-catalyst- separator
- Advanced membranes/ separator

Proposed Future Work

- Improve fundamental understanding of degradation mechanisms of electrodes separator materials and supporting electrolyte:
  - Effect of dynamic operation and temperature on Gas cross over
  - Develop methods to track and quantify electrode morphology changes and evaluate separator integrity
  - Effects of Start/Stop cycles or other stressors
- Propose specific ASTs protocol to study components degradation:
  - Dynamic operation, High current density operation, and Start-up and Shut-down
- Develop standardized testing protocol (together with the IEA)
- Investigate Ni-based anode structures
  - With enhanced ECSA, graded pore structures, and control of surface composition
  - Optimize catalyst layer deposition, thermal treatment, and catalyst infiltration
  - Parametric studies to determine impact of electrode structure on performance
- Integration of bubble and dissolved gas effects in cell modeling
- Establish modeling framework for catalyst/membrane stability under different operating conditions.
- Optimization of coating for performance enhancement and stable catalysts-electrode-separator interface
- Evaluate the micro-domain morphological impact on catalyst-layer/bubble interfacial behavior and potential impact on liquid alkaline water electrolyzer performance

Proposed Future Work

- Tailoring the catalyst layer micro-domain by laser ablation and anodization
- Understanding and Mitigating Electrocatalyst Degradation
    - in situ experiments to gain insights into the dynamics of dissolution.
    - Complete activity/stability evaluation at higher temperatures.
    - Conduct surface analysis before and after cycling to understand the surface evolution.
    - Explore the degradation of Zirfon component along with the impact of Fe in Zirfon performance.
    - Screen other SS grades for optimal OER activity and stability
- Understanding Component Degradation
    - Determine in situ the degradation rates and reaction products from organic and inorganic electrolyzer components by using a direct injection triple-quad (QqQ) mass spectrometer and ICP-MS
    - Explore the influence of electrode potential and in the presence of trace impurities on performance and material degradation processes
    - Understanding anode catalyst oxidation state and structure using In situ and Ex situ Surface Raman Spectroscopy

Technical Back-up and Additional Information

Technology Transfer

- **Standardization of liquid alkaline testing protocol and identifying baseline components for H2NEW.** Baseline components have been identified and set. Multiple activation processes were conducted investigating operating variables that included different current and potential cycles and holds, coordinated with characterization efforts to identify overall electrodes mechanisms. These findings will provide valuable insights into the impact of operating conditions and can be related to the techno-economic considerations of cell operation for achieving the lowest hydrogen cost.

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