Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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6 to 9 PM - Grand Ballroom  

Project ID #  
PDP_07_Ingher

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Overview

Timeline

• Project start date: 10/13/2004
• Project end date: 05/31/2010
• Percent complete: 50%

Budget

• Total project funding
  – DOE share: $2,921,501
  – Contractor share: $760,492
• Funding received in FY07: $400,000, $200,000 for NREL
• Funding received in FY08: $500,000
• Funding received for FY09: $0

Barriers

• DOE MYPP Objective for PEC:
  – Develop advanced renewable PEC hydrogen generation technologies.
  – By 2018, verify the feasibility of these technologies to be competitive in the long term.
• Technical Targets:
  – 2013: STH Eff > 8%; Durability >1,000 hours;
  – 2018: STH Eff > 10%; Durability >5,000 hours;
• PEC Hydrogen Generation Barriers - MYPP 3.1.4:
  – Y. Materials Efficiency
  – Z. Materials Durability
  – AA. PEC Device and System Auxiliary Material
  – AC. Device Configuration Designs
  – AD. Systems Design and Evaluation

Partners

• Xunlight Corporation
  - Dr. Anke Abken
• University of Toledo
  - Dr. William B. Ingler Jr.
• National Renewable Energy Lab.
  - Dr. John Turner
Project Objectives (Relevance)

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

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

Year 1:

- Identify materials that meet the performance criteria for transparent, conducting, corrosion-resistant (TCCR) materials, including having stability for up to 300 hours. First round of materials to be produced at 350°C or lower with 70% or greater transparency and at least 3 mA/cm² photocurrent.
- Identify materials that meet the performance criteria for photoactive semiconductor (PAS) materials, including having stability for up to 300 hours. First round of materials to be produced at 350°C or lower with 70% or greater transparency and at least 3 mA/cm² photocurrent.

Year 2:

- Develop TCCR material with a stability up to 700 hours. Second round of materials to be produced at 300°C or lower with 85% or greater transparency and at least 5 mA/cm² photocurrent.
- Develop high-quality PAS material with a stability up to 700 hours. Second round of materials to be produced at 300°C or lower and at least 5 mA/cm² conductivity.
- Go/No-Go Decision Point (this decision point will occur at the end of Year 2 and will coincide with the end of Budget Period 1): Go/no go decision will be based, in part, on progress toward developing TCCR and PAS materials capable of meeting the following performance criteria: ≥700 hours of stability, capable of being fabricated at ≤300°C, ≥85% or greater transparency, and ≥5 mA/cm² photocurrent (TCCR material); ≥700 hours of stability, capable of being fabricated at ≤300°C, and ≥5 mA/cm² photocurrent (TCCR material).

Year 3:

- Develop TCCR material with stability up to 1,000 hours. Second round of materials to be produced at 250°C or lower with 90% or greater transparency and at least 8 mA/cm² photocurrent.
- Develop high-quality PAS material with stability up to 1,000 hours. Second round of materials to be produced at 250°C or lower and at least 8 mA/cm² photocurrent.
- Complete techno-economic analysis and energy analysis for the PEC systems for hydrogen production.
Two approaches are taken for the development of efficient and durable photoelectrochemical (PEC) cells.

An immersion-type PEC cell

A substrate-type PEC cell
Research Tasks (Approach)

• **Task 1:** Transparent, conducting and corrosion resistant coating for triple-junction tf-Si based photoelectrode;  
  [Phase 1: 100%; Phase 2: 50%; Total: 50%]

• **Task 2:** Hybrid multijunction PEC electrode having semiconductor-electrolyte junction;  
  [Phase 1: 100%; Phase 2: 50%; Total: 50%]

• **Task 3:** Understanding and characterization of photoelectrochemistry;  
  [Phase 1: 100%; Phase 2: 50%; Total: 50%]

• **Task 4:** Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems;  
  [Phase 1: 100%; Phase 2: 50%; Total: 50%]

• **Task 5:** Development of device designs for large-area, substrate-type PEC panels;  
  [Phase 1: 100%; Phase 2: 50%; Total: 50%]
Technical Accomplishments - Task 1

• Study of In$_2$O$_3$-Fe$_2$O$_3$ as a TCCR material.

• Research has focused on maximizing the long-term stability and current density of the film while maximizing transparency.

• The best sample so far was made at 275°C, 100 W Fe$_2$O$_3$ and 30 W In in 6% oxygen gas for two hours of deposition, and had an increasing current density of 4.32 mA/cm$^2$ at 1.6 V after 28 cycles.

