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PHOTOELECTROCHEMICAL BASED DIRECT CONVERSION SYSTEMS FOR HYDROGEN PRODUCTION

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Abstract

Current fundamental bottlenecks to developing long-lasting high-efficiency photoelectrochemical systems for fuel production are a) poor matching of the semiconductor bandgap with the solar spectra, b) instability of the semiconductor in the aqueous phase, c) energetic mismatch between the semiconductor band edges and the electrochemical reactions of interest, and d) poor kinetics of the H_2 generation reaction. Our studies this year to address these issues focused on new nitride semiconducting materials for increased stability, and metal ion surface treatments for control of band edge energetics. We also performed experiments directed at the determination of the realizable efficiency for PEC water splitting systems.

Introduction

The direct photoelectrolysis of water has been termed the “Holy Grail of Photoelectrochemistry”. This is the process whereby light, illuminating a semiconductor, is used to split water into hydrogen and oxygen. The incident light, absorbed in a semiconductor electrode, splits the water directly. A one-step monolithic system eliminates the need to generate electricity externally and subsequently feed it to an electrolyzer. Since current commercial electrolysers suffer from high capital costs, they are a major contributor to the cost of electrolytically produced hydrogen. Combining the electrolyser with the PV system eliminates one of the high cost components of a PV-hydrogen generation system. This type of monolithic system also reduces semiconductor processing since surface contacts, interconnects and wiring are no longer necessary. This configuration requires only the piping necessary for the transport of hydrogen to an external storage system or gas pipeline.

The major road blocks in doing direct photoelectrolysis of water are well known. The main problems are efficient light absorption (for reasonable solar efficiencies, the bandgap must be less than 2.0 eV), corrosion of the semiconductor (most useful semiconductors are thermodynamically unstable in water), and energetics (the matching of the semiconductor band edge energies with the hydrogen and oxygen evolution reactions). The most stable semiconductors in aqueous solution are oxides, but their bandgaps are either too large for efficient light absorption, or their semiconductor characteristics are poor. Semiconductors with better solid state characteristics are typically thermodynamically unstable with respect to oxidation.

Figure 1 gives the energetic picture for a semiconductor electrode immersed in an aqueous electrolyte (a photoelectrolysis system). Hydrogen is produced at the surface of an illuminated p-type semiconductor; oxygen is produced at the surface of an illuminated n-type semiconductor. This occurs due to injection of electrons into the solution (for p-type) or because holes (electron vacancies) appear at the semiconductor/electrolyte interface (for n-type). The other component of water, oxygen or hydrogen is produced at a separate electrode. Either system, n- or p-type, would have the same efficiency for water splitting. However, photo-generated holes can be considered strong oxidizing agents and may oxidize the semiconductor itself, causing decomposition. Stability then depends on the competition between semiconductor decomposition and water oxidation or reduction. The most stable situation is the p-type semiconductor where electron flow is directed towards the illuminated side effecting the evolution of hydrogen. The p-type semiconductors offer some protection against photocorrision, because under illumination the surface is cathodically protected. Oxygen evolution at the surface of the semiconductor, therefore, is a less desirable situation. Systems based on n-type electrodes therefore are inherently less stable than systems based on p-type electrodes.

