Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Project ID: P148c

Photoelectrochemical (PEC) Water Splitting

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Presenter: Joel W. Ager, PEC Technology Lead, LBNL

Date: May 7, 2024

DOE Hydrogen Program

2024 Annual Merit Review and Peer Evaluation Meeting

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NREL Transforming ENERGY | BERKELEY LAB Bringing Science Solutions to the World | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory

HydroGEN Project Goal

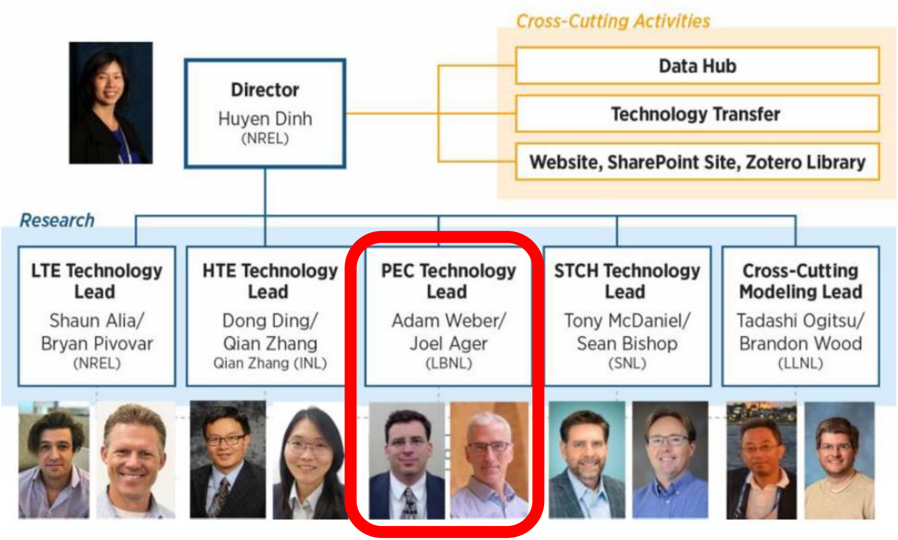
Website: https://www.h2awsm.org/

Goal: Accelerate foundational R&D of innovative materials for advanced water splitting (AWS) technologies to enable clean, sustainable, and low-cost (\$1/kg H_2) hydrogen production

H_2 Production Target: \$1/kg

HydroGEN is focused on early-stage R&D in H_2 production and fosters cross-cutting innovation using theory-guided applied materials R&D to advance all emerging water-splitting pathways for hydrogen production

HydroGEN PEC Overview



Barriers

- Efficiency
- Durability
- Cost

National Lab PEC Team

NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

Lawrence Livermore National Laboratory

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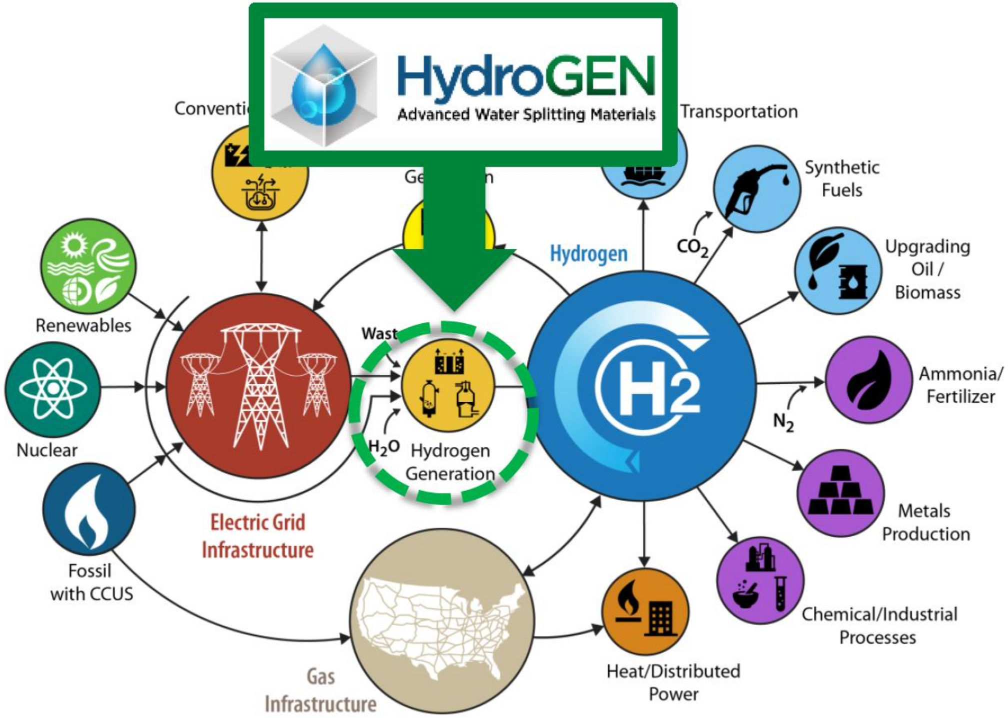
H2@Scale: Enabling Affordable, Reliable, Clean and Secure energy

