Proposal

SOLAR PHOTOCATALYTIC HYDROGEN PRODUCTION FROM WATER USING A DUAL BED PHOTOSYSTEM

Phase I Final Report and Phase II Proposal

Submitted to:
U.S. Department of Energy
Golden Field Office
1617 Cole Boulevard
Golden, CO 80401-3393

Submitted by:
Florida Solar Energy Center
University of Central Florida
1679 Clearlake Road
Cocoa, Florida 32922-5703

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FLORIDA SOLAR ENERGY CENTER

PROPOSAL FACT SHEET

If you have questions about:

Contact:

Technical Matters

Principal Investigator(s):

Dr. Clovis Linkous
Phone: (321) 638-1447
Fax: (321) 638-1010
Email: calink@fsec.ucf.edu

Proposal Budget

Ms. Mary Huggins, Associate Director, FSEC

Phone: (321) 638-1480
Fax: (321) 638-1488
Email: mary@fsec.ucf.edu

Contractual Matters

Ms. Mary Stanley, Contract Manager

Phone: (407) 823-2836
Fax: (407) 823-3299
Email: mstanley@mail.ucf.edu

If you wish to send a contract:

Please make the contract out to the **University of Central Florida** and send it to:

Ms. Mary Stanley, Contract Manager
Office of Sponsored Research
University of Central Florida
Orlando Tech Center
12443 Research Parkway
Orlando, FL 32826

The Florida Solar Energy Center is a research institute of the University of Central Florida.

**SOLAR PHOTOCATALYTIC HYDROGEN PRODUCTION FROM WATER
USING A DUAL BED PHOTOSYSTEM**

Phase I Final Report and Phase II Proposal

Clovis A. Linkous
and
Darlene K. Slattery

Florida Solar Energy Center
University of Central Florida
Cocoa, FL 32922

September 11, 2000

Prepared for the United States
Department of Energy
Under cooperative agreement
#DE-FC36-99G010449

TABLE OF CONTENTS

Technical Summary.....	i
PHASE I REPORT.....	1
Introduction.....	1
Experimental Section.....	2
Theoretical Calculations.....	2
Ultraviolet Photoelectron Spectroscopy.....	3
Voltammetry.....	3
UV-visible Spectrophotometry.....	4
Results and Discussion.....	4
Semiempirical MO Calculations.....	4
Voltammetric Studies.....	6
Spectrophotometric Studies.....	7
O ₂ Evolution Studies.....	11
Photocatalytic H ₂ Evolution.....	13
Proof of Concept Operation.....	14
References.....	15
PHASE II PROPOSAL.....	17
Statement of Work.....	17
Performance Schedule.....	20
Budget.....	21
Qualifications.....	25
Key Personnel.....	25
Facilities Description.....	25
Résumés of Key Personnel.....	27
Appendices.....	33
Appendix A: Structures of Pigments Evaluated in Phase I.....	33
Appendix B: Future Embodiments of the Dual Bed Photocatalytic System...	36

Technical Summary

A body of work has been performed in which the feasibility of photocatalytically decomposing water into its constituent elements using a dual bed, or modular photosystem, under solar radiation has been demonstrated. The system envisioned consists of two modules, each consisting of a shallow, flat, sealed container, in which microscopic photocatalytic particles are immobilized. The photocatalysts would be chosen as to whether they specifically promote H_2 or O_2 evolution in their respective containers. An aqueous solution containing a redox mediator is pumped between the two chambers in order to transfer electron equivalents from one reaction to the other. The photosystem would feature:

- separate evolution of H_2 and O_2
- potentially higher utilization of the solar spectrum, since the two light-absorbing modules will be able to use more abundant, lower energy photons.
- cheap reagents, photocatalysts, and construction materials, plus minimal processing result in a low cost module.

Using semiempirical molecular orbital calculations, ultraviolet photoelectron spectroscopy, voltammetric analysis, and UV-visible spectrophotometry, a number of organic pigment compounds were identified that are good absorbers of solar radiation, and are energetically capable of performing the various photoredox processes. Both modules by themselves were shown to work, selectively evolving either H_2 or O_2 while respectively oxidizing or reducing the iodate/iodide redox mediator. The chemical potential of the solution, as determined by the concentration ratio of the oxidized and reduced forms of the mediator, was identical for both modules, proving the necessary condition that the effluent of one module can be acted on by the other. For the O_2 -evolving module, the best photocatalyst material proved to be a perylene diimide, while the best material for H_2 -evolution was copper phthalocyanine.

The objective of the Phase II effort is to perform R&D tasks that will enable engineering and economic analysis of the technology. Our preliminary determination, based on materials costs, is that the dual bed could produce H_2 at \$13/mBtu if the solar-to- H_2 energy conversion efficiency of the system is 8%. Accordingly, we propose to perform a systems analysis of several dual bed configurations (series-connected, tandem membrane, and perforated membrane) to evaluate whether these alternative configurations would accrue efficiency improvements. We will also include the effect of using a redox conformer as mediator, to ascertain the effect of utilizing a more complex mediator whose reversibility is a function of molecular conformation. Now that we have a good idea about what molecular structures make the best photocatalysts, we will design, synthesize, and test a number of compounds that would appear to have optimum characteristics. Pending favorable results on the aforementioned activities, we will construct square foot-sized modules and test them under solar simulated conditions. Support is also requested to be able to attend and participate in experts meetings associated with Annex 14 of the International Energy Agency on Photoelectrolytic Production of Hydrogen.

PHASE I REPORT

Introduction

In this work we are attempting to perform the highly efficient storage of solar energy in the form of H_2 via photocatalytic decomposition of water. While it has been demonstrated that H_2 and O_2 can be evolved from a single vessel containing a single suspended photocatalyst (Sayama 1994; 1997), we are attempting to perform net water-splitting by using two photocatalysts immobilized in separate containers, or beds. A schematic showing how the device would work is shown in Figure 1.

Figure 1. Schematic of a Dual Bed Photocatalytic Water-Splitting System.

Two pairs of photocatalytic reactions would occur. In one container, water is reduced to H_2 ; the electron equivalents for the reaction come from a redox mediator, M . In the second container, water is oxidized to evolve O_2 ; here the oxidized form of the mediator acts as electron acceptor. By circulating the mediator in an aqueous solution between the beds, the transfer of charge equivalents between the two water decomposition half-cell reactions is accomplished. While the maximum quantum efficiency for water-splitting is automatically cut in half, one is now able to utilize lower energy photons to perform less energetically demanding chemical steps, and so achieve better utilization of the solar spectrum.

The direction of reaction is controlled largely by the electronic structure of the photocatalysts. In order to perform H_2 evolution, the conduction band edge of the semiconductor must exceed, or on the electrochemical voltage scale, be more negative

than, the electronic energy level for H_2 . The valence band edge must lie below the redox state of the mediator. A similar argument can be made for the O_2 -evolving photocatalyst.

One of the principle advantages of the photocatalytic approach to water-splitting is the module cost. Previous work has shown that photocatalyst dispersions at only a few milligrams per square centimeter can effectively collect the incoming light (Linkous 1995). To scale up the units, one would need 10 g photocatalyst/ m^2 , or 45 m^2/lb . With a projected cost of 10's of dollars per pound, the photocatalyst would have a negligible impact on overall system cost. In a comparative analysis of several semiconductor-electrolytic H_2 -generating systems (Block 1998), it was estimated that a dual bed reactor operating at 8.0% efficiency would be able to produce H_2 at \$13/Mbtu.

