

SOLAR PHOTOCATALYTIC H₂ PRODUCTION FROM WATER USING A DUAL BED PHOTOSYSTEM

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Abstract

Organic pigments, surface-modified with catalytic metals, are being employed in various dual modular configurations so as to effect the solar-driven decomposition of water to its constituent elements, particularly hydrogen. Utilizing a UV-filtered Xe lamp, various perylene diimides and indanthrones have been observed to preferentially oxidize water to evolve O₂ in alkaline IO₃⁻/I⁻ solution, while phthalocyanine and quinacridones reduced water to evolve H₂. Voltammetric study of Ir, Pt, and Ni co-catalyst materials provided a means of comparing their ability to use the iodine species as electron donors and acceptors. Iodate reduction on Ir appeared to be much faster than iodide oxidation, possibly explaining why Ir is a better co-catalyst for O₂ evolution under these conditions. Interdigitated Ni wire arrays were used as electrochemical equivalents of the dual bed cell in a simulation scheme. It was demonstrated that H₂ and O₂ could proceed at the 10's of mA/cm² level using a redox mediator, in this case ferro/ferricyanide, as the electron donor/acceptor. It was also shown that the rate of gas evolution was strongly tied to the Ox/Red ratio in the working fluid, suggesting that it may be necessary to connect the two modules through an electrolytic concentration cell to sustain vigorous gas evolution.

Introduction

Semiconducting compounds in particulate form are being employed in various dual modular configurations so as to effect the solar-driven decomposition of water to its constituent elements, particularly hydrogen. The goal is to develop a module with low manufacturing cost, safe evolution of H₂ and O₂ in separate compartments, and efficient use of the solar spectrum.

The objective of the current 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 H₂ at \$13/mBtu if the solar-to-H₂ energy conversion efficiency of the system is 8% (Block 1998). Having determined a number of molecular structures that make active photocatalysts (Slattery 2000, 2001), our intent is to design, synthesize, and test a number of compounds that would appear to have optimum characteristics.

A schematic of the dual bed concept is shown below in Figure 1. Two pairs of photocatalytic reactions occur. In one container, water is reduced to H₂; the electron equivalents for the reaction come from a redox mediator, M. In the second container, water is oxidized to evolve O₂; 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.

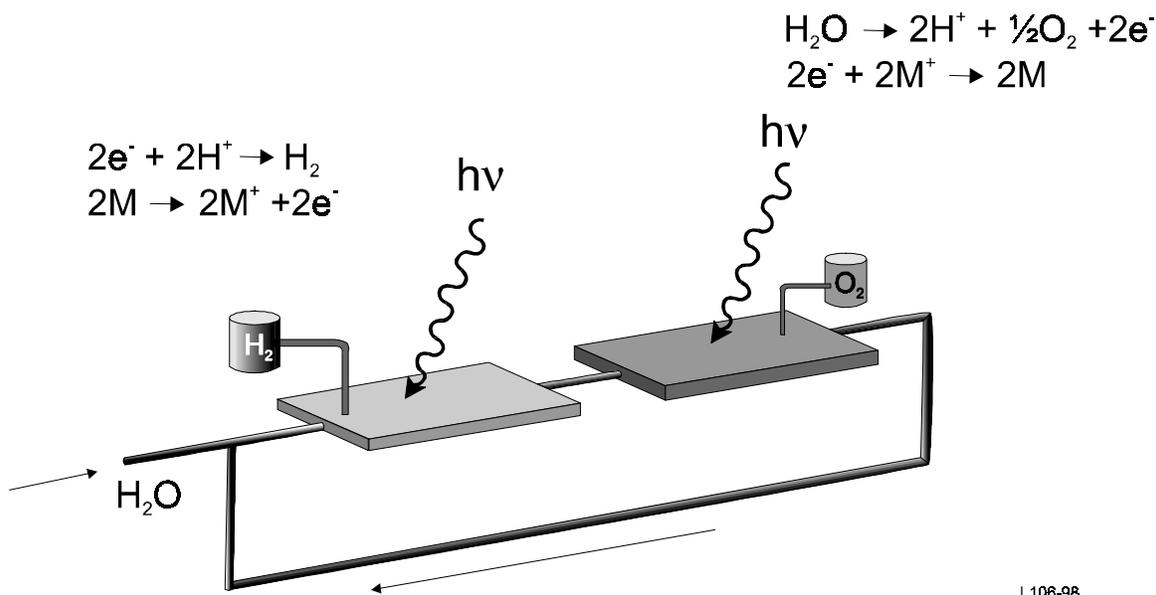


Figure 1. Schematic of a dual bed photocatalytic water-splitting system.

Results and Discussion

Our objective is to perform R&D tasks that will enable engineering and economic analysis of the technology. With that end in mind, our research efforts have gone along two basic directions: 1) photocatalyst development; and 2) systems development.

Photocatalyst Development

Our first task was to revisit many of the photocatalyst/electrolyte systems that we had investigated in the previous contract period, except that now we employed a 400 nm (UV cut-off) filter. This eliminated interfering gas evolution reactions from alkaline iodate solution (UV photochemical disproportionation) and polymer substrate light absorption. The gas evolution levels went down (in 6 h trials, we obtained 32 μl O_2 for the ditridecyl perylene diimide system and 19 μl for indanthrone; 8 μl H_2 for quinacridone and 7 μl for copper phthalocyanine), but nevertheless we still achieved our Phase 1 objective, namely, observation of H_2 and O_2 evolution from respective photocatalysts with the same redox electrolyte (1:1 I^-/IO_3^-). Production efficiencies for the two gases are now at similar levels. In retrospect, as will be discussed in the modeling section of the report, the use of 1:1 Ox/Red likely constituted a substantial limitation on performance.

While a lengthy evaluation process in the search for effective photocatalysts has already been traversed, we nevertheless maintained a modest effort in the synthesis and evaluation of new organic pigment candidates for H_2 and O_2 evolution. For H_2 evolution, we examined representatives of merocyanine family. The band edges looked promising and it has achieved the best performance in solid state organic PV cells (Sayama 2000). However, when we examined it in our aqueous alkaline photocatalytic system, it was found to be photochemically unstable—not just in water, but even in dry air. Thus the transition from solid state to solution can often lead to new decomposition mechanisms.

In the area of O_2 evolution, the companion reaction to H_2 derived from water, we synthesized perfluoroalkyl chain derivatized perylene diimides. We had tested short chain alkyl derivative before with no real improvement over the base compound. However, recent reports have suggested that perfluoroalkyl side chains can afford up to an order of magnitude improvement in photoconductivity. This was an intriguing idea, as it would be thought that long chain substituents would tend to decrease crystalline order, and in so doing shorten charge carrier diffusion length and ultimately quantum efficiency.

As indicated above, we chose to make the perfluoroditridecyl derivative. This is done by heating a solution of the perfluorooctyl iodide in the presence of the base diimide. While work-up and characterization continues, thus far an increase