

II.C.1 Semiconductor Materials for Photoelectrolysis

Todd Deutsch (Primary Contact), John Turner,
Heli Wang, Huyen Dinh
National Renewable Energy Laboratory (NREL)
15013 Denver West Parkway
Golden, CO 80401
Phone: (303) 275-3727
Email: Todd.Deutsch@nrel.gov

DOE Manager
Eric Miller
Phone: (202) 287-5829
Email: Eric.Miller@ee.doe.gov

Subcontractor:
University of Nevada Las Vegas (UNLV), Las Vegas, NV

Project Start Date: 2005
Project End Date: Project continuation and direction
determined annually by DOE

Overall Objectives

Identify, synthesize, and characterize new semiconductor materials that have the capability of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device, either as a single absorber or as part of a high-efficiency multi-junction device

Fiscal Year (FY) 2013 Objectives

- Optimize semiconductor surface modification for passivation against corrosion while maintaining high solar-to-hydrogen efficiency.
- Demonstrate improved durability for state-of-the-art high-efficiency III-V semiconductor electrodes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.5) 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 as follows:

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

This project made progress towards the stability target with material that exceeds the efficiency target. The main achievements were over 300 hours of high photocurrent operation under bias with minimal corrosion and surpassing a 100-hour lifetime at short-circuit.

FY 2013 Accomplishments

- We fabricated an acrylic photoreactor for testing PEC materials that is able to collect hydrogen and oxygen gases separately for quantitative analysis which is necessary for solar-to-hydrogen efficiency benchmarking. The photoreactor was designed for mounting on a two-axis solar tracker for outdoor testing and can be equipped with lenses for moderate optical concentration.
- Surface spectroscopic results from UNLV uncovered additional elements that played a key role in the successful nitride passivation treatment allowing us to reproduce the protective effect on additional GaInP₂ surfaces. In partnership with UNLV, we filed a provisional patent application on the treatment process.
- Feedback from nitrogen K-edge X-ray emission spectroscopy taken by our UNLV collaborators at the Advanced Light Source has provided quantitative results on the degree of nitride that provides the best electrode durability, giving us a target level of incorporation for ion dosing.
- We led an effort, along with Stanford and DOE, to compile and streamline PEC standardized methods documents that did not fit into our Journal of Materials Research publication [1] and submitted them to Springer for publication as a short book.
- We tested multiple treated tandem GaInP₂/GaAs electrodes for durability under bias and had some last for several hundred hours with little sign of physical degradation or loss of performance.

- We tested several tandem GaInP₂/GaAs electrodes at short-circuit that had initial starting solar-to-hydrogen efficiencies in excess of 10%. They were tested until failure and the average lifetime of fourteen electrodes was 60 hours, with three operating longer than 100 hours.



INTRODUCTION

Photoelectrochemistry combines 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 towards 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 (i) splits water into hydrogen and oxygen spontaneously upon illumination without an external bias, (ii) has a solar-to-hydrogen efficiency of at least 10% with a clear pathway to 15%, and (iii) can ultimately be synthesized via high-volume manufacturing techniques with a final hydrogen production cost of \$2.10/kg.

APPROACH

Our approach is to study the current material sets used in commercial solar cells as well as related materials that meet near-term solar-to-hydrogen efficiency targets and to extend their durability by surface passivation techniques. The surface passivation treatments are engineered not only to stabilize the semiconductor at the electrolyte interface but also to maintain the high native efficiencies by ensuring that charge transfer is not compromised. To help us identify the steps that initiate corrosion reactions and develop mitigation strategies, we collaborate with partners who apply state-of-the-art spectroscopic characterization skills and theory to better observe and understand our system. Another area of focus is to investigate new materials that have lower band gaps and high quantum efficiencies that could allow them to achieve the ultimate DOE solar-to-hydrogen efficiency target, which is very high.

