
Professor Thomas Jaramillo
Stanford University
June 8, 2016
Project ID#: PD119

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline and Budget

- Project Start Date: 1/1/15
- Project End Date: 12/31/2017
- Total Project Budget: $750,000
  - Total Recipient Share: $750,000
  - Total Federal Share: $750,000
  - Total DOE Funds Spent*: $434,826
    * as of 3/31/16

Barriers and Targets

Barriers

- Materials Efficiency – Bulk and Interface (AE)
- Materials Durability – Bulk and Interface (AF)
- Integrated Device Configurations (AG)

Targets

- Photoelectrochemical Hydrogen Cost
- Annual Electrode Cost per TPD H₂
- Solar to Hydrogen (STH) Energy Conversion Ratio
- 1 sun Hydrogen production rate

Partners

- National Renewable Energy Laboratory (NREL)
- PEC Working Group
Origin of worldwide H₂ production of ~50 billion kg/year

Hydrogen is an important industrial chemical and potential future fuel. Photoelectrochemical (PEC) water splitting offers the potential for sustainable H₂ production from sunlight and water. Technoeconomic analysis of centralized PEC H₂ production facilities shows that this process can become economically competitive with further improvements in device efficiency, durability, and cost.


Relevance and Impact

Objectives

• Method and protocol development to understand photoelectrode corrosion in acid.

• Interfacial engineering of the Si surface to provide enhanced catalytic activity and corrosion resistance in acid by means of molybdenum sulfide nanomaterials.

• Interfacial engineering of III-V photocathode surfaces with similar approaches, in collaboration with Dr. Todd Deutsch at the National Renewable Energy Laboratory (NREL).

• Interfacial engineering of the BiVO₄ surface to provide enhanced electronic properties, catalytic activity and corrosion resistance in acid with a series of ultra-thin metal / metal oxide films.

• Quantification of H₂ and O₂ and true solar testing at NREL.

Technical Targets we are aiming to meet:

10% STH Efficiency
100 J/s per m² of Hydrogen Production
Approach
Testing Design and Tandem Device Engineering

1. Stability testing methods
2. Protecting layer and HER catalyst for Si photocathode
3. III-V photocathodes from NREL
4. Protective layer and OER catalyst for photoanode
5. Unassisted water splitting photoelectrode

True solar testing at NREL
Quantification of H₂ and O₂
Modeling of realistic STH efficiency as a function of band gaps for a tandem absorber PEC system shows that 20% STH can be achieved with a tandem device with band gaps of 1.2 and 1.8 eV.

MoS$_2$ is promising as a protection layer for materials unstable in acid.

Approach
Stability measurement setup

We have developed a photoelectrochemical (PEC) setup improves the reliability of our long term stability measurements

- Precise control over the position of the electrode
- High illumination uniformity
- 1 – 10 sun intensity
Accomplishments and Progress
Stability of MoS$_2$-Si Photocathodes

- Silicon photocathodes were prepared with MoS$_2$ protection layers.
- Stability testing in 0.5 M sulfuric acid, under 1 sun illumination at 0.0 V vs. RHE, found the samples to be stable for 25 days of continuous operation.
- The electrode subsequently failed catastrophically during Day 26.


Accomplishments and Progress
Understanding failure mechanisms of MoS$_2$-Si

Comparison by XPS measurement pre and post PEC stability testing

- After the 26 days of PEC testing and catastrophic failure, no molybdenum or sulfur species are detected by XPS evidencing the absence of the MoS$_2$ protection layer.
- Additionally, silicon is uncovered with evidence of additional silicon dioxide formation.
- Ongoing efforts are aimed at probing failure mechanisms and at increasing stability.

We used MoS$_2$ to protect GaInP$_2$ in acid increasing its stability >500x without losing significant photocurrent density.

The MoS$_2$ further functions as a catalyst for the Hydrogen Evolution Reaction improving onset potential.

