II.H.9 Progress in the Study of Amorphous Silicon Carbide (a-SiC) as a Photoelectrode in Photoelectrochemical (PEC) Cells

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Objectives

- Work closely with the DOE Working Group on 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 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-H_2 plant production cost. Table 1 shows detailed milestones year by year.

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Task #	Milestone	Note
Year 1	Material photocurrent ≥3 mA/cm^2	Achieved
	Durability ≥100 hr	Achieved
Year 2	Material photocurrent ≥4 mA/cm^2	Achieved
	Durability ≥200 hr	
	Device STH efficiency ≥5%	
GO/NO-GO decision evaluated		
Year 3	Device STH efficiency ≥6.15% over 300 hours	
Year 4	Device STH efficiency ≥7.5% over 500 hours	

Accomplishments

New Approaches in Tungsten Oxide Surface Treatment:

- Photocurrent above 3.5 mA/cm^2 (at 1.6 V vs. saturated calomel electrode, SCE) demonstrated with molybdenum incorporation in WO_3 near surface (approximately 300 nm) to form a bilayer.
- Evaluation of RuO_2 as catalyst for oxygen evolution reaction. Enhancement of devices performances demonstrated with both RuO_2 thin film and nanoparticles.

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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 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 project. 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 have been also in development for incorporation in the PEC photoelectrode designs (i.e., the hybrid photovoltaic [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 material 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 reporting period of the project (June 2008 – June 2009), 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. Specific progress in developing the tungsten-based materials is detailed in the following subsections.

Tungsten-Based Compound Films

Several experiments on tungsten oxide surface modifications have been initiated during this period. A WO_3 surface modification using molybdenum (referred as WO_3:Mo) was fabricated using a reactive co-sputtering process. Molybdenum incorporation was performed at the end of the WO_3 film synthesis to form a WO_3:Mo(300 nm)/WO_3 (2 µm) bilayer. Photo-electro-chemical tests performed under simulated AM1.5 illumination in 0.33 M H_3PO_4 pointed out a saturated photocurrent increase of approx. 20% at 1.6 V vs. SCE with the bilayer PEC electrode (3.6 mA/cm^2) when compared to pure WO_3 materials (2.9 mA/cm^2), as presented in Figure 1. Subsequent surface analyses performed at the University of Nevada, Las Vegas (UNLV) revealed a WO_3 work function increase of approx. 0.2 eV after Mo incorporation. The difference in the Fermi level positions between the two materials would create a built-in potential at the WO_3:Mo/WO_3 interface that could enhance hole transfer to the electrolyte.

Surface modification with RuO_2 nanoparticles to increase catalytic activity on WO_3 was also investigated. First, a series of experiments were conducted on RuO_2 thin films to establish a baseline deposition process.

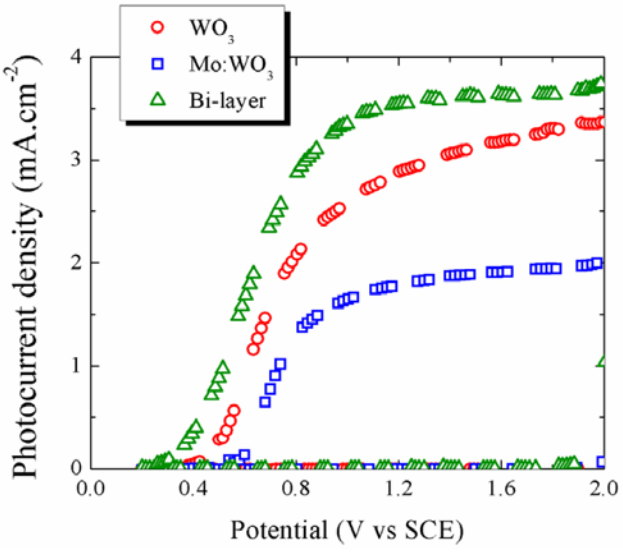

FIGURE 1. Current-potential characteristics measured for WO_3 (open circles), WO_3:Mo (open squares), and WO_3:Mo/WO_3 bi-layer (open triangles) PEC electrodes in 0.33M H_3PO_4 under chopped simulated AM1.5G illumination (scan rate: 25 ms/V).