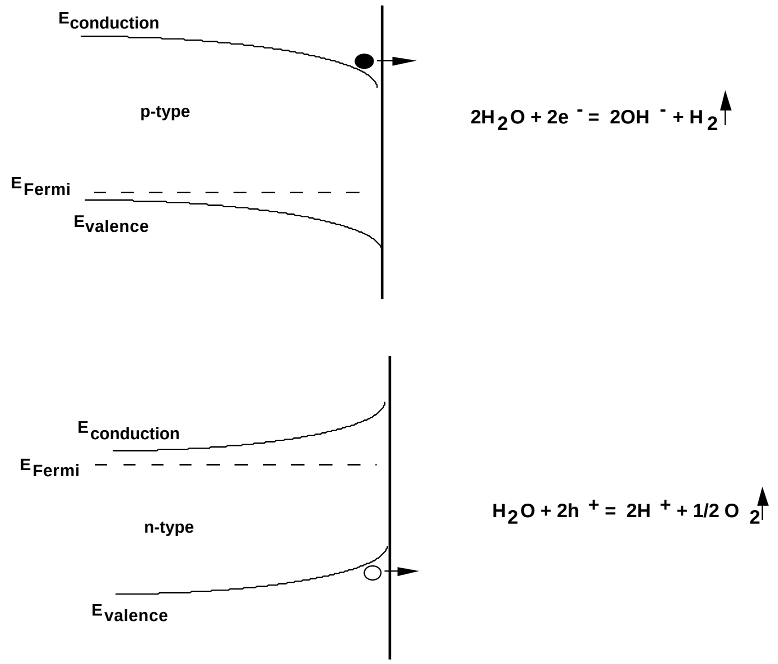

Fig. 1. Energetics of p- and n-type semiconductors immersed in aqueous electrolytes.

For a one-step process to be viable, the light harvesting system must generate sufficient voltage to effect the decomposition of water, and the system must be stable in an aqueous environment. Splitting water into hydrogen and oxygen requires a thermodynamic potential of 1.229 eV at 25°C. At current densities appropriate to normal sunlight intensities (10-20 mA/cm^2), typical values of the overvoltage for the cathode (hydrogen evolving) and anode (oxygen evolving) reactions are 50 mV and 275 mV respectively. A potential then, of at least 1.6 V, is required for a water splitting system. For a single gap semiconductor based direct conversion water splitting system, the fundamental requirement of at least 1.6 V coupled with the internal losses from the semiconductor, implies a minimum bandgap greater than 1.8 electron volts. Catalysts are required on both the hydrogen and oxygen evolving surfaces to speed up the redox reactions and stabilize the semiconductor.

In earlier work, we identified p-type gallium indium phosphide (p-$GaInP_2$) as perhaps an ideal semiconductor for water splitting. While its bandgap was in the ideal range (1.83 eV), the energetics of its band edges were not correct for water splitting, needing an additional 500mV bias. While it is possible to move the band edges to some extent, it is still insufficient to effect water splitting.

Band Edge Engineering

The flat-band potential and, therefore the energetics of the band edges of any semiconductor/electrolyte system are controlled by the charge in the Helmholtz inner layer. Any change in charge in that layer changes the measured flat-band potential and subsequently the energetics of the band edges. The variation of the semiconductor flat-band potential with pH is due to the change in the adsorbed charge (H+ and OH-) on the electrode surface. Adding negative charge (such as OH- ions) shifts the bands to more negative potentials, whereas adsorption of a positive charge (such as H+ ions) shifts the bands positive.

The ability to control the positions of semiconductor band edges at the semiconductor/electrolyte interface is an indispensable prerequisite to align them with the reaction of interest in solution (*vide supra*). Simply put, it is desirable to be able to shift the band edges of the semiconductor without changing the pH of the solution and to be able to change the solution pH without affecting the semiconductor band edge positions. Surface modification with transition-metal ions makes use of the former approach while derivatization with organic molecules mainly relies on the latter approach.

Surface Modification Schemes

Surface modification schemes are chosen based on the likelihood of achieving one or more of the following fundamental goals: a) control over the energetic positions of the semiconductor band edges (band edge engineering), b) catalyze charge transfer across the semiconductor/water interface and c) chemical and electrochemical stability of the semiconductor surface in aqueous media.

Transition metal compounds have a rich chemistry both in terms of their ability to catalyze reactions, and also in their varied state of charge. Many modification schemes are available that would allow us to attach these moieties to semiconductor surfaces. Our procedure involved immersing the bare, etched semiconductor surfaces into dilute solutions of various transition metal ions. In situ, physisorption or chemisorption of the metal ions would be expected to create a layer of charges at the semiconductor surface within the Helmholtz layer. Adsorption of positively charged ions at the semiconductor surface (within the Helmholtz layer) will shift the band edges positive. Similarly, negatively charged ions will shift the band edges negative. Control over the extent of band edge shift will be achieved by selecting the charge on each ion (monovalent, divalent etc.) and by controlling how many ions adsorb on the surface, by selecting the appropriate ion size and its concentration in the solution (Figure 2). Before adsorption, no reaction can occur because the valance band edge is too positive to effect oxidation of water. After adsorption of a positively charged metal ion, the band edges have shifted to more positive potentials, allowing the oxidation of water to proceed. From our earlier work, we know that for $GaInP_2$ the band edges need to be shifted 0.1-0.4 V positive to align its band edges with the H_2/H_2O and O_2/H_2O redox potentials

