

II.D.2 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Subcontractors

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Overall Objectives

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

Fiscal Year (FY) 2014 Objectives

- Focus on immersion-type photoelectrochemical (PEC) systems. Further improve the performance of the photoelectrode with the corrosion-resistant transparent protective (CRTP)/corrosion-resistant conducting catalytic (CRCC) novel layer design in an effort to improve the solar-to-hydrogen (STH) conversion efficiency and the durability to achieve a cost-effective PEC system.
- Complete techno-economic analysis of MWOE's PEC system.
- Explore new kinds of transparent, conducting, and corrosion-resistant (TCCR) coating material to improve the durability of the electrode.

- Work towards commercial-size PEC electrodes and PEC systems, and improve their efficiency and lifetime performance.

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 - Bulk and Interface
- (AF) Materials Durability - Bulk and Interface
- (AG) Integrated Device Configurations
- (AI) Auxiliary Materials
- (AJ) Synthesis and Manufacturing

Technical Targets

This project focuses on the development of low-cost photoelectrode materials and systems using triple junction tf-Si-based PEC cells to split water and generate hydrogen using sunlight.

FY 2014 Accomplishments

- Worked on the novel design for immersion-type PEC cells, where the illuminated side of the PEC electrode is divided into areas coated with a CRTP layer for light absorption and areas coated with a CRCC layer for oxygen generation.
- Investigated the use of electroplated Pt as the CRCC layer in a CRCC/CRTP device.
- Developed an electroplated Ni/Pt bi-layer as the CRCC layer in a CRCC/CRTP device.
- Studied the sputter deposition of thick Co_3O_4 layer in selective regions for the CRCC layer in a CRCC/CRTP device.
- Studied the use of a sputter-deposited SiO_2 layer as the CRTP layer for both a CRCC (Ni/Pt)/CRTP (SiO_2) device and a CRCC (Co_3O_4)/CRTP (SiO_2) device. Studies included the first deposition of CRCC then CRTP, or, the first deposition of CRTP then CRCC layers.
- Investigated the use of TiO_2 as a CRTP layer in a CRCC/CRTP device.
- Performed techno-economic analysis of MWOE's PEC system using DOE's H2A model. The results indicate that with 50-ton-per-day ("TPD") production capacity,

our system has the potential to achieve a hydrogen generation cost of \$2/gasoline gallon equivalent (gge).

- Worked towards commercial-size PEC electrodes; achieved 3.3% STH conversion efficiency for immersion-type PEC cells of 4-inch x 4-inch size using low-cost electroplated Ni hydrogen evolution reaction (HER).
- Worked with different PEC groups around the world to supply both standard and custom-made triple-junction solar cells and to further PEC research. Sent a triple-junction PEC device to Caltech for collaboration.
- Fabricated p-i-n structure solar cells (different from our normal n-i-p device) for PEC application so that the HER would take place on the front surface and the oxygen evolution reaction (OER) would take place on the back surface.



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 solar cells are an ideal material for making cost-effective PEC systems for hydrogen generation. They have the following key features: (1) an open-circuit voltage (V_{oc}) of ~ 2.3 V and an operating voltage around 1.6 V, ideal for water splitting; (2) they can be put on a conducting stainless steel substrate which serves as an electrode; (3) they can be 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 equipment, so that 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 electrolytes, especially under light working conditions. In order to develop a PEC system using triple-junction tf-Si solar cells, we need to develop a coating that can be applied onto the solar cell surface and that has 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 either an OER catalyst (for n-i-p structure) or an HER catalyst (for p-i-n structure).

APPROACH

Three technical tasks were performed during this reporting period:

- Development of TCCR coating for triple-junction tf-Si-based photoelectrodes.
- Understanding and characterization of photo-electrochemistry.
- Development of device designs for low-cost, durable, and efficient immersion-type PEC cells and systems.

RESULTS

Development of a Durable PEC Device Having a CRCC/CRTP Structure

Development of a Pt/Ni Plated Layer as a CRCC

We investigated coating the Pt electrode as a CRCC layer/OER catalyst on top of Co_3O_4 coated on a a-Si triple-junction solar cell, using H_2PtCl_6 as the electrolyte (pH ~ 1) and a Pt mesh as the counter electrode. It is found that corrosion of Co_3O_4 starts after 90 seconds of electrodeposition. A similar plating process on the stainless steel back side as the HER catalyst was successful. When the pH level was increased to ~ 6 , minimal corrosion occurred. We explored the plating of Pt onto Co_3O_4 coated with a-Si with varying plating current densities and varying plating times. A typical plating condition used is 8 mA/cm^2 for 60 sec. In order to form a Pt coating in certain areas for a CRCC layer and expose certain other areas for the application of a CRTP layer, Kapton[®] tapes are applied to areas to prevent Pt plating. A clear coating used in the automotive industry is used to create the CRTP layer region. Certain overlap of CRCC and CRTP areas are designed into the process to avoid undercut corrosion. The effort in generating a CRCC/CRTP structure using plated Pt is challenged by device shunting issues, as the plating process corrodes the transparent conductive oxide layer and the a-Si device. Future effort will be focused on plating deposition of Pt on a-Si films under less acidic conditions.

