II.J.4 Photoelectrochemical System for Hydrogen Generation

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Fiscal Year (FY) 2011 Objectives

- Fabrication of components of scaled-up prototype photoelectrochemical (PEC) reactor cell.
- Integration of scaled-up prototype of a PEC reactor cell.
- Demonstration of the scaled-up prototype reactor cell with photoelectrodes and performance evaluation.

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	2011 Status
Usable Band Gap	eV	2.3	2.2
Chemical Efficiency	%	10	To be determined
Solar-to-Hydrogen Efficiency	%	8	~5% - to be verified
Durability	hr	1,000	0.5 - to be verified

FY 2011 Accomplishments

- Fabricated A2B6 photoelectrodes using solution deposition to produce CdS/ZnS bilayer (n-type) films.
- Designed, fabricated, and tested a third generation PEC reactor cell panel and mechanical framework (0.5 m x 0.5 m).
- Conducted techno-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 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. Previously we selected a CdS/ZnS bilayer and also ZnTe as promising A2B6 material combinations with band gaps in the 2.2-2.4 eV range. Recently, we concentrated on the CdS/ZnS architecture and explored and evaluated different processes for producing the films. These processes included an electrodeposition approach for co-depositing CdS with the ZnS capping layer from a single solution and a sequential deposition of CdS followed by ZnS via chemical solution deposition. We concluded our investigation of the ZnTe film, based on additional testing which revealed that the durability of the electrodeposited ZnTe films was insufficient for system integration.

In addition to fabricating photoelectrode materials, we developed and assembled the third generation in a series of prototype reactor cell systems to house the photoelectrodes and capture the generated hydrogen. This PEC reactor housing is the final prototype for this project and will be used for testing and demonstration purposes. Technoeconomic evaluations of the hydrogen production cost have been 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 PEC reactor cell housing.

Electrodeposited A2B6 Photoelectrode Development

Previously we had developed a process for co-deposition of an *n-n* CdS/ZnS bilayer film using electrochemical deposition. Recently we have refined the deposition process to increase the thickness of the films as shown in Figure 1. The thicker films have higher overall durability, however the uniformity of the coating, particularly of the ZnS window layer requires further improvement. The co-deposition process utilizes both zinc and cadmium salts simultaneously in the reaction vessel along with a single organic sulfur source. Due to the electrodeposition of CdS proceeding more rapidly than the solution-deposited ZnS, as well as the lack of stirring during the electrodeposition, local concentration effects may be among those contributing to the poor uniformity.

To improve the ZnS coating uniformity, a solution deposition process was developed for coating previously electrodeposited CdS samples with a ZnS window layer. First, single layer ZnS films were developed and characterized. These samples bandgap around 3.5 eV which is consistent with zincblende ZnS. Next the coating process was applied to the electrodeposited CdS films immediately upon their removal from the CdS bath. These two fabrication step samples were tested and compared to the co-deposited samples, and test results indicated that while the two-step samples were more durable, the co-deposited films provided superior PEC performance. This is attributed to the continuous variation in stoichiometry that results from the co-deposited films allowing carriers to transfer between layers more efficiently, when compared to the abrupt interface present in the two-step samples. In the future, the next step would be to apply a hybrid procedure where the thickness of the ZnS layer of a co-deposited is incrementally increased through a second deposition in a fresh bath. This hybrid process may provide both a gradual stoichiometry change from CdS to ZnS along with an increased total ZnS coating thickness.

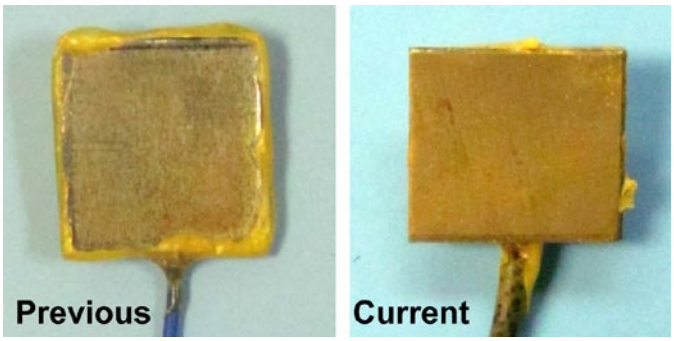

FIGURE 1. CdS/ZnS bilayer films showing increased thickness through two-step process as compared to previously deposited samples through the optimization of the coating process.

PEC Reactor Cell Development

After the successful testing of the second generation prototype for the PEC reactor cell which houses the photoelectrode, counterelectrode, water and evolved H_2 and O_2 gases, we scaled up the design and fabricated a third generation prototype as shown in Figure 2. The prototype takes advantage of the scalable and modular design to increase the total size of the system area to 65 cm x 50 cm with an available harvesting area of approximately 20 cm x 20 cm (due to excess area allocated to the counterelectrode and for gas capture). The system is designed to allow simple and flexible integration of photoelectrodes for loading and maintenance, as well as autonomous extraction of the hydrogen gas and refilling of the aqueous electrolyte. The prototype system has recently been evaluated for system cost and durability based on testing and projected performance parameters.

Conclusions and Future Directions

Physical Optics Corporation has explored a novel electrodeposition and chemical solution deposition approaches to fabricating CdS/ZnS bilayer films for PEC hydrogen generation. In addition, a third generation prototype of the reactor cell mechanical framework has been designed, assembled, and is being evaluated. Future work would work to improve the film uniformity and durability by optimizing the deposition process. We plan to continue to investigate opportunities for verification of PEC test results through collaboration with other members of the PEC workgroup. The results of the system development and economic analysis will provide a strong basis for further commercial development of PEC hydrogen production components or systems in the future while working to overcome DOE technical barriers.

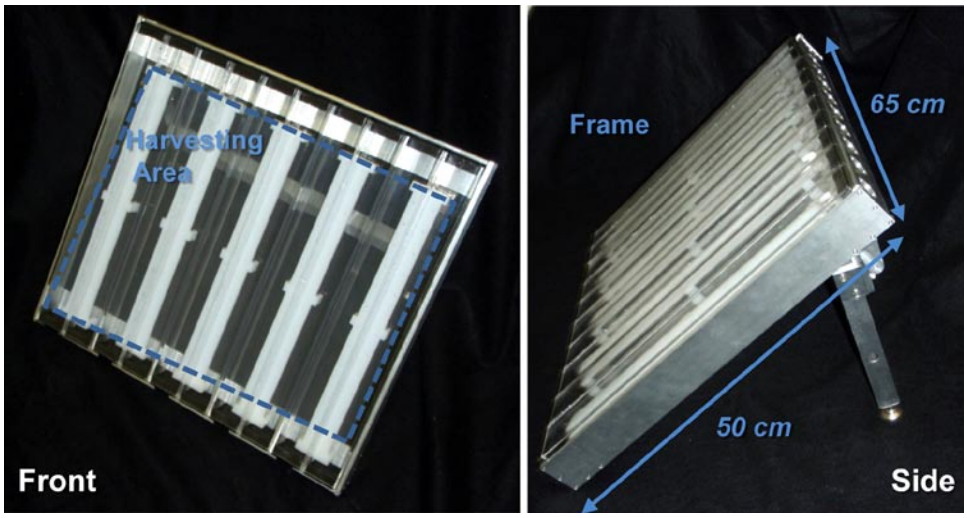

FIGURE 2. Third generation prototype PEC reactor photographed with electrodes removed. The prototype reactor was designed and built to be modular and scalable, and to have a low cost to fabricate and maintain.