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

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WBS 12.1.0.519

Project ID # P196h

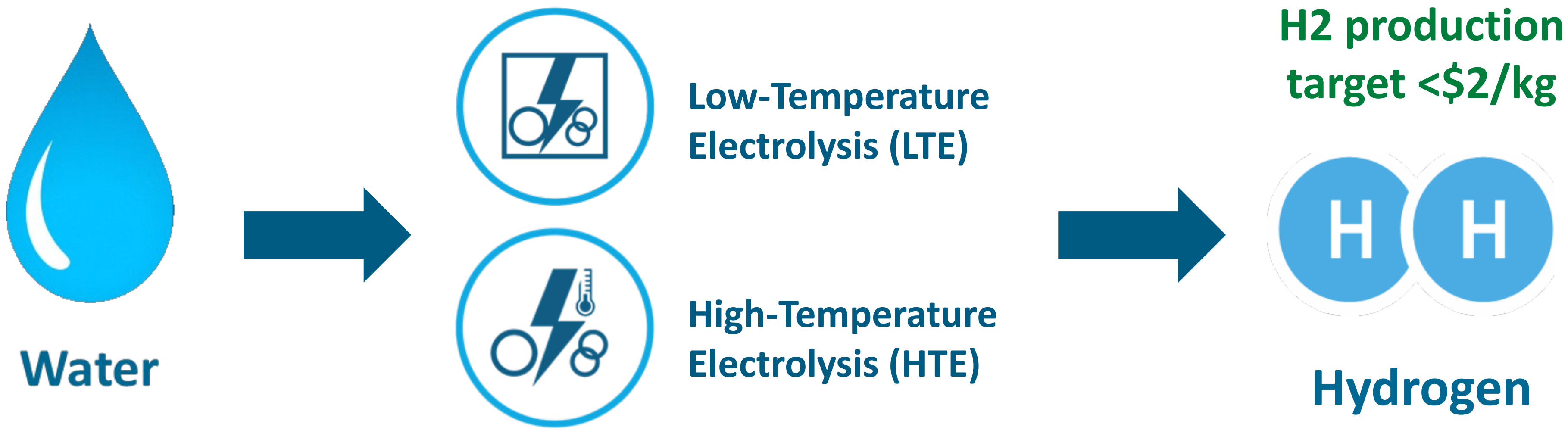
Date: June 6, 2023

DOE Hydrogen Program

2022 Annual Merit Review and Peer Evaluation Meeting

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

Relevance: Liquid Alkaline Water Electrolysis Experts Meeting

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- **Virtual Workshop January 26-27, 2022**
  - **Build a detailed picture of the status and challenges of commercially-available LA water electrolyzers and opportunities for developing next-generation LA electrolyzer technology**
  - **Prioritize R&D opportunities to overcome current limitations and challenges**
  - **Help shape HFTO's strategy for LA electrolyzer research and development**
- **Significant H2NEW engagement/leadership on organizing/executing Experts Meeting**
- **Full report and presentations available on line (https://www.energy.gov/eere/fuelcells/advanced-liquid-alkaline-electrolysis-experts-meeting)**
- **Provides basis of much of H2NEW workscope and approach**

Round 1		
Session Title	***Moderator***	***Scribe***
Fundamental Degradation Mechanisms	*Rangachary Mukundan, LANL*	*Elliot Padgett, NREL*
Characterization & Diagnostic Needs	*Debbie Myers, ANL*	*Haoran Yu, ORNL*
Performance Targets & Status	*James Vickers, HFTO*	*Tobias Schuler, NREL*
Manufacturing	*Alexey Serov, ORNL*	*McKenzie Hubert & Colin Gore, HFTO*
Cell Integration	*Plamen Atanassov, UC Irvine*	*Julie Fornaciari, LBL*

Round 2		
Session Title	***Moderator***	***Scribe***
Technoeconomic & System Analysis	*Mark Ruth, NREL*	*Anne Marie Esposito, HFTO*
Separator Materials	*Marcelo Carmo, Nel Hydrogen, US*	*Sandipkumar Maurya, LANL*
Catalysts & Dimensionally Stable Anodes	*Shaun Alia, NREL*	*Ahmed Farghaly, ANL*
Porous Transport Layers	*Guido Bender, NREL*	*Jason Keonhag Lee, LBL*
Stack & System	*Eric Miller, HFTO*	*Andrew Tricker, LBL*

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 1: Durability and AST Development

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Timeline and Budget

- Start date (launch): January 1, 2023
- Awarded through September 30, 2025
- FY23 DOE funding: ~$5M

Barriers/Targets

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

Consortium Task Team

NREL NATIONAL RENEWABLE ENERGY LABORATORY
BERKELEY LAB
Argonne NATIONAL LABORATORY
Los Alamos NATIONAL LABORATORY
OAK RIDGE National Laboratory

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

Other lab leads:
Xiong Peng (LBNL)
Sandip Maurya (LANL)
Debbie Myers (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

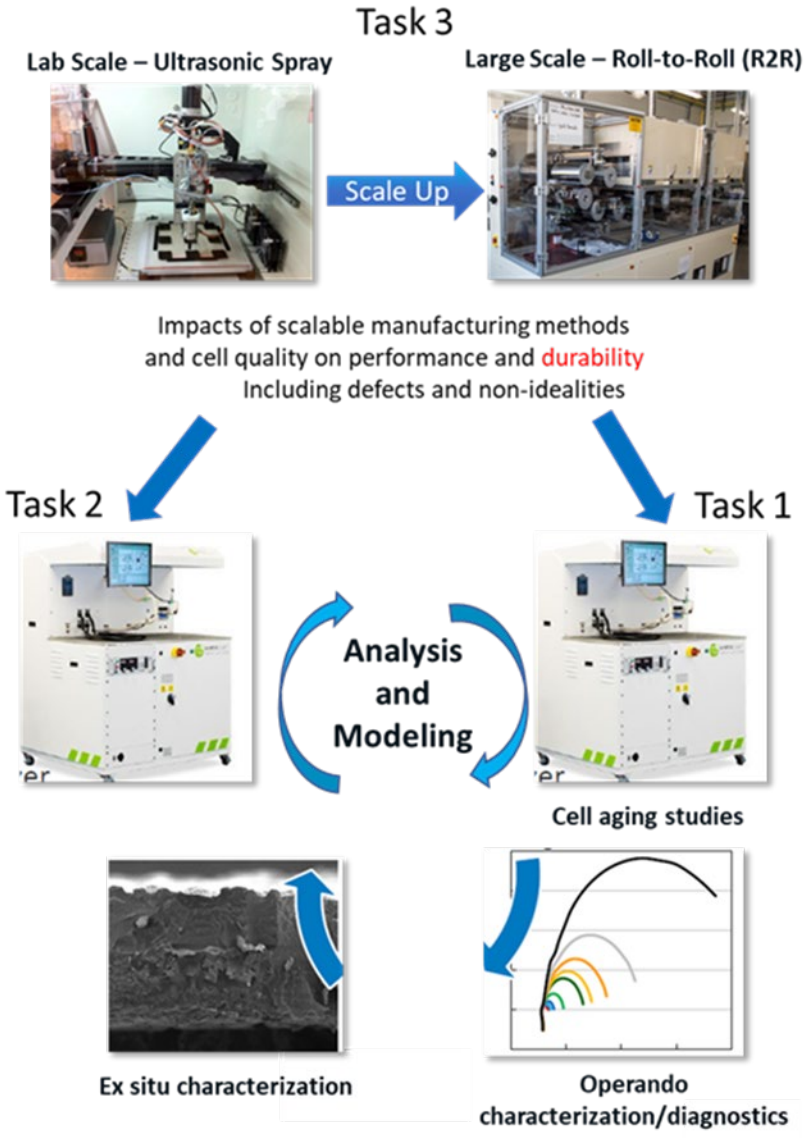
ii. Component engineering
   - Modification of Zirfon
   - Zirfon alternatives

iii. Systems/Technoeconomic analysis
   - System design, operating strategy, and performance tradeoffs
   - Identifying key differences in performance and cost between PEM and LAWE