We then explored the use of plated Ni as a buffer layer prior to the plating of the Pt layer. We investigated plating of Ni films on Co_3O_4 coating a a-Si device using $\text{NiSO}_4/\text{NiCl}_2$ electrolyte with a pH of ~ 3 . A typical plating condition used is 20 mA/cm^2 current for 30-180 sec. Again, Kapton[®] tapes are used to pre-define areas for plating so that the clear coat can be applied to create CRTP regions. The device structure in the CRCC region is stainless steel (SS)/a-Si triple cell/indium tin oxide/ Co_3O_4 /Ni/Pt. Many sets of PEC electrodes with such a structure were fabricated and studied. The results show that a Pt/Ni-coated device is more stable than a Pt-coated device, with an initial STH efficiency of 3.7%.

The performance drops 50% after approximately 5 hours of operation. It is interesting to notice that after the sample is kept overnight in the dark, the STH efficiency is recovered almost back to its initial value (see Figure 1). This repeats for five consecutive days. The mechanism for the degradation of STH efficiency under light and the recovery of efficiency in dark needs to be further understood.

Development of Co₃O₄ as the CRCC Layer

As electroplating an OER catalyst layer exposes the semiconductor under corrosive environment, a vacuum coating process is used to deposit a CRCC layer using sputter deposition. In this approach, we explored the use of a thick Co₃O₄ layer as the OER catalyst. Thick Co₃O₄ is deposited on top of a thin Co₃O₄ layer. A thick Co₃O₄ layer is acceptable even though its transparency is not high, since only a partial area of the device front surface is covered with the thick Co₃O₄ layer. An automotive clear coat, with a thickness of around 0.5 mm, is used as the CRTP layer. Kapton® tape is used to define the areas for clear coat coverage. Alternatively, a sputter-deposited SiO₂ layer is used as the CRTP layer. Certain overlap of CRCC and CRTP areas are designed into the process to avoid undercut corrosion.

Specifically, we deposited Co₃O₄ layers with a thickness in the range of 500 nm and 1,500 nm as the CRCC layer, over the 70 nm Co₃O₄ coating that covers all areas, using magnetron sputter deposition with a power density of around 100 W over a 3” round sputter target. Various devices with such a Co₃O₄ (CRCC) and clear coat (CRTP) combination were fabricated. Initial results show an initial STH efficiency of 3.5% and performance degraded 50% after 55 hours. Studies of the degraded samples show a change of color in the clear coat CRTP layer, suggesting the lifetime of the Co₃O₄ layer may be much longer.

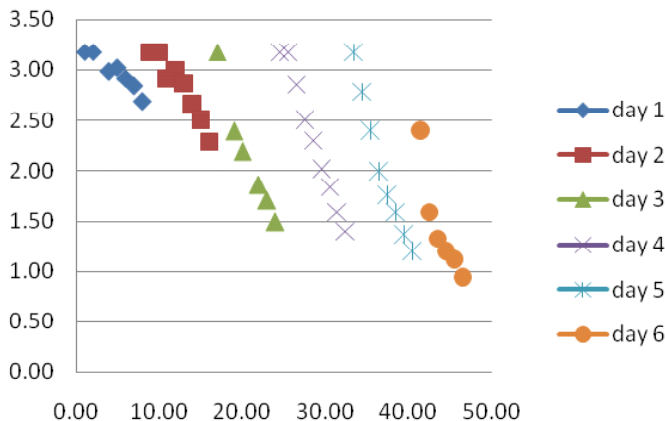


FIGURE 1. STH efficiency (%) as a function of PEC hydrogen production time (in hours) for a CRCC (electroplated Ni/Pt)/CRTP (clear coat) device, showing the recovery of its degradation when the sample is placed in the dark

In order to have a stable CRTP layer, we used magnetron sputtering process to deposit the SiO₂ layer. This is done for both CRCC layers made using electroplated Ni/Pt layers and a sputter-deposited Co₃O₄ layer. For CRCC (Ni/Pt)/CRTP (SiO₂) combination, the initial STH efficiency is around 3.5%, and the STH efficiency drops 50% in about 12 hours, representing an improvement from CRCC (Ni/Pt)/CRTP (clear coat). It is also observed that the STH efficiency recovers to 90% of its initial value after the sample is kept in the dark overnight.

