

H2NEW: <u>Hydrogen (H2) from Next-generation</u> <u>Electrolyzers of Water</u> H2NEW LTE: Manufacturing, Scale-Up, and Integration

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Project Goals



<u>Goal</u>: 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

H2NEW Task 3a,b: Manufacturing, Scale-Up, and Integration Overview



Timeline and Budget

- Start date (launch): October 1, 2020
- Awarded through September 30, 2025
- FY23 DOE funding for Task 3a,b: **\$2.3M**
- FY24 DOE funding for Task 3a,b: **\$3.6M**
- Total DOE funds received to date: **\$10.5M**

Barriers

- Durability
- Cost



Relevance and Impact





H2NEW Figure of Merit

- Ink and electrode activities (Task 3ai and 3aii) support transition to low catalyst loading and increased cell performance
- Defect and integration activities (Task 3aiii) address H2NEW performance and durability targets
- PTL and membrane activites (Task 3b) cross-cuts with Tasks 2 to engineer MEA subcomponents for improved performance and durability.

Relevance and Impact



Technical Targets for PEM Electrolyzer Stacks and Systems

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



Source: https://www.energy.gov/eere/fuelcells/technical-targets-proton-exchange-membrane-electrolysis

For details on footnotes a-i see above-referenced website.

Task 3 activities specifically focus on how MEA fabrication and component design impacts the capital cost, efficiency, and durability targets targets



Task 3a: MEA fabrication, Interface engineering

- i. Inks
 - Constituent interactions ink, formulation and preparation of the ink predefine the micro- and macro-scale behaviors
 - Ink morphology: particle size/agglomeration, stability, level of adsorption of ionomer, supported and unsupported catalysts
- ii. Electrodes
 - Coatability: rheology, wettability, drying, particle size, coating method
 - Electrode morphology: porosity, distribution of ionomer, thickness homogeneity
 - Novel electrodes: conductive additives, supported catalysts
- iii. Cell Integration, Interfaces, and Defects
 - Engineered cell interfaces: PTL surface modifications (laser ablation, protective coatings)
 - Impact of cell defects: modifications to PTL surface (abrasion, protective coating variations) and membrane thickness
 variations

Task 3b: Components

- i. Porous Transport Layers
 - Develop understanding of structure and function, design of new structures (bilayers, MPLs)
 - Porous transport electrodes
- ii. Recombination Layer Membranes
 - Develop understanding of structure and function, aid in design of new structures



Please see H2NEW Oral Presentation File for the overall H2NEW consortium safety planning and culture.



Milestone Name/Description		Туре	Status	
Probe gas recombination layer properties, performance and durability using model systems fabricated using two different methods at three different loadings and ionomer contents, provide data for modeling efforts.		QPM	Completed (Slide 21)	
Quantify properties (volume fraction, pore size distribution, tortuosity, and catalyst spatial distribution) of porous transport layers and porous transport electrodes, with and without microporous layers toward quantifying the impact of these properties on performance and durability	12/30/2023	QPM	Completed (Slide 12-14)	
Conduct in-cell performance and durability studies and ex situ analysis (e.g., TEM, CT, SEM, EIS) for anode catalyst layers fabricated from inks with different formulations (including incorporation of electron conductors), properties, and preparation histories to determine the impact of these factors on catalyst layer structure, performance, and durability.	03/31/2024	QPM	On going (Slides 18-19)	
Perform systematic investigation of anode fabrication to assess the impact of different PTL/MPLs on performance and durability. Investigate features such as catalyst loading, catalyst type, processing parameters, and PTL/MPL variations.		QPM	On going (Slide 13)	
Down-select to 1-2 baseline RC architectures based on repeatability, ease of fabrication, compatibility with recombination reaction mechanism studies, and ability to produce sufficient amounts for testing/characterization across consortium activities.	6/30/2024	QPM	In Progress	

Accomplishments and Progress: Explored organic solvents to improve ink stability



• **Objective:** Improve anode ink stability against agglomeration and gravitational settling using organic solvent to alter typical wateralcohol mixtures



NMP: N-methyl 2-pyrrolidone | DMSO: Dimethyl sulfoxide | PG: Propylene glycol | DMAc: Dimethyl acetate | DMF: Dimethylformamide | BG: 1, 2 Butylene glycol | EG: Ethylene glycol

