# II.G.10 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen


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- University of Toledo, Toledo, OH
- National Renewable Energy Laboratory (NREL), Golden, CO

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## Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin-film silicon (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.

## Technical Barriers

This project addresses the following technical barriers from 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
(AB) Bulk Materials Synthesis
(AC) Device Configuration Designs
(AD) Systems Design and Evaluation

## Technical Targets

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

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

| Characteristic | Units | DOE 2012 Targets | 2010 Status |
|---|---|---|---|
| Solar-to-Hydrogen Efficiency | % Efficiency | 8 | To Be Determined |
| Durability | Hours | 1,000 | 500 |
| Cost | $ gasoline gallon equivalent (gge) | 2-3 | To Be Determined |
| Photocurrent of TCCR | mA/cm$^2$ | 8 (Project Target) | 37.8 (Cobalt Oxide) |
| Photocurrent of PAS | mA/cm$^2$ | 8 (Project Target) | 0.0334 (Indium Iron Oxide) |
| Deposition Temperature | °C | 250 (Project Target) | 250 |
| Transparency of TCCR | % Transmission | 90 (Project Target) | 90 |
| Voltage Drop Across TCCR/PV-Cell Layer Stack | V | ≤0.15 | To Be Determined |

TCCR = transparent, conducting and corrosion-resistant; PAS = photo-active semiconductor; PV = photovoltaic

## Accomplishments

- A 12"×12" substrate-type PEC cell model was fabricated and has been tested twice so far, however leaks exist in the framework.
- TCCR coatings and $H_2$ evolution catalysts were developed (Task 1).

  - For use as TCCR material $In_2O_3$-$Fe_2O_3$ work was completed and published in the Journal of Materials Research.
  - Large-area electroplating of porous Ni as $H_2$ evolution catalyst has been developed using precursor salts in order to improve and optimize the porous structure of the films for improved performance.
- Facilities for large-area processing of substrate-type PEC cells have been established; processes for PEC components are under development (Task 5).
  - The effect of back reflector on amorphous silicon (a-Si) photoelectrodes was studied and material properties were optimized.
  - The current collection grid for a-Si photoelectrodes, which will incorporate a PAS layer, was optimized considering optimal bus bar thickness.

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## Introduction

This project and its subcontractors are jointly developing the critical technologies required for cost-effective production of hydrogen from sunlight and water using tf-Si-based photoelectrodes. These triple-junction tf-Si-based electrodes include triple cells with either amorphous silicon germanium alloy (a-SiGe) or microcrystalline silicon (µc-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/µc-Si) are used to generate the voltage bias necessary for hydrogen generation. A TCCR coating is deposited on top of the photoelectrode for protecting 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 PAS and the electrolyte.

State-of-the-art a-Si/a-SiGe/a-SiGe and/or a-Si/a-SiGe/µc-Si devices are used as photoelectrodes. The corrosion resistance and PEC mechanisms for a range of oxide-, nitride- and carbide-materials, and II-VI compounds are under investigation. High-performance, durable PEC cells and systems will be developed, optimized and demonstrated in this project.

## Approach

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

- Task 1: Transparent, conducting and corrosion resistant 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.

## Results

Tasks 1 focuses on the preparation of TCCR coatings deposited onto the top of the tf-Si photoelectrode. During this reporting period emphasis was focused on the completion of work on fabricating and characterizing $In_2O_3$-$Fe_2O_3$ films; results and findings were published in the Journal of Materials Research. The TCCR films were deposited using radio-frequency magnetron sputter deposition in argon and oxygen using multiple sputter guns simultaneously. From the completed work, the results indicate that samples made at 250°C with 30 W of In and 100 W of $InFe_2O_4$, and a sputter deposition time of ninety minutes produced optimal results.

Under Task 2 a method for large-area electroplating of porous Ni used as $H_2$-evolution catalyst has been developed. Over the past year work has focused on the addition of precursor salts such as zinc chloride, zinc nitrate, and copper sulfate to the plating solution in order to improve micro- and macro-structures of the porous nickel films. The method uses the co-deposition of Ni and Zn (or another precursor metal) onto the back-side of tf-Si photoelectrodes; after Ni/Zn electrodeposition Zn is leached out leaving a porous Ni-structure behind. At this stage of research, zinc chloride shows the best results, which is shown in Table 2. The goal of electroplated nickel project is to develop materials that meet or exceed the performance of the industry standard of platinum-coated nickel. Table 2 is presented to show results from our latest experiments to improve upon the standard that we have developed previously in our lab.

