II.I.1 Photoelectrochemical System for Hydrogen Generation

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Objectives

- Optimize and refine selection of A2B6 semiconductor photoelectrode materials.
- Synthesize and characterize the A2B6 semiconductor photoelectrode materials.
- Develop large-area photoelectrode panels.
- Develop a scaled-up prototype of a photoelectrochemical (PEC) reactor cell.
- Integrate the scaled-up prototype reactor cell with photoelectrodes and evaluate its performance.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y) Materials Efficiency

(AC) Device Configuration Designs

(AD) Systems Design and Evaluation

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for PEC Hydrogen Production

Characteristic	Units	2013 Target	2010 Status
Usable Band gap	eV	2.3	2.2
Chemical Efficiency	%	10	TBD
Solar-to-Hydrogen Efficiency	%	8	TBD
Durability	hours	1,000	TBD

TBD = to be determined

Accomplishments

- Fabricated A2B6 photoelectrodes using low-cost electrodeposition to produce two distinct architectures: a CdS/ZnS bilayer (n-type) and a ZnTe (p-type).
- Demonstrated CdS/ZnS absorption band edge at 2.2 eV and performed photoelectrochemical testing of samples.
- Designed, fabricated, and tested two generations of photoelectrochemical (PEC) reactor cells.
- Conducted preliminary economic analysis for PEC reactor system.

Introduction

Sunlight is an abundant, renewable and domestically available energy source that can provide a significant proportion of carbon-free energy in the future, particularly if sunlight can be harnessed to generate hydrogen fuel for transportation. PEC hydrogen generation is an approach to generate hydrogen fuel directly from water by using sunlight to drive a water-splitting reaction on the surface of novel semiconductor materials. The primary technical barriers to the development of these semiconductor materials are that they absorb a sufficient amount of the incoming solar energy, efficiently transfer that energy to drive the water-splitting reaction, and remain durable and efficient for long operational times while remaining cost-competitive with other hydrogen generation approaches. In this project, Physical Optics Corporation (POC) is developing an approach for the low-cost fabrication of A2B6 semiconductor photoelectrode architectures and building a prototype PEC reactor cell for testing and demonstration.

Approach

The approach of this project is to increase the solar-to-hydrogen efficiency by using lower band gap A2B6 semiconductor materials (addressing the Materials Efficiency technical barrier). Using a lower band gap enables increased solar absorption due to capturing the abundant lower energy photons inaccessible to traditional high band gap PEC materials. Through a review of potential A2B6 material combinations we selected CdS and ZnTe absorbing materials with band gaps in the 2.2-2.4 eV range. Both materials can be deposited using the low cost, solution process of electrochemical deposition, which is also highly scalable for manufacturing. To address the well-known lack of

durability of CdS we designed a Type-II heterojunction architecture which uses wide band gap ZnS as a capping or window layer to provide photocorrosion protection (addressing the Device Configuration Designs technical barrier). A process for co-depositing CdS with the ZnS capping layer from a single solution was adopted and refined for photoelectrode fabrication.

In addition to fabricating photoelectrode materials, a series of generations of prototype systems to house the photoelectrodes, the PEC reactor cell, were designed, assembled, and tested as part of an iterative design process. Ultimately the photoelectrodes and PEC reactor housing will be assembled as a final prototype for testing and demonstration purposes. Technoeconomic evaluations of the hydrogen production cost will be made based on the prototype fabrication costs, the material costs, and the projected photoelectrode efficiency and lifetime of the mature system. This work directly addresses the Systems Design and Evaluation technical barrier.

Results

Our efforts on this project have focused on the development of the two major cell components: the semiconductor photoelectrode structure and the photoelectrochemical reactor cell housing.

Electrodeposited A2B6 Photoelectrode Development

We developed and refined the process for co-deposition of an *n-n* CdS/ZnS bilayer film using electrochemical deposition. The bilayer film shown in Figure 1, consists of an approximately 2 micron thick layer of CdS capped with roughly 100 nm of ZnS. After a base layer of CdS is deposited, the incorporation of ZnS is gradual starting around the third hour of the deposition process. Due to the large band gap of ZnS (Eg = 3.5 eV) the CdS/ZnS bilayer films are visibly and spectroscopically (for absorption spectroscopy) indistinguishable from CdS single layer films. Figure 2 shows the Tauc plot for an electrodeposited CdS/ZnS film showing a direct band edge around 2.2 eV, which achieves the DOE target. The reduction in band gap compared to bulk CdS (Eg = 2.4 eV) is attributed to a reduced amount of strain present in the solution deposited film. The influence of different substrate materials on the growth of CdS/ZnS was investigated, which revealed that due to the process by which CdS deposits (i.e., mediated by proton reduction on the cathode) more uniform CdS films were deposited using substrate materials that had slow proton reduction kinetics (e.g., Ti and ITO).

