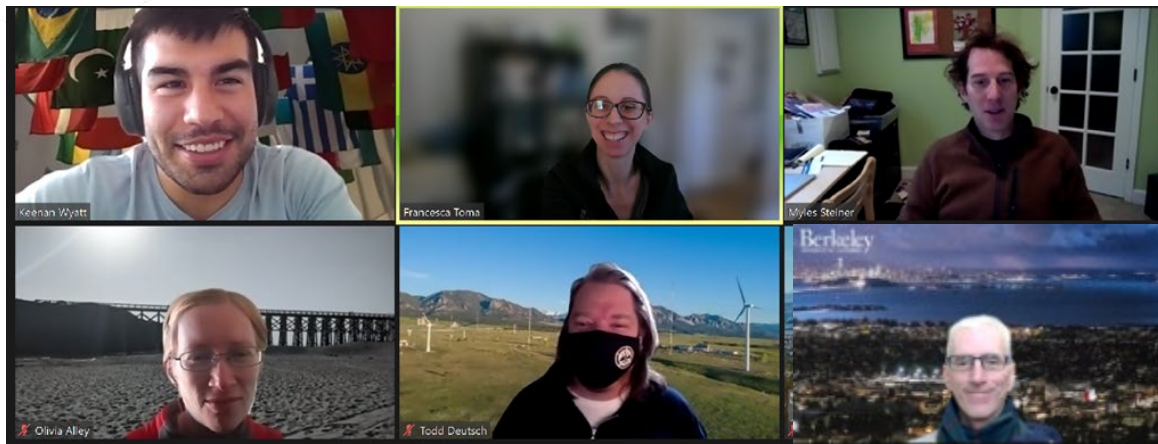




Photoelectrochemical Water Splitting (PEC): Joel W. Ager (March 2023-present), Francesca Toma (to March 2023)



Not in the picture:

James Young (NREL)
Alex King (LBNL)
Adam Weber (LBNL)
Ethan Crumlin (LBNL)
Rebecca Hamlyn (LBNL)
Anh Pham (LLNL)
Tadashi Ogitsu (LLNL)

Alumni:

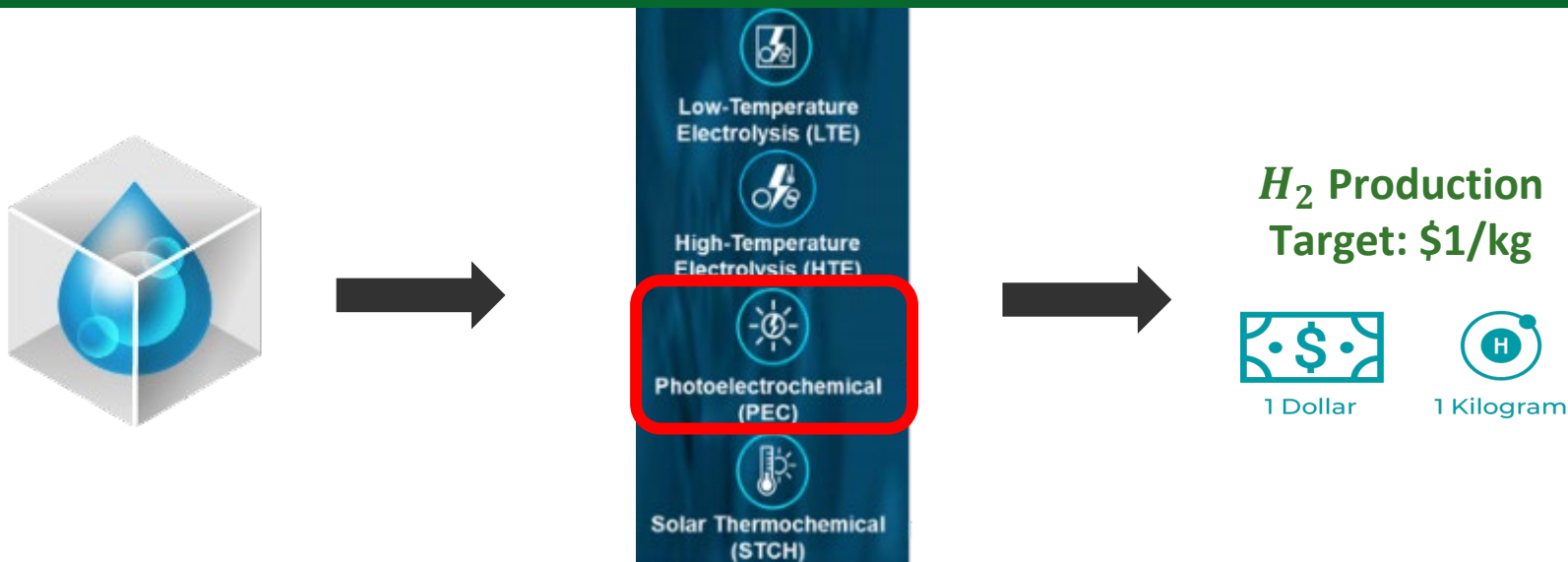
Guosong Zeng – Assistant Professor at Sustech
David Larson -- Twelve (Senior Prototyping Engineer)
Guiji Liu -- eJoule International (Senior Scientist)



