
II.D.1 High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production

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Subcontractors:

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- University of Hawaii, Honolulu, HI (XGJ-5-52227-01)

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Project End Date: September 30, 2017

Overall Objectives

- Develop a semiconductor-based, solar-driven, water-splitting photoelectrochemical (PEC) device with greater than 20% solar-to-hydrogen (STH) efficiency and several thousand hours of stability under normal operating conditions.
- Incorporate components that can be fabricated cost-effectively and are straightforward to scale up such that a plant scaled to 50,000 kg H₂/d can achieve an estimated production cost of \$1–\$2/kg hydrogen using only sunlight and water as feedstocks.
- Demonstrate a prototype photoreactor that produces 3 L of standard hydrogen within an 8-hour period under moderate solar concentration (~10X).

Fiscal Year (FY) 2016 Objectives

- Perform techno-economic analysis on higher-concentration (100X) systems and use H2A hydrogen analysis tool to generate a tornado plot that shows the sensitivity of a Type 4 reactor to optical concentration.
- Using a surface-modified semiconductor device capable of over 15% STH efficiency, show less than a 20% loss in efficiency after 875 h of continuous operation at short-circuit.
- Fabricate a photoreactor for use on a tracker.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production (3.1) section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (AE) Materials Efficiency – Bulk and Interface
- (AF) Materials Durability – Bulk and Interface
- (AG) Integrated Device Configurations
- (AI) Auxiliary Materials

Technical Targets

This project is a materials discovery investigation to identify a single semiconductor material that meets the technical targets for efficiency and stability. The 2015 technical targets from the Multi-Year Research, Development, and Demonstration Plan PEC hydrogen production goals in Table 3.1.8.A are the following:

- 15% solar-to-hydrogen (STH) conversion efficiency
- 900-hour replacement lifetime (1/2 yr at 20% capacity factor)
- \$300/m² PEC electrode cost

FY 2016 Accomplishments

- We discovered and quantified systematic errors in efficiency measurements that consistently lead to over-reporting by our lab and others. We published a manuscript on the topic in *Energy & Environmental Science*.
- Using actual, direct solar illumination that is collimated and precisely characterized, we measured over 16% STH efficiency, which is a new world record, on an inverted metamorphic multijunction (IMM) cell.
- We used H2A to model the effect that varying solar concentration (10X, 50X, 100X) for a Type 4 PEC reactor system has on the levelized cost of hydrogen.
- We used COMSOL Multiphysics® to model a PEC reactor under solar concentration and calculated that the ohmic potential drop in solution under 10X is less than 300 mV, but calculated that a pressure of 147 atm is required to keep the hydrogen in solution and prevent bubbles from scattering incident light.
- We discovered that GaAs has a high intrinsic stability as a photocathode, which we hypothesized is due to the in situ formation of a protective metallic As layer. We

published a manuscript on our results in the *Journal of Materials Chemistry A* special issue on water splitting and photocatalysis.

- We used scanning transmission electron microscopy (STEM) to image the original champion GaInP₂ sample that had nitrogen ion bombardment and unintentional PtRu applied to its surface and confirmed the University of Nevada, Las Vegas observation that recent attempts to replicate the champion sample have much higher PtRu loadings.
- We characterized CuGaSe₂ from the University of Hawaii and determined that it has an ideal bandgap and sufficient below-bandgap transmission to serve as the top electrode in a dual-absorber water-splitting system.
- We designed and fabricated a photoreactor for outdoor testing and procured a solar tracker to dedicate to this effort.
- We filed a non-provisional patent application on IMM cells for high-efficiency water splitting.



INTRODUCTION

Photoelectrolysis cells combine a light-harvesting system and a water-splitting system into a single, monolithic device. The catalyzed surface of a semiconductor is the light-harvesting component, as well as one part of the water-splitting system, with the balance consisting of a spatially separated counter electrode. Discovering a semiconductor system that can efficiently and sustainably collect solar energy and direct it toward the water-splitting reaction could provide renewable and economically competitive fuel for the hydrogen economy.

The goal of this work is to develop a semiconductor material set or device configuration that:

- Splits water into hydrogen and oxygen spontaneously upon illumination without an external bias.
- Has a solar-to-hydrogen efficiency of at least 15%, with a clear pathway to exceed 20%.
- Can ultimately be synthesized via high-volume manufacturing techniques with a final hydrogen production cost below \$2/kg.