A device structure with CRCC (sputtered-Co₃O₄)/CRTP (sputtered-SiO₂) was also explored. Two approaches were studied: (1) first SiO₂, then Co₃O₄ (the “SiO₂/Co₃O₄” device); and (2) first Co₃O₄, then SiO₂ (the “Co₃O₄/SiO₂” device). Kapton® tapes were used to mask out the area during sputtering so that the deposition would not occur in the unwanted areas. The Kapton® tapes were applied in such a way to allow certain overlap of Co₃O₄ and SiO₂ layers to avoid undercut corrosion. The Co₃O₄/SiO₂ device showed less durability, with the device failing after around 30 hours of PEC operation. The SiO₂/Co₃O₄ device showed an interesting increase in STH efficiency during the first 250 hours of run time, followed by a drop after 300 hours (Figure 2). Further research is needed to understand such an increase in STH efficiency.

Use of TiO₂ as a CRTP Layer

We have previously investigated TiO₂ as a TCCR material. However, the conductivity of TiO₂ limits the performance of the PEC device. In this study, TiO₂ is used as the CRTP layer, where the conductivity is not a requirement due to the unique CRCC/CRTP design. After various baseline depositions on various substrates and various deposition conditions, a device with CRCC (sputtered-Co₃O₄)/CRTP (sputtered-TiO₂) was fabricated. The device has shown

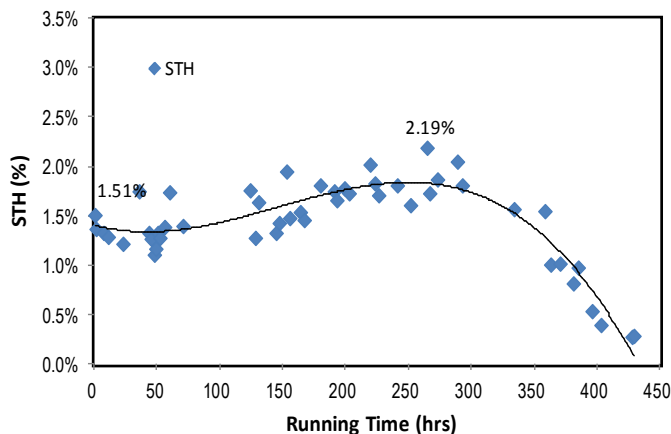


FIGURE 2. STH efficiency (%) as a function of PEC hydrogen production time (in hours) for a CRCC (Co₃O₄)/CRTP (SiO₂) device, showing an increase in STH efficiency during the first 200 hours of operation

improved stability, with performance down to 50% at ~40 hours and with >1% STH efficiency even after 100 hours.

Development of a Large-Area PEC Device

Our most efficient PEC device with STH efficiency of 5.7% was obtained on a 1.5" x 1.5" device with a Co_3O_4 OER catalyst and a Ru HER catalyst. A standard lower-cost Ni HER led to a STH efficiency of around 4.1%. During this year, effort was made to produce a larger-area PEC device, with an active area of 4" x 4". One objective is to see whether a larger device would show reduced performance due to shunting and degradation, or, size-related reduction in performance. Results show that the larger 4" x 4" device exhibits a 3.3% STH efficiency with electroplated Ni as the HER catalyst, which is about 25% lower than the STH efficiency obtained on smaller-size devices. The device lifetime is also reduced to around 40 hours (>1% STH efficiency), which is reduced from the previously obtained 170 hours for smaller devices. Further work is needed to reduce the size dependence of the STH efficiency.

Development of Techno-Economic Analysis Using the H2A Model

During this period, we have performed the techno-economic analysis of MWOE's immersion-type PEC system using the H2A model provided by DOE. The a-Si triple-junction photovoltaic cells, coated with appropriate corrosion-resistant catalyst material and/or protective coatings, are in direct contact with the electrolyte and produce oxygen gas on the anode side and hydrogen gas on the cathode side. Circulation pumps are used to maintain electrolyte concentration and to provide filtration. The evolved hydrogen is compressed, water is allowed to condense, and the stream is passed through an intercooler system to provide cool, dry hydrogen at 300 psi at the factory gate.

The current variable manufacturing costs of triple-junction solar cells on a stainless steel substrate are in the range of \$25/m² (assuming full production of a 25 MW plant), and many technology improvements and the use of alternative materials will lead to a reduction of variable manufacturing cost down to about \$15/m² by 2017 (with expanded capacity). We expect that the corrosion-resistant catalytic coatings and durable protective layers will add some additional cost, but no more than \$15/m², for a total PEC electrode cost less than \$30/m². The electrode will be contained in a polymeric housing. The cost of the housing, electrical terminals, etc. is expected to be approximately \$10/m², which is a reasonable assumption

given the packaging costs of current (2014) commercially available photovoltaic panels. For example, current 8% a-Si modules are reported to have a manufacturing cost around \$0.5/Watt, corresponding to a panel cost of \$40/m² for a fully encapsulated and framed panel with junction box and all other functional components.

