

II.C.3 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Contract Number: DE-FG36-05GO15028

Subcontractors:

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

Project Start Date: April 1, 2005

Project End Date: March 31, 2014

Overall Objectives

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

Fiscal Year (FY) 2013 Objectives

- Focus on immersion-type PEC systems, and work on improving the solar-to-hydrogen (STH) conversion

efficiency and durability to achieve a cost-effective PEC system.

- Develop new designs of PEC electrodes, and explore new kinds of transparent, conducting, and corrosion-resistant coating material to improve the durability of the electrode.
- Develop new oxygen and hydrogen generation catalysts and understand how they affect the performance of the PEC system.
- Improve the PEC module case design, carry out outdoor testing of immersion-type PEC systems and study their performance under real-time conditions.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section 3.1.5 of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (AE) Materials Efficiency
- (AF) Materials Durability
- (AG) Integrated Device Configuration
- (AI) Auxiliary Material
- (AJ) Synthesis and Manufacturing

Technical Targets

This project focuses on the development of photoelectrode materials and triple junction tf-Si-based PEC cells to split water and generate hydrogen using sunlight. The status of this project towards the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan objective for PEC production of hydrogen is shown in Table 1.

FY 2013 Accomplishments

- Transparent, conducting, and corrosion-resistant (TCCR) coatings have been developed (Task 1). Successfully transferred results from research and development to the prototype roll-to-roll production machine for depositing cobalt oxide film on large area amorphous silicon (a-Si) triple-junction cells.
- Submitted two provisional patent applications on a novel design for immersion-type PEC cells where the illuminated side of the PEC electrode is divided into areas coated with corrosion-resistant transparent protective (CRTP) layer for light absorption and areas

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

DOE Barriers	Performance Measure	Units	DOE 2013 Targets	DOE 2015 Targets	MWOE current Status
(AE) Materials Efficiency	STH Efficiency	%	8	15	5.7 (immersion-type)
(AF) Materials Durability	Hours under PEC Operation	Hours	≥1,000	≥0.5 year	480 hr (STH efficiency >1%)
	Cost	gge		\$4 (2020)	TBD

gge – gasoline gallon equivalent; TBD – to be determined

coated with corrosion-resistant conducting catalytic (CRCC) layer for oxygen or hydrogen generation depending on the structure of the solar cells (Tasks 1 and 4).

- Developed complete procedures starting with standard solar cells from large-scale production, going through shunt passivation, next applying the TCCR layer and oxygen evolution reaction (OER) catalyst, and then adding hydrogen evolution reaction (HER) catalyst, and finally make a PEC electrode for photovoltaic hydrogen generation (Task 1 and 4).
- Have achieved 5.7% STH conversion efficiency for immersion type PEC cells (Task 4). This is, to our knowledge, the highest STH efficiency ever achieved for low-cost thin-film PEC electrode.
- Have achieved ~480 hours of operating life time for immersion-type PEC cells with final STH efficiency >1% (Task 4).
- Developed and evaluated a variety of hydrogen evolution catalyst materials such as plated platinum, ruthenium, electro-plated and sintered nickel (Task 4).
- Various immersion-type PEC module designs have been built to optimize the STH conversion efficiency, to extend the lifetime and reduce the cost (Task 4).



INTRODUCTION

In this project, MWOE and its subcontractors are jointly developing critical technologies for cost-effective production of hydrogen from sunlight and water using tf-Si-based photoelectrodes.

Triple junction a-Si/a-SiGe/a-SiGe is an ideal material for making cost-effective PEC systems for hydrogen generation. It has the following key features:

- It has an open-circuit voltage (V_{oc}) of ~2.3 V and has an operating voltage around 1.6 V. This is ideal for water splitting. There is no need to add a bias voltage or to inter-connect more than one solar cell.
- It is made by depositing a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/ μ c-Si(or nc-Si) thin films on a conducting stainless

steel substrate which can serve as an electrode. When we immerse a triple-junction solar cell in electrolyte and illuminate it under sunlight, the voltage is large enough to split water, generating oxygen at the Si solar cell side (for n-i-p type cells) and hydrogen at the back, which is the stainless steel side. This results in a simple and low-cost system which does not need a counter electrode or any wire connections.

