Photoelectrochemical Hydrogen Production

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Final Report

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Photoelectrochemical Hydrogen Production – Final Report

Eric L. Miller, Daniela Paluselli, Bjorn Marsen, Richard Rocheleau

Executive Summary

Abstract
The scope of this photoelectrochemical hydrogen research project is defined by multijunction photoelectrode concepts for solar-powered water splitting, with the goal of efficient, stable, and economic operation. From an initial selection of several planar photoelectrode designs, the "Hybrid Photoelectrode" (*HPE*) has been identified as the most promising candidate technology. This photoelectrode consists of a photoelectrochemical (PEC) junction and a solid-state photovoltaic (PV) junction. Immersed in aqueous electrolyte and exposed to sunlight, these two junctions provide the necessary voltage to split water into hydrogen and oxygen gas. The efficiency of the conversion process is determined by the performance of the PEC- and the PV-junctions and on their spectral match.

Based on their stability and cost effectiveness, iron oxide (Fe_2O_3) and tungsten oxide (WO_3) films have been studied and developed as candidate semiconductor materials for the PEC junction (photoanode). High-temperature synthesis methods, as reported for some high-perfomance metal oxides, have been found incompatible with multijunction device fabrication. A low-temperature reactive sputtering process has been developed instead. In the parameter space investigated so far, the optoelectronic properties of WO_3 films were superior to those of Fe_2O_3 films, which showed high recombination of photo-generated carriers.

For the PV-junction, amorphous-silicon-based multijunction devices have been studied. Tandem junctions were preferred over triple junctions for better stability and spectral matching with the PEC junction. Based on a tandem a-SiGe/a-SiGe device and a tungsten trioxide film, a prototype hybrid photoelectrode has been demonstrated at 0.7% solar-to-hydrogen (STH) conversion efficiency.

The PEC junction performance has been identified as the most critical element for higher-efficiency devices. Research into sputter-deposited tungsten trioxide films has yielded samples with higher photocurrents of up to 1.3 mA/cm^2. An improved a-Si/aSi tandem device has been demonstrated that would provide a better voltage match to the recently improved WO_3 films. For a hybrid photoelectrode based on these component devices the projected STH efficiency is 1.3%.

For significant efficiency enhancements, metal oxide films with increased optical absorption, thus lower bandgap, are necessary. Initial experiments were successful in lowering the WO_3 bandgap by nitrogen doping, from 3.0 eV to 2.1 eV. Optimizing the electronic properties of these compounds, or other reduced-bandgap materials such as Fe_2O_3, is the most immediate challenge. As the photocurrent levels of the PEC junction are improved, increasing attention will have to be paid to the matching PV junction.

Conclusions

- The viability of the hybrid photoelectrode concept has been demonstrated

- Optical/electronic properties of present hybrid-compatible metal-oxides are still the *key limiting factor* to hydrogen-production efficiency in *HPE*s
- Modified tungsten trioxide with reduced bandgap and modified iron oxide with reduced photocarrier recombination are seen as promising pathways to *HPE* development.

Recommendations

- Expand efforts to develop high-performance *HPE*-compatible metal oxide materials by high-throughput and classical materials science & engineering
- Pursue integrated device design for optimum spectral match of PEC and PV junctions
- Study scalability of metal oxide thin films and *HPE* devices to assess viability of commercialization

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Project Summary

Objectives

- Develop cost-effective materials and systems for efficient photoelectrochemical (PEC) hydrogen production
- Demonstrate viability of such a PEC system

Technical Barriers

The "Hydrogen, Fuel Cells & Infrastructure Technologies" (HFCIT) Multiyear Program 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 listed include:

- Material Durability. Durable materials with the appropriate characteristics for PEC hydrogen production that meet the program element goals have not been identified.
- Photoelectrochemical Efficiency. Materials with appropriate bandedge and bandgap for hydrogen production must be developed.
- Materials and System Engineering. Hybrid designs that combine multiple layers of materials could address issues of durability and efficiency.

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 Fe_2O_3 and WO_3
  - Photovoltaic (PV) thin films such as amorphous silicon and copper indium gallium diselenide (CIGS)
- Develop UH-patented "Hybrid Photoelectrode" (*HPE*) technology
  - Materials Research: Development of low-temperature & scalable processes to fabricate stable PEC metal oxide films and suitably matched PV films
  - Photoelectrode Optimization: Continued optimization of materials and device designs to demonstrate high-performance / low-cost hydrogen production

Accomplishments

Phase I.

