Task 2 Report

Solar Photocatalytic Hydrogen Production from Water Using a Dual Bed Photosystem

DOE/AL/85802--T2-Pl.2

Annual Report

FSEC-CR-857-95

DOE Contract #DE-FG04-94AL85802

December 1995

Submitted to:
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PREFACE

This report describes the Sustainable Hydrogen Production research conducted at the Florida Solar Energy Center (FSEC) for the past year. The report presents the work done on the following four tasks:

- Task 1. Production of Hydrogen by Photovoltaic-Powered Electrolysis - This task represents the final effort of a cooperative project between the U.S. Department of Energy, NASA/Kennedy Space Center, FSEC and the Florida Energy Office. The activities covered five years of effort at a total funding of \$216,809. These results represent a successful coordination of two state agencies and two federal agencies.
- Task 2. Solar Photocatalytic Hydrogen Production from Water Using a Dual-Bed Photosystem - This task established the basis of the dual-bed concept by selectively evolving hydrogen or oxygen. A number of redox mediators were found to facilitate hydrogen production.
- Task 3. Development of Solid Electrolytes for Water Electrolysis at Intermediate Temperatures - Several ionomers were synthesized and fabricated into proton exchange membranes. Laboratory testing in an electrolysis cell gave comparable performance to the commercial product.
- Task 4. Production of Hydrogen by Thermocatalytic Cracking of Natural Gas - The experimental unit was constructed and a number of catalysts for methane cracking reactions were tested. Laboratory experiments established catalyst activity and identified stability problems.

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SOLAR PHOTOCATALYTIC H_2 PRODUCTION FROM WATER USING A DUAL BED PHOTOSYSTEM

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1.0 SUMMARY

This work is an investigation into the use of photocatalytic particles in a dual bed configuration, so as to effect the solar-driven decomposition of water to its constituent elements, particularly hydrogen. The system envisioned would consist of two modules, each consisting of a shallow, flat, sealed container, in which micron-sized photocatalytic particles are immobilized. An aqueous solution containing a redox mediator is pumped between the two chambers. Different photoparticles and catalysts are chosen for their respective modules so as to effect oxidative water-splitting in one vessel to evolve oxygen gas, and reductive water-splitting in the other to evolve hydrogen. This is a direct photoconversion scheme that breaks down the energetic requirement for water decomposition into a 2-photon process, and enables separate production of hydrogen and oxygen.

Titanium dioxide, TiO_2 , and indium phosphide, InP, were employed as photoparticles in the O_2 - and H_2 -evolving beds, respectively. Platinum catalysts were evaluated to promote H_2 - evolution. Calculations on the energy band structure of free and immobilized particles provided guidance as to how the microstructure of the particles should be configured. A series of redox mediators, spanning a range of redox potentials, were tested. While many electron donors facilitated H_2 - evolution, only the most oxidizing ones enabled O_2 - evolution. A single redox couple, capable of charge exchange in both modules, is desirable to avoid system design complexity.

2.0 INTRODUCTION

In 1972 Fujishima and Honda pointed out that irradiation of wide band gap semiconductors such as TiO_2 could supply much of the energy required to electrolytically decompose water, evolving O_2 and generating protons that could be reduced at a dark electrode to produce hydrogen. This introduced photoelectrochemistry as a new approach to solar energy conversion.

Various problems arose as work progressed. One, the original wide band gap semiconductors, such as TiO_2 and SnO_2 , required light energy well into the ultraviolet, making poor utilization of the solar spectrum; two, only highly crystalline, highly pure semiconductor specimens gave large photocurrents and quantum efficiencies, because of the limited lifetimes of the photogenerated charge carriers in the solid state; and three, semiconductors whose band gaps were better matched to the solar spectrum were subject to photoanodic corrosion, where the photogenerated hole could decay by dissolving a surface metal atom into the electrolyte.

It was also realized that the classic electrochemical configuration of two planar electrodes standing parallel to one another did not lend itself well to efficient use of the incoming solar photons. One either had to use an optically transparent counter electrode so that light could pass through it and the electrolyte to reach the semiconductor electrode, or deposit a thin film of semiconductor on glass and irradiate from the backside.

