

II.E Photoelectrochemical Production

II.E.1 Photoelectrochemical Systems for H₂ Production

John A. Turner (Primary Contact), Todd Deutsch, Jennifer Leisch**, Heli Wang*
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, Colorado 80401
Phone: (303) 275-4270; Fax: (303) 275-3033; E-mail: jturner@nrel.gov
**Colorado School of Mines*
***University of Colorado*

DOE Technology Development Manager: Roxanne Danz
Phone: (202) 586-7260; Fax: (202) 586-9811; E-mail: Roxanne.Danz@ee.doe.gov

Objective

- Identify and characterize new semiconductor materials that have appropriate band gaps and are stable in aqueous solutions.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- M. Material Durability
- O. Photoelectrochemical Efficiency

Approach

- Materials Research: Perform semiconductor materials research, discovery, and development.

Accomplishments

- Initial results from potentiodynamic analysis showed that the GaPN material is stable, with no photocorrosion, and can also split water. This could be the first stable material that has been identified that has a band gap of less than 2 eV and that is capable of spontaneously splitting water upon illumination.
- Identified barriers for the synthesis of CuInGaSSe material with band gaps in the range 1.6-2.0 eV.

Future Directions

- Continue to synthesize and characterize nitride materials (GaPN, GaInN) for longer lifetimes.
- Investigate thin-film (CuInSSe) materials as low-cost water splitting systems.
- Evaluate additional materials for longer lifetime and lower costs in collaboration with others.
- Develop coatings that act as catalysts and provide corrosion protection in photoelectrochemical (PEC) systems.
- Develop and evaluate multijunction structures for high efficiency.

Introduction

Direct conversion systems combine the capture of solar light energy with a water splitting system with the goal of producing hydrogen in a single step; water is split directly upon illumination with no external electron flow. An illuminated semiconductor immersed in aqueous solution—termed a photoelectrochemical, or PEC, system—exemplifies such a direct conversion system. Light impinging on the semiconductor material generates an internal electric field within the material and water can be split, with hydrogen (for example) being generated at the illuminated surface and oxygen being generated on the back (dark) side. These PEC systems have been a focus of a number of researchers for over 30 years. One of the major advantages of these PEC systems is that they operate under direct solar light. At solar intensities, the effective current density that is generated at the surface is 10-20 mA/cm², depending on the type of material used. At these current densities, the energy required for electrolysis is much lower than that for commercial electrolyzers, and therefore, the corresponding electrolysis efficiency is much higher. At a current density similar to short circuit photocurrent from a solar cell, hydrogen and oxygen generation is achieved at an applied voltage of approximately 1.35 V, giving rise to an electrolysis efficiency of 91%. This then is one of the advantages of a direct conversion hydrogen generation system; not only does it eliminate most of the costs of the electrolyzer, it also has the possibility of increasing the overall efficiency of the process.

Approach

PEC hydrogen production is in an early stage of development and depends on a breakthrough in materials development. The primary effort in this project is to synthesize a semiconducting material or a semiconductor structure with the necessary properties. For the direct PEC decomposition of water to occur, three key energetic conditions and the criteria of stability for the semiconductor must be met. For the energetic conditions, the semiconductor's band gap must be sufficiently large to split water and yet not too large as to prevent efficient absorption of the solar spectrum (ideally 1.8-2.2 eV), the band edges of the semiconductor

must overlap the hydrogen and oxygen redox potentials, and the charge transfer across the semiconductor/liquid interface must be fast enough to prevent band edge migration. In addition, the semiconductor's surface must be stable against corrosion both in the dark and under illumination. For FY 2004, our study of PEC direct conversion systems involved two areas of materials research focusing only on the issues of semiconductor band gap and corrosion resistance.

Our materials research in this area is progressing on two fronts: 1) working on the high-efficiency materials in order to apply basic scientific understanding to lower-efficiency, low-cost materials, and 2) working on the durability of low-cost materials in order to apply basic scientific understanding to higher-efficiency, lower-durability materials. Currently, the highest-efficiency systems have the shortest lifetimes and the lower-efficiency systems have the longest lifetimes. The optimal system will likely be a compromise between efficiency and lifetime.