Project Goal

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

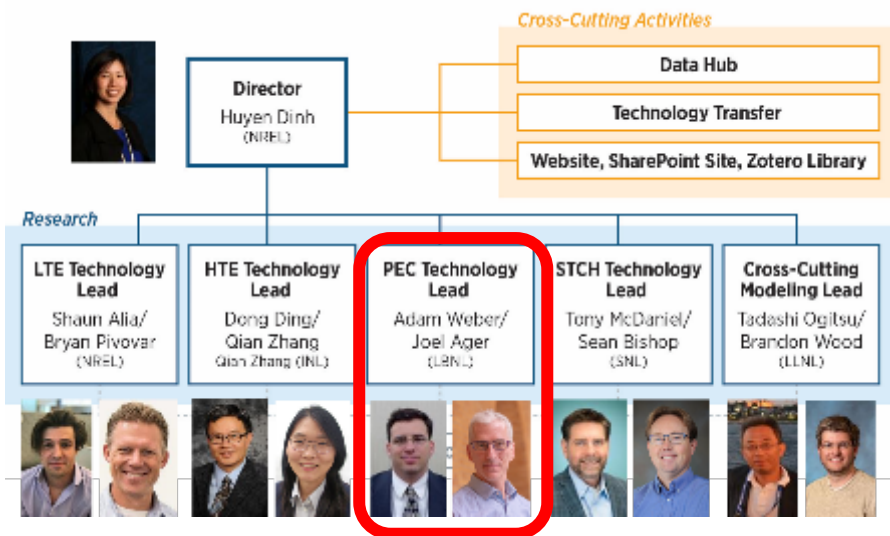
Goal: Accelerate foundational R&D of innovative materials for advanced water splitting (AWS) technologies to enable clean, sustainable, and low-cost (\$1/kg H_2) hydrogen production.



