II.H.1 Photoelectrochemical Hydrogen Production: DOE PEC Working Group Overview

Eric L. Miller
University of Hawaii at Manoa (UH)
1680 East-West Road, Post 109
Honolulu, HI 96822
Phone: (808) 956-5337; Fax: (808) 956-2336
E-mail: ericm@hawaii.edu

DOE Technology Development Manager:
Roxanne Garland
Phone: (202) 586-7260; Fax: (202) 586-2373
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

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Project End Date: Various funded projects within the DOE PEC Working Group with different end dates within 2009/2010.

Objectives

The U.S. DOE's photoelectrochemical (PEC) Hydrogen Production Working Group's primary objective is to collaboratively develop practical solar hydrogen-production technology, using innovative semiconductor materials and devices research and development (R&D) to foster the needed scientific breakthroughs for meeting DOE Hydrogen Program goals.

Technical Barriers

The DOE PEC Working Group is working to address all of the technical barriers identified in the "Photoelectrochemical Hydrogen Production" section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y) Materials Efficiency
(Z) Materials Durability
(AA) PEC Device and System Auxiliary Material
(AB) Bulk Materials Synthesis
(AC) Device Configuration Designs
(AD) Systems Design and Evaluation
(AE) Diurnal Operation Limitations

Technical Targets

As recognized within the PEC Hydrogen research community and the DOE PEC Hydrogen program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. This is reflected in Table 1, a reprint of the DOE Targets for PEC Hydrogen Production from the DOE's Multi-Year RD&D Plan [1].

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target
Usable semiconductor bandgap	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency	%	4	4	10	12
Plant solar-to-hydrogen efficiency	%	not available	not available	8	10
Plant durability	hr	not available	not available	1,000	5,000

The DOE PEC Working Group is utilizing its collective expertise in theoretical materials modeling, synthesis, characterization and analysis to study a diverse portfolio of promising PEC thin-film materials classes with the potential for meeting the technical targets.

Accomplishments

Important milestones have been achieved this past year through the collaborative efforts of the DOE PEC Working Group, and the associated DOE-funded projects. Significant progress has been made in the development of the Working Group's "Tool Chest" of materials theory, synthesis, characterization and analysis techniques; and this tool chest has been instrumental in the development and optimization of important PEC materials classes. For example, "useable band gaps" of 2.6 eV have been demonstrate in tungsten-based films compatible with integration into multi-junction devices with 5% chemical conversion efficiency, and even lower band gaps have been demonstrated in other PEC materials classes, including iron-oxide, silicon-carbide, copper-chalcopyrites, molybdenum-sulfide, and III-V compounds. DOE PEC Working Group efforts are ongoing to render these band gaps "useable" for high-efficiency PEC hydrogen production. The PEC Working Group accomplishments, detailed further in following sections, can be summarized broadly as follows:

- Successful Development and Application of New PEC "Tool-Chest" Capabilities.
- Advances in Focus Materials Classes Using the DOE-PEC Working Group's "Tool-Chest."
- Further Expansion of Collaborative Research Efforts.

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Introduction

PEC hydrogen production, the splitting of water into hydrogen and oxygen using sunlight, is an important enabling technology for a future green economy which will rely, in part, on hydrogen as an energy currency [2]. The traditional semiconductor-based PEC material systems studied to date, however, have been unable to meet all the performance, durability and cost requirements for practical hydrogen production. For example, PEC semiconductors such as titanium-dioxide and other metal-oxides have proven to be stable in aqueous solutions, but suffer from low solar conversion performance due to their high band gaps [3]. Based on these inherent limitations, it has become increasingly clear that new, more advanced materials need to be developed. Technology enabling breakthroughs in materials R&D are needed for the success of PEC hydrogen production.

