II.F.5 Photoelectrochemical Hydrogen Production

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

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Fiscal Year (FY) 2012 Objectives

- Work closely with the DOE Working Group on Photoelectrochemical (PEC) Hydrogen Production for optimizing PEC materials and devices.
- 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 Program Multi-year Research, Development and Demonstration Plan:

(Y) Materials Efficiency
(Z) Materials Durability
(AA) PEC Device and System Auxiliary Material
(AB) Bulk Materials Synthesis
(AC) Device Configuration Designs

Technical Targets

Table 1 lists the technical targets for PEC hydrogen production using amorphous silicon carbide-compound (a-SiC), metal oxide-compound (i.e. WO_3) and I-III-VI_2 (copper chalcopyrite-based) films.

FY 2012 Accomplishments

1. Improvement in performance of the hybrid photovoltaic (PV)/a-SiC device:
   - Increase of photocurrent density up to 2 mA/cm^2, or equivalent solar-to-hydrogen efficiency (STH) of ~2.5%, by surface modification using Ru nano-particles.
2. Improvement in performance of the metal oxide photoelectrode, including:
   - Durability of WO_3 (tungsten oxide) sputtered material has been improved to 600 hrs.
   - Photocurrent density in copper tungsten oxide ($CuWO_4$, 2.2 eV) is increased to ~1.2 mA/cm^2 @1 V (V vs. saturated calomel electrode), an order of magnitude higher than in 2011.
   - Bifacial monolithic integration is demonstrated.
3. Improvement in performance of the I-III-VI_2 photoelectrode, including:
   - Novel coplanar hybrid device achieved 3.53 mA/cm^2 (or 4.34% STH efficiency).
   - Durability of $CuGaSe_2$ PEC cell is increased to 420 hrs.
   - Device design pathway developed to quantify material development goals to obtain 10% and 20% STH efficiency.

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/cm^2, 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

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 ≥5%	32% Achieved	60% Achieved	62% Achieved
Passed Go/No-Go decision evaluation in November, 2010				
Year 3*	Device STH efficiency ≥5%	32% Achieved	60% Achieved	85% Achieved
	Durability ≥300 hr	Achieved	83% Achieved	66% Achieved
Year 4	Device STH efficiency ≥5%	50% Achieved	60% 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			

* As of writing this report.

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.

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 is being employed to facilitate the R&D process. Specifically, the feedback approach is 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 2011–June 2012), 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. In order to reduce the surface barrier, surface modification using Ru nanoparticle was performed. The Ru nanoparticle catalyst was fabricated at University of Hawaii by sputtering technique. It was observed that the sputter time of 10-20 sec gave best treatment results. The Ru-coated hybrid PV/a-SiC device is of configuration of SnO_2/pin/pin/a-SiC(p)/a-SiC(i)/Ru. Prior to Ru deposition, SiO_2 on a-SiC(i) surface was removed in 5% hydrofluorhydric acid solution for 90 sec. The current density vs. potential characteristics were measured in pH2 buffer electrolyte and in 2-electrode setup using a RuO_2 counter electrode. The illumination intensity conformed with AM1.5G spectrum. The 2-electrode current-voltage characteristics obtained before and after Ru nanoparticle treatment are shown in Figure 1. It was observed that such treatment led to a systematic photocurrent density increase, up to 2 mA/cm^2 without bias. Also, measurement after the durability test showed that the current density recovered to nearly its original value. Subsequent illuminated open-circuit potential measurements confirmed the anodic flat band potential shift of ca. 500 mV, an ideal situation for photocathode systems. Improvement was also confirmed by the National Renewable Energy Laboratory with outdoor test conditions.