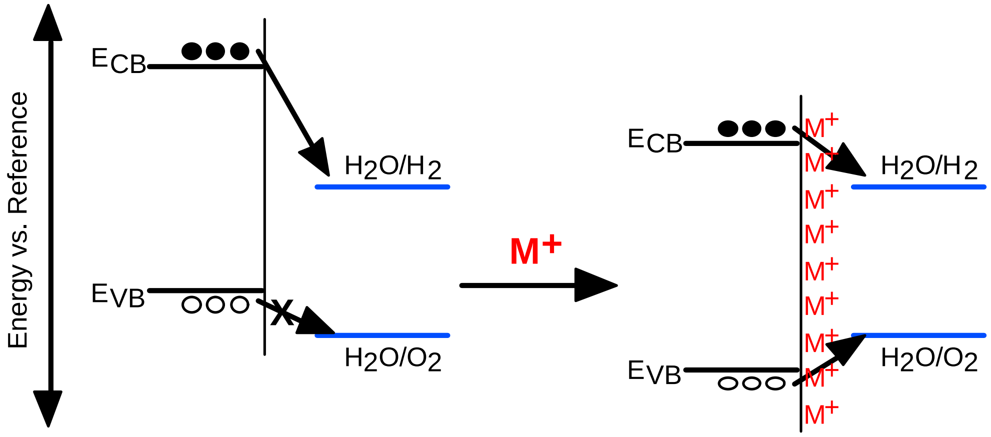

Figure 2. Idealized band edge control by adsorption of charged metal ions.

Figure 3 shows the effect of adding Fe^{3+} to an acid solution with an illuminated p-$GaInP_2$ electrode. A positive shift of 0.2 V in the onset of the photocurrent for hydrogen production is noted (probably due to the specific adsorption of Fe^{2+}). This shows the possibilities of this approach.

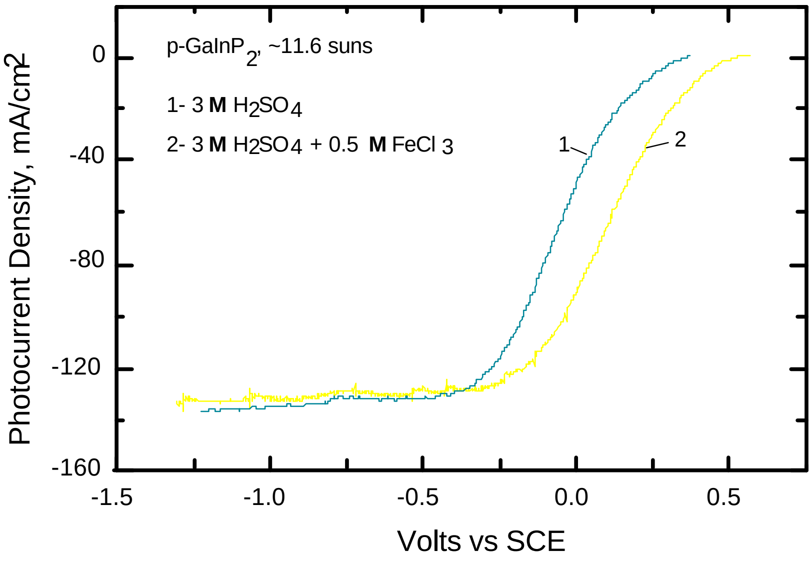

Figure 3. Photocurrent onset potential shift due to Fe^{+3} treatment.

In addition to the primary band edge control effect described above, the metal ions can also exert a secondary effect. It is known that the band edges for many semiconductors shift under illumination due to accumulation of photogenerated charges at the interface caused by poor rate of charge transfer across the semiconductor/liquid interface (Figure 4). Under illumination, the surface becomes negatively charges (due to the accumulation of electrons at the surface) and the band edge shifts to more negative potentials. This is exactly the opposite direction needed for this system.

