

# **H2NEW: Hydrogen (H2) from Next-generation Electrolyzers of Water H2NEW LTE: Manufacturing, Scale-Up, and Integration**

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Project ID # P196C



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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.



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: **\$2.3M**
- Annual budget adjustments anticipated

# **Barriers**

- **Durability**
- **Cost**







- Task 3 specifically focuses on manufacturing cost reductions through enabling high throughput fabrication techniques:
	- Understanding inks
	- Catalyst layer optimization and fabrication
	- Porous Transport Layer (PTL) design and optimization
- MEAs, PTLs and other components developed within Task 3 crosscut with Tasks 2 and 3



#### **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
- 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 pinholes

## **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
	- Model impact, develop understanding of structure and function, aid in design of new structures





# **Accomplishments and Progress: Further Understanding of Ink Thickening**

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- $1rO<sub>2</sub>$  catalyst inks are challenging to handle and process due to low viscosity and high sedimentation
- In FY22, we found that water-rich inks leads to a gelation with aging
- FY23 work focus on understanding mechanism and determining impact on MEA



- **Demonstrated that ink age/viscosity not showing impact on performance**
- **Experiments show thickening is caused by ionomer, likely due to bridging**
- **Thickening not dependent on catalyst type or dispersing process**

# **Accomplishments Progress: Understanding shelf-life stability of IrO<sub>2</sub> inks**

- There is a critical need to understand catalyst particle and ink stability over time relative to use and storage in an industrial setting
- Catalyst, ink, and electrodes were studied over two weeks to investigate if changes occur







- **Measurements of ink and catalyst layers do not show significant differences in properties**
- **Age of ink does not impact MEA performance indicating good shelf stability of inks**

# **Accomplishments and Progress: In situ measurements of Ink Mixing Methods on Particle Size Distribution**



## Quantified catalyst ink particle size distribution through in situ and ex situ x-ray scattering measurements ink mixed with different methods

Alfa Aesar IrO<sub>y</sub>/D2020 (I:C=0.2)/Water-nPA (1:1) Ink Mixing Methods:

- Bath sonication (Ink 1)
- Horn sonication (Ink 2)
- High shear mixing Turrax18G (Ink 3)
- High shear mixing Turrax 25F (Ink 4)
- Ball Milling (Ink 5)

## **Ultra-small angle X-ray and small-angle**



#### Mixing Methods High-Shear Mixing Time Ball Milling Time -ink5 ball mill 1hr -Ink1 Bath -Ink4\_Turrax\_25F\_1 min -Ink2 Horn -ink5\_ball mill\_24 hr -Ink4\_Turrax\_25F\_30 mins **Volume Fraction** -Ink3 Turrax 18G 30 mins -Ink4 Turrax 25F 30 mins  $P<sub>2</sub>$ -ink5 ball mill 24 hr  $P<sub>1</sub>$ 100 1000  $\mathbf{1}$ 10 100 1000 10 10 100 1000 Particle size (nm) Particle size (nm) Particle size (nm)

# **Aggregate size (P1):**

• **Similar for all processing methods**

**Agglomerate size (P2):** 

• **Horn < Bath < Turrax 25F < Turrax 18G < Ball mill**

#### **Aggregate and Agglomerate Size Distributions from SAXS/USAXS** Fitting range:  $Q = 0.09$  to 0.00012 Å<sup>-1</sup>

# **Accomplishments and Progress: Determining Impacts of Coating Method Durability**





AST protocol: 30,000 cycles square wave  $(1.4 V - 2.0 V)$ , 1 minute per cycle (500 hr total)

# **Accomplishments and Progress: Addressing challenges of ultra- low loaded anodes**

- •DOE 2030 Goal 0.125 mg<sub>PGM</sub>/cm<sup>2</sup>
- •Conducted work towards developing inks and scalable coating processes to produce catalyst layers with target loading and performance
- •Investigating impacts of ink formulation, ink-substrate interactions, drying on catalyst layer uniformity



