

II.F.6 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Subcontractors:

- Xunlight Corporation, Toledo, OH
- University of Toledo, Toledo, OH
- National Renewable Energy Laboratory, Golden, CO

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Project End Date: June 30, 2013

- Two approaches are taken for the development of efficient and durable photoelectrochemical (PEC) cells:
 - An immersion-type PEC cell in which the photoelectrode is immersed in electrolyte.
 - A substrate-type PEC cell in which the photoelectrode is not in direct contact with electrolyte.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section (3.1.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYPP):

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AC) Device Configuration Designs
- (AD) Systems Design and Evaluation

Technical Targets

This project focuses on the development of photoelectrode materials and triple junction tf-Si-based PEC cells required to achieve or exceed DOE's technical targets. The status of this project towards the DOE MYPP objective for PEC production of hydrogen for 2013 is:

Accomplishments

- TCCR coatings were developed (Task 1).
 - After extensive study of many different types of material classes for TCCR application, cobalt oxide has been identified as the major material class of

Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film (tf)-Si based photoelectrodes.

TABLE 1. Progress towards Meeting Technical Targets for Immersion-Type PEC Cells and Systems

DOE Barriers	Performance Measure	Units	DOE 2013 Targets	2010 Go/No-Go	MWOE current Status
Y. Materials Efficiency	Solar-to-Hydrogen (STH) efficiency	% Efficiency	8	N/A	4.0 (immersion-type)
Z. Materials Durability	Durability	Hours	≥1,000	≥700	1,000 (Co ₃ O ₄) 330 (PEC)
	Cost	gge	\$2-3	N/A	TBD
	Deposition temperature	°C	≤250 (MWOE Target)	≤300	200
	Transparency of TCCR	% Trans-mission	≥90 (MWOE Target)	≥85	95
	Voltage drop across TCCR layer	V	≤0.15	≤0.35	0.086

gge = gasoline gallon equivalent; TCCR = transparent, conducting and corrosion resistant; TBD = to be determined

study, moving into the Phase Two of the project period.

- $\text{In}_2\text{O}_3\text{-Co}_3\text{O}_4$ has also shown promising results, will be optimized for TCCR performance.
- Successfully transferred the results from the lab to the prototype roll-to-roll production machine to deposit cobalt oxide film on large area a-Si triple junction cells. The PEC electrodes with cobalt oxide coating have been used to build the immersion-type PEC systems (Task 1 and 4).
- Have achieved 4.1% initial solar to hydrogen conversion efficiency and over 330 hours life time for immersion type PEC cells (Task 3).
- Various immersion-type PEC module designs have been built to optimize the STH conversion efficiency, to extend the lifetime and reduce the cost. Reasonable STH efficiency has been obtained and further improvements are under way (Task 4).
- Worked with Dr. Nocera's group at the Massachusetts Institute of Technology and Sun Catalytix on solar water splitting project, by providing triple junction a-Si solar cells. Their research results were published in Science Magazine and were selected as one of Top 50 Innovations of Year 2011 by Time Magazine ("Artificial Leaf") (Task 4).



Introduction

In this project, MWOE and its subcontractors are jointly developing the critical technologies for cost-effective production of hydrogen from sunlight and water using tf-Si-based photoelectrodes. These tf-Si based electrodes include triple junction cells with either amorphous silicon germanium alloy (a-SiGe) or microcrystalline silicon ($\mu\text{-Si}$) as the narrow band gap absorber material.

In this project two separate approaches have been pursued for the development of immersion- and substrate-type PEC photoelectrodes:

- In one approach, triple-junction tf-Si based photoelectrodes (a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/ $\mu\text{-Si}$) are used to generate the voltage bias necessary for hydrogen generation. A TCCR coating is deposited on top of the photoelectrode to protect the semiconductor layers from corrosion while forming an ohmic contact with the electrolyte.
- The second approach uses a hybrid structure, in which two tf-Si-based junctions (middle and bottom junctions of the present triple-junction tf-Si cell) provide a voltage bias of about 1.1 V, and a third junction (the top junction) forms a rectifying junction between a photo-active

semiconductor and the electrolyte. This approach was down-selected during a Go/No-Go review in Dec 2010.

Approach

Five technical tasks are being performed under this grant to accomplish the project objectives:

- Task 1: TCCR coating for a triple-junction tf-Si-based photoelectrode.
- Task 2: Hybrid multi-junction PEC electrode having semiconductor-electrolyte junction.
- Task 3: Understanding and characterization of photo-electrochemistry.
- Task 4: Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems.
- Task 5: Development of device designs for large area, substrate-type PEC cells.