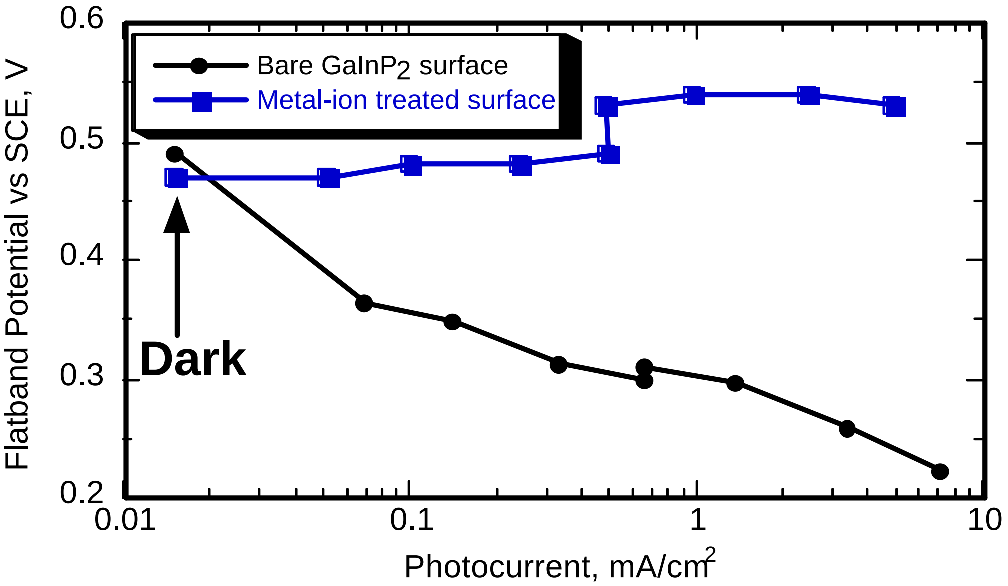

Figure 4. Band edge movement as a function of light intensity with and without metal ion treatment.

The catalytic ability of the metal ions (*vide infra*) prevent accumulation of charges at the semiconductor interface and hence suppress the undesirable and uncontrollable band edge shift under illumination. Transition metal ions can stabilize semiconductor surfaces by effectively removing (catalyzing) photogenerated charges which may otherwise participate in undesirable side reactions resulting in corrosion.

Nitride materials

Recent work in our laboratory with III-V materials has shown that it is possible to split water with an efficiency greater than 12% utilizing a unique structure based on a $GaInP_2/GaAs$ tandem system. Water is split directly upon illumination, using light as the only energy input. This device is a PEC device, voltage-biased with an integrated PV device. The GaAs cell generates the additional voltage needed to overcome the energetic mismatch between the $GaInP_2$ and the water oxidation/reduction reactions. Although the efficiency of this system is high, the cost of the material is also high, leading to an expensive water splitting system. In addition, while the system showed some stability, the long-term stability is unknown. For a viable water splitting system, other materials need to be explored.

Nitride semiconductors have been established as extremely promising candidate materials for applications such as blue, green, and UV LEDs and lasers, solar blind photodetectors, piezoelectric and electro-optic modulators, and high power electronics. The market for blue LED's and lasers alone is driving an intense growth in research and development focussed on these materials. It seems likely that the cost, availability, and quality of nitride based thin film devices will all improve substantially in the next few years. In addition, Group III-nitrides have not yet been investigated for use in hydrogen-evolving solar cells. It is known that GaN is very chemically stable, so much so that device fabricators have not been able to develop a suitable wet chemical etchant for it. It is also known that the composition of $In_xGa_{1-x}N$ can be adjusted to produce a band gap suitable for solar applications. In order to decide whether the III-nitrides are suitable for use in hydrogen-evolving solar cells, it must be determined whether they are electrochemically stable and whether the dopants in the p-type material will be passivated by the hydrogen evolution process. We have completed a preliminary investigation on these two subjects using GaN.