Since the essential feature of photoelectrochemical energy conversion was development of a barrier voltage at the semiconductor/electrolyte interface, it was realized that this could just as well be accomplished with the semiconductor in powder form. Conceptually this was a much simpler way to perform solar photoelectrolysis: just pour the semiconductor powder into water, expose the system to light, and H_2 and O_2 would bubble out.

New problems arose, however. The main one was separation of products. In an electrochemical cell, chemistry is performed by the occurrence of two half-cell reactions, each reaction proceeding at its own respective electrode. In the case of electrolyte-soluble products, an ion-conductive separator can also be included to ensure that the two chemical product streams do not mix with one another and back react. For the semiconductor particle system, the

microscopic nature of the half-cell reaction surfaces causes H_2 and O_2 to be evolved essentially together. The gas stream released from the photoparticle slurry would be 66% H_2 by volume, the balance mostly O_2 , well within the combustible range.

Our work to date has been geared toward understanding how photoparticle systems operate, and how a large scale reactor system might be configured. We have found that fixed bed arrays of particulates would make the most economic use of the solar energy-converting material. Furthermore, the loss in conversion efficiency compared to loose colloidal systems is compensated by the technical advantages of having a flow system that moves the dissolved products of reaction out the photoreactor, lessening the extent of back reaction.

3.0 DESCRIPTION OF CONCEPT

We are attempting to take the fixed particle bed approach and apply it to the photocatalytic water splitting problem. The intrinsic problem of gaseous product separation could be solved by employing 2 particle beds, one for oxidation of water to evolve O_2 , the other for reduction of water to evolve H_2 . Figure 1 depicts how the system would work.

The general chemical mechanism for a dual bed concept photosystem would be as follows:

where, PC-R: photocatalyst for the reductive stage of the process

PC-O: photocatalyst for the oxidative stage of the process

M: redox mediator

The immediate task was to identify photoactive materials that could be used for either H_2 or O_2 evolution, and devise ways to immobilize them on a surface. Much of the work done over the

Figure 1. Schematic of the Dual Photoparticle Bed Concept for Water Splitting.

years in photoelectrochemical work could be built on for this task. As for O_2 evolution, one can identify 6 metal oxides that have achieved some measure of success as photoanodes: TiO_2 , ZnO , SnO_2 , WO_3 , MoO_3 , and Fe_2O_3 . We have used TiO_2 , as the greatest photoelectrochemical successes have been achieved with this material.

As for hydrogen evolution, comparably fewer materials have been identified. This is partly due to difficulties in p-type doping of materials that are stable in water, and also due to the use of Pt and other noble metals as rapid H_2 -evolving electrodes that work in the dark while the anode is illuminated. Even so, a number of metal phosphides, such as InP and GaP, have been studied. We chose InP as the base material.

Also, a redox equivalent transfer agent or mediator should be identified to provide an anodic half-cell reaction in the H_2 -evolving reactor and the cathodic half-cell back reaction in the O_2 -evolving reactor. Charge transfer kinetics with the respective semiconductor powders should be reasonably rapid in order to make use of the photogenerated electrons and holes, but not so fast that the reverse reaction proceeds with equal facility. The respective back reactions between O_2 and M in one chamber and H_2 and M^+ in the other also represent an efficiency loss that should be accounted for.

The band characteristics of PC-R and PC-O will limit what redox agents could possibly serve as mediator in the dual particle bed system. As shown in Figure 2, the positive limit of redox potential is determined by the valence band edge of the p-type, H_2 -evolving photocatalyst, while the negative limit is determined by the conduction band edge of the n-type, O_2 -evolving photocatalyst. As band edges are difficult to determine, researchers frequently approximate them by measuring the flat band potential, V_{fb} .

To give an example, let PC-O be n- TiO_2 . At pH 9, V_{fb} is calculated to be -0.375 V vs NHE, based on -0.7 V at pH 13. The previously mentioned approximation for n-type semiconductors is that $E_{cb} = V_{fb}$, and so -0.375 is the negative limit. Also let PC-R be p-InP. At the same pH, $V_{fb} = +0.7$ V, which approximates the InP valence band position. That enables a $0.7 - (-0.375) = 1.07$ volt range to work with.

