II.E.9 Photoelectrochemical Hydrogen Production: MVSystems Incorporated

Arun Madan
MVSystems, Incorporated
372 Lamb Lane
Golden, CO 80401
Phone: (303) 271-9907
E-mail: ArunMadan@aol.com

DOE Technology Development Manager:
Roxanne Garland
Phone: (202) 586-7260; Fax: (202) 586-2373
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

Contract Number: DE-FG36-07GO17105

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

Project Partner:
National Renewable Energy Laboratory (NREL), Golden, CO

Project Start Date: November 1, 2007
Project End Date: August 31, 2009

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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration (Multi-Year RD&D) Plan:

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

Technical Targets

As recognized within the PEC hydrogen research community and the DOE Hydrogen Program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. Of the four DOE technical characteristics outlined in the Multi-Year RD&D Plan for PEC hydrogen production (see Table 1), targets in the first category ("useable semiconductor band gap") are the primary focus of research, with secondary emphasis on the second category targets ("chemical conversion process efficiency").

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristic	Units	2006 Status	2013 Target	2018 Target
Useable Semiconductor Band Gap	eV	2.8	2.3	2.0
Chemical Conversion Process Efficiency (EC)	%	4	10	12
Plant STH Efficiency	%	N/A	8	10
Plant Durability	hrs	N/A	1,000	5,000

N/A - not applicable

The specific targets of this project are the demonstration of a PEC solar-hydrogen production system with 7.5% solar-to-hydrogen (STH) conversion efficiency and operational life up to 500 hours; and the identification of commercialization paths toward a \$22/kg-H_2 plant production cost.

Accomplishments

- New Approaches in Tungsten Oxide Surface Treatment:
  - Baseline photocurrents in excess of 3.0 mA/cm^2 for bulk films established in previous projects have been reliably reproduced.

  - Surface optimization of WO_3 films using Grätzel-type dye-sensitized cells approach was initiated, with preliminary tests being performed using wide band gap TiO_2 films.
- Copper Chalcopyrite-Based PEC Electrode Performances Enhancement:
  - Continuing efforts initiated to enhance copper-chalcopyrite alloy film photocurrent generation through optimization of deposition process, with current specific emphasis on copper-gallium-diselenide ($CGSe_2$).
  - Initiated development of thinner $CGSe_2$ film required to allow sufficient photon passage to reach the photovoltaic (PV) bottom layer of a multi-junction device.
  - Initiated studies of impurity incorporation such as sulfur to further increase the material band gap past the $CGSe_2$ limit of 1.6 eV.
- Durability of Amorphous Silicon Carbide Films in Acidic Solution:
  - The a-SiC photoelectrode has shown good durability for up to 100 hours. Localized holes have been observed at the edge and within a part of a-SiC film, caused possibly by pinholes.
  - After the durability test, the photocurrent onset shifts toward a lower bias voltage. Shift appears to be permanent (for at least two weeks), indicating that there may be a change in the a-SiC surface structure under test.
  - The Pt surface treatment improves the durability of a-SiC photoelectrodes on stainless steel (SS) and SS/Mo substrates whereas it has no effect on a SnO_2 type substrate and it is worse on a ZnO substrate. In addition, a photocurrent onset shift towards a lower bias voltage (by ~0.4 V) has been observed on SS and SS/Mo substrates; but not on SnO_2 and ZnO type substrates. The dark current on all four substrates with Pt treatment increases.

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 will be put 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 greater than 6 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 $CIGSe_2$, $CGSe_2$, etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) is the specific focus of this R&D effort. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is also included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components are also in development for incorporation in PEC photoelectrode designs, including attention to the necessary process integration techniques. 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

During this initial phase of the project, extensive studies of the three materials classes under investigation have focused on understanding and improving photoelectrochemical behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Specific progress in developing each of the focus materials is detailed in the following subsections.