0.1 wt% IrO₂: Nafion D2020 (0.2 I/C) 40:30:30 Solvent:water:nPA

- Examined stability of dilute inks in 13 solvent mixtures which include polar protic (aliphatic alcohols, aliphatic glycols, glycerol) and polar aprotic solvents
- Water-alcohol mixtures show least stability with the stability degree decreasing with increasing alcohol polarity or the length of the aliphatic chain
- Glycols and glycerol appear to be resulting in greater ink stability than alcohols





Dynamic Light Scattering



- DLS measurements indicate intermolecular interactions play a predominant role in the enhanced ink stability, particularly in viscous solvents (glycerol and glycols) that significantly reduce gravitational settling rate
- Size trends are consistent with gravitation settling behavior, supporting the visual observations
- Particle size and polydispersity appears to be minimal in glycerol, propylene glycol, and NMP solvents.
- Further validation of the particle size/stability measurements using additional H2NEW capabilities such as x-ray scattering techniques

Accomplishments and Progress: Impact of Ionomer EW on Ink Rheology and Stability



Objective: Explore the impact of ionomer equivalent weight on ink rheology and stability against agglomeration



Impact of ionomer EW on ink rheology is very weak in water-rich media, where for both 725 and 930 EWs, increasing I/C led to a weak increase in viscosity above a certain I/C

The addition of ionomer leads to transition in their rheological response from non-Newtonian to Newtonian suggesting stabilization of IrO2 particles against agglomeration for all EWs.



a [A-1]



- Ionomer EW has dramatic effect on ink rheology
- At high I/Cs, low EW ionomer (725) led to a more dramatic increase in the ink viscosities compared to high EW ionomer (930).
- Comparison of inks rheology against neat ionomer dispersions indicated low-EW ionomer likely induced catalyst flocculation in alcohol-rich media
- Results show ionomer EW and dispersion media impact ink morphology

η [Pa·s]

Accomplishments and Progress: Improve Uniformity of Rollto-Roll Coated, Low Loaded Iridium Oxide Anode

- U.S. DEPARTMENT OF ENERGY
- In FY22, attempts to fabricate low loaded IrO₂ PEMWE electrodes (≤ 0.2mg_{Ir}/cm²) at scale resulted in catalyst layer homogeneity issues
- FY23 work focused on improving this homogeneity and determining impact on MEA performance/durability









- Homogeneity was improved through new mixing and coating processes
- Steady-state MEA behavior at 3A/cm² showed significant differences between FY22 anode (red) and FY23 anodes of similar loading
- Cell performance at end of life reflected similar trends to steady state voltage measurements
- Collaborating with durability task to better understand results

 $0.260 \, mg_{Ir}/cm^2$

Accomplishments and Progress: XPS Characterization of MEAs

lr 4f

59

M=O Oxide

M-OH Hydroxide





• XPS used to characterize changes in MEA composition as a function of fabrication method and testing protocol

Effect of Testing:

- **Spray coating and Gravure:** The relative amount of Ir to Ionomer changes – increases with testing for all samples
- **Spray Coating: Higher** hydroxide vs oxide amount before and after testing
- Gravure: Lower or similar amount of hydroxide vs oxide

Accomplishments and Progress: Platinum Black as Electron Conductive Additive in Anode





Iridium fraction	In-plane e ⁻ conductivity (S/cm)			
1.00	2.69			
0.80	16.64			
0.52	24.15			
0.20	30.43			
0.01	82.72			

- Incorporation of Pt in anode CL increases in-plane conductivity enhancing Ir utilization
- Replacing ~80% of Ir with Pt only results in a 14 mV loss at 0.2 A cm⁻².
- Durability Impact of replacing Ir with Pt under study; initial results promising

Substituting Ir with Pt could significantly reduce the cost without loss in performance

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Accomplishments and Progress: Characterization of Commercial PTL Architectures up to 30 bar



- Investigated 6 Commercial PTL/MPL samples
 - 3D microstructure characterized using synchrotron-based tomography
 - Samples were tested *in operando* up to 30bar cathode backpressure using FuGeMEA configuration