APPROACH

All proven zero-bias PEC devices with STH over 1% rely on two series-connected semiconductor junctions (tandem cell) to increase the majority-carrier potential at the counter electrode [1-4], providing sufficient potential difference (photovoltage) for water splitting. Tandem devices also

overcome the band-alignment challenge common to PEC materials.

For maximum efficiency, the subcell currents in series-connected devices must be equal, creating the requirement of current matching. The maximum theoretical current generated by a semiconductor can be calculated by assuming unity quantum yield for every above-bandgap photon in the solar spectrum. Using the accepted lower heating value efficiency equation [5], 20% STH corresponds to a short-circuit current density of 16.26 mA/cm² under AM1.5G (1-sun). The largest bottom-cell bandgap that can be used and still achieve 20% STH is 1.41 eV. However, quantum yields are never 100% and semiconductors are not true step-function devices. Therefore, to realistically achieve STH values in excess of 20%, we must use lower top-cell and bottom-cell bandgap combinations, which guides our selection of candidate semiconductors.

An additional variable that can be used to match the currents is the thickness of the top cell—a thinner cell will allow more photons through to the bottom cell. This gives us some additional flexibility in the bandgaps that may be used. The lower limit of useable bandgaps is ~0.8 eV [6], dictated by the short penetration depth of lower-energy photons through water.

We will focus on III-V semiconductors, which exhibit the highest conversion efficiencies among all photoabsorber materials, and design tandem junctions to maximize the spectrally split device current, while achieving sufficient voltage to drive the maximum current through the device. We plan to initially focus on devices grown by conventional III-V metal-organic vapor-phase epitaxy to demonstrate maximum possible efficiencies. We will then port successful device structures to emerging synthesis techniques—such as spalling, epitaxial lift-off, or hydride vapor-phase epitaxy—that have the potential to meet low-cost absorber targets. We plan to improve the stability of III-V semiconductor water-splitting electrodes by a variety of surface-protecting modifications that include nitridation and sputtering, atomic layer deposition of oxides or nitrides, and thin coatings of MoS₂.

RESULTS

Surface Stability

In an effort to better understand the PtRu surface microstructure of the “champion” durability sample, we obtained STEM images of the last-remaining untested piece of it. This champion sample was from our original discovery of nitridation and PtRu sputtering and had the highest durability yield of any surface modification we have ever observed, with every electrode exhibiting remarkable stability (several 10s of hours), even after durability testing, electrode deconstruction, reconstruction, and retesting.

One of these electrodes even survived a cumulative 115 h of testing [7].

The imaging mode used was high-angle annular dark-field (HAADF) STEM under which heavier elements, such as Pt and Ru, appear as a lighter contrast against a darker background. Comparison of HAADF-STEM of the champion and an attempt to replicate it (Figure 1) suggest a much higher PtRu loading on the replicate. The HAADF-STEM images corroborate our University of Nevada, Las Vegas collaborators' discovery, based on X-ray photoelectron spectroscopic analysis, that the replication attempts have significantly higher amounts of PtRu than the champion. Our goal is to adjust the surface-modification treatment parameters to achieve surfaces that are more similar to

