Photoelectrochemical System for Hydrogen Generation (PHESHYG)

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Physical Optics Corporation
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## Overview

### Timeline
- Start: 06/20/2007
- End: 08/14/2010
- ~75% Completed

### Barriers
- Y: Materials Efficiency
- AC: Device Configuration Designs
- AD: Systems Design and Evaluation

### Budget
- Total Project Funding: $849,996
  - DOE share: $849,996
  - Contractor share: $0
- Funding received in FY09: $359,355
- Funding for FY10: $389,644

### Partners
- National Renewable Energy Lab (NREL)
- PEC Working Group
Relevance - Objectives

**Project Objective:** To demonstrate electrodeposited II-VI photoelectrodes as viable, low cost, materials for solar hydrogen generation and design a prototype reactor system.

**2010 Objective:** Assemble prototype photoelectrochemical (PEC) cell array based on II-VI photoelectrodes along with cost analysis.

### DOE 2007 MYPP TARGETS

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>2013 Target</th>
<th>2018 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Usable Band gap</td>
<td>2.3 eV</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>Chemical Efficiency (EC)</td>
<td>10 %</td>
<td>12%</td>
</tr>
<tr>
<td>Solar-to-Hydrogen Efficiency (STH)</td>
<td>8 %</td>
<td>10%</td>
</tr>
<tr>
<td>Durability</td>
<td>1000 hrs.</td>
<td>5000 hrs.</td>
</tr>
</tbody>
</table>

**How approach relates:**
- Narrow band gap II-VI materials
- Use of multilayers and p-type materials
- System level design and fabrication

PEC-based Solar Reactor Array
## Relevance - Barriers

<table>
<thead>
<tr>
<th>Barrier</th>
<th>POC’s Approach</th>
<th>Challenge</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Y: Materials Efficiency</strong></td>
<td>Address efficiency barrier by using narrow band gap II-VI materials CdS ($E_g = 2.3$ eV), ZnTe ($E_g = 2.3$ eV), and CdSe ($E_g = 1.7$ eV)</td>
<td>Overcoming reduced efficiency due to use of electrochemical deposition (polycrystalline film), which inhibits carrier transport</td>
</tr>
<tr>
<td><strong>AC: Device Configuration Designs</strong></td>
<td>Developing “multijunction” structure to allow use of both narrow band gap absorbing material and wider band gap, more durable materials</td>
<td>Engineering a high quality junction interface with solution processing techniques</td>
</tr>
<tr>
<td></td>
<td>Electrochemical deposition (solution processing) is a scalable, cost-effective technique that is widely used in manufacturing</td>
<td></td>
</tr>
<tr>
<td><strong>AD: Systems Design and Evaluation</strong></td>
<td>Designing and fabricating a prototype scale reactor (~1 m² area) to explore materials, components, geometries, and other considerations necessary to productize PEC cells</td>
<td>Fabricating a large number of good quality photoelectrodes</td>
</tr>
<tr>
<td></td>
<td>Applying economic modeling to estimate cost of hydrogen from reactor cell at production level</td>
<td>System level testing</td>
</tr>
</tbody>
</table>
## Approach - Milestones

### Overall technical approach: Electrodeposited II-VI Materials

<table>
<thead>
<tr>
<th>Item</th>
<th>Action</th>
<th>Result/Comment</th>
</tr>
</thead>
</table>
| **2009 Milestone:**     | downselected II-VI materials to 2 combinations (one n-type, one p-type) | (1) CdS(n)/ZnS(n) multijunction: strong absorption in CdS increases efficiency while ZnS increases durability  
(2) ZnTe (p-type): use of low band gap p-type material with promise for durability by eliminating photocorrosion |
| **2010 Planned Milestones:** | (1) Design and fabrication of PEC cell reactor array including materials evaluation and cost analysis  
(2) Demonstration of system test results | (1):  
- 25% complete  
- Timeline depends on photoelectrode fabrication  
(2): Developing collaborations for system tests |
| Relation to past efforts: | - II-VI materials approach                                             | - Approach targets weaknesses of II-VI materials previously studied                                                                       |
| Relation to current efforts: | - II-VI materials approach  
- PEC Reactor Design                                                   | - Complements current work on oxides, III-V, multijunctions  
- Supplements work on system level studies and economic analysis |
PHESHYG Phase II Objectives: (from proposal)