Relevance and Potential Impact



Source: DOE Hydrogen and Fuel Cell Technologies Office, https://energy.gov/eere/fuelcells/h2-scale

Transportation and Beyond

Large-scale, low-cost hydrogen from diverse domestic resources enables an economically competitive and environmentally beneficial future energy system across sectors

Hydrogen can address specific applications that are hard to decarbonize

Today: 10 MMT H_2 in the US

Economic potential: 2x to 4x more

Materials innovations are key to enhancing performance, durability, and reduce cost of hydrogen generation, storage, distribution, and utilization technologies key to H2@Scale

"Hydrogen at Scale (H_2@Scale): Key to a Clean, Economic, and Sustainable Energy System," Bryan Pivovar, Neha Rustagi, Sunita Satyapal, Electrochem. Soc. Interface Spring 2018 27(1): 47-52; doi:10.1149/2.F04181if.

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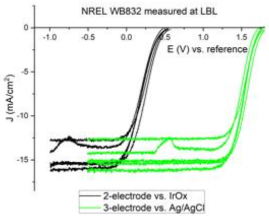
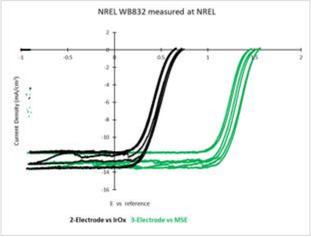
HydroGEN PEC
Relevance and *Potential Impact*

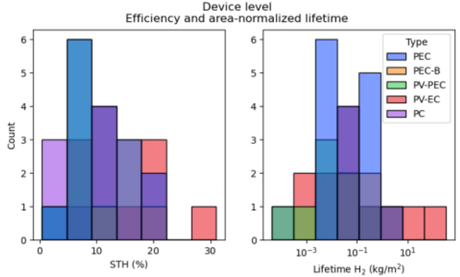
- Lead development of standardized PEC device measurement techniques
  Improves reproducibility between labs

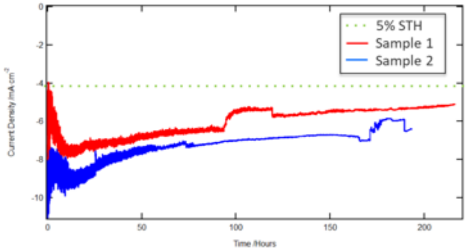
- Lead the identification of device and system-level performance metrics
  Clearly defines improvements needed for economic viability

- Lead in developing reliability science needed for closing the durability gap
  New materials for durable PEC water-splitting devices
  Accelerated wear protocols to quantify progress