- It is being produced on large rolls of 3-ft wide and up to 5,000 ft long stainless steel web in a 25-MW roll-to-roll production machine. Therefore, the corresponding PEC electrodes and systems can be made at very low cost.

However, the tf-Si solar cell is not highly stable in a strongly acidic or strongly basic electrolyte, which is typically needed for efficient and simultaneous evolution of oxygen and hydrogen. The tf-Si layers could be corroded by such electrolyte, especially under working conditions under light. In order to develop a PEC system using triple-junction tf-Si solar cells, we need to develop a coating which can be applied onto the solar cell surface, and which needs to have the following features: 1) transparent, so that the light can pass through the coating and reach the solar cells, 2) conducting, so that the voltage generated by the solar cell under sunlight can be applied to the electrolyte-electrode interface and generate oxygen and hydrogen, 3) corrosion resistant, so that it can protect the solar cell surface from being corroded in the electrolyte, and 4) capable of being deposited onto the solar cell surface at 200°C or lower, since the solar cell could be damaged if the temperature is higher than 200°C. In addition, it needs to act as an OER catalyst.

APPROACH

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

- Task 1: Transparent, conducting and corrosion-resistant coating for triple-junction tf-Si-based photoelectrodes.
- Task 2: Hybrid multi-junction PEC electrodes having semiconductor-electrolyte junctions.
- 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.



FIGURE 1. PEC electrode under operation conditions in KOH/H₃BO₃ electrolyte.

- Task 5: Development of device designs for large area, substrate-type PEC cells.

RESULTS

During last year, more work has been carried out to improve the TCCR coating (Task 1) and develop procedures to fabricate PEC electrodes from the standard solar cells by shunt passivation, applying the TCCR coating and OER catalyst and applying the HER catalyst. One of the focuses was to develop various HER catalyst materials, which have a substantial impact on the STH efficiency and durability of immersion-type PEC systems. We have studied five different types of HER catalyst. They are electroplated platinum, ruthenium, electroplated smooth Ni and porous nickel, and sintered nickel. While noble metals such as platinum and ruthenium are very good HER catalysts, Ni is considered a low-cost option for commercial-scale PEC systems for hydrogen generation. Platinum was plated from an H₂PtCl₆ solution and ruthenium was plated from a RuCl₃ solution. Smooth Ni was plated from a NiCl₂/NiSO₄ solution. To obtain porous Ni, we developed a method to co-deposit Ni and zinc from a NiCl₂/NiSO₄/ZnCl₂ solution and then leach out the zinc, which will leave a porous Ni coating. Sintered Ni is obtained by annealing Ni powders in a mixture of other metal powders acting as filler which then are leached out, leaving a porous Ni structure behind. The HER catalyst sheet is then attached to the backside of tf-Si-based PEC electrodes which use Co₃O₄ as the TCCR coating.

Table 2 summarizes the initial STH efficiency values obtained for PEC electrodes using these five HER materials. The highest initial STH efficiency of 5.7% has been obtained using plated ruthenium as the HER catalyst followed by plated platinum providing an STH efficiency of 5.6%. The

STH for electrodes with Ni HER are somewhat lower: 4.1% for plated porous Ni, 3.0% for sintered Ni and 1.5% for plated smooth Ni catalyst materials. In comparison, the PEC electrode without any HER catalyst (last one in Table 2) has the lowest STH efficiency and worst durability, which indicates that a HER catalyst, although on the backside of photoelectrode, is essential.

