II.E.2 Photoelectrochemical Hydrogen Production

Eric L. Miller (Primary Contact), Daniela Paluselli, Bjorn Marsen, Richard Rocheleau Hawaii Natural Energy Institute, University of Hawaii at Manoa 1680 East-West Road, POST 109 Honolulu, Hawaii 96822 Phone: (808) 956-5337; Fax: (808) 956-2336; E-mail: ericm@hawaii.edu

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

Objectives

- To assist DOE in the development of technology to produce hydrogen using solar energy to photoelectrochemically split water
- Develop cost-effective materials systems for efficient photoelectrochemical (PEC) hydrogen production
- Demonstrate viability of such a PEC system
- Initiate plans for future development to commercialization

Technical Barriers

The Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan describes photoelectrochemical hydrogen production technologies as "...not mature. Several technical barriers must be overcome before economic barriers can be considered. Methods of engineering and manufacturing these systems have not been fully evaluated." The general technical barriers addressed by this project are:

- M. Material Durability
- O. Photoelectrochemical Efficiency
- N. Materials and System Engineering

Approach

- Utilize multi-junction planar photoelectrodes based on low-cost materials for direct water splitting
 - Stainless steel foil substrates
 - Photoelectrochemically active metal oxide thin films such as Fe₂O₃ and WO₃
 - Photovoltaic (PV) thin films such as amorphous silicon (a-Si) and copper-indium-gallium-diselenide (CIGS)
- Develop University of Hawaii (UH)-patented "Hybrid Photoelectrode" (*HPE*) technology
 - <u>Materials Research</u>: Development of low-temperature and scalable processes to fabricate stable PEC metal oxide films and suitably matched PV films
 - <u>Photoelectrode Optimization:</u> Continued optimization of materials and device designs to demonstrate high-performance/low-cost hydrogen production

Accomplishments

The "Hybrid Photoelectrode" developed as a system with potential for efficient and cost-effective (PEC) hydrogen production

• Pathways to success identified and pursued

- Focus on metal oxide films (Fe₂O₃ and WO₃) for the top layer
- Integrate with proven amorphous silicon tandem technology
- Critical research issues in materials R&D and in photoelectrode design, fabrication and testing identified and attacked
 - Ability to engineer key properties of Fe₂O₃ and WO₃ films demonstrated
 - Excellent film adhesion and stability in corrosive electrolytes achieved
 - Photocurrents up to 1.3 mA/cm^2 achieved (1 sun) in WO₃ films
 - Bandgap reduction of WO₃ achieved through controlled doping of films
 - Tailored a-Si tandem device designed for next-generation prototype

Viability of a "Hybrid Photoelectrode" system demonstrated

- Prototype demonstrated based on WO₃ and amorphous silicon, operating in acid electrolyte
- Stable hydrogen production in 1N H₂SO₄ measured for over 10 hours
- Photocurrents up to 0.5 mA/cm² in 1-sun outdoor tests (0.7% solar-to-hydrogen)
- Key factors for efficiency enhancements identified

Future Directions

- · Plans initiated to address critical technical barriers and development issues
- Industry, academic and government lab partnerships established for further development toward commercialization

Introduction

Under the sponsorship of the U.S. Department of Energy (DOE), the Thin Films Laboratory at the Hawaii Natural Energy Institute of the University of Hawaii (UH) has been developing high-efficiency, potentially low-cost, photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source. The main thrust of the PEC systems research at UH has been the development of integrated multi-junction photoelectrodes based on low-cost semiconductor, catalytic, and protective thin films [1].

In order to meet the DOE's goals, the photoelectrode system must be low-cost and must be capable of operating stably in corrosive aqueous electrolyte environments with solar-to-hydrogen (STH) conversion efficiencies greater than 9% by 2010 and greater than 10% by 2015 [2]. In an attempt to meet the cost and performance goals, UH has been concentrating on the development of a "Hybrid Photoelectrode" (*HPE*) which incorporates low-cost metal-oxide and photovoltaic-grade semiconductor thin films, as described in the following section.

