Proceedings of the 2000 Hydrogen Program Review
NREL/CP-570-28890

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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Abstract

High efficiency photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source have been identified by DOE as one of the promising technologies to meet long-term hydrogen-production goals. In the PEC research at UH, our approach has been to compare alternate materials and system configurations using reactor modeling, and to identify and address the critical materials and photoelectrode-operation issues through extensive experiments in materials synthesis and in photoelectrode fabrication and testing. In 1996 we demonstrated direct solar-to-hydrogen conversion efficiencies of 7.8% using a photocathode fabricated from 10% efficient triple-junction amorphous silicon solar cells. These prototypes were configured with a separate anode connect by wire to a photocathode. In subsequent years, our focus shifted toward the development of photoelectrodes with fully integrated cathodes/anodes. This year, we advanced the design of a new fully integrated and self-contained photoelectrode fabricated entirely with thin film processing and demonstrated a process sequence to fabricate prototypes. The new photoelectrodes again used multi-junction a-Si cells and sputter-deposited catalyst, contact, and protective films developed at UH. We also continued the development of optimal transparent-conductive and protective films. A deposition system for copper-indium -gallium diselenide (CIGS) films was installed (cost shared with other projects and UH support) as part of a new effort to develop higher efficiency photoelectrodes. The encapsulated design with side-by-side series-connected CIGS junctions has the potential to achieve 15% solar to hydrogen conversion efficiency. Plans are underway to demonstrate hydrogen-production using the a-Si photoelectrodes and to develop a fabrication process for high efficiency CIGS-based photoelectrodes.

Introduction

One of most ambitious goals of the US Department of Energy's Hydrogen Program is the large-scale production of hydrogen utilizing a renewable energy source to split water. High efficiency photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source is one of the more promising technologies to meet this mission. A schematic illustration of a PEC hydrogen production using solar energy as the renewable source is shown in Figure 1a (Rocheleau et. al., 1989). Sunlight shining on a photoelectrode comprising a semiconductor photovoltaic generator coated with catalytic thin films produces electric current which drives the hydrogen and oxygen evolution reactions (HER, OER) at the respective surfaces. In one possible conceptual design for a large-scale reactor, shown in Figure 1b, arrays of photoelectrodes are arranged in tubular reactors which include gas-separating membranes to facilitate the collection of high-purity hydrogen and oxygen.