TABLE 2. Comparison of Different Hydrogen Generation Catalyst

HER Catalyst	Initial STH Efficiency	Operating Hours with STH Efficiency >1%
Plated Platinum	5.6%	42 hrs
Plated Ruthenium	5.7%	37 hrs
Plated Smooth Nickel	1.5%	80 hrs
Plated Porous Nickel	4.1%	170 hrs
Sintered Nickel	3.1%	480 hrs
No HER catalyst	1.2%	8 hrs

Although the highest STH efficiency values were obtained using platinum and ruthenium as HER catalyst materials, the PEC system using Ni as the HER catalysts demonstrates much better durability (480 hours). Figure 2 shows STH efficiency versus operation time for PEC electrodes with different HER catalyst materials. More work is underway to improve both the efficiency and durability.

Examining the electrodes with decayed efficiency, corrosion is observed at the oxygen generating side, which is the solar cell/TCCR coating side of the electrode. Therefore, we concluded that even though Co₃O₄ itself is stable in electrolyte, the thickness (~70 nm) that we have been using might be too thin to protect the solar cell underneath. On the other hand, if we increase the thickness of Co₃O₄, the

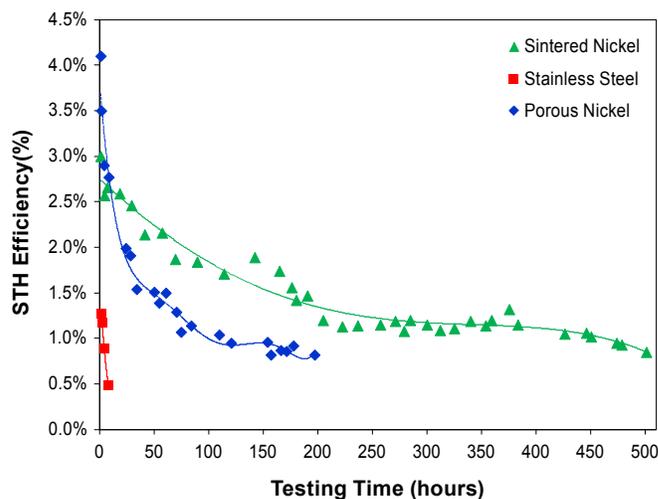


FIGURE 2. STH efficiency versus operation time for PEC electrodes with different HER catalyst materials.

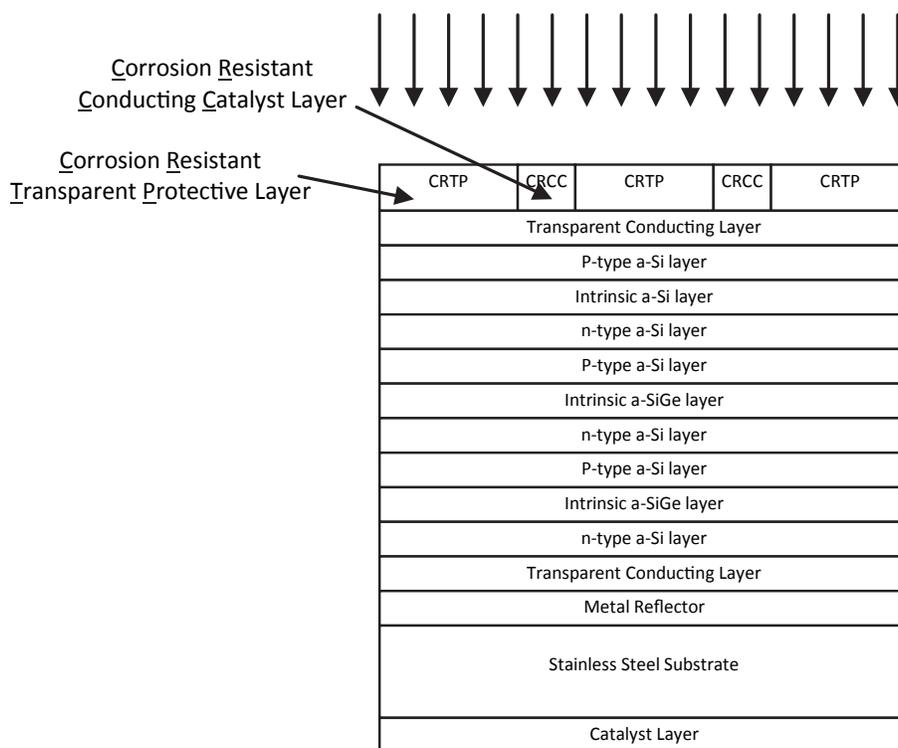


FIGURE 3. Schematic of the PEC electrode with the novel design of alternating CRCC and CRTP coating.