# **Accomplishments and Progress: Quantifying Impact of Drying Rates on Anode Structure**



Utilized X-ray scattering to quantify aggregate and agglomerate structure of catalyst layers dried under difference conditions



#### **3 different ink drying conditions:**

- Slow solvent removal: solvent removal in presence of solvent vapor
- Room temp: solvent removal at room temp
- Rapid: solvent removal at 100° C



- **Rapid drying results in larger IrO<sub>x</sub> agglomerates**
- **Drying rate can be used control electrode structure**

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# **Accomplishments and Progress: Development of PTL with improved performance**

Control of Pore Size with PMMA Porogen



#### Objectives:

- Develop PTLs with optimized structure using scalable processing methods
- Improve understanding of critical structural parameters (pore size, pore shape, pore volume, graded porosity)
- PTL/MPL structures
- **Accomplishments**
	- **Demonstrated good control of structure via tape casting**
	- **Surpassed performance of baseline commercial PTL**



#### Support/MPL Bilayers



# **Accomplishments and Progress: Improving CL/PTL Interface via Laser Ablation**





- Investigated use of laser ablation to improve CL/PTL interface and impacts on performance and durability
- Laser ablated PTLs show increase in the measured double layer capacitance, indicating larger ECSA.
	- Observed less indentation to the CL/Membrane seed with laser ablated PTLs after AST
- **Demonstrated that laser ablation improves MEA IV performance and durability**

3500 4000

2000 2500 3000

Current density [mA/cm<sup>2</sup>]

**From Baseline PTL Laser Ablated PTL Laser Ablated PTL** 

500 1000

Current density [mA/cm<sup>2</sup>]

# **Accomplishments and Progress:**

# **Effect of CL/PTL Interface on Performance**

## **Performance Effects of PTL Pt-coating quality**

- Uncoated strip patterns = scratches or local delamination  $\Rightarrow$  Low impact
- Uncoated patches = global delamination or poor coating  $\Rightarrow$  High impact

#### ⇒ **Continuous defect size/shape matters**





#### **Performance Effects of PTL abrasions**

- Improvement up to  $\sim$ 80 mV at 4 A cm<sup>-2</sup>.
- Possible causes:
	- Removing or reducing the  $TiO<sub>x</sub>$  layer
	- Increasing the PTL surface roughness and improving contact area at interface
	- Flattening top surface for more contact



# **Accomplishments and Progress:**

# **Performance and Efficiency Effects of Pinholes**





- Tear- and open-shaped pinholes intentionally added to CCMs
- Pinholes have minimal (beneficial) impact on VI-performance of cell
- Tear-shaped pinholes may close or obstruct  $H_2$  permeation to some extent
- Pinholes significantly impact H<sub>2</sub> crossover, specifically during differential pressure operation
- NREL | 16 • The bigger and the more open the pinhole, the higher the H<sub>2</sub>:O<sub>2</sub> ratio and the lower H<sub>2</sub> efficiency

# **Accomplishments and Progress: Leveraging unique capabilities of discretionary projects to study catalysts and catalyst layers**



# **Electrode Porosity and Pore Size Distribution Comparison (pFIB-SEM) – Carnegie Mellon**

Objective: Investigate differences in pore morphology between regions of heterogeneity within an  $IrO<sub>2</sub>$ electrode



**Locally compressed region had significantly lower porosity and mean pore size than locally uncompressed region**

# **Catalyst and Electrode Composition (XPS) Colorado School of Mines**

Objective: Investigate potential changes in catalyst chemistry and electrode composition as function of ink age





- **No changes in iridium states**
- **Increased ionomer at top surface with ink age**