Approach: Advanced Liquid Alkaline Electrolysis

Significant parallels to H2NEW approach for PEM

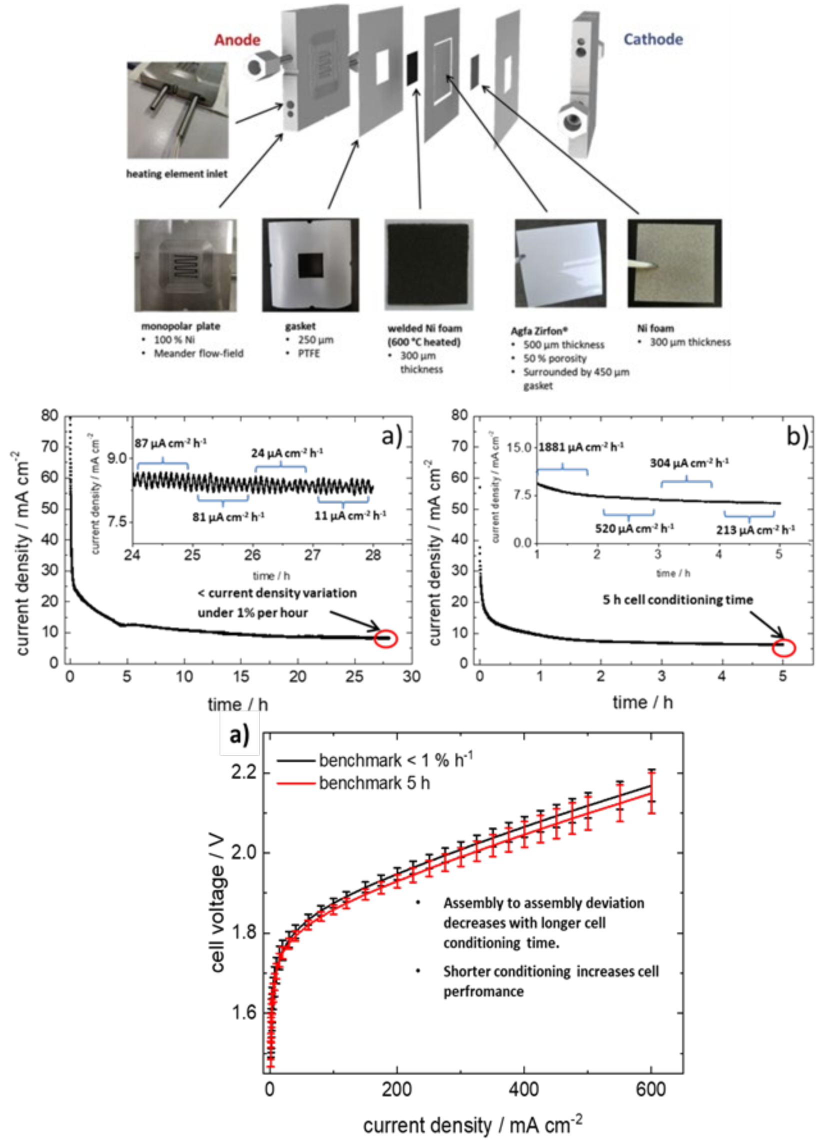
- Durability
  - Establish fundamental degradation mechanisms
  - Develop accelerated stress tests
  - Determine cost, performance, durability tradeoffs
  - Develop mitigation
- Performance
  - Benchmark performance
  - Novel diagnostic development and application
  - Cell level models and loss characterization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



Accomplishments and Progress: Challenges and important considerations in liquid alkaline

- Previous work identified the difficulties associated with the benchmarking of liquid alkaline single cells.
- Cell conditioning needs to be established prior to performance testing being performed
  - Conditioning at 1.7 V for at least 20h (A conditioning method with a current density variation of less than 1% per hour)
- Low reproducibility (Large deviation between tests)
- sufficient conditioning time and procedure is needed

- ***Direct comparison of results between different facilities***



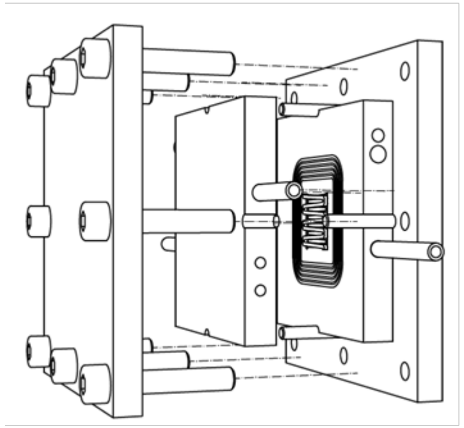
C. Karacan...M. Shviro et al., international journal of hydrogen energy 47 (2022) 4294

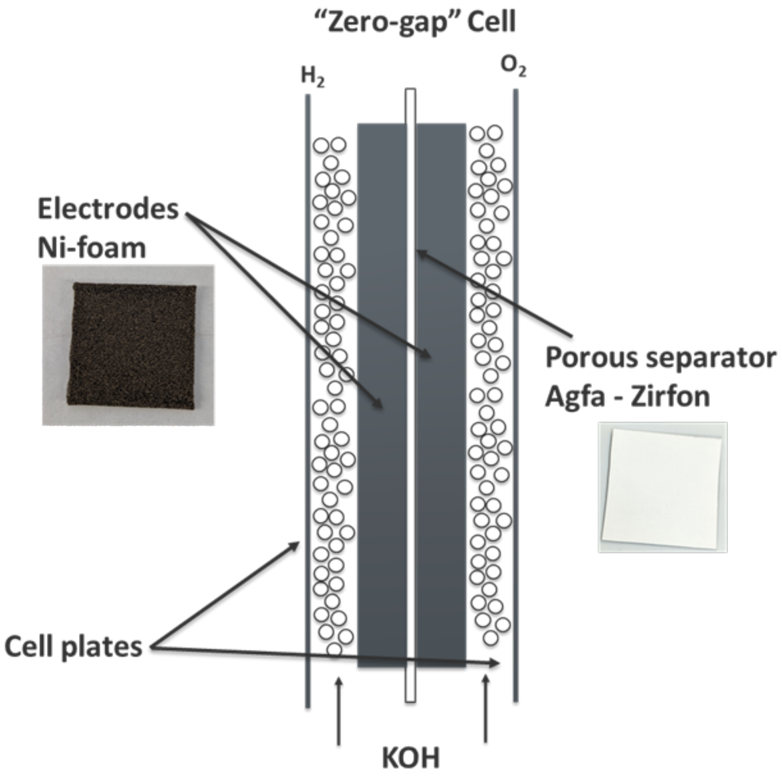
Accomplishments and Progress: Baseline state-of-the-art commercial liquid alkaline components

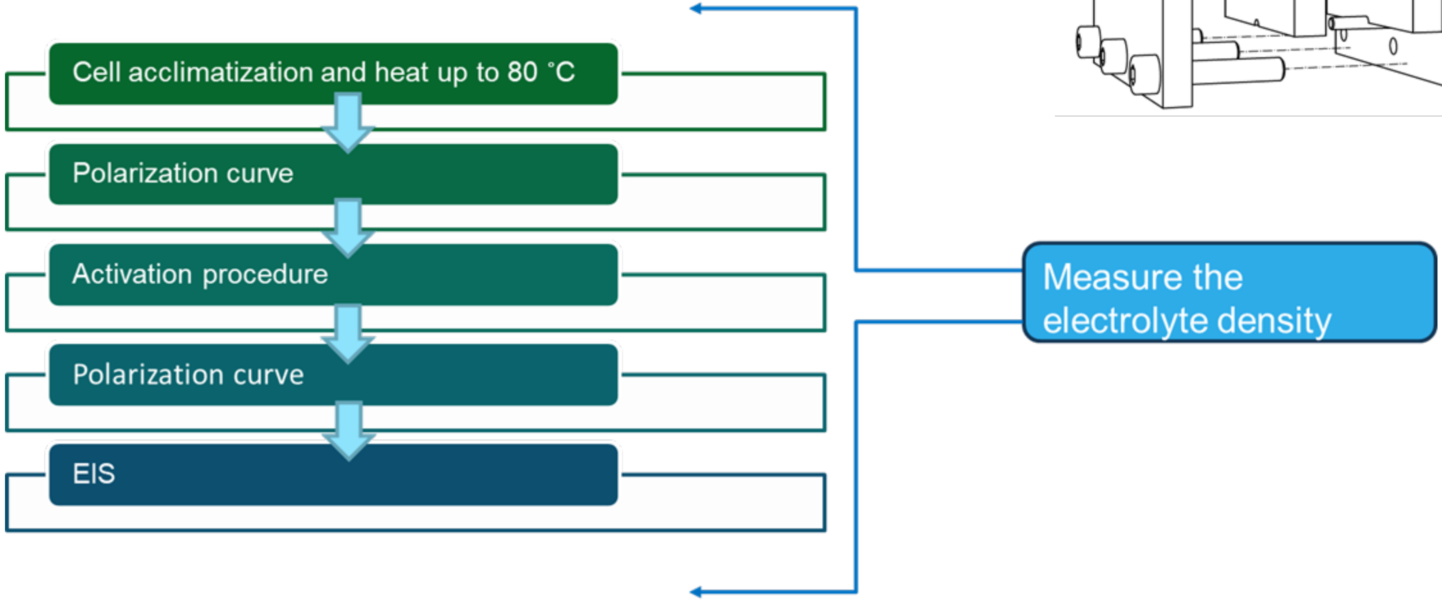
- Developing **testing protocol** and cell for straightforward **evaluation of state-of-the-art materials and components** to validate them through accurate comparison of performance.