Figure 2. Energy band diagram showing range of possible mediator redox potentials

Various iron complexes, quinones, halogens, and other reasonably rapid charge transfer agents within the optimum redox potential range were examined. A listing of these reagents with their respective standard reduction potentials is given in Table I.

Table I. Listing of Redox Mediators

<u>Ox</u>	<u>Red</u>	<u>E° (V vs NHE)</u>
Sn ⁴⁺	Sn ²⁺	0.139
Anthraquinone-2,6-disulfonate	-	0.228
K ₃ [Fe(CN) ₆]	K ₄ [Fe(CN) ₆]	0.46 (NaOH)
1,4-Napthoquinone-2-sulfonate	-	0.47
Toluidine Blue	R.T.B.*	0.534
-	KI	0.535
thionine	leucothionine	0.563
-	FeSO ₄	0.68
1,4-benzoquinone	hydroquinone	0.699
NO ₃ ⁻	-	0.84
V ₂ O ₅ (VO ₂ ⁺)	VOSO ₄	1.00
-	KBr	1.087
-	HCl	1.358
HIO ₆	-	1.7

*R.T.B. = "reduced Toluidine Blue", produced via Zn reduction of the Ox form.

We tried wherever possible to test both the "Ox" and "Red" forms of the mediator, since positive results (i.e., H₂ and O₂ evolution, respectively) for both forms would constitute unambiguous proof that a good candidate had been found. In a few instances, where a particular redox state was not commercially available, it was generated in-house, as in Zn reduction of Toluidine Blue.

4.0 RESULTS

4.1 Theory: Band Structure of Catalyst/Photoparticle Configurations

On the microscopic level, there are many ways to configure the arrangement of catalyst and photoparticle. Certainly they must be in close proximity to each other, so that the photogenerated charge can flow from semiconductor to catalyst phase without recombination or other loss mechanisms. One normally thinks of a catalyst as precious material, dispersed as fine particles on an inert support. In our case, the catalyst would be deposited on a semiconductor powder, which is certainly not inert. The optimum size of a catalyst deposit, both in terms of its absolute size and size relative to the semiconductor particle that supports it, needs to be determined. Also, the proximity of one catalyst island to another is important, because too much catalyst could block the incoming light that is to be absorbed by the semiconductor.

If the catalyst is not too expensive, one could just as well consider depositing the semiconductor on the catalyst, or better still, deposit both semiconductor and catalyst on an inexpensive, but electronically conductive, substrate. That way, islands of semiconductor and catalyst could be placed side by side. This would cause some segregation of the respective oxidation and reduction reactions in each module, and would enable maximum light absorption by the photoparticle. It is intended to establish a theoretical basis for this approach.

Potential Distribution for a Flat, Infinite Semiconductor Surface

The model for the potential field in a semiconductor immersed in an electrolytic solution assumes a flat infinite semiconductor surface. A potential will develop according to Poisson's equation as follows:

$$\nabla^2 V(x) = \frac{-4\pi}{\epsilon_1} \rho \quad , \quad (1)$$

which states that the potential is a function of the charge density, ρ , and semiconductor dielectric constant, ϵ_1 . The charge density can be written in terms of concentrations of electron, holes, donor levels, and acceptor levels as follows (n, p, N_D, N_A respectively):

$$\rho = e(-n + p + N_D - N_A) \quad (2)$$

Assuming complete ionization of donors and acceptors, free carrier concentration in the electric field can be determined by a Boltzmann distribution. Thus,

$$n(x) = n^0 \exp \frac{e(V - V_b)}{kT}; \quad p(x) = p^0 \exp \frac{-e(V - V_b)}{kT}, \quad (3)$$

