

II.G.9 Progress in the Study of Copper Chalcopyrites as Photoelectrodes in Photoelectrochemical Cells

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 National Renewable Energy Laboratory (NREL),
 Golden, CO

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Objectives

- Work closely with the DOE Working Group on Photoelectrochemical (PEC) Hydrogen Production to develop and employ new theoretical, synthesis and analytical techniques for optimizing PEC materials and devices.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices based on amorphous-silicon-compound, tungsten-compound and copper-chalcopyrite compound classes of thin films.
- Demonstrate functional multi-junction device incorporating best-available PEC film 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

The specific targets of this project are (a) the demonstration of a PEC solar-hydrogen production system with 7.5% solar-to-hydrogen (STH) conversion efficiency (b) operational life up to 500 hours and (c) the identification of commercialization paths toward a \$22/kg-H₂ plant production cost by 2010 and \$5/kg by 2015. Table 1 shows detailed milestones year by year.

TABLE 1. Progress towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production with Copper Chalcopyrite-based Materials

Task #	Milestone	Note
Year 1	Material photocurrent ≥ 3 mA/cm ²	Achieved
	Durability ≥ 100 hours	10%
Year 2	Material photocurrent ≥ 4 mA/cm ²	Achieved
	Durability ≥ 200 hours	5%
	Device STH efficiency $\geq 5\%$	*Pending Fabrication
Go/No-Go decision evaluated (End of 2010)		
Year 3	Device STH efficiency $\geq 6.15\%$ over 300 hours	
Year 4	Device STH efficiency $\geq 7.5\%$ over 500 hours	

*Components are available that, combined numerically, can achieve 5% STH efficiency

Accomplishments

- Material photocurrents are in excess of goals.
- Surface and bulk modifications are improving feasibility of completed device.
- Planned device can achieve 5% STH efficiency.



Introduction

Based on its potential to meet long-term goals, research and development (R&D) centering on multijunction hybrid photoelectrode technology defines the scope of this collaborative project. Within this scope, particular emphasis is placed on the most critical materials-research components in terms of efficiency, durability and cost. To achieve 7.5% STH conversion efficiency and up to 500-hour operational life along with production cost goals, the development of low-cost photoactive materials with photocurrents $>6 \text{ mA/cm}^2$ and with sufficient durability to meet the lifetime requirement will be the key focus. Development of specific thin-film materials classes with promising PEC potential, including tungsten-based compounds (such as metal and mixed-metal oxides, oxy-nitrides, oxy-sulfides, etc.), copper-chalcopyrite compounds (including CIGSe, CGSe, etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) are the specific focus of this R&D project. In addition to the materials R&D activities, development of laboratory scale demonstration devices and generation of preliminary commercialization studies is included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been developed for incorporation in the PEC photoelectrode designs (i.e., the hybrid PV/a-SiC PEC cells). It is the central objective of the MVSystems project team to work closely with the DOE Working Group on PEC Hydrogen Production to develop pathways for successful PEC hydrogen technologies.

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 tungsten-, copper-chalcopyrite- and silicon-based compounds, to enhance understanding of fundamental performance parameters, and expedite development of process-compatible forms of these materials. The primary objective of the materials research efforts is the development of films which meet photocurrent and durability goals and which are compatible with device fabrication. The most promising candidate materials will be 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

Progress in the study of copper chalcopyrite-based thin films of the formula $(\text{Cu}_x\text{Ag}_{1-x})(\text{In}_y\text{Ga}_{1-y})(\text{S}_z\text{Se}_{1-z})$ for PEC water splitting this period has been focused on device integration. While copper chalcopyrite-based films are capable of high photocurrents, band misalignments currently preclude current extraction without superfluous external voltages. This particular problem has been addressed through bulk, surface and device modifications.