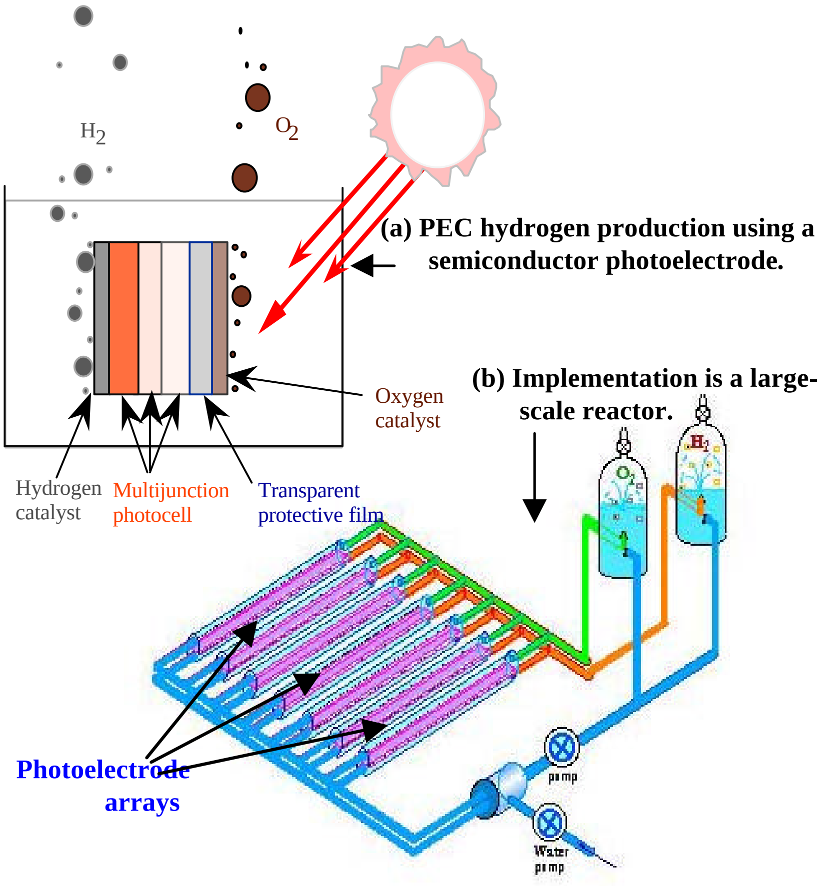


Figure 1 – Photoelectrochemical Hydrogen Production

In order to meet DOE goals, a PEC system must be low cost, must operate at solar-to-chemical conversion efficiencies greater than 10% and must have long operating lifetimes. Numerous approaches involving a variety of semiconductors have been explored since the early 1980's, but none have been successful. The high voltage required to dissociate water and corrosiveness of the aqueous electrolytes have been major hurdles. The use of multijunction PV devices provides sufficient voltage to split water and allows use of a wide range of catalytic and protective films. Modeling and proof-of-concept experiments conducted at UH have provided strong evidence that future direct solar-to-hydrogen conversion efficiency greater than 10% can be expected with photoelectrodes fabricated from low-cost, multijunction amorphous silicon (a-Si) solar cells (Rocheleau & Miller, 1997). Moreover, conversion efficiencies approaching 15% are possible using advanced photoelectrode designs (described in this paper) in which series-connected cells of high-efficiency materials, such as copper-indium-diselenide (CIS), can be stacked in a side-by-side configuration. Based on the very thin semiconductor layers involved and on compatibility with high-throughput manufacturing processes, both the a-Si and CIS photoelectrode systems have the potential for low cost.

Long Term Goals

The ultimate goal of this research is to develop high efficiency (greater than 10%), and low cost thin-film semiconductor photoelectrodes for PEC reactors to directly produce hydrogen from water using sunlight as the energy source. To reach this goal, our approach has included parallel research efforts in: 1) reactor modeling to compare alternate materials and system configurations (Rocheleau et al., 1994); 2) extensive experiments in materials synthesis and testing to identify critical materials issues (such as stability and catalytic activity); and 3) photoelectrode fabrication and testing to identify and address critical photoelectrode-operations issues. Work to date has identified promising high-efficiency PEC systems based on a-Si photoelectrodes coated with specially-developed thin-film catalysts (Rocheleau & Miller, 1997), and even higher efficiency systems based on CIS photoelectrodes. An important near-term goal is to identify which of the materials systems is best suited for achieving the long-term goals in efficiency, stability, scalability and cost.

Past Results

In the past, our effort was mainly focused on demonstrating the feasibility of the photoelectrochemical approach. Optimizing efficiency and stability of all necessary thin-film components of the photoelectrode, including semiconductor layers, the hydrogen and oxygen catalysts, and transparent contact and protective films, has been a significant part of the effort. Early demonstration prototypes were based the configuration shown in Figure 2 with a photoactive cathode and a separate anode. Potassium hydroxide (KOH) was chosen based on the demonstrated chemical activity and long-term stability of thin film HER and OER catalysts previously developed at UH for in this particular electrolyte (Miller & Rocheleau, 1997). For the cathode in the prototype, a triple-junction pinpinpin solar cell on a glass/SnO superstrate (Solarex Thin Film) was used. A CoMo HER thin-film catalyst was sputter-coated on the backside. The separate anode, connected via wires to the SnO layer of the solar cell was sputter-coated with a Fe:NiOx OER catalyst.

The hydrogen production performance of the prototype system operated in Honolulu on a day with intermittent cloud coverage is shown in Figure 3. Solar-to-hydrogen efficiencies as high as 7.8% were achieved in this configuration using a 10.3% efficient a-Si solar cell (Rocheleau et. al., 1998).