Zinc telluride films were also fabricated using electrochemical deposition which showed a strong dependence on the substrate and growth potential due

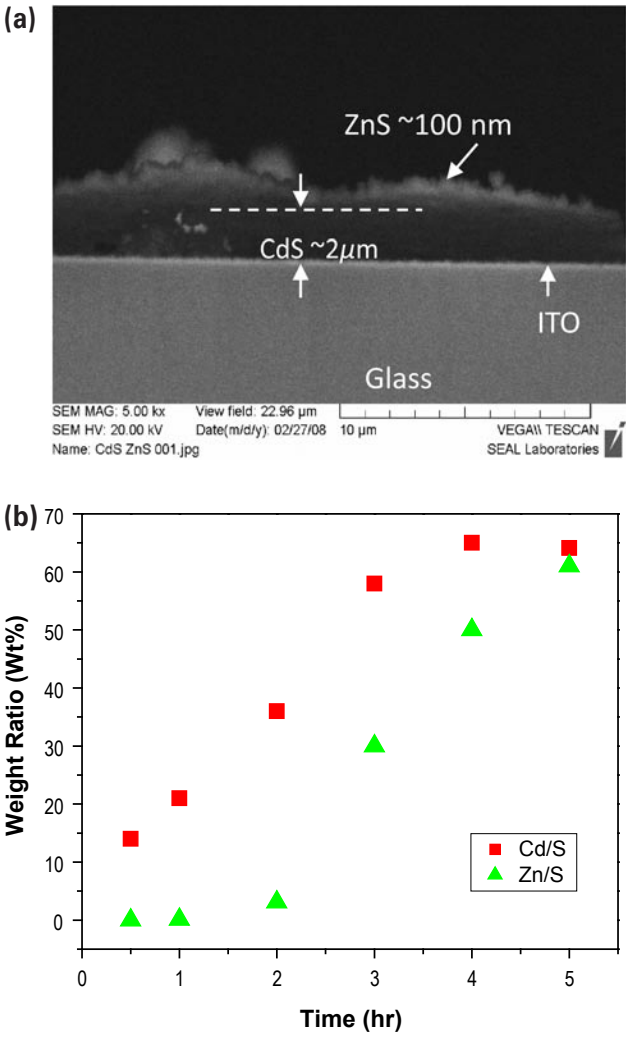

FIGURE 1. CdS/ZnS bilayer film characterization showing (a) scanning electron microscopy cross-section of the film; and (b) the weight ratio of Cd/S and Zn/S plotted versus deposition time as measured by EDX. Initial layers of the film show much higher concentrations of Cd with an increase in Zn concentration in outer layers of the film.

to the large difference in reduction potential between Zn and Te. Films with an excess of one material or another were typical, as confirmed by energy dispersive X-ray (EDX) and X-ray diffraction (XRD) measurement.

The electrodeposited CdS/ZnS were characterized following standard PEC procedures. The open circuit potential measurement confirmed the n-type doping with an estimated flatband potential of -0.50 V vs. Ag/AgCl in 0.1 M H_2SO_4. Results of PEC testing are shown in Figure 3, which shows the 3-electrode current density-voltage (JV) and unbiased photocurrent characteristics for electrodeposited CdS/ZnS. Air annealing (at 200-300°C) has been investigated as a means of improving crystallinity. Initial results showed similar PEC properties with a decrease in durability attributed to the formation of cracks in the film during