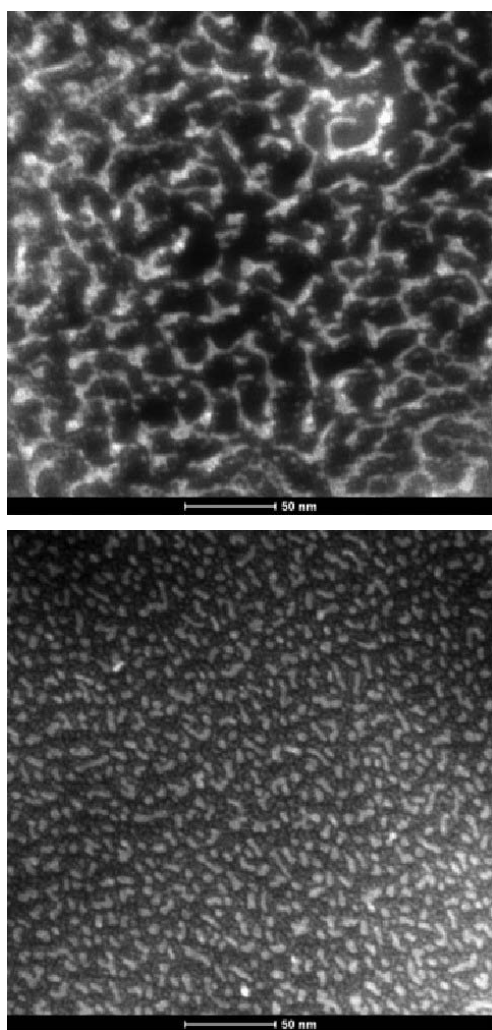


FIGURE 1. HAADF-STEM of the champion durability sample (top) and a recent attempt to replicate its surface (bottom). The heavier elements, such as Pt and Ru, are the lighter contrast against the dark background. Although the particles are nominally similar sizes in the two surfaces, the replicate clearly has a much higher level of PtRu loading. (Images by Andrew Norman, National Renewable Energy Laboratory).

the champion surface, with the hope of observing similar remarkable durability.

We also discovered that GaAs has unexpected stability during operation as a photocathode in acidic electrolytes, which we attribute to the in situ formation of a metallic As layer. The details can be found in Publication 1. The discovery that arsenides have a greater intrinsic stability than phosphides is significant because it makes accessible several possible new III-V material compositions that had previously been considered too unstable for PEC applications.

Techno-Economic Modeling

This year we used the H2A Future Central Hydrogen Production from the Photoelectrochemical Type 4 version 3.0 case study [8] to evaluate the sensitivity of hydrogen production costs to optical concentration. All values were calculated assuming a 1,000 kg/d (1 tonne per day or TPD) plant scaled to 2,000 kg/d with 98% operating capacity factor. A 25% solar capacity factor was used and a hydrogen production rate of 1.702×10^{-6} kg/m²-s is assumed for a 20% STH device. Using these inputs, the solar capture area required for 1 TPD at 20% STH is 20,400 m², 25% STH is 16,320 m², and 15% is 27,199 m². Because H2A requires inputs to be in 2005 dollars, the component costs have to be adjusted in the following ways. The lens array was assumed to be \$75/m² in 2010 dollars and Plexiglas was \$124/m² in 2007 dollars, giving \$67.17 and \$116.8 in 2005 dollars, respectively. To calculate capital (and replacement) costs, the lens cost was multiplied by the capture area whereas the Plexiglas cost was multiplied by three times the absorber area. The lens cost was assumed to be independent of concentration factor. The PEC absorber area required was calculated by dividing the capture area by the concentration factor. Lenses and Plexiglas reactor parts were replaced every 10 years. Within the range of the inputs used, hydrogen levelized costs are most sensitive to PEC absorber costs, followed by concentration factor (Figure 2a). Using current PEC absorber costs of \$10,000/m², concentration is by far the most effective route to reducing hydrogen levelized cost (Figure 2b). If PEC absorber costs are able to achieve the \$200/m² “ultimate” target, then hydrogen levelized cost becomes more sensitive to efficiency as balance-of-system costs dominate (Figure 2c).

Although concentration up to 100X may demonstrate a route to economic plausibility, technological feasibility is limited by physical processes occurring in actual photoreactor cells. We used COMSOL Multiphysics® modeling to calculate physical parameters of our photoreactor cell to estimate losses under operating conditions. Our COMSOL Multiphysics® modeling calculated minimal (<300 mV) ohmic losses at 10X concentration, but losses can exceed several volts at 100X using our current reactor geometry. Much higher concentrations are reasonable with redesigned reactor geometry, specifically ones that more