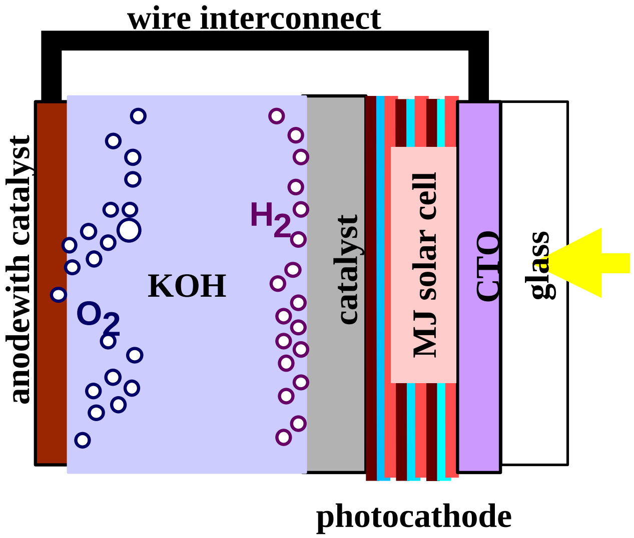


Figure 2 – Photocathode with Separate anode

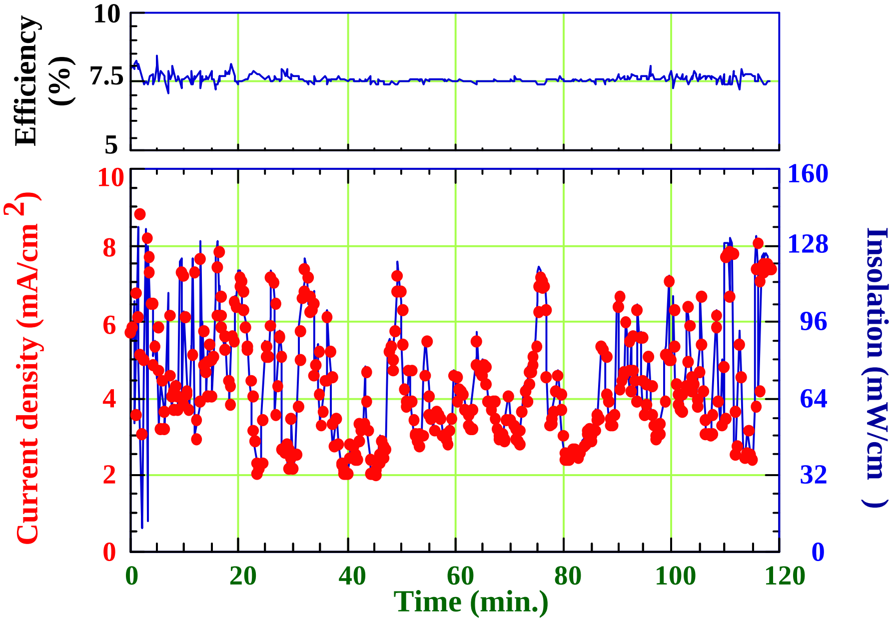


Figure 3 – Solar Hydrogen Production Data

After successful demonstration of proof of concept using the separated anode/cathode configuration, we focussed last year on the critical engineering issues for practical implementation. The primary goal was the development of fully integrated photoelectrode configurations based on planar fabrication of thin films onto inexpensive substrates. Design requirements included high solar-to-hydrogen efficiency, long term stability in aqueous electrolyte, and ease of scale-up. The first fully integrated photoelectrode design that was considered is shown in Figure 4. A nipnipnip a-Si cell (Energy Conversion Devices) on stainless steel substrate was used. The back surface of the SS substrate was coated with CoMo HER catalyst while the front surface of the solar cell was coated with Fe:NiOx OER catalyst. Unfortunately, the relatively thick (1 micron) Fe:NiOx layers introduced high optical losses (Miller, 1996), while thinner, more transparent films layers suffered from loss of catalytic activity and reduced corrosion protection.