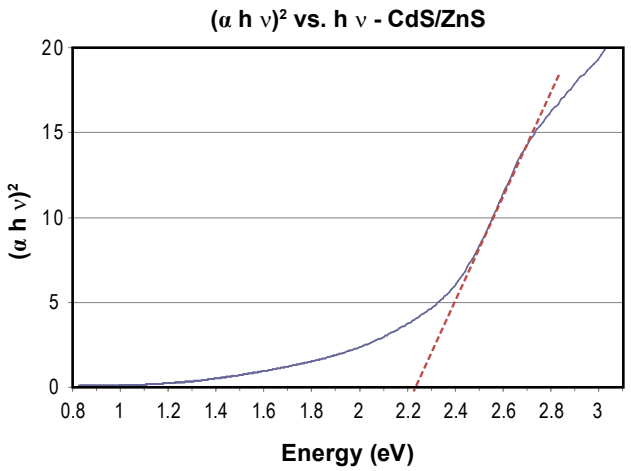

FIGURE 2. Tauc plot $(\alpha h\nu)^2$ vs. $h\nu$ based on the ultraviolet-visible absorption of the CdS/ZnS film. The linear fit corresponds to an allowed direct band gap around 2.23 eV.

annealing due to the mismatch in thermal expansion between the substrate and film. PEC characterization of ZnTe films are in progress and are expected to offer increased photocorrosion stability due to being p-type and generating hydrogen during the water-splitting reaction (i.e., due to being the photocathode).

PEC Reactor Cell Development

We have designed and fabricated a second generation prototype for the PEC reactor cell which will house the photoelectrode, counterelectrode, water and evolved H_2 and O_2 gases. The second generation design shown in Figure 4 was developed based on the testing of the first generation design performed by using electrolysis on metal electrodes installed in the unit in the locations where the photoelectrode and counterelectrode would sit. Through this testing we observed H_2/O_2 gas evolution and identified potential bottlenecks, weak seals, and other drawbacks. The resulting second generation design improved on the first by including a drastically reduced number of seals, eliminating bottlenecks, and improving the layout of the photoelectrode and counterelectrode configuration to better utilize space. The new design is both scalable (by increasing the size of the basic unit cell) and modular (by allowing multiple cells to be combined together) while providing easy maintenance. While awaiting system level tests with photoelectrodes, the second generation design is being further refined through studies of the durability of the materials (plastics, metals, etc.) to extended exposure to harsh electrolytes and ultraviolet light. This study includes both a literature review and laboratory lifetime testing of various reactor materials in electrolyte solutions.

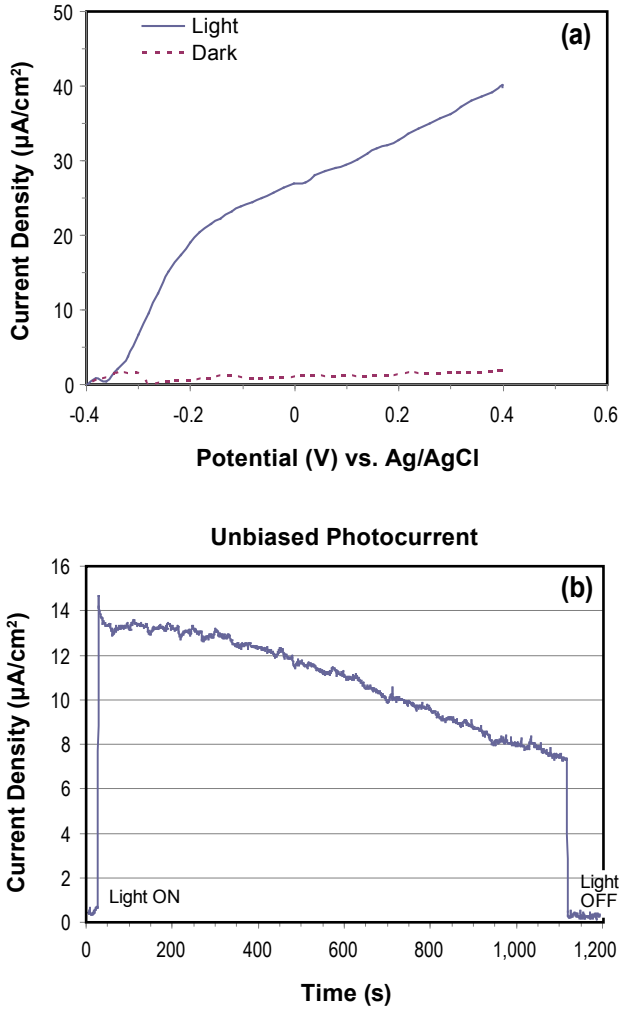

FIGURE 3. PEC measurement results for the ZnS/CdS sample of 1x1 cm size under 112 mW/cm^2 illumination (AM1.5 spectrum) in 0.1 M H_2SO_4 with Pt counterelectrode. (a) 3-electrode JV curves showing 27 μA of photocurrent at 0 V vs. Ag/AgCl. (b) The sample provides stable unbiased photocurrent for up to 2,100 s in the 0.1 M H_2SO_4 solution.

