

II.F.3 Characterization and Optimization of Photoelectrode Surfaces for Solar-to-Chemical Fuel Conversion

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Project End Date: Project continuation and direction
determined annually by DOE

Fiscal Year (FY) 2012 Objectives

- Develop theoretical tool chest for modeling photoelectrochemical (PEC) systems, including experimental validation using model III-V systems.
- Compile publications database of research on relevant photoelectrode materials.
- Uncover key mechanisms of surface corrosion of semiconductor photoelectrodes.
- Understand dynamics of water dissociation and hydrogen evolution at the water-photoelectrode interface.
- Evaluate electronic properties of the surface and water-electrode interface.
- Elucidate relationship between corrosion and catalysis.
- Provide simulated X-ray spectra to the University of Nevada, Las Vegas (UNLV) for interpretation of experimental results and validation of theoretical models.
- Share research insights with the PEC Working Group members.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Z) Materials Durability
- (Y) Materials Efficiency

Technical Targets

This project is conducting fundamental theoretical studies of mechanisms of corrosion and catalysis in III-V semiconductor-based photoelectrode materials for PEC hydrogen production. Insights gained from these studies will be applied toward the optimization and design of semiconductor materials that meet the following DOE 2013 PEC hydrogen production targets:

- Usable semiconductor bandgap: 1.8-2.3 eV
- Chemical conversion process efficiency: 10%
- Plant solar-to-hydrogen efficiency: 8%
- Plant durability: 1,000 hrs.

FY 2012 Accomplishments

- Continued with compilation, review, and sharing of available information on III-V electrode materials, catalysts, and related subjects (ongoing).
- Performed quantum molecular dynamics of water-electrode interfaces:
 - Summarized studies on III-V surface morphology.
 - Published discussion of effect of surface oxidation and hydroxylation in a peer-reviewed journal.
- Investigated simple model Hamiltonian approach for feasibility of theoretical screening of co-catalysts.
- Group discussion of results pointed to supporting evidence for hole-trap corrosion mechanism, which is one of three possible corrosion mechanisms identified in FY 2011.
- Continued collaborations with unfunded external collaborators to develop theory/computational tool chest for PEC hydrogen research.
- Continued joint theoretical/experimental study on III-V electrode surface (continue through FY 2012 and beyond).



Introduction

Certain III-V based photoelectrochemical cells, notably the GaInP₂/GaAs tandem cell developed at the National Renewable Energy Laboratory (NREL), are known to demonstrate high solar-to-hydrogen conversion efficiencies that already exceed the DOE FY 2013 goal. However, durability of these cells has remained the key unresolved

issue so far. The primary purpose of this project is to perform a detailed investigation into the microscopic properties of the water-electrode interface, and to use this information to identify correlations with device performance, as measured in terms of solar-to-hydrogen conversion efficiency and corrosion resistance. The results will provide key feedback to collaborators at NREL, helping them develop a coherent performance optimization scheme for III-V based photoelectrodes. State-of-art X-ray spectroscopic measurements performed by the UNLV team will bridge remaining gaps in the knowledge obtained from our atomistic modeling, facilitating comparison with actual electrode properties. In FY 2012, we had four major accomplishments [1]. First, our findings on the surface morphology and its chemical properties were summarized and published in a peer-reviewed journal [2]. Second, key evidence that supports one of three corrosion mechanisms identified in FY 2011 was found. Third, we adapted and tested a simple model Hamiltonian-based method, which can be used to screen for good co-catalyst materials in a computationally efficient manner. Fourth, calculation procedures for X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) of phosphorous L-edge and nitrogen K-edge spectra were established, with preliminary results showing excellent agreement with experiments [3]. The last accomplishment is particularly significant in light of recent activity at NREL, which found that specific nitrogen surface treatments can improve the durability of GaInP₂ electrode beyond 1,000 hours [4]. The NREL results have motivated a shift in focus for FY 2013, during which we will investigate the chemical and physical state of nitrogen incorporated into the electrode surface, using both simulations and interpretation of the UNLV-generated X-ray spectroscopic measurements. The results will be used to provide feedback to NREL in order to optimize the nitrogen treatment process.