- Evaluation of multijunction photoelectrode concepts completed
  - Amorphous silicon based device structures explored
  - CIGS based device structures explored
  - Hybrid photoelectrode design conceived
- Hybrid Photoelectrode (HPE) developed
  - Dedicated double- and Triple-junction a-Si devices fabricated
  - Initial Fe_2O_3-based prototype fabricated

Phase II.

- Fe_2O_3 films for HPE devices successfully deposited using low temperature sputter process
  - Ability to engineer key film properties successfully demonstrated.
  - Excellent film adhesion and stability in alkaline media achieved.
  - Photocurrents up to 0.1 mA/cm^2 achieved under 1-sun.
- WO_3 films for HPE devices successfully deposited using low temperature sputter process
  - Ability to engineer key film properties successfully demonstrated.
  - Excellent film adhesion and stability in acid media achieved.
  - Photocurrents up to 1.2 mA/cm^2 achieved under 1 sun.
- Stable operation of HPE (based on WO3) demonstrated:
  - Structure: amorphous silicon alloy tandem (U. Toledo) with sputtered ITO and low-temperature sputtered WO_3 (UH) - 2.5 cm^2 area.
  - Stable hydrogen production in 1N H_2SO_4 measured for over 10 hours.
  - Photocurrents up to 0.5 mA/cm^2 in 1-sun outdoor tests (0.7% STH).
  - Performance consistent with measured properties of the WO_3 material and the tandem silicon cell.

Phase III.

- Pathways to improved HPE efficiency identified and pursued:
  - Optimized metal oxide films (Fe_2O_3 and WO_3) for higher photocurrent
  - Tailored photovoltaic component device for optimum voltage assist
- Metal oxide research advanced:
  - Expanded parameter-space for WO_3 sputter deposition explored
  - Photocurrents up to 1.3 mA/cm^2 achieved (1 sun) in WO_3 films.
  - Bandgap reduction of WO_3 achieved through controlled doping of films
- Photovoltaic component device for HPE advanced
  - Tailored a-Si tandem device designed for next-generation prototype

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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.

Approach

Research at UH to develop integrated multijunction photoelectrodes for direct solar splitting water has evolved through several stages, as traced in Figure 1. Implementations of the various configurations based on amorphous silicon-germanium and on CIGS thin film technologies were investigated. Each of the configurations represented in Fig. 1 was found to suffer from serious disadvantages, in terms of either performance, stability, or complexity. As a result of this experience, the concept of the "Hybrid Photoelectrode" (*HPE*) was conceived and developed.

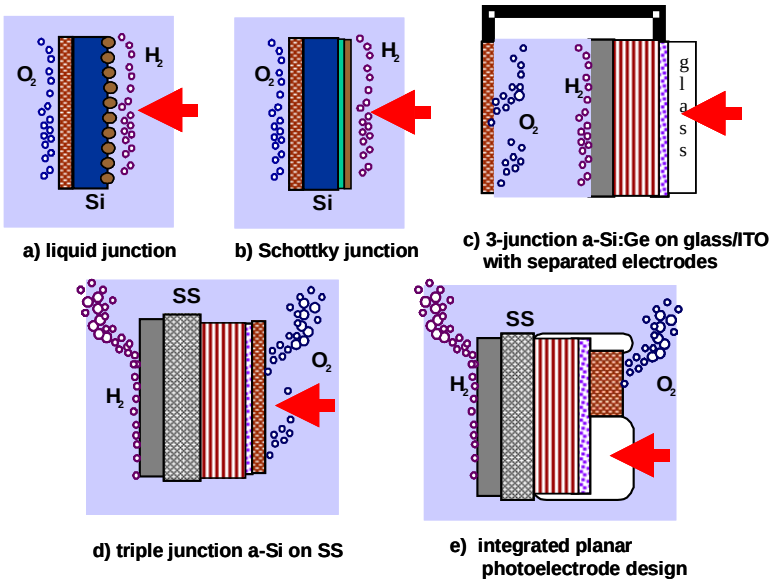

Figure 1. Evolution at UH of planar photoelectrodes for solar-to-hydrogen conversion.

The basic *HPE* structure developed at UH is shown in Figure 2. This multi-junction 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 metal-oxide layer. The primary focus of our current work has been the development of *HPE*s 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).