In earlier work on this concept, we tried to identify combinations of redox mediators and photocatalysts that would perform their respective functions. We identified the alkaline IO_3^-/I^- redox couple as being optically transparent, highly soluble, and active for electron transfer in both Ox and Red states (Linkous 1996). For the O_2 -evolving photocatalyst, we first studied TiO_2 . While it was able to evolve O_2 under a variety of conditions, the 3.0-3.2 eV band gap absorbed too little of the solar spectrum. For the H_2 -evolving photocatalyst, we identified indium phosphide, InP. While initial H_2 yields were good, it proved unstable under illumination in the alkaline solution. Moreover, it was eventually discovered that InP could be attacked by IO_3^- even in the dark.

That result led us to consider organic pigments as photocatalysts for the respective water-splitting reactions. The number of pigments commercially available is quite large, however, and so we sought to develop a battery of testing methods, both theoretical and experimental, for estimating whether a given compound could effectively absorb visible wavelength light and be able to either photooxidize or photoreduce water. The list of pigments studied, along with their calculated ionization potentials in electron volts and their λ_{max} in nanometers are shown in Appendix A. As for a theoretical method, we evaluated several semi-empirical molecular orbital calculation methods and determined that the PM3 method gave the most reliable gas phase ionization potentials for fused ring compounds. The results were not necessarily accurate, but did yield a linear plot by which a correction factor could be obtained. The application of the PM3 method to pigments of interest, plus the development photoelectron and voltammetric methods of testing, are described below.

Experimental

Theoretical Calculations

Calculation of the HOMO (highest occupied molecular orbital in the ground state) and LUMO (lowest unoccupied molecular orbital) for each pigment was accomplished using CAChe[®] 3.0 software from Oxford Molecular Group, run on a Pentium II, 233 MHz computer. The molecule was drawn within the program and the valence, hybridization, and initial geometry were corrected using the "beautify" option. After a preliminary geometry optimization by molecular mechanics, MM2, additional optimization was

performed using PM3 parameters. The fully optimized molecule was then submitted for PM3 determination of the wavefunctions, including the HOMO and LUMO.

Ultraviolet Photoelectron Spectroscopy

The required apparatus to perform these measurements was found at the University of Arizona, under the supervision of Dr. Nadine Gruhn. The gas-phase ultraviolet photoelectron spectra were recorded using an instrument and procedures that have previously been described in detail (Westcott 1998). The argon $^2P_{3/2}$ ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy, and the difference between the argon $^2P_{3/2}$ ionization and the methyl iodide $^2E_{1/2}$ ionization at 9.538 eV was used to calibrate the ionization energy scale. During data collection the instrument resolution (measured using FWHM of the argon $^2P_{3/2}$ peak) was 0.015-0.030 eV. Ionization peak positions are reproducible to ± 0.02 eV.

Voltammetry

The various pigments were largely intractable in aqueous solution and in most organic solvents as well, so that voltammetric data had to be obtained by casting pigment films directly onto the working electrode and performing the electrolysis on the film in a blank supporting nonaqueous electrolyte. The pigments were solubilized by making a Lewis acid complex with $AlCl_3$ which could then be subsequently acted on by organic solvents. Even though the pigments could be solubilized in this way, it was still necessary to cast films, because the ligand binding effect shifted the energy levels we were hoping to probe, and the organic solvents employed were electroactive themselves in the anodic potential region.

Solutions were prepared under an inert atmosphere in a glovebox. Using a process recently developed at Xerox (Hsieh 1998), 6 mL of nitromethane and 4 mL of methylene chloride were combined and 0.33 g of aluminum chloride was added. After stirring to dissolve the $AlCl_3$, 0.4 mmol of the pigment were added. The flask was stoppered and the solution allowed to stir for 6-18 hours.

The working electrode was a 1.0 cm^2 platinum foil. The electrode was passed through a hydrogen flame and then, under an inert atmosphere, was dipped in the pigment/nitromethane solution 1-7 times to coat, allowing time to dry between coats. After coating, the electrode was removed from the glove box and dipped in deionized water to remove any residual nitromethane, methylene chloride and aluminum chloride. It was then placed in a warm oven at approximately 110°C until dry.

Voltammetric experiments were run using an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A with data being recorded using a Hewlett Packard 7015B chart recorder. A three electrode, single compartment configuration was used, with a platinum mesh counter electrode, and a $Ag/AgClO_4$ reference electrode. Solutions were 0.1 M tetraethylammonium perchlorate in DMSO when investigating reduction potentials or 0.1 M $LiClO_4$ in acetonitrile for oxidation potential studies. The solvents were Aldrich brand anhydrous and were used as received.

UV-Visible Spectrophotometry

Initial spectra were run on a Milton Roy Spectronic 601 UV-vis Spectrophotometer. Readings were made manually at 10 nm increments from 400 to 800 nm, with the instrument being zeroed after each change of wavelength. Samples run on this instrument were either sublimed onto glass, prepared as a pigment/polymer film or prepared as a dilute solution. Solvents included chloronaphthalene, N-tert-butyl formamide, propylene carbonate, sulfuric acid, DMSO, water and the methylene chloride/nitromethane/ AlCl_3 solution. For the pigment/polymer films, the polymer was polystyrene with a weight ratio of 50:1, polymer to pigment. Films were cast from a methylene chloride solution onto microscope slides.

Later measurements were made on a Shimadzu UV-2401 PC UV-vis Recording Spectrophotometer fitted with an integrating sphere attachment for reflectance measurements. Samples were run as powders, manually packed into the sample holder, with a barium sulfate powder as the blank. The instrument was run by, and the data acquired on, a Gateway 2000 computer running UVPC Personal Spectroscopy Software, version 3.9. The data was collected as percent reflectance and then transformed using the Kubelka-Munk equation. This data, as well as that obtained on the Spec 601, was ultimately imported into Microsoft Excel for graphing.

Results and Discussion

Semiempirical MO Calculations

As stated in the Introduction, we had shown that one could perform PM3 semi-empirical molecular orbital calculations on organic molecules, derive gas phase ionization potentials based on the calculated HOMO's of the molecules, and then plot these values versus the literature IP values to derive a linear equation containing the correction factor between theory and experiment. However, we soon found that good linear correlations could only be obtained for structurally analogous series of compounds. The addition of heteroatoms in the fused aromatic rings of many of the more interesting pigments caused energy shifts that warranted a new correction factor. Unfortunately, rather little experimental ionization potential data exists for organic pigments. Plenty of optical spectral data is available, but IP is not recognized as a significant parameter for the dye and pigment industry, even though it undoubtedly correlates with factors of considerable interest, such as lightfastness.

Hence it became necessary to obtain experimental gas phase ionization potential data. This was done via ultraviolet photoelectron spectroscopy (see Experimental section). A representative spectrum for indigo is shown in Figure 2. The ionization potential is determined by extending the slope of the lowest energy transition peak until it crosses the

horizontal axis. The values are shown for a number of pigments in Table 1 below. As expected, the experimental values were generally somewhat less than the calculated values. If nothing else, this is due to the fact that the experimental value is an "onset" of ionization, while the calculated value represents the maximum of the thermal Gaussian distribution of

Figure 2. Gas Phase Ultraviolet Photoelectron Spectrum for Indigo

energies. It may also be true that PM3 typically overestimates some of the overlap integrals for fused aromatics. A plot of experimental versus theoretical ionization potential for a number of similar compounds (indanthrone, quinacridone, isoviolanthrone, indanthrene gold orange, perylene TCDA, and dimethoxyviolanthrone) are shown in Figure 3. Units are in electron volts (eV). The equation shown is a least squares fitting of the data. Our expectation is that we will now be able to take any prospective fused

aromatic quinonoid structure, perform a 20 minute PM3 calculation on it, and then substitute the result into the fitted equation to derive the true ionization potential.