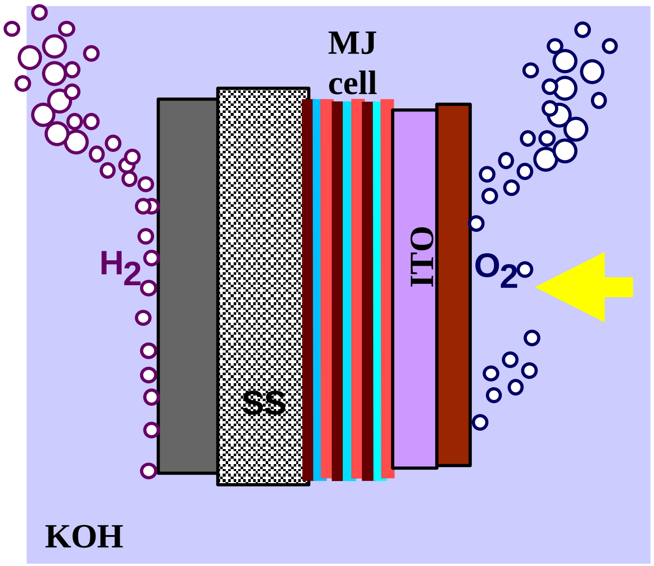


Figure 4 – Integrated Photoelectrode with Monolithic Stacked Cells

At the Hydrogen Program Review in May 1999 (Miller & Rocheleau, 1999), we introduced the conceptual design shown in Figure 5 for a new fully-integrated photoelectrode design structure incorporating planar, series connected solar cells. In this new structure, front surface regions for light collection and for oxygen evolution are separated laterally on the substrate eliminating the requirement for transparency in the OER catalyst material. A highly transparent and inert encapsulation film protects the solar cell under the light-collection area. Compared with the simple integrated structure in Figure 4, the new design has more intricate film geometries and therefore requires a more complex fabrication process. However, as described in the following sections, it opens the door to use of higher efficiency semiconductor materials, such as copper-indium-diselenide cells which have reported solar efficiencies exceeding 18% (Tuttle et al., 1995), previously not feasible for solar hydrogen production.

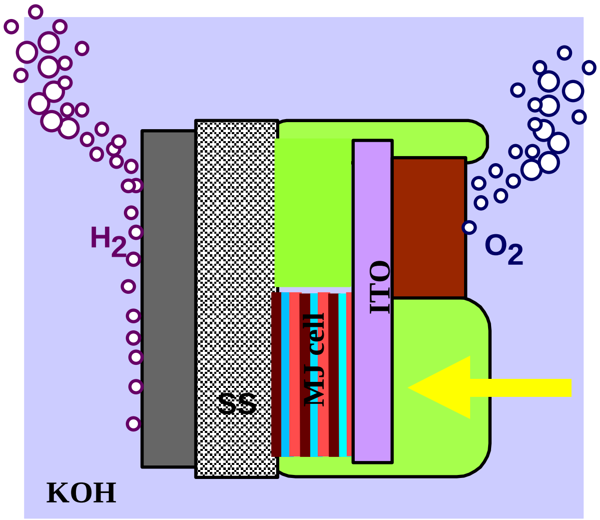


Figure 5 – New Lateral Photoelectrode with Encapsulated Cells

Along with the design of specific integrated photoelectrode configurations, the research last year continued to focus on optimization of the electronic and corrosion-resistance properties of the catalysts films, and of the underlying semiconductor and transparent contact films. Significant progress was made in enhancing the KOH-resistance of amorphous silicon, of transparent/conductive ITO, and of highly transparent TiO_2 encapsulation films.

Current Year Objectives/Tasks

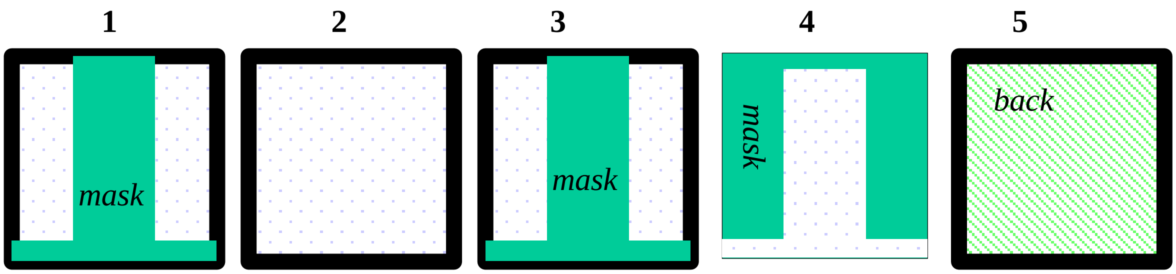
The primary objective of the photoelectrode research effort this year was to identify fully-integrated configurations (i.e., no external wires to connect the anode and cathode) which could achieve high efficiency using thin film semiconductors and which would be compatible with large scale manufacturing.