Where n_0 , p_0 , and V_b are concentrations of electrons, holes and the potential at the bulk of the semiconductor, k is the Boltzmann constant, and T is temperature. Substituting this result into equation (2) yields

$$\rho = e \left(-n^0 e^{\frac{e(V - V_b)}{kT}} + p^0 e^{\frac{-e(V - V_b)}{kT}} + N_D - N_A \right) \quad (4)$$

Substituting this into (1) results in

$$\nabla^2 V = -\frac{4\pi}{\epsilon_1} e \left(-n^0 e^{\frac{e(V - V_b)}{kT}} + p^0 e^{\frac{-e(V - V_b)}{kT}} + N_D - N_A \right) \quad (5)$$

For an n-type semiconductor for which $N_D \gg N_A$ and $n^0 \gg p^0$ equation (5) can be simplified to

$$\nabla^2 V = -\frac{4\pi}{\epsilon_1} e \left(-n^0 e^{\frac{e(V - V_b)}{kT}} + N_D \right) \quad (6)$$

Using only the first term of the series expansion of the exponential, equation (6) further simplifies to

$$\nabla^2 V = -\frac{4\pi}{\epsilon_1} e \left(-n^0 \left(1 + \frac{e(V - V_b)}{kT} \right) + N_D \right) \quad (7)$$

Because there is no space charge in the bulk of the semiconductor, $-n^0 + N_D \approx 0$. Taking this into account,

$$\nabla^2 V = \frac{4\pi n^0 e^2}{\epsilon_1 kT} (V - V_b) \quad (8)$$

Asserting that V_b is the reference potential, hence equal zero, the solution to the flat infinite surface is:

$$V(x) = (V_0 - V_b) e^{-\frac{x}{L}} - V_b \quad (9)$$

where L is the Debye length defined as

$$L = \sqrt{\frac{\epsilon_1 kT}{4\pi e^2 n^0}} \quad (10)$$

Free Semiconductor Particle

Expanding on this general development, a spherical semiconductor particle immersed in an electrolytic solution will be considered. The form of Poisson's equation is shown below after simplifications of the same nature as those above have been applied. Additionally, $V_b = 0$ is assumed.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V}{\partial r} \right) = \frac{1}{L^2} V \quad (11)$$

Equation (11) is of the form of a modified spherical bessel function as generally shown below:

$$z^2 w'' + 2zw' - [z^2 + n(n+1)] = 0 \quad (12)$$

Because the potential at the center of the particle must be finite ($V|_{r=0}=\text{constant}$), rejection of all solutions except the i-type bessel functions is possible. Also because our initial equation restricts n to 0 or -1 we can consider the case of $n=0$. Because $i_0(r)=\sinh(r)/r$ the appropriate solution is:

$$V = \frac{r_0 V_o}{r} * \frac{\sinh\left(\frac{r}{L}\right)}{\sinh\left(\frac{r_0}{L}\right)} \quad (13)$$

for the boundary for the boundary conditions $V=1|_{r=r_0}$ and $V=\text{constant}|_{r=0}$.

Potential Distribution for Interstitial Catalyst System

The potential for a semi-spherical semiconductor particle interfaced to a conductive substrate on the flat side and immersed in an electrolytic solution is in the following.

It is assumed that symmetry exists in the θ direction. Thus equation (1) takes the form below in 2 dimensional spherical coordinates.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V}{\partial r} \right) + \frac{1}{r^2 \sin \phi} \frac{\partial}{\partial \phi} \left(\sin \phi \frac{\partial V}{\partial \phi} \right) = \frac{-4\pi}{\epsilon_1} \rho(r, \phi) \quad (14)$$

Applying the same assumptions as in the first section equation (8) is as follows:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V}{\partial r} \right) + \frac{1}{r^2 \sin \phi} \frac{\partial}{\partial \phi} \left(\sin \phi \frac{\partial V}{\partial \phi} \right) = \frac{1}{L^2} (V - V_b) \quad (15)$$

Substituting $u=\cos \phi$, and again asserting that V_b is the reference potential ($V_b=0$) this becomes

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V}{\partial r} \right) - \frac{1}{r^2} \frac{\partial}{\partial u} \left((1-u^2) \frac{\partial V}{\partial u} \right) = \frac{1}{L^2} V \quad (16)$$