Figure 3. Plot of experimental versus theoretical ionization potential for photocatalytic pigments.

Voltammetric Studies

While UPS proved useful as a means of acquiring experimental ionization potential data, we also sought to develop an in-house method by which we could make the same determination. The first oxidation and reduction potentials in an electrochemical experiment can approximate the ionization potential and electron affinity, respectively, although a correction involving solvation energies would be necessary for a rigorous determination.

The difficulty of preparing samples that would yield voltammetric data is described in the Experimental section. Even so, once the Lewis acid pigment solubilization technique was mastered, voltammetric data for nearly all the prospective organic photocatalysts could be obtained. A representative voltammogram, obtained for Indanthrene Yellow, is shown in Figure 4. The results for all the pigments are also shown in Table 1. In general, there was fair agreement between the ΔV value, based on the difference between the E_{ox} and E_{red} measurements, and the ΔE value based on spectroscopy. Sometimes the voltammetric wave was irreversible, so that the measured redox potential was more of an upper bound than the actual value. While the correlation between calculation and experiment was less than with the UPS measurements, it should be noted that the

electrochemical experiment better reflects the solid state energy levels that would participate in the photocatalytic reaction. It is also true that there is no limitation having to do with structural analogues; the voltammetric waves are unambiguous indications of the energies where charge transfer would be expected from a given compound. Certainly the general trend of calculated HOMO increasing with E_{ox} was observed, especially for the perylenes.

Figure 4 . Cyclic Voltammogram for the Oxidation of Indanthrene Yellow

Spectrophotometric Studies

The visible spectra of the pigments were of interest for two major reasons: knowledge of the region in which the pigments absorb and determination of the band gaps. As mentioned in the Introduction, a compound that absorbs a large proportion of the incident radiation will be more efficient than one that absorbs only a small fraction. Therefore, it was in our best interest to evaluate the spectra to determine how much of the solar spectrum would be absorbed.

From the literature, it was easy to obtain a λ_{max} for most of the pigments. However, these values are the wavelength of the maximum absorption; they tell nothing about the shape of the absorption band or the location of the edges. Light striking a sample will contain photons over a range of energies and, therefore, electrons will be promoted to numerous

energy levels. While this absorption band will strongly influence the color of the material, it is the longest wavelength, which gives us the lowest energy transition and, thus, the band gap.

Initial spectroscopic studies were done using a Milton Roy Spectronic 601. This instrument was not equipped to do reflectance measurements on solids, so it was either necessary to make dilute solutions of the pigments or to make thin films through which the radiation could be transmitted. While it was possible to make solutions of some of the pigments, most were too insoluble and resulted in fine suspensions that promoted light scattering, leading to low signal to noise ratios. Most of the pigments were soluble in concentrated sulfuric acid but drastic color changes resulted, preventing accurate determination of the absorption band edge.

Figure 5. Visible Spectrum of Quinacridone

Eventually, literature information led to a method to solubilize the pigments using a nitromethane/methylene chloride/ AlCl_3 solution. The same two problems exhibited with the other solutions again were seen: many were actually fine suspensions while others resulted in color changes. None satisfactorily gave the required information. Forming thin films was also attempted. In this method, a solution of polystyrene and methylene chloride was prepared and a small amount of the pigment was added. This mixture was then spread in a thin film onto a precut microscope slide. A great deal of difficulty was encountered in forming uniform films because the pigment was suspended in the polymer mixture, not dissolved. Additionally, many of the films formed tiny bubbles and ripples during the solvent evaporation. All of these imperfections led to difficulty in obtaining acceptable spectra.

Eventually, a Shimadzu UV-vis recording spectrophotometer fitted with an integrating sphere attachment was obtained. Using this attachment allowed reflectance

measurements to be made on the powdered samples, eliminating the problems encountered with the earlier approaches. The sample was tamped into the sample holder and inserted directly into the instrument. The data was recorded as a percent reflectance measurement but this could be converted to the more familiar absorption curves by use of the Kubelka-Munk equation, the transformation being a part of the packaged software. A representative spectrum is shown in Figure 5. The quinacridone spectrum clearly illustrates the necessity of examining the spectrum rather than using the $\lambda_{\max}$ for calculating the transition energy. The manufacturer, Ciba-Geigy, reports $\lambda_{\max}$ to be 523 nm but the edge of the absorption band is about 600 nm. To determine the edge of the absorption band in each spectrum, a linear portion of the curve was extrapolated to zero. This wavelength was converted to the band gap using the equation

$$\Delta E = hc/\lambda$$

where

h = Planck's constant

c = speed of light

λ = absorption wavelength

The compilation of all ΔE values for the pigments under study, as determined from their optical spectra, are shown in Table 1.

Table 1. Energy Levels of Various Organic Pigments as Determined by PM3 Semi-Empirical MO Calculation, UV-Photoelectron Spectroscopy, Voltammetry, and UV-Visible Spectrophotometry.

PIGMENT	I.P. theory (eV)	I.P. exp (eV)	E° _{ox} (V)*	E° _{red} (V)*	λ (nm)	ΔE (eV)
Indanthrone	7.25	6.78	0.99	-0.29	622	1.99
Quinacridone	7.65	7.23	1.39	-1.11	595	2.08
Dimethoxy Violanthrone	7.90	~7.6	1.16	-0.34	706	1.75
Isoviolanthrone	8.22	7.87	1.54	-0.34	712	1.74
Indigo	8.34	7.23	1.19	-0.37	737	1.68
Bis(chlorophenyl) DPP	8.50	7.47	<1.49	-0.70	600	2.06
Pyranthrone	8.54	----	1.39	-0.30	585	2.12
Indanthrene Black	8.83	----	----	----	----	----
Indanthrene Gold Orange	8.84	8.07	1.50	-0.03	562	2.20
Perylene TCDA	9.31	8.22	<2.29	-0.05	604	2.05
Indanthrene Yellow	9.41	----	1.09	----	510	2.43
Perylene Diimide	8.87	----	<2.09	-0.14	652	1.90

* vs NHE reference electrode

O₂ Evolution Studies

Having established a number of methods for estimating the available oxidation potential of a photocatalyst, it was time to see whether water could indeed be oxidatively decomposed to evolve O₂. Accordingly, the prospective photocatalysts were suspended with 2.0 weight percent co-catalyst in a dichloroethane solution and deposited by painting onto an acrylic substrate.

This represented something of a departure from past methods. Formerly, we had made co-catalyst modifications of the primary photocatalysts by a number of methods, such as photoreduction or direct borohydride reduction of a noble metal salt. The direct chemical reduction method has been found to be difficult and counterproductive with the organic pigments. The reducing effect of the BH₄⁻ ion often served to irreversibly reduce and discolor the pigment.

Consequently, we have been directly physically mixing the photocatalyst and co-catalyst powders. While this does not make for as intimate a mixture as the aforementioned methods, nevertheless, related studies in photocatalytic detoxification studies with similarly intractable materials has shown that positive effects can indeed be observed by direct blending of the photocatalyst and co-catalyst powders (Linkous, 2000).

The O₂ evolution data from the photocatalytic experiments is shown in Table 2. Each value represents a 6-hour photolysis with a Xe lamp using iodate ion as electron acceptor in 1.0 M NaOH solution. The co-catalyst was iridium black.

Most of the pigments performed better than TiO₂ tested under the same conditions. The value obtained for the acrylic blank (which also included Ir co-catalyst) was a matter of concern, since the unpigmented sample could not have absorbed any visible light. Imposition of a 400 nm longpass filter eliminated the gas evolution, so that it was concluded that the 1.7 ml value represented a UV background effect. The nature of the UV effect was initially thought to be due to oxidative water-splitting via UV light-generated valence band holes, the same O₂-evolving mechanism ascribed to the various semiconductor powders.