The specific objectives are:

- **Evaluation and selection of liquid alkaline cell components**
- **Definition and execution of a harmonize testing protocol**



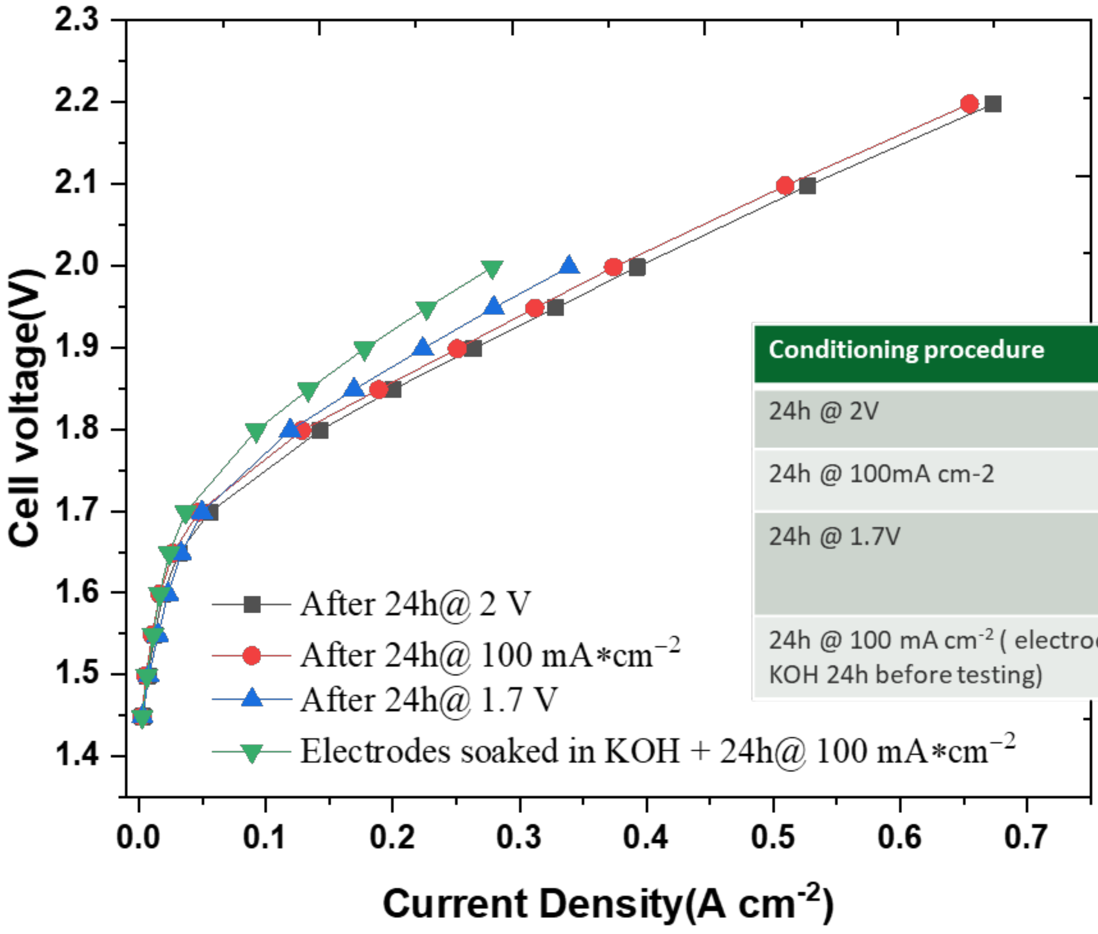


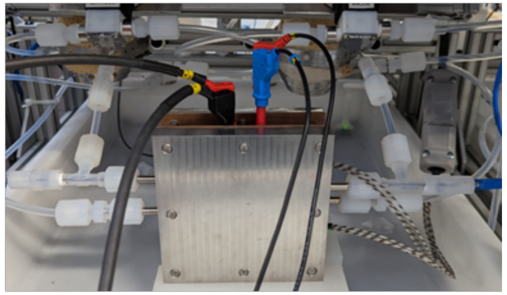


Accomplishments and Progress: Preliminary study of the Activation Procedure

- It is of utmost importance that a stable cell condition is established prior to performance testing.
- The effects of the conditioning process are essential to understanding the electrodes, separator, and cell performance.

- Anode: Ni foam 1.5mm
- Cathode: Ni foam 1.5mm
- Temp: Cell 80 °C
- Flow: 50 ml min^{-1}
- KOH: 30 wt.%



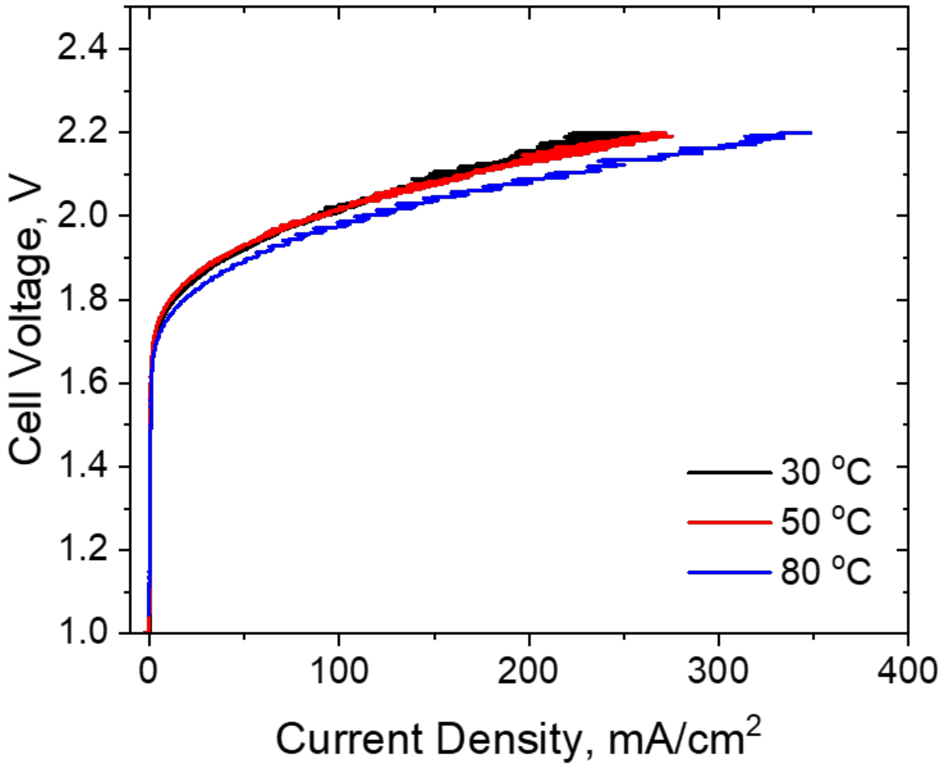


Conditioning procedure	Current @ 2 V
24h @ 2V	394 mA cm^{-2}
24h @ 100mA cm-2	374 mA cm^{-2}
24h @ 1.7V	338 mA cm^{-2}
24h @ 100 mA cm^{-2} (electrodes soaked in KOH 24h before testing)	278 mA cm^{-2}

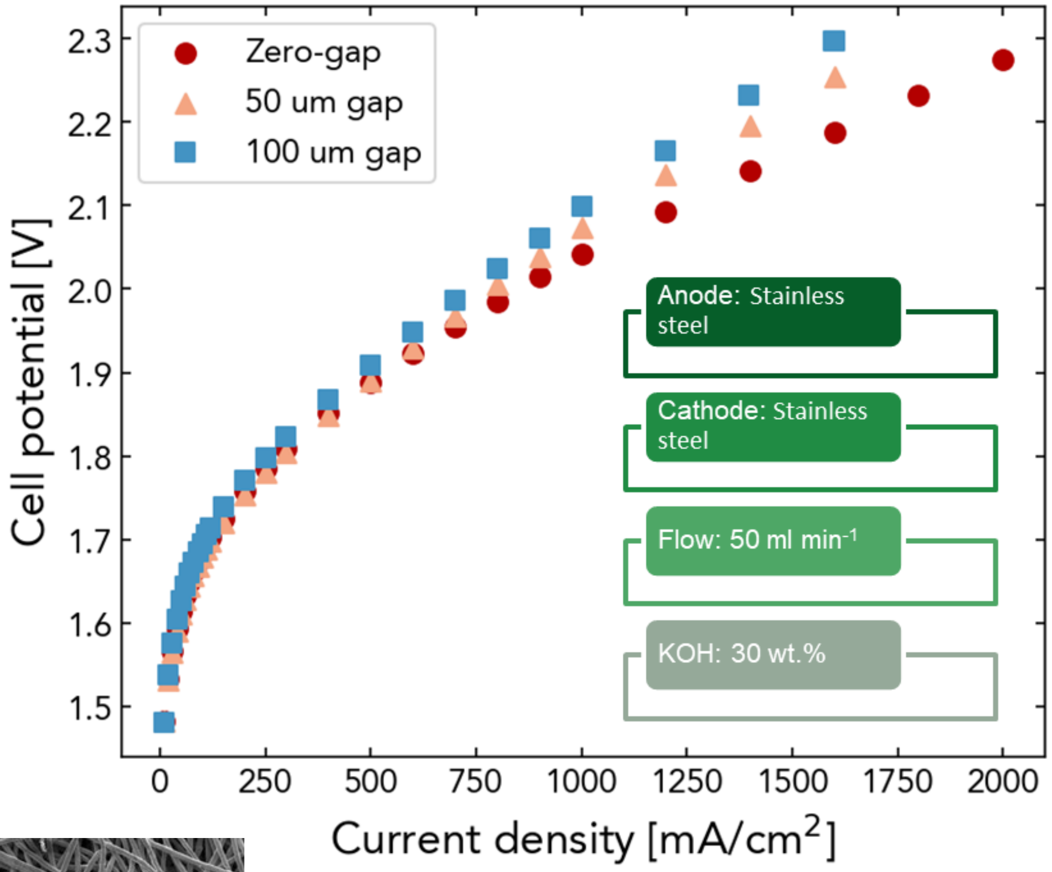
Accomplishments and Progress: Preliminary study of Temperature effect