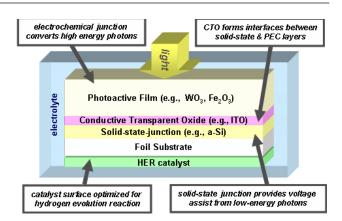


Figure 1. The multi-junction "Hybrid Photoelectrode" structure, showing constituent thin-film layers. Photons are absorbed both at the metal-oxide/ electrolyte interface and at the buried solidstate junction to generate sufficient voltage to split water.

Approach

The basic "Hybrid Photoelectrode" structure developed at UH is shown in Figure 1. This multijunction device combines thin-film solid-state with PEC junctions to meet the voltage, current and stability requirements for hydrogen production. The development effort has relied on continued use of integrated models for photoelectrode design [3], establishment of industry and university partners with thin-film materials expertise, and fabrication and evaluation of photoelectrode test devices. Significant advantages of the HPE design over other structures investigated at UH [4] include elimination of lateral current collection; simplification of device geometry for ease of fabrication; and improved stability based on the thick, seamless outer metaloxide layer. The primary focus of our current work has been the development of HPEs based on low-cost solid-state junction materials such as amorphous silicon (a-Si) and copper-indium-gallium-diselenide (CIGS) coated with photoactive metal oxides such as iron oxide (Fe_2O_3) and tungsten trioxide (WO_3).

There has been extensive investigation into Fe₂O₃ and WO₃ films for their PEC water splitting properties. Hydrogen production currents can be quite high in the metal-oxide PEC junctions, but only at sufficient levels of voltage bias [5,6]. In the HPE configuration, the necessary voltage bias is automatically generated in the buried solid-state junction utilizing low-energy photons not absorbed at the PEC interface. An important part of our research approach has been the development of lowtemperature (<300°C) processes yielding photoactive and stable metal-oxide films for HPE fabrication. Specific emphasis has been on developing reactively sputtered Fe₂O₃ and WO₃ films, along with fabrication and testing of HPE prototypes using amorphous silicon solid-state junctions with these sputter-deposited oxides.

Results

Significant progress was made this year in the development of the "Hybrid Photoelectrode" towards the goal of cost-effective PEC hydrogen production. The most promising materials systems for near-term demonstration were established, and the critical research issues in materials R&D and in photoelectrode design, fabrication and testing were identified and addressed. Importantly, all major milestones in materials research and photoelectrode development have been consistently met throughout the course of this project.

Key milestones this year were the establishment of promising HPE pathways based on tungsten trioxide and iron oxide, and completion of initial investigations of WO₃ and Fe₂O₃ films fabricated using a low-temperature reactively sputtered deposition process [7]. It was found that critical structural, electronic and photoelectrochemical properties of the sputtered films are significantly altered by varying the sputter deposition conditions, including oxygen partial pressure and substrate temperature (limited to 300°C for this research). For example, it was found that Fe₂O₃ film conductivity ranged from 10^{-9} to 10^{-2} S/cm, with the most conductive films deposited at the high end of our 'low-temperature' range with low oxygen percentages – an effect attributable to large grain structure and oxygen vacancy levels [8]. Similar correlations of conductivity with oxygen content and temperature were seen in WO₃ films, with conductivities ranging from 10^{-10} up to 10^{-1} S/cm. In general, the tungsten trioxide exhibited superior electronic behavior. All the Fe₂O₃ and WO₃ films from this study exhibited excellent stability in electrolyte; however, the hydrogen photocurrents in the best Fe_2O_3 films were limited to 0.1 mA/cm² in outdoor tests, while in contrast, photocurrents up to 1.2 mA/cm² were readily achieved in the sputtered WO₃ films, as seen in Figures 2a and 2b, respectively [9].