Results

This year, research has focused on the continued development of group III nitrides (GaPAsN, GaPN) and thin films of CuInGaSSe for use as PEC materials.

Nitride materials as high-efficiency corrosion-resistant PEC devices

GaPAsN: While this material set has band gaps in the range necessary for water splitting, we have determined through our corrosion analysis that this material is inherently unstable. Given the much higher stability of our As-free materials (see below), we have discontinued our work on this material and are focusing on the GaPN material.

GaPN: Four samples were subjected to potentiodynamic analysis to determine material stability. Photocorrosion was minimal for three of the electrodes under all conditions, which included both acidic and basic solutions, with and without platinum treatment. Figure 1 is an example from potentiodynamic analysis of an electrode that exhibits nearly ideal behavior against photocorrosion. The fourth sample exhibited significant photocorrosion

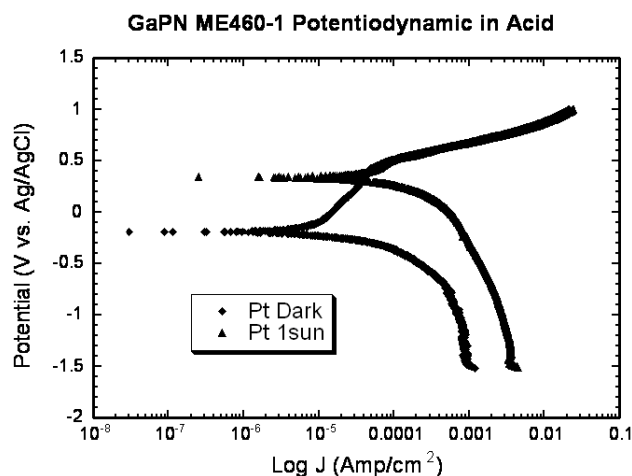


Figure 1. Evaluation of Photocorrosion Showing the Overlap of the Anodic Current Density Branches in Darkness and Light. For this electrode the dark cathodic current density after platinum treatment was unusually high.

under all conditions. This behavior is most likely due to this sample having the lowest nitrogen composition of this series of GaPN samples.

Illuminated potentiodynamic plots in acid and base, with and without platinum, for all electrodes are quite similar. This indicates that these materials are equally resistant to photocorrosion in both acidic and basic solutions. As expected, the platinum treatment raises the cathodic current density slightly and reduces the potential required to bring about hydrogen evolution. Since the current densities are slightly higher in acidic solutions, acidic electrolyte is probably the best choice for operation of these materials. Stability must be determined from current density vs. time plots before the operating electrolyte can be determined conclusively.

GaPN electrodes were then subjected to current-time analysis to assess their corrosion resistance in acidic and basic solutions. The samples were tested for 60 minutes in 3 M H_2SO_4 and had projected lifetimes an order of magnitude higher than GaAsPN under the same conditions. This result suggests that arsenic has a destabilizing effect for these materials. GaPN evaluated for 60 minutes in KOH appears to have a shorter lifetime than in acid, similar to GaAsPN in KOH. GaPN is more stable in acid than base, which is the opposite stability criteria for the GaAsPN material. Acidic solutions are therefore the

Table 1. Current Density vs. Time Durability Results. GaPN is more stable in H_2SO_4 . Extending the duration of experiments led to increased projected lifetimes, indicating passivation of the surface during operation.

GaPN Sample	ME477	Acid ME460	60min ME463	ME461
% Nitrogen	1.6	2.1	2.6	3.5
Initial J (Acm^{-2})	2	1.8	2.2	4
Lifetime (hrs)	15.4	25.6	11.9	3.6
Extended Acid	ME463	ME461	ME461	
Duration	4.3 hours	18 hours	42 hours	
Lifetime (hrs)	21	57.8	104.1	
		KOH	60min	
Sample	ME477	ME460	ME463	ME461
Initial J (Acm^{-2})	2.9	2.4	7.9	3.9
Lifetime (hrs)	6.6	11.1	5.9	9.2
Extended KOH	ME461			
Duration	18 hours			
Lifetime (hrs)	27.7			

preferred electrolyte for GaPN photoelectrolysis. Longer lifetime experiments indicated that the 60-minute studies did not adequately predict stability. The lifetime projection for the best electrode increased in the longest duration study to 104 hours. The data from this experiment were also quite unique and promising (see Table 1). At 19 hours of operation, the current density was $1.6 \text{ mAc}m^{-2}$ and remained steady for 8 hours. At 27 hours, the current density increased to $1.7 \text{ mAc}m^{-2}$ and remained constant for 8 hours. The performance dropped off at a constant rate over the next 8 hours to a low of $1.3 \text{ mAc}m^{-2}$ at the conclusion of the study. The improvement in gas evolution provides hope that stability can be enhanced under some conditions. The testing, however, yellowed the acid solution, which points to some sample dissolution.