Sample		Porosity % (through plane, avg)	Average Pore Radius (µm)	Average Parti cle Size (µm)	Tortuosity	
	Thickness (µm)				In-plane	Through- plane
Felt PTL (H2NEW Baseline)	271 ± 1.5	74.1 ± 1.8	14.6 ± 9.3	22.3 ± 2.5	1.29	1.52
Sinter #1 PTL	278 ± 5.5	33.3 ± 6.1	6.28 ± 2.7	8.75 ± 2.6	2.85	3.46
Sinter #1 MPL	142 ± 2.3	30.3 ± 7.0	4.57 ± 1.8	7.85 ± 2.4	3.56	3.20
Sinter #2 PTL	250. ± 2.8	41.6 ± 5.6	3.66 ± 1.3	4.38 ± 1.0	2.43	2.02
Sinter #2 MPL	46.0 ± 1.9	29.4 ± 1.4	2.09 ± 0.53	3.65 ± 0.95	4.78	2.87



 PTL performance determined by HFR due to either contact or bulk e⁻ transport resistance

Accomplishments and Progress: Examining Effects of PTL and Catalyst Layer



- Testing conducted to determine appropriate MEA for screening PTL materials
- Compared BOL performance of 0.1 and 0.4 mg_{lr}/cm² anodes with commercial PTLs
- Lower loadings are more impacted by PTL structure than higher loadings
- Cell performance dominated by changes in HFR from PTL/CL contact area



Accomplishments and Progress: Quantifying Mechanical Deformation at PTL/Anode Interface





Accomplishments and Progress: Development of MPL/PTL with improved performance

2.1

2.0

Cell potential [V] ^{8.1} ^{9.1} ^{9.1}

BL-P30-Powder

BL-P30-Fiber



- Develop PTLs with optimized structure using scalable processing methods
- Improve understanding of critical structural parameters (pore size, pore shape, pore volume, graded porosity)
- MPL/PTL structures

New structures significantly improve performance

- **One-step preparation of MPL/PTL** structure using phase inversion tape casting
 - **Reduced tortuosity, enhanced** permeability
- Sintered MPL onto commercial PTLs
 - Enhanced surface area, reduced gap size •

J.K. Lee, M.C. Tucker, et al., Pioneering Microporous Layers for Proton-Exchange-Member Water Electrolyzers via Tape Casting



Accomplishments and Progress: Electrospun Titanium Based Microporous Layers for PTLs





SEM of Electrospun MPL





- Electrospinning offers precise control over the morphology of titanium fibers for highly customizable MPLs
- On going work to optimizing the sintering environment and surface treatment for increasing corrosion resistance of PTL without PGM coating



Electrospun MPL improves interface with CL increasing performance

Anode: IrO₂, 0.12 mg/cm²; Pt-coated 2GDL10-0.25. Cathode: catalyst loading, 0.1 mg_{Pt}/cm² TEC10V50E; MGL370. Membrane: N115

Accomplishments and Progress: Impact of Membrane Thickness Variations





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Accomplishments and Progress: Ionomer-free Electrodes





Ink infiltration into PTLs and MPLs leads to poor PTE and MPE performance FY23 work focused on mitigating this infiltration to improve performance

Accomplishments and Progress: QPM—Ink-Based PTEs and





MPEs



High Viscosity Ink: Cross Sections and Performance Ink PTE Ink MPE



PTE and MPE BOL Performance



Ink infiltration was reduced by coating with high-viscosity anode inks onto MPLs

- Regardless, high (>1mg_{Ir}/cm²) loadings were required to achieve similar performance to baseline CCMs
- Different ink avenue or coating method (spray, sputtering) may be needed to achieve desired performance

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Accomplishments and Progress: Investigating Impact of Recombination Catalyst Location





H2NEW: Hydrogen from Next-generation Electrolyzers of Water Cell Temperature: 80 °C; Anode H₂O: 75 ml min⁻¹; Gas flow rate: 300 sccm; Active area: 50 cm²



NREL Team Members: Sunil Khandavalli, Diana Zhang, Scott Mauger, Chance Parrish, Elliot Padgett, Chang Liu, Guido Bender, Jake Wrubel, Ricardo Duarte, Robin Rice, Chai Engtrakul, Sarah Blair [Ink characterization and studies, Electrode coating, In situ testing, MPL studies, Recombination Layer Fabrication]

LBNL Team Members: Grace Lau, Jason Lee, Michael Tucker, Adam Weber, Anyka Bergeson-Keller, Ahmet Kusoglu, Elizabeth Greenberg, Ashley Bird, Xiong Peng, Rangachary Mukundan[Fundamental material interactions and interfaces studies, Electrode coating, PTL fabrication and surface modification, In situ studies]