• This was part of a relatively small region of stability in the parameter space including temperatures from 250°C to 275°C and oxygen concentrations from 5% to 6%.

• Stable current density appears to peak for total flow of around 11 sccm during deposition, at least for samples made at 250°C.

• Current study on In$_2$O$_3$-InFe$_2$O$_4$.

• Optimized conditions being used for deposition on 4” × 4” substrates.
Technical Accomplishments - Task 1

- Experimental data and deposition parameters of samples deposited onto TEC-15 (SnO$_2$:F) glass, with data from cyclic voltammetry and UV-Vis spectro-photometry. 'S' denotes stable, 'U' denotes unstable. Samples marked with a star (*) were made with a new iron oxide target.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (°C)</th>
<th>In (W)</th>
<th>Fe$_2$O$_3$ Ar (sccm)</th>
<th>Ar/O$_2$ (%)</th>
<th>Total Flow (sccm)</th>
<th>Dep. Time (min)</th>
<th>Stability</th>
<th>1st cycle Cycles (mA/cm$^2$)</th>
<th>28 cycles Cycles (mA/cm$^2$)</th>
<th>Eg (eV)</th>
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<td>2.67</td>
<td>5.005%</td>
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<td>730</td>
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<td>100</td>
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<td>3.43</td>
<td>6.002%</td>
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<td>U 0</td>
<td>16.5</td>
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<td>6.002%</td>
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<td>U 0</td>
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<td>5.005%</td>
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<td>5.005%</td>
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<td>11.08</td>
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<td>S 8</td>
<td>9.33</td>
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</table>
Technical Accomplishments - Task 1
Technical Accomplishments - Task 2

- Fabrication of triple-junction a-Si/a-SiGe/a-SiGe solar cells (Photoelectrodes)
- Fabrication of triple-junction a-Si/a-SiGe/nc-Si solar cells (Photoelectrodes)

- Effect of GeH$_4$/Si$_2$H$_6$ flow ratio effect on the performance of a-SiGe solar cells was studied.

- I-V curves of a-SiGe solar cells deposited with various GeH$_4$/Si$_2$H$_6$ flow ratios are shown:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>GeH$_4$/Si$_2$H$_6$ Flow ratio</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (I-V)</th>
<th>FF (%)</th>
<th>EFF (%)</th>
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<tr>
<td>GD2590</td>
<td>0</td>
<td>0.99</td>
<td>11.34</td>
<td>70.14</td>
<td>7.89</td>
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<td>GD2593</td>
<td>0.8</td>
<td>0.90</td>
<td>14.97</td>
<td>59.24</td>
<td>7.95</td>
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<tr>
<td>GD2572</td>
<td>1.1</td>
<td>0.87</td>
<td>16.95</td>
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<td>9.05</td>
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<tr>
<td>GD2571</td>
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<td>0.83</td>
<td>17.01</td>
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<td>0.78</td>
<td>18.19</td>
<td>58.53</td>
<td>8.35</td>
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</table>
Technical Accomplishments - Task 2

- The effect of different plasma treatments on the photovoltaic parameters of a-Si solar cells on SS substrates was studied;

<table>
<thead>
<tr>
<th>Sample No</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
<th>plasma</th>
</tr>
</thead>
<tbody>
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<td>3mw176(A)</td>
<td>0.924</td>
<td>11.004</td>
<td>53.459</td>
<td>5.433</td>
<td>No any</td>
</tr>
<tr>
<td>3mw179(B)</td>
<td>0.924</td>
<td>11.179</td>
<td>45.845</td>
<td>4.738</td>
<td>Ar + O</td>
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<tr>
<td>3mw181(C)</td>
<td>0.925</td>
<td>10.703</td>
<td>59.608</td>
<td>5.904</td>
<td>Ar</td>
</tr>
<tr>
<td>3mw182(D)</td>
<td>0.919</td>
<td>10.881</td>
<td>63.301</td>
<td>6.332</td>
<td>H</td>
</tr>
</tbody>
</table>

The IV-curves show the effect of plasma pretreatment on the I-V curves of a-Si solar cells deposited on stainless steel substrates;

(a) without any plasma treatment,  
(b) with Ar (95%) + O (5%) plasma,  
(c) with Ar (100%) plasma, and  
(d) with H (100%) plasma treatment.
Technical Accomplishments - Task 4

• The effect of electroplating parameters on ZnO back reflector coatings was studied;

Electroplating set-up

- Parameter:
  - Temperature
  - Nylon Mesh
  - ZnO Thickness

• The total and diffused reflectance of electroplated ZnO layer deposited at different deposition temperatures was measured.