RESULTS

Photoreactor Design and Fabrication

With the aid of intern Adolfo Alvarez, we designed a photoreactor to facilitate on-sun testing of promising

PEC water-splitting electrodes. The body was made of poly(methyl methacrylate) for optimal chemical resistance and optical transparency. The design incorporated a bracket for mounting on a two-axis solar tracker at NREL's Solar Radiation Research Laboratory. Two lower ports allow interchangeable semiconductor and counter electrode insertion and permit electrical contacts between the electrodes for circuit measurements (Figure 1). Two upper ports on the reactor allow separate hydrogen and oxygen collection and were engineered to be the high points during the full range of inclinations the cell experiences as it tracks the sun's path throughout the day. Solar-to-hydrogen efficiency can be evaluated using real-time solar spectral and intensity data collected on instruments adjacent to the tracker and compared with current measured between the water splitting electrodes. The product gas volumes can be used to determine the Faradaic efficiency. Testing of III-V tandem electrodes under on-sun conditions to benchmark efficiency and durability is ongoing.

Durability Testing on Tandem Electrodes

High efficiency III-V tandem semiconductor photoelectrochemical electrodes were tested for durability under water splitting conditions. A protective surface modification developed at NREL was applied and resulted in improved photocorrosion resistance. The best performing electrodes had lifetimes that exceeded 100 hours when tested at short-circuit and several hundred hours when a bias was applied. The durability of the modified surfaces at unprecedented photocurrent densities is a significant improvement over the severe degradation observed after only 24 hours for untreated electrode surfaces. These results demonstrate noteworthy progress towards the DOE's

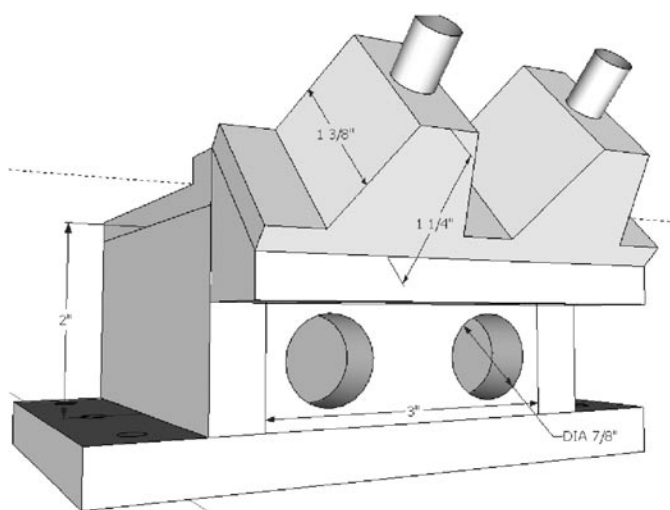


FIGURE 1. Computer-aided design rendering of the back-side of the photoreactor. The two lower ports are for the semiconductor and counter electrodes. The two upper ports connect to tubing for hydrogen and oxygen gas collection.

efficiency and durability targets required to achieve cost-competitive hydrogen production via photoelectrolysis.

After undergoing nitrogen ion implantation-based surface passivation treatments, tandem p-GaInP₂/GaAs photoelectrodes were potentiostatically tested for durability in 3M H₂SO₄ electrolytes with the fluorosurfactant Zonyl[®] FSN-100. Electrodes were illuminated by a 250-watt tungsten light source calibrated to AM1.5G with a 1.81 eV band gap GaInP₂ reference cell. Previously we reported 115 hours of stability on epilayer (non-tandem) p-GaInP₂ where a constant current of 10 mA/cm² was applied. The testing for tandem electrodes either had a constant circuit bias of -1.5 V or -1 V, or had no bias at all between the working and platinum black counter electrodes (short-circuit). All of the tests were accomplished in a two-terminal configuration because reference electrodes are not robust enough to withstand the harsh durability conditions.