Conclusions and Future Directions

POC has applied a novel CdS/ZnS bilayer electrodeposition approach to fabricate a semiconductor architecture for photoelectrochemical hydrogen generation. The resulting films exhibit broad absorption of the solar spectrum with a band gap of 2.2 eV. The characterization of the bilayer film using PEC methods demonstrated a photocurrent of 27 uA at 0 V vs. Ag/AgCl under AM1.5 illumination. Future work aims at improving the photocurrent through investigation and optimization of the carrier transport properties of the electrodeposited films to be achieved by optimizing the deposition process. Verification of PEC test results through collaboration with other members of the PEC workgroup are planned. In addition to developing

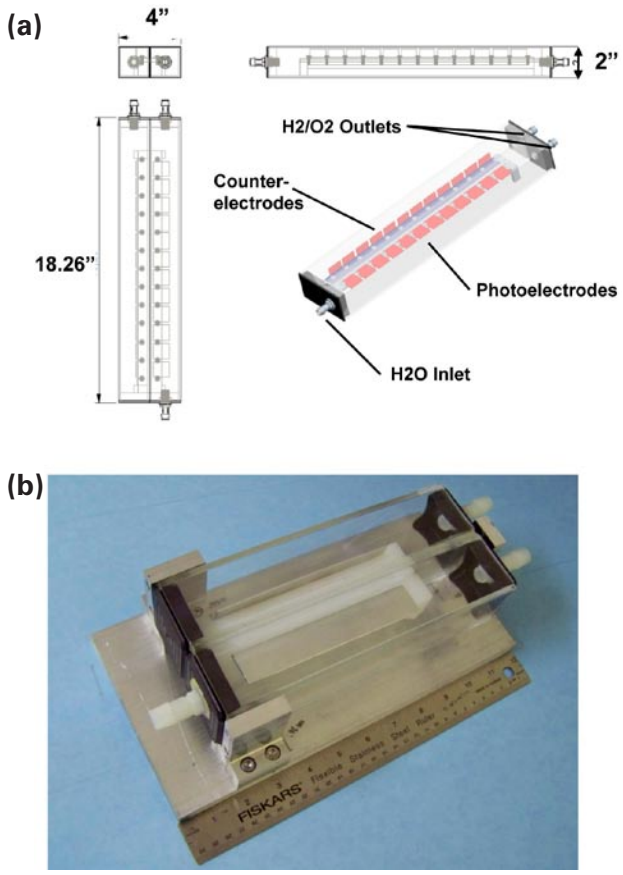

FIGURE 4. POC's Prototype PEC Reactor (a) Reactor design showing (red) electrodes mounted on removable table enclosed in clear tubing with gas outlets and water inlet. (b) The prototype reactor fabricated at POC photographed with metal electrodes installed for testing via electrolysis.

photoelectrode materials, we constructed a small-scale prototype PEC reactor, based on the testing of the first generation prototype. The second generation prototype improved on the collection and partitioning of gases, an improvement of the counterelectrode-photoelectrode arrangement, the durability of the materials used in the system, and the modularity and scalability of the design. The future development of the PEC reactor system will include integration with photoelectrodes for full system testing and evaluation. Based on the final prototype system, an evaluation of the commercial potential for the system will be performed including the calculation of the cost of hydrogen production through technoeconomic analysis. The results of the system development and economic analysis will provide a strong basis for further commercial development of photoelectrochemical hydrogen production components or systems in the future while working to overcome DOE technical barriers.

FY 2010 Presentations

1. J.F Hodelin and A. Parfenov, *Photoelectrochemical system for Hydrogen Generation*, Fuel Cells Technologies Program SBIR Presentation- Phase 2 Production and Delivery Projects, Washington, D.C., October 2009.

2. J.F Hodelin and A. Parfenov, *Photoelectrochemical system for Hydrogen Generation*, 2010 Vehicle Technologies and Hydrogen Programs Annual Merit Review and Peer Evaluation Meeting , Washington, D.C., June 2010.