• The blue curves show a reference sample with sputtered ZnO/Ag layer.
Technical Accomplishments - Task 4

- The graphs show the effect of different processing parameters (current density, Nylon mesh) and the impact of EP-ZnO layer thickness on diffused reflectance;

- Increasing the EP-ZnO thickness increases the diffused reflectance and surface roughness;
Technical Accomplishments - Task 5

- Work on developing photoassisted electrochemical process for shunt passivation focuses on metal salt selection used as electrolyte.

- Metal salt A was previously used for shunt passivation of PEC devices (no back reflector). Passivating with salt A requires using a low pH of the electrolyte, which might lead to corrosion when back reflectors (Al/Ag/ZnO layer stacks) are used.

- As an alternative metal salt B was tested. The low light open circuit voltage (LLV$_{OC}$) improves for passivation conditions using 5-7V for 20 sec.

- Work on shunt passivation using metal salt B,C for samples with back reflectors from Xunlight’s 2 MW roll-to-roll (RTR) system is in progress. Salt B,C contain the same metal cation but a different anion; they are less corrosive than salt A and allow environmental friendly disposal. Although promising results for salt B have been achieved it is not as effective as using salt A.
Technical Accomplishments - Task 5

• A method for ink-dot application was developed; the method will support lead to reliability improvements of substrate-type PEC cells.

• A method for increasing the durability of the metal foil adhesion to the silver current collection grid was developed. The robot is used to apply ink dots, or “tabbing”, along a central metal foil conductor.

• The following procedure was used for the ink-dot application:
  ➢ The operator will load a single 11” × 17” PV cell into the robot and engage a vacuum hold-down plate mechanism. The robot dispenser arm will be aligned to the start and stop points.
  ➢ Then, all ink application points in between are calculated and the program runs accordingly.
  ➢ After the robot tabber runs its program the ink tabbing is cured in a conveyor oven.

Device after ink dot application

Fisnar ink tabbing robot
Collaborations

Partners:

- NREL (Federal):
  NREL is working on improved understanding of PEC process for a-Si based photoelectrodes (in collaboration with Dr. John Turner).

- University of Toledo (Academic):
  UT is developing TCCR coatings, H₂ catalysts for immersion and substrate-type PEC cells. Developing prototype 1ft × 1ft PEC devices with UT.

Technology Transfer:

- NREL:
  NREL is supporting with device measurements on a-Si. a-SiGe, etc. solar cells (device characterization, stability testing etc.).

- University of Toledo:
  UT is integral as they finished another DOE H₂ grant that was on basic research transferred to this project. UT is continuing development of the material work they started on the previous grant.
Proposed Future Work

• Task 1: Continue study and optimization of In$_2$O$_3$-InFe$_2$O$_4$ TCCR coatings on solar cell surfaces.

• Task 2: Develop chemical plating for II/VI-semiconductors (CdS) as PAS & TCCR coating for immersion-type hybrid PEC cells.

• Task 4: Supported by University of Toledo 4” × 4” immersion-type PEC cells will be developed.

• Task 5: Supported by University of Toledo a 1ft × 1ft substrate-type PEC cell will be developed.
  - Long-term reliability studies and measurements will be done.

• Task 5: The shunt passivation process will be improved focusing on salt studies used as electrolytes.
Project Summary

• **Relevance:** Addresses DOE program objectives, specifically high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.

• **Approach:** An immersion-type photoelectrochemical cell where the photo-electrode is immersed in electrolyte and a substrate-type photo-electrochemical cell where the photoelectrode is not in direct contact with electrolyte.

• **Technical Accomplishments and Progress:**
  Demonstrated a 4” × 12” substrate-type PEC cell with 12” × 12” model under development.
  Have secured external funding for development of roll-to-roll unit for a-Si solar cell deposition at Xunlight.

• **Technology Transfer/Collaborations:**
  Active collaboration with UT towards commercialization of research done at MWOE and Xunlight.

• **Proposed Future Research:**
  Will leverage research done at UT to develop substrate-type PEC. Computational components at UT and NREL will be used for improved identification of material classes for sputter deposition of PAS and TCCR layers.