Specific tasks included: 1) demonstrating a fabrication sequence for the new encapsulated photoelectrode design (i.e. Figure 5) using triple-junction a-Si cells supplied by the University of Toledo and thin-film catalyst and protective coatings developed at UH; 2) further optimization of the catalyst and protective coatings for use in the new photoelectrodes, primarily the indium-tin-oxide (ITO) transparent contact layer; 3) refinement of the new photoelectrode design to allow use of high efficiency CIGS (gallium-doped CIS) solar cells.

Current Year Progress

Photoelectrode Fabrication

Initial prototypes of the new encapsulated photoelectrode design were fabricated using triple-junction a-Si solar cells (University of Toledo). The contact layers, catalysts and encapsulation thin films were deposited in-house by sputtering. The process sequence including schematics of the shadow masks for the individual sputter steps is shown in Figure 6. Photoelectrodes were fabricated on 1” square substrates cut from the 2”x2” cells provided by the University of Toledo. A thin TiO_2 passivation layer was deposited onto the non-photo active regions of the front surface, followed by the ITO lateral conduction layer and the patterned Fe:NiOx OER catalyst. The photoactive region was encapsulated using transparent, chemically inert TiO_2. The final step in the process was deposition of a CoMo HER catalyst layer onto the back of the SS substrate. Photographs showing front and back sides of one of the fabricated photoelectrodes are seen in Figure 7.



1) TiO_2 passivation of non-PV areas (FS).
2) ITO contact over entire front surface.
3) NiFe:Ox catalyst on non-PV areas (FS).
4) TiO_2 encapsulation of PV area (FS).
5) CoMo catalyst over entire back surface.

Figure 6 – Fabrication Sequence for Encapsulated Cells

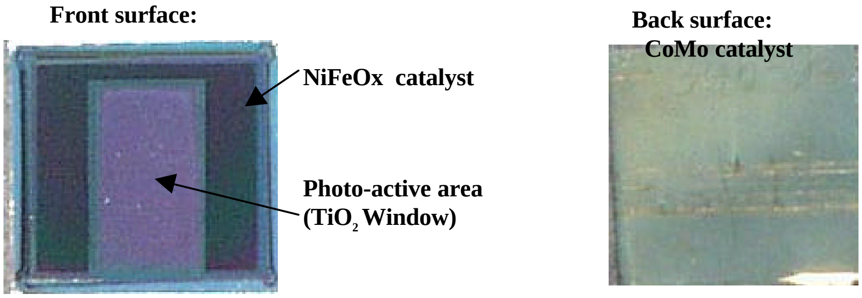


Figure 7 – Photographs of Fabricated Photoelectrodes

Preliminary tests were conducted on the fabricated photoelectrodes in 1N KOH under simulated solar light. The experimental setup is pictured in Figure 8. Observations from these early experiments indicate that hydrogen and oxygen gases are evolved at the photoelectrode surfaces, but performance is limited by device instabilities originating around the edges. The highest concentration of light-induced bubbles appears around the front surface edges of the photoelectrode. After about 15 minutes of operation, the front surface films begin to degrade, with the degradation initiating at these edge regions. Plausible explanations for the degradation include high electric fields occurring at the abrupt edges between the cathodic and anodic surfaces resulting in structural damage in the outer protective films or microcracks between the different lateral layers. Either problem could allow penetration of the corrosive KOH into the more vulnerable underlying a-Si layers. We plan to refine the fabrication sequence to produce a photoelectrode geometry that minimizes edge interfaces and eliminates the high-field edge effects.

