

II.C.2 Photoelectrochemical Hydrogen Production

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University of Hawaii at Manoa (UH), Honolulu, HI

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Project End Date: September 30, 2013

Overall Objectives

- 5% solar-to-hydrogen (STH) conversion efficiency
- Operational life up to 500 hours
- Identify commercialization paths toward a \$22/kg-H₂ plant production cost

Fiscal Year (FY) 2013 Objectives (towards end of September)

- Work closely with the DOE Working Group on Photoelectrochemical (PEC) Hydrogen Production for optimizing PEC materials and devices, with the STH efficiency improved to 5% from current level of 4.34% (reported in May 2012), and durability at the working condition up to 500 hours.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices.
- Demonstrate functional multi-junction device incorporating materials developed.
- Explore avenues toward manufacture-scaled devices and systems.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production 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
- (AJ) Synthesis and Manufacturing

Technical Targets

Table 1 lists the technical targets for PEC hydrogen production using amorphous silicon carbide-compound (a-SiC), metal oxide-compound (i.e. WO₃), and I-III-VI₂ (copper chalcopyrite-based) films.

Task 2

FY 2013 Accomplishments

- 1) Improvement in performance of the hybrid photovoltaic (PV)/a-SiC device: Increase of photocurrent density up to 4.9 mA/cm² (equivalent to ~6.1% STH efficiency) by combining surface modification (Ru nano-particles) and high-performance PV cells.
- 2) In metal oxides: theory-driven quaternary oxides engineering.
- 3) In copper chalcopyrites: synthesis of 'Red' (2.0 eV) copper indium gallium diselenide (CIGS).



INTRODUCTION

Based on its potential to meet long-term goals, research and development (R&D) centering on multi-junction hybrid photoelectrode technology defines the scope of this collaborative project. Within this scope, particular emphasis is put in the development of low-cost photoactive materials integrated with a-Si-based solar cells as a driving force with photocurrents greater than 4 mA/cm², and with sufficient durability to meet lifetime requirement, i.e., ≥500 hours. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary energy/economic analysis for hydrogen production cost based on the developed PEC technology is included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components are being developed for incorporation in PEC photoelectrode designs, including attention to the necessary process integration techniques.

TABLE 1. Technical Targets

Task #	Milestone	a-SiC	WO ₃	I-III-VI ₂
Year 1	Material photocurrent ≥ 3 mA/cm ²	Achieved	Achieved	Achieved
	Durability ≥ 100 hr	Achieved	Achieved	10% Achieved
Year 2	Material photocurrent ≥ 4 mA/cm ²	Achieved	90% Achieved	Achieved
	Durability ≥ 200 hr	Achieved	Achieved	Achieved
	Device STH efficiency $\geq 5\%$	32% Achieved	60% Achieved	62% Achieved
Passed Go/No-Go decision evaluation in November 2010				
Year 3	Device STH efficiency $\geq 5\%$	32% Achieved	60% Achieved	85% Achieved
	Durability ≥ 300 hr	62% Achieved	83% Achieved	66% Achieved
Year 4	Device STH efficiency $\geq 5\%$	Achieved	62% Achieved	87% Achieved
	Durability ≥ 500 hr	62% Achieved	Achieved	84% Achieved
	Completion of Final Energy/Economics report on scale up and commercialization toward a \$22/kg-H ₂ plant production cost			

APPROACH

The general approach of this collaborative effort focuses on the DOE PEC Working Group's "feedback" philosophy integrating state-of-the-art theoretical, synthesis, and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability, and cost. Materials modeling, bulk-film optimization, film-surface enhancement, along with comprehensive material and device characterization are being employed to facilitate the R&D process. Specifically, the feedback approach are being applied to our focus material classes, including the metal oxide-, copper-chalcopyrite-, and silicon-based compounds, to enhance understanding of fundamental performance parameters and expedite development of process-compatible forms of these materials. The most promising candidate materials are being identified, with the short-term goal of demonstrating laboratory-scale water-splitting devices, and with a long-term goal of transferring the fabrication processes toward the commercial scale.

RESULTS

During this reporting period (June 2012–June 2013), extensive studies of the three materials classes under investigation have focused on understanding and improving PEC behavior, specifically by applying our theoretical, synthesis, and analytical techniques in identifying relevant aspects of structural, optoelectronic, and electrochemical properties.