The electrochemical stability of p-GaN was studied by examining the current-voltage characteristics in 3 M H_2SO_4 and 0.1 M KOH solutions under conditions of room light and intense (approximately 10 sun) illumination. Because the 3.4 eV band gap of GaN is significantly larger than the energy of visible photons, testing in room light is essentially the same as testing in darkness. Figure 5 shows the I-V data for a sample in 0.1 M KOH.

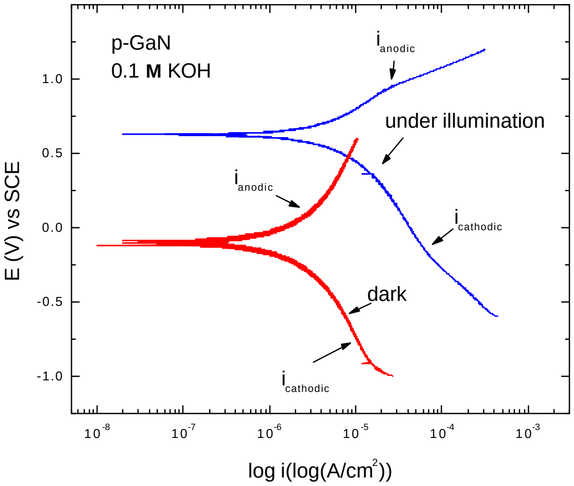

Figure 5. Potentiodynamic scans for p-GaN in 0.1M KOH

The positive voltage shift of the current reversal point under illumination is consistent with the known cathodic protection that illumination provides to p-type semiconductors in aqueous solutions. The cathodic current density is observed to increase significantly under illumination, is attributed to hydrogen production at the semiconductor surface. The anodic current density, is not so strongly affected by illumination and is attributed to oxidation reactions. The anodic current densities measured for p-GaN are several orders of magnitude lower than those for p-$GaInP_2$, indicating that it is far more stable than p-$GaInP_2$ in basic solutions.

Early research on hydrogen-evolving solar cells showed that the carrier concentration in TiO_2 could be affected by absorption of hydrogen from electrolyte solutions. Research on the growth of p-GaN has shown that the Mg dopant atoms are passivated upon exposure of the material to NH_3 at elevated temperatures. In order to determine whether the p-type doping of GaN can be passivated by during hydrogen evolution, the carrier concentrations of different samples were measured before and after 4000 s of hydrogen evolution in 3 M H_2SO_4, 1 M KOH, and pH 7 phosphate buffer. The hydrogen evolution current as a function of time is shown for each of the three cases in Figure 6. For each sample, illumination was provided by a 150 W Xe arc lamp. For all three solutions, Hall measurement showed identical carrier concentrations (1.7 x 10^{17} cm^{-3} p-type) before and after the hydrogen evolution session. This shows that exposure to hydrogen evolution in acid, neutral, and basic aqueous solutions does not cause passivation of the Mg dopant atoms in p-GaN.