Toward this end, the U.S. DOE currently funds a number of research institutions from the academic, industrial and national laboratory sectors with the objective of discovering, engineering and optimizing such advanced PEC materials systems for solar water-splitting. To facilitate progress, the project participants, have formed a national Working Group on PEC hydrogen production, bringing together experts in analysis, theory, synthesis and characterization from the academic, industry and national laboratory research sectors. The 2009 DOE Hydrogen Program Annual Merit Review (AMR) held in Crystal City, VA featured 13 presentations from participating PEC Working Group institutions, as illustrated in Figure 1. An overview of the collective approach and past-year's progress is presented in the following sections.

Approach

The general approach of the collaborative effort among the DOE PEC Working Group researchers is to integrate state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost. From the application of density-functional theory to calculate band-structures and effects of co-incorporants on valence and conduction band positions; through the use of diverse synthesis techniques, including combinatorial methods, to create tailored materials; and by employment of microstructural, electron spectroscopic, and electrochemical characterization techniques, a comprehensive picture of the materials properties and resulting performance is being developed. Within the DOE PEC Working Group, the approach has been applied to a number of "focus materials" deemed of particular interest for PEC applications.

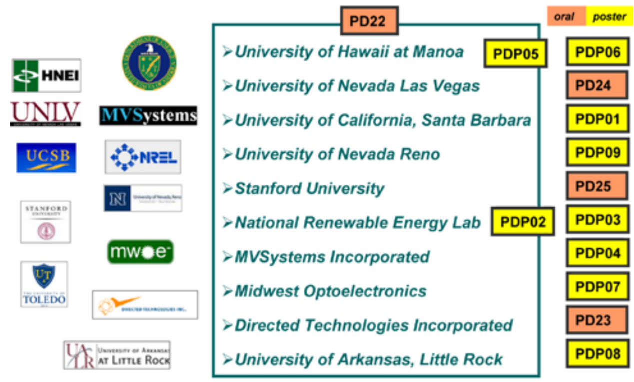

FIGURE 1. PEC Working Group Members with current DOE financial support, including the 2009 DOE Hydrogen Program Annual Merit Review oral/poster presentation designations.

It is important to stress that PEC hydrogen production has already been successfully demonstrated on the laboratory scale. High solar-to-hydrogen (STH) efficiencies, between 12-16%, have been demonstrated for limited durations in devices based on expensive high-quality crystalline semiconductors, such as the III-V tandem GaAs/$GaInP_2$ cell [4]. In addition, lower STH efficiencies, in the 3-5% range have been demonstrated in devices based on lower priced thin-film semiconductor materials. Multi-junction devices, for example using WO_3 films as a PEC top-junction, have been reported in this performance category [5]. To achieve practical PEC hydrogen production, new semiconductor materials systems with both high performance and low cost are needed. One specific approach is the further development of the traditional PEC semiconductor thin-films and nano-structures for higher efficiencies. Examples include improvements to iron-oxide and tungsten trioxide. Another approach is the adaptation of efficient photovoltaic (PV) semiconductor thin-films and nano-structures for effective use in PEC. This includes, for example, copper chalcopyrites and amorphous silicon compounds. Other innovative approaches include the development of entirely new materials classes, such as quantum-confined WS_2 and MoS_2 nanoparticle systems; and the development of breakthrough synthesis technologies to reduce the cost of high-performance crystalline semiconductors, such as $GaAs/GaInP_2$. Future progress in all these approaches will be integrally tied to the DOE PEC Working Group's continued development and deployment of its tool-chest, and continual feedback among the theory, synthesis and characterization efforts

Results

To expedite technical progress, the DOE PEC Working Group has initiated task forces to coordinate important PEC research activities. While some of the collaborative task forces center on the R&D of specific PEC materials classes, others focus on critical activities to advance the supporting science and technologies in the PEC tool-chest. Important activities in the latter category include:

- Development of standardized testing and reporting protocols for evaluating candidate PEC materials systems on a level playing-field. In the past, the lack of standardized conditions and procedures for reporting PEC results has greatly hampered research progress across the board. To date, the Standardized Testing Task Force, which is being coordinated by the National Renewable Energy Laboratory (NREL), has made significant initial progress, recently drafting 18 detailed testing protocol documents that are under continued refinement for near term publication [6].
- Development and refinement of techno-economic analyses of PEC hydrogen production systems incorporating performance and processing cost feedback from the broader materials R&D efforts. The objective is to provide a basis for evaluating the long-term feasibility of large-scale PEC production technologies in comparison with other renewable approaches. Techno-economic analysis activities with the Working Group have been coordinated through Directed Technologies Incorporated [7].
- Development of advanced characterization techniques to enhance understanding of PEC materials and interfaces and promote breakthrough discoveries [8]. The materials characterization efforts employ the most advanced microstructural, optoelectronic, and electrochemical characterization techniques available to paint a comprehensive picture of the materials properties in relation to PEC performance. Example techniques include X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, Auger, inverse photoemission spectroscopy, in ex situ as well as new, advanced in situ methods. Figure 2 shows the materials characterization facility developed at the University of Nevada, Las Vegas (UNLV), which is a cornerstone of the PEC research characterization activities.

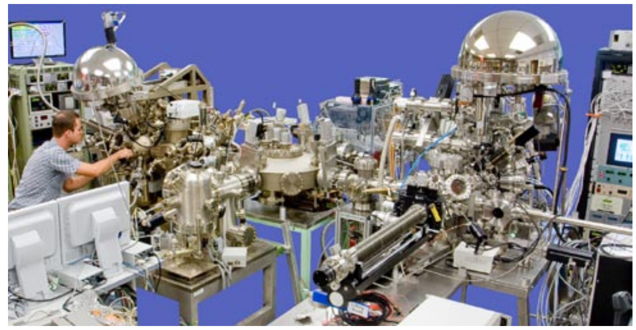

FIGURE 2. Advanced Solid-State/Surface Characterization Tool at UNLV

- Development of new theoretical models of PEC materials and interfaces critical to the design and engineering of new semiconductor systems [9]. For PEC semiconductor materials, the effects of impurity incorporation and other asymmetries on the band structures need to be calculated using both traditional and enhanced density-functional theory algorithm. Developing these sophisticated models of band states and bandgap, including effects of surface, interfaces and grain-boundaries, has been initiated within the PEC Working Group at NREL and the Lawrence Livermore National Laboratory.
- Development and implementation of innovative synthesis techniques to facilitate the PEC materials discovery process [10] represent important Working Group research activities. A broad spectrum of chemical, electrochemical and physical deposition methods are being employed to tailor material compositions and properties at the University of Hawaii, the University of California, Santa Barbara, and MVSystems, Incorporated, for example. Additionally, rapid throughput combinatorial methods based on the different synthesis routes are being explored. Innovative synthesis routes can make or break the viability of a semiconductor system, a fact well-appreciated by the PV community.
- Development of standardized screening procedures for the "Up-Selection" and "Down-Selection" of DOE-supported PEC materials classes. The screening procedures are being developed in close coordination with the standardized testing, advanced characterization, and materials-theory activities. A hierarchy of screening protocols, ranging from top level device performance to detailed measurement of performance limiting materials and interface properties, is being formulated within the Working Group, as illustrated in Figure 3. Standard and consistent application of the best available theoretical and experimental