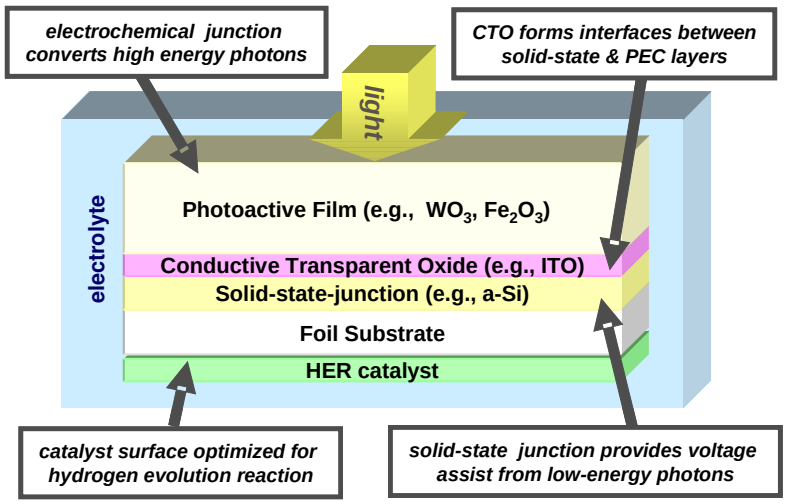

Figure 2. The multi-junction "Hybrid Photoelectrode" structure, showing constituent thin-films

There has been extensive investigation into Fe_2O_3 and WO_3 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 low temperature (<300°C) processes yielding photoactive and stable metal-oxide films which are compatible with *HPE* fabrication. Specific emphasis has been on developing reactively-sputtered Fe_2O_3 and WO_3 films, along with fabrication and testing of *HPE* prototypes integrating amorphous silicon solid-state junctions with these sputter-deposited oxides.

Results

Significant progress has been made towards the project goals with the development of the "Hybrid Photoelectrodes". 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 & testing were identified and addressed. All major milestones in materials research and photoelectrode development have been consistently met throughout the course of this project.

A key element of this project has been the development of WO_3 and Fe_2O_3 films 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 Fe_2O_3 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 WO_3 films, with conductivities ranging from 10^{-10} up to 10^{-1} S/cm. In general, the tungsten trioxide exhibited superior electronic behavior. All the Fe_2O_3 and WO_3 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/cm^2 in outdoor tests, while in contrast, photocurrents up to 1.2 mA/cm^2 were readily achieved in the sputtered WO_3 films, as seen if Figures 3a and 3b, respectively [9].

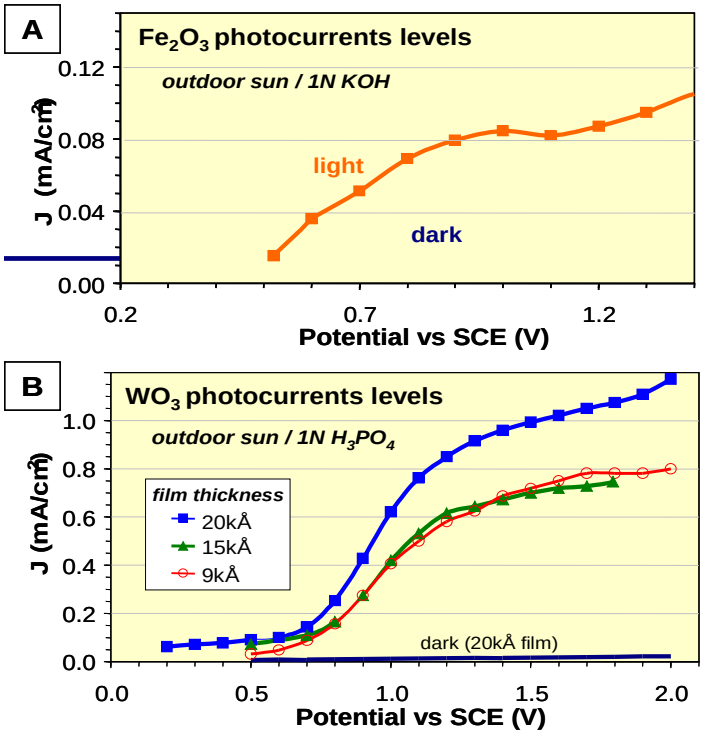

Figure 3. Photocurrent levels measured in reactively sputtered metal-oxide films: A) best Fe_2O_3 sample; B) WO_3 samples of different thickness deposited under standard conditions.

Critical issues for continued enhancement of the photocurrent levels include the development of Fe_2O_3 films with better electronic properties (reduced photo-generated carrier recombination), and development of WO_3 films with reduced bandgap. Initial work to demonstrate bandgap engineering of sputtered WO_3 films using nitrogen doping was completed by the end of the research program. As can be seen in Figure 4, showing the optical bandgaps for sputtered films as a function of the nitrogen content in the sputter ambient, WO_3 bandgaps can be reduced from 3.0 down to 2.1 eV using nitrogen as the doping gas. Further work on doped metal oxide materials is warranted based on these results. In particular, high-throughput screening of a wide range of doped films is recommended.