Accordingly, a series of alternative polymer binders were tested in order to identify a binder that would be non-oxidizing under Xe lamp irradiation. These results are shown in Table 3. It is seen that all of the binders tested, including very inert ones such as ethylene/propylene copolymer, evolved at least some O₂. Finally, another control experiment was run where a quartz window, known to be UV transparent in the region of the lamp spectral output, was put in place instead of a polymer substrate. The O₂ evolution still occurred, indicating that the source of the O₂ evolution lay in the alkaline iodate solution itself. A transmission spectrum for iodate ion, shown in Figure 6, shows how deep UV light (< 300 nm) may be absorbed. The solar spectrum has negligible intensity in this region, however, so that use of iodate ion as redox mediator in a solar-based dual bed system should not be a problem.

Table 2. Volume of O₂ Evolved in Water-Splitting Experiments using Organic Pigments

Photocatalyst	O ₂ Evolved (ml)
Perylene Diimide	4.4
bis(p-chlorophenyl) DPP	3.6
Indanthrone	3.3
Perylene TCDA	3.2
Pigment Red 177	2.6
Indanthrene Yellow	2.0
Quinacridone	1.8
Isoviolanthrone	1.5
Acrylic blank	1.5
Indigo	1.4
Dimethoxyviolanthrone	1.3
TiO ₂	1.3
Indanthrene gold orange	0.9
Indanthrene Black	0.7

Table 3. O₂ Evolution from Polymeric Substrates.

Substrate	Window	mL O ₂ Evolved
Polymethacrylate	Quartz	1.70
Polycarbonate	Quartz	2.00
Ethylene/Propylene Copolymer	Quartz	2.40
PVC	Quartz	1.99
None	Quartz	1.70
None	Pyrex	0.06
None	UV Filter	0.02

Solution: 0.2 M IO₃⁻ in 1.0 M NaOH

Figure 6. Transmission Spectrum of Potassium Iodate Solution

Despite the modest yields of O_2 and the difficulty in establishing a gas evolution baseline, it was apparent that we accomplished our goal in finding more active O_2 -evolving photocatalysts than TiO_2 .

Photocatalytic H_2 Evolution

Having achieved some measure of success with the O_2 -evolving photocatalysts, it was time to turn our attention toward H_2 -evolving photocatalysts. From the literature and from our PM3 calculations, it was apparent that the phthalocyanine (Pc) family of compounds could serve as photocatalysts in this regard (Kearns 1961; Giraudeau 1980). A number of phthalocyanine compounds were acquired and submitted to testing in the same manner as the O_2 -evolving photocatalysts above, except that the electrolyte contained 0.2 M iodide ion to serve as electron donor, and the co-catalyst was 2.0 weight percent platinum black.

These results are shown in Table 4 below. The chloro-aluminum Pc was chosen as a representative trivalent metal center. Earlier work had shown that these MPc-X's could perform well as electrode materials in a photoelectrochemical cell (Klofta 1985). Because of its above-plane central moiety, the vanadyl Pc has a unique crystal structure and optical spectrum, and so was of interest for this application (Griffiths 1976). As it turned out, the more common copper Pc evolved the most H_2 . This may correlate with its superior extinction coefficient in the solid state (Moser 1963).

Table 4. Volume of H₂ Evolved in Water-Splitting Experiments using Phthalocyanine Organic Pigments

photocatalyst	H ₂ evolved (μl)
CuPc	113.0
VOPc	25.6
AlPc-Cl	16.0
NiPc	22.6

While the amounts of gas evolved are considerably less than with the O₂-evolving photocatalysts, we are confident better photocatalysts will be identified with time. The challenge to date has been to identify organic materials whose HOMO was sufficiently positive on the voltage scale to oxidize water, but whose LUMO was also sufficiently positive so that the band gap energy could be surmounted using visible wavelength light. More often than not, LUMO levels for organic pigments are energetically capable of performing water reduction, and so with time more favorable materials will be found.

Proof of Concept Operation

Having found organic pigments that would support O₂ evolution and H₂ evolution, it was time for proof of concept, i.e., to show that the separate photocatalytic systems could evolve their respective gas using the same redox electrolyte. Our best O₂-evolving photocatalyst was the ditridecyl perylene diimide and our best H₂-evolving photocatalyst was copper phthalocyanine. Their structures are shown in Figures 7 and 8. The two photocatalysts were tested as before, except that instead of using entirely Ox or Red forms of the redox mediator, the experiment was begun at equal parts IO₃⁻ and I⁻. In each case, the respective gas was obtained in ~80% of the amount obtained with 100% of Ox or Red, respectively, thus showing that net water-splitting would occur in closed cycle operation.

Figure 7. Structure of O₂-Evolving Photocatalyst N,N'-Ditridecyl-3,4,9,10-Perylene Tetracarboxylic Diimide.

Figure 8. Structure of Copper Phthalocyanine.

In future work, modifications of the existing configuration will be attempted to increase system efficiency. We will attempt this objective in several ways. One is to demonstrate tandemized versions of the dual bed system using organic pigments and polymer membrane technology. Subsequently, we will introduce porosity or microperforations into the photocatalytic membranes. Finally, we will try to prevent back reaction by developing controlled conformation redox mediator complexes.

References

- Block, D.L. 1998. "Comparative Costs of Hydrogen Produced from Photovoltaic Electrolysis and from Photoelectrochemical Processes," In *Proceedings of the 12th World Hydrogen Energy Conference*, vol 1:185-194. Buenos Aires, Argentina: International Association for Hydrogen Energy.
- Giraudeau, A., F.-R.F. Fan, and A.J. Bard. 1980. "Semiconductor Electrodes. 30. Spectral Sensitization of the Semiconductors n-TiO₂ and n-WO₃ with Metal Phthalocyanines," *J. Am. Chem. Soc.* 102:5137-5141.
- Griffiths, C.H., M.S. Walker, and P. Goldstein., 1976. *Mol Cryst. Liq. Cryst.* 33:149.
- Hsieh, B.R., and A.R. Melnyk. 1998. *Chem. Mater.* 10:2313-2316.
- Kearns, D.R., and M. Calvin. 1961. "Solid State Ionization Potentials of Some Aromatic Organic Compounds," *J. Chem. Phys.* 34: 2026-2030.
- Klofta, T.J., P.C. Rieke, C.A. Linkous, W.J. Buttner, A. Nanthakumar, T.D. Mewborn, and N.R. Armstrong, "Tri- and Tetravalent Phthalocyanine Thin Film Electrodes: Comparison with Other Metal and Demetallated Phthalocyanine Systems," *J.*

Electrochem. Soc. 132: 2134-2144.

Linkous, C.A., N.Z. Muradov, and S.N. Ramser. 1995, "Consideration of Reactor Design for Solar Hydrogen Production from Hydrogen Sulfide Using Semiconductor Particulates," *Int. J. Hydrogen Energy*, 20:701-710.

Linkous, C.A., D.K. Slattery, A.J.A. Ouelette, G.T. McKaige, and B.C.N. Austin. 1996. "Solar Photocatalytic H₂ from Water Using a Dual Bed Photosystem." In *Hydrogen Energy Progress XI: Proceedings of the 11th World Hydrogen Energy Conference*, vol. 3, 2545-2550.

Linkous, C.A., G.J. Carter, D.B. Locuson, A.J. Ouelette, D.K. Slattery, and L.A. Smitha. 2000. "Photocatalytic Inhibition of Algae Growth Using TiO₂, WO₃, and Co-catalyst Modifications," submitted to *Env. Sci. Technol.*

Moser, F.H., and A.L. Thomas. *Phthalocyanine Compounds*. New York:Reinhold Publishers.

