II.D.2 Wide Bandgap Chalcopyrite Photoelectrodes for Direct Water Splitting

Overall Objectives

In line with the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, our project aims to identify suitable semiconducting materials for efficient and durable photoelectrochemical (PEC) hydrogen production at a cost of $2/kg or less. Specifically, our project aims to

- Develop efficient copper chalcopyrite (Cu(In,Ga)S\(_2\)) based materials with ideal optoelectronic properties for PEC water splitting.
- Identify appropriate surface treatments to prevent photocorrosion, improve surface energetics, and enhance the hydrogen evolution reaction.
- Demonstrate 3 L of hydrogen produced in 8 hours using a copper chalcopyrite-based standalone PEC device.

Fiscal Year (FY) 2016 Objectives

- Demonstrate copper chalcopyrite photoelectrode material with bandgap >1.7 eV that generates at least 10 mA/cm\(^2\).
- Improve chalcopyrite stability in aqueous electrolytes using MoS\(_2\) as protection layers, with a durability goal of 750 h continuous operation at 8 mA/cm\(^2\).
- Demonstrate CuInGaS\(_2\) solar cells with a photoconversion efficiency >6%.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(AE) Materials Efficiency
(AF) Materials Durability
(AG) Integrated Device Configurations
(AJ) Synthesis and Manufacturing

Technical Targets

This project aims to develop efficient and durable PEC devices using low-cost semiconducting materials. Specifically, our project aims to modify the optoelectronic properties of the photovoltaic (PV)-grade copper chalcopyrite material class for PEC water splitting. Alongside, we are engineering new surface treatments to improve chalcopyrites’ surface energetics, their catalysis toward the hydrogen evolution reaction, as well as their resistance against photo-corrosion. The status of this project’s technical targets is documented in Table 1.

TABLE 1. Progress towards This Project’s Technical Targets for FY 2016

<table>
<thead>
<tr>
<th>FY 2016 Milestones</th>
<th>Due date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(In,Ga)S(_2) solar cells with a photoconversion efficiency &gt;6%</td>
<td>12/2015</td>
<td>Complete</td>
</tr>
<tr>
<td>Photocurrent density relevant to 15–16% STH with chalcopyrite 12–13 mA/cm(^2)</td>
<td>03/2016</td>
<td>90%</td>
</tr>
<tr>
<td>Durability &gt;750 hrs at mA/cm(^2), with a stretch goal of 1,000 hrs</td>
<td>06/2016</td>
<td>30%</td>
</tr>
<tr>
<td>Fabricate Cu(In,Ga)S(<em>2) cells with V(</em>{OC}) &gt;750 mV</td>
<td>09/2016</td>
<td>95%</td>
</tr>
</tbody>
</table>

STH – solar-to-hydrogen; V\(_{OC}\) – open circuit voltage

FY 2016 Accomplishments

Accomplishments during the current project period include:

- Over 10 mA/cm\(^2\) achieved with CuGa(S,Se)\(_2\), CuGa\(_2\)Se\(_4\), and CuInGaS\(_2\) chalcopyrite materials (go/no-go criteria for Year 1).
- Modeling of optical bandgap and electronic defects in CuGa(S,Se)\(_2\).
• Validation of in situ studies of chalcopyrites/electrolyte interface.
• Improvement of CuGaSe₂ photoelectrode durability using TiO₂ and MoS₂ as a protective coating.

INTRODUCTION

The goals of this project are to demonstrate PEC hydrogen production with a dual absorber system capable of generating at least 3 L of hydrogen in 8 hours as well as to develop a standalone system with a STH conversion efficiency of 15% and operational life up to 2,000 hours.