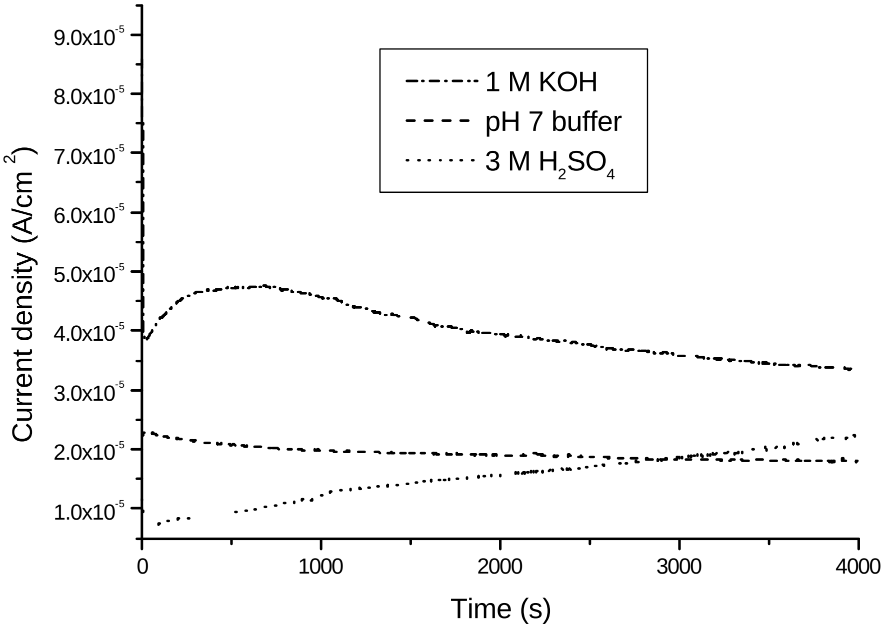

Figure 6: Hydrogen evolution current-time profile for p-GaN

A notable feature of the hydrogen evolution plot in Figure 6 is that the hydrogen evolution rate is not constant in time. The hydrogen current in the basic and neutral solutions appears to be asymptotically approaching a steady state value, while the hydrogen current in the acidic solution increases linearly with time over the 4000 s measurement period. Although the changes in current are not on an order of magnitude scale, which would indicate material instability, these smaller changes do indicate that some surface modification of the p-GaN is occurring during the hydrogen evolution process.

Efficiency of Direct Conversion Processes

The focus of the hydrogen production task is to generate hydrogen utilizing solar energy. The efficiency of this process is extremely important because an area of land must be covered and any efficiency losses must be made up by an increase in the collector area.

This will ultimately have a significant impact on the overall cost of such a system. For this work we are interest in looking at the factors that affect the overall efficiency of a PEC solar-hydrogen generation system.

The efficiency of electrolysis can be defined as the chemical potential of hydrogen divided by the voltage required for electrolysis. At the normal operating current density of commercial electrolyzers (~1 A/cm^2), this voltage ranges from 1.8-2.0 volts. An electrolyzer, then operating at 1.9 volts operates with an energy efficiency of 65% (1.23/1.9). Coupling this electrolysis efficiency with a 12% PV efficiency would give an overall solar-to-hydrogen efficiency of 7.8%. To increase the electrolysis efficiency, one must operate at a lower voltage. This requires better catalysts, or a decrease the current density (which results in a decrease in the rate of hydrogen production). Increasing the area of the electrodes in an electrolyzer would also reduce the current density, but costs would increase due to an increase in the amount of material.

One of the major advantages of a direct conversion PEC system is that the area available for electrolysis approximates that of the solar cell. At solar intensities, this current density is 10-20 mA/cm^2, depending on the type of cell. At these current densities, the voltage required for electrolysis is much lower, and therefor the corresponding efficiency is much higher. Figure 7, presents current-voltage curve for water splitting in an electrochemical cell consisting of two Pt electrodes of identical area. At a current density similar to short circuit photocurrent from a solar cell, hydrogen and oxygen generation is achieved at an applied voltage of approximately 1.35 V, giving rise to an electrolysis efficiency of 91%. Coupling this to a 12% efficient PV array leads to an overall solar-to-hydrogen efficiency of 10.9%. This then is one of the advantages of a PEC hydrogen generation system, not only does it eliminate most of the costs of the electrolyzer, it also has the possibility of increasing the overall efficiency of the process.

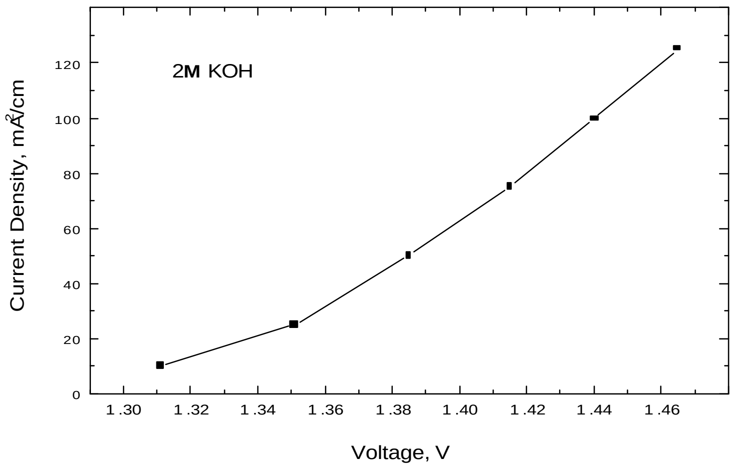

Figure 7. Current density vs. voltage curve for water splitting with two identical Pt electrodes