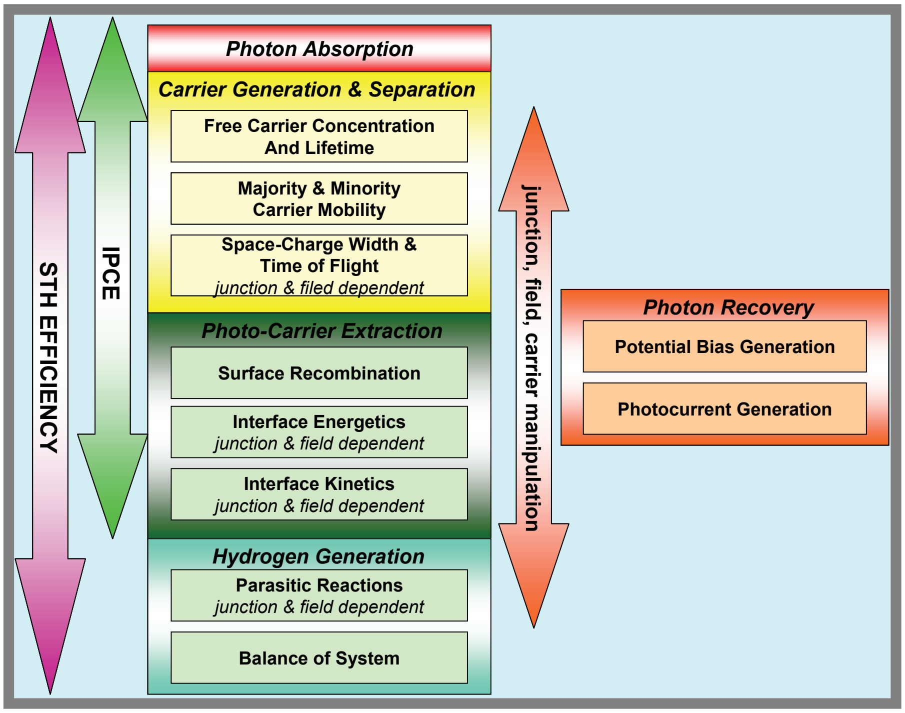

FIGURE 3. Block Diagram of PEC Screening Hierarchy under Development by the DOE PEC Working Group

techniques to direct research efforts is the objective of this important Working Group activity.

In the PEC Working Group, continued feedback between the theory, synthesis, characterization and analysis is providing fundamental insights needed to promote technical breakthroughs in a broad spectrum of promising PEC materials classes. The Working Group has initiated a white paper approach to the organization and tracking of scientific research progress. For each material class under investigation, a white paper is maintained as a living document which concisely summarizes the benefits, barriers, research status and approaches for addressing the barriers, all closely tied to the new advancements in theory, synthesis and characterization concurrently under development. The white papers also maintain a record of active research participants as well as a database of references documenting past achievements. To date, white papers have been drafted for a number of key focus materials classes including:

- **Tungsten-Oxide and Related Modified Compounds** - Tungsten oxide, particularly in thin-film and nano-particle forms, has been a workhorse in PEC applications for years. It is inexpensive and stable, but its high bandgap (~2.6 eV) is limiting to PEC performance. Photocurrent densities of approximately 3 mA/cm^2 have been achieved [11], with STH efficiencies over 3% in tandem configurations. To break the performance barrier, current research is focused on reducing bandgap through ion incorporation into the tungsten oxide structure [12], and further integration in multi-junction devices.
- **Iron-Oxide and Related Modified Compounds** - Iron-oxide is abundant, stable, inexpensive and has a near-ideal bandgap (~2.1 eV) for PEC applications. Unfortunately, its poor absorption, photo-carrier lifetime and transport properties have been prohibitive to practical water-splitting. Current research to overcome these barriers have been encouraging, with recent progress in thin films and nano-structured materials [13,14]. Iron-oxide in tandem configurations may also be of interest for practical solar water-splitting.
- **Amorphous Silicon Compounds, including Silicon Carbides and Nitrides** - Amorphous silicon compounds have recently demonstrated interesting performances in PEC applications [15,16]. The progress of this material class in PEC applications has benefitted from decades of research in the PV community. Technical barriers remain in PEC stability and interface properties, and electrolyte and surface modification studies could help overcome these barriers. With material and interface improvements, monolithically fabricated multi-junction devices using amorphous silicon compound films have practical appeal for PEC water splitting.
- **Copper Chalcopyrite Compounds** - Copper chalcopyrite thin films are among the best absorbers of solar energy. As a result, chalcopyrite alloys formed with copper and gallium, indium, sulfur and