The typical baseline absorber film is CuGaSe_2 (CGSe), which has the highest attainable bandgap in the $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ system of $\sim 1.68 \text{ eV}$. CGSe is capable of high photocurrents but only at an impractically high external voltage bias. Bulk modification has led to the best cells produced in this material class which are CuInGaS (CIGS) films (fabricated at the Helmholtz Zentrum Berlin in 2009). While performing well, these "sulfide" cells are still inadequate for a monolithically integrated hybrid (photovoltaic [PV]/PEC) photoelectrode (HPE) device shown in Figure 1 where voltage is supplied by underlying PV cells harvesting passed sub-bandgap photons.

Bulk modification was also pursued by replacing Cu with Ag, which can raise the bandgap and more properly align the band edges. Films were fabricated with a formula of $\text{Ag}(\text{In}_{0.2}\text{Ga}_{0.8})\text{Se}_2$ (AIGSe) with a bandgap only slightly lower than CGSe showing an expected n-type conduction, which is not ideal but, with a sufficient voltage, photocurrents nearly as high as that in typical CGSe films ($\sim 15 \text{ mA/cm}^2$) could be extracted from AIGSe films (Figure 2). These films showed that Cu replacement with Ag did indeed move the band edges, but full replacement moved them an extreme amount beyond our desired levels. Further tests exploring *partial* replacement of Cu with Ag will

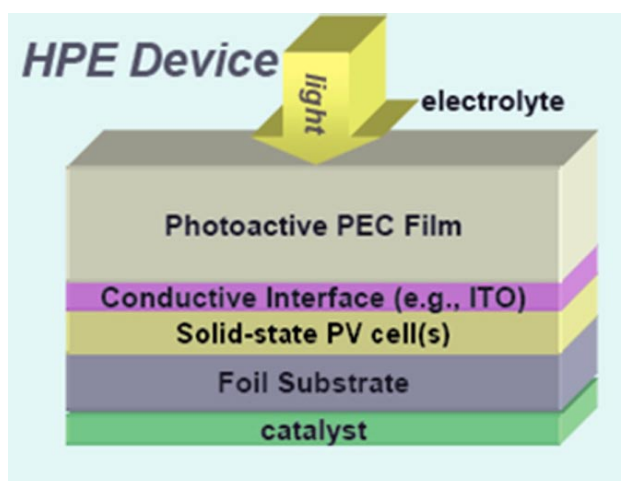


FIGURE 1. HPE device incorporating a PEC device on top of one or more PV devices, supplying the required voltage bias.

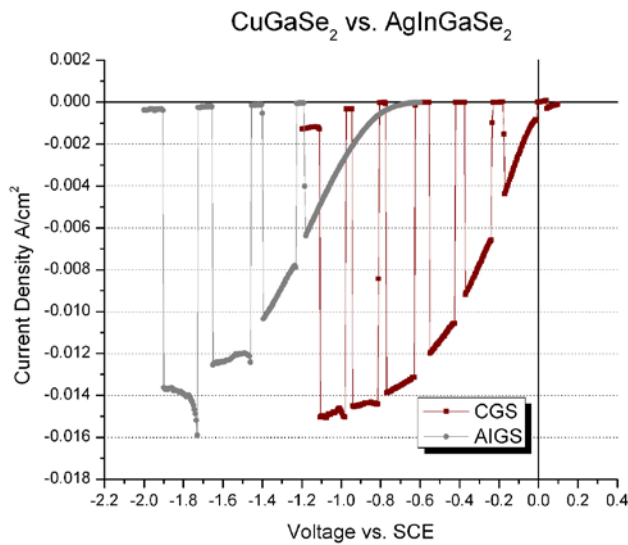


FIGURE 2. Current-voltage (J-V) characteristics of AlGaSe vs. CGSe films showing comparable photocurrents, but an exceeding higher external voltage requirement for Ag-incorporated cells in 0.5 M H₂SO₄ under 1-sun AM1.5G illumination.

be conducted to gain more control over band edge positions.

Surface modifications were also performed with PdAu nanoparticles sputtered onto the surface of CGSe films. The results, shown in Figure 3, show an improvement in the “fill factor”, however, onset voltage remains unchanged. These surface treatments can be used to extract a few more mA/cm² of any as-fabricated film in this material class.

