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

Todd G. Deutsch (Primary Contact),
John A. Turner, James L. Young, Myles A. Steiner, Henning Döscher, Ellis Klein
National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO  80401
Phone: (303)275-3727
Email: Todd.Deutsch@nrel.gov

DOE Manager: David Peterson
Phone: (240) 562-1747
Email: David.Peterson@ee.doe.gov

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• University of Nevada, Las Vegas, Las Vegas, NV (XGB-2-11673-01)
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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 per day 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).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery 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 PEC hydrogen production goals in Table 3.1.8.A of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan are the following.

• 15% STH conversion efficiency
• 900-hour replacement lifetime (half a year at 20% capacity factor)
• $300/m² PEC electrode cost

FY 2017 Accomplishments

• We tested a new III-V alloy, GaInAsP, as a candidate for the 1.7-eV bandgap top cell in a higher-efficiency tandem device, and discovered it has good intrinsic stability and photocurrent efficiency. We sent a series of GaInAsP samples to the Heske group, our surface validation team collaborators at the University of Nevada, Las Vegas to get a better understanding of the surface stabilization mechanism.

• We achieved very good durability results with the Jaramillo group at Stanford University on buried-junction pn-GaInP₂ capped with MoS₂. We measured 100 h with little degradation and plan to extend the testing.

• We designed a capillary mass-spectrometer-based faradaic yield system and measured trace signals of H₂ and O₂ from GaAs water-splitting microcells from Jongseung Yoon’s laboratory at the University of Southern California, testing the limit of quantitative detection for this custom instrument.
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 air mass 1.5 global (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 usable 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 absorber 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/spattering, atomic layer deposition of oxides/nitrides, and thin coatings of MoS₂.

RESULTS

Solar-to-Hydrogen Efficiency Benchmarking

During the course of benchmarking over 16% STH efficiency on our inverted metamorphic multijunction (IMM) cells [7], we identified and documented two more potential sources of measurement error that were not included in our Energy & Environmental Science manuscript [8] that detailed ways of improving STH measurement accuracy. One systematic error we discovered is a consequence of applying light from a diverging illumination source through the multiple interfaces of an electrochemical cell. The different indices of refraction between air/glass/electrolyte cause a concentration error that can increase the light intensity on the sample by 10%, relative to the calibrated value, under commonly used experimental conditions. We recommended using a highly collimated source (i.e., sunlight with a collimating tube) to mitigate this source of error. We also made a recommendation against setting light intensity from a solar simulator with the reference diode inside the electrochemical cell, either with air or electrolyte inside the cell. In the case of an air-filled cell, reflection at the glass/
electrolyte interface is significantly lower than at a glass/air interface, resulting in a light intensity on the PEC sample that is about 5% greater than the calibrated value. Immersing the reference cell in electrolyte during light-intensity calibration can eliminate the reflection error at the inner electrochemical cell interface, whereas the infrared absorption of water attenuates light on a typically used Si reference cell, leading to an overcompensated simulator intensity.

To report STH water-splitting efficiency, the fraction of current going to hydrogen and oxygen generation (Faradaic efficiency) must be known. We designed and built a new Faradaic efficiency measurement system based on product gas detection by a capillary mass spectrometer. Using a mass spectrometer has several advantages over the more commonly used gas chromatograph in detecting product gases, including the following: greater sensitivity, continuous measurement, and ability to provide qualitative as well as quantitative information. We demonstrated the capability of this system by measuring the Faradaic efficiency of solar water splitting on GaAs microcells synthesized by our collaborator. We were able to quantitatively determine oxygen and hydrogen generated on 0.0025-cm² microcells at only 50 μA of current. The corresponding concentrations of oxygen and hydrogen under the measurement conditions were 200 ppm and 400 ppm, respectively. Confirming a near-unity Faradaic yield, we were able to use collimated sunlight to benchmark 13.1% STH efficiency from these GaAs microcells [9].

For longer-term performance assessment under more realistic conditions, i.e., those that include temporal intermittency from clouds and diurnal cycles, we designed and fabricated a photoreactor for testing on a two-axis solar tracker. The photoreactor (Figure 1) can be fitted with a Fresnel lens for measurements at low optical concentrations (~10x), and it is equipped with quantitative gas-collection capabilities, can accommodate a variety of sample dimensions, and has Nafion® membrane separators to prevent mixing of hydrogen and oxygen.

Durability Testing

IMM cells have advantages over upright tandems when in pursuit of higher STH efficiencies. However, the stability of the IMM cells is significantly lower than we previously observed with upright tandem water-splitting PEC cells. Corrosion on upright cells tends to be characterized by a more uniform etching from the surface toward the substrate. Degradation of IMM cells initiates locally—apparently centered around native defects in the material—leading to blistering and delamination from the Si handle, and ultimately resulting in catastrophic failure (Figure 2). It is possible that these native defects are also present in the upright cells, but their tendency to lead to catastrophic failure is tempered by the 700-μm-thick GaAs substrate. The IMM form factor of a very thin (~5 μm) absorber layer in direct contact with a gold hole Collecting back contact appears to be a less stable configuration than the upright cells that have GaAs substrate between the absorber layer and gold back contact. Similar single-crystal epitaxial III-V semiconductors are flexible when removed from their substrates—a property often highlighted as advantageous for solid-state photovoltaics—and would be expected to be susceptible to delamination should adhesion with its rigid handle become compromised. It is unclear whether the GaAs substrate provides a chemical buffer, slowing etching progression of acidic electrolyte to the gold back contact, or is merely additional mechanical support for a flimsy absorber layer.

We have attempted to passivate the IMM surfaces with epitaxial capping layers (GaInAsP and GaInAsN), which, based on experience, should have greater stability than GaInP₂. However, the mechanical instability of the IMM cells prevents us from evaluating their chemical stability. An example of this can be seen in Figure 3, where the GaInAsN-capped IMM structure exhibits good stability under electrochemical durability testing, but physical observation of the surface (Figure 3 inset) reveals a surface that is already deteriorating in discrete locations. Initial attempts have been unsuccessful to map native defects with optical microscopy and locally passivate them.
CONCLUSIONS AND UPCOMING ACTIVITIES

- We have established robust protocols for accurately benchmarking solar-to-hydrogen efficiency that have their foundations in the methodology used to certify the efficiency of multijunction solid-state solar photovoltaic cells.

- IMM cells are a good platform for meeting the STH efficiency targets established in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, but they are more susceptible to corrosion than upright tandems.

- Upcoming activities will focus on surface modifications that increase STH efficiency by reducing reflection at the semiconductor/electrolyte interface. We will also focus on durability by potentially developing upright metamorphic cells.

SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

1. 2017 DOE Hydrogen and Fuel Cells Program R&D Award (Young, Steiner, Deutsch)

2. (Pending) Devices and methods for photoelectrochemical water splitting. Application No. 15/078,206
**FY 2017 PUBLICATIONS AND PRESENTATIONS**


10. “Advanced device design for photoelectrochemical water splitting derived by a detailed balance approach,” Pacific Rim Meeting of Electrochemical and Solid State Science (PRiME), Honolulu, HI. October 6, 2016. (Döscher)


**REFERENCES**