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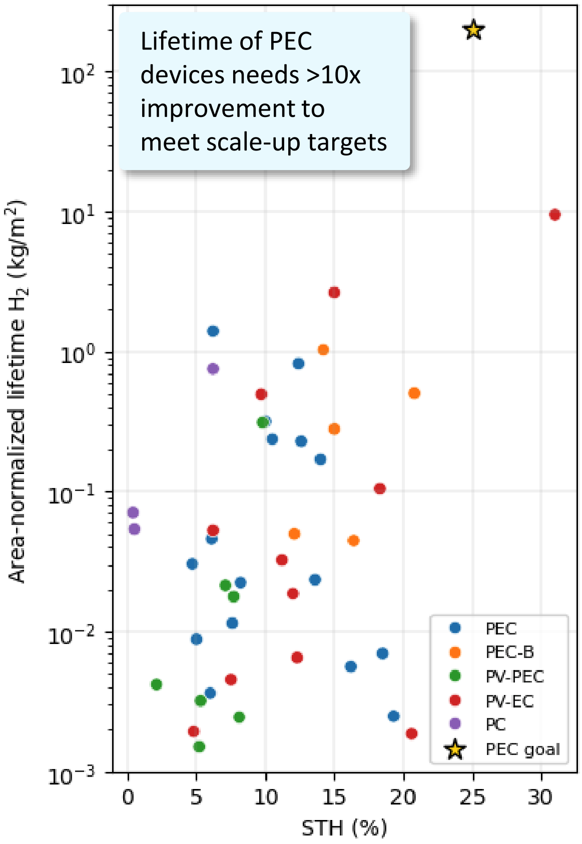
HydroGEN 2.0 PEC Approach



- Prioritize durability stressors and establish PEC device durability protocol
- Use density functional theory (DFT) and microkinetic modeling to describe the local environment at the electrode/electrolyte interface under operation
- Provide mechanistic understanding of PEC device degradation guided by theory and in operando characterization

Comparison of the solar to hydrogen efficiency (STH) and lifetime H_2 produced for unassisted water splitting devices. Data sourced with permission from Cheng et al. in 2022 Solar Fuels Roadmap, *J. Phys. D. Appl. Phys*. **2022**, 55 323003. PEC goal from Ben-Naim et al., *ACS Energy Lett.* **2020**, 5, 2631–2640. Data published on AWSM Data Hub.

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Safety in AWSM laboratories – LBNL and NREL

- LBNL has robust safety oversight through its Work Planning and Control (WPC) system
- LBNL implements continuous Feedback and Improvement through its Integrated Safety Management (ISM) plan
- <u>Improvements specific to AWSM-funded research</u>
  - Improved SOPs for unattended experiments, including experimenter documentation and remote camera monitoring
  - Centralized H_2 supply for B30
  - Improved connections to high-current experiments
  - Safer use of heat tapes, including GFCI protection, over-temperature shutoff, and low-voltage power supply
- Developing comprehensive questionnaire to assist PEC seedling projects with safety associated with outdoor testing (temperature control, gas handling, etc.)

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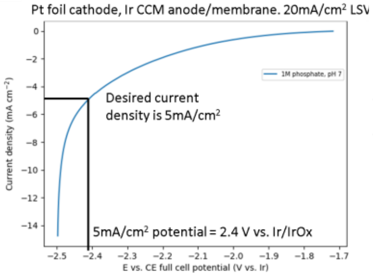
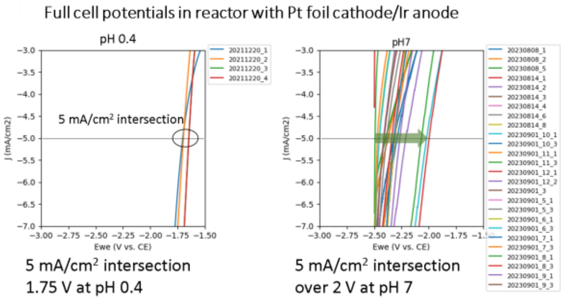
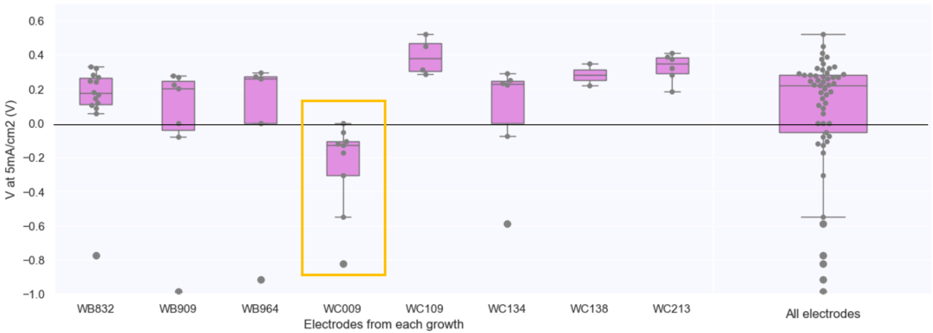
HydroGEN 2.0 PEC Accomplishment
Rigorous analysis of PEC reproducibility