Utilizing separation of variables, it is assumed that the solution takes the form:

$$V(r, \phi) = R(r)M(u) , \quad (17)$$

which leads to

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{1}{L^2} r^2 = \frac{1}{M} \frac{\partial}{\partial u} \left((1-u^2) \frac{\partial M}{\partial u} \right) \quad (18)$$

Because functions of r are equal to functions of u the two sides of equation (18) must be equal to an arbitrary constant λ . Thus,

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - Kr^2 = \lambda \quad (19a)$$

$$\frac{1}{M} \frac{\partial}{\partial u} \left((1-u^2) \frac{\partial M}{\partial u} \right) = \lambda , \quad (19b)$$

Where equation (19a) is recognizable as a Bessel equation, equation (19b) is of the form of Legendre's equation and λ is a positive integer and separation parameter.

The solution to equation (19b) is the well known Legendre polynomial expressed as

$$M(u) = A_n P_n(u) , \quad (20)$$

where

$$P_n(x) = \sum_{m=0}^n (-1)^m \frac{(2n-2m)!}{2^n m! (n-m)! (n-2m)!} x^{n-2m} . \quad (21)$$

The solutions of equation (19a) are the spherically modified bessel function $i_n(x)$ and $k_n(x)$. Because the potential must be finite at $r=0$ only the i function is possible. Thus, the solution is of the form:

$$R(r) = D_n i_n \left(\frac{1}{L} r \right), \quad (22)$$

where

$$i_n \left(\frac{r}{L} \right) = 2^{-(n+1)} \sqrt{\pi} \left(\frac{r}{L} \right)^n \sum_{k=0}^{\infty} \frac{\left(-\frac{r e^{\frac{\pi i}{2}}}{4L} \right)^k}{k! \Gamma(n + .5 + k + 1)} \quad (23)$$

Finally, substituting equations (20) and (22) into equation (17) results in the general form of the solution.

$$V(r, \phi) = \sum_{n=1}^{\infty} A_n D_n J_n \left(\frac{1}{L} r \right) P_n(\cos \phi) \quad (24)$$

Letting $a_n = A_n D_n$,

$$V(r, \theta) = \sum_{n=1}^{\infty} a_n i_n \left(\frac{1}{L} r \right) P_n(\cos \theta) \quad (25)$$

The coefficient a_n is readily obtained by applying B.C. $V=1$ at $r=r_0$ and the condition of orthogonality to the Legendre polynomial.

$$a_n = \frac{(2n+1)k}{2i_n \left(\frac{r_0}{L} \right)} \int_0^{\pi} P_n(\cos(\phi)) \sin(\phi) d\phi \quad (26)$$

Thus, the complete solution is

$$V(r, \phi) = \sum_{n=1}^{\infty} \left(\left(\frac{(2n+1)k}{2i_n \left(\frac{r_0}{L} \right)} \int_0^{\frac{\pi}{2}} \sin(\phi) \cdot P_n(\cos(\phi)) d\phi \right) i_n \left(\frac{r}{L} \right) P_n(\cos(\phi)) \right) . \quad (27)$$

At this point, the particular solution awaits imposition of additional boundary conditions. Discontinuities are found at the edges the semiconductor particle where it contacts both the electrolyte and the conductive substrate. Finite element analysis may be necessary to define the potential distribution.

4.2 Redox Mediator Photochemistry

The first objective was to show that the two types semiconductor particles together can generate a sufficient photovoltage to break down water; at ambient temperature, the theoretical value is about 1.23 V. Based on realistic values of overpotentials and other losses, about 1.0 V per module needs to be generated. We chose n-TiO₂ and p-InP as the initial pairing of powders to be tested.

A series of redox reagents were irradiated with a Xe lamp in aqueous slurries of photocatalytic powders to probe the limits of energy storage that each semiconductor is capable of. It also provided some insight into what compounds may prove to be useful redox mediators. For example, if the voltage generation requirement is shared equally between the two photoreactors, the redox mediator will have a standard redox potential of 0.6 V (acidic standard state). The further the mediator's redox potential departs from that value, the more uneven the energy storage load becomes.