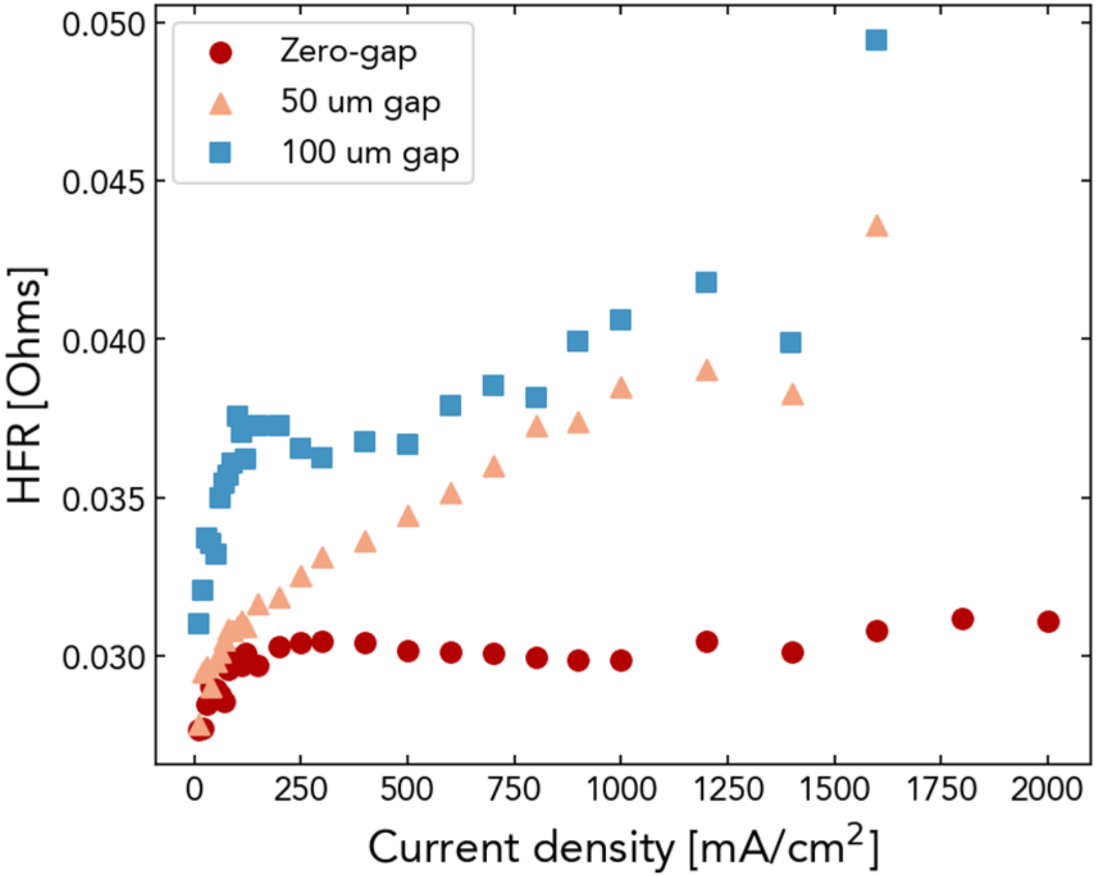
- optimal operating temperature for alkaline electrolysis depends on various factors such as the electrode material, the electrolyte concentration, and the system design.
- Cell efficiency increase at 80 C due to lower viscosity, higher conductivity of the electrolyte and high kinetics.

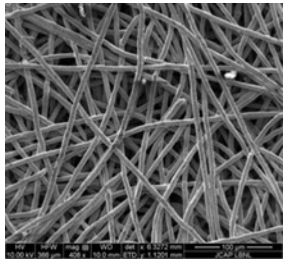
- Anode: Thermally treated Ni foam, 1mm
- Cathode: Ni foam, 1 mm
- Flow: 50 ml min^{-1}
- KOH: 30 wt.%



Accomplishments and Progress: Investigating Zero-gap and Finite-gap impact on the performance







Stainless steel (SS) electrode

- Finite-gap underperform even with very small gap due to increased HFR especially at high currents
- HFR increases as currents: more gas bubbles get trapped between the gap, leading to bubble-induced ohmic loss
- **Regulating bubble transport pathway will be a potential method to improve finite-gap performance**

Accomplishments and Progress: *Ex-situ* Components study- Effects of Thermal Treatment on Nickel Surface

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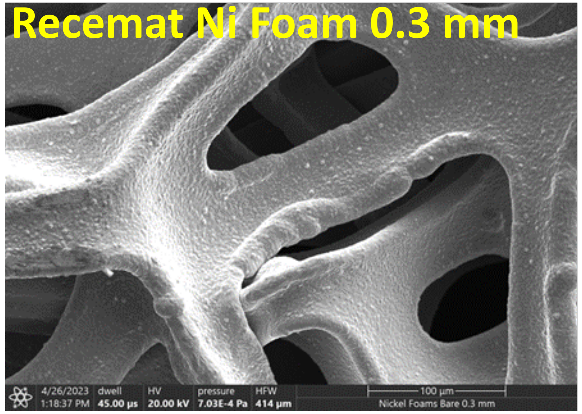
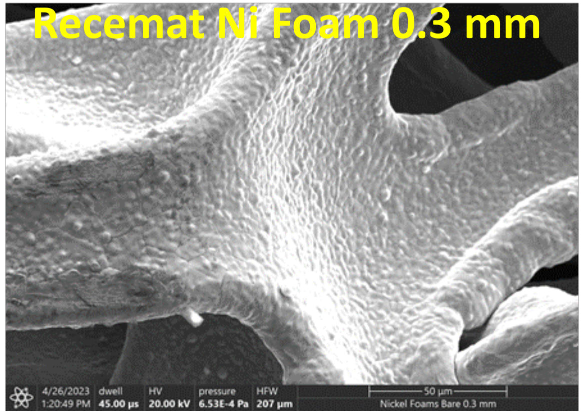
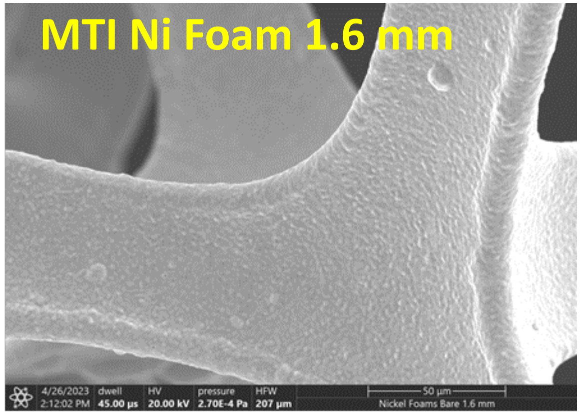
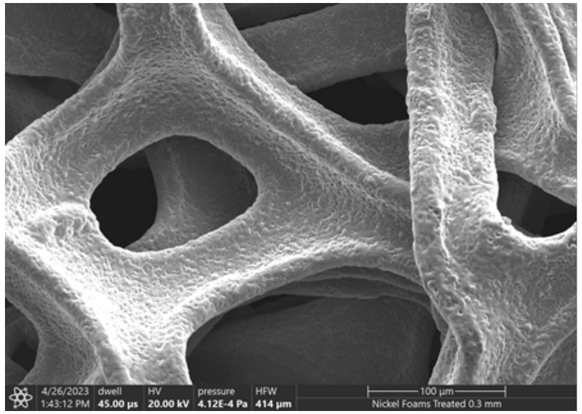
Bare Foam

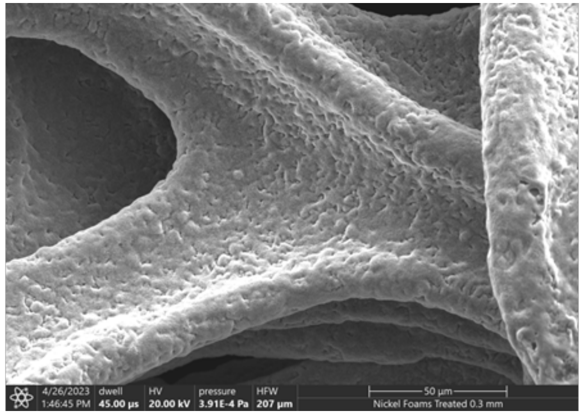


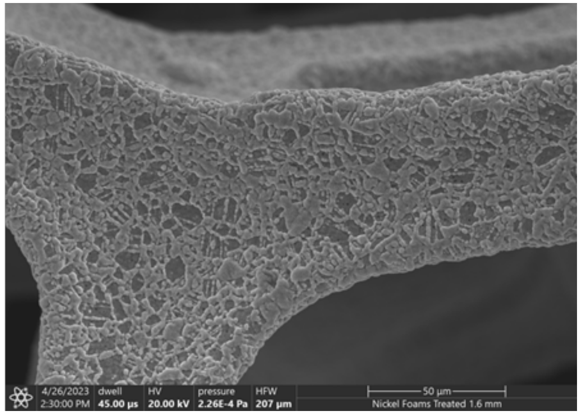




Treated Foams





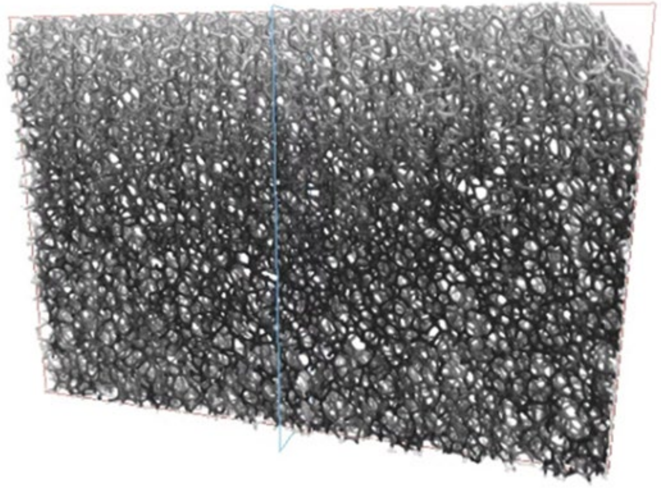


5-8% Weight gain observed

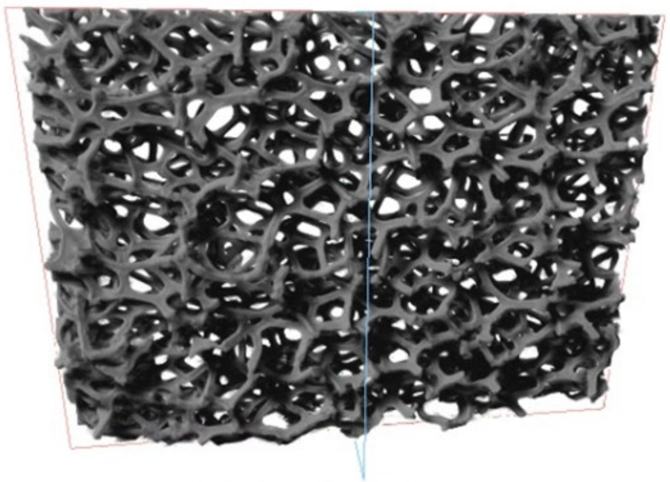
Anode annealing at 600 ^{o}C (24 h), results into a rough catalyst surface of NiO. Irrespective of Nickel foam source