APPROACH

The chalcopyrite material class, typically identified by its most popular PV-grade alloy CuInGaSe₂, provides exceptionally good candidates for PEC water splitting. A key asset of this bandgap tunable, direct absorber, thin film semiconductor material is the outstanding photon-to-electron conversion efficiency, as demonstrated with CuInGaSe₂ (CIGSe)-based PV cells. A STH efficiency of 4% was achieved by our team in 2012 using a 1.6 eV bandgap CuGaSe₂ (CGSe) photocathode connected in series with three a-Si PV drivers (side-by-side architecture). The use of such coplanar architecture was dictated by the bandgap of CuGaSe₂, which was too narrow for a “stacked” multijunction integration. With wide bandgap chalcopyrites, we will be able to stack the PEC device over the PV driver and increase the STH efficiency.

RESULTS

PV-grade wide bandgap absorbers: theoretical modeling. To better inform the experimental synthesis of desirable alloys, we have focused on assessing the bandgap and thermodynamic stability of absorber alloys as a function of composition and have also begun calculations to characterize how point defects may influence the resulting properties of the alloys. We have focused on the CuGa(S,Se)₂ (CGSSe) alloys that have received the most attention from our experimental efforts and summarize the calculated bandgap and stability as a function of S content in Figure 1. We find that these alloys are readily mixed to form solid solutions and are stable against phase separation at modest processing temperatures. Additionally, CGSSe alloys exhibit bandgaps within the target range of ~1.8–2 eV for Ga-contents ranging from ~20–40%, with a nearly linear dependence on composition. Additional calculations on Cu(In,Ga)S₂ alloys identify that the bandgaps of these alloys display slightly more nonlinear behavior with composition than those of the CGSSe alloys. This is evident in our calculated bandgap bowing parameter of 0.05 eV, as seen in Figure 1a, compared to the 0.2 eV calculated for Cu(In,Ga)S₂ alloys. We also continue to evaluate the solubilities and electronic character of native and extrinsic defects in pure CGSe and CuGaS₂ (CGS). We are currently assessing the stability of defects with deep states like the Ga_{Cu} deep donors that have previously been suggested to play a role in limiting the performance of high-Ga CIGSe photovoltaics. In Figure 1c we include the deep levels associated with this defect in both CGSe and CGS and find that they are deeper in the CGS bandgap by ~0.5 eV relative to CGSe and may also be problematic for pinning the Fermi level if their concentrations are high enough.

PV-grade wide bandgap absorbers: synthesis. During this reporting period, development of new wide bandgap chalcopyrites with great potential for PEC water splitting continued. Theoretically, wide bandgap chalcopyrites may be obtained by replacing some of the selenium with sulfur in CuGaSe₂, creating the alloy CuGa(S,Se)₂. We were able to experimentally verify this by synthesizing CGSSe alloys with

![FIGURE 1.](image_url)
a bandgap between approximately 1.7 eV and 2.4 eV, which is shown in Figure 2. CGSe films were fabricated with a two-step process first involving the co-evaporation of a selenide-based precursor and then a sulfurization step. By controlling the amount of sulfur present during the sulfurization process, we were able to synthesize films anywhere within the aforementioned bandgap range. With this material class, our team has demonstrated a current density of approximately 11.0 mA/cm² with a 1.72 eV bandgap CGSSe. Also during this reporting period, ordered defect chalcopyrite CuGa₅Se₅ electrodes were grown in an ultrahigh vacuum cluster tool system. A photocurrent density of 11 mA/cm² was achieved with a 1.84 eV CuGa₅Se₅. Both CGSSe and CuGa₅Se₅, along with CuInGaS₂, satisfied the go/no-go criteria for Year 1.