ANL Team Members: C. Firat Cetinbas, Nancy Kariuki, Debbie Myers, Jaehyung Park [X-ray characterization studies for inks and electrodes]

ORNL Team Members: Xiang Lyu, Alexey Serov, Dave Cullen, Haoran Yu, David Arregui-Mena [Ink characterization and studies, Electrode coating, Electron microscopy]

LANL: Tanvir Arman, Sergio Diaz-Abad, Kaustubh Khedekar, Siddharth Komini Babu, Kui Li, Yuanchao Li, Jacob Spendelow [Recombination layer fabrication and testing, PTL and MPL fabrication]

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







Bringing Science Solutions to the World







Accomplishments and Progress: Response to Previous Year's Reviewers' Comments



This poster is part of the H2NEW consortium oral presentation and was not reviewed separately at the last AMR.



Please see the H2NEW Oral Presentation File (AMR Project ID # p196) for the overall H2NEW consortium Diversity Equity Inclusion and Accessibility and Community Benefit Plan Accomplishments

Remaining Challenges and Barriers

- Relate ionomer-catalyst interactions to MEA performance and durability
- Catalyst and electrode improvements for improved utilization and durability
- Optimize MEA interfaces, especially catalyst layer-PTL
- Understand MPL coating and target properties/design
- Advanced membranes for reduced/mitigated crossover

Overall Goal: Understand component integration and scaling while maintaining or improving durability



Proposed Future Work



Task 3a: MEA fabrication, Interface engineering

- i. Inks
 - Better understanding of ink thickening mechanism to control this behavior
 - Develop inks for next-generation commercial materials (supported and unsupported)
- ii. Electrodes
 - Fabrication of catalyst layers with next-generation commercial materials
 - Continue work on incorporation of electron conductors
- iii. Cell Integration and Interfaces
 - Effects of local membrane thinning and pinholes on cell performance and durability
 - Studying the effect of TiO_x and PTL coating defects on the performance and durability
 - Nanostructure fabrication of PTL surface with laser ablation

Task 3b: Components

- i. Porous Transport Layers
 - i. Optimize MPL and phase inversion structures; downselect and scale up best structures
 - ii. Porous transport electrode (PTE) fabrication and testing using commercial and H2NEW-made materials
- ii. Recombination Layers
 - Model impact; develop understanding of structure and function, aid in design of new structures

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

Summary—Task 3



- The task 3 effort focuses on cell integration and scale-up aspects of the overall H2NEW goals
 - Efforts are highly integrated with Task 1 durability and Task 2 performance efforts
- Task 3 work areas include inks, electrodes, integration and interfaces, PTLs, and MPLs
 - Developed MPL fabrication processes

- Key findings to date include:
 - Several methods for MPL fabrication are successful, and final choice should depend on performance, scalability, and projected cost

Technical Back-up and Additional Information



Publications



- 1. Khandavalli, S., Park, J., Winter, H. Myers, D.; Ulsh, M.; Mauger, S. (2023) Viscoelasticity enhancement and shear thickening of perfluorinated sulfonic acid ionomer dispersions in water-alcohol solvent mixtures. *Macromolecules* **2023**, 56, 6988–7005.
- 2. J.K. Lee, G. Y. Lau, A. Bergeson-Keller, A. Kusoglu, X. Peng, and M.C. Tucker, Pioneering Microporous Layers for Proton-Exchange-Member Water Electrolyzers via Tape Casting, Applied Functional Materials, Submitted
- 3. Jason K. Lee, Grace Anderson, Andrew W. Tricker, Finn Babbe, Arya Madan, David A. Cullen, José' D. Arregui-Mena, Nemanja Danilovic, Rangachary Mukundan, Adam Z. Weber, Xiong Peng, "Ionomer-free and recyclable porous-transport electrode for high-performing proton-exchange-membrane water electrolysis". *Nat Commun.* 14, 4592, 2023
- Lyu, X.; Foster, J.; Rice, R.; Padgett, E.; Creel, E. B.; Li, J.; Yu, H.; Cullen, D. A.; Kariuki, N. N.; Park, J. H.; Myers, D. J.; Mauger, S.; Bender, G.; Pylypenko, S.; Serov, A. Aging Gracefully? Investigating Iridium Oxide Ink's Impact on Microstructure, Catalyst/Ionomer Interface, and PEMWE Performance. Journal of Power Sources 2023, 581, 233503. <u>https://doi.org/10.1016/j.jpowsour.2023.233503</u>.
- 5. Ferner, K. J.; Park, J.; Kang, Z.; Mauger, S. A.; Ulsh, M.; Bender, G.; Litster, S. Morphological Analysis of Iridium Oxide Anode Catalyst Layers for Proton Exchange Membrane Water Electrolysis Using High-Resolution Imaging. *International Journal of Hydrogen Energy* **2024**, *59*, 176–186. https://doi.org/10.1016/j.ijhydene.2024.02.020.
- 6. Liu, C.; Wrubel, J. A.; Padgett, E.; Bender, G. Impacts of PTL Coating Gaps on Cell Performance for PEM Water Electrolyzer. *Applied Energy* **2024**, *356*, 122274. <u>https://doi.org/10.1016/j.apenergy.2023.122274</u>.
- Liu, C.; Wrubel, J.; Padgett, E.; Bender, G. The Impacts of Membrane Pinholes on PEM Water Electrolysis. *Journal of Power Sources* 2023, 581, 233507. <u>https://doi.org/10.1016/j.jpowsour.2023.233507</u>.