2. Oxide Mineral-Based Compound Films

With an electronic band-gap of 2.2 eV and more favorable surface energetics for water splitting than most

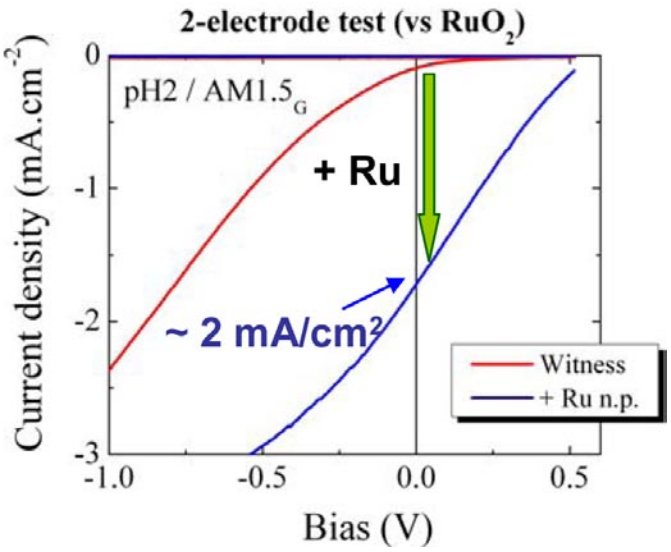

FIGURE 1. The 2-electrode current density-potential characteristics in pH2 buffer solution on hybrid devices

oxide systems (i.e. WO_3, TiO_2, Fe_2O_3), copper tungstate ($CuWO_4$) is a material-class that merits further investigation. We reported last year on the effect of thermal treatment on the crystallographic, surface energetics and PEC properties of reactively co-sputtered $CuWO_4$. A major improvement was observed on $CuWO_4$ films after a post-annealing at 500°C in argon for 8 hours, exhibiting a photocurrent density of approx. 400 μA/cm^2 at 1.6 V vs. saturated calomel electrode. More importantly, electrochemical impedance spectroscopy study indicated that $CuWO_4$ transport properties must be improved in order to achieve better performing photoanodes. This issue was addressed this year by adding conductive carbon nanotubes (CNTs) directly into the matrix of $CuWO_4$ photoanodes. To do so, $CuWO_4$-CNT nanocomposites were obtained via spray pyrolysis deposition process using a solution containing all building blocks (i.e. Cu, W precursors and CNT) required to fabricate this unique system (Figure 2).

Subsequent current-voltage characteristics pointed out a net improvement in photocurrent generation, with a maximum current density of c.a. 1 mA/cm^2. This corresponds to a doubling of the photocurrent density when compared with $CuWO_4$ witness samples.

3. I-III-VI$_2$ (Copper Chalcopyrite-Based) Films

The largest technical barrier in this material class is a misalignment of the energy band levels in the semiconductor-electrolyte interface in the baseline material $CuGaSe_2$ with a relatively low bandgap of 1.65 eV. This makes monolithic integration with PV driving devices difficult, and the misaligned band levels result in a high required voltage bias from PV cells. Material development is focused on modifying the group I (Cu, Ag) to group VI (S, Se) bond to