NREL and LBNL quantified within- vs between- growth variations for eight MOVPE photocathodes





(left) Determination of the 5mA/cm² potential from the initial LSV scan. Center: four LSV curves from measurements done in 0.5 M H_2SO_4 (pH 0.4), showing an approximate potential of -1.75 V. Right: 26 LSV curves from pH 7.0 measurements, including from long-path and short-path configurations of the reactor. Decreasing the path length and additional optimizations led to ~0.5 V decrease in the full cell potential.



V_onset is the potential difference between working electrode (WE) and counter electrode (CE) under simulated 1 sun illumination (2 electrode measurements, 0.5 M H_2SO_4, pH 0.4, CE is IrO_x, ca. 1 cm², WE is PEC cell, ca. 0.2 cm²). A positive value predicts that bias-free operation is possible in acid at at least 5 mA cm². 67% of the runs have a positive value and there are 5 statistical outliers.

We recommend that similar statistical methods be used for comparing the initial performance and durability of different groups of PEC devices (i.e. t-tests for pairs of conditions, ANOVA for multiple comparisons).

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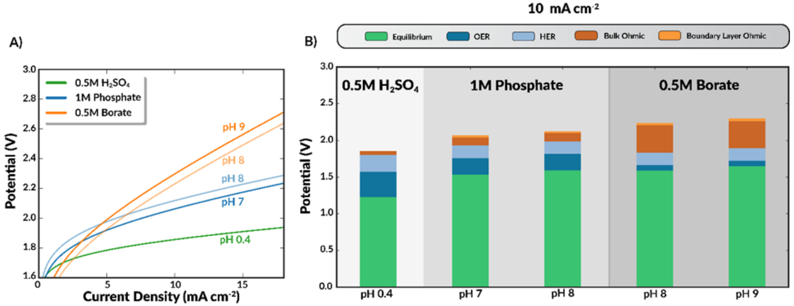
HydroGEN 2.0 PEC Accomplishment

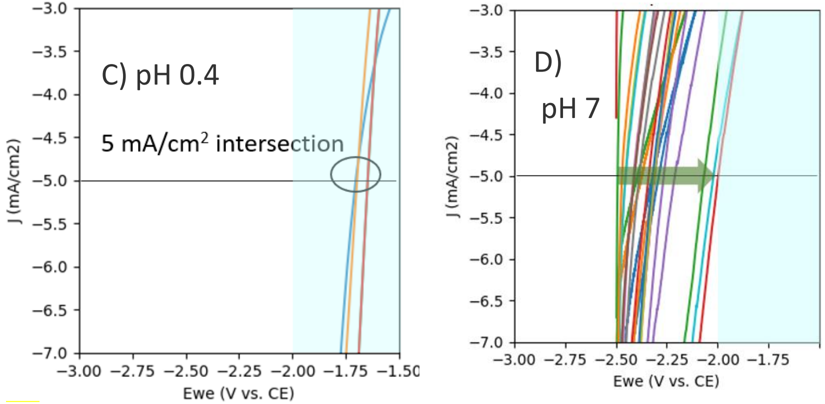
NREL and LBNL defined optimal conditions for neutral pH operation

Modeling and Simulation

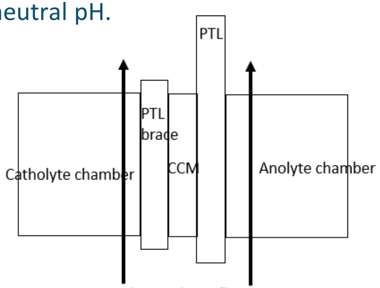


A) Polarization curves of the PEC cell with 0.5M H_2SO_4 (pH 0.4), 1M phosphate (pH 7 and 8), and 0.5 M borate (pH 8 and 9) electrolytes. B) Breakdown of contributions to voltage at average HER current density for all the electrolytes tested at electrolyte flow rate. 0.5 M H_2SO_4 exhibits the lowest ohmic losses, but large kinetic losses. 0.5 M Borate at pH 8 has the highest ohmic losses, but the lowest kinetic potential losses.