Approach

Further progress in semiconductor-based PEC photoelectrodes requires in-depth understanding of the complex relationship between surface stability and catalytic activity. This in turn relies on knowledge of the fundamental nature of the electrode-water interface, and of the chemical pathways explored during surface-active hydrogen evolution. As such, we are carrying out finite-temperature ab initio molecular dynamics simulations and energetics calculations based on density-functional theory to understand the chemical, structural, and electronic properties of water/electrode interfaces under equilibrium conditions, as well as to understand the competing chemical reaction pathways visited during photocatalysis. Our approach uses (001) surfaces of InP, GaP and GaInP₂, which have known water-splitting activity, as model semiconductor electrodes. We are investigating on effect of the foreign chemical species on the stability and reactivity of the electrode surfaces, as suggested

by our collaborators in J. Turner and T. Deutsch's group at NREL [5], as well as independent reports in the literature that surface oxygen may play a key role in motivating both the surface photocorrosion and the catalytic water splitting reaction [6,7]. Accordingly, we are evaluating the stability, structure and reactivity of the III-V(001)/water interfaces in the presence of surface oxygen, hydroxyl, and nitrogen, in order to correlate the results to experimentally observed surface compositions and morphologies. We also provide ab-initio derived X-ray spectroscopic data to enable direct comparison with experimental results from Prof. C. Heske's group at UNLV. This information is intended to suggest a strategy for device improvement.

Results

Over 800 papers related to PEC hydrogen research have been collected, indexed, and stored. Those deemed especially relevant to III-V semiconductor-based approaches have been summarized and shared with members of the III-V Surface Validation Team (LLNL/NREL/UNLV) of the DOE Photoelectrochemical Hydrogen Production Working Group using a limited-access community web forum and traditional email communication. Particular emphasis was put on GaInP₂, In₂O₃, and the growth interface between the two, since these are expected to be crucial for identifying the agent responsible for corrosion resistance and hydrogen evolution.

Detailed studies of InP and GaP (001) surfaces, and in particular, of the effect of surface oxide and hydroxyl on material properties, were summarized and published in a peer reviewed journal [2]. Specifically, the paper details the relationship between local atomic configurations, electronic structure, and chemical properties of these surfaces. Based on observations of general trends widely observed across various types of surface morphologies, we proposed that despite their structural and morphological complexity, the most important chemical properties of real electrode surfaces could be described by a simple local model. This represents a crucial development, as it allows us to dramatically simplify our models of real photoelectrode surfaces without loss of generality. The local bond-topological model also simplifies the calculation of X-ray spectra of the III-V photoelectrode surfaces, which are an important bridge that can connect the microscopic photoelectrode properties to actual measured device performance. Our paper also identified a few local atomic configurations whose specific electronic signatures point to a possible role in photocorrosion due to hole trapping. Notably, this hole trapping mechanism was one of the three possible mechanisms we identified in FY 2011.

During a PEC Working Group teleconference held in FY 2012, we proposed a "dark" current experiment, in which electrons are provided by the power source to the cathode rather than via photoillumination. This allows one to identify whether cathodic hole transport, which is relevant only in

the case of photoillumination where electrons and holes are co-generated, plays a role in the corrosion mechanism. If hole trapping is the major source of corrosion, the rate of corrosion should be greatly suppressed in a dark current experiment. We were able to determine that the NREL team had already conducted such experiments in 1998 (for an unrelated purpose) [8], and that they indeed observed a reduced rate of corrosion when applying current in the dark. This supports our assertion that the hole-trapping corrosion mechanism is the major contributor for III-V based photocathode. Developing a robust method to eliminate the hole-trap levels is the rational next step. One possibility would be to induce controlled growth of a high-quality surface oxide that avoids the local atomic configurations responsible for the hole trapping.

As was highlighted at the 2012 Annual Merit Review, T. Deutsch (NREL) has successfully shown that by using specific ion energies and durations, nitrogen bombardment of GaInP₂ surfaces can yield significant enhancements in durability, with one nitrogen-treated sample showing durability in excess of 1,000 hours. At this moment, the underlying mechanism of the enhanced durability is not understood. To this end, the spectroscopy team at UNLV recently performed a series of measurements (including XES) and found that the aforementioned sample showed a strong nitrogen-related peak with a shape indicating a unique but unidentifiable chemical environment. Simultaneously, at LLNL, we established the calculation procedures for P L_{2,3}-edge XAS (see Figure 1) and XES of GaP and InP [1], N K-edge of GaN. We anticipate that the information obtained from these analysis will allow us to properly interpret the measured spectra, which will be crucial in understanding the stabilization mechanism due to low energy nitrogen bombardment [5].