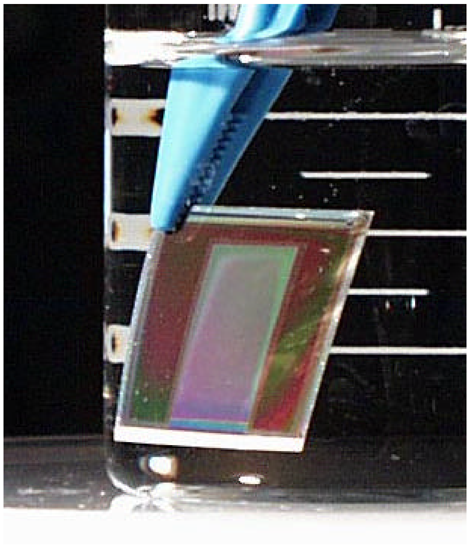


Figure 8 – Testing of Encapsulated a-Si Photoelectrode

ITO Optimization

The properties of the indium-tin-oxide (ITO) for use as a transparent conductive front contact are extremely important in the new photoelectrode design. The ITO must transmit light to the solar cell while laterally conducting photocurrent to the catalyzed areas. It should also assist in the protection of the underlying a-Si from chemical attack by KOH. Last year we initiated an extensive research effort to optimize the balance between conductivity, light transmission and chemical resistance in KOH in sputtered ITO films. This year, we completed the study (Chin, 2000), and are in the process of preparing publications to present our findings.

Central to the study, ITO films were RF sputter-deposited from a compound target under a range of process conditions. Variables in the test matrix of films included: sputter gas composition from 0 to 0.67% oxygen in argon; RF sputter power from 50 to 150W and substrate temperature from 50 to 200°C. For each set of conditions, films were deposited onto glass for conductivity (4-point probe), transparency (spectrophotometer) and structural (XRD) measurements; onto silicon for thickness (profilometer) and composition (EDX) measurements; and onto 302 stainless-steel to characterize corrosion rates in KOH. Electrical and optical properties varied significantly over the range of conditions used in the sputtering system. Optimal conductivity and transmittance (for the solar spectrum) were achieved in films deposited at 200°C with 0.25% oxygen in the argon sputtering gas. We attribute this result to the crystal orientation and grain sizes found in the polycrystalline films deposited under these conditions, which influence scattering mechanisms and optical bandgap in the material (Wu and Chiou, 1996).

Corrosion experiments revealed that the degree of chemical stability of the ITO films in KOH also depends strongly on process conditions during deposition. It was found that films deposited at 200°C exhibited the best corrosion resistance in KOH. Figure 9 shows the percentage weight loss of different ITO films (on SS302) as a function of time immersed in 1N KOH. A substantial fraction of the film was removed in the films deposited at 100°C, while little to no change was observed in the films deposited at 200°C . Again we attribute the result to film grain structure and orientations. Figure 10 shows SEM micrographs (40000x) of film surfaces for ITO on SS302 deposited at 100 and 200°C, before and after a 96-hour immersion in KOH. While the 200°C film appears unchanged, the 100°C film shows clear indications of chemical attack, particularly along grain boundaries. The fortunate result of this study is that corrosion-resistant ITO can be deposited under conditions also yielding high conductivity and transparency. We have thus identified a material well suited for the top conductive contact layer in the integrated photoelectrode structure.