# **Responses to Previous (2021) Year Reviewers' Comments**



- The project is focused on standard technologies and material sets. It would be great to see some investigation into promising alternatives that have the potential to leapfrog over the existing state of the art. The recommendation is not necessarily for an in-depth study but rather for some assessment of the potentials and problems with these promising alternatives
	- *Work in FY22 and FY23 has included work on the development of new PTL structures and nextgeneration catalyst materials (supported, unsupported, alloy)*
- There should be even more emphasis on facilitating scale-up of electrolyzer production. The benefits of economies of scale are a huge assumption behind estimates of future low-cost electrolyzers. Manufacturability should be a key lens for the entire consortium
	- *The research activities addressing ink stability, coating methods, and low-loading challenges for R2R coating are directly addressing the manufacturability of electrolyzers.*



NREL Team Members: Carlos Baez-Cotto, Sunil Khandavalli, Scott Mauger, Chance Parrish, Jason Pfeilsticker, Elliot Padgett, Chang Liu, Guido Bender, Michael Ulsh, Jake Wrubel, Robin Rice [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, 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, Jacob Spendelow, Mahlon Wilson, Abdurrahman Yilmaz [Recombination layer fabrication and testing, PTL and MPL fabrication]

University Collaborators: Svitlana Pylypenko, Jayson Foster (CSM) [Electron microscopy and XPS]; Shawn Litster, Kara Ferner, Fausto Pasmay (CMU) [Tomography]









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# **Remaining Challenges and Barriers**

- Improve anode ink stability for new IrO<sub>2</sub> catalysts
- Understand and predict ink interactions
- Improve coating uniformity of low-loaded R2R electrodes
- Optimize MEA interfaces, especially catalyst layer-PTL
- Understand MPL coating and target properties/design
- Validate benefit of new concepts
	- Laser ablation/structuring of PTL
	- Multilayer coatings
- 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
	- Improve homogeneity for R2R-coated catalyst layer with loadings  $< 0.2 \text{mg}_{1r}/\text{cm}^2$
- iii. Cell Integration and Interfaces
	- Effects of local membrane thinning and pinholes on cell performance and durability
	- Studying the effect of  $TiO<sub>x</sub>$  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 bi-layer, phase inversion, and freeze tape cast 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

# **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
	- Completed foundational studies of the impacts of and interactions between ink constituents
	- Completed studies to understand the efficacy of scalable coating methods compared to the spray-coated baseline fabrication
	- Coordinated across labs on ink and anode coating baselining
	- Explored laser modification of PTL surfaces and control of PTL properties via processing routes
- **Key findings to date include:**
	- Interactions between ink constituents as well as levels of agglomeration are highly dependent on formulation
	- Anode ink stability is a practical processing issue formulation thickening can improve stability and processability
	- R2R coatings can perform comparably to spray-coated baseline at FuGeMEA loading of 0.4 mg<sub>Ir</sub>/cm2, but further work required to achieve uniform coatings at lower loading
	- Laser ablation or mechanical abrasion of the PTL surface can improve performance and mass transport
	- Pinholes have minor VI-performance impacts but potentially large safety implications
	- Engineering PTL porosity can result in performance improvements

# Technical Back-up and Additional Information



# **Publications**



- 1. Lee, J.K., Schuler, T., Bender, G., Sabharwal, M., Peng, X., Weber, A.Z., Danilovic, N. Interfacial Engineering via Laser Ablation for High-Performing PEM Water Electrolysis. *Applied Energy* 336, (2023), 120853.
- 2. J.K. Lee, G. Y. Lau, M. Sabharwal, A.Z. Weber, X. Peng, and M.C. Tucker, Titanium porous-transport layers for PEM water electrolysis prepared by tape casting, J. Power Sources 559 (2023) 232606
- 3. 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. *Submitted to Macromolecules*
- 4. Lyu, L., Foster, J., Rice, R., Padgett, E., Creel, E., Li, J., Yu, H., Cullen, DA., Kariuki, N., Park, J., Myers, D., Mauger, S., Bender, G., Pylypenko, S., Serov, A. (2023) Aging Gracefully? Investigating Iridium Oxide Ink's Impact on Microstructure, Catalyst/Ionomer Interface, and PEMFC Performance. Submitted to Energy & Environmental Science

