Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Overview

Timeline

- Project start date: 10/13/2004
- Project end date: 3/1/2009
- Percent complete: 33%

Budget

- Total project funding
  - DOE share: $2,921,501
  - Contractor share: $760,492
- Funding received in FY05: $100,000
- Funding received in FY06: $200,000
- Funding received in FY07: $400,000, $200,000 for NREL
- Funding for FY08: $500,000

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

- University of Toledo
  - Dr. Xunming Deng
- National Renewable Energy Lab.
  - Dr. John Turner
Objectives

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

• To develop and demonstrate, at the end of the 3-year program, tf-Si based PEC photoelectrodes and device designs with the potential to achieve systems with 10% solar-to-hydrogen efficiency with a durability of 5,000 hours by 2018.
Milestones

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 cells.

An immersion-type PEC cell

A substrate-type PEC cell
Research Tasks

• **Task 1:** Transparent, conducting and corrosion resistant coating for triple-junction tf-Si based photoelectrode [Phase 1: 100%; Total: 33%]

• **Task 2:** Hybrid multijunction PEC electrode having semiconductor-electrolyte junction [Phase 1: 100%; Total: 33%]

• **Task 3:** Understanding and characterization of photoelectrochemistry [Phase 1: 100%; Total: 33%]

• **Task 4:** Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems [Phase 1: 100%; Total: 33%]

• **Task 5:** Development of device designs for large-area, substrate-type PEC panels [Phase 1: 100%; Total: 33%]
Approaches for PEC electrodes

Two separate approaches for the development of high-efficiency and stable PEC photoelectrode for the immersion-type PEC cells:

Approach 1A (Task 1):
• Develop triple junction tf-Si photoelectrodes covered with a transparent, conductive, and corrosion resistant (TCCR) protection layer

Approach 1B (Task 2):
• Develop hybrid, triple junction photoelectrodes with a semiconductor-electrolyte junction as the top junction and tf-Si alloys as the middle and bottom junctions
Major Activities under Task 1 and 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)
- Construction and operation of a 3 ft × 3 ft chamber for fabrication of thin film silicon solar cells on stainless steel substrate
- Deposition of transparent, conducting and corrosion-resistant coating using sputtering
- Optimization of a sputter system with four linear targets (4”x15”), capable of making TCCR films on 1ft × 4ft substrates.
Large area tf-Si solar cell are readily available for immersion-type PECs

1ft x 3ft a-Si Photoelectrodes from new PECVD system
tf-Si Deposition Chambers

A second new PECVD system, capable of making 3 ft x 3ft photoelectrodes have been designed and constructed. Amorphous Si photoelectrodes (solar cells) have been fabricated in this new system.
1’ x 3’ single junction amorphous silicon based photo cells were fabricated. I-V characteristics of 0.25 cm² single-junction amorphous silicon based photo cells taken from these larger samples, measured with AM1.5 illumination. One of the cells incorporates back-reflecting layers. The cells show good photoelectric conversion efficiency and fill factor. Although these cells are single junction, this is an important step towards fabricating multijunction, semiconductor-electrolyte junction photoelectrodes.
Task 3: Understanding and Characterizing PEC

- Several efforts are on going under this task.
  - NREL team is currently developing improved understanding of PEC process for a-Si based photoelectrodes in collaboration with John Turner.
  - An outdoor solar testing facility has been utilized and used for outdoor testing of PEC panels for long-term stability and output.
Task 4: Immersion-type PEC cell

- Focus on Task 4 is on the construction and optimization of deposition system that will be used for making large-area photoelectrode for immersion-type PEC cells.
- Designed and constructed a system capable of making 3ft × 3ft photoelectrodes.
- Improved deposition uniformity over large area.
- Focused on electrodeposited ZnO that will be used for BR optimization.
- Continued the design and optimization of immersion-type PEC cells.
Electrodeposited ZnO Films

- **Film quality improvement of electrodeposited ZnO**
  - One of the main drawbacks with tank electrodeposition of ZnO is the non-uniform deposition. For optoelectronic applications such as photovoltaic back reflectors and TCCRs a higher film quality is expected. This problem has been addressed by two different approaches.

- **Modifications to Bath**
  - The objective of this approach was to control the ionic reactions. Two main processes that were run,
    - Increase ionic conductivity by adding KCl
      - No significant improvement
    - Change pH by using HNO₃ or KOH
      - pH 5.4 to 5.7 showed improvement in uniformity but the solution becomes unstable
  - X-ray diffraction measurements verify that for all these bath conditions we get uncontaminated ZnO films.
XRD spectra for various bath conditions to produce electrodeposited ZnO films

The advantages of this new method:
• Uniform plating
• Edge effect is minimum
• Uniform temperature distribution
• Possibility to be done at higher temperatures
  • Zn(OH)$_2$ to ZnO is favorable at higher temperatures
• Need less solution to run experimental run
Quantum Efficiency with Electro-deposited ZnO used in the Back Reflector

- Quantum efficiency plots for three solar cells with ZnO electrodeposited at 2, 3, and 4 mA/cm²
Task 5: Fabrication of Substrate-Type PEC cells

- Focus under this task has been on establishing facilities to make substrate-type PEC cells in large area.
- Improved screen-printing techniques.
- Designed and built a fabrication facility for making substrate-type PEC electrodes.
- Designed, developed and constructed a photo-assisted electrochemical shunt passivation system to remove shunts and shorts in the photoelectrodes.
- Long-term testing of substrate-type modules.
Improved Equipment for Screen-Printing Techniques

Grids are 1 mil thickness for adequate conductivity
Investigation into cheaper electrocatalyst materials

• The sintered nickel-cobalt oxide catalyst. The left and right side photos are 20× magnification of the porous structure of the catalytic surface.

• Fabrication of 12” × 12” substrate-type solar cells is in progress. Optimization of triple junction amorphous silicon cell for use in the substrate PEC cell is also under progress.
Degradation in photoelectrochemical cell was observed after 140 days. The measurements were made at 88 to 95 mW/cm² solar radiation.
Future Work

• Continued study into optimization of present oxide materials – Identify classes of materials most promising to phase 2 goals.
  – Material classes are focusing on iron oxide and titanium dioxide material classes with various dopants such as antimony and indium for iron oxide and nitrogen and carbon for titanium dioxide.
  – Deposition of oxides under higher power and with metallic targets to improve stability and oxide structure study new materials beyond present set.
• Leveraging our resources on a substrate-type PEC as all the materials required to build one on site are now available – large area solar cell, electrolyzers.
  – Production of final module design (substrate-type PEC) with electroplated nickel on back of stainless steel with triple junction a-Si on front.
• Improvement in voltage and efficiency of large area solar cells.
Project Summary

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

- Approach: An immersion-type photoelectrochemical cells where the photoelectrode is immersed in electrolyte and a substrate-type photoelectrochemical cell where the photoelectrode is not in direct contact with electrolyte.

- Technical Accomplishments and Progress: Demonstrated a 4” × 12” substrate-type PEC 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 integrate computational components at UT and NREL to better identify classes of materials to sputter for PAS and TCCR layers.