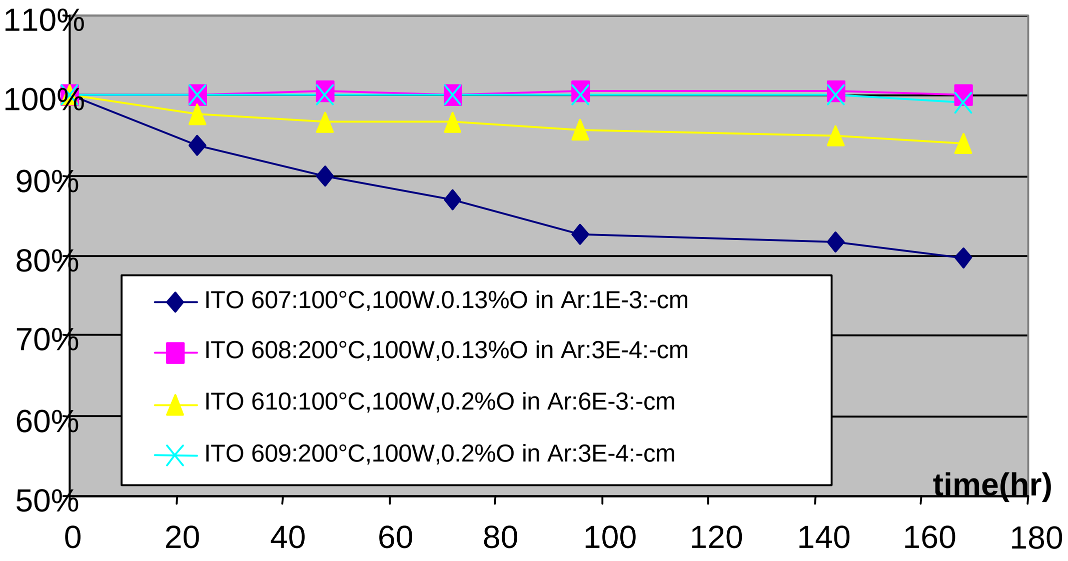
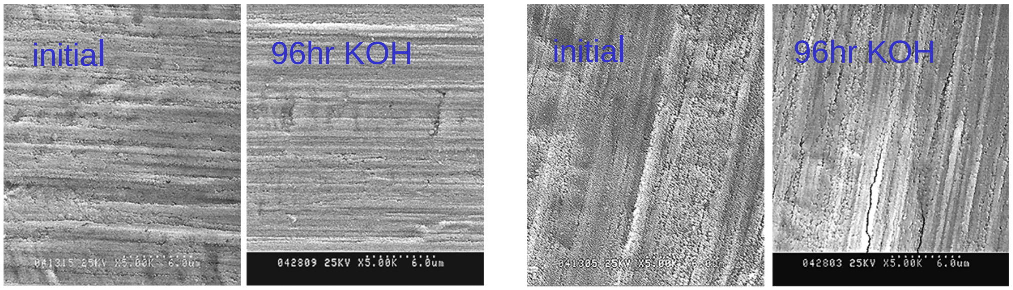


Figure 9 – Degradation of Different ITO Films in 1N KOH



ITO 609 (200° film) **ITO 607 (100° film)**

Figure 10 – SEM Surface Images of ITO Films Exposed to KOH

Photoelectrode Design for CIS

The new photoelectrode design allows use of side-by-side series-connected single-junction solar cells in addition to the stacked multijunction configuration. This has opened the door to using alternative low cost, high-efficiency thin film materials, such as copper-indium-diselenide, which have reported solar efficiencies exceeding 18%. These materials were not previously considered because of the low voltage of a single junction device and the inability to fabricate monolithic-stacked multi-junctions. However, the newly proposed encapsulated photoelectrode design was further developed to incorporate side-by-side CIGS cells, taking advantage of the potential for efficiency enhancement. A cross sectional view of a CIGS photoelectrode using three series-connected CIGS/CdS junctions is shown in Figure 11.

