NSF/DOE Solar Hydrogen Fuel
Engineering Surfaces, Interfaces, and Bulk Materials for Unassisted Solar Photoelectrochemical (PEC) Water Splitting

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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*: $685,000 (as of 3/31/15)

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
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).
- Integration of BiVO₄ to Si to make a tandem photoelectrochemical cell capable of unassisted water splitting.
- Quantification of H₂ and O₂ and true solar testing at NREL.
- Study the mechanistic degradation of PEC water splitting devices by developing an operando electrochemical flow cell coupled to both an optical and confocal Raman microscope to inform new strategies for improving our catalysts and protection layers.

Technical Targets from DOE Fuel Cell Technologies Office MYRDD Plan:

- 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. Photoanode design for unassisted water splitting

5. True solar testing at NREL

Quantification of $H_2$ and $O_2$
Approach
Material Selection

**Photoabsorber materials**

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.

**Protection layer material**

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


The photoelectrochemical 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
Silicon photocathodes were prepared with MoS$_2$ protection layers. Stability testing in 0.5 M sulfuric acid found that the samples were stable for 64 days of continuous 1 sun illumination. The electrode subsequently failed catastrophically.
After the 64 days of PEC testing and catastrophic failure, XPS characterisation reveals a drastic transformation in the chemical oxidation states of the elements present. Specifically, the proportion of oxidized molybdenum increased from 10 % to 75 %.
Accomplishments and Progress
Understanding the Failure Mechanism of MoS$_2$-Si

Microscopy post PEC stability testing

After the 64 days of PEC testing and catastrophic failure, SEM reveals a highly roughened surface with both pits and agglomerates across the surface. TEM of the same sample reveal significant roughening with pits of up to 30 nm deep. By STEM-EDS mapping, it is clear that the pits extend through the protective molybdenum layers into the silicon and that silicon has been etched away.
MoS₂ was used to protect pn⁺ GaInP₂ for >100 hrs in 3M sulfuric acid.

The MoS₂ further functioned as a catalyst for the hydrogen evolution reaction with an earlier onset potential than a platinum-modified pn⁺ GaInP₂ photocathode.
Accomplishments and Progress
Protecting the surface of GaInP$_2$

Reuben J. Britto, Jesse D. Benck, James L. Young, Christopher Hahn, Todd G. Deutsch, and Thomas F. Jaramillo. The Journal of Physical Chemistry Letters 2016 7 (11), 2044-2049
Reuben J. Britto, James L. Young, Ye Yang, Miles Steiner, David LaFehr, Mathew Beard, Todd G. Deutsch, and Thomas F. Jaramillo. In Prep.
Laurie A King, T. Hellstern, S. Park, R. Sinclair and T. F. Jaramillo Submitted 2017
Accomplishments and Progress

Operando flow cell development

Preliminary operando data collection from a p-GaInP₂/MoS₂ photocathode in our flow cell.

Once in operation, we can investigate pinhole formation as it occurs.

SEM of p-GaInP₂/MoS₂ after 100 h of testing in 3 M H₂SO₄
Accomplishments and Progress
Unassisted Tandem Photoelectrochemical Water Splitting Cell

We developed a device design and a scalable fabrication scheme of a tandem heterojunction photoanode structure: \( p^+n \) black-Si core/SnO\(_2\) interface/W-doped BiVO\(_4\) shell/CoPi catalyst. When coupled with CoP NPs, the device demonstrates a unassisted water splitting without any precious metal.

Chakthranont, P., Hellstern T. R., McEnaney, J. M., and Jaramillo T. F. *In Preparation*
Towards the development of a monolithic device we designed and fabricated a backside illuminated silicon photoanode with approximately 510 mV photovoltage.
Proposed Future Work

Continuing work

Explore different materials for tandem device to enable higher efficiency and stability

Combining current and future innovations to make a non-precious metal unassisted water splitting device with high stability

Further in situ investigation of MoS$_2$ failure mechanisms to improve GaInP$_2$ stability using a flow combined with microscopy

Further work into stabilization strategies for III-V photo-absorbers for unassisted water splitting devices with NREL
Collaborations

National Renewable Energy Laboratory (NREL)
We work with Todd Deutsch and James Young on the GaInP₂ stability project. Our collaboration involves:
- Fabrication
- Sample exchange
- Parallel testing
- Discussion and idea sharing
- Process optimization

Manuscript published together:

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.

EMN Workshop at Stanford (2016)
Summary

Approach

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

  Stability testing design  Si protection  III-V protection  Photoanode design  Unassisted PEC device

- The photoelectrochemical setup provides precise control of the electrode illumination, which improves the reliability of our long term stability measurements.
Summary

Accomplishments

• Achieved long-term stability of MoS$_2$-Si photocathode in acid for 64 days
  
  Laurie A King, T. Hellstern, S. Park, R. Sinclair and T. F. Jaramillo. Submitted 2017

• Protected GaInP$_2$ in acid for over 100 hours with MoS$_2$
  

  Reuben J. Britto, James L. Young, Ye Yang, Miles Steiner, David LaFehr, Mathew Beard, Todd G. Deutsch, and Thomas F. Jaramillo. In Prep.


• Developed a highly active and stable CoP HER catalyst - Si photocathode
  

• Engineered a wafer-scaled nanostructure heterojunction BiVO$_4$/Si photoanode that can perform unassisted water splitting
  
  Pongkarn Chakthranont, Thomas R. Hellstern, Joshua M. McEnaney, and Thomas F. Jaramillo. In Prep