Experiment



C) Cells operating in acid require a full cell voltage <2 V, which is lower than the expected output of employed tandem solar cells. D) Use of catalyst-coupled membrane (CCM, schematic below) reduces required potential for 5 mA cm^{-2} operation to close to 2 V in neutral pH.



Neutral pH operation below 2 V is possible if ohmic losses are reduced

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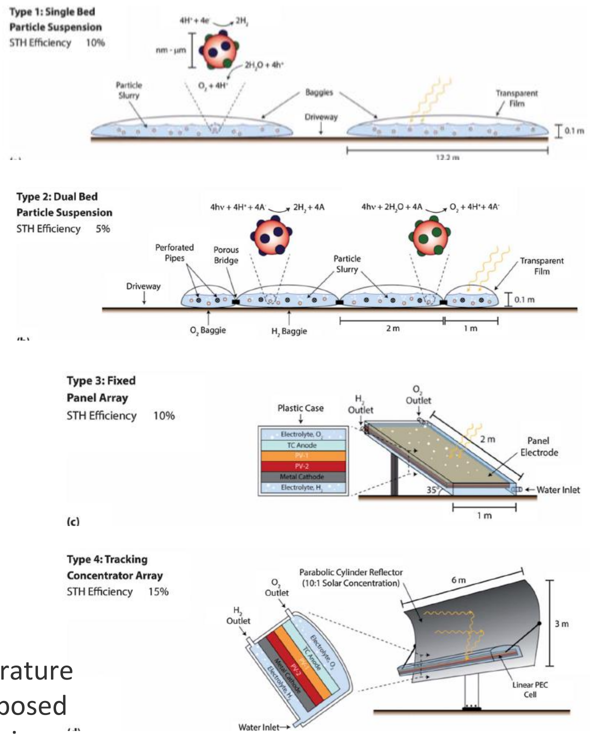
HydroGEN 2.0 PEC Accomplishment
Proposed device and system-level performance metrics

Device-level metrics

- Solar to hydrogen conversion efficiency
  STH (%)
- Area-normalized lifetime production of H_2
  kg/m^2
  normalized to PV area for concentrators

System-level metrics

- Area
  m^2
  receiver area for concentrators
- Lifetime
  hours
  as reported by source
- System H_2 production rate
  kg/hr



Parkinson, B. *Acc. Chem. Res.* **1984**, *17*, 431–437

James *et al*., *DOE Rep.* **2009**.

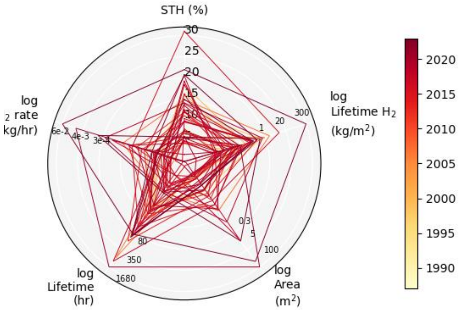
Pinaud et al, Energy Env. Sci. **2013**.

Ager, J. W.; Shaner, M. R.; Walczak, K. A.; Sharp, I. D.; Ardo, S. *Energy Environ. Sci.* **2015**

Ben-Naim, M.; Britto, R. J.; Aldridge, C. W.; Mow, R.; Steiner, M. A.; Nielander, A. C.; King, L. A.; Friedman, D. J.; Deutsch, T. G.; Young, J. L.; Jaramillo, T. F. *ACS Energy Lett.* **2020**,

Cheng, W.-H., Deutsch, T. G., Xiang, X. in 2022 Solar Fuels Roadmap, *J. Phys. D. Appl. Phys.* 2022

Holmes-Gentle, I.; Tembhurne, S.; Suter, C.; Haussener, S. *Nat. Energy* **2023**



Analysis of 44 literature reports using proposed performance metrics

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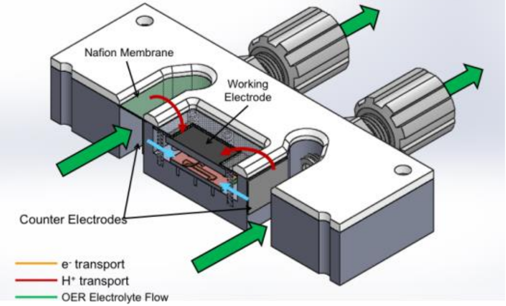
HydroGEN 2.0 PEC Accomplishment – NREL