Sayama, K., and H. Arakawa. 1994. "Effect of Na₂CO₃ Addition on Photocatalytic Decomposition of Liquid Water over Various Semiconductor Catalysts." *J. Photochem. Photobiol. A: Chem.*, 77: 243-247.

Sayama, K. and H. Arakawa. 1997. "Effect of Carbonate Salt Addition on the Photocatalytic Decomposition of Liquid Water over Pt-TiO₂ Catalyst." *J. Chem Soc., Faraday Trans.*, 93: 1647-1654.

Westcott, B.L., N.E. Gruhn, and J.H.J. Enemark. 1998. *J. Am. Chem. Soc.* 120:3382-3386.

PHASE II PROPOSAL

Statement of Work

Photocatalytic compounds in particulate form will be employed in various dual modular configurations so as to effect the solar-driven decomposition of water to its constituent elements, particularly hydrogen. The system advantages are low manufacturing cost, safe evolution of H_2 and O_2 in separate compartments, and more efficient use of the solar spectrum.

Each module has its own distinctive photocatalyst according to whether it is to evolve H_2 or O_2 . Earlier studies concentrated on conventional inorganic semiconductor materials. It was eventually realized that new photocatalytic materials needed to be developed to avoid lifetime problems due to corrosion and to absorb lower energy photons. A combination of semi-empirical molecular orbital calculations and voltammetric, UV-visible spectroscopic, and UV photoelectron analysis identified several organic pigment families as promising materials. These materials were tested as to their respective O_2 - and H_2 -evolving ability. A perylene diimide gave the best results for O_2 evolution, while copper phthalocyanine proved best for H_2 evolution.

The tasks to be performed over the next year are as follows:

1. **System/configuration modeling.** Our system calculations based on materials costs indicate that if an 8% solar to hydrogen conversion efficiency could be obtained, the resulting H_2 would sell for \$13/mbtu. To achieve this efficiency, it is anticipated that a combination of photocatalyst materials and system configuration development will be necessary. The various configurations under consideration are shown in Appendix B. The effect of various module designs can be estimated by modeling calculations.
 - a. **Dual planar modules.** Mass transport considerations would indicate that there will be a redox mediator concentration gradient across the face of each module, so that the rate of water-splitting would fall in the direction of flow of the working fluid. Diffusion and forced flow calculations will be performed to correlate the movement of the redox mediator to the module performance.
 - b. **Tandem module.** One trade-off in employing dual modules or any tandem systems is that the quantum efficiency of the water-splitting process is automatically halved. This is justified by being able to utilize more of the solar spectrum. An approach successfully exploited in the photoelectrochemical area is to use tandem electrodes, that is, semiconductor electrodes made from dissimilar lamina that complement each other in terms of their electronic characteristics. It is possible to formulate a photocatalytic version of the dual bed by conceptually folding one module underneath the other. Modeling the use of tandem modules should provide a basis of comparison to the series planar arrangement.

c. **Perforated tandem module.** In this modification, we will consider whether perforating the photoactive surface to enable mediator flow from front to back through the supporting membrane, as opposed to transverse flow around it, will reduce mass transport difficulties.

d. **Redox conformation effect.** One obvious deficiency of the photocatalytic approach to water-splitting is that little provision exists for preventing the reverse reaction, i.e., the consumption of H_2 and O_2 inside the module via reaction with the respective form of the redox mediator. It may be possible to prevent the back reaction by employing redox mediators that undergo conformational change due to change in oxidation state. The effect of reversible and irreversible mediator kinetics will be including into the modeling calculations.

2. **Continued photocatalyst development.** An experimental component of this year's work will involve further development of the photocatalyst materials. Now that we have a good idea about what molecular structures make the best photocatalysts, we will design, synthesize, and test a number of compounds that would appear to have optimum characteristics.

a. **O_2 -evolving photocatalyst.** For O_2 evolution, derivatization of the imide moiety on the perylene diimide is expected to improve its photocatalytic performance. A recent article in *Nature* (Vol 404, 30 March 2000) described an organic semiconductor that had increased electron mobility when a fluorinated sidechain was added. The semiconductor compound, naphthalenetetracarboxylic diimide, is analogous to the perylene diimide that we have been investigating for oxidative water splitting. We therefore have become interested in the influence that would result from fluorinated N,N'-alkyl groups on the perylene compound. Such a compounds are not available commercially, so we would have to synthesize them ourselves.

b. **H_2 -evolving photocatalyst.** The work done on phthalocyanines will be expanded to include other pigment families. Most notably, our earlier work on PM3 calculations would indicate that quinacridones and indanthrones should be facile H_2 evolution photocatalysts. Indeed, preliminary work has corroborated that these pigments will preferentially evolve H_2 (D.K. Slattery, Ph. D. thesis, Florida Institute of Technology, 1999). We also intend to investigate the cyanine and merocyanine dyes. Well known in the color photographic community, there is a substantial literature base as to their chemical and physical characteristics. These compounds were not studied earlier, because their energetic characteristics were not conducive toward O_2 evolution. Now that we are giving equal emphasis to H_2 and O_2 evolution, we will evaluate them as H_2 -evolving photocatalysts.

3. **Module construction.** Successful completion of tasks 1 and 2 will lead to construction and testing of photocatalytic modules. It is in this endeavor that one of the prime advantages of the photocatalytic approach will be apparent: scaling up to whatever module size is necessary (square inch, square foot, or even square yard) can be easily accomplished.

a. **Photocatalyst and co-catalyst distribution.** It seems clear that co-catalysts must be included to promote acceptable charge transfer rates. The means of applying a 1.0 weight percent co-catalyst uniformly distributed over a large photocatalyst deposit area is a technique that must be developed. Chemical reduction, electrochemical deposition, and simple physical blending of co-catalysts have been attempted in the past. Each method has its advantages and disadvantages. Of the three, chemical reduction is likely the preferred approach, but only if the co-catalyst can be deposited without altering the state of the photocatalyst itself. The task here is to develop a combination of photocatalyst, co-catalyst, and reducing agent that are compatible with each other.

b. **Testing under solar simulator.** This will be the critical milestone, to construct a module and test it under solar simulated illumination. We have at our disposal a solar simulator that can produce up to 1.5 AM1 solar irradiance over an area of many square meters. Other groups at the Center have used it for testing solar hot water heaters, photovoltaic cells, and calibrating of optical test equipment. If necessary we can secure beam time on the simulator and construct a module of whatever area is necessary to obtain a measurable gas evolution rate.

4. **Participation in IEA Annex activities.** The former "Photoproduction of Hydrogen" Annex 10 agreement of the International Energy Agency has been reconstituted as Annex 14 on "Photoelectrolytic Production of Hydrogen." Investigators from Switzerland and Japan that formed collaborations with us during the previous agreement will be participating again in the new annex, so that it is expected that those interactions will continue. The specific interaction is under negotiation at this point, but it is anticipated that common ground will be found with the use of our pigments in dye-sensitization systems.