At the conclusion of the biased durability testing, the semiconductor electrodes were disassembled and their surfaces were analyzed using an optical profilometer to determine if any physical degradation had occurred. The corrosion electrolytes were also tested for gallium and indium concentrations by inductively coupled plasma mass spectrometry (ICP-MS). The analytes were detected in ppb quantities and converted to nanomoles per Coulomb to account for variation in testing cell volumes, electrode surface areas, and overall charge passed. The ICP-MS results from the biased tests (Figure 2) demonstrate that the surface passivation treatment is effective in providing protection at very high cathodic current densities for long durations. Interference microscopy (Figure 3) revealed that nominal etching occurred for this particular electrode surface over 315 hours of passing, on average, 14.55 mA/cm² cathodic, hydrogen-evolution photocurrent. While untreated electrode

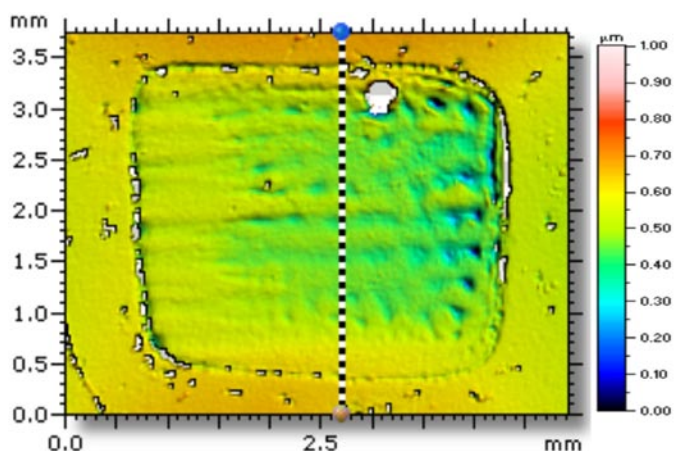


FIGURE 3. Surface profile of the deconstructed electrode subjected to 315 hours of testing at -1.5 V generated by optical interference microscopy. The perimeter of the rectangular chip was masked with epoxy leaving only the interior area exposed to electrolyte during testing. The etching of the exposed surface was minimal compared to that observed on untreated electrodes.

surfaces exhibit widespread, uniform etching about 1 μm deep after only 24 hours at 10 mA/cm², 315 hours at a higher current density resulted in localized surface etching that was only a few hundred nanometers deep on treated electrode surfaces.

Short-circuit testing was a measure of lifetime as all of the tests ended in catastrophic failure of the electrodes with large craters that perforated the entire epilayer and substrate. Optical profilometry and ICP-MS are not useful tools for quantitative comparisons under such failure conditions. Electrode failure under short-circuit conditions was indicated by the first appearance of anodic current, and on average the 14 treated tandem electrodes operated for 60 hours before failing. The most durable electrodes had lifetimes of 102.6, 103.2, and 110.1 hours. Even though three out of the 14 electrodes exceeded 100 hours of unbiased operation, the durability under short-circuit was not as great as when the electrodes were biased. It appears that sustaining a high cathodic photocurrent is critical to the long-term stability of the treated tandem electrode surfaces.

In addition to semiconductor degradation, another possible reason for the decline in photocurrent with time could be fouling of the counter electrode, which was observed at the conclusion of each of the durability tests. When biased testing was performed in a surfactant-free electrolyte, the counter electrode did not get fouled; however, large bubbles formed on the working electrode and severe physical degradation of the semiconductor occurred within a few hours. At the rate of gas evolution for these high efficiency water-splitting tests, surfactant is required and a fluorosurfactant was chosen because it should be resistant to oxidative decomposition. It is clear that alternative surfactants should be investigated to identify those that can

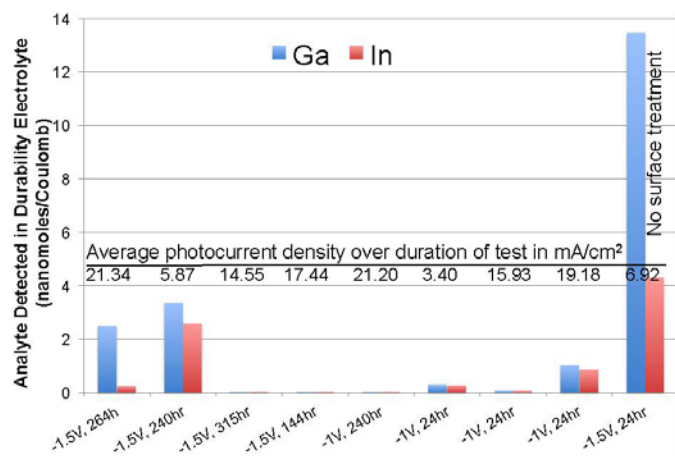


FIGURE 2. Ga and In present in 3M H₂SO₄ durability solutions of tandem electrodes detected by ICP-MS. Results are from multiple, unique electrodes that were all treated except for the one noted. Lower values for the treated electrodes suggest stability compared with the untreated sample.

still aid bubble removal and also resist degradation. We are optimistic that the durability at short-circuit can be pushed to several hundred hours as we continue to optimize the surface treatment conditions and refine electrolyte composition.