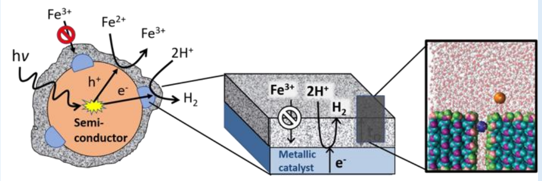
- Led a breakout session at the September AWSM benchmarking workshop that focused on
  - NREL's experience and challenges with outdoor photoreactor testing
  - Synergies among the six new awarded PEC seedling projects
- Developed comprehensive questionnaire to assist PEC seedling projects with photoreactor setup, evaluation of device performance, and logistical considerations
  - All seedling projects will be performing on-sun testing at NREL for 2 weeks
  - Seedling final deliverable should produce 0.1 g H_2/h (approximately 200 cm^2)
  - Testbed will be instrumented to monitor and record solar-to-hydrogen efficiency

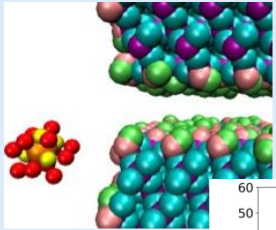
- Provided seedlings materials as well as characterization support and contributed to publications
  - Rutgers: "TiO_2/TiN bifunctional interface enables integration of Ni_5P_4 electro-catalyst with III-V tandem photoabsorber for stable solar-driven water splitting" Hwang…Dismukes et al., *ACS Energy Lett.* 2024, 9, 789−797.
  - Rice: "Technoeconomic model and pathway to <$2/kg green hydrogen using integrated halide perovskite photoelectrochemical cells" Fehr…Mohite et al., *ACS Energy Lett.* 2023, 8, 4976−4983.



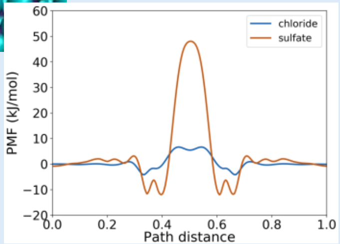
Cross-cut accomplishments in low-temperature technologies (PEC/LTE)
Atomistic insights into transport, OER activities, stability

PEC: Selective Transport





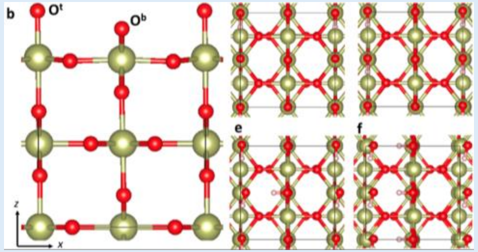
Oxide overlayer for selective transport

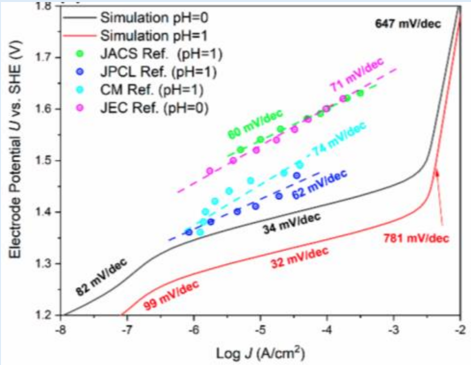


Aydin et al., EES Catalyst (Submitted)

Optimize porosity and chemistry to enhance hydrogen production

PEC: OER Activity

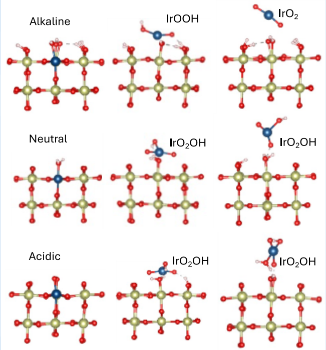




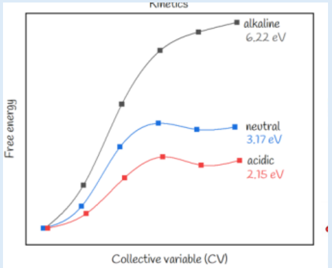
Developed models for predicting catalytic activities