GaPN current densities and lifetimes appear to be independent of the nitrogen composition of the sample. The increase in lifetime observed with longer testing illustrates a passivating process occurring on the surface of GaPN. This phenomenon means short-duration experimental results cannot be used to determine expected lifetime. The materials must be run until hydrogen evolution ceases in order to determine true electrode lifetimes.

Thin-film Materials

Large-area fabrication possibilities and low-cost material requirements combine to make thin-film materials a desirable option for photoelectrochemical hydrogen production. Electrodeposition provides a low-cost, scalable technique for the production of large-area thin-film materials for this application. Electrodeposited CuInSe_2 (CIS) thin-film materials have been extensively studied; however, their band gaps are too low for application as a top junction in these devices. It is known that addition of Ga and S into the CIS lattice can increase the material band gap to within the desired range of 1.7-2.0 eV [1]. The addition of sulfur in the electrodeposition process has proved to be extremely difficult. In this research, Cu(In,Ga)Se_2 materials were electrodeposited on molybdenum-coated glass substrates and then vapor-enriched in several different atmospheres containing sulfur.

Film Preparation Results

Copper in solution affects the overall deposited film composition. Greater copper concentration in solution correlated to more Cu and less Se deposited in the film. Successive depositions from the same fresh solution resulted in little change in the composition of the films. However, deposition from the same solution after sitting overnight, or from a different solution with the same composition, often resulted in deviation from the previous stoichiometry.

Annealing these precursor materials in a sulfur-containing atmosphere enriches them from the surface down. Due to diffusion limitations, sulfur is seen in higher concentration near the material surface versus the material bulk. Phase separation is evident in many of these materials, most likely due to this compositional gradient. Some materials show multiple band gap characteristics due to this effect. Figure 2 shows the x-ray diffraction (XRD) pattern of an enriched sample. This film shows higher sulfur and gallium concentration at the surface. Splitting in the CIS peaks is seen, representing these variations in the lattice.

Films with a high Ga/In ratio and $\text{S/Se} = 1$ show a band gap around 1.9 eV, with a second apparent

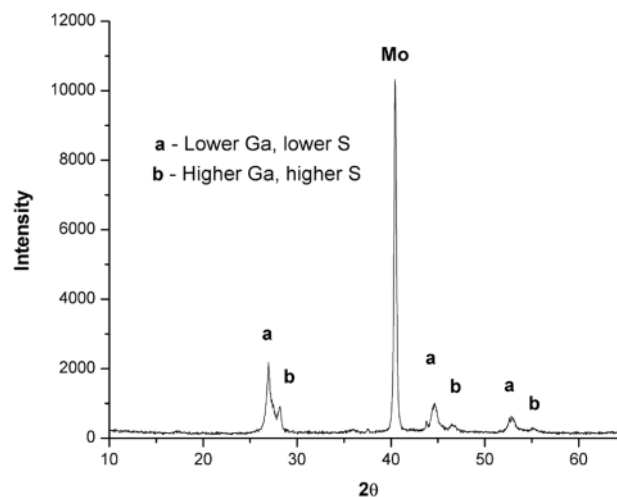


Figure 2. XRD Pattern Showing Peak Splitting Due to Annealing in a Sulfur-Containing Atmosphere and Consequent Film Inhomogeneity

band gap in the CIS range. Films with a very low Ga/In ratio show a single, much lower band gap, closer to 1.1 eV. All of the former films showed splitting in the XRD patterns.