Key issues for continued enhancement of the photocurrent levels include the development of Fe₂O₃ films with better electronic properties (reduced photo-generated carrier recombination) and development of WO₃ films with reduced bandgap. Initial work to demonstrate bandgap engineering of sputtered WO₃ films using nitrogen doping was completed this year. As can be seen in Figure 3, showing the optical bandgaps for sputtered films as a function of the nitrogen content in the sputter ambient, WO₃ bandgaps can be reduced from 3.0 down to 2.1 eV using nitrogen as the doping gas. A more detailed analysis of this promising result will provide critical guidance for future HPE development. In future work, combinatorial discovery methods will be useful, both in the reduced-bandgap WO3 and in the reducedrecombination Fe₂O₃ development process. A wide range of doped films, including WO₃ doped with

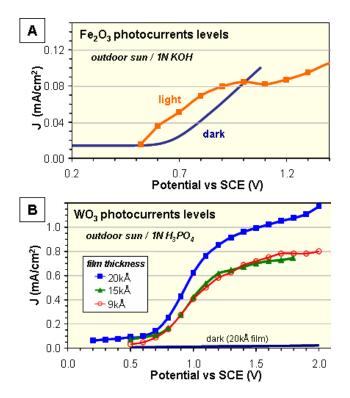


Figure 2. Photocurrent levels measured in reactively sputtered metal-oxide films: A) best iron oxide sample; B) tungsten trioxide samples of different thickness deposited under standard conditions.

nitrogen, sulfur, molybdenum (and others), and Fe_2O_3 doped with iodine (and others), will be thoroughly screened for their PEC performance.

A critical milestone in our photoelectrode development effort last year was the successful demonstration of functional "Hybrid Photoelectrodes" using un-optimized tandem amorphous silicon junctions (fabricated by the University of Toledo) coated with reactively sputtered WO₂ films [9]. The best devices tested generated hydrogen at up to 0.7% STH without serious degradation over a 10-hour operating period. Although the efficiency was low in these initial prototypes, clear pathways toward improvement have been identified this year, including (1) further development of metal-oxide films with increased photocurrent levels and (2) development of solidstate junctions with better current-matching and higher voltage boost. While the former has been the central focus of our work, initial efforts have been made to develop a better solid-state junction for the

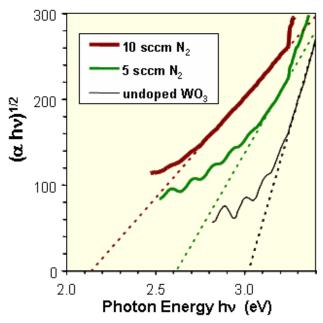


Figure 3. Tauc plot for undoped and nitrogen-doped tungsten trioxide samples with extrapolations for optical bandgap determination.

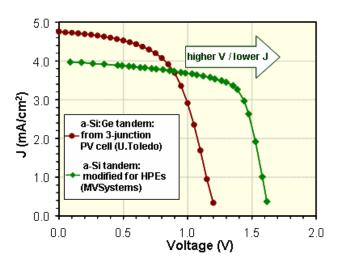


Figure 4. Current-voltage curves of double-junction a-Si/a-SiGe and a-Si/a-Si devices.

next-generation prototypes. Amorphous silicon tandem junctions can be tailored by varying the thicknesses and bandgaps of the two intrinsic absorber layers. Figure 4 compares the photovoltaic performance of the a-Si double junction from the initial prototypes with devices modified for improved PEC matching. It can be seen that some "unused" current has been traded for voltage in the modified

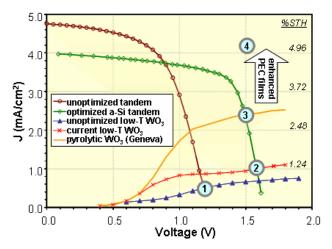


Figure 5. Performance levels of WO₃-based *HPE* systems determined by load-line analysis of the solid-state and PEC layer current-voltage characteristics. Current levels at the device operating points (i.e., curve intersections) translate linearly to STH efficiencies.

tandem. With a photocurrent of 3.65 mA/cm² (at 1.1 V), this device will enable demonstration of a 4.5% STH efficient device, provided an appropriate top junction is available (emphasizing the importance of further materials development to enhance the metal-oxide films).