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: FY16-FY23



Barriers

- Cost
- Efficiency
- Durability

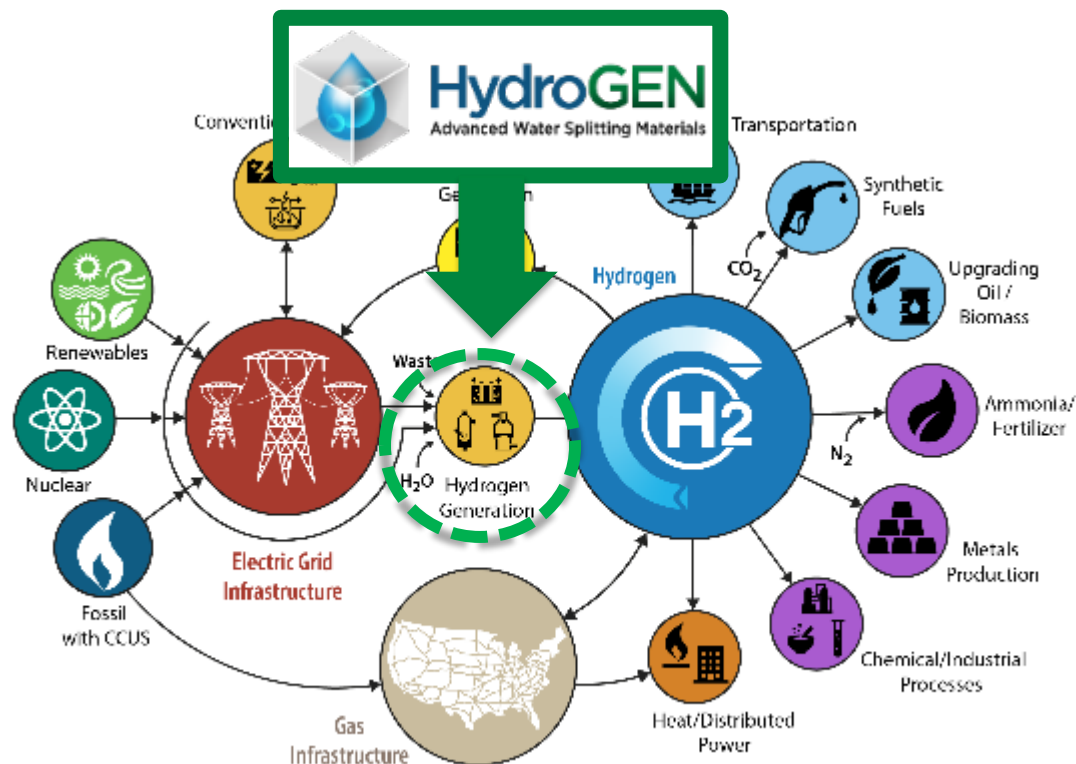
National Lab PEC Team





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

Relevance and Potential Impact



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 H₂ in the US

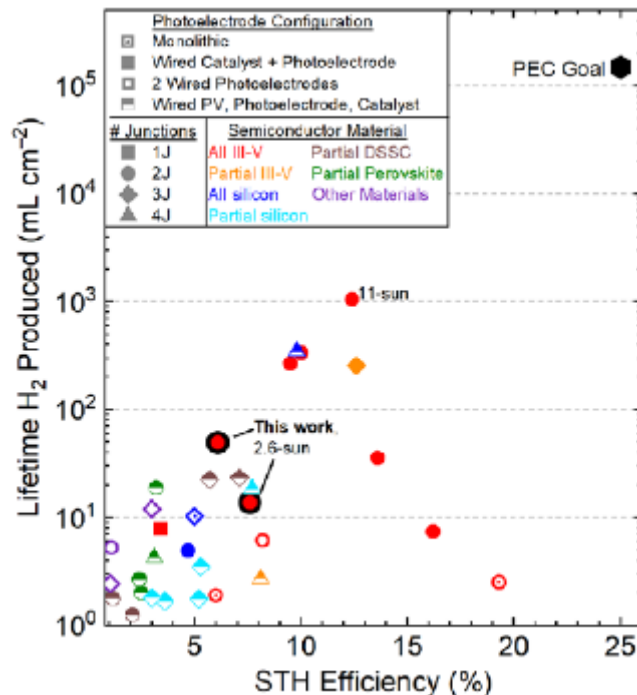
Economic potential: 2x to 4x more

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



HydroGEN 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

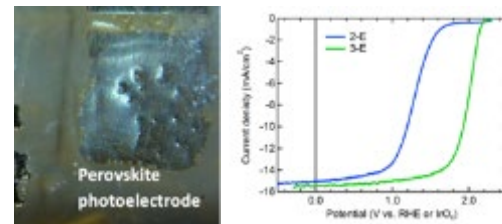


Comparison of the solar to hydrogen efficiency (STH) and lifetime H₂ produced for unassisted water splitting devices. The “PEC Goal” point in the upper right was calculated assuming a 20% capacity factor over a 10 year lifetime (15).



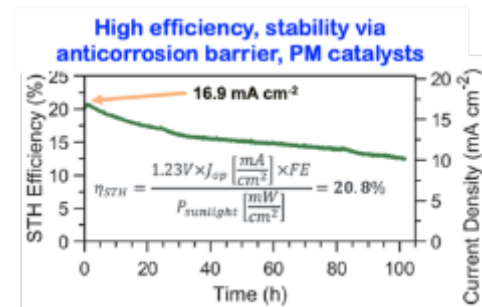
HydroGEN 2.0 PEC Top Accomplishments

- NREL**, in collaboration with the **University of Toledo** (Prof. Yanfa Yan), worked on the characterization of halide perovskite/ halide perovskite tandem photoelectrodes for unassisted water splitting demonstrating higher than 18% in a two-electrode configuration under one sun illumination without an external bias with 500 h stability.

