Photoelectrochemical Water Splitting

2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

John A. Turner
National Renewable Energy Laboratory
jturner@nrel.gov 303-275-4270
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This presentation does not contain any proprietary or confidential information.
The goal of this research is to develop a stable, cost effective, photoelectrochemical based system that will split water using sunlight as the only energy input. Our objectives are:

1. Identify and characterize *new semiconductor materials* that have appropriate bandgaps and are stable in aqueous solutions.
2. Study *multijunction semiconductor systems* for higher efficiency water splitting.
3. Develop techniques for the *energetic control* of the semiconductor electrolyte interphase.
4. Develop techniques for the preparation of transparent *catalytic coatings* and their application to semiconductor surfaces.
5. Identify environmental factors (e.g., pH, ionic strength, solution composition, etc.) that affect the energetics of the semiconductor, the properties of the catalysts, and the stability of the semiconductor.

Our work this year has only been on Objective #1
**Budget**

Funding for FY2004 = $400k

**Staff:**
- Todd Deutsch, PhD Student, University of Colorado
- Jennifer Leisch, PhD Student, Colorado School of Mines
### PEC Targets from Multi-Year Plan

<table>
<thead>
<tr>
<th>Target Dates</th>
<th>2005</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar-to-hydrogen efficiency (%)</td>
<td>7.5</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td>Durability (hours)</td>
<td>1,000</td>
<td>10,000</td>
<td>20,000</td>
</tr>
<tr>
<td>Projected H₂ Cost ($/kg)</td>
<td>360</td>
<td>22</td>
<td>5</td>
</tr>
</tbody>
</table>

2010 goal: Projected Cost of PEC hydrogen within 50% of that for PV/Electrolysis.

Current NREL Status is a 12% efficiency, but only a 20-hour lifetime.
Technical Challenges *(the big three)*
Barriers for Photoelectrochemical Hydrogen Production

- **Material Durability: Barrier M**
  - The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption (~3 eV), or their semiconductor characteristics are poor.

- **Efficiency (Bandgap): Barrier O**
  - For reasonable solar efficiencies, the band gap must be less than about 2.2 eV, unfortunately, most useful semiconductors with bandgaps in this range are photochemically unstable in water.

- **Energetics: Not Included in Multi-Year Plan**
  - In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energies where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.
Summary of Approach

The primary task is to synthesize the semiconducting material or the semiconductor structure with the necessary properties. This involves material research issues (material discovery), multi-layer design and fabrication, and surface chemistry. Activities are divided into the task areas below – funded ones in **black**:

- **GaInP$_2$ - NREL** (fundamental materials understanding)
- **GaPN - NREL** *(high efficiency, stability)*
- **InGaN - CSM, NREL** *(high efficiency, stability)*
- **CuInGa(Se,S)$_2$ - UNAM (Mexico), NREL** *(Low cost)*
- Multi-junction Amorphous Silicon - University of Toledo and ECD *(Low cost)*
- **Energetics**
  - Band edge control
  - Catalysis
  - Surface studies
PEC Project Timeline


- **Phase I - Feasibility**
  1. Project definition and laboratory set-up
  2. Materials identification, experimental design and implementation.

- **Phase II – Development of High-Efficiency direct water splitting system.**
  3. Select materials and structure
  4. Structural modification and testing
  5. World Record result – 12.4% solar-to-hydrogen (Science)

- **Phase III – Alternative materials for longer lifetime and lower costs.**
  6. Studies of a-Si triple junctions
  7. Low cost thin-films
  8. Nitrides for longer lifetimes
Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions

\[ 2\text{H}_2\text{O} + 2e^- = 2\text{OH}^- + \text{H}_2 \uparrow \]

\[ \text{H}_2\text{O} + 2h^+ = 2\text{H}^+ + \frac{1}{2} \text{O}_2 \uparrow \]
Material and Energetic Criteria

- **Band Gap** ($E_g$) must be at least 1.6-1.7 eV.
- **Band Edges** must straddle $H_2O$ redox potentials.
- **Rapid** charge transfer.
- **Stable** in aqueous solution.

All must be satisfied simultaneously.
Potentiodynamic Curves for p-GaInP$_2$ - Base

In order to meet lifetime goals we must discover materials with inherently higher stability.
One possibility is nitride materials, an example of which is p-GaN.

It shows excellent stability...

...and water splitting capability

But... >3.0eV bandgap
Preliminary Investigation of GaP$_x$N$_{(1-x)}$ for PEC Water Splitting Systems

with Professor Carl Koval University of Colorado at Boulder

\[
y = 9E-08x - 2E-07 \\
R^2 = 0.9926 \\
E_g = 1.88 \text{ eV}
\]

<table>
<thead>
<tr>
<th>Electrode</th>
<th>% Nitrogen</th>
<th>Meas. Direct $E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME477-3</td>
<td>1.6</td>
<td>2.07</td>
</tr>
<tr>
<td>ME477-4</td>
<td>1.6</td>
<td>2.06</td>
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<tr>
<td>ME460-3</td>
<td>2.1</td>
<td>2.01</td>
</tr>
<tr>
<td>ME460-4</td>
<td>2.1</td>
<td>2.01</td>
</tr>
<tr>
<td>ME463-3</td>
<td>2.6</td>
<td>2</td>
</tr>
<tr>
<td>ME463-4</td>
<td>2.6</td>
<td>2</td>
</tr>
<tr>
<td>ME461-3</td>
<td>3.5</td>
<td>1.96</td>
</tr>
<tr>
<td>ME461-4</td>
<td>3.5</td>
<td>1.96</td>
</tr>
</tbody>
</table>
These low bandgap nitride materials exhibit exceptional stability.
GaPN - Preliminary Results