# **Presentations**



- 1. Lee, J.K., Tricker, A.W., Peng, X., Danilovic, N., Weber, A.Z., (2022) Advanced Porous-Transport-Layer Interface Design for PEM Electrolyzers. *242nd Electrochemical Society Meeting,* Abstract ID: 165344. Oral Presentation.
- 2. Lee, J.K., Tricker, A.W., Peng, X., Danilovic, N., Weber, A.Z., (2022) Porous-transport-layer interface design for PEM electrolyzers via laser ablation. 3rd *International Conference on Electrolysis 2021*. Poster Presentation.
- 3. S. Khandavalli, J. Park, R. Rice, G. Bender, D. J. Myers, M. Ulsh, and S. A. Mauger, Tuning the Rheology of Anode Inks with Aging for Low-Temperature Polymer Electrolyte Membrane Water Electrolyzers, 242nd Electrochemical Society Meeting, Atlanta, Georgia, October 2022, I01B-1483. Oral Presentation
- 4. S. Khandavalli, J. Park, R. Rice, G. Bender, D. J. Myers, M. Ulsh, and S. A. Mauger, Tuning the Rheology of Anode Inks with Aging for Low-Temperature Polymer Electrolyte Membrane Water Electrolyzers, 3rd International Conference on Electrolysis 2021, Golden, Colorado, June 2022. Oral Presentation.
- 5. S. A. Mauger, S. Lee, E. Padgett, S. Khandavalli, G. Stelmacovich, T. Schuler, S. M. Alia, S. Pylypenko, and M. Ulsh, Fabrication, Performance, and Durability of Roll-to-Roll Coated Iridium-Based Anodes, 242<sup>nd</sup> Electrochemical Society Meeting, Atlanta, Georgia, October 2022, I01F-1656. Oral Presentation.
- 6. S. A. Mauger, S. Lee, E. Padgett, S. Khandavalli, G. Stelmacovich, T. Schuler, S. M. Alia, S. Pylypenko, and M. Ulsh, Fabrication, Performance, and Durability of Roll-to-Roll Coated Iridium-Based Anodes, 3rd International Conference on Electrolysis 2021, Golden, Colorado, June 2022. Oral Presentation.
- 7. M. Sabharwal, J. K. Lee, G. Lau, X. Peng, M. Tucker, A.Z. Weber, Impact of pore morphology of porous transport layers on the performance of PEM water electrolyzers, Gordon Research Conference, RI, July 2022
- 8. Foster, J., Zaccarine, S.F., Baez-Cotto, C., Kim, S., Dzara, M.J., Batool, M., Shepherd, M., Lyu, X., Serov, A., Jankovic, J., Mauger, S., Ulsh, M., Pylypenko, S. X-ray photoelectron spectroscopy characterization of polymer electrolyte membrane fuel cell and water electrolyzers, *ICE 2021 3rd International Conference on Electrolysis 2021*, Golden, CO, June **2022**, Poster.
- 9. Foster, J., Lyu, X., Creel, E.B., Li, J., Yu, H., Cullen, D.A., Kariuki, N.N., Park. J.H., 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.
- 10. Pylypenko, S. Catalyst/Ionomer Interactions: What We Learned from XPS Analysis, Telluride Science Research Center (TSRC) Workshop 4 Platinum Group Metal and Platinum Group Metalfree Electrocatalysts: Catalyst/Ionomer Interactions, Telluride, CO, March **2023**, Oral.
- 11. X. Peng, "The Cutting-edge in Clean Electrolysis for Green Hydrogen Production", Invited talk, U.S. Frontiers of Engineering Symposium, Seattle, WA, September 22, **2022**
- 12. X. Peng, "Pathways to Terawatt Scale Electrolysis- Importance of Interfaces and Underexplored Opportunities", Fuel Cell Gordon Research Conference, Providence, RI, July 27, 2022
- 13. A. Serov "Design of Catalyst Layers for Fuel Cell and Electrolyzer Application", ICE 2021, Golden, CO, June **2022**
- 14. A. Serov "Catalyst Layers: From Materials to Roll-to-Roll Manufacturing", Fuel Cell Seminar, Long Beach, CA, February **2023**
- 15. C. Liu, J. Wrubel, E. Padgett, G. Bender, "The impacts of membrane pinholes on PEM water electrolysis", 242<sup>nd</sup> Electrochemical Society Meeting, Atlanta, Georgia, October 2022, I01F-1656. Oral Presentation.