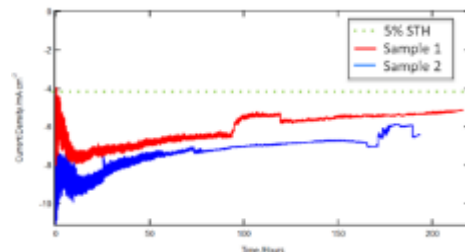


- LBNL and NREL** worked with **Rice University** (Prof. Aditya Mohite) to characterize halide perovskite photoelectrodes coated with catalysts and a hydrophobic graphene-based barrier which ensures optimal charge transfer at the light absorber/catalyst interface.

- We achieved >100 hours stability with peak efficiency exceeding 20% STH. A paper which report this results is under revision.
- We developed a techno-economic analysis for PEC systems based on perovskite absorbers. A paper reporting these results is in preparation.



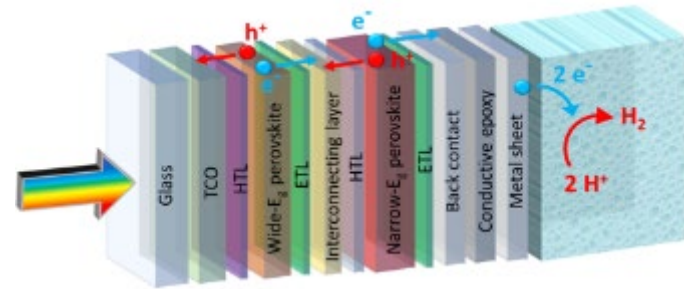
- LBNL and NREL** published a protocol on standardized PEC measurements at both Labs that has been greatly appreciated by the community. We met our Go/No-Go and are working towards the end-of-the-project goals. Here, we show progress towards our FY23Q4 milestone and achieved > 5% STH, 200+h stability at near neutral pH by testing similar samples and comparing results at both Labs.





Project Goals:

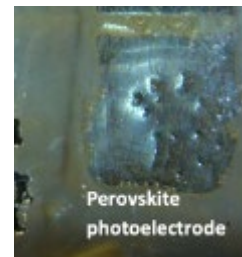
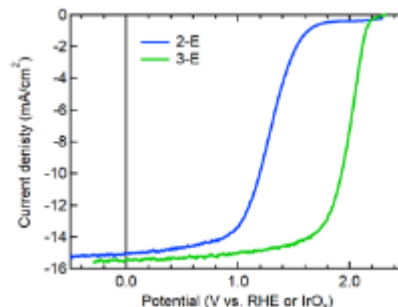
- Demonstrate perovskite/perovskite tandem photoelectrodes for wireless and unassisted water splitting
- Develop water impermeable coating to protect tandem photoelectrodes during the operation in water
- Demonstrate tandem photoelectrodes with an STH efficiency of up to 20%



Schematic of a perovskite/perovskite tandem photoelectrode

Highlights for BP3:

- Demonstrated prototype integrated perovskite/perovskite tandem photocathodes for unassisted solar-driven water splitting.
- The perovskite/perovskite tandem photoelectrodes deliver a solar-to-hydrogen efficiency of > 18% in a two-electrode configuration under one sun illumination without an external bias.
- The perovskite tandem photoelectrodes show a continuous operation lifetime in an aqueous acid solution for more than 500 hours.



(left) LSV curves of perovskite tandem photoelectrodes under AM 1.5G illumination. (right) Photo of perovskite/perovskite tandem photoelectrodes under operation.



Seedling Projects Accomplishments: Highly Efficient Solar Water Splitting Using 3D/2D Hydrophobic Perovskites with Corrosion Resistant Barriers

Rice University PI: A. Mohite

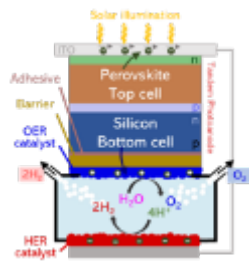


Project Goals:

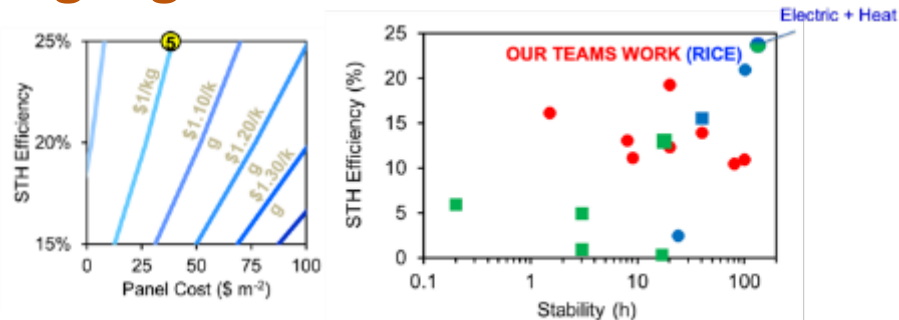
- Develop high-efficiency 3D/2D halide perovskite solar cells that reach 20% solar to hydrogen (STH) efficiency
- Incorporate HER/OER catalysts into an autonomous PEC platform
- Using corrosion-resistant barriers, including hydrophobic polymers, carbons, and ALD oxides (Al_2O_3 , HfO_2), reach 500 hours stability
- Understand degradation mechanisms in PEC and mitigate
- Demonstrate 5x5 in² module to show scalability

Measured STH 24.3% best literature HaP

Developed and tested a 3D printed PEC reactor incorporating 3D/2D perovskite HER+OER catalysts:

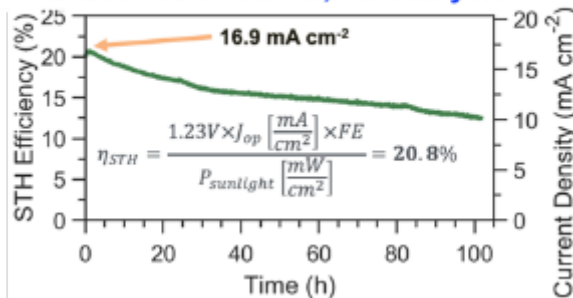


Highlights for BP3

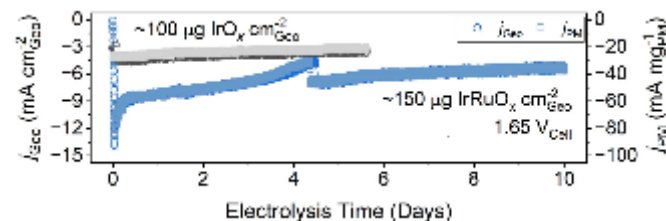


Solar-to-Hydrogen η = 20.8% and 102 hours of durability

High efficiency, stability via anticorrosion barrier, PM catalysts



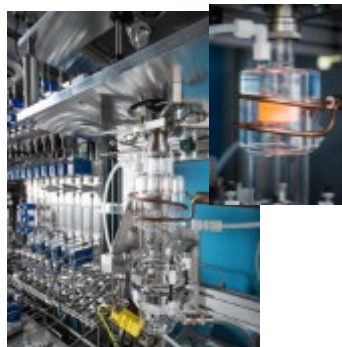
Towards earth abundant OER catalysts



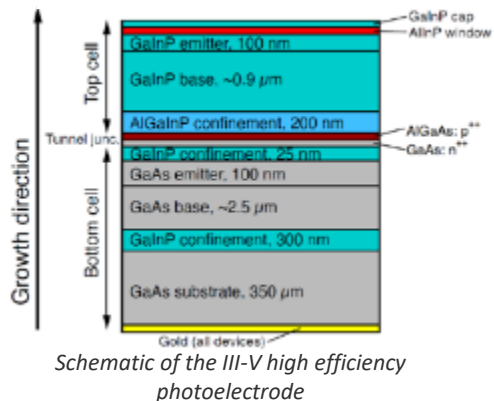


HydroGEN 2.0 PEC Progress

Photoelectrode Growth by metal organic vapor phase epitaxy



MOVPE at 620°C growth temperature

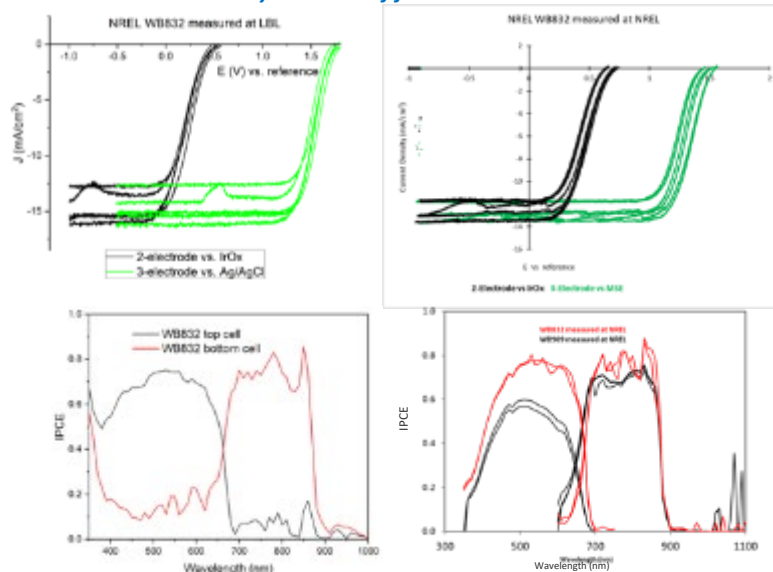


HydroGEN: Advanced Water Splitting Materials

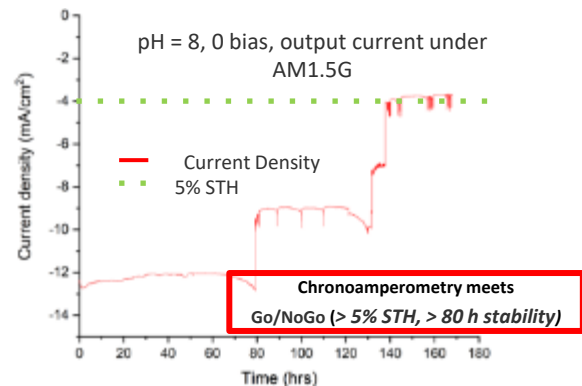
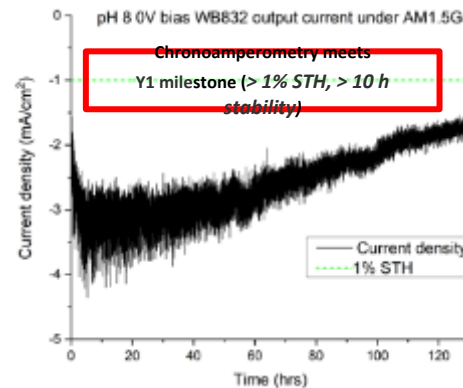
Photoelectrode Fabrication and Testing at NREL and LBNL



Dual anode cell with high modularity and ease of fabrication



Progress to Date



Reproducibility achieved at both Labs

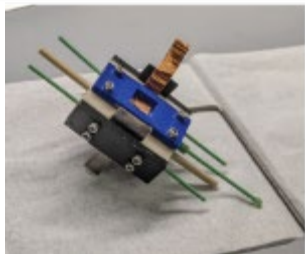
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HydroGEN 2.0 PEC Accomplishment: Publication

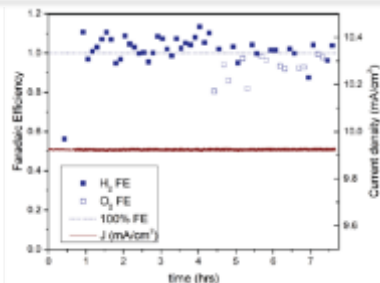
Best Practices in PEC Water Splitting: How to Reliably Measure Solar-to-Hydrogen Efficiency of Photoelectrodes¹

- Publication shares with PEC community best practices when measuring and reporting STH efficiency of new photoelectrodes and will improve the reproducibility of results across the field.
“This is a great paper for the community, thank you for dedicating the time to put this together, especially during this challenging historical time (pandemic)”
–2023 attendee, Solar Fuels Gordon Conference
- Publication benchmarks a flow reactor for H₂/O₂ measurement, that any lab can produce from readily available materials using a CNC miller and 3D printer.
- 4098 views, 491 downloads, 10 mentions in news articles (4/10/2023)