CONCLUSIONS

- We have developed a surface passivation treatment that significantly improves the durability of p-GaInP₂/GaAs tandem electrode surfaces. The durability of tandem electrodes at short-circuit is greater for treated than for untreated surfaces, but still needs improvement.
- The PEC performance metrics necessary to achieve the DOE goals for cost-competitive hydrogen could be met using the high water-splitting efficiencies of these tandem devices coupled with the durability provided by an optimized surface modification.
- The durability was not as great as for electrodes tested at short-circuit as it was for those that were biased. Because a real PEC reactor will not have a bias applied, durability testing should utilize short-circuit conditions to determine how a candidate semiconductor material will perform in an actual deployed device.

FUTURE DIRECTIONS

- We will continue to optimize the surface passivation treatment by varying ion implantation parameters based upon critical feedback provided by our UNLV collaborators.
- We will evaluate the efficacy of the surface passivation treatment on other III-V PEC semiconductors to see if the protection could apply to this whole material class.
- To minimize ancillary system component contributions to circuit failure in two-electrode durability testing, we will examine alternative electrolyte/surfactant compositions and investigate other counter electrodes that are more catalytically active for water oxidation.

FY 2013 PUBLICATIONS

1. “Titanium and magnesium Co-alloyed hematite thin films for photoelectrochemical water splitting” Houwen Tang, Wan-Jian Yin, M.A. Matin, Heli Wang, Todd Deutsch, Mowafak M. Al-Jassim, John A. Turner and Yanfa Yan, *J. Appl. Phys.* **111**, 073502 (2012).
2. “Photoelectrochemical activity of as-grown, α -Fe₂O₃ nanowire array electrodes for water splitting” Boris D. Chernomordik, Harry B. Russel, Uros Cvelbar, Jacek B. Jasinski, Vivekanand Kumar, Todd Deutsch, and Mahendra K. Sunkara, *Nanotechnology*, **23**, 194009 (2012).
3. “Novel Micropixelation Strategy to Stabilize Semiconductor Photoelectrodes for Solar Water Splitting Systems” Fatima Toor, Todd G. Deutsch, Joel W. Pankow, William Nemeth, Arthur J. Nozik and Howard M. Branz, *J Phys. Chem. C*, **116**, 19262-19267, (2012).

4. “The stability of illuminated p-GaInP₂ semiconductor photoelectrode” Heli Wang, Todd Deutsch, Adam Welch, John A. Turner, *Int. J. Hydrogen. Energ.*, **37**, 14009-14014, (2012).
5. “BiVO₄/CuWO₄ Heterojunction Photoanodes for Efficient Solar Driven Water Oxidation” Satyananda Kishore Pilli, Todd G. Deutsch, Thomas E. Furtak, Logan D. Brown, John A. Turner and Andrew M. Herring, *Phys. Chem. Chem. Phys.*, **15**, 3273-3278, (2013).
6. “Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry” Blaise A. Pinaud, Jesse D. Benck, Linsey C. Seitz, Arnold J. Forman, Zhebo Chen, Todd G. Deutsch, Brian D. James, Kevin N. Baum, George N. Baum, Shane Ardo, Heli Wang, Eric Miller and Thomas F. Jaramillo, *Energy Environ. Sci.* **6**, 1983-2002, (2013).
7. “Electronic structure study of N, O related defects in GaP for photoelectrochemical applications” Muhammad N. Huda, Todd G. Deutsch, Pranab Sarker, and John A. Turner, *J. Mater. Chem A*, **1**, 8425-8431, (2013).
8. “Efficient photoelectrochemical water oxidation over cobalt-phosphate (Co-Pi) catalyst modified BiVO₄/1D-WO₃ heterojunction electrodes” Satyananda Kishore Pilli, Todd G. Deutsch, Thomas E. Furtak, John Turner, Logan D. Brown, and Andrew M. Herring, *Phys Chem Chem Phys*, IN PRESS First published online July 9, 2013. DOI: 10.1039/C3CP52401A