During the Go/No-Go review in Dec 2010, it was decided that the immersion-type PEC work (Task 4) will proceed into the second phase and the substrate-type PEC work (Task 5) would come to an end. It was also determined the TCCR work (Task 1) will proceed and the photo-active semiconductor work (Task 2) will be halted.

Results

The immersion-type PEC system utilizing a-Si triple junction solar cell should be a very efficient and low-cost approach for renewable hydrogen generation. The most challenging part of this approach is to develop a TCCR coating to protect the tf-Si solar cells in electrolyte. The focus of Task 1 has been to identify promising materials to use as the TCCR layer. After extensive studies of various material classes for this purpose, cobalt oxide and cobalt oxide co-deposited with other metal oxides have been identified as the most promising material that we would focus on moving into Phase II of this project. Over the past year the film properties were further optimized in Xunlight's roll-to-roll deposition system. This prototype production system allows large-area PEC electrode fabrication, including the deposition of TCCR layer without breaking the vacuum. Cobalt oxide has been sputtered on a-Si triple junction solar cells at 200°C. Reducing the sputtering power from 1.5 kW (Run 4) to 0.8 kW (Run 5) leads to transmission values of 90-100% in a wavelength range between 300-900 nm (Figure 1). The average thickness of these Co_3O_4 layer is ~70 nm. The oxygen flow was varied between 100-140 sccm and it seems that the transmission of the Co_3O_4 layer does not change with the oxygen flow in the sputtering gas. Under one-sun condition, the voltage drop on the cobalt oxide layer is only 0.086 V, which is excellent since this indicates

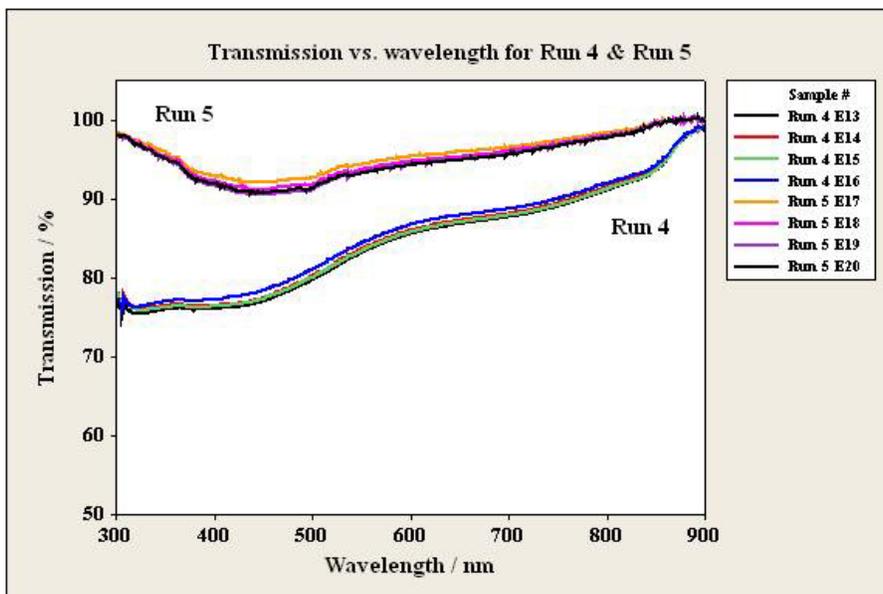


FIGURE 1. Transparency of cobalt oxide films (TCCR layer) deposited in Xunlight's roll-to-roll deposition system for large-area fabrication of PEC electrodes

that almost all the voltage generated by the solar cell can be used for water splitting and hydrogen generation. All of the above performance metrics meet or exceed the DOE goals and MWOE project goals. Cobalt oxide films deposited on fluorine-doped tin oxide (TEC 15) have been shown to be electrochemically stable for over 1,000 hrs under an applied bias of 1.8 V which reassembles the operating conditions for an immersion-type PEC cell assembly. With the roll-to-roll deposition system, not only can we optimize the deposition conditions for cobalt oxide, we can also adjust the solar cell deposition conditions and optimize the solar cell and TCCR layer deposition parameters for PEC performance instead for solar-to-electricity performance. This is a great advantage that we have comparing to many other groups that have to rely on commercially available solar cells which are always optimized for solar to electricity performance.

Under Task 4, we have focused our efforts in two major areas during last year. The first area was to develop immersion-type PEC electrodes with good STH efficiency and life time. We have fabricated PEC electrodes with cobalt oxide coating on the oxygen generating side and porous Ni catalyst on the hydrogen generation side. We have achieved a 4.1% initial STH efficiency and over 330 hrs of lifetime with a 2.5 cm² electrode (Figure 2). This efficiency was calculated by the actual measurement of hydrogen gas collected over time under AM 1.5 illumination (1 sun). It seems the main cause for performance decay overtime is the edge corrosion of the cell by electrolyte. We have been addressing this issue by applying a clear coat at the edge and employ some special design for the electrode holder in the large area PEC module design.