Objective 1. Optimization and Refinement of the A2B6 Semiconductor PE Materials (100% complete)

Objective 2. Characterization of the A2B6 Semiconductor-Based PE Materials (80% complete)

Objective 3. Systematic Reorganization of the A2B6-Based Photoelectrode and Development of Large-Area PE Panels (80% complete)

Objective 4. Development of Scaled-up Prototype of PHESHYG Cell (80% complete)

Objective 5. Integration of the Scaled-up Prototype PHESHYG System, and Evaluation of Its Performance (25% complete)

Objective 6. Evaluation of Application Scenarios for the PHESHYG Technology (70% complete)
Technical Accomplishments:

Electrodeposition of CdS/ZnS Bilayer on ITO

- Fabricated bilayer CdS/ZnS films using single step ED process. (Obj. 1)

- Type II heterojunction allows carrier transport from CdS absorption layer to ZnS capping layer

- Weight ratio determined via EDX shows increased proportion of Zn over time
Technical Accomplishments:

UV-Vis Absorption Measurements

\[ A \sim \frac{1}{E_g - h\nu} \]

- Linear coefficient of absorption
- \( E_g \): band gap energy
- \( h\nu \): energy of photon

\[
(Ah\nu)^2 = C'(h\nu - E_g)
\]

- Reduced band gap compared to bulk CdS (2.4 eV) attributed to reduced strain in chemically deposited film.

CdS/ZnS films show band gap in range of DOE target 2.0-2.3 eV. (Obj. 2)
Technical Accomplishments:

Cyclic Voltammetry Substrate Study

Films grown on ITO Substrates

Films grown on Ti Substrates

- Films can be grown on variety of conducting substrates
- CdS growth takes place before Cd2+ reduction, mediated by H+ reduction
- As a result, substrates with slow H+ reduction kinetics slow rate of film growth
- Selecting ITO and Ti for testing due to reduced kinetics mitigating effect of pinholes to substrate during testing

CV of CdS/ZnS Electrodeposition Solution

High overpotential for H+ reduction slows growth, limits substrate effects. (Obj. 1&2)
Technical Accomplishments:

3-electrode J-V and Photocurrent Measurements

Open Circuit Potential Measurement (vs. Ag/AgCl in 0.1 M H2SO4)

<table>
<thead>
<tr>
<th></th>
<th>OCP dark</th>
<th>OCP light</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP dark</td>
<td>-0.069 V</td>
<td>-0.166 V</td>
<td>-0.097 V</td>
</tr>
</tbody>
</table>

- n-type behavior
- Vfb measurement still needed (light intensity here insufficient to flatten bands)

3-electrode J-V (37 uW/cm², Xe lamp)

• estimated efficiency $\eta_{STH} = 0.94\%$
  (with applied bias = 0.4 V vs. Ag/AgCl)

Biased Photocurrent (38 mW/cm², Xe)

Preliminary OCP, JV, and photocurrent measurements. Show $\eta_{STH} \sim 1\%$. (Obj. 2-3)
Technical Accomplishments:

Stability of as-deposited and Annealed CdS/ZnS

- Lifetime by extrapolation ~ 12 minutes under ~ 5 suns.
- Possibly due to non-uniform ZnS layer

Initial measurements of stability and annealing, improvements underway. (Obj. 2)
## Technical Accomplishments:

### ZnTe photoelectrode fabrication

<table>
<thead>
<tr>
<th>Property</th>
<th>Value/Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Band gap energy, $E_g$(eV)</strong></td>
<td>~2.20</td>
</tr>
<tr>
<td><strong>Type of Conductivity</strong></td>
<td>$p$</td>
</tr>
<tr>
<td><strong>Type of PE</strong></td>
<td>Photocathode</td>
</tr>
<tr>
<td><strong>Stability</strong></td>
<td>photo-corrosion may be stable as cathode</td>
</tr>
</tbody>
</table>

Stoichiometry from EDX:
- Zn: 55%, Te: 45% (+/- 15%)
  - *sensitive to deposition conditions*

XRD indicates primarily cubic ZnTe (squares) with small amount of hexagonal Te (triangles).