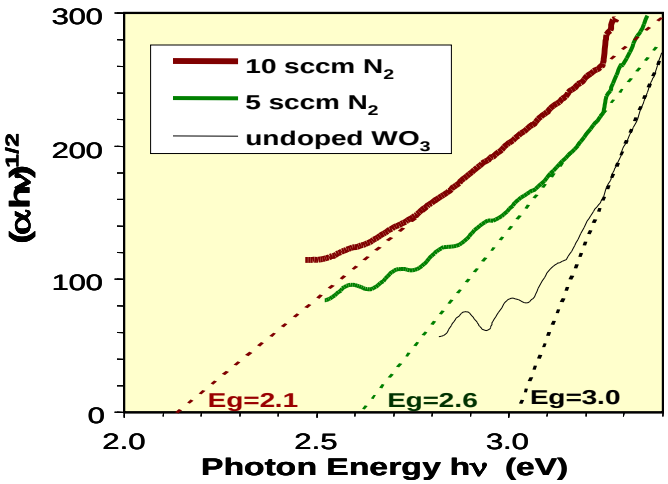

Figure 4. Tauc plot for undoped and nitrogen-doped tungsten trioxide samples with extrapolations for optical bandgap determination.

The most critical milestone in our photoelectrode development effort has been the successful demonstration of functional "Hybrid Photoelectrodes" using un-optimized tandem amorphous silicon junctions (fabricated by the University of Toledo) coated with reactively-sputtered WO_3 films [9]. The test structure is shown in Figure 5a. The performance of the component devices and the integrated hybrid photoelectrode are shown in Figure 5b.

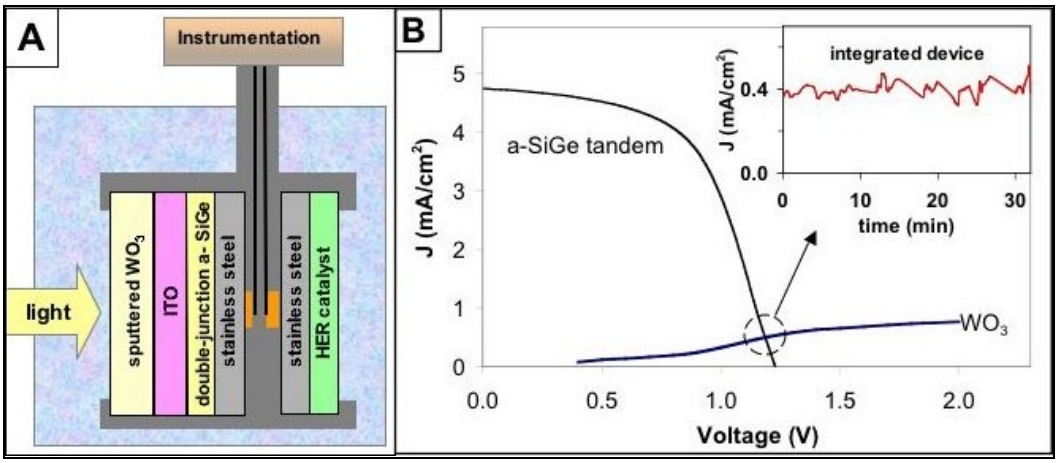

Figure 5. Successful "Hybrid Photoelectrode" demonstration. A) Test structure. B) Analysis based on performance of component films, and measured performance of the integrated device.

This particular device 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, including: (1) further development of metal-oxide films with increased photocurrent levels, and (2) development of solid-state 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 next-generation prototypes. Amorphous silicon tandem junctions can be tailored by varying the thicknesses and bandgaps of the two intrinsic absorber layers. Figure 6 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 tandem. With a photo-current of 3.65 mA/cm ^{2}(at 1.1V), 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.)