Solar Photocatalytic H₂ Production from Water Using a Dual Bed Photosystem

Florida Solar Energy Center

Task Designation/Milestone	Qtr 1	Qtr 2	Qtr 3	Qtr 4
1. System/configuration modeling				
a. dual planar modules	◆			
b. tandem module		◆		
c. perforated tandem module			◆	
d. redox conformation effect				◆
2. Continued photocatalyst development				
a. O ₂ -evolving photocatalyst		◆		
b. H ₂ -evolving photocatalyst			◆	
3. Module construction				
a. photocatalyst and co-catalyst distribution				◆
b. testing under solar simulator				◆
4. Participation in IEA Annex 14 activities				
a. attend fall '00 experts meeting	◆			
b. attend spring '01 experts meeting			◆	

BASE HOURLY

SALARY & WAGES

FRINGE BENEFITS

**TOTAL
COSTS**

FSEC
Cost Share

Agency Funding Requested

DIRECT LABOR:

Project Manager	\$46.00	201	\$9,246	\$2,270	\$11,516	\$0	\$11,516
Principal Research Engr/Scientist	\$33.08	1040	\$34,403	\$8,446	\$42,849	\$40,622	\$2,227
Senior Research Engr/Scientist	\$27.38	0	\$0	\$0	\$0	\$0	\$0
Research Engr/Scientist	\$20.74	4160	\$86,278	\$21,181	\$107,460	\$0	\$107,460
Associate Research Engr/Scientist	\$17.30	0	\$0	\$0	\$0	\$0	\$0
Technical Support/Technician	\$13.43	0	\$0	\$0	\$0	\$0	\$0
Secretarial/Clerical	\$11.26	520	\$5,855	\$1,437	\$7,293	\$0	\$7,293
Undergraduate Student Assistant	\$7.48	1040	\$7,779	\$23	\$7,803	\$0	\$7,803
Graduate Student Assistant (PhD)	\$18.54	0	\$0	\$0	\$0	\$0	\$0
SUBTOTAL			\$143,562	\$33,358	\$176,920	\$40,622	\$136,298

SUBCONTRACT:

None	\$0	\$0	\$0
SUBTOTAL:	\$0	\$0	\$0

EXPENSE:

Travel (out of state)	\$5,317	\$0	\$5,317
Travel (in-state)	\$0	\$0	\$0
Equipment Maintenance (SEM, FTIR)	\$2,500	\$0	\$2,500
Chemicals	\$2,500	\$0	\$2,500
General Supplies	\$500	\$0	\$500
Optical Supplies	\$2,000	\$0	\$2,000
Laboratory Supplies	\$1,500	\$0	\$1,500
Vacuum Accessories	\$1,500	\$0	\$1,500
Machine Shop	\$1,000	\$0	\$1,000
Computer Searches & Numerical Analysis Software	\$1,500	\$0	\$1,500
Solar Simulator Tests	\$2,344	\$0	\$2,344
Outside Chemical Analysis	\$2,000	\$0	\$2,000
SUBTOTAL:	\$22,661	\$0	\$22,661

EQUIPMENT:

Waveform Generator	\$5,000	\$0	\$5,000
SUBTOTAL:	\$5,000	\$0	\$5,000

TOTAL DIRECT COSTS:

INDIRECT COSTS:	41.5%	of base:	\$199,581	\$82,826	\$16,858	\$65,968
TOTAL PROPOSED COSTS:				\$287,407	\$57,480	\$229,926

TOTAL PROPOSED COSTS:

Cost Share: 20%

TRAVEL DETAILS

Out of State Travel

Destination: Geneva, Switzerland

1 trips

1 persons

4 days

3 nights

	Unit	Unit Cost	Total
Airfare	each trip	\$ 1,150	\$ 1,150
Lodging	each night	\$ 128	\$ 384
Per diem	each day	\$ 100	\$ 400
Rental car	each day	\$ -	-
Local travel	miles per trip	80	23 (@ \$0.29/mile)
Parking	per day	\$ 12	\$ 48
Misc. & tolls	per trip	\$ 25	\$ 25
			\$ 2,030 Total

Destination: Tokyo, Japan

1 trips

1 persons

4 days

3 nights

	Unit	Unit Cost	Total
Airfare	each trip	\$ 1,150	\$ 1,150
Lodging	each night	\$ 175	\$ 525
Per diem	each day	\$ 95	\$ 380
Rental car	each day	\$ -	-
Local travel	miles per trip	80	23 (@ \$0.29/mile)
Parking	per day	\$ 12	\$ 48
Misc. & tolls	per trip	\$ 25	\$ 25
			\$ 2,151 Total

Destination: Annual Review Meeting

1 trips

1 persons

4 days

3 nights

	Unit	Unit Cost	Total
Airfare	each trip	\$ 400	\$ 400
Lodging	each night	\$ 125	\$ 375
Per diem	each day	\$ 21	\$ 84
Rental car	each day	\$ 45	\$ 180
Local travel	miles per trip	80	\$ 23 (@ \$0.29/mile)
Parking	per day	\$ 12	\$ 48
Misc. & tolls	per trip	\$ 25	\$ 25

\$ 1,135 Total

Total Travel: \$ 5,317

FLORIDA SOLAR ENERGY CENTER

Proposal Rates for Direct Labor

(Actual 10/01/99 labor rates with salary escalation)

Period of Performance Start Date 10/01/2000
Period of Performance End Date 09/30/2001
Number of Months = 12

		Staff	OPS
	Hourly	Hourly Rate +	Hourly Rate +
	Rate	Benefits (24.55%)	Benefits (8.15%)
Project Manager	\$46.00	\$57.29	N/A
Principal Research Engr/Scientist	\$33.08	\$41.20	\$35.78
Senior Research Engr/Scientist	\$27.38	\$34.10	\$29.61
Research Engr/Scientist	\$20.74	\$25.83	\$22.43
Associate Research Engr/Scientist	\$17.30	\$21.55	\$18.71
Program Assistant	\$13.14	\$16.37	\$14.21
Computer Programming/Support	\$25.65	\$31.95	\$27.74
Technical Support/Technician	\$13.43	\$16.73	\$14.52
Secretarial/Clerical	\$11.26	\$14.02	\$12.18
General Support	\$10.07	\$12.54	\$10.89
Undergraduate Student Assistant	\$7.48		\$7.50
Graduate Student Assistant (PhD)	\$18.54		\$18.60

Unless otherwise noted in the proposal/contract, actual salary and fringe benefit costs will be charged. The above proposal rates are based on the averages of actual salaries of employees in the labor categories listed.

Actual fringe benefit costs will vary, but are estimated at 24.55% for salaried employees (calculated above), 8.15% for OPS (Other Personal Services) temporary employees, and 0.30% for student assistants.

Annual salary increases are included in the above rates, using 3% for professional employees and 3% for support staff. These escalation rates are applied for professional and for support staff each October 1 during the expected project period of performance.

The Florida Solar Energy Center's Indirect Cost Rate is 41.5% of mod. total direct costs for the period 07/01/98 through 06/30/00. Modified Total Direct Costs are defined as all direct costs excluding equipment over \$1,000 per item (OCO), tuition, and that portion of each subcontract in excess of \$25,000. This rate may be provisionally applied beyond that period until the rate agreement with the Federal Government is amended.

QUALIFICATIONS

Key Personnel

The principal investigator will be Dr. Clovis A. Linkous, Senior Research Scientist at the Solar Energy Center. He will be responsible for technical aspects of the project, assisting with experiment planning and interpretation of results. He will also be responsible for fulfilling the various technical reporting requirements associated with the project, including the Phase II presentation at the DOE annual technical review. He will maintain the relationship with participants in the International Energy Agency. Finally, he will be in charge of designing and directing the construction of the demonstration photocatalytic modules.

Dr. Darlene K. Slattery, Research Chemist at FSEC, will be responsible for synthesizing new photocatalysts and characterizing them. The characterization will involve setting up experimental apparatus, conducting experiments (voltammetry, photoconductivity, and photolysis testing), and interpreting results, and will also assist with the reporting requirements.

Eric D. Martin is currently a Research Engineer at FSEC where he performs research in the areas of detoxification, hydrogen, and the building environment. He will be responsible for performing the system calculations necessary to predict ultimate efficiencies. His previous hydrogen research includes design, optimization, and simulation of stand-alone renewable hydrogen energy systems, and CO₂-free production of hydrogen from fossil fuels

Résumés of the 3 investigators are attached.