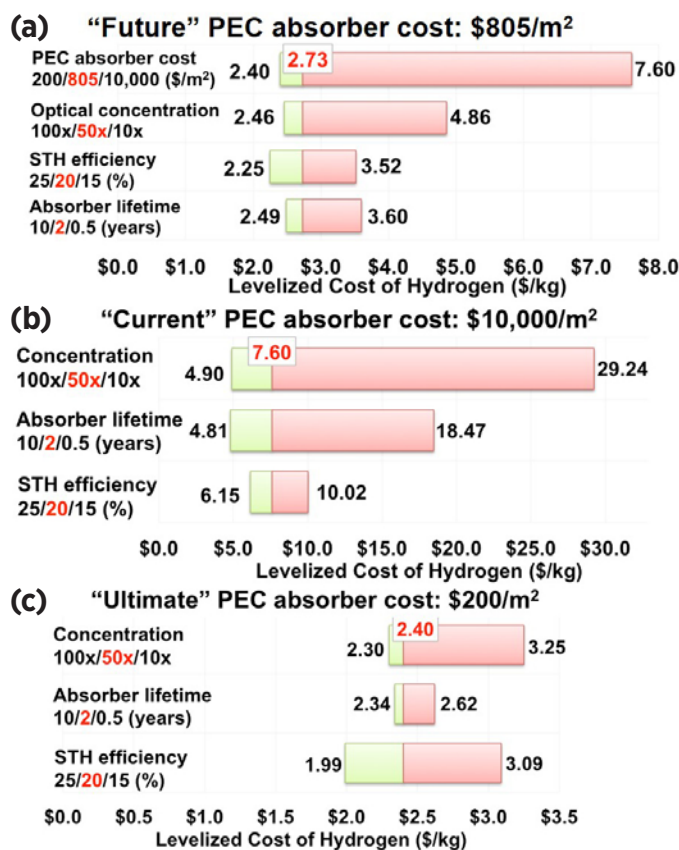


FIGURE 2. Sensitivity analysis showing influence of absorber costs, concentration factor, STH efficiency, and absorber lifetime on hydrogen costs. Hydrogen costs from a Type 4 concentrator PEC reactor using (a) future, (b) current, and (c) ultimate absorber costs for baseline projections.

closely approximate electrolyzers where current densities can reach several A/cm². The use of buried-junction devices allows the flexibility to make these geometries attainable. We also used COMSOL Multiphysics® to calculate the pressure—specifically, 147 atm—required to keep hydrogen in solution, which could prevent bubbles from scattering incident light. Operating at this pressure is not practical, so other engineering measures must be considered in designing a reactor that minimizes the light attenuation due to hydrogen gas evolution from the illuminated photocathode surface.

Solar-to-Hydrogen Efficiency Benchmarking

We discovered several potential sources of experimental error while performing efficiency measurements on our IMM cells. Almost all of these errors lead to artificially higher photocurrents and overrate the measured efficiency. The errors are a consequence of common experimental techniques, so we published a manuscript to raise awareness of this issue and proposed specific remedies that we hope will be adopted by the PEC community.

The errors are due to two main categories of uncertainty: absorber area and illumination. We discovered that the Hysol Loctite 9462 epoxy we use, although nominally opaque, actually transmits a significant fraction of incident illumination (20–60%) at thicknesses up to 1.2 mm. We (and many others) typically use this epoxy to define the active area of the electrode and had assumed only the exposed area was responsible for collecting light. We found that photons absorbed by the semiconductor under the area masked by epoxy can inflate photocurrent density measurements by 20% or more, depending on the ratio of total semiconductor area to the area exposed. We have moved to a more transparent epoxy and settled on a more conservative definition of active area that includes the total area of the semiconductor chip, including the portion covered by epoxy.

The other main sources of error are due to spectral mismatch between the simulated light source and the reference light spectrum, as well as light piping and concentration effects of photoreactor cells. The spectral mismatch is especially important in multi-junction absorbers, where one junction is typically current-limiting. Over-illuminating the current-limiting junction can lead to measured device photocurrent densities that exceed what is possible under real solar illumination. Additionally, exposing an entire photoreactor to diffuse (scattered) light—as is present in the “global” spectrum—can cause coupling of photons to the sample via light piping that would otherwise not be available to it. We propose making efficiency measurements under “direct” solar illumination with a collimating tube and a well-defined electrode area to minimize the above sources of error. The current density measured under these conditions should be validated by integrating the incident photon-to-current efficiency response over the AM1.5D reference spectrum to check for self-consistency. Publication 2 discusses these issues in much greater detail. We used these advanced benchmarking protocols to confirm over 16% STH efficiency on an IMM III-V device and have submitted a manuscript to a peer-reviewed journal describing the study.