1. Amorphous Silicon Carbide-Based Compound Films

The surface barrier at a-SiC/electrolyte interface impedes photocurrent to be extracted from the hybrid PV/a-SiC device. Last year, we reported improvement in surface

energetics and improvement of photocurrent in the hybrid PV/a-SiC device via Ru nanoparticle surface treatment. Over this reporting period, a further improvement in the device performance has been achieved through combination of the surface treatment by Ru nanoparticles, improvement of the solar cell performance, and use of electrolyte of higher conductivity. Figure 1 shows the 2-electrode current density-voltage (JV) characteristics obtained before (blue line) and after Ru nanoparticle treatment (red line). The Ru-coated hybrid PV/a-SiC device is of the configuration SnO₂/X cell/a-SiC(p)/a-Si(i)/a-SiC(n)/Ru, where the X cell is a high-performance solar cell¹ and is series-connected with the a-SiC photoelectrode by a metal wire. Compared with the previous hybrid device, where the a-SiC photoelectrode was

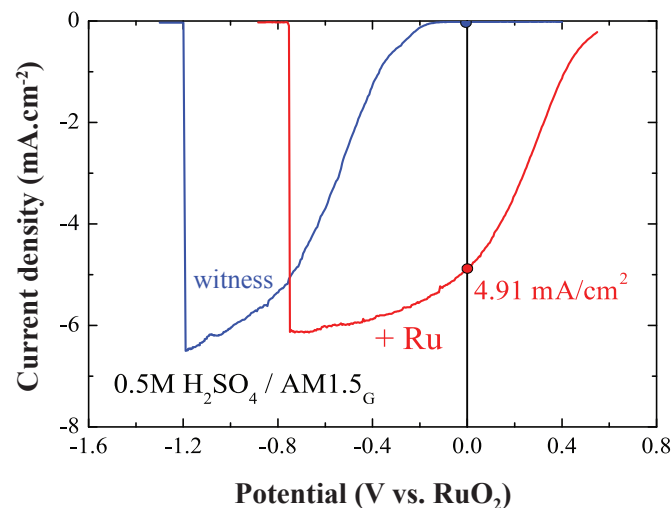


FIGURE 1. The 2-electrode current density-potential characteristics in 0.5 M H₂SO₄ solution on hybrid devices.

¹ For proprietary purpose, the details of this solar cell are not disclosed here.

of p-i configuration, the p-i-n structure here provides extra photovoltage, i.e., by 0.4-0.5 V. The Ru nanoparticle catalyst was fabricated at the University of Hawaii by sputtering technique for 15 sec. Prior to Ru deposition, SiO₂ on a-SiC photoelectrode surface was removed in 5% hydrofluorhydric acid solution for 90 sec. The current density vs. potential characteristics were measured in 0.5 M H₂SO₄ electrolyte and in 2-electrode setup using a RuO₂ counter electrode. The illumination intensity conformed with air mass 1.5_G spectrum. It was observed that the resultant photocurrent density increase up to 4.9 mA/cm² without external bias, or equivalent to a STH efficiency of ~6.1% (assuming 100% Faradaic efficiency). The illuminated open-circuit potential measurements confirmed an anodic shift in the flat band potential of ca. 600 mV, an ideal situation for photocathode systems.

2. Oxide Mineral-Based Compound Films

With an electronic band-gap of 2.2 eV and optimum surface energetics for water splitting, copper tungstate (CuWO₄) is a promising material for PEC hydrogen production. During this reporting period, our efforts were focused on improving the electronic transport properties of this system, especially evaluating the effect of the addition of foreign chemical elements on CuWO₄ bulk resistivity. With the help of Prof. Huda's group at the University of Texas in Arlington, we were able to identify several new tungstate-based multi-cation metal-oxides. For example, from a combined mineral data-based search and density functional theory (DFT) calculations, we were able to predict that the addition of bismuth to form quaternary copper bismuth tungstate (CuBiW₂O₈) should: i) lower the electron effective mass in the conduction band, and ii) suppress unfilled states present in the forbidden gap of CuWO₄. In other words, CuBiW₂O₈ should have a higher electrical conductivity when compared to CuWO₄. This was tested by electrical impedance analyses performed on ceramic pellets of CuBiW₂O₈ and CuWO₄ formed by solid-state reaction (powder sintering). As predicted, the bulk resistivity decreased by two orders of magnitude after addition of bismuth to a value much closer to that of our high-performance WO₃ material.

3. Copper Chalcopyrite-Based Films

Amongst all material classes currently studied for PEC H₂ production, the chalcopyrite system is the system that probably offers the best compromise between efficiency and synthesis costs. In order to integrate this class into an efficient standalone hybrid photoelectrode system, one must i) lower overpotentials originating from a valence band sitting too far from the O₂/H₂O redox level, and ii) increase its optical bandgap from 1.6 eV (the highest value for the selenide class, CuGaSe₂) to 2.0 eV. This year, our research was focused on selenium substitution with sulfur. Using co-evaporated 1 μm-thick CuGaSe₂ as the baseline system, we demonstrated that selenium could be substituted by sulfur

using a simple annealing step. With this protocol, a dramatic change in optical properties was observed, with a band-gap increase from 1.6 eV (CuGaSe₂) to 2.4 eV (CuGaS₂). Then, by simply adjusting the indium content in the film during the initial growth process, the band-gap of sulfurized copper chalcopyrite was decreased from 2.4 eV to 2.2 eV and finally to 2.0 eV, as shown in Figure 2. X-ray photoelectron spectroscopy analysis performed by Prof. Heske's group at the University of Nevada in Las Vegas on the 2.0 eV copper indium gallium sulfide (CuInGaS₂) material indeed confirmed that all selenium at the surface of the films was replaced with sulfur. Preliminary PEC analyses reveal an anodic shift of the flatband potential with increasing band-gap. This suggests that the bandgap modification in sulfurized films primarily stems from a downward shift of the valence band, an ideal situation for p-type PEC systems.