The goal of this study was to quantify the efficiency gains from a direct conversion PEC system. For this work, we used an integrated PV/electrolysis design to emulate a PEC system. Unlike a direct conversion PEC system, an integrated PV/electrolysis system has separated PV and electrolyzer parts (Fig 8). For these experiments, the area of the electrolyzer system is identical to the area of the PV collector. These integrated systems allow us to study the issues involving the effects of current density, solar intensity variability, and light concentration on the overall efficiency for hydrogen production. In this study we utilized an integrated PV/electrolysis design, based on two multijunction solar cells: a highly efficient GaInP/GaAs cell and a low cost multijunction device based on amorphous silicon (a-Si). Both cells are capable of generating voltage sufficient for water splitting. It is demonstrated that this monolithic PV/electrolysis configuration can lead to higher solar to hydrogen conversion efficiency than coupled systems involving electrolyzers and photovoltaic solar cells.

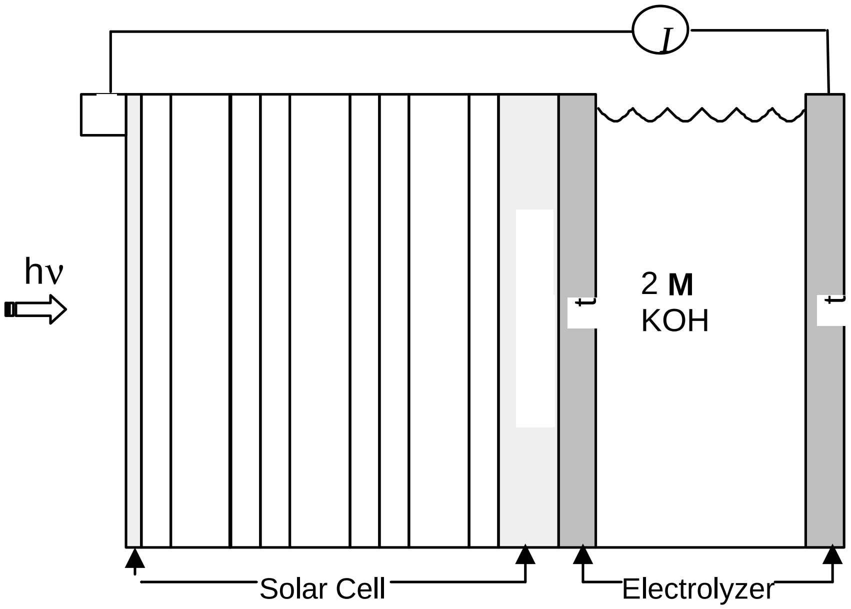

Figure 8. Integrated solar cell-electrolyzer design

In a practical application this PV/electrolysis system would operate at short circuit conditions. For such a configuration, the efficiency for hydrogen production can be calculated using the equation: efficiency = (power out)/(power in). The input power is the incident light intensity of 100 mW/cm^2. For the output power, assuming 100% photocurrent electrolysis efficiency, the hydrogen production photocurrent is multiplied by 1.23 volts, the ideal fuel cell limit (lower heating value [LHV] of hydrogen). Using this calculatation, our experimental results for the hydrogen production efficiency for the n/pn/p-$GaInP_2$/GaAs/(Pt)/2**M** KOH/Pt system is:

$$1.23\ \text{V}*13.4\ \text{mA/cm}^2/100\ \text{mW/cm}^2=16.5\%$$

and for triple junction a-Si(Pt)/2M KOH/Pt it is:

$$1.23\text{V}*6.4\text{mA/cm}^2/100\text{mW/cm}^2=7.8\%.$$

The value for the a-Si system is significant, in that this efficiency is realized by a PV cell with only a 9% solar-to-electrical efficiency. Because of the lower current density, this system is performing water electrolysis with an equivalent efficiency of 86% (effective electrolysis voltage of 1.42 volts). This means that the maximum operating voltage of the a-Si PV cell is close to that required for electrolysis.