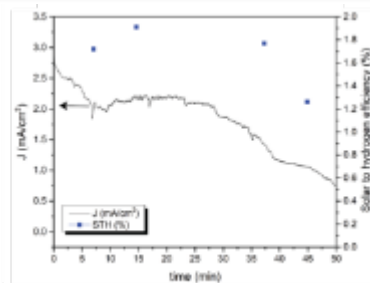


Reactor

HydroGEN: Advanced Water Splitting Materials



Validation: dark FE



STH of III-V tandem at pH 0.4

¹Front. Energy Res., 27 October 2022 Volume 10 - 2022 |
<https://doi.org/10.3389/fenrg.2022.884364>

This presentation does not contain any proprietary, confidential, or otherwise restricted information



Best Practices in PEC Water Splitting: How to Reliably Measure Solar-to-Hydrogen Efficiency of Photoelectrodes

A methodical approach: We provided an in depth, step-by-step description of each factor that goes into the solar to hydrogen efficiency calculation.

2-electrode current density

Description of an accurate measurement of the photoelectrode area

GC quantification of H₂/O₂

Detailed protocol for quantification of H₂ and O₂ by gas chromatography

$$\eta_{STH} = \frac{j_{sc} \left(\frac{mA}{cm^2} \right) * 1.23V * \eta_{FE}}{P_{total} \left(\frac{mW}{cm^2} \right)}$$

AM1.5G source calibration

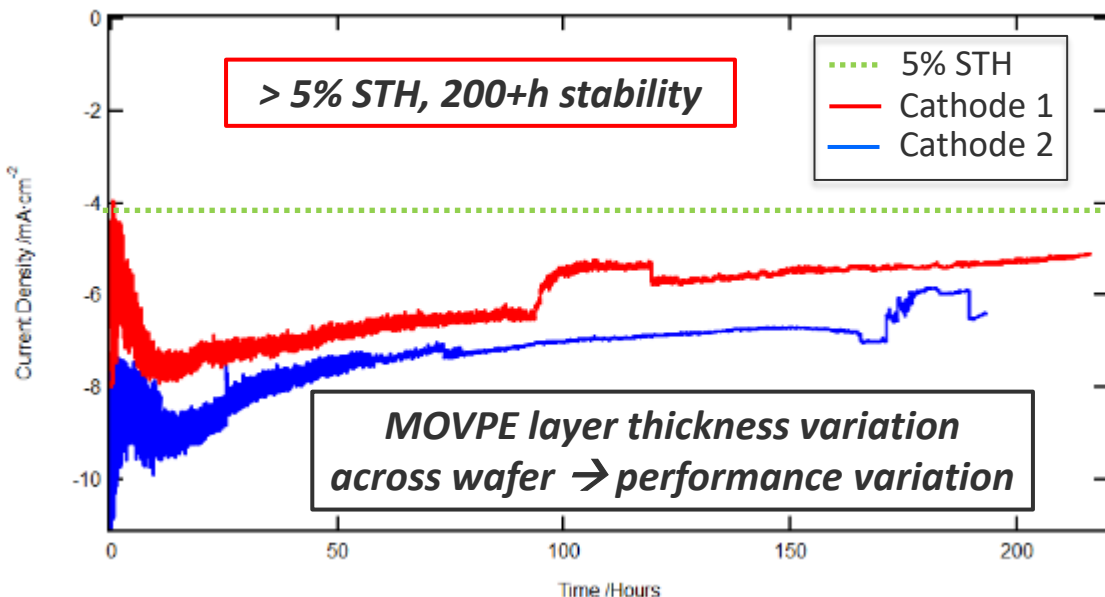
Step-by-step procedure for solar simulator calibration that accounts for the current-limiting junction of a tandem photoelectrode



HydroGEN 2.0 PEC Accomplishment: progress towards Q4 milestone

Annual milestone (FY23Q4): Demonstrate a completely integrated system and neutral pH conditions that achieve >220 h durability at short circuit and > 5% STH efficiency. Scale-up to a hand-held >4 cm² active area device that will split water under direct sunlight illumination with appreciable hydrogen bubble generation.

