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

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

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Fiscal Year (FY) 2011 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.

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 the MWOE project towards the DOE technical targets for PEC production of hydrogen for 2013 is:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE 2013 Target</th>
<th>MWOE 2011 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar-to-Hydrogen Efficiency</td>
<td>% Efficiency</td>
<td>8</td>
<td>5 (4”×12” module)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Substrate-type)</td>
</tr>
<tr>
<td>Durability</td>
<td>Hours</td>
<td>&gt;1,000</td>
<td>1,000 (Cobalt Oxide)</td>
</tr>
<tr>
<td>Cost</td>
<td>$/gasoline gallon equivalent</td>
<td>2-4</td>
<td>To Be Determined</td>
</tr>
<tr>
<td>Photocurrent of TCCR</td>
<td>mA/cm²</td>
<td>&gt;8 (MWOE Target)</td>
<td>37.8 (Cobalt Oxide)</td>
</tr>
<tr>
<td>Photocurrent of PAS</td>
<td>mA/cm²</td>
<td>&gt;8 (MWOE Target)</td>
<td>0.0334 (Indium Iron Oxide) (Down-selected)</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>°C</td>
<td>&lt;250 (MWOE Target)</td>
<td>180-200 (Cobalt Oxide)</td>
</tr>
<tr>
<td>Transparency of TCCR</td>
<td>% Transmission</td>
<td>&gt;90 (MWOE Target)</td>
<td>90 (Cobalt Oxide)</td>
</tr>
<tr>
<td>Voltage drop across TCCR/PV-cell layer</td>
<td>Volts</td>
<td>≤0.15</td>
<td>0.07 (Cobalt Oxide)</td>
</tr>
</tbody>
</table>

TCCR - transparent, conducting and corrosion resistant; PAS - photoactive semiconductor; PV - photovoltaic

FY 2011 Accomplishments

- A 12”×12” substrate-type PEC cell prototype was fabricated and has been tested.
- TCCR were developed (Task 1):
  - From a Go/No-Go meeting Co₃O₄ and In₂O₃-Fe₂O₃ were identified as the major material classes of study moving into the final grant period.
- Facilities and procedures for large-area deposition of Co₃O₄ for use in immersion-type PEC cells have been established and some runs have been carried out with very promising results (Task 1).
• Large-area electroplating of porous Ni as H₂ evolution catalyst has been developed using precursor salts in order to optimize the porous structure of the catalyst films (Task 4):  
  - Many new precursors were studied for Ni electroplating and it was found that using (NH₄)₂SO₄ yielded the best results due to the increased porosity of the Ni layer.

Introduction

In this project, MWOE 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. This approach was down-selected during a Go/No-Go review in December 2010.

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 3: Understanding and characterization of photoelectrochemistry.
- 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 December 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 PAS work (Task 2) will be halted.