Accomplishments and Progress: High Throughput *Ex-situ* Activation of Ni and Steel Electrodes

Commercial Ni Foam

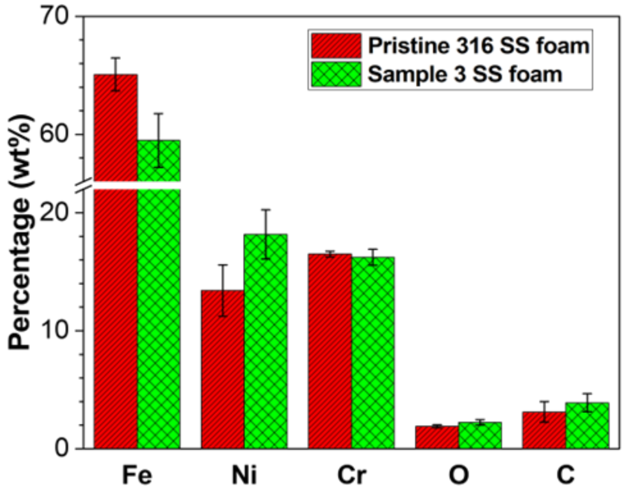


Voids Fraction: 90%

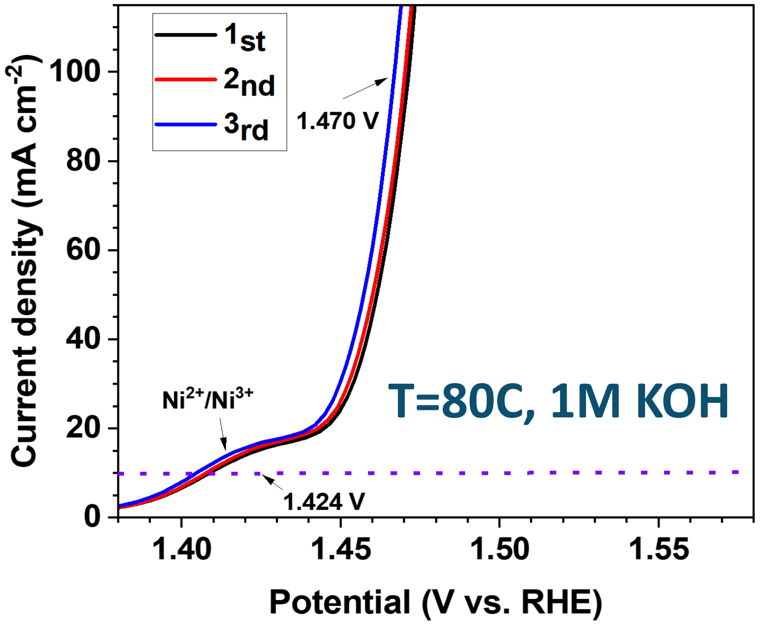


6-vessels Electrochemical Activation Setup and Activation Parameters

Voltage, V	Media	Duration, min	T, C
0.5, 1, 2	KOH	30, 60, 120	50, 80



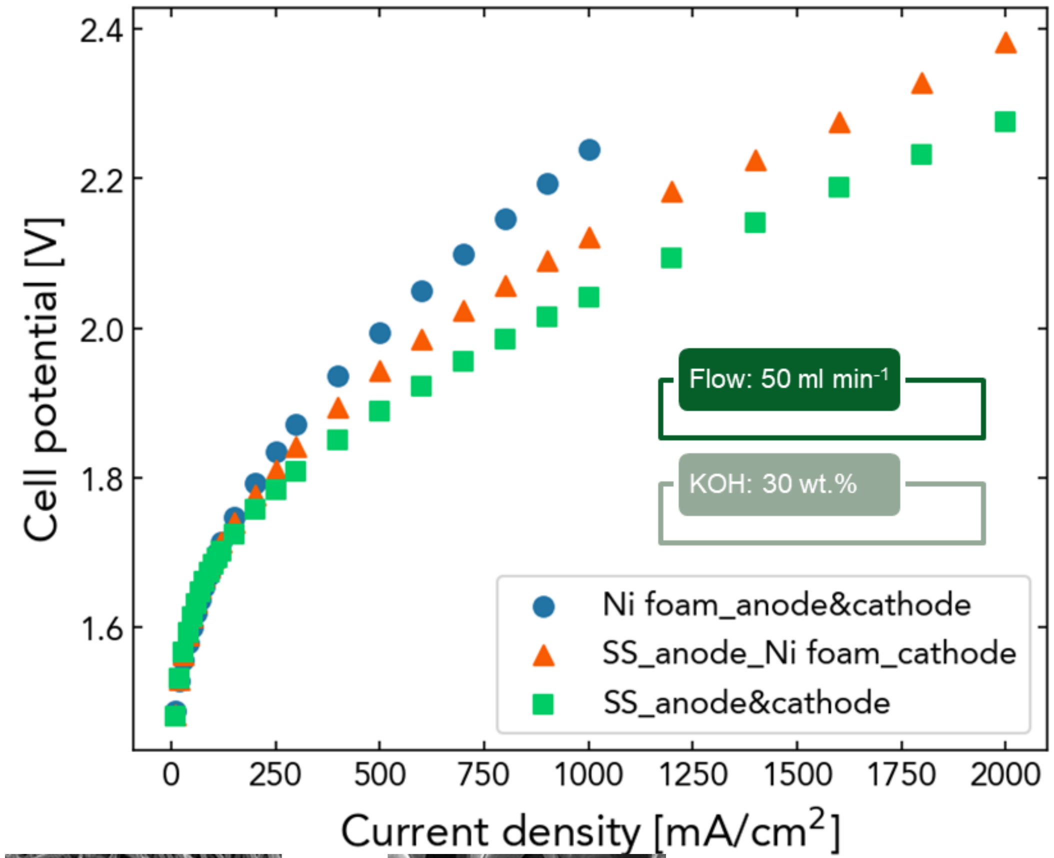
316 Stainless Steel

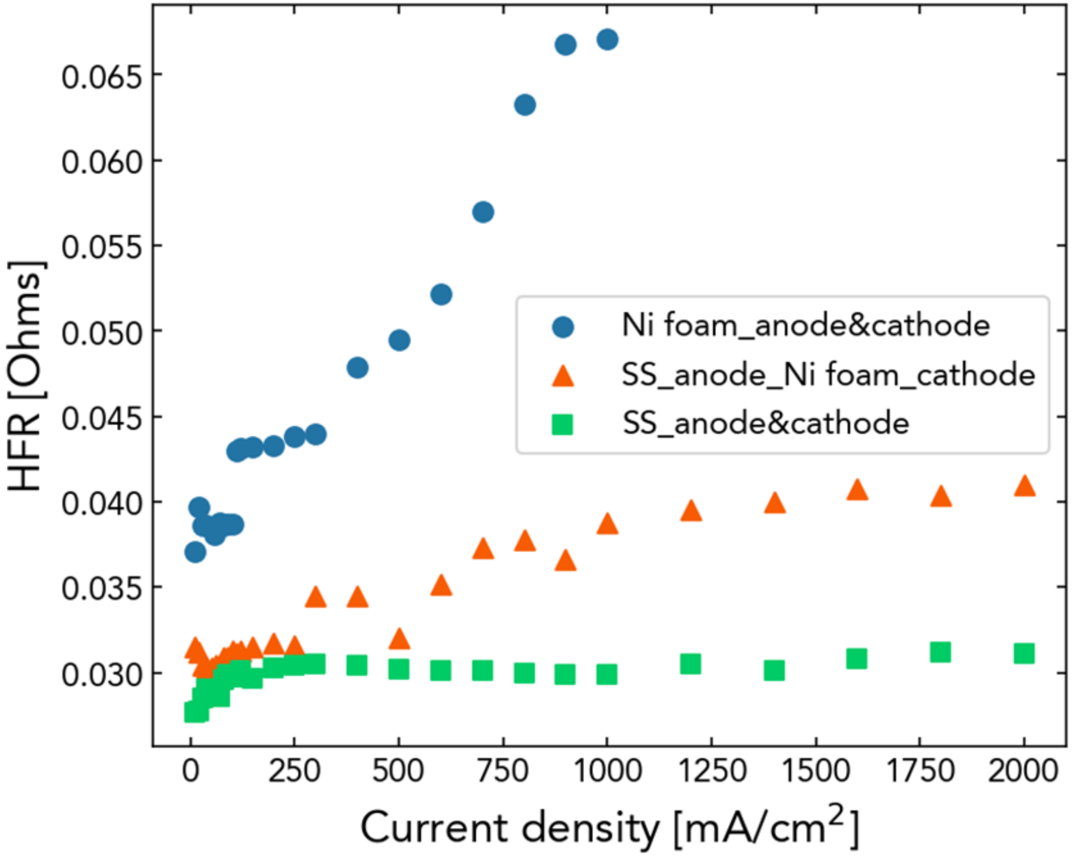


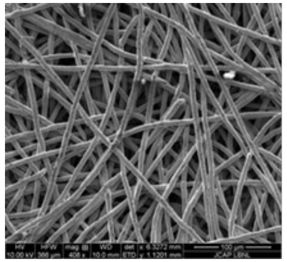
- Ex-situ activate stainless steel produced 100mA/cm^2 @ 1.47V