(Preliminary two-electrode multimeter measurements in acid (in mV and microA except where noted). Pt counter electrode.)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Dark OCP</th>
<th>6sun OCP</th>
<th>Dark SSC</th>
<th>6sun SSC</th>
<th>type</th>
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</thead>
<tbody>
<tr>
<td>MF097-1</td>
<td>-28</td>
<td>-1.45 V</td>
<td>0.1</td>
<td>-3.5 mA</td>
<td>n</td>
</tr>
<tr>
<td>MF097-2</td>
<td>-20</td>
<td>-1.49 V</td>
<td>0.1</td>
<td>-5.0 mA</td>
<td>n</td>
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<tr>
<td>MF097-3</td>
<td>-7</td>
<td>-0.67 V</td>
<td>0.1</td>
<td>-3.0 mA</td>
<td>n</td>
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<tr>
<td>MF097-4</td>
<td>-5</td>
<td>-0.81 V</td>
<td>0.1</td>
<td>-1.5 mA</td>
<td>n</td>
</tr>
<tr>
<td>MF098-1</td>
<td>16</td>
<td>250</td>
<td>0.05</td>
<td>0.4</td>
<td>p</td>
</tr>
<tr>
<td>MF098-2</td>
<td>-201</td>
<td>-3</td>
<td>-0.3</td>
<td>-0.4</td>
<td>p</td>
</tr>
<tr>
<td>MF098-3</td>
<td>-230</td>
<td>28</td>
<td>-0.25</td>
<td>0.2</td>
<td>p</td>
</tr>
<tr>
<td>MF098-4</td>
<td>-203</td>
<td>3</td>
<td>-0.1</td>
<td>0.2</td>
<td>p</td>
</tr>
</tbody>
</table>
New Materials - Band Gap Requirements for Electrodeposited CIGSS

- Dependence on sulfur content noted.
- However, this is convoluted by varying concentrations of other elements (5 component system!)

Goal: Consistent synthesis of high bandgap material
Technical Challenges (Cont.)

- Catalysts:
  - Oxygen (most important -- highest energy loss).
  - Hydrogen
  - Transparency might be necessary
  - Non-precious metal (lower current density!)
- Band edge engineering
- Semiconductor hybrid designs
- Low cost system designs featuring passive controls
Project Safety

- Hydrogen generation from our samples is small (a few µl/min), so no special precautions over standard engineering controls for chemical laboratories are taken at this time.
  - Sample sizes are small (<0.5 cm²) so hydrogen production even from the most efficient cells is low.
  - Cells are open to allow rapid diffusion of the hydrogen (no build-up).
  - Air exchanges are 6-10/hour in the lab.
  - For PEC H₂ and O₂ are produced at separated electrodes.

- For scale-up, a complete hazard identification and risk assessment will be done to identify issues relating to personnel, equipment and environmental factors.
  - Hardware and material analysis will be done to identify possible component failure modes.
  - This will be integrated into the design of the test facility and modules, and guide the write-up of the operational procedures.
Collaborations

In the US
Colorado School of Mines
University of Colorado
Program Production Solicitation

Outside of the US
Switzerland, Mexico, Armenia, Sweden, Japan
### Reviewers’ Comments from 2003 Poster

<table>
<thead>
<tr>
<th>Comments</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Focus on candidate light absorbing materials.</td>
<td>1. Focused on nitrides and thin-film CIGSSe material</td>
</tr>
<tr>
<td>2. Efforts should continue to include amorphous silicon photoelectrodes as well as other newer materials.</td>
<td>2. No funding for a-Si</td>
</tr>
<tr>
<td>3. Without some intermediate goals, the work will go on for 5 years without an off-ramp strategy.</td>
<td>3. Intermediate goals concentrate on specific material studies. Materials with poor properties are discarded, e.g. the multijunction GaInP₂ system and GaAsPN.</td>
</tr>
<tr>
<td>4. Concentrating on the semiconductor and PEC device has left him less time for catalyst questions – developing the electrodes for the O₂ and H₂ generation.</td>
<td>4. No funding for catalysts studies.</td>
</tr>
</tbody>
</table>

“A great apostle of the program to a skeptical industrial world.”
PEC Project Timeline - Outyears

Phase IV – Synthesis and characterization of Nitride materials and thin-film materials
9 GaNP and CuInSSe materials – perhaps a-Si
10 GaInN materials

Phase V – High-Efficiency direct water splitting system based on nitrides.
11 Select materials and structure
12 Structural modification and testing
13 8% and 1000 hours

Phase VI – Module development and testing
14 Design development and safety assessment
15 Build and test
16 IPO and retire!
Future Plans

• Remainder of FY2004:
  – Continue evaluation of nitride material
  – Continue evaluation of thin-film CIGSSe

• For FY2005:
  – Additional materials with LBNL, CSM, …
  – Coatings: SiN, SiC, …
  – Band-edge engineering (perhaps with Office of Science.
  – Multijunction structures