Facilities description

The Florida Solar Energy Center (FSEC) functions as the energy research institute of the State University System of Florida. Created in 1974 as a non-profit, Type I Institute, FSEC is administered by the University of Central Florida.

FSEC employs a staff of 150 individuals. Of that number, approximately 90 are professionals with expertise in engineering and energy research, architectural research, energy analysis, policy analysis, and education and training. The remainder of the staff comprises technical and clerical support personnel, and university student assistants.

Under state and contract funding, FSEC conducts research and provides technical services in the following program areas, among others:

- Hydrogen energy from renewable resources
- Photovoltaic systems and applications
- Energy and building systems
- Advanced air conditioning systems
- Active solar thermal systems.

Nearly all the instrumentation needed for performing the various analyses described in the statement of work are available in-house. Possibly, some visits to the Chemistry Department at the University of Central Florida and some elemental analysis by Galbraith Laboratories or other commercial service would be necessary. We have also had good interactions with the Microchemical Analysis Division of the nearby Kennedy Space Center and the Surface Analysis Group at the University of Arizona.

The H₂ Laboratory is outfitted the following relevant equipment:

- For voltammetric and impedance analysis, we have a Princeton Applied Research 5210 Two-Phase lock-in amplifier, coupled with a PAR 273 voltammetric analyzer and several high current/low voltage power supplies.
- For surface analysis, we have an Amray 1810 scanning electron microscope and a Stereomaster specimen microscope.
- For safe use of various organic solvents and air sensitive measurements, we have two 4' and one 6' fume hoods, and 2 Labconco controlled-atmosphere glove boxes.
- For product identification and other analyses, we have a Perkin-Elmer Spectrum 2000 Fourier Transform Infrared Spectrophotometer with a Harrick Scientific DRA-2-PE9 diffuse reflectance and HVC-DR2 reaction chamber attachments.
- For gas analysis we have a SRI gas chromatograph equipped with a 30' Haye-Sep DB column, and with thermal conductivity and flame photometric detectors.
- For trace gas analysis, we have a Varian Saturn II gas chromatograph/mass spectrometer with septum equipped temperature programmable capillary injector and single split/splitless capillary ultra clean injector;

Finally, ready access to the University Library enables FSEC personnel to keep track of the latest developments in the physical and engineering sciences.

CLOVIS ALAN LINKOUS
Florida Solar Energy Center
1679 Clearlake Road
Cocoa, Florida 32922-5703
(407) 638-1000 ext. 1447

<calink@fsec.ucf.edu>

EDUCATION:

Ph.D. degree: Michigan State University, 1983; Chemistry
Department; Prof. Neal R. Armstrong, advisor; thesis title: "Light-Activated
Electrochemical Reactions on Chloro-Gallium Phthalocyanine-Modified
Electrode Surfaces."

B.S. degree: Purdue University, 1976; Chemistry and Physics major.

EMPLOYMENT HISTORY:

1990 - Present	Senior Research Scientist, Florida Solar Energy Center
1987 - 1989	Scientist, Brookhaven National Laboratory
1984 - 1987	Associate Scientist, Brookhaven National Laboratory
1982 - 1984	Assistant Scientist, Brookhaven National Laboratory
1978 - 1982	Research Associate, Department of Chemistry, University of Arizona.

Research interests:

- Kinetics and mechanisms of semiconductor particulate chemistry
- The organic solid state
- Fabrication and characterization of solid polymer electrolytes
- Batteries, fuel cells, electrolysis
- Hydrogen energy systems
- Electrochemistry and properties of superoxide ion

Awards:

1996	Outstanding Chemist Award, American Chemical Society, Orlando Section.
1994	Centers and Institutes Researcher of the Year, University of Central Florida.

Professional Affiliations

International Association for Hydrogen Energy
American Chemical Society
Electrochemical Society

Biographical Information

Born: April 27, 1954, Fort Wayne, Indiana
Married, 3 sons
Interest and activities: distance running, Chinese language
and culture, music, camping and hiking

Selected publications

1. C.A. Linkous, D.K. Slattery, and N.F. Gruhn, "Organic Pigments as Photocatalytic Agents in a Solar Water-Splitting Scheme" Proceedings of the 13th World Hydrogen Energy Conference, Beijing, China.
2. D.K. Slattery, C.A. Linkous, and N.F. Gruhn, "Photocatalytic Water-Splitting Using Organic Pigments as Semiconductors," *Polymer Preprints*, American Chemical Society National Meeting, San Francisco, CA, March 28th, 2000.
3. C.A. Linkous, G.J. Carter, "Closed Cycle Photocatalytic Process for Decomposition of Hydrogen Sulfide to its Constituent Elements," *Division of Fuel Chemistry Preprints*, American Chemical Society National Meeting, San Francisco, CA, March 27th, 2000.
4. C.A. Linkous, "Hydrogen Energy: The Good, the Bad, and the Environmentally Acceptable," Symposium on Fuels for the Year 2000 and Beyond, Division of Fuel Chemistry Preprints, 216th National Meeting, American Chemical Society, Boston, MA, August 23-27, 1998.
5. C.A. Linkous and D.K. Slattery, "Solar Hydrogen via a Photosynthetic Z-Scheme Analogue Based on Semiconductor Powders," Symposium on Fuels for the Year 2000 and Beyond, Division of Fuel Chemistry Preprints, 216th National Meeting, American Chemical Society, Boston, MA, August 23-27, 1998.
6. C.A. Linkous, "Photocatalytic Recycling of H₂ in Hydrodesulfurization," Symposium on Recent Advances in Heteroatom Removal, Division of Petroleum Chemistry Preprints, 215th National Meeting, American Chemical Society, Dallas, TX, March 29-April 3, 1998, p 101.

Resume

Darlene Kay Slattery
Florida Solar Energy Center
1679 Clearlake Road
Cocoa, FL 32922

Education

Undergraduate University of Central Florida
Orlando, Florida
Chemistry Major, B.S. 1986

Graduate University of Central Florida
Orlando, Florida
Industrial Chemistry Major, M.S. 1989

Thesis: "Alkaline hydrolysis of 1,3-Dibromo-1,1-difluoroalkanes: a Two-Step Vinyl Carboxylation Scheme."

Florida Institute of Technology
Melbourne, Florida
Chemistry Major, Ph.D. 1999

Dissertation: "Photocatalytic Decomposition of Water Using Organic Pigments"

Experience

Graduate Teaching and Research, University of Central Florida, Department of Chemistry, Fall 1986 through Spring 1989

Research Chemist, Florida Solar Energy Center, June 1989 to Present

Adjunct Professor, Florida Institute of Technology, June through August 1993

Research

Organic Chemistry: Synthesis and characterization of difluoroalkanes

Hydrogen Storage Compounds: Synthesis and characterization of compounds for storage of hydrogen for automotive use

Photocatalytic Decomposition of Water: Study of organic and inorganic semiconductors for use in water splitting schemes

Awards and Memberships

Celebrate Excellence Student Research Award 1989

Member American Chemical Society (ACS)
1992 - 93 Chair of the Orlando Section ACS
1994 - 96 Treasurer of the Orlando Section ACS