Sub-surface energetics improvement: advanced characterization. This project year, the world-wide first S L₂,₃ X-ray emission spectroscopy (XES) measurements of a solid–liquid interface of a PEC material were collected at the Advanced Light Source, Lawrence Berkeley National Laboratory. Such measurements allow for the characterization of the solid–electrolyte interface between custom-deposited CuInGaS₂ thin films on Au-coated, C-based membranes and a highly acidic, sulfur-free electrolyte. The S L₂,₃ XES spectra of the first two solid–liquid interface experiments, along with corresponding reference samples, are shown in Figure 3. Furthermore, we have continued our ion treatment regime for surface and bulk compositional analysis of two CGSe-based absorbers: one “bare absorber” composed of CGSe and one sulfurized absorber (CuGaSe₂, CGSSe). Ion treatments at variable ion energies allowed us to determine whether certain elements (carbon, oxygen, and sodium in particular) are only present as surface adsorbates, or integrated into the surface and/or bulk of the respective films. X-ray photoelectron spectroscopy survey spectra of the CGSSe absorber surface before and after low-energy ion treatments revealed a small reduction of C, O, and Na surface adsorbates (“ion-treated”) and a complete removal of C and Na (but not of O) after sputtering. Next project steps include additional sputter treatments to further identify the presence or absence of oxygen in the bulk of the films, a detailed analysis of the S L₂,₃ and the Se M₂,₃ XES measurements recently completed at the Advanced Light Source, as well as an analysis of a new sample series specifically designed to allow for a full band alignment determination of the CdS–Cu(In,Ga)Se₂ interface.

Surface catalysis and corrosion resistance. During the second year of our project we worked to develop conformal MoS₂ coatings to protect CGSe electrodes from corrosion in sulfuric acid electrolyte during photoelectrochemical hydrogen evolution. In Year 1, we showed that physical vapor deposition methods, which have been effective in protecting silicon photodevices from corrosion in the past, were effective in protecting CGSe for only short periods of time. Physical vapor deposition is a directional deposition method and was unable to conformally coat the CGSe electrodes.

Instead, atomic layer deposition (ALD), a gas-phase self-limiting method, was used to deposit conformal films. We developed an oxygen plasma assisted method to deposit molybdenum oxide (MoOₓ) by ALD and then converted the MoOₓ to molybdenum sulfide (MoS₂), a material known for its high durability in acid electrolyte, using a 10% H₂S–90% H₂ sulfidizing gas. Unfortunately, the oxygen plasma damages the surface of the CGSe electrode, leading to high resistivity.
and low hydrogen evolution activity. We determined that it was necessary to add a barrier layer of TiO$_2$ deposited by thermal ALD to protect the CGSe samples from oxygen plasma damage during MoO$_x$ deposition. The TiO$_2$ also has the added benefit of enhancing durability. Figure 4 shows the results of our surface protection schemes and includes durability measurements for bare CGSe electrodes, CGSe electrodes with 15 nm of TiO$_2$ deposited by ALD and 1 nm Pt as a catalyst, and CGSe electrodes with 7 nm of ALD-deposited TiO$_2$ and 4 nm of ALD-deposited MoO$_x$ that has been converted to MoS$_2$. All samples were tested by measuring the potential required to obtain a constant current density of -8 mA cm$^{-2}$. Both the TiO$_2$-coated samples significantly outlast the uncoated CGSe electrode. The Pt-catalyzed CGSe electrode catastrophically fails after about 250 h of continuous operation, while the MoS$_2$-containing sample has operated approximately 270 h as of this writing without failure. Likely there is some additive effect to durability by employing both MoS$_2$ and TiO$_2$ films, both of which are known to resist electrochemical corrosion.

**CONCLUSIONS AND FUTURE DIRECTIONS**

- Over 10 mA/cm$^2$ achieved with 1.73 eV CuGa(S,Se)$_2$, 1.84 eV CuGa$_3$Se$_5$, and 1.75 eV CuInGaS$_2$ chalcopyrite materials (go/no-go criteria for Year 1). Materials development will continue to increase the photocurrent output of newly formed chalcopyrites.
- Over 250-h durability demonstrated with MoS$_2$- and TiO$_2$-coated chalcopyrites. Coating methods will be adjusted to improve material coverage and enhance photoelectrode durability.
- Over 700 mV $V_{oc}$ demonstrated with wide bandgap chalcopyrite materials. New buffers and surface treatments will be evaluated to meet Year 2 go/no-go criteria (750 mV $V_{oc}$).
- Complete PEC structures made of wide bandgap-based photoelectrodes and narrow bandgap PV drivers will be fabricated and tested.

**FY 2016 PUBLICATIONS/PRESENTATIONS**