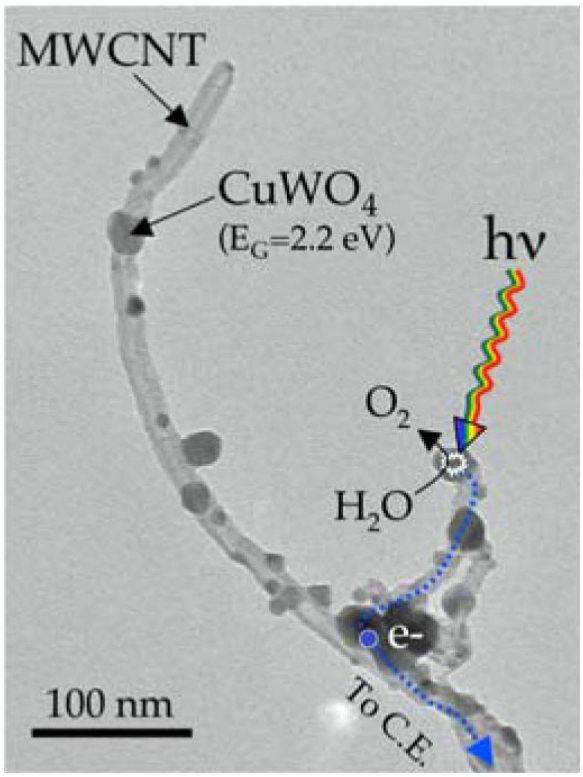

FIGURE 2. Micrograph of a $CuWO_4$-CNT nanocomposite used for PEC hydrogen production

more favorably align the energy levels and raise the bandgap. The validation of the novel coplanar device achieving 4.34% STH efficiency using low-cost a-Si PV cells lays out a design pathway towards DOE project goals. The coplanar device cannot achieve much more than 5% STH, and so material advances are needed to allow bandgaps closer to the ideal bandgap of 2.0-2.1 eV. With the addition of either silver or sulfur to raise the bandgap to ~1.8 eV, one PV cell can be buried beneath it and required voltage bias should be reduced, allowing performance beyond the 5% STH threshold. Further raising the bandgap (towards 2.1 eV) will allow a second PV cell to be buried and can potentially extend performance beyond the 20% STH range. Current durability success with $CuGaSe_2$ achieving 420 hrs of continuous operation at 4 mA/cm^2 is very promising. Surface treatments of nano- and micro-scale catalysts are being explored to further extend durability towards 1,000 hrs. These same catalytic treatments are, of course, also expected to improve device performance.

Conclusions and Future Directions

Surface treatment of the hybrid PV/a-SiC device using Ru nanoparticles was found to reduce the photocurrent onset and enhance photocurrent up to ~2 mA/cm^2 at zero potential. In metal oxide-based compound such as $CuWO_4$, the post-deposition annealing improves its conductivity and

photo-response while the bandgap remains unchanged (2.1 eV). Finally, a STH efficiency of ~4.3% is achieved in the novel co-planar integrated a-Si (PV)/$CuGaSe_2$ (PEC) device. Incorporation of Ag and/or S in baseline $CuGaSe_2$ cells remains the highest priority in the I-III-VI_2 material class to achieve >5% STH efficiency and beyond. The hybrid PV/a-SiC device, and other two-photoelectrode thin film materials (WO_3 and Copper Chalcopyrite) show excellent durability in electrolyte for ≥200 hours.

FY 2012 Publications/Presentations

1. Nicolas Gaillard, Yuancheng Chang, Artur Braun and Alexander DeAngelis, Copper Tungstate (CuWO4)–Based Materials for Photoelectrochemical Hydrogen Production, 2012 MRS Spring Meeting, mrss12-1446-u02-08.

2. Yuancheng Chang, Artur Braun, Alexander Deangelis, Jess Kaneshiro, and Nicolas Gaillard, Effect of Thermal Treatment on the Crystallographic, Surface Energetics, and Photoelectrochemical Properties of Reactively Cosputtered Copper Tungstate for Water Splitting, J. Phys. Chem. C, 25490–25495, DOI: 10.1021/jp207341v (2011).

3. J.M. Kaneshiro, A. Deangelis, X. Song, N. Gaillard and E.L. Miller "I-III-VI_2 (Copper Chalcopyrite-based) Thin Films for Photoelectrochemical Water-Splitting Tandem-Hybrid Photocathode) MRS Proceedings 1324 (2011) mrss11-1324-d15-08 doi:10.1557/opl.2011.964.

4. J. Kaneshiro, Dissertation Thesis, University of Hawai`i at Mānoa, 2012.

5. PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION, 2012' DOE H_2 Annual Merit Review meetings, Washington, D.C., May 13, 2012 (presented by Jian Hu and Nicolas Gaillard).