We anticipate that some electrodes will require refurbishment/catalyst regeneration every two years, at a cost of \$6/m² (i.e., 20% of the PEC electrode cost).

We also assume 10% STH conversion efficiency and 1,825 hours of standard sunlight per year. Land costs are taken to be \$500/acre, and 50% coverage is assumed due to the use of tilt structures. The plant is designed for 1 TPD, and costs have been scaled to 50 tons/day using a "learning factor" of 0.78 (supported by Williams et al. 2007). Balance-of-system costs are based on a Type 3 PEC example system in a report by Strategic Analysis, Inc. with a projected reduction in installation costs due to modular design.

This calculation demonstrates that by Year 2017, the 1 TPD system will be able to produce hydrogen at a cost of approximately \$5/gge with an electrode lifetime of 2 years before refurbishment. Scaling the system by a factor of 50 using a 0.78 learning factor, to 50 TPD, is projected to reduce costs to under \$2/gge, thus meeting DOE's goal. Table 1 summarizes H2A Model parameters and results stated above.

From the model calculation, about 73% of hydrogen generation cost results from direct capital cost and 26% from operation and maintenance. As shown in Figure 3, the cost of PEC cells accounts for about 37% of total direct capital costs, which is about \$2.2M for a plant of 1 TPD production scale. The second most costly item is installation, and most of it is for the PEC reactors. The installation cost does not depend on the total installed wattage, but on the number of panels installed. If the STH efficiency is improved by 10%, it is

TABLE 1. H2A Model Parameters and Results for MWOE's PEC System

Parameter	2017 (1TPD)	Ultimate Case (50 TPD)
Solar to Hydrogen Conversion Ratio	10%	10%
Plant Size	1 TPD	50 TPD
PEC Electrode Cost	\$30.00/m ²	\$12.80/ m ²
PEC refurbishment/Catalyst Regeneration Cost	\$6.00/ m ²	\$2.56/ m ²
Catalyst Replacement Schedule	2 years (expected)	2 years
Balance of Plant Cost	\$2.8 million	\$1.2 million/1 TPD base
Cost of Hydrogen	\$4.97/gge	\$1.95/gge

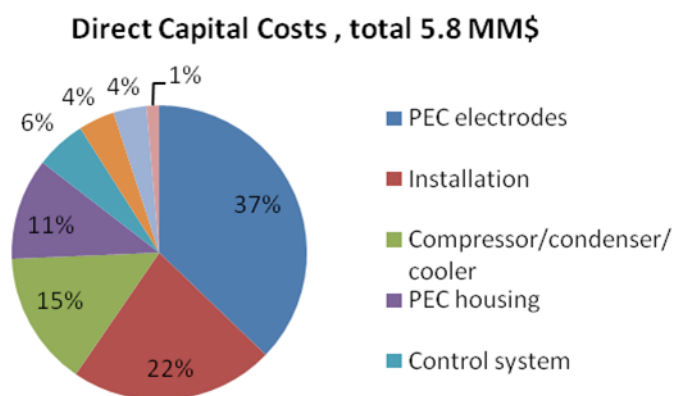


FIGURE 3. The Capital Cost Allocation for a Flat PEC Array (for a production scale of 1 TPD)

expected that the installation cost will drop roughly by 10% because PEC reactors are reduced by 10%. The rest of the capital cost allocation is also shown in Figure 3.

CONCLUSIONS

- The novel design for immersion-type PEC cells where the illuminated side of the PEC electrode is divided into areas coated with a CRTP layer for light absorption and areas coated with a CRCC layer for oxygen generation has shown promising results.
- Techno-economic analysis using DOE's H2A model indicates that MWOE's immersion-type PEC system based on triple-junction a-Si solar cells has the potential to achieve a hydrogen generation cost of \$2/gge.
- Effective TCCR material, oxygen and hydrogen generation catalyst material, and a PEC electrode fabrication method have been developed, and a potentially low-cost PEC system is made possible using these materials and approaches.
- The team collaborated with different research groups around the world to further extend PEC hydrogen generation research and development.
- As this project is approaching its final phase, we documented progress made and lessons learned to position for further research and commercialization in the future.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Xu, L., Deng, X., Abken, A.E., Chen, C., Turner, J., "Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen", 2014 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Oral presentation, Washington Marriott Wardman Park, Washington, D.C., June 19, 2014.