CONCLUSIONS AND FUTURE DIRECTIONS

The photocurrent of the hybrid PV/a-SiC device has been enhanced to 4.9 mA/cm² at zero bias due to improved surface energetics using Ru nanoparticle surface treatment and incorporating the high-performance PV cell. Durability of such hybrid devices will be tested in a working condition, i.e., under a current bias of ~4 mA/cm². Progress continued on metal oxide-based compound with the evaluation of quaternary systems (CuBiW₂O₈), directed by advanced theoretical calculations. Copper tungstate material resistivity has been decreased by two orders of magnitude with the addition of bismuth. Several new tungstate-based multi-cation metal-oxides have also been identified. Thin film synthesis is currently underway. In copper chalcopyrite-based systems, CuInGaS₂ of 2 eV has been successfully fabricated by replacing Se with S and adjusting the indium

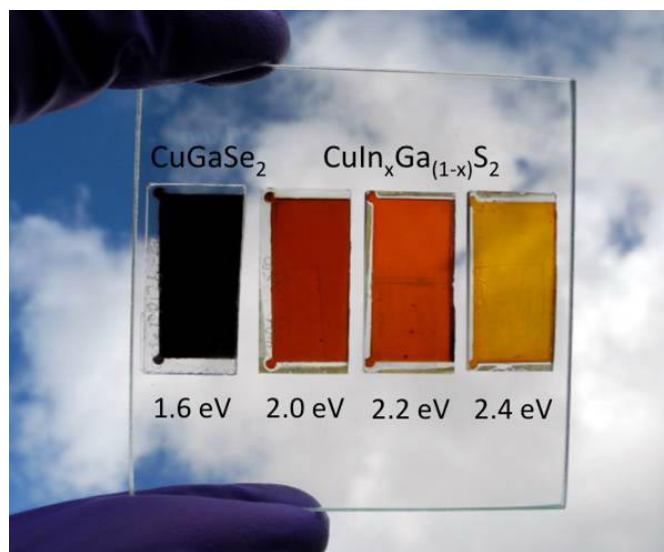


FIGURE 2. Optical image of as-deposited CuGaSe₂ and sulfur-annealed CuInGaS₂ thin films.

content in the film. A downward shift in the valence band was confirmed. Durability testing will be performed on this new type of material.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Surface Modification of a-SiC Photoelectrode Using Metal Nanoparticles, Feng Zhu, Ilvydas Matulionis, Nicolas Gaillard, Yuancheng Chang, Jian Hu, Josh Gallon, and Arun Madan, presented at MRS Spring Meeting, San Francisco, April 1–5, 2013.
2. PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION, 2012 DOE H₂ Annual Merit Review meetings, Washington, DC, May 16, 2013 (presented by Nicolas Gaillard).
3. A nanocomposite photoelectrode made of 2.2 eV band gap copper tungstate (CuWO₄) and multi-wall carbon nanotubes for solar-assisted water splitting, Nicolas Gaillard, Yuancheng Chang, Alexander DeAngelis, Scott Higgins, Artur Braun, International Journal of Hydrogen Energy, Volume 38, Issue 8, 19 March 2013, Pages 3166–3176.
4. Photoelectrochemical Reforming of Glucose for Hydrogen Production using a WO₃-based Tandem Cell Device, D.V. Esposito, R.V. Forest, Y. Chang, N. Gaillard, S. Hou, K.H. Lee, B.E. McCandless, R.W. Birkmire, and J. Chen, Energy Environ. Sci. 5, 9091-9099 (2012).
5. Theory-driven Metal Oxide Down-selection for Photoelectrochemical Hydrogen Production: The Case of Metal Tungstates, Nicolas Gaillard, Yuancheng Chang, Dixit Prasher, S. Sarker, Muhammad N. Huda, presented at MRS Spring Meeting, San Francisco, April 1–5, 2013.
6. Development of Chalcogenide Thin Films Materials for Photoelectrochemical Hydrogen Production, Nicolas Gaillard, Stewart Mallory, Jess Kaneshiro, presented at MRS Spring Meeting, San Francisco, April 1–5, 2013.
7. Performance and Limits of 2.2eV Copper Tungstate (CuWO₄) Mineral for Photoelectrochemical Hydrogen Production, N. Gaillard, Electrochemical Society PRIME meeting, symposium B10, 1741 (2012).
8. Ruthenium-Based Materials for Oxygen and Hydrogen Evolution Catalysis in Photoelectrochemical Applications, Y. Chang, J.M. Kaneshiro, N.M. Gaillard, Electrochemical Society PRIME meeting, Abstract MA2012-02 1775 (2012).