- **Scott Mauger** was awarded the L.E. Scriven Young Investigator Award from the International Society of Coating Science and Technology (2022)
- **Jacob Spendelow** was awarded the ECS Toyota Young Investigator Award (2022)
- **Kara Ferner** received an NSF Graduate Research Fellowship (2023) and the best poster award at the Carnegie Mellon Graduate Research Symposium for her work in H2NEW
- Jayson Foster received the best poster award at the ICE 2021 3<sup>rd</sup> International Conference on Electrolysis for his work on XPS of catalyst and catalyst layers as part of H2NEW (2022)

# **Technology Transfer**



- No patents filed or awarded since 2022 AMR
- H2NEW members are subrecipients on existing industry-led FOA projects
	- $3M P197$
	- Nel Hydrogen P198
	- Plug Power P199

# **Accomplishments and Progress: Initiated work on fabricating PTEs**



- Porous transport electrodes (PTEs) may provide benefits for MEA performance by increasing catalyst layer – PTL contact and improving electrical and thermal conduction
- Initial coating trials were performed on commercial materials with smaller pore sizes and/or lower porosity than standard PTL materials
- PTEs fabricated with PVD Ir showing good performance in early tests



#### **Liquid-Coated PTEs**



# **Accomplishments and Progress: Initiated Fabrication of Membranes with Recombination Catalysts**



- $H_2$  recombination catalysts are a strategy to reduce safety concerns related to  $H_2$  crossover
- There are still many unknowns about optimized designs and performance under dynamic operation
- Samples have been fabricated to probe:
	- Membrane variables including catalyst loading, catalyst type, catalyst location, layer thickness, and deposition method
	- Operating conditions such as current density and differential pressure
- Coordinating with Task 2 to provide data to better model recombination reaction and better understand mechanism





Hydrogen pressure (bar)

# **Accomplishments and Progress: Leveraging unique capabilities of discretionary projects**





#### **Objective:**

Use XPS to determine coating quality (reproducibility) and the effect of catalyst ink storage on the surface composition of catalyst layers.

**Reproducibility:** CL composition is very similar in different areas indicating

**Ink aging effect:** No visible changes to Ir states are observed; increase in relative amount of surface ionomer compared to  $\text{IrO}_2$  catalyst from elemental ratios and signal from ionomer peaks in O 1s; some minor changes in proportion of iridium oxide and hydroxide

# **Accomplishments and Progress: Characterized Electrode Thickness Distribution with Nano-CT**



- **Objective**: Quantify differences in electrode thickness between IrO<sub>2</sub> catalyst layer coating methods of spray coating vs. blade coated and between pristine and tested electrodes
	- CMU nano-CT used for 3D phase contrast imaging of electrodes for high contrast between solid and void phases
	- Image-processing and segmentation used to extract electrode thickness distributions
- Between pristine electrodes, spray coated catalyst layer had a lower mean electrode thickness and narrower distribution compared to blade coated catalyst layer
- Tested blade coated catalyst layer showed the lowest electrode thickness distribution due to electrolyzer compression effects
- Increased thinning shown in regions of tested catalyst layer, due to direct contact with individual PTL titanium fibers during electrolyzer operation  $\rightarrow$  possible differences in internal structure/morphology between locally compressed and uncompressed regions