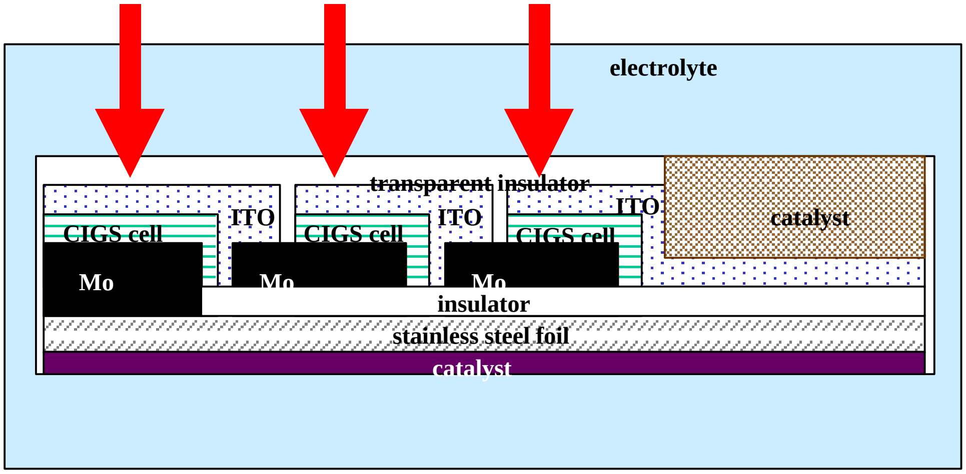


Figure 11 – Integrated Photoelectrode with 3 CIS Single-Junction Cells

In addition to the advancements in the photoelectrode design, progress was made this year in several areas necessary for the development of a practical CIGS photoelectrode. Most significantly, a thermal deposition system for CIGS was installed and tested at UH. CIS/CdS single-junction solar cells with efficiencies exceeding 10% were successfully fabricated on CIS films deposited in this system. Improved efficiencies are expected with incorporation of Ga and further optimization of the process conditions. Corrosion testing of CIGS devices is planned.

Summary and Plans

For the past several years, our approach has been to compare alternate materials and system configurations using reactor modeling, and to identify and address the critical materials and photoelectrode-operation issues through extensive experiments in materials synthesis and in photoelectrode fabrication and testing. We have demonstrated direct solar-to-hydrogen conversion efficiencies of 7.8% using a photocathode fabricated from low cost triple junction amorphous silicon solar cells with 10% photovoltaic efficiencies configured with a separated anode. Our focus has since shifted from the glass superstrate cells used in the separate anode/cathode configuration to devices grown on metal substrates for compatibility with proposed conceptual designs. These reactor designs, prepared in collaboration with NREL, indicated several important advantages of using the conductive (metal) substrates.

This year, we advanced the design of a fully integrated photoelectrode fabricated on a metal substrate using only thin film processing techniques. We demonstrated a process sequence to fabricate prototypes of the new photoelectrode using stacked triple-junction a-Si cells and sputter-deposited catalyst, contact, and protective films developed at UH. At the same time we continued optimization of the electronic properties and corrosion resistance of the semiconductor, transparent-conductor and transparent-protective films for the new photoelectrode. A deposition system for CIS and CIGS films was set up and tested as part of a new effort to develop higher efficiency photoelectrodes using the encapsulated design configured with side-by-side series-connected junctions.

The objective for FY2000-20001 is to demonstrate high efficiency, stable production of hydrogen using amorphous silicon photoelectrodes in the new encapsulated photoelectrode configuration and to evaluate the feasibility of using high efficiency copper-indium-gallium-diselenide cells in the side-by-side series-connected configuration. We plan to refine the specific processing steps for fabrication of the integrated a-Si photoelectrode to improve photoelectrode lifetime and to develop a processing sequence for the more complicated CIS photoelectrode.

During FY2000-2001, we will also continue the development of an integrated electrical/optical/electrochemical computer model to aid in the design and evaluation of alternate material systems and photoelectrode geometries. We plan to continue the optimization of catalyst and protective films integral to the encapsulated photoelectrode structure. To meet the objectives of a near-term hydrogen-producing demonstration, our strategy of working closely with the solar cell manufacturers to obtain high-efficiency solar cell device structures tailored specifically for hydrogen production remains an important part of the planned research.

Acknowledgments

We wish to thank the US Department of Energy for support of this work under Grant DE-FG04-94AL85804. We also thank Solarex Thin Film, Energy Conversion Devices, and the University of Toledo for amorphous silicon samples and Maggie Mann of NREL for useful discussions and input in the development of conceptual designs for large-scale systems.

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Figure Captions

Figure 1 – Photoelectrochemical Hydrogen Production

Figure 2 – Photocathode with Separate anode

Figure 3 – Solar Hydrogen Production Data

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Figure 5 – New Lateral Photoelectrode with Encapsulated Cells

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