Presentations



 Foster, J., Liu, X., Creel, E., Li, J., Yu, H., Cullen, D.A., Kariuki, N.N., Park, J., Myers, D.J., Serov, A., Pylypenko, S. Investigation of Surface Chemistry of Pemwes Iridium Oxide Catalyst Layers as a Function of Ink Aging Time, *243rd Meeting of the Electrochemical Society,* Boston, MA, May, **2023**, oral
 Foster, J., Lyu, X., Padgett, E., Mauger, S., Serov, A., Pylypenko, S., X-ray Photoelectron Spectroscopy Analysis of PEMWE Catalyst Layers with Focus on Catalyst-Ionomer Interface, *AVS 69th International Symposium and Exhibition*, Portland, OR, November **2023**, Poster
 Foster, J., Lyu, X., Padgett, E., Mauger, S., Serov, A., Pylypenko, S., X-ray Photoelectron Spectroscopy Analysis of PEMWE Catalyst Layers with Focus on Catalyst-Ionomer Interface, *18th Topical Conference on Quantitative Surface Analysis*, Portland, OR, November **2023**, Poster
 Alexey Serov, Xiang Liu, Jayson Foster, Robin Rice, Elliot Padgett, Scott Mauger, Guido Bender, Erin B. Creel, Haoran Yu, David A. Cullen, Nancy N. Kariuki, Jae Hyung Park, Deborah J. Myers, Svitlana Pylypenko "Catalysts, Inks and Electrodes for PEM Water Electrolysis: Scalable Approach for Highly Performed Catalyst Layer Fabrication", 243rd Meeting of the Electrochemical Society, Boston, MA, May, **2023**, *Invited* Kaustubh Khedekar, Kui Li, Ryan Gebhardt, Andrew Park, Rod L. Borup, and Siddharth Komini Babu. "Fundamentals of Gas Permeation in PEM Water Electrolyzers Operated at High Pressures", 244th Fall ECS Meeting, Gothenburg, Sweden, October, **2023**.
 Siddharth Komini Babu, Tanvir Arman, Sergio Diaz Abad, Abdurrahman Yilmaz, Jacob LaManna, Daniel S. Hussey, Jacob S. Spendelow. "Novel Porous Transport Layers for Polymer Electrolyte Membrane Water Electrolyzers", 2023 AlChE Annual Meeting, Orlando, FL, December, **2023**. *Invited*



- Enter patent applications here
 - LBNL record of invention: Porous titanium structures for water electrolyzers (Tucker, Shen, Lee, Lau)
 - LBNL&UCI Patent: Nemanja Danilovic, Keonhag Lee, Devashish S Kulkarni, Iryna Zenyuk, Adam Weber, Xiong Peng. 'Treatment of a porous transport layer for use in an electroylyzer'. US20230407457A1

- H2NEW members are subrecipients on existing industry-led FOA projects
 - 3M-P197
 - Nel Hydrogen P198
 - Plug Power P199



• Xiang Lyu and Alexey Serov received "ORNL Director's Award for Team Accomplishment in Outstanding Research Output", November 5, 2023