Finally, during FY 2012, we began investigating a new method for quickly screening the feasibility of candidate co-catalysts, based on a model Hamiltonian approach developed by Santos and others [9]. This method is based on Markus-Hush theory and the Anderson-Newns model,

and is able to simultaneously address H⁺ solvation, charge transfer reactions, and chemisorption very simply and with relatively low computational cost. In the original paper, it was demonstrated that the protonation of a Pt surface under bias could be described using this approach, yielding qualitatively correct descriptions of the free energy profile (indicative of exothermic, barrierless reaction) and of the barrier suppression mechanism (strong hybridization between Pt *d* and proton *s* levels). We have applied this method to examining protonation of a GaInP₂ surface under an applied bias potential and have confirmed that the model gives qualitatively correct behavior. In particular, we were able to properly predict protonation to be an exothermic reaction, with a large kinetic barrier that can be traced to poor hybridization between the proton and the GaInP₂ surface (see Figure 2). The fact that we are able to successfully discriminate between the free energy profile of a good catalyst (Pt) from a bad one (untreated GaInP₂ surface) indicates that the method may be used to efficiently screen candidate low-cost co-catalyst materials.

Conclusions and Future Directions

- The studies of surface chemistry and morphology performed during FY 2010 and FY 2011 were summarized and published in a peer-reviewed journal.
- Group discussions during a PEC Working Group teleconference led to finding evidence that specifically supports a hole-trapping mechanism as a major source of cathodic corrosion of III-V photoelectrodes.
- Computational procedures for accurate XAS/XES calculations for P L-edge, O K-edge, and N K-edge spectra were established.
- A simple model Hamiltonian approach to screen candidate co-catalysts was shown to be feasible.
- The compilation of past studies will continue in order to refine our growing understanding of the relevant issues of photoelectrochemistry, particularly with respect to III-V surfaces, their oxides, and interfaces between them.