Bias-free water splitting at neutral pH in cuvette cell



Chronoamperometry shows significant progress towards Q4 milestone

Cathode: two electrodes from growth # WC106 of GaInP/GaAs III-V tandem, with PtRu catalyst

Cathode active area: 0.2 cm²

Anode: IrOx, separated from the photocathode via Ti mesh

Electrolyte: pH 7.2 potassium phosphate *remains at neutral pH in bulk throughout 200 hours*

Measurement vessel: cuvette cell



Collaboration and Coordination

- Partnership between LBNL and NREL
 - To demonstrate reproducibility of PEC measurements on the same material
 - To publish protocol for community to lay out best practices for accurate PEC measurements
 - Aim is to demonstrate efficient and durable bias-free water splitting at neutral pH
- Partnerships with seedling labs at Rice University and University of Toledo



Accomplishments and Future Work: PEC 2.0

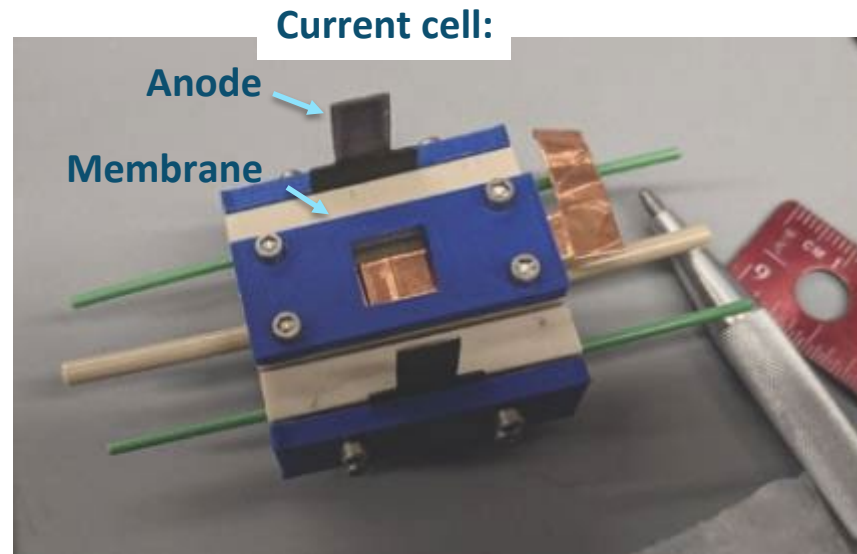
- **Future work:** aimed at end-of-the-project goals
 - Development of a hand-held portable device with 4 cm² active area
 - Towards 5% STH, 200+h stability

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



HydroGEN 2.0 Future Work: cell design

- **Aim: perform bias-free water splitting at neutral pH in this cell, to quantify STH efficiency**
- Resistance due to ion transport is too high at neutral pH
- To decrease resistance, ion transit path from anode to membrane will be eliminated by **merging anode and membrane into catalyst-coated membrane**.
- *Proposed future work subject to changed based on funding levels*



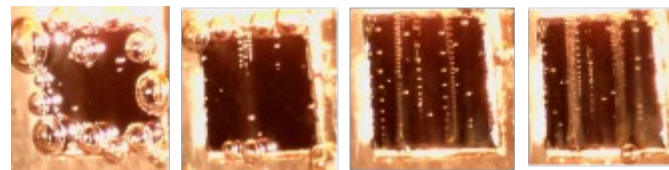
Future cell:
Replace separate Ir/IrOx anodes with Ir CCMs



HydroGEN 2.0 Future Work: III-V lifetime and durability

- To increase lifetime, will compare capping layers and protective layers to address electrodeposition and/or other corrosive mechanisms
 - GaN or GaP capping layer
 - TiO_2 or Al_2O_3 protective layers
- Will use pre-post analysis to further study corrosive mechanisms
 - Optical and SEM: structural changes
 - SPM: nanomechanical and conductivity changes
 - ICP-MS: quantify dissolved compounds in post-run electrolyte
 - EDS or XPS: elemental changes
- *Proposed future work subject to changed based on funding levels*

Evolution of photocathode at zero bias under illumination (III-V with GaP capping layer):



0 hr

30 hr

150 hr

250 hr

Increased roughness from photoreduction and Ga/In electrodeposition processes leads to more bubble nucleation sites on surface over time



HydroGEN 2.0 PEC: Summary

- Benchmarked and shared with community a flow reactor for H_2/O_2 quantification (NREL/LBNL)
- 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 in acid at 18% STH efficiency with a perovskite tandem photoelectrode, with a 500+ hour lifetime (U Toledo)
- Demonstrated bias free water splitting at 20.8% STH efficiency with a perovskite/silicon tandem photoanode, with a 100+ hour lifetime (Rice U)
- 8 publications, 5 under review/in press, 12 presentations/invited talks, 1 award