Zhou et al., ACS Appl. Energy. Mater (2023)

LTE: Catalyst Stability



Dissolution pathways of Ir at different pH conditions



pH-dependence dissolution kinetics

Explore impacts of morphology and environment on stability

Zagalskaya et al., (in preparation)

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Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- *The focus on standards development and benchmarking is fantastic to see, and the team is encouraged to consider how to do more of this.*
  - We are continuing to lead in this area, including leading a dedicated session at the upcoming Benchmarking Meeting
  - HydroGEN PEC team has joined IEA Hydrogen TCP – Task 45 Renewable hydrogen Subtask 2 PEC and will work to define standards worldwide
- *The techno-economic analysis (TEA) seems to be used a little inconsistently in the seedlings (though only the PEC seedlings were reviewed)*
  - We are leading the development of performance metrics and consistent TEA methodologies which will address this concern.
- *Regarding PEC, the project has made significant progress in terms of demonstrating high solar-to-hydrogen (>17%), durability, as well as prototyping that represents a notable step forward in terms of TRL for this class of technology.*
  - We agree that improvements in durability are the key to advancing the TR level

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Accomplishments and Progress: Responses to Previous Year Reviewers' Comments, continued

- *The PEC branch is the most challenging in terms of seeing a potential impact, as a realistic chance of success is hard to see*
  - Our initial analysis of performance metrics has highlighted recent progress in this area, including large area (100 m^2) and durable (months) demonstrations. We also note several start-up companies (all in Europe) in the PEC H_2 space.
- *A focused research on degradation mechanisms is suggested.*
  Degradation mechanisms studies should be planned.
  The project should give greater emphasis on TEA/performance metrics
  - We intend to continue the focus on durability, sharing best practices and methods with the LTE team who have a similar focus.

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HydroGEN STCH Seedling Projects & Lab Collaboration

PEC Node Labs

NREL — National Renewable Energy Laboratory

Berkeley Lab

Lawrence Livermore National Laboratory

Support through:

Personnel

Equipment

Expertise/Protocols

Capability

Materials/cells

Data

Interactive PEC projects

Rice

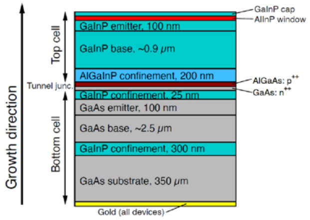
Yale

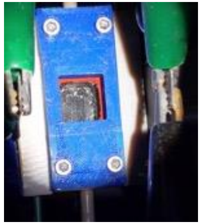
California Institute of Technology

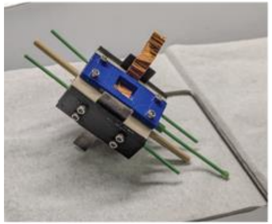
The University of Toledo

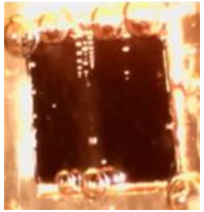
University of Michigan

University of Hawai'i









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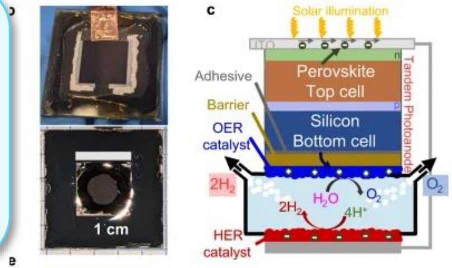
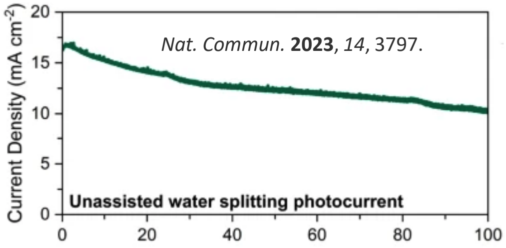
HydroGEN PEC Seedling Accomplishments: 3 continuing projects

P216: Aditya D. Mohite, Rice University
LBNL and NREL worked with **Rice University** to characterize halide perovskite photoelectrodes coated with catalysts and a hydrophobic graphene-based barrier which ensures optimal charge transfer at the light absorber/catalyst interface.