selenium have been widely characterized in the PV world. A great advantage of this material class for PEC applications is the bandgap tailoring based on composition, with bandgaps ranging from 1.0 eV in $CuInSe_2$ to 1.6 eV in $CuGaSe_2$, and up to 2.43 eV in $CuGaS_2$ [17]. The $CuGaSe_2$ bandgap is attractive for PEC applications. Photo-current densities exceeding 13 mA/cm^2 have been demonstrated with this material [18] in biased PEC cells. Stability, surface kinetics and surface energetics remain as barriers, but if research can successfully address these, high STH efficiency could be achievable in low-cost thin-film copper chalcopyrite systems.

- **Tungsten- and Molybdenum-Sulfide Nano-Structures** - As bulk materials, tungsten- and molybdenum-sulfides are excellent hydrogen catalysts, but their bandgaps (below 1.2 eV) are too low for PEC water-splitting. Quantum confinement using nano-structuring, however, can increase the bandgap up to 2.5 eV. Current studies in nanostructured MoS_2 are focused on stable synthesis routes and integration of the nano-structures into practical bulk PEC devices [19].
- **III-V Semiconductor Classes** - High-quality crystalline semiconductor compounds of gallium, indium, phosphorous and arsenic have been studies for decades. In PEC experiments to date, STH efficiencies between 12 and 16 percent have been demonstrated in $GaInP_2$ /GaAs hybrid tandem photocathodes [20]. High cost and limited durability are the barriers to practical PEC hydrogen production, and breakthroughs in synthesis and in surface stabilization are being pursued.

Although there is still much work ahead for achieving high-performance low-cost PEC hydrogen production, research in these promising candidate materials has seen significant recent progress. The reader is referred to the cited references and to the progress reports for all of the DOE PEC Working Group 2009 AMR presentations (i.e., the presentations listed in Figure 1) for detailed progress in the individual materials categories.

Conclusions and Future Directions

The U.S. Department of Energy's Working Group on PEC hydrogen production has taken a collaborative approach in the R&D of novel PEC material systems. This approach, incorporating a broad spectrum of state-of-the-art techniques in theory, synthesis, characterization and analysis, is proving invaluable in the identification and development of the most promising materials for practical PEC hydrogen production. Continued Working Group efforts in conjunction with expanded international collaborations are expected to greatly facilitate the discovery and optimization of material systems and devices capable of meeting the DOE PEC hydrogen production targets. The current collaborative pathway is expected to greatly facilitate the discovery and optimization of material systems and device configurations capable of meeting the DOE PEC production targets. Specific future directions include:

- Continued Advancement of DOE PEC Working Group Efforts:
  - Further PEC "Tool-Chest" development efforts.
  - Standardization of materials and device testing protocols.
  - Refinement of materials selection and prioritization criteria.
- Continued Expansion of Collaboration Efforts, Nationally and Internationally:
  - DOE PEC Working Group expansion.
  - U.S.-led "International Energy Agency PEC Annex-26".

The ultimate aim is to make the materials and device breakthroughs necessary for high-efficiency, low-cost PEC hydrogen production.

Special Recognitions & Awards/Patents Issued

1. 2008 DOE Hydrogen Program R&D Award for DOE PEC Working Group Efforts: E. Miller.

2. IEA-HIA PEC Annex-26 Operating Agent Appointment: E. Miller.

FY 2009 Publications/Presentations

The publication list of the U.S. DOE PEC Working Group Members is extensive. The reader is referred to the progress reports of the 2009 DOE AMR presentations of the Working Group Participants (including oral presentations PD 23, 24, 25, as well as poster presentations PDP 05, 06, 07, 08 and 09) for a comprehensive list of publications.

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