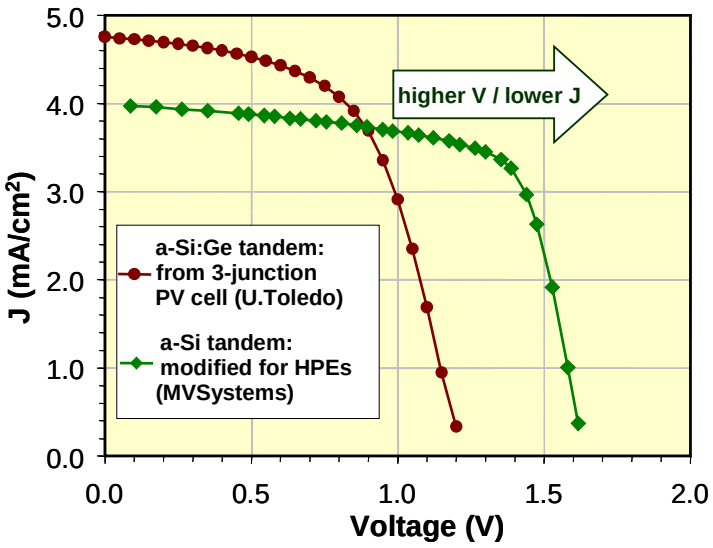

Figure 6. Current-voltage curves of double-junction a-Si/a-SiGe and a-Si/a-Si devices.

Another important milestone from this work has been 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 solid-state junction layer; and demonstration of integrated devices, both on the laboratory and manufacture scale. Figure 7 indicates the specific directions in WO_3 based devices. Current and future performance levels of WO_3-based *HPE* systems are shown through the load-line analysis curves in Fig. 7, indicating: (1) 0.7% STH is possible using unoptimized solid-state and sputtered WO_3 films (as demonstrated); (2) 1.3% STH is possible using the solid-state and sputtered WO_3 films developed so far; (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 WO_3 and further optimization of the solid-state junction.

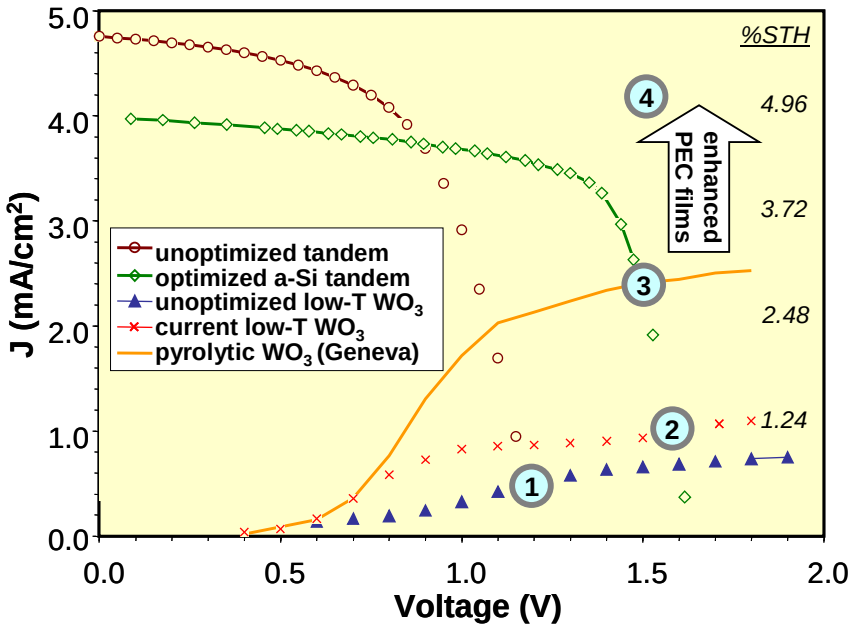

Figure 7. Performance levels of a WO_3-based *HPE* systems determined by load-line analysis of the solid-state and PEC layer current-voltage characteristics. Current levels at the device operating points (i.e., curve intersections) translate linearly to STH efficiencies.

Conclusions

- The viability of the hybrid photoelectrode has been demonstrated
- The optical/electronic properties of present hybrid-compatible metal-oxides are still the *key limiting factor* to hydrogen-production efficiency in *HPE*s
- Modified tungsten trioxide with reduced bandgap and modified iron oxide with reduced photocarrier recombination are seen as promising pathways to *HPE* development.

Recommendations

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References

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2. S. Marsillac, S. Dorn, R. Rocheleau,, E. Miller, "Low-temperature deposition of Cu(InGa)Se2 solar cells on various substrates", *Solar Energy Materials & Solar Cells* **82**, 45-52 (2004).
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Special Recognitions & Awards/Patents Issued

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

Acronyms

a-Si: Amorphous Silicon
a-SiGe: Amorphous Silicon Germanium
CIGS: Copper-Indium-Gallium-Diselenide
DOE: Department of Energy
Fe_2O_3: Iron Oxide
HFCIT: Hydrogen, Fuel Cells and Infrastructure Technologies
HNEI: Hawaii Natural Energy Institute
HPE: Hybrid Photoelectrode
ITO: Indium Tin Oxide
PEC: Photoelectrochemical
PV: Photovoltaic
STH: Solar to Hydrogen
UH: University of Hawaii
WO_3: Tungsten Trioxide