- >100 hours stability with peak efficiency >20% STH.

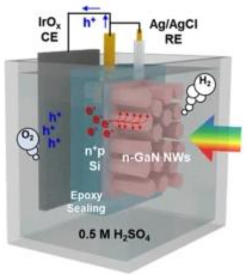




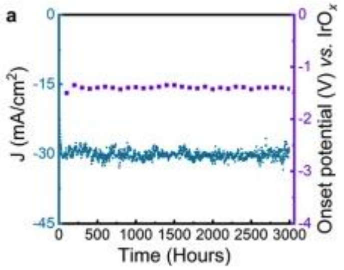
Nat. Commun. **2023**, *14*, 3797.

P209: Zetian Mi, University of Michigan
LBNL and NREL worked with **the University of Michigan** to demonstrate stable operation of a photocathode comprising Si and GaN, the two most produced semiconductors in the world

- Operation for 3,000 h without any performance degradation in two-electrode configurations.

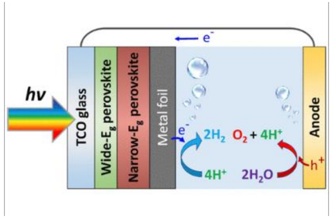


Nat. Commun. **2023**, *14*, 2047.

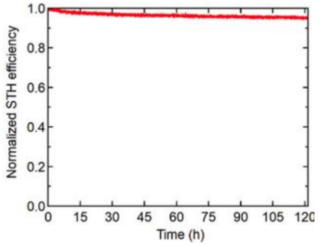


P218: Yanfa Yan, University of Toledo
NREL worked with the **University of Toledo** (Yanfa Yan) to monolithically integrate all-perovskite tandem photocathodes for unassisted solar water splitting with 15% STH.

- Continuous operation in water for >120 h at 1 sun



ACS Energy Lett. **2023**, *8*, 2611.



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HydroGEN PEC Seedlings: 3 new starts

P213
Shu Hu, Yale University

>200 cm^2 Type-3 PEC Water Splitting Prototype Using Bandgap-Tunable Perovskite Tandem and Molecular-Scale Designer Coatings

Node support: NREL and LBNL

P214
Joel Haber, Caltech

Demonstration of a Robust, Compact Photoelectrochemical (PEC) Hydrogen Generator

Node support: NREL and LBNL

P215
Nicolas Gaillard, University of Hawaii

Semi-Monolithic Devices for Photoelectrochemical Hydrogen Production

Node support: NREL and LLNL

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HydroGEN PEC: Future Work

PEC Lab R&D work

- End of FY2024 goal: Stand-alone solar water splitting device of at least 4 cm^2 illuminated area capable of indoor and outdoor operation with neutral (pH ~ 7) water
- End of project goal in FY2026: Photoreactor capable of indoor or outdoor operation accommodating illuminated areas of up to 200 cm^2. Reactor will be instrumented to measure the H_2 generation rate and, optionally, to accommodate diagnostic tests meant to assess and predict durability
- Leadership in PEC community: develop and publicize device and system-level performance metrics required for PEC water splitting to meet DOE cost targets

PEC Lab support of seedlings

- Provide platform for verifying performance of prototype devices from seedling projects

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

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HydroGEN 2.0 PEC: Summary

- Used previously developed protocols for robust benchmarking and statistical analysis of stand-alone PEC water-splitting devices (NREL/LBNL)
- Developed initial set of performance metrics for PEC devices and systems (LBNL/NREL/LLNL)
- Demonstrated bias-free water splitting with a III-V photocathode at over 5% STH efficiency for more than 200 hours at neutral pH (NREL/LBNL)
- Demonstrated bias-free water splitting at 20.8% STH efficiency with a perovskite/silicon tandem photoanode, with a 100+ hour lifetime (Rice/NREL/LBNL)
- Demonstrated Si/GaN photocathode with 3000+ hours stability (U. Michigan/NREL)
- Demonstrated bias-free water splitting in acid at 18% STH efficiency with an all-perovskite tandem photoelectrode, with a 120+ hour lifetime (U Toledo/NREL)
- 7 publications

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