transparency will decrease. Recently, we have developed a novel design which would address this problem and which could lead to a PEC electrode that can generate hydrogen effectively and have a good durability.

In this novel design as shown in Figure 3 and Figure 4, we separate the solar cell surface into two types of regions, Region I and Region II. For Region I, we coat the surface with a CRTP layer, which does not need to be electrically conducting. There are many materials we can use, for example, clear coat, SiO₂ coating, etc. For region II, we coat the surface with a CRCC layer, such as Co₃O₄ material. In this design, Region II does not need to be transparent, it only needs to have good electrical conductivity and act as a good oxygen generating site. Since there is no need to be transparent, we can make much thicker Co₃O₄ coating, not being limited by the 70-nm thickness, or we can use a metal catalyst, such as platinum. Effectively, Region I will act as solar energy absorbing and electrical voltage generating sites; the indium tin oxide (ITO) layer on top of the solar cell and underneath the CRTP and CRCC coating transfers the voltage from Region I to Region II, and Region II will act as oxygen generating site with Co₃O₄ as the oxygen generating catalyst. We have filed two provisional patents based these new ideas. The experiment work is underway.

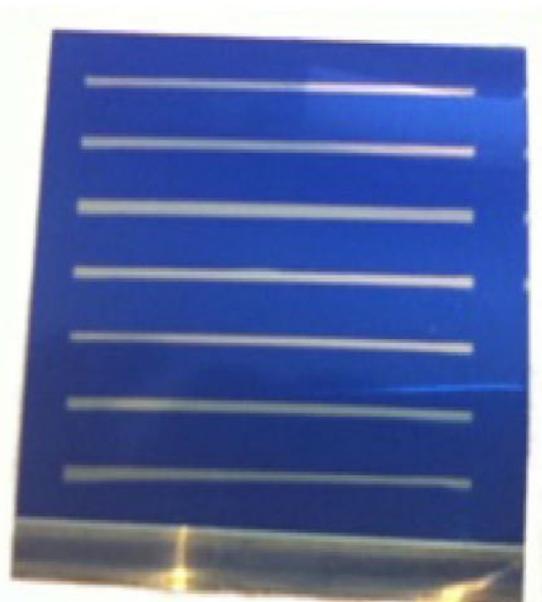


FIGURE 4. PEC electrode with CRCC/CRTP design. The silver lines are Co₃O₄-coated regions (CRCC), and the blue regions are for light absorption (CRTP). The ratio between the areas of CRCC and the CRTP regions can be adjusted to optimize the PEC performance.

CONCLUSIONS AND FUTURE DIRECTIONS

- Fabricate PEC electrodes with the novel CRTP/CRCC design which potentially could extend the durability of the PEC electrodes substantially.
- Experiment with different fabrication methods for PEC electrode preparation with respect to solar cell and ITO deposition conditions, different catalyst and fabrication process, 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 large-area, commercial-size PEC systems and carry out tests in real-life conditions.
- Complete concept design of large-area, low-cost PEC system.

- Perform preliminary techno-economic analysis of the immersion-type PEC system based on the concept design.
- Collaborate with different research groups around the world to further PEC hydrogen generation research and development.
- This project is approaching its final phase, and one of the priorities is to document progress made and lessons learned to position for further research and commercialization in the future.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Xu, L., Deng, X., Abken, A.E., Chen, C., Turner, J., “Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen”, 2013 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation, Oral presentation, Crystal Gateway Marriott, Arlington, VA., May 16, 2013.