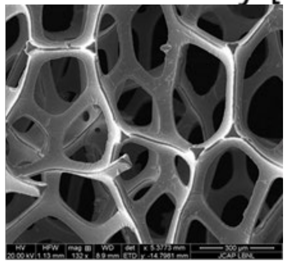
Micro-CT images provided by Dr. Angela Criswell; Rigaku Americas Corporation, TX, USA

Accomplishments and Progress: Investigated how various electrodes can improve the cell performance





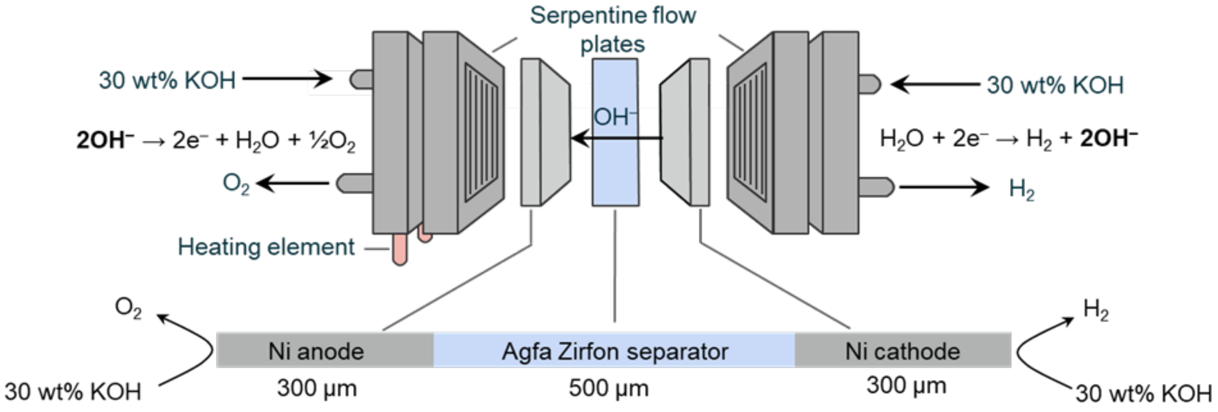


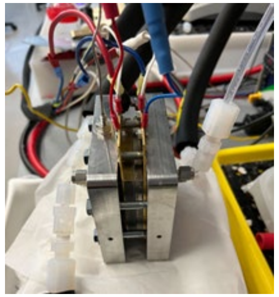


Stainless steel (SS) electrode (left) and Ni foam (right)

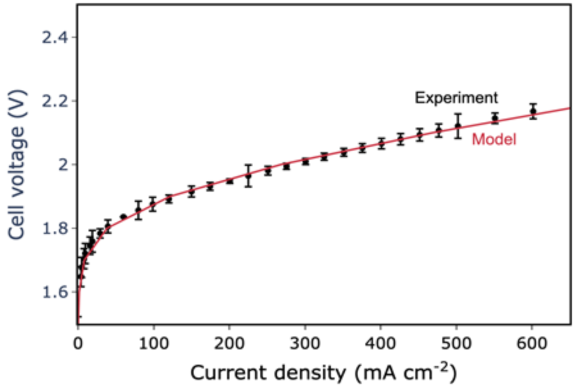
- Stainless steel electrodes enhances LAWE performance for both anode and cathode
- Electrode porosity can impact HFR by impacting bubble behavior
- **Electrode engineering is an efficient pathway for achieving advanced LAWEs**

Accomplishments and Progress: Cell Modeling





- **Utilize physics-based cell modeling to understanding limiting phenomena and be able to conduct sensitivity studies**



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

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

$$\sum_i z_i c_i = 0$$

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

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

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

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

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

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

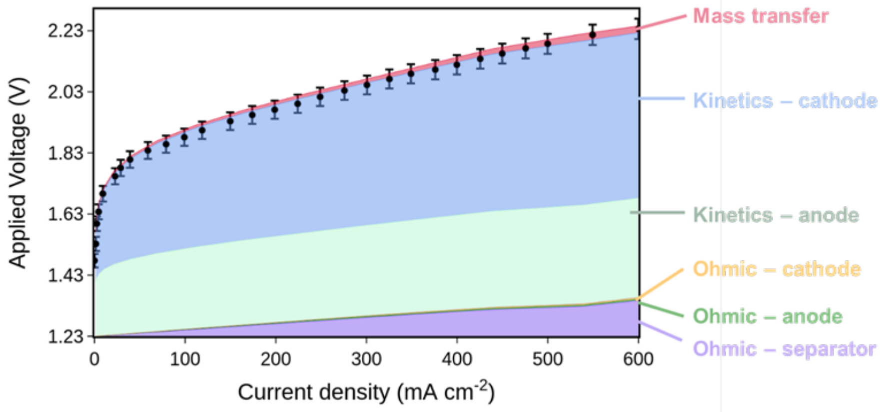
$$\mathrm{pH} = -\log K_W - \log \frac{a_W}{\gamma_{\mathrm{OH^-}} m}$$

Bubble coverage

$$a_v = a_v^0 (1 - \theta)$$

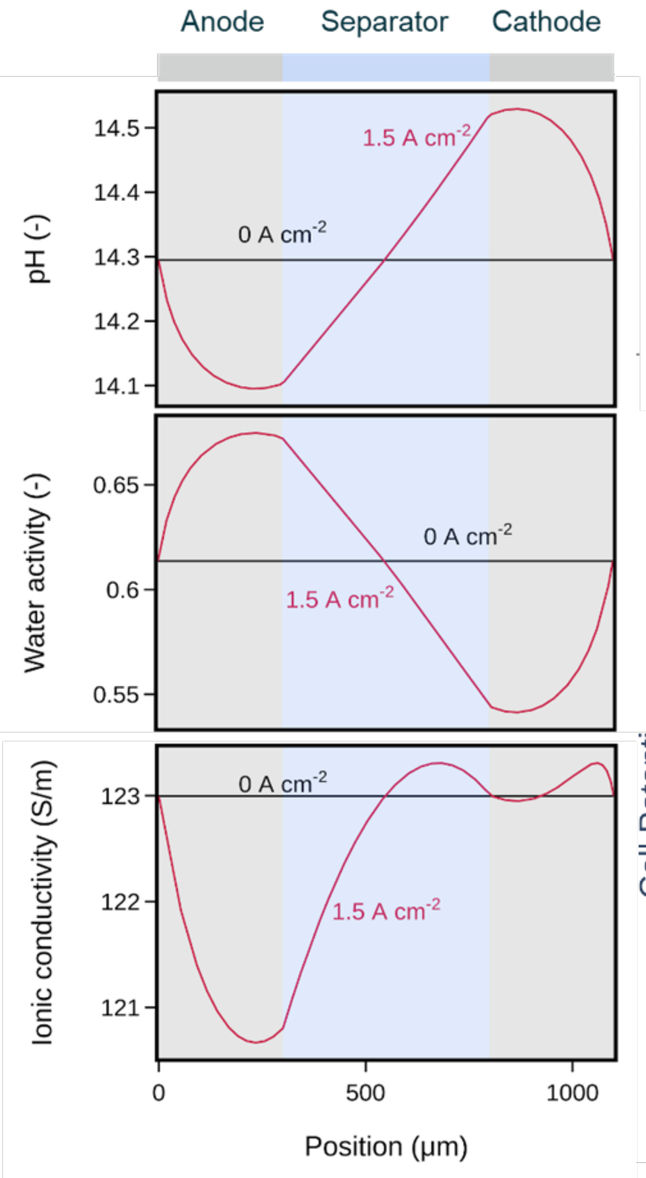
$$\theta = 0.023 i_{total}^{0.3}$$

Applied Voltage Breakdown



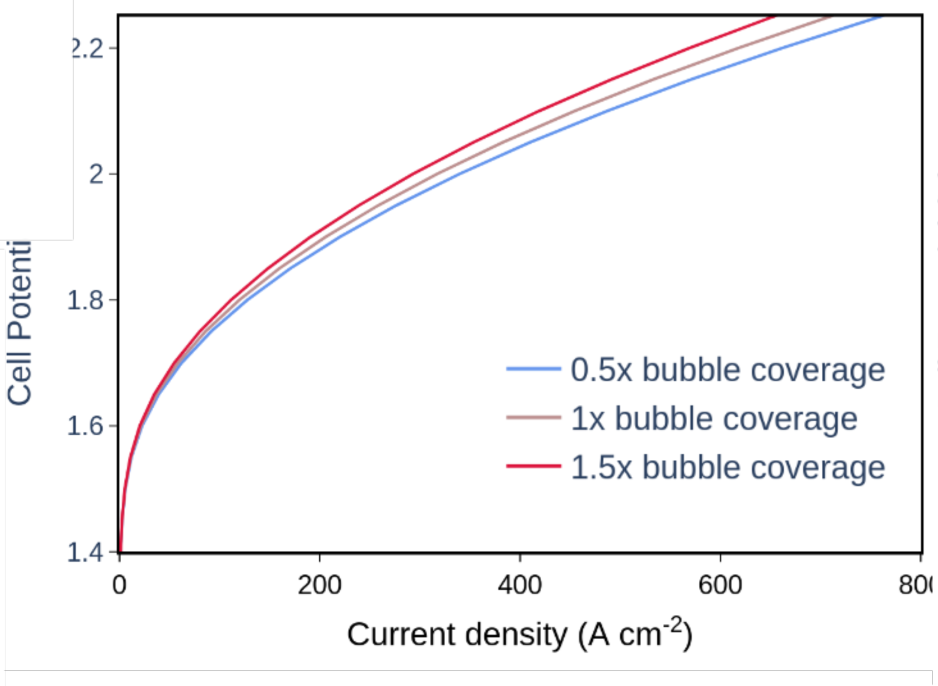
Karacan et al., **2022** *Int. J. Hydrog. Energy*, 47, 7, 4294-4303