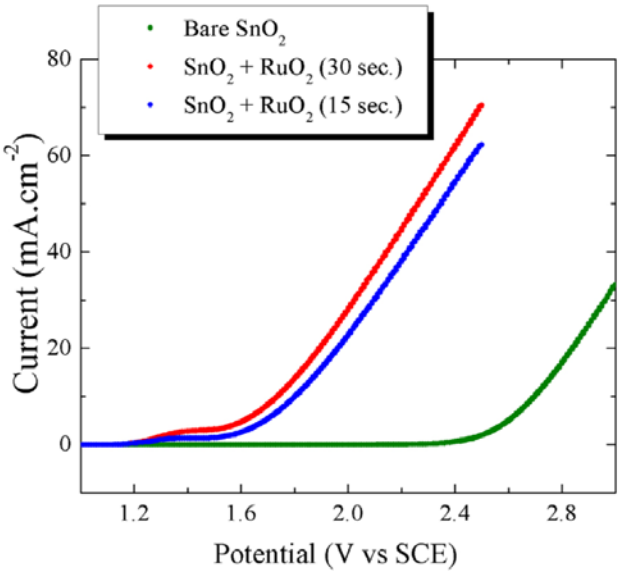

FIGURE 2. Current vs. potential curves measured in 0.33 M H_3PO_4 electrolyte on TEC15 substrate before (green curve) and after a 15 second (blue curve) or 30 second (red curve) RuO_2 nanoparticles deposition.

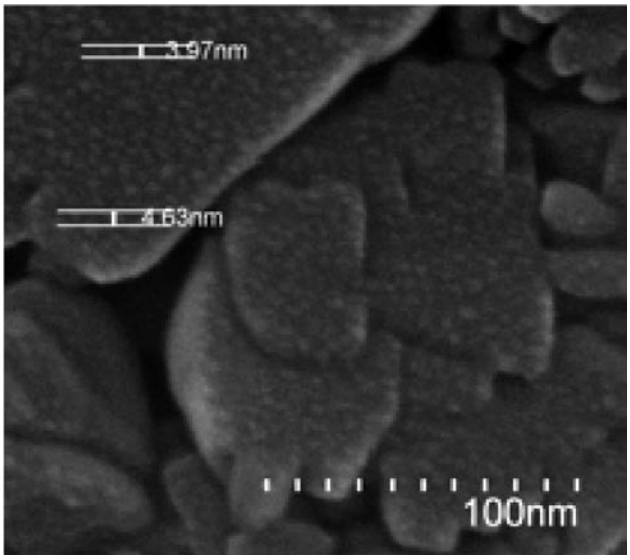

FIGURE 3. Scanning electron microscopy micrograph of WO_3 film treated with RuO_2 nanoparticles. The resulting 3-5 nm particles cover approximately 35% of the total area.

Catalytic activity for the oxygen evolution reaction was validated using RuO_2 thin film as a counter electrode for a p-type PEC electrode test. Onset potential reductions of about 400 mV were observed for both a-SiC and CGSe-based PEC electrodes. Nanoparticles were then deposited on TEC15 substrates using the same process with a 15 or 30-second long deposition time. High catalytic activity of RuO_2 nanoparticles was observed, with a reduction of the oxygen evolution reaction onset potential of more than 1 V (see Figure 2). More important, the effect of deposition time (i.e. the size of the particles) has a negligible effect on the onset potential. This important discovery will be crucial to maximize light harvesting of tungsten oxide film treated with nanoparticles. In fact, a 30 second RuO_2 deposition process covers 35% of the WO_3 surface with 5 nm particles, as presented in Figure 3.

Conclusions and Future Directions

The MVSystems/UH project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO_3 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, including oxide etch (a-SiC), bilayer formation and nanoparticles deposition (WO_3). Bulk modifications were also investigated, such as CIGSe film sulfurization to modify energy band position. Resulting interface and bulk energy band positions will be characterized using UNLV advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.

FY 2009 Publications/Presentations

1. F. Zhu, J. Hu, I. Matulionis, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, A. Madan, *Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight,* Phil. Mag. B85, (2009) 1-16.

2. J. Hu, I. Matulionis, F. Zhu, J. Gallon, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, and A. Madan, Development of a photovoltaic (PV)/photoelectrochemical (PEC) hybrid device with amorphous silicon carbide as the photoelectrode for water splitting, MRS spring meeting, San Francisco, 2009.

3. F. Zhu, J. Hu, I. Matulionis, A. Kunrath, and A. Madan, *Properties of Nano-crystalline Silicon-Carbide Films Prepared Pulse Using Modulated RF- PECVD*, MRS spring meeting, San Francisco, 2009.

4. Y. Zhang, K. George, M. Bär, C. Heske, J. Hu, F. Zhu, and A. Madan, *Chemical and electronic structure of SiC thin films for photoelectrochemical water splitting,* MRS spring meeting, San Francisco, 2009.

5. N. Gaillard, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Surface Modification of Tungsten Oxide-Based Photoanodes for Solar-Powered Hydrogen Production*, MRS spring meeting, San Francisco, 2009.

6. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Improved current collection in WO_3:Mo/WO_3 bilayer photoelectrodes*, to be published in Journal of Material Research.

7. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion,* to be published in Sol. Energy Mater. and Sol. Cells.