Currently unable to monolithically integrated devices, Figure 4 shows a co-planar HPE device. The DOE goal of 5% STH can be theoretically (from numerical calculations) achieved using available materials. This device is of course impractical, however it develops a pathway towards creating a viable device. Work is underway to both fabricate these cells as standalone devices and improve upon their design.

Conclusions and Future Directions

The MVSystems/UH project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO₃ and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting. The project benefits from existing knowledge of the three PEC thin-film materials and their PV performances to apply them to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC performances. New surface modification techniques were investigated, surface treatments (a-SiC, CGSe, WO₃), bilayer formation (WO₃) and new device integration schemes (CGSe and WO₃). Bulk

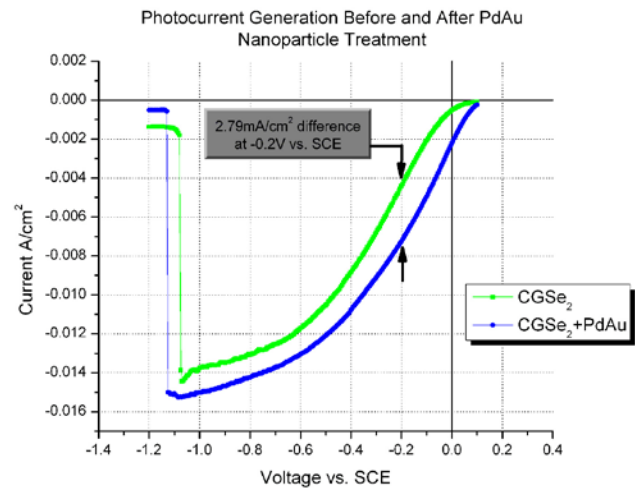


FIGURE 3. J-V characteristics of a CGSe film before and after PdAu nanoparticle deposition by sputtering. Measured in 0.5 M H₂SO₄ under 1-sun AM1.5G.

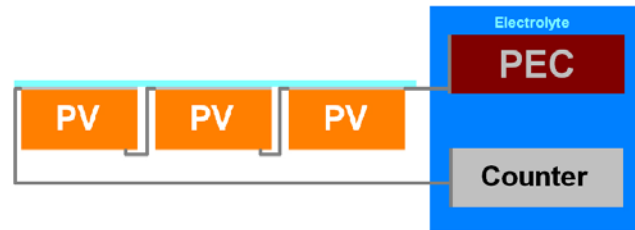


FIGURE 4. A schematic diagram of a co-planar hybrid HPE. Materials available can produce a device capable of reaching the DOE goal of 5% STH conversion efficiency.

modifications were also investigated, such as partial copper replacement with silver to form CAIGSe film to modify energy band position. Resulting interface and bulk energy band positions will be characterized using advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.

FY 2010 Publications/Presentations

1. Ilvydas Matulionis, Jian Hu, Feng Zhu, Josh Gallon, Nicolas Gaillard, Todd Deutsch, Eric Miller, and Arun Madan, “Surface modification of a-SiC:H photoelectrodes for photocurrent enhancement,” to be presented at SPIE, San Diego, August, 2010.
2. Feng Zhu, Jian Hu, Ilvydas Matulionis, Todd Deutsch, Nicolas Gaillard, Eric Miller, and Arun Madan “The Potential of Using a-SiC:H as the Photoelectrode for Water Splitting”, presented at NHA hydrogen conference and Expo., Long beach, CA, May 3–6, 2010.
3. Book chapter :“Solar Energy”: Feng Zhu, Jian Hu, Ilvydas Matulionis, Todd Deutsch, Nicolas Gaillard, Eric Miller, and Arun Madan, “Amorphous Silicon Carbide

Photoelectrode for Hydrogen Production from Water using Sunlight , edited by: Radu D. Rugesu, ISBN 978-953-307-052-0, pp. 432, February 2010, INTECH,

4. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Improved current collection in WO₃:Mo/WO₃ bilayer photoelectrodes*, J. Mat. Res. **25** (2010) 45.

5. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion*, Sol. Energy Mater. and Sol. Cells. **94** (2010) 12-16.