Accomplishments and Progress: Cell Modeling

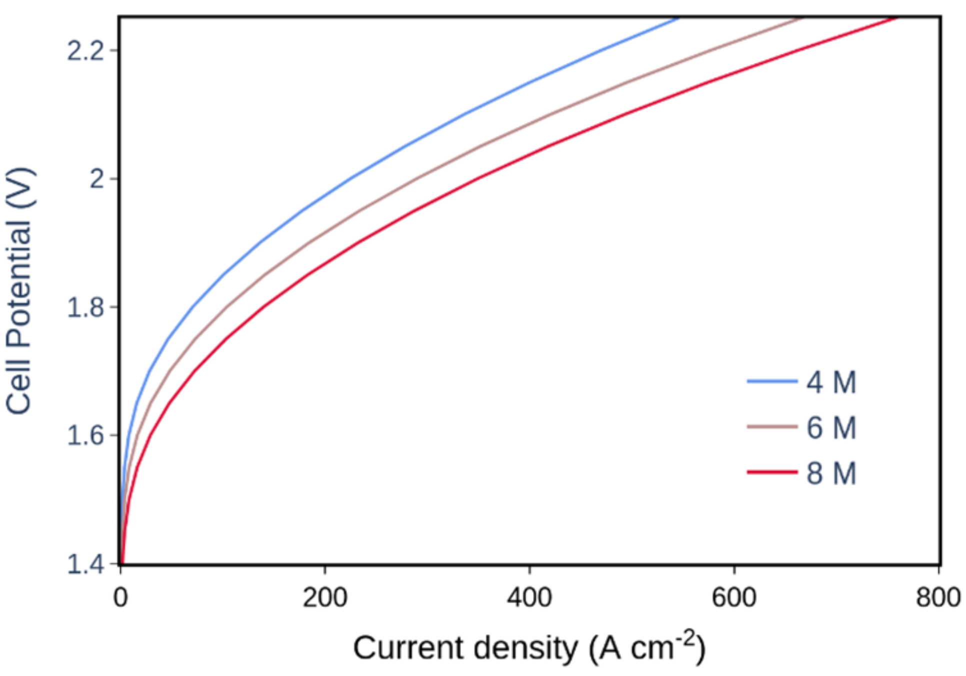


- Complex properties and gradients at higher current densities
- Initial sensitivity studies demonstrate importance of mass transport and ionic concentration on performance

Bubble Effects



KOH concentration



Accomplishments and Progress: Reference Liquid Alkaline Water Electrolysis (LAWE) System

- ➢ Develop reference system configurations for performance, durability and cost studies
- ➢ Develop quantitative understanding of mechanisms that determine system dynamic response to load changes, turndown, efficiency at rated power and partial loads, and durability.

Distributed LAWE System

1. Electrolyzer Stack
- MEA
  Separator: ZrO_2 Diaphragm (Zirfon)
  OER Anode Catalyst: Raney Ni (Ni-Al)
  HER Cathode Catalyst: Mo-doped Raney Ni (Ni-Al-Mo)
  Electrode Substrate: Ni-coated Expanded SS Sheet
- Anode O_2 PTL: Sintered Porous Ni
- Cathode H_2 PTL: Sintered Porous Ni
- Bipolar Plates: Ni Coated SS
- Current Collectors: Ni Coated Expanded SS
- End Plates: SS

2. Electrical BOP System
- Transformer
- Rectifier

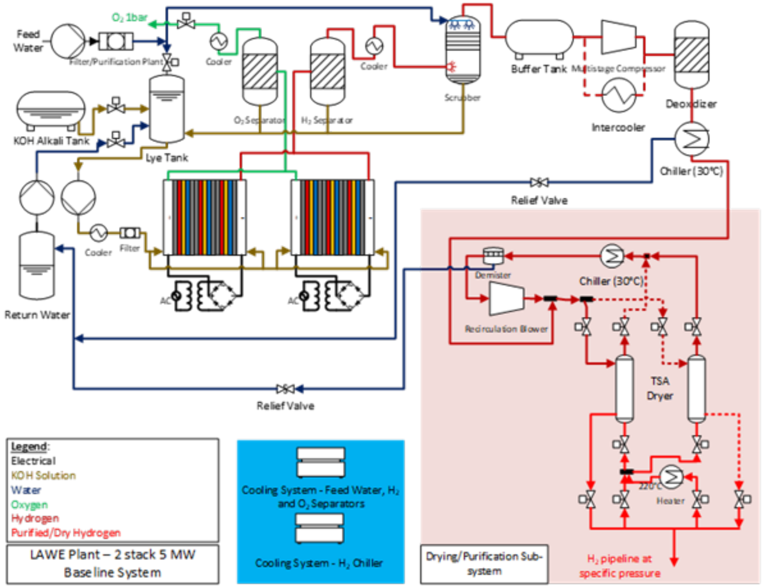
3. Feed Water System
- Feed Pumps
- Water Purification Plant
- Water Reservoir

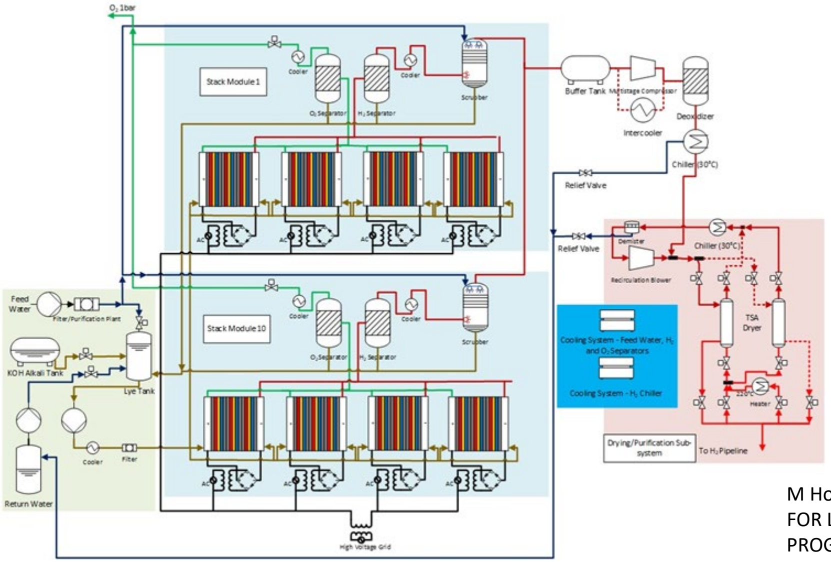
4. KOH System
- KOH Recirculation Pump
- KOH Cooler

5. Gas Treatment System
- Anode H2-Water Separator
- H2 Cooler
- H2 Scrubber
- Cathode O2-Water Separator
- O2 Cooler

6. H_2 Purification System
- H_2 Buffer
- H_2 Compression Unit
- Deoxidizer
- Condenser
- H_2 TSA Dryer

7. Cooling Water System
- Compression Chiller
- Dry Cooler





Centralized LAWE System

1. Stack Modules
- 1.1 4 X 2.5 MW stacks
- 1.2 Electrical BOP Subsystem
- 1.3 KOH Subsystem
- 1.4 Gas Treatment Subsystem