FY 2013 PRESENTATIONS

1. “Photoelectrochemical water splitting”, Inter-Continental Advanced Materials & Photonics (I-CAMP), 2012 Summer School on Renewable and Sustainable Energy, University of Colorado, Boulder, July 19, 2012. (Turner) *Invited*
2. “Material Properties and Economic Considerations for Photoelectrochemical Water-Splitting Systems”, JX Nippon Oil & Energy Corporation”, Yokohama, Japan, July 23, 2012. (Turner) *Invited*
3. “Semiconducting Materials and Structures for Photoelectrochemical Hydrogen Production”, University of Tokyo, Tokyo, Japan, July 24, 2012. (Turner) *Invited*
4. “Material Properties and Economic Considerations for Photoelectrochemical Water-Splitting Systems”, 1st International Workshop on Solar-Chemical Energy Storage (SolChES), Sendai, Japan, July 25, 2012. (Turner) *Invited Plenary*
5. “Protecting p-GaInP₂ from Corrosion for Durable Photoelectrochemical Water Splitting”, 2012 SPIE’s Optics + Photonics, San Diego, CA, August 12, 2012. (Wang) *Invited*
6. “Photoelectrochemical Hydrogen Production”, CRSP Fall Research Symposium, University of Colorado, Boulder, August 29, 2012. (Turner) *Invited*
7. “Material Properties and Economic Considerations for Photoelectrochemical Water-Splitting Systems”, Toyota Central Research and Development Laboratory, Toyota, Japan, September 19, 2012. (Turner) *Invited*

8. “The Promise and Challenges for Photoelectrochemical Hydrogen Production”, Nagoya Institute of Technology (NITech), Nagoya, Japan, September 20, 2012. (Turner) *Invited*
9. “Challenges in Photoelectrochemistry and the Impact of Coordination Chemistry”, 62nd Japan Society of Coordination Chemistry Symposium, Toyoma, Japan, September 21, 2012. (Turner) *Invited Plenary* -JSCC Lectureship Award presentation.
10. “The Hydrogen Economy and Photoelectrochemical Water Splitting”, NREL Fall Interns, October 3, 2012. (Turner) *Invited*
11. “Hydrogen Production from Photoelectrochemical Cells: Economic and theoretical considerations and experimental results”, PRiME 2012: Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan. Honolulu, Hawaii. October 7th, 2012. (Turner) *Invited Plenary*
12. “Photoelectrolysis on p-GaInP₂; Extended Durability by Nitrogen Ion Implantation”, PRiME 2012: Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan. Honolulu, Hawaii. October 9th, 2012. (Deutsch) *Contributed*
13. “Corrosion protection of p-GaInP₂ for durable photoelectrochemical water splitting”, PRiME 2012: Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan. Honolulu, Hawaii. October 9th, 2012. (Wang) *Contributed*

14. “Photoelectrochemical Water Splitting and the Hydrogen Economy”, South Dakota School of Mines, October 18, 2012. (Turner) *Invited Sigma Xi lecture*
15. “Photoelectrochemical Water Splitting and the Hydrogen Economy”, Black Hills State University, October 19, 2012. (Turner) *Invited Sigma Xi lecture*
16. “Material Properties and Economic Considerations for Photoelectrochemical Water-Splitting Systems”, University of Nevada, Reno, November 30, 2012. (Turner) *Invited*

REFERENCES

1. Chen, Z., Jaramillo, T.F., Deutsch, T.G., Kleiman-shwarsstein, A., Forman, A.J., Gaillard, N., Garland, R., et al. (2010). Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols. *Journal of Materials Research*, 25(1), 3–16. doi:10.1557/jmr.2010.0020