Tungsten-Based Compound Films

As part of WO_3 R&D development work at the UH this period, new experimental evaluation techniques were initiated. As part of the evaluation, tungsten oxide samples have been sent to NREL for incorporation into modified Grätzel-type dye-sensitized cells. Grätzel cells, traditionally based on titanium-dioxide semiconductor thin films, use an organic dye to accept electrons from an I-/I3 redox couple, enhancing photon absorption. As a drawback to water-splitting applications, however, the dyes are unstable in aqueous electrolytes. As a remedy, oxygen-based heteropolyacids, also known as polyoxometallates, are being investigated at NREL to accept electrons from the water instead of the I-/I3 redox couple in the typical Grätzel cell. Preliminary tests will be performed using TiO_2 to test how the dye absorbs light in the visible range and injects electrons into the wide band gap oxide. Once the sensitization has been characterized and validated, TiO_2 will be replaced by lower-band-gap, higher-performance WO_3 films. This is expected to shed new light on tungsten oxide behavior, and potentially lead to a solution to overcome the band-gap limitations to PEC hydrogen production efficiency in WO_3 materials. As they become available, results from these experiments will be presented in subsequent progress reports.

Copper-Chalcopyrite-Based Compound Films

During this period, progress was also made at the UH in the R&D of copper-chalcopyrite-based materials for PEC hydrogen production. In particular, $CIGSe_2$ and $CGSe_2$ studies were conducted to better understand the potential use of these material classes. Under appropriate biasing conditions, $CIGSe_2$ has produced very high photocurrents in PEC water cleavage experiments. However, it has been observed that the low bandgap (~1.1-1.3 eV) can make it difficult to transmit significant light through such films. In multi-junction devices, this limited light transmission could restrict the effectiveness of a PV cell bottom layer to provide the needed potential bias conditions. $CGSe_2$, on the other hand, has a bandgap around 1.65 eV, which in theory could transmit sufficient light to drive a PV cell bottom layer for incorporation into a monolithic stack device. In recent optical measurements with 1.0-1.3 µm $CGSe_2$ films, however, it was observed that insufficient light is still being transmitted, primarily related to film thickness. Ultraviolet (UV)-visible spectrophotometer (Figure 1) and current-voltage (IV) curves of PV cells optically filtered by a $CGSe_2$ film both confirm this deficiency. Recent depositions have focused on optimizing PEC performance of the thicker (>1 µm) films, and our most recent depositions have exhibited a 40% increase of the photocurrent over earlier films. It is postulated that thinner films deposited with this optimized process could transmit sufficient light to the bottom PV cell

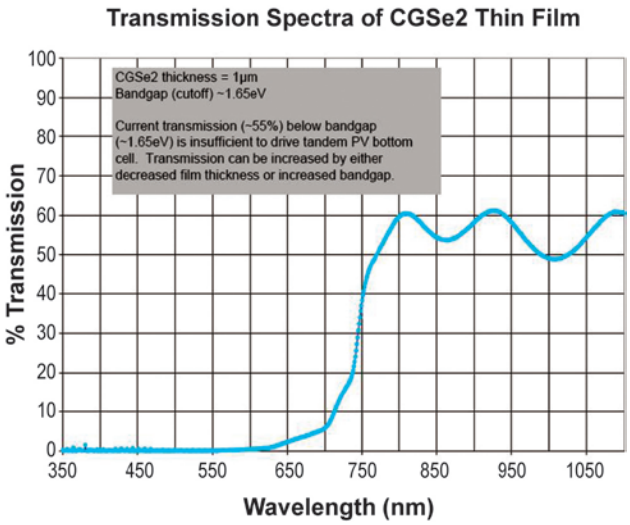

FIGURE 1. UV-visible spectra of transmission through a 1 μm CGSe2 film. Transmission is insufficient to drive a tandem PV bottom cell, necessitating a thinner top film.

while maintaining sufficient photocurrent for efficient water cleavage. Work is in progress in the investigation of these thinner films. In addition, future experiments will deal with $CGSe_2$ bandgap increase using different deposition methods or impurity incorporations such as sulfur. Surface treatments after deposition will also be investigated for band-edge optimization and device improvement. Deposition equipment maintenance has temporarily delayed progress in these R&D areas, but arrangements to re-instate operations of the improved hardware have been completed.