2. High Voltage Transformer

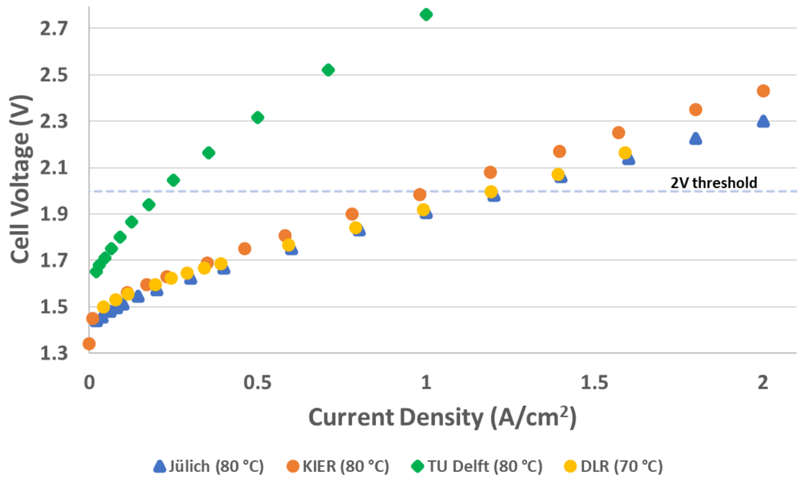
3. Feed Water System

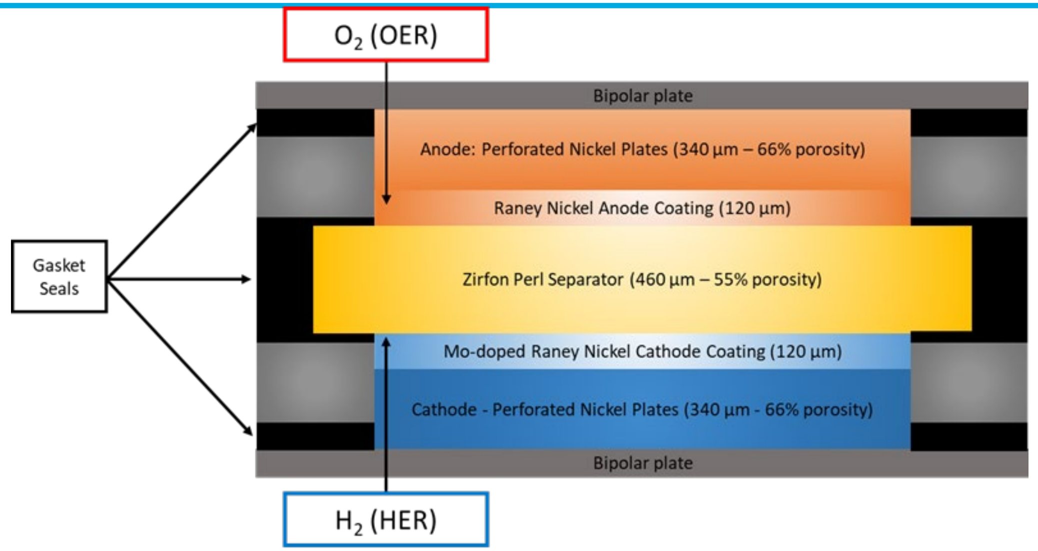
4. H_2 Purification System

5. Cooling Water System

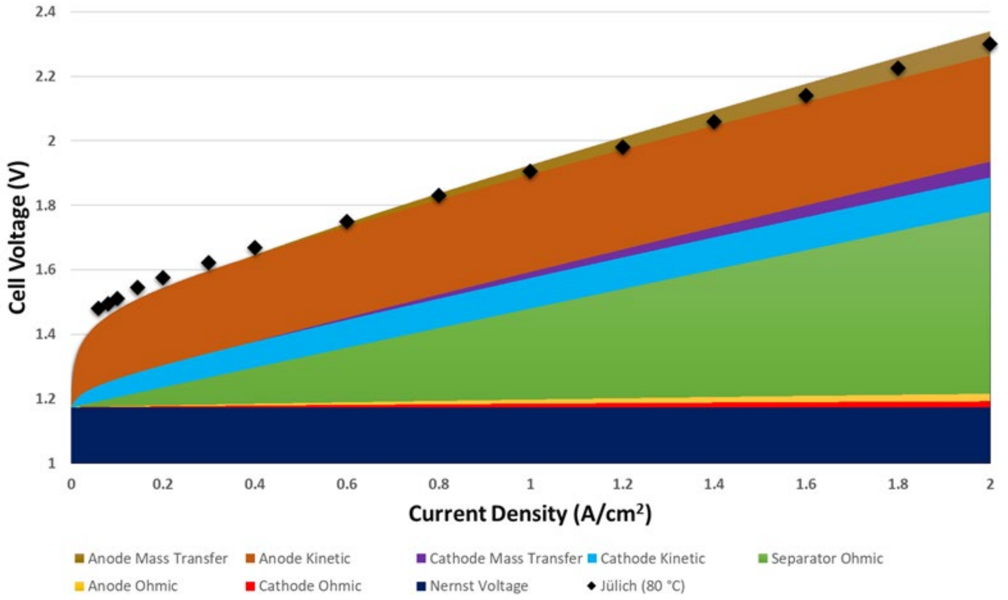
M Holst, S Aschbrenner, T Smolinka, C Voglstätter, G Grimm, COST FORECAST FOR LOW TEMPERATURE ELECTROLYSIS – TECHNOLOGY DRIVEN BOTTOM-UP PROGNOSIS FOR PEM AND ALKALINE WATER ELECTROLYSIS SYSTEMS, Fraunhofer Institute for Solar Energy Systems ISE, Oct 2021

Accomplishments and Progress: 1-D Distributed Kinetics Cell Model





Parameter	Unit	Value
Operating Temperature	°C	80
Operating Pressure	bar	1
Electrolyte Concentration	wt.% KOH	30
Cathode Catalyst	-	Ni-Al-Mo
Cathode Catalyst Coating	µm	120
Anode Catalyst	-	Ni-Al
Anode Catalyst Coating	µm	120
Separator	-	Zirfon PERL
Separator Thickness	µm	460
Cell Setup	-	Zero-gap



Approach: Expanding PEM focused technoeconomic and systems analysis capabilities to alkaline electrolyzers

H2NEW
U.S. DEPARTMENT OF ENERGY

H2NEW task 3c activities

- Technoeconomic cost modeling
- Electricity market analysis
- Systems analysis

Key hydrogen levelized cost factors

- Electrolyzer capital cost
- Electricity price and operating strategy
- Performance and durability

1 Dollar
1 Kilogram

Hydrogen levelized cost $/kg H2

Experimental R&D

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See p196d for H2NEW analysis poster

Proposed Future Work

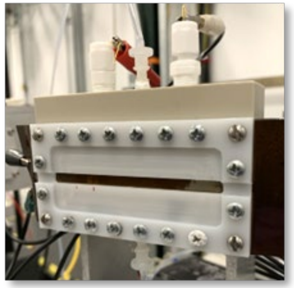
- Improve fundamental understanding of degradation mechanisms of electrodes separator materials and supporting electrolyte:
  - Effect of dynamic operation and temperature on Gas cross over
  - Short term durability study
  - Develop methods to track and quantify electrode morphology changes and evaluate 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)
- Improved separators : Modification of Zirfon and Zirfon alternatives
  - Explore inclusion of GRCs in alkaline separators
- Investigate Ni-based anode structures; fabricate various porous structures
  - Prepare Ni anode structures with graded porosity, low-tortuosity pores, and various pore sizes using modified tape-casting processing and inert-atmosphere sintering

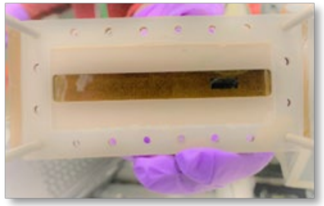
Proposed Future Work

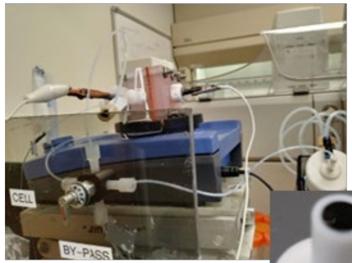
- Investigate the durability of stainless-steel based electrodes by potential-cycling or constant current hold
- Investigate Ni-based anode structures; fabricate various porous structures and deliver to cell testing task
- Prepare Ni anode structures with graded porosity, low-tortuosity pores, and various pore sizes using modified tape-casting processing and inert-atmosphere sintering
  - Develop control over pore size, pore shape, total porosity, and surface area/roughness
  - Parametric studies to determine impact of electrode structure on performance
  - Deliver samples to other sub-tasks for ablation, etching, catalyst deposition, etc
- Tailoring the catalyst layer micro-domain by laser ablation and anodization
- Evaluate the micro-domain morphological impact on catalyst-layer/bubble interfacial behavior and potential impact on liquid alkaline water electrolyzer performance

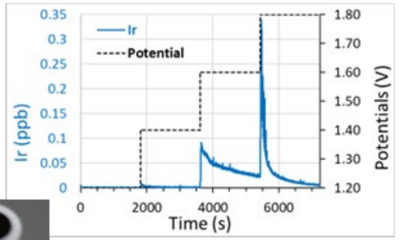
Proposed Future Work

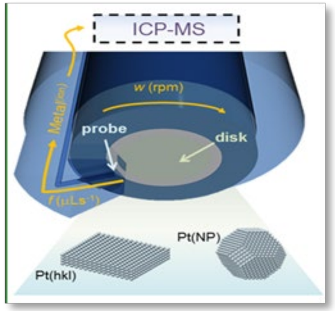
- Understanding and Mitigating Electrocatalyst Degradation
  - On-line ICP-MS of catalyst dissolution products as a function of potential and potential profile coupled with *in situ* X-ray absorption spectroscopy as input to component and cell degradation models
  - Ex situ or on-line HPLC coupled with conductivity measurement to study of impact of KOH concentration, dissolved H_2 and O_2 gases, impurities derived from another cell and system components on separator material degradation and conductivity
- 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











Proposed Future Work: Literature review and operating strategies

- Identify literature values for economic parameters for current (traditional) and future (zero-gap) LAWE
  - Data sources: operational plants, technoeconomic analysis, journals
  - Key variables: capital and operating costs, voltage, current, efficiency, part-load capacity, degradation rates, lifetime, replacement costs
- (Goal) Given an hourly electricity price dataset, calculate the operating profile which will minimize average electricity price while meeting a minimum capacity factor
- (Goal) From the operating profile, calculate the yearly degradation rate. This allows for calculating the replacement profile of the stack to input into H2A-Lite
- Identify pathways and tradeoffs that enable low-cost hydrogen production
  - Increasing durability (overall degradation and stack replacement timelines. Higher replacement frequency yields better efficiency but increases costs)
  - Economic and operational tradeoffs between PEM and LAWE