Selected Publications

- Zidan, R.; D.K. Slattery; J. Burns *Int. J. Hydrogen Energy*, **1991**, 16(12), 821.
- Linkous, C., and D. Slattery. 1992. "Development of Solid Electrolytes for Water Electrolysis at Intermediate Temperatures" In Proceedings of the 1992 DOE/NREL Hydrogen Program Review, 31-43. Honolulu, Hawaii.
- Slattery, D. 1992. "The Characteristics of Chemically Prepared Magnesium Hydrides" In Proceedings of the 9th World Hydrogen Energy Conference, 871. Paris, France.
- Slattery, D.; R. Zidan and M. Hampton. 1993. "Hydrogen Storage by Chemical Synthesis Techniques." In Proceeding of the 1993 DOE/NREL Hydrogen Program Review. Cocoa Beach, FL.
- Slattery, D.K., "Hydrogen from Renewables Research", Final Report FSEC Report #CR-669-93 Prepared for U.S. DOE, September 1993.
- Slattery, D. 1994. "Chemically Synthesized Hydrogen Storage Compounds." In Proceedings of the 1994 DOE/NREL Hydrogen Program Review. Livermore, CA.
- Slattery, D.K. "Hydrogen From Renewables Research." Final Report FSEC #CR- 767-94. Prepared for DOE, December 1994.
- Slattery, D.K. "The Hydriding - Dehydriding Characteristics of $\text{La}_2\text{Mg}_{17}$." *International Journal of Hydrogen Energy*, **1995** 20, 971.
- Linkous, C.A.; D.K. Slattery; A.J.A. Ouellette; G.T. McKaige, and B.C.N. Austin, 1996. "Solar Photocatalytic H_2 From Water Using a Dual Bed Photosystem" In Proceedings of the 11th World Hydrogen Energy Conference, 2545. Stuttgart, Germany.
- Slattery, D.K.; C.A Linkous, 1996. "Photocatalytic H_2 Evolution over Semiconductor Particles Deposited on Conductive Substrates" In Proceedings of the 11th World Hydrogen Energy Conference, 2551. Stuttgart, Germany.
- C.A. Linkous and D.K. Slattery, "Development of New Materials and Approaches to Photocatalytic Systems", Proceedings of the 1998 U.S. DOE Hydrogen Program Review, April 28-30, 1998, Alexandria, VA.
- C.A. Linkous and D.K. Slattery, "Solar Hydrogen via a Photosynthetic Z -Scheme Analogue Based on Semiconductor Powders," Symposium on Fuels for the Year 2000 and Beyond, Division of Fuel Chemistry Preprints, 216th National Meeting, American Chemical Society, Boston, MA, August 23-27, 1998.
- C.A Linkous,.; D.K. Slattery,. "Development of New Materials and Approaches to H_2 Evolving Photocatalytic Systems" In Proceedings of the 12th World Hydrogen Energy Conference, 1987. Buenos Aires, Argentina, June 1998.
- Slattery, Darlene K.; Linkous, Clovis A.; Gruhn, Nadine E., *Photocatalytic Water-Splitting Using Organic Pigments as Semiconductors, Polymer Preprints* **2000**, 41(1).
- Slattery, Darlene K.; Linkous, Clovis A.; Gruhn, Nadine E.; Baum, J. Clayton, "Semi-Empirical MO and Voltammetric Estimation of Ionization Potentials of Organic Pigments. Comparison to Gas-Phase Ultraviolet Photoelectron Spectroscopy." *Dyes and Pigments*. Submitted.

Eric D. Martin

Florida Solar Energy Center
1679 Clearlake Rd.

Cocoa, FL 32922

(321) 638-1450 martin@fsec.ucf.edu

Education:

1994 - Bachelor of Science, Chemical Engineering
Florida Institute of Technology, Melbourne, FL

Senior Project: Design of an industrial scale plant for production
of hydrogen
by the UT-3 Process: Thermochemical
Decomposition of Water.

1996 - Master of Science, Environmental Engineering
Florida Institute of Technology, Melbourne, FL

Thesis: A Flow Reactor Model for Photocatalysis of Acetone
Contaminated Airstreams

Experience:

1995-April 1997

April 1997-present

February

Research Engineer
Assistant

Graduate Student

Florida Solar Energy Center, Cocoa, FL
Solar Energy Center

Florida

Design, fabrication, and testing of pilot and industrial scale photocatalytic reactors for detoxification of airborne nitrate esters and VOCs. Conducted ASPEN Plus simulations of these as well as Chemical Heat Pump systems. Responsible for management of laboratory supplies and analytical instruments.

Design, optimization, and simulation of an integrated renewable hydrogen energy system for remote applications using TRNSYS transient simulation software. Develop a process for CO₂-free production of hydrogen from fossil fuels.

Utilize simulation software to identify cost effective energy efficient retrofits for existing buildings; energy savings used to offset the cost of disaster mitigation retrofits. Brief local government agencies on sustainable community redevelopment issues. Develop training modules on water/wastewater conservation and reuse. Develop residential standards for a statewide green building program.

1993-1994

Volunteer Research

Dr. J. Clayton Baum, Chemistry Department, Florida Institute of Technology

Calculated dipole moments for various π -bonded monocyclic compounds to determine polarity using Ampac and Spartan molecular modeling software.

Computer Skills: ASPEN Plus ChemCAD III Strawberry Tree (data acquisition)

Sigma Plot FORTRAN FEDS
AutoCAD TRNSYS EnGauge

Analytical Skills: Varian GC Dionex HPLC, IC Chemiluminescence NOx Analyzer

Varian GCMS Perkin Elmer FTIR

Affiliations: 1993-present American Institute of Chemical Engineers - Associate Member

1998-present Surfrider Foundation – Active Member

2000-present Florida Green Building Coalition, Inc. – Organizing Committee Member

Patents:

Co-Inventor of five pending patents in the United States and Canada in the area of environmental remediation.

Publications:

T-Raissi, A., E.D. Martin, N.Z. Muradov, C.R. Painter, S.N. Stiles, and M.R. Kemme. *Mass Transfer Considerations in the Design of Vapor-Phase Photocatalytic Reactors*. Journal of Advanced Oxidation Technologies. 3, No. 2: pp. 188-198, 1998.

Muradov, N.Z., A. T-Raissi, E.D. Martin, C.R. Painter, M.L. Lateulere, and M.R. Kemme. *DR-FTIR Characterization of the TiO₂/Support for the Gas-Phase Photocatalytic Destruction of NG*. Journal of Advanced Oxidation Technologies. 4, No. 2, 1999.

Martin, E. and N. Muradov. *Modeling of Sustainable Hydrogen Production/Storage Energy Systems for Remote Applications*. ACS 218th National Meeting. Division of Fuel Chemistry, Symposium on Hydrogen Production, Storage, and Utilization. New Orleans, LA, Aug. 22-26, 1999.

Martin, E. and N. Muradov. *Modeling of Integrated Renewable Hydrogen Energy Systems for Remote Applications*. Advances in Hydrogen Energy, Padro, C. and F. Lau eds.; Kluwer Academic/Plenum Publishers; New York, NY; 2000.

Appendix A. Structures of Photocatalytic Organic Pigments Studied in Phase 1

Quinacridone Red	Red	6.67	380
Isoviolanthrone	Bluish green	7.26	250
Indanthrone	Blue	6.24	>200

Indigo

Blue

7.42

240

Perylene tetracarboxylic dianhydride

Red

8.45

350

bis(chlorophenyl) DPP

Violet

7.02

300

Pyranthrone

Orange

7.62

230

Indanthrene Yellow GCN	Yellow	8.56
Indanthrene Black BBN	Black	7.93
Dimethoxy Violanthrone (Vat Green	Green	6.93
Indanthrene Gold Orange	Orange	7.96
		<300	

Appendix B. Future embodiments of dual bed photocatalytic system

Configuration Microview

Macroview

Dual Bed

Tandem Membrane

Perforated Tandem Membrane

Perforated Photo-conductive Tandem Membrane