Amorphous Silicon Carbide-Based Compound Films

During this project period, extensive characterizations have been performed on a-SiC material durability in acidic solution. Those tests have been performed on films deposited on textured SnO_2 substrates, since samples on SnO_2 were found to be much more stable in the previous 24-hour durability test. Here, a constant current of 3 $mAcm^{-2}$ has been applied to the a-SiC-based PEC electrodes for 100 hours. It has been observed that voltage decreases linearly over time, from -2.9 V to -3.3 V. Further observation pointed out that SiC films are largely intact after the test, but shows localized holes at edges and part of the film (Figure 2). Additional characterization will be performed to understand the origin of those pinholes. However, it is interesting to note that performance of a-SiC-based PEC electrodes is enhanced after the 100-hour durability tests, as evidenced by IV characteristics obtained before and after the test (Figure 3). In fact, since the dark current remains almost unchanged, the absolute onset potential is noticeably reduced (by ~0.6 V) after the test leading to higher photocurrent. It is important to note

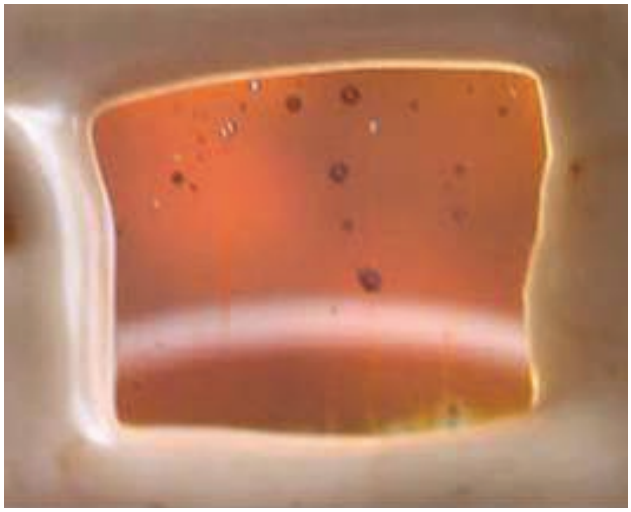

FIGURE 2. Morphology of a-SiC photoelectrodes after the 100-hour durability test. Illumination is from the backside of the samples.

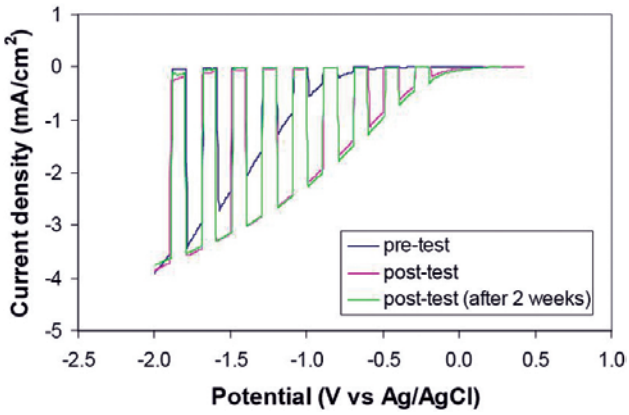

FIGURE 3. IV characteristic measured on an a-SiC photoelectrode before (blue line), right after (pink line) and two weeks after (green line) to the 100-hour durability test.