Results

Tasks 1 focuses on the preparation of TCCR coatings deposited onto the top of the tf-Si photoelectrode. Many different material classes have been studied, including Fe₂O₃, TiO₂ and WO₃. Co₃O₄ has been identified as a promising candidate for use as a TCCR material: it can be sputtered at temperatures <250°C and provides sufficient transparency if the layer thickness is kept below ~50nm; Co₃O₄ layers are corrosion resistant in alkaline electrolytes which are used in immersion type PEC cells, and these layers provide good electrical conductivity. Co₃O₄ layer (sputtered onto Tec 15 glass) provides a current density of 37.8 mA/cm² at 1.8 V, which is the voltage of the PEC cell under operating conditions. The voltage drop across the TCCR layer for the TCCR/PV cell stack is ~0.07 V. For small-area studies, the TCCR films were deposited using radio frequency magnetron sputter deposition system for argon and oxygen using multiple sputter guns simultaneously. From the completed work, the results indicate that samples made at 250°C with 100 W and a sputter deposition time of 30 minutes produced optimal results. These Co₃O₄ layers have demonstrated 1,000 hours of stability in ~30% KOH as electrolyte at the time of this report. During this reporting period emphasis was focused on fabricating and characterizing Co₃O₄ films and on developing a large-area deposition process for Co₃O₄ using Xunlight’s roll-to-roll deposition system (Figure 1, Figure 2). Xunlight’s roll-to-roll deposition system allows large-area fabrication of PEC electrodes including the deposition of TCCR layer without breaking the vacuum: the equipment simulates processing conditions which are comparable to a manufacturing environment. Process parameters such as sputtering power, line speed and oxygen content in the sputtering gas were optimized in order to achieve the best performing Co₃O₄ TCCR layer and PEC electrodes. Transmission measurements performed on the Co₃O₄ layer deposited onto glass slides showed that reducing the layer thickness by increasing the line-speed to 6”/min improved the transparency of the Co₃O₄ layer significantly. Reducing the sputtering power to 1.5 kW lead to transmission values of 80-100% in a wavelength range between 300-900 nm. The average thickness of these Co₃O₄ layers were ~135 nm.
Noteworthy is that the transmission of the Co\textsubscript{3}O\textsubscript{4} layer does not change with the oxygen flow in the sputtering gas.

Under Task 4, a method for large-area electroplating of porous Ni used as H\textsubscript{2}-evolution catalyst has been developed. Over the past year work has focused on the continued study of the addition of precursor salts such as ammonium sulfate, cobalt chloride, zinc acetate, and zinc sulfate to the Ni plating solution in order to improve micro- and macro-structures of the porous nickel films. The method uses the co-deposition of Ni and a precursor metal (Zn, Co) onto the back-side of tf-Si photoelectrodes; after Ni/Zn or Ni/Co electrodeposition the precursor metal is leached out leaving a porous Ni-structure behind. At this stage of research, using ammonium sulfate as a precursor material shows the best result, which is illustrated in Figure 3. The porosity of the nickel catalyst is shown in Figure 4.

Task 5 focuses on the development of large-area substrate-type PEC systems. Under this task several prototypes for 12”×12” PEC cell assemblies were fabricated. The porous Ni layer used as a hydrogen evolution catalyst was electroplated onto the backside of a tf a-Si device. The surface of the PEC electrode was encapsulated using a lightweight ethylene vinyl acetate-based encapsulation material, which protects the electrode from environmental impact under outdoor operating conditions. The generation of hydrogen and oxygen was confirmed under illumination. At this point of research solar-to-hydrogen efficiency data are not available for 12”×12” PEC systems. However, earlier experiments showed that a solar-to-hydrogen efficiency of 5% has been obtained for a 12”×4” substrate-type PEC system.
Conclusions and Future Directions

The proposed future work will include:

- **Continue optimization of oxide materials suitable for TCCR coatings:**
  - Material class studies will be focusing on $\text{In}_2\text{O}_3$–$\text{Co}_2\text{O}_3$.
  - Optimization work on $\text{Co}_3\text{O}_4$ TCCR will continue.

- **Optimize large-area deposition of $\text{Co}_3\text{O}_4$ TCCR layer in the roll-to-roll system and fabricate large-area $\text{tf Si}$ PEC electrodes with a $\text{Co}_3\text{O}_4$ TCCR coating:**
  - Improve performance of large-area photoelectrodes.

- **Demonstrate 4”×4” and 12”×12” immersion-type PEC systems:**
  - Design of immersion-type PEC systems using triple-junction a-Si photoelectrodes with a TCCR layer.
  - The PEC system will employ porous Ni as $\text{H}_2$ evolution catalyst electroplated onto the backside of the triple-junction a-Si device.

- Long-term reliability studies and solar-to-$\text{H}_2$ efficiency measurements will be performed.

- Complete techno-economic analysis and energy analysis for the PEC systems for hydrogen production.

**FY 2011 Publications/Presentations**