FIGURE 2. The experiment set-up for measuring the STH efficiency of the PEC electrodes

The second area that we have focused on was to design and develop PEC system with our large-area PEC electrodes. The basic design (Figure 3) uses an insert to hold the PEC electrode and to separate the unit into two chambers with an open void at the bottom for ion flow in the electrolyte. An insert holds the PEC electrode which allows for easy



FIGURE 3. Prototype PEC module design with four inch by four inch PEC electrodes

replacement of different PEC electrode materials. A STH conversion efficiency of 2.5 has been achieved with the PEC module in actual outdoor condition. Figure 4 shows the PEC module in operation under normal outdoor condition. We are working on exploring different PEC module designs to further improve the performance.

We have worked with Dr. Nocera's group at the Massachusetts Institute of Technology and Sun Catalytix on solar water splitting project, by providing triple junction a-Si solar cells. Their related research results were published in Science Magazine and were selected as one of Top 50 Innovations of Year 2011 by Time Magazine. MWOE has received many requests for collaboration on PEC hydrogen generation research projects from multiple research groups around the World, including University of Texas at Austin, Toyota Technical Center in Ann Arbor, University of California at San Diego, Energy Research Institute at

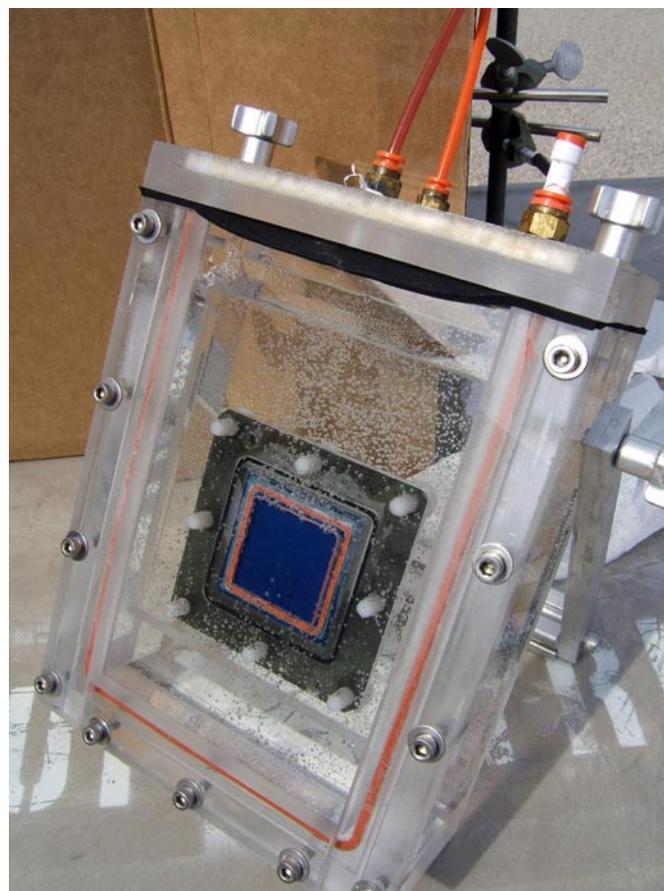


FIGURE 4. An immersion-type PEC module in operation under actual outdoor conditions

Nanyang Technological University in Singapore, Imperial College London in England. As far as we know, MWOE/Xunlight is the only company in the world which can supply triple junction solar cells which are ideal for renewable water splitting and hydrogen generation.

Conclusions and Future Directions

- Continue to improve the STH conversion efficiency for the large-area immersion-type PEC system, understand the different factors which could affect the efficiency such as cell uniformity, optimum operating voltage and operating current of the solar cell, the effect of the TCCR characteristics on the PEC performance, and the hydrogen and oxygen generation catalyst, etc.
- Experiment with different fabrication methods for PEC electrode with respect to solar cell and indium tin oxide deposition conditions, electrode preparation and different conditions for applying TCCR coating both in the lab and in the large scale roll-to-roll deposition system.

- Continue to develop different module designs to optimize the STH efficiency, extend lifetime and reduce cost.
- Develop more TCCR materials in addition to Co_3O_4 .
- Develop 1'x1' commercial size PEC system and carry out test in real life conditions.
- Collaborate with different research groups around the world to further PEC hydrogen generation research and development.
- Carry out the preliminary techno-economic analysis of the immersion-type PEC system.