Another important milestone this year was the development of a detailed roadmap outlining the direction of future work to enhance efficiency in HPE devices through accelerated R&D of novel metal-oxide films; further optimization of the solidstate junction layer; and demonstration of integrated devices, both on the laboratory and manufacture scale. Figure 5 indicates the specific directions in WO₃-based devices. Current and future performance levels of WO₃-based HPE systems are shown through the load-line analysis curves in Figure 5, indicating that (1) 0.7% STH is possible using unoptimized solid-state and sputtered WO₃ films (as demonstrated); (2) 1.3% STH is possible using the solid-state and sputtered WO₂ films developed this year; (3) > 3% STH is possible from a system using WO_3 without bandgap modification; and (4) >5% STH will require both bandgap modification of the WO₃ and further optimization of the solid-state junction. To meet DOE goals, a collaborative effort has been initiated to tackle the key technical issues in future work. Coordinated materials research and device integration efforts are planned at UH, MVSystems Inc., the Southwest Research Institute, Duquesne University and the National Renewable Energy Laboratory, with complementary "combinatorial discovery" efforts at Intematix Corp. and the University of California Santa Barbara.

Conclusions

- The optical/electronic properties of present hybrid-compatible metal oxides are still the *key limiting factor* to hydrogen production efficiency in *HPE*s at this time, clearly defining the primary focus for continued research efforts.
- Modified tungsten trioxide with reduced bandgap and modified iron oxide with reduced photocarrier recombination have been identified as promising pathways to *HPE* development.
- Continued *HPE* development is planned, based on expanded collaborative efforts including work in materials R&D, combinatorial discovery, and device integration and scale-up, which will enable *meeting the 2010 DOE goals*.

References

- E. Miller, R. Rocheleau, X. M. Deng, "Design Considerations for a Hybrid Amorphous Silicon/ Photoelectrochemical Multijunction Cell for Hydrogen Production." *International Journal of Hydrogen Energy*, 28 (6) (2003) 615-623.
- Multi-Year Research, Development and Demonstration Plan Planned Activities for 2003-2010 (draft 6/3/03), U.S. Department of Energy: www.eere.energy.gov/ hydrogenandfuelcells/mypp/.
- R. Rocheleau, E. Miller, "Photoelectrochemical Production of Hydrogen: Engineering Loss Analysis." *International Journal of Hydrogen Energy*, 22 (8) (1997) 771-782.
- R. Rocheleau, E. Miller, A. Misra, "High-Efficiency Photoelectrochemical Hydrogen Production Using Multijunction Amorphous Silicon Photoelectrodes." *Energy and Fuels*, 12 (1998) 3-10.

- S. Khan, J. Akikusa, "Photoelectrochemical Splitting of Water at Nanocrystalline n- Fe₂O₃ Thin Films Electrodes." *Journal of Physical Chemistry B*, 103 (1999) 7184-7189.
- C. Santato, M. Ulmann, J. Augustynski, "Photoelectrochemical Properties of Nanostructured Tungsten Trioxide Films", *J. Phys. Chem. B*, 105 (2001) 936-940.
- 7. A. Elshabini-Riad & F. D. Barlow III, "Thin Film Technology Handbook" McGraw-Hill (1998).
- E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, "Low-Temperature Sputtered Iron Oxide for Thin Film Devices." *Thin Solid Films*, in press (2004).
- 9. E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, "Development of Reactively Sputtered Metal Oxide Films for Hydrogen-Producing Hybrid Multijunction Photoelectrodes." *International Journal of Hydrogen Energy*, in press (2004).

FY 2004 Publications/Presentations

- E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, "Low-Temperature Sputtered Iron Oxide for Thin Film Devices", *Thin Solid Films*, in press (2004).
- E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, "Development of Reactively Sputtered Metal Oxide Films for Hydrogen-Producing Hybrid Multijunction Photoelectrodes", *International Journal of Hydrogen Energy*, in press (2004).
- E. Miller, R. Rocheleau, S. Khan, "A Hybrid Multijunction Photoelectrode for Hydrogen Production Fabricated With Amorphous Silicon/ Germanium and Iron Oxide Thin Films", *International Journal of Hydrogen Energy* 29, 907 (2004).

Special Recognitions & Awards/Patents Issued

 E. Miller & R. Rocheleau, "Hybrid Solid-State/ Electrochemical Photoelectrode for Hydrogen Production": patent pending through the UH Office of Technology Transfer and Economic Development.