Britto R.J., Benck J.D., Young J.L., Hahn C., Deutsch, T.G., Jaramillo T.F. *Journal of Physical Chemistry Letters* (accepted, 2016)
Accomplishments and Progress
Characterizing failure mechanisms of MoS$_2$-GaInP$_2$

The Auger spectra reveals the failure mechanism for MoS$_2$ on GaInP$_2$. Pores form in the MoS$_2$ exposing the GaInP$_2$ underneath. The GaInP$_2$ is then corroded to expose the degenerately doped GaAs substrate.
Stability of CoP-n⁺p Si Photocathodes

The CoP catalyst grown on n⁺p Si shows excellent activity and stability. This performance puts it among the best non-precious metal Si photocathodes ever tested in acidic or basic electrolyte.

Spray pyrolysis was developed to deposit a thin film of W-doped BiVO$_4$ on a scaffold of Si NWs to improve the charge separation of BiVO$_4$ and increase the photovoltage of the heterojunction photoanode.

Accomplishments and Progress
Precious metal-free Unassisted Water Splitting Photoanode

- By optimizing the doping profile of the Si NWs, a heterojunction BiVO$_4$/Si photoanode can achieve a photocurrent onset as early as -0.2 V vs. RHE
- When paired with a CoP nanoparticle cathode, the device can perform unassisted water splitting at 0.4 mA/cm$^2$ without any precious metals

Sulfite oxidation I-V curves of W-doped BiVO$_4$/Si heterojunction photoanode with various types of Si p-n junction

Water oxidation I-V curve of CoPi-decorated BiVO$_4$/Si photoanode paired with CoP nanoparticle cathode

Collaborations

National Renewable Energy Laboratory (NREL)
Todd Deutsch, James Young

We work with Todd and James on the GaInP₂ stability project. Our collaboration involves:
- Fabrication
- Sample exchange
- Parallel testing
- Discussion and idea sharing
- Process optimization

PEC Working Group
The PEC Working Group meets regularly to review technical progress, develop synergies, and collaboratively develop common tools and processes for PEC water splitting. Organized through the Department of Energy led by Eric Miller.

Energy Materials Network Workshop
Consortium that will accelerate the research, development and deployment of advanced water splitting technologies for renewable hydrogen production. Scientific experts in these technology areas will come together to identify key materials, metrics, and targets essential to commercial viability.

Molybdenum Disulfide as a Protection Layer and Catalyst for Gallium Indium Phosphide Solar Water Splitting Photocathodes
Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, Thomas F. Jaramillo

Manuscript under review
Proposed Future Work

Immediate goals

Applying acid stabilization strategies developed for BiVO$_4$ in acid to heterojunction device

Further \textit{in situ} study of MoS$_2$ failure mechanisms to improve GaInP$_2$ stability

Protection layer on BiVO$_4$/Si heterojunction photoelectrode

PEC Flow Cell combined with microscopy

Combining current and future innovations to make a non-precious metal unassisted water splitting device that is stable in acid
Proposed Future Work

Long term goals

Developing methods to identify photoelectrode failure mechanisms and predict long-term performance using short-term tests

(a) Failure Analysis

1. Electrochemistry
   - Chart showing changes in potential over time.

2. Spectroscopy
   - Spectrogram showing elements such as S, Mo, C, and O.
   - Chart showing kinetic energy vs. counts.

3. Microscopy
   - SEM image with scale of 200 μm.

(b) Accelerated Testing Methods

1. Potential cycling
   - Chart showing potential vs. time.

2. Light/dark cycling
3. Increased light intensity
   - Diagram showing light intensity comparison between 1 sun and 10 suns.
4. Varied temp + pH
   - Chart showing temperature range of 25 – 90 °C and pH range of 0 – 7.
Approach

- We are developing protection layers for addressing stability and activity of both the photoanode and photocathode in acid.

- The photoelectrochemical setup provides precise control of the electrode illumination, which improves the reliability of our long term stability measurements.
Achieved long-term stability of MoS$_2$-Si photocathode in acid for 25 days


Protected GaInP$_2$ in acid for over 70 hours with MoS$_2$

Britto R.J., Benck J.D., Young J.L., Hahn C., Deutsch, T.G., Jaramillo T.F. *Journal of Physical Chemistry Letters* (accepted, 2016)

Developed a highly active and stable photocathode consisting of CoP HER catalyst on Si


Engineered a wafer-scaled nanostructure heterojunction BiVO$_4$/Si photoanode that can perform unassisted water splitting