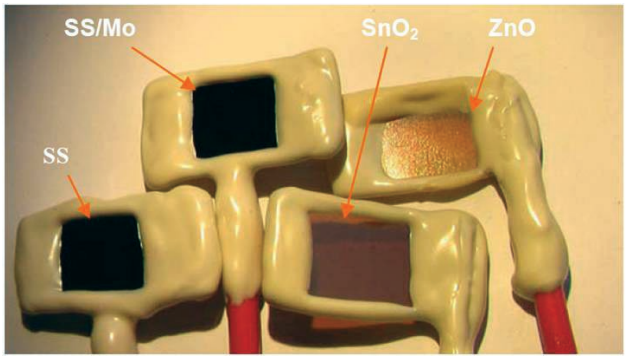

FIGURE 4. Surface morphology of a-SiC photoelectrodes on Pt-coated SS, SS/Mo, ZnO and SnO_2 substrates after 24-hour test.

that those improvements also remain two weeks after the durability test. Implantation of hydrogen ions (H^+) into the a-SiC film during the 100-hour test (negative bias applied to the film) could explain those results. Another explanation may reside in a surface barrier, such as SiO_x, which could be etched during the test. To confirm this hypothesis, hydrofluorhydric acid etching will be performed on a-SiC films before PEC electrode testing. In order to improve durability of a-SiC photoelectrodes on metal substrates and reduce the required external bias to drive water splitting, additional surface treatments using platinum were performed on a-SiC films deposited on SS/Mo, SS, ZnO_2 and SnO_2. The Pt layer was deposited by a pulsed electrodeposition technique under 1-sun (AM 1.5G) illumination. Durability tests performed on those samples over 24 hours show that Pt surface treatment improved durability of a-SiC photoelectrodes on SS and SS/Mo substrates whereas it had no effect on a SnO_2-type substrate. It is important to note that severe degradation of ZnO_2 films (caused by corrosion) is observed after the 24-hour test (Figure 4). Current vs. voltage characteristics performed on those samples evidence initial high dark current when all four substrates are used. After a 24-hour test, the dark current decreases on SS and SnO_2 substrates but remains unchanged on SS/Mo substrate, and increases on ZnO substrate (due to corrosion). The photocurrent on SnO_2, however, decreases with Pt treatment. The photocurrent onset shift towards a lower bias voltage (by ~0.4 V) has been observed on SS and SS/Mo substrates; but not on SnO_2 and ZnO type substrates. Additional open-circuit-measurement under illumination vs. pH roughly follows a correlation of ≈59 mVpH, as predicted by the Nernst equation. It is also seen that at pH=2, the flatband voltage of all a-SiC films is +0.26 V vs. Ag/AgCl reference electrode, which is above the H_2O/O_2 redox potential by ≈0.7 V.

Conclusions and Future Directions

This project's close working relationship with the DOE Working Group on PEC Hydrogen Production is tightly focused on integrating state-of-the-art theoretical, synthesis and analytical techniques toward the identification and development of the most promising materials for practical PEC hydrogen production. Initial progress has been demonstrated in the project's three focus thin-film materials classes of amorphous-silicon-compounds, tungsten-compounds and copper-chalcopyrite-compounds; and accelerated progress in material development and device demonstration is expected in the upcoming year.

FY 2008 Publications/Presentations

1. A. Stavrides, A. Kunrath, J. Hu, R. Treglio, A. Feldman, B. Marsen, B. Cole, E. Miller, and A. Madan, "Novel Materials for use as Photoelectrodes for Hydrogen Production in Photoelectrochemical Cells", presented at TMS 2007 Annual Meeting (Orlando, 2007).

2. I. Matulionis, F. Zhu, J. Hu, T. Deutsch, A. Kunrath, E Miller, B. Marsen, and A. Madan, "Development of a corrosion-resistant amorphous silicon carbide photoelectrode for solar-to-hydrogen photovoltaic/ photoelectrochemical devices", to be presented at SPIE conference, San Diego, August 11-15, 2008.

3. J. Hu, F. Zhu, I. Matulionis, A. Kunrath, T. Deutsch, E. Miller, and A. Madan, "Solar-to-Hydrogen Photovoltaic/ Photoelectrochemical Devices Using Amorphous Silicon Carbide as the Photoelectrode", to be presented at 23rd European Photovoltaic Solar Energy Conversion Conference, Spain, September 1-5, 2008.