Task 5 focuses on the development of processing procedures for large-area photoelectrodes. Under this task sintered electrocatalysts employed as anodes in substrate-type PEC cells were developed. Thin film Si-based PEC cells employ preferentially back reflectors for re-directing unabsorbed incident light back through

**TABLE 2.** Current-Voltage Characteristics for Porous Nickel Catalyst Layer using Zinc Chloride as a Precursor Salt

| Voltage (V) | Current @ Electrode Spacing 1 cm | Current Density ($mA/cm^2$) | Current @ Electrode Spacing 2 cm | Current Density ($mA/cm^2$) | Current @ Electrode Spacing 3 cm | Current Density ($mA/cm^2$) |
|---|---|---|---|---|---|---|
| 1.6 | 0.01 | 0.388 | 0.01 | 0.388 | 0.00 | 0.000 |
| 1.7 | 0.02 | 0.775 | 0.02 | 0.775 | 0.01 | 0.388 |
| 1.8 | 0.04 | 1.550 | 0.05 | 1.938 | 0.03 | 1.163 |
| 1.9 | 0.10 | 3.875 | 0.09 | 3.488 | 0.07 | 2.713 |
| 2.0 | 0.24 | 9.300 | 0.18 | 6.975 | 0.15 | 5.813 |
| 2.1 | 0.42 | 16.275 | 0.31 | 12.013 | 0.29 | 11.238 |
| 2.2 | 0.67 | 25.963 | 0.53 | 20.538 | 0.52 | 20.150 |
| 2.3 | 0.94 | 36.425 | 0.85 | 32.938 | 0.80 | 31.000 |
| 2.4 | 1.34 | 51.925 | 1.24 | 48.050 | 1.12 | 43.400 |

the semiconductor layer enhancing the solar-to-hydrogen conversion efficiency of the device. A study was conducted addressing the long-term reliability of the back-reflector: tests conducted in a high humidity environment were used for evaluating the device stability. The fill factor for devices employing different back-reflector films were measured after numerous hours of highly accelerated stress test exposure. The experimental variable in this study is the composition of the back-reflector the tf-Si material is deposited onto. We tested numerous back-reflector compositions and we identified a specific composition providing the best stability under hot and humid conditions, which will translate into improved long-term reliability of PEC cells. We are planning to use this back-reflector for fabricating large-area PEC systems.

## Conclusions and Future Directions

The proposed future work will include:

- Continue optimization of present oxide materials suitable for TCCR coatings:
  - Material class studies will be focusing on $In_2O_3$-$Co_2O_3$.
- Continue optimization of present oxide materials suitable for PAS coatings:
  - Material class studies will be focusing on $Fe_2O_3$-$WO_3$.
- Develop chemical plating for materials suitable for PAS and TCCR coatings for immersion-type hybrid PEC cells.
- Leveraging our resources on building a prototype for large-area (1 ft×1 ft) substrate-type PEC.
  - Design of final substrate-type PEC will employ porous Ni as $H_2$ evolution catalyst electroplated onto the backside of stainless steel substrates with a triple junction a-Si device on the front-side.
  - Long-term reliability studies and solar-to-$H_2$ efficiency measurements will be performed.
- Develop 4"×4" immersion-type PEC cells:
  - Long-term reliability studies and solar-to-$H_2$ efficiency measurements will be performed.
- Improve performance of large-area photoelectrodes.
- Complete techno-economic analysis and energy analysis for the PEC systems for hydrogen production.

## FY 2010 Publications/Presentations

**1.** Ingler Jr., W.B.; Naseem, A.: "Indium Oxide / Indium Iron Oxide Thin Films for Photoelectrochemical Hydrogen Production with a-Silicon Solar Cells" J. Mater. Res. **2010**, 25, 25.

**2.** Fan, Q.H.; Chen, C.; Liao, X., Xiang, X.; Cao, X.; Ingler Jr., W.B.; Adiga, N.; Deng, X.: "Spectroscopic aspects of front transparent conductive films for a-Si thin film solar cells" J. Appl. Phys. **2010**, 107, 034505.

**3.** Fan, Q.H.; Chen, C.; Liao, X.; Xiang, X.; Zhang, S.; Ingler, W.B.; Adiga, N.; Hu, Z.; Cao, X.; Du, W.; Deng, X.: "High efficiency silicon-germanium thin film solar cells using graded absorber layer" Sol. Ener. Mat. Sol. Cells, **2010**, 94 (7), 1300-1302.