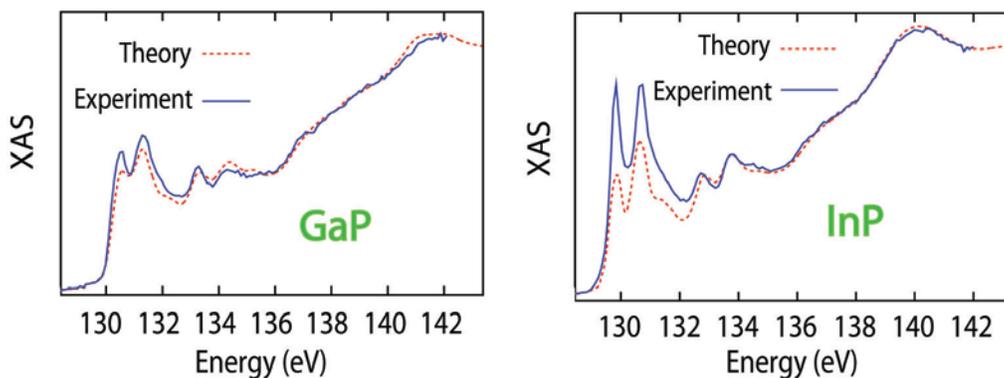


FIGURE 1. P L_{2,3}-edge XAS of bulk GaP and InP

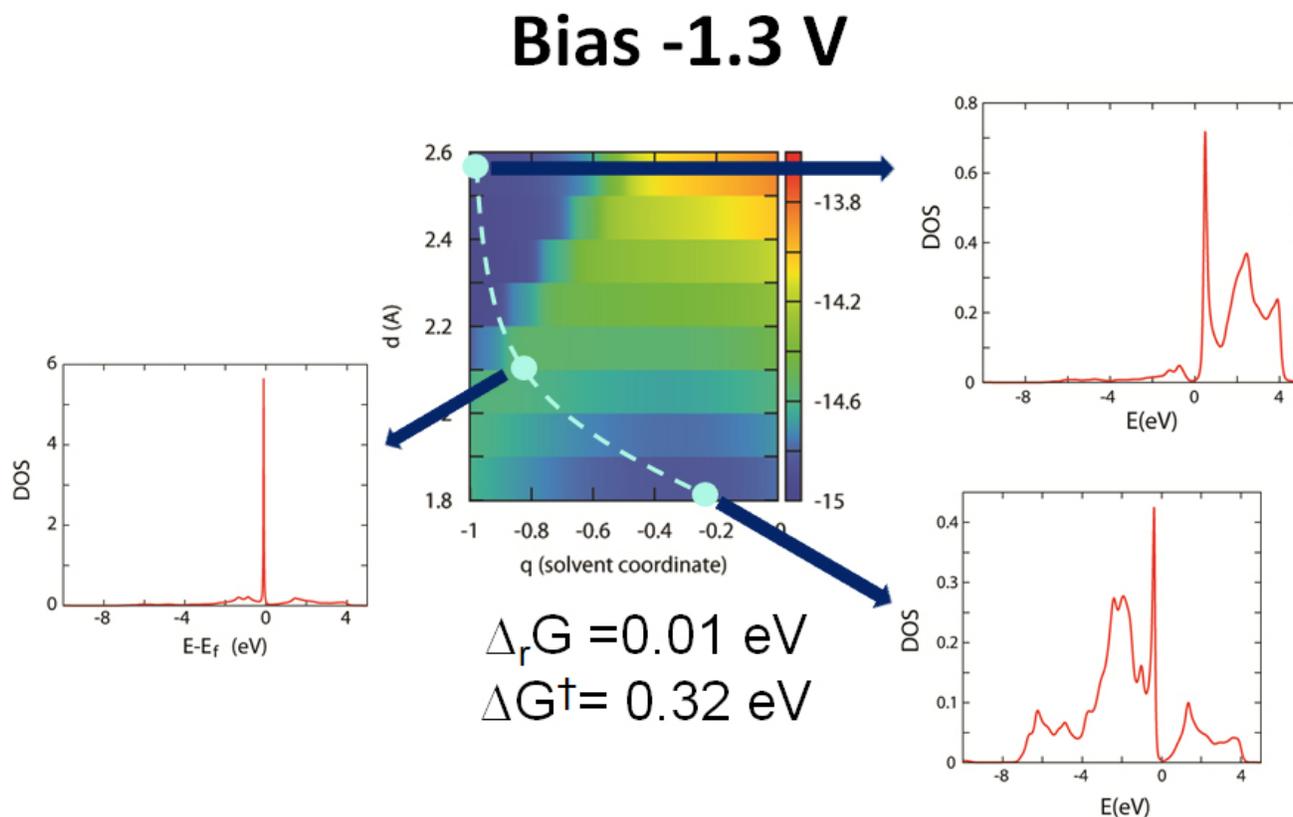


FIGURE 2. Free energy profile of protonation of GaInP₂ surface under a bias potential, calculated using the method described in reference [9]

- In FY 2013, our major focus will be to investigate on the state of nitrogen in nitrogen-bombarded GaInP₂. Successful identification of the optimal state of nitrogen will lead to improve durability of this electrode with minimal compromise of the solar-to-fuel conversion efficiency.
- We are currently summarizing the interface *ab initio* simulations performed in FY 2010-FY 2012 for publication in a high-profile peer-reviewed journal.

FY 2012 Publications/Presentations

Publications

1. T. Ogitsu, B. Wood, W. Choi, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2012).
2. B. Wood, T. Ogitsu, and E. Schwegler, *J. Chem. Phys.* **136**, 064705 (2012).

Presentations

1. The Molecular Foundry Annual Users Meeting in Berkeley, Oct 2011.
2. 220th ECS meeting in Boston, Oct 2011.

3. Workshop for U.S.-Japan DOE-METI Collaboration on Clean Energy Technology Action Plan in Pleasanton, CA, in Feb. 2012.
4. American Physical Society March Meeting in Boston, March 2012 (two presentations).
5. 2012 Materials Research Society Spring Meeting in San Francisco, April 2012.
6. DOE EERE Fuel Cell Technology Annual Merit Review in Arlington, May 2012.
7. Materials Simulation in Petaflops era in Kashiwa, Japan, June-July 2012 (two invited talks).
8. 19th International Conference on Photoelectrochemical Conversion and Storage of Solar Energy at Caltech, July-Aug 2012 (two presentations).

References

1. T. Ogitsu, B. Wood, W. Choi, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2012).
2. B. Wood, T. Ogitsu, and E. Schwegler, *J. Chem. Phys.* **136**, 064705 (2012).
3. C. Heske *et al.*, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2012).
4. T. Deutsch *et al.*, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2012).

5. T.G. Deutsch, C.A. Koval, and J.A. Turner, *J. Phys. Chem. B* **110**, 25297 (2006).

6. A. Heller, *Science* **223**, 1141 (1984).

7. J. Vigneron, M. Herlem, E. M. Khoumri, and A. Etcheberry, *Appl. Surf. Sci.* **201**, 51 (2002).

8. T. Deutsch, C. Koval, and J. Turner, *J. Electrochem. Soc.* **145**, 3335 (1998).

9. E. Santos *et al.*, *Phys. Rev. B* **79**, 235436 (2009).