CONCLUSIONS AND FUTURE DIRECTIONS

- Using higher optical concentration in solar-hydrogen photoreactors is one way to offset the disproportionately large contribution of the current cost of III-V semiconductor absorbers to achieve reasonably priced hydrogen in the short term. Managing the elevated current densities achieved under higher optical concentration requires re-engineering of the photoreactor to minimize electrode distances to achieve an acceptable ohmic (internal resistance) potential loss due to ion transport.
- Our new higher-efficiency devices have a buried *p-n* junction at the surface closest to the electrolyte. Using

a buried *p-n* junction allows incorporation of more robust encapsulation schemes because current can be collected through a conduit and does not require the passivating layer to be conductive. Transparent, insulating encapsulants that have known stability, such as poly(methyl methacrylate) and silicone, can now be considered. We plan to leverage these encapsulating strategies to achieve several hundred hours of stability at a high solar-to-hydrogen efficiency.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. “Remarkable Stability of Unmodified GaAs Photocathodes during Hydrogen Evolution in Acidic Electrolyte,” James L. Young, K. Xerxes Steirer, Michael J. Dzara, John A. Turner, and Todd G. Deutsch, *J. Mater. Chem. A*, **4**, 2831–2836 (2016).
2. “Solar to Hydrogen Efficiency: Shining Light on Photoelectrochemical Device Performance,” H. Döscher, J.L. Young, J.F. Geisz, J.A. Turner, and T.G. Deutsch, *Energy Environ. Sci.*, **9**, 74–80 (2016).
3. “Reversible GaInP₂ Surface Passivation by Water Adsorption: A Model System for Ambient-Dependent Photoluminescence,” James L. Young, Henning Döscher, John A. Turner, and Todd G. Deutsch, *J. Phys. Chem. C*, **120**, 4418–4422 (2016).
4. “Molybdenum Disulfide as a Protection Layer and Catalyst for Gallium Indium Phosphide Solar Water Splitting Photocathodes,” Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, Thomas F. Jaramillo, *J. Phys. Chem. Lett.*, **7**, 2044–2049 (2016).
5. “III-V Semiconductor Systems as the Only Viable Candidates for Commercial PEC H₂ Production Devices,” Solar Fuels Network: Moving from Materials to Devices, London, England. July 7, 2015. (Turner) *invited*
6. “Photoelectrochemical Water Splitting, from Fundamentals to Devices,” Modern Topics in Energy and Power Technical Meeting, Army Research Lab, Adelphi, MD. July 14, 2015. (Turner) *invited*
7. “Inverted Metamorphic Tandem Devices for Efficient Photoelectrochemical Water Splitting” 20th American Conference on Crystal Growth and Epitaxy, Big Sky, MT. August 4, 2015. (Döscher)
8. “Semiconductor Systems and Catalysts for Photoelectrochemical Water Splitting,” ALS User’s Meeting, LBNL, Berkeley CA. October 5, 2015. (Turner) *invited*
9. “Improving Onset Potential for Higher Efficiency Water Splitting with III-V Tandems,” American Vacuum Society 62nd Meeting, San Jose, CA. October 20, 2015. (Young)
10. “Inverted Metamorphic Multijunction Semiconductors for Exceptionally High Photoelectrolysis Efficiencies: Materials Development and Measurement Challenges,” Physics Department seminar, Denmark Technical University, Copenhagen, Denmark. November 18, 2015. (Deutsch) *invited*
11. “Tandem Device Design for Photoelectrochemical Water Splitting: The Impact of Sunlight Absorption in Aqueous

Electrolytes and the Role of Inverted Metamorphic III-V Epitaxy,” Institut für Solarenergieforschung Hameln (ISFH), Kolloquium, Hameln, Germany. November 24, 2015. (Döscher)

12. “Solar Energy to Hydrogen Fuel via Highly Efficient III-V Semiconductors,” Postdoctoral Researcher Candidate Seminar, NREL, Golden, CO. January 21, 2016. (Young)
13. “The Hydrogen Economy and Photoelectrochemical Water Splitting,” REMRSEC graduate student seminar, Colorado School of Mines, Golden, CO. February 9, 2016. (Turner) *invited*
14. “Frontiers, Opportunities and Challenges for a Hydrogen Economy,” IGERT graduate student seminar, Arizona State University, Glendale, AZ. February 12, 2016. (Turner) *invited*
15. “Maximizing Photocurrent Onset Potential of III-V Photoelectrochemical Junctions,” Materials Research Society Spring Meeting, Phoenix, AZ. March 31, 2016. (Young)

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