Fabricated ZnTe photoelectrodes and verified composition. (Obj. 1).
Testing in progress.
Technical Accomplishments:

PEC Reactor Design: 1st Generation

Sealed container with PEC
(electrolyte, counterelectrodes, photoelectrodes)

Benefits:
- Easy to scale-up
- Modular
- Novel approach
- Build using COTS

Individual photoelectrode
Same in a mount/connector
Mounted photoelectrode with seal

Outlet with H₂ delivery
Outlet with O₂ delivery

Created design based on commercially available components for prototyping. (Obj. 4)
Technical Accomplishments:

PEC Reactor 1st Generation Testing

Scaled Down Design

Fabricated 1st Generation Design

Test apparatus used electrolysis to generate H2/O2 in electrode locations

Design Improvements Identified:

- Reduce number of seals
- Increase counterelectrode area
- Review material selection
- Keep modular design and scalability

Fabricated and tested 1st design and identified key modifications needed. (Obj. 4)
Technical Accomplishments:

PEC Reactor 2\textsuperscript{nd} Generation Design

- Modular
- Scalable
- Less seals needed
- Fabricated Prototype

Designed and fabricated 2\textsuperscript{nd} generation design based on results from 1\textsuperscript{st} tests. (Obj. 4-5)
Technical Accomplishments:

PEC Reactor Materials Testing

Material Weight Loss/Gain and in KOH (28% 4 weeks)

<table>
<thead>
<tr>
<th>Bottle #</th>
<th>Material</th>
<th>Initial Weight (g)</th>
<th>Final Weight (g)</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-empty-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>PVC</td>
<td>0.961</td>
<td>0.965</td>
<td>0.416</td>
</tr>
<tr>
<td>3</td>
<td>Nickel</td>
<td>0.455</td>
<td>0.452</td>
<td>-0.659</td>
</tr>
<tr>
<td>4</td>
<td>Aluminum 6061</td>
<td>2.375</td>
<td>0</td>
<td>-100% (dissolved)</td>
</tr>
<tr>
<td>5a</td>
<td>Neoprene</td>
<td>1.233</td>
<td>1.235</td>
<td>+0.1622</td>
</tr>
<tr>
<td>5b</td>
<td>EPDM</td>
<td>0.05735</td>
<td>0.057</td>
<td>-0.61</td>
</tr>
<tr>
<td>6</td>
<td>Acrylic</td>
<td>0.966</td>
<td>0.970</td>
<td>+0.141</td>
</tr>
<tr>
<td>7</td>
<td>18-8 Stainless Steel</td>
<td>7.845</td>
<td>7.857</td>
<td>+0.1529</td>
</tr>
<tr>
<td>8</td>
<td>Viton® Fluoroelastomer</td>
<td>1.311</td>
<td>1.356</td>
<td>+3.432</td>
</tr>
<tr>
<td>9</td>
<td>Acrylic + epoxy</td>
<td>1.830</td>
<td>1.841</td>
<td>+0.601</td>
</tr>
<tr>
<td>10a</td>
<td>Nylon (hex nut)</td>
<td>0.846</td>
<td>0.856</td>
<td>+1.182</td>
</tr>
<tr>
<td>10b</td>
<td>Nylon 6/6 (screw)</td>
<td>0.224</td>
<td>0.233</td>
<td>+4.01</td>
</tr>
<tr>
<td>11a</td>
<td>Polyethylene (black)</td>
<td>0.415</td>
<td>0.416</td>
<td>+0.241</td>
</tr>
<tr>
<td>11b</td>
<td>Polyethylene (white)</td>
<td>2.003</td>
<td>2.010</td>
<td>+0.349</td>
</tr>
<tr>
<td>12a</td>
<td>PC/ABS (black)</td>
<td>1.797</td>
<td>1.846</td>
<td>+2.726</td>
</tr>
<tr>
<td>12b</td>
<td>ULTEM (creamy white)</td>
<td>0.504</td>
<td>0.519</td>
<td>+2.972</td>
</tr>
</tbody>
</table>

Reactor component testing in KOH identifies acrylic as viable component. (Obj. 4-5)

- Conducted reactor material analysis based on 1st generation testing conclusions
- More data analysis currently underway including H2SO4 tests

Discoloration

Material
Untested
Tested

[Image of material samples]
Technical Accomplishments:

PEC Reactor System Cost Analysis

<table>
<thead>
<tr>
<th>CdS/ZnS PE materials of 1 cm² (1 m² unit = 400 small PE cells 5x5 cm² each)</th>
<th>NRE² ($K)</th>
<th>Production Cost³ ($/unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Quantity 100 m²</td>
</tr>
<tr>
<td>Raw Materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td>COTS</td>
<td>$1.15</td>
</tr>
<tr>
<td>ITO glass</td>
<td>COTS</td>
<td>$3.20</td>
</tr>
<tr>
<td>Glassware</td>
<td>COTS</td>
<td>$0.15</td>
</tr>
<tr>
<td>Potentiostats (lifetime of 10 years)</td>
<td>COTS</td>
<td>$0.45</td>
</tr>
<tr>
<td>Sub Total</td>
<td>-</td>
<td>$4.95</td>
</tr>
<tr>
<td>Labor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthesis processing</td>
<td>20</td>
<td>$0.83</td>
</tr>
<tr>
<td>Characterization/testing labor</td>
<td>10</td>
<td>$0.50</td>
</tr>
<tr>
<td>Sub Total</td>
<td>30</td>
<td>$1.33</td>
</tr>
<tr>
<td>TOTAL ($/m²)</td>
<td>30</td>
<td>$6.28</td>
</tr>
</tbody>
</table>

Initial H₂ cost estimate using above values ($/m²) with $\eta = 1\%$ and lifetime = 5 yrs. and the similar parameters to James et al. (2)

- Cost of hydrogen is: $14.34 - $15.02/kg despite low cost/m² due to low efficiency.


(2) 1 ton per day plant, excludes O&M costs, cost at plant gate (well-to-gate)
Collaborations

DOE H2 Program:

• Member of PEC Hydrogen Working Group
• John Turner (NREL-federal) : subcontracting for photoelectrode materials testing in progress
# Proposed Future Work

<table>
<thead>
<tr>
<th>Item</th>
<th>Action</th>
<th>Comment</th>
</tr>
</thead>
</table>
| **2010 Planned Milestones:** | (1) Design and fabrication of PEC cell reactor array including materials evaluation and cost analysis  
(2) Demonstration of system test results | (1) : - 25% complete  
- Timeline depends on photoelectrode fabrication  
(2): Developing collaborations for system tests |
| **2010 Selected Objectives:**  
- Tests of ZnTe photoelectrodes  
- Full study of sample annealing | - Particular emphasis on characterizing and improving stability through study of ZnS - CdS interface properties  
- Need stronger collaboration for help testing samples |
| Obj. 4: Development of Scaled-up Prototype of PHESHYG Cell | - Perform reactor materials stability using other electrolytes  
- Select materials for next prototype | - Materials selection directly influences reactor cost, lifetime, and O&M  
- Selection will be based on resilience to electrolyte, UV/Vis transparency, H2 permeability and cost |
| Obj. 6: Evaluation of Application Scenarios for the PHESHYG Technology | - Refine H2 cost analysis using actual materials selected for PHESHYG reactor | - Build on work by B. James and H2A model |
Summary

Relevance:
- Demonstrate electrodeposited II-VI photoelectrodes as viable (i.e. meet band gap, and stability requirements), low cost, materials for solar hydrogen generation and design a prototype reactor system.

Approach:
- Downselected II-VI materials to 2 combinations: CdS/ZnS bilayer (n/n), ZnTe p-type

Accomplishments:
- Fabrication and characterization of CdS/ZnS and ZnTe films
- Absorption of CdS/ZnS structure acceptable (Eg ~ 2.2 eV)
- CdS/ZnS efficiency ~ 1 % with applied bias, 12 min. lifetime; optimization required
- Constructed and tested 1st generation PEC reactor cell using COTS components
- Designed and fabricated 2nd generation reactor based on test results
- Preliminary economic analysis performed showing strong dependence of cost on efficiency due to present low efficiency with potential improvements to $4/kg with $\eta = 4\%$

Collaboration:
- Developing testing collaboration with NREL, Member of PEC workgroup

Future Work:
- Refine PEC testing with CdS/ZnS, perform testing on ZnTe
- Assembly and integration of large area PEC reactor
- Refine economic analysis based on actual PEC reactor material costs