On the other hand, the $GaInP_2$/GaAs PV/electrolysis system operates at a much higher voltage than is required for electrolysis at this current density. If the cell were operated at its maximum power point, rather than at short circuit conditions, it would deliver significant electrical power and thereby increase the total efficiency of the system. The output power then can be calculated as (1.23-**V**)***i**, where **V** and **i,** are bias voltage and current density at maximum power point. For n/pn/p-$GaInP_2$/GaAs/(Pt)/2**M** KOH/Pt system, the maximum power point for water photoelectrolysis was at -0.57 V with a current density of 13.1 mA/cm^2. The total efficiency for then for simultaneous hydrogen production and power generation is 23.6%. For maximum efficiency in a direct conversion PEC device, this cell would require some modification to decrease the operating voltage. Ideally, this would increase the photocurrent such that the overall efficiency of 23% could be maintained.

An important characteristic of PV/electrolysis system is its ability to generate hydrogen for during the day with a changing light intensity, in particular maintaining high solar-to-hydrogen conversion efficiency under low sun insolation. Two possible reasons can diminish the efficiency of hydrogen production: (1) the voltage generated by PV cell is not sufficient for water splitting and (2) a current density in the system decreasing to the extent that oxygen rather than water is be reduced at the cathode. Figure 9 shows photocurrent during the day for the n/pn/p-$GaInP_2$/GaAs/(Pt)/2**M** KOH/Pt cell operating at short circuit condition.

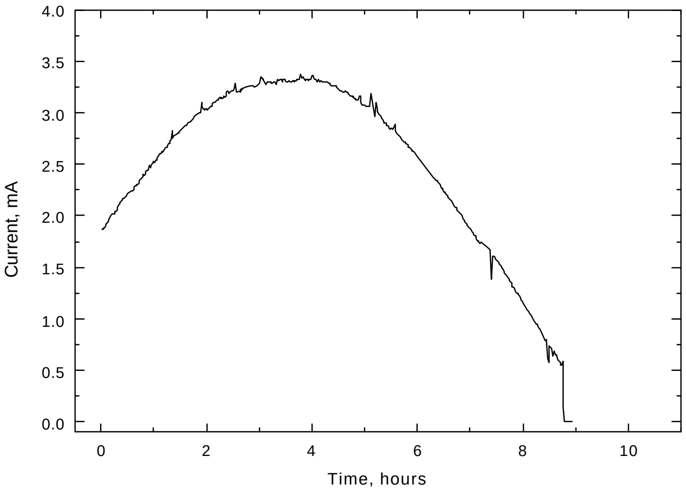

Figure 9

Note that the short circuit current follows the solar insolation during the day. A copious amount of gas was evolved from both electrodes during the whole period. The efficiency of hydrogen production in this experiment can be calculated as time integrated ratio of (power in)/(power out). That would be 108mWh/cm^2/659 mWh/cm^2= 16.4%, where 659 mWh/cm^2 is the solar radiation during the time of experiment. This result is in good agreement with indoor measurements under similar conditions, indicating that hydrogen was generated during the most of the day.

Goals

The goal of this research is to develop a stable, cost effective, photoelectrochemical based system that split water upon illumination, producing hydrogen and oxygen directly, using sunlight as the only energy input. We believe that for a commercial system, the overall solar-to-hydrogen efficiency must be near 10%, with a lifetime of at least 10 years. The basis for our goals lies in the requirements for a viable photoelectroysis device. We hope to accomplish our goals by (1) identifying and characterizing possible semiconductors that have appropriate bandgaps and stability, (2) developing techniques for the preparation of transparent catalytic coatings and their application to semiconductor surfaces, (3) controling the semiconductor energetics so that the band edges are matched for water splitting, (4) and promising multijunction cell systems that generate sufficient voltage for the water splitting reaction such as our novel integrated photovoltaic/photoelectrochemical system.

Acknowledgment

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