Discussion

It has been demonstrated that successive electrodepositions yield thin films with reproducible compositions. The enrichment process can result in phase separation in certain precursor films, due to diffusion limitations. One of the phases in these materials exhibits a band gap in the desired range for photoelectrochemical water splitting. Further work is needed in the annealing and enrichment process to obtain single-phase materials with the desired band gap. These materials show potential in attaining the appropriate band gap for the top junction in photoelectrochemical water splitting cells. However, consistent deposition methods, including sulfur incorporation, need further development. Phase separation and annealing losses are problems being addressed.

Conclusions

- Initial studies on GaPAsN showed that although we were able to achieve the necessary band gap, the material stability was unsatisfactory, and our work on this material was discontinued.

- Initial studies on GaPN showed that achieving the necessary band gap was possible and that this material showed exceptional stability in acid under hydrogen evolution conditions.
- Work on the thin-film CuInGaSSe system showed that while it is possible to synthesize a material with a band gap in the range 1.6-2.0 eV, understanding and controlling all the variables involved in material growth remains a challenge.

References

1. Leisch, J.E., et al., Solar Energy Materials and Solar Cells, 2003(81): p. 249-259.

FY 2004 Publications

1. McConnell, R. D.; Turner, J. A.; Lasich, J. B.; Holland, D. (2004). Concentrated Solar Energy for the Electrolytic Production of Hydrogen. International Solar Concentrator Conference for the Generation of Electricity or Hydrogen, 10-14 November 2003, Alice Springs, Australia. NREL/CD-520-35349. Golden, CO: National Renewable Energy Laboratory; 24 pp.; NREL Report No. PR-520-36256.
2. Turner, J. A. (2004). Hydrogen Could Fuel the Digital Electric Grid. *Electronic Design*. Vol. 52(1), 12 January 2004; p. 24; NREL Report No. JA-560-35976.
3. Leisch, J. E.; Bhattacharya, R. N.; Teeter, G.; Turner, J. A. (2004). Preparation and Characterization of Cu(In,Ga)(Se,S)₂ Thin Films from Electrodeposited Precursors for Hydrogen Production. *Solar Energy Materials and Solar Cells*. Vol. 81(2), 6 February 2004; pp. 249-259; NREL Report No. JA-590-33791.
4. Fernandez, A. M.; Dheree, N.; Turner, J. A.; Martı́nez, A. M.; Arriaga, L. G.; Cano, U. Photoelectrochemical Characterization of the Cu(In,Ga)S₂ Thin-Film Prepared by Evaporation. *Solar Energy Materials* (in press).

FY 2004 Presentations

1. "Materials and Band-edge Engineering Approaches to Photoelectrochemical Water Splitting", at the XXIst International Conference

on Photochemistry, session on "Solar Light Energy Conversion: from Artificial Photosynthesis Technology to Solar Cells", Nara, Japan.

2. "Nitride Semiconducting Materials for Hydrogen Production from Water and Sunlight via Photoelectrolysis", at the XII International Materials Research Congress, Symposium on Solar-Hydrogen-Fuel Cells, Mexico.
3. "A Vision for a Renewable Hydrogen Economy", Platts Global Energy Group, Boulder, Colorado.
4. "Overview of Hydrogen and Fuel Cell Research at NREL" to the Renewable Energy Conversion Working Group of the Interagency Advanced Power Group, Golden, Colorado.
5. "A Vision for a Renewable Hydrogen Economy" at the Massachusetts Institute of Technology Emerging Technology Forum, Cambridge, Massachusetts.
6. "Photoelectrochemical Direct Water Splitting Systems", invited talk at the Chesapeake Conference sponsored by DuPont.
7. "The Renewable Hydrogen Economy", invited talk at University of Texas, Arlington, Texas.
8. Invited talk at the workshop on Photosynthesis that was organized at Lawrence Berkeley National Laboratory as part of their energy initiative workshop series. The presentations can be found at: <http://www.lbl.gov/pbd/energy/>.
9. Presentation (at NREL) to Stanford's Global Climate and Energy Program leadership.
10. Presentation (at NREL) on hydrogen and fuel cells to a group of cadets and faculty from the Air Force Academy.
11. Lecture on hydrogen and fuel cell technologies to the Ted Scripps Fellows in Environmental Journalism.
12. H. Wang participated in the Electrochemical Society Meeting, presenting a poster.