In Table II below, gas evolution results are given for one-hour irradiation of TiO_2 slurries in the presence of various redox reagents. It was expected that those with the highest redox potentials would perform best, while those with low redox potential would exhibit little or no gas evolution. As it turned out, gas evolution was observed in nearly every case. Therefore, gas chromatographic analysis of the product gases were performed to confirm the presence of O_2 . In the majority of cases, the gas evolved was not O_2 . Not surprisingly, the only clear cut case of O_2 evolution was found for H_5IO_6 , periodic acid, the reagent with the highest redox potential.

Table II. Gas Evolution from TiO_2 Slurries

1 hr Xe lamp illumination

<u>redox substrate</u>	<u>gas evolved (ml)</u>	<u>O_2 detection</u>
1,4-naphthoquinone disulfonic acid	12	no
2,6-anthraquinone disulfonic acid	15	no
toluidine blue	5	no
thionine	0	no
VO_2^+	10	?
	20*	yes
H_5IO_6	5	yes
	13*	yes
NO_3^-	4	no

* ground admixture of TiO_2 and dried carbon paint.

O₂ evolution with H₅IO₆ does not clearly represent energy storage at all, since its redox potential is positive of water oxidation--the TiO₂ is acting as a photocatalyst, but not as an energy transducer.

Many representatives from the previous series of redox agents were tested as electron donors in the photocatalytic evolution of H₂ using InP. The experiment was essentially the same: irradiation of an InP semiconductor particle suspension, measurement of net gas evolution, and gas chromatographic analysis for H₂. Nine different redox agents were tested representing a span of approximately 1 volt of redox potential energy. Results are summarized in the Table III below:

Table III. Gas Evolution from InP slurries

Mediator	Solvent	Gas Evolution?	H ₂ Evolution?
hydroquinone	NaOH	yes	no
K ₄ [Fe(CN) ₆]	NaOH	yes	yes
SnCl ₂	HCl	yes	yes
FeSO ₄	H ₂ SO ₄	yes	yes
Toluidine Blue	H ₂ SO ₄	yes	?
KI	HCl	yes	yes
KBr	HCl	yes	yes
none	HCl	yes	yes
KI	H ₃ PO ₄	yes	yes
KBr	H ₃ PO ₄	yes	yes
VOSO ₄	H ₃ PO ₄	yes	no

The solvent is listed in each case, because it was determined midway through the experiments sequence that HCl was an active substrate for H₂ evolution. This was an unexpected result, as

the redox potential for Cl_2 evolution was thought to be too positive. Enough testing with alternative electrolytes was done to insure against false results.

In contrast to what had been seen earlier for TiO_2 , all the redox agents tested evolved gas, and all but 2 or 3 of them had at least some H_2 as part of that gaseous evolution. Even the halides were found to work as redox substrates. In terms of redox potential, the hydroquinone should have worked, but also underwent uncharacterized decomposition reactions.

4.3 Future Work

Even though many possible redox mediator candidate were identified in the H_2 - evolution module, the lack of positive results in the O_2 - evolution module precluded identification of a reagent capable of shuttling electrons between the two modules. Either the TiO_2 needs to be made more active through doping or catalyst modification, or alternatives need to be found; ultimately, chromophore/photoconductor systems for O_2 and H_2 evolution must be developed.

It will also be necessary to: a) Determine level of sophistication needed for redox mediator. b) Balance light absorptive and catalytic activity of the chromophore. c) Consider whether the H_2 cell would benefit from a dye sensitization approach.

Finally, we will need to: 1. on the theoretical work, incorporate reverse chemical reaction kinetics into steady state equation. 2. use supersensitizers in conjunction with base chromophore. 3. catalysts for redox mediator oxidation and reduction.

5.0 ACKNOWLEDGEMENT

The author would like to thank Beverly Austin, Tom McKaige, Anthony Ouellette, and Darlene Slattery for their technical assistance on this work. The financial support of the Department of Energy, Office of Advanced Utility Systems, is gratefully acknowledged.