Nanotube Array
Photoelectrochemical Hydrogen Production

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Project ID # PD062

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## Overview

### Timeline
- Project start date: 08/15/08
- Project end date: 08/15/10
- Percent complete: 81%

### Budget
- Total: $750,000
  - DOE share: $750,000
  - Contractor share: $0
- FY09 Funding: $260,000
- FY10 Funding: $365,225

### Barriers
- Photoelectrochemical Hydrogen Production
  - AC. Device Configuration Designs

### Partners
- John Turner at NREL is a subcontractor for evaluation of PEC samples
- Synkera has the project lead as the SBIR company
Relevance: Photoelectrochemical (PEC) Hydrogen

Requirements of PEC material:
• Band gap must be at least 1.7 eV
• Band edges must straddle H₂O redox potentials
• Must be stable in aqueous solution

Relevance

The project objective is to develop hybrid photoelectrochemical (PEC) devices that meet or exceed the 2018 performance targets.

Synkera is addressing the barrier of PEC Device Configuration Designs by creating a hybrid design that combines multiple layers of materials to simultaneously address issues of durability and efficiency. As part of this effort, techniques are being developed that can manufacture devices at commercial scales.

<table>
<thead>
<tr>
<th>Performance Measure</th>
<th>Units</th>
<th>2013 Target</th>
<th>2018 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Usable bandgap</td>
<td>eV</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Chemical conversion efficiency</td>
<td>%</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Solar to hydrogen efficiency</td>
<td>%</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Plant Durability</td>
<td>hours</td>
<td>1000</td>
<td>5000</td>
</tr>
</tbody>
</table>
Relevance: Key Milestones for Phase II Project

<table>
<thead>
<tr>
<th>Key Milestone</th>
<th>% Completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete and test upgrade of ALD reactor</td>
<td>100</td>
</tr>
<tr>
<td>Complete fabrication of architecture prototypes</td>
<td>100</td>
</tr>
<tr>
<td>Complete membranes for development of absorber materials.</td>
<td>100</td>
</tr>
<tr>
<td>Determine process for InGaN deposition</td>
<td>90</td>
</tr>
<tr>
<td>Complete fabrication of absorber prototypes</td>
<td>75</td>
</tr>
<tr>
<td>Prototype able to meet all DOE goals</td>
<td>50</td>
</tr>
</tbody>
</table>
Approach: Anodic Aluminum Oxide as a Scaffold for PEC Materials

- High quality self-organized material with regular nanoporous lattice
- Uniform & aligned arrays of cylindrical nanopores
  - Pore diameter: 5 - 300 nm
  - Pore density: $10^{12} - 10^8$ cm$^{-2}$
  - Thickness: 0.1 - 300 µm
- Formed by anodic oxidation of Aluminum
- Scaleable, manufacturing-friendly
- Platform for nano/microfabrication
Approach: AAO a Scalable Material

World’s largest nanoporous AAO membrane produced at Synkera
Technical Accomplishment

Engineered Nanotemplates for PEC

Synthesis of anodic aluminum oxide with large pore sizes.

Increasing Etch Time

Anodic aluminum oxide with minimally reflective surface.
Approach: Nanorod Arrays for PEC Hydrogen (Phase I design)

- Based on AAO nanotemplate
- Short distance to conductors allows for efficient electron-hole separation
- Small pore size will reduce gas bubble formation
- TiO$_2$ is doped to reduce the band gap, but conductivity through TCO is unaffected
- Fabricated using atomic layer deposition (ALD)
Approach: Fabrication by Atomic Layer Deposition

ALD consists of sequential self-limiting surface reactions using gaseous precursors applied in ABAB... fashion.

Synkera ALD Reactor

ALD inside AAO

Alumina
Technical Accomplishment

Transparent Conductor and TiO₂ by ALD

Conductive and Titania Coatings

Resistance of nanotubes

SEM images of AAO coated with conductive layer

EDX linescan of Materials inside AAO

SEM images of AAO coated with both materials

Demonstrated conformal coatings inside high-aspect ratio pores.
Technical Accomplishment

Phase I Results

Able to reduce bandgap to 2.5 eV

Sample was active with zero applied potential!!!

We conclusively showed that nanostructuring increased the efficiency of photoelectrolysis
Technical Accomplishment

Phase II PEC Data

Test System
- 3-electrode setup
- Calibrated to 1 sun exposure
- 0.1 M K₂SO₄ test solution

Typical Cyclic Voltammogram

Highest current density obtained on undoped TiO₂ using test conditions listed was 400 μA/cm².
Phase II Approach: Nanorod Absorber Arrays for PEC Hydrogen

- Instead of modifying the TiO$_2$, we will add a separate absorber material to harness light
- This absorber can (in principle) be vertically graded in order to absorb a wider range of the solar spectrum.
Phase II Approach Absorber Layer

III-V Absorbers: InN, GaN, and $\text{In}_x\text{Ga}_{1-x}\text{N}$

- TCO is the electron conductor
- Absorber material is used to harness light
- $\text{TiO}_2$ provides protective surface

EDX linescan of $\text{In}_x\text{Ga}_{1-x}\text{N}$ inside AAO
Conduction bandedge of GaN is insufficient to drive photoelectrolysis of water. Similar results with InN.
Collaborations

Partners

• National Renewable Energy Laboratory (Federal): Investigation of PEC efficiency and position of bandedges

• University of Colorado (Academic): High resolution SEM images of ALD coated samples

Commercialization

• HyGenera LLC was founded as a spin-off from Synkera for a variety of hydrogen related technologies, including PEC.

• Interested parties: Protonex Technology Corp., ITN Energy, McGuffy Energy Group, and CTI Petroleum, among others.

• Completed Technology Niche Assessment with Foresight Science & Technology to identify markets for spin-off applications.
Proposed Future Work

• Investigate \( \text{WO}_3 \) as a PEC material
• Revisit N-doping of \( \text{TiO}_2 \) as a means to push bandgap down to 2 eV
• Measure long-term stability of nanostructured films
• Investigate other absorber materials
Summary Slide

**Relevance:** to develop hybrid photoelectrochemical devices that meet or exceed the 2018 performance targets.

**Approach:** Develop hybrid nanostructured devices where electron conduction, light absorption, and PEC reaction take place in separate materials.

**Technical Accomplishments:** Demonstrated photoelectrolysis without any external bias. Demonstrated integration of all materials into a device.

**Collaborations:** Synkera founded Hygenera LLC, a spinoff company designed to work with a variety of hydrogen related technologies.

**Proposed Future Research:** Examine other absorber and PEC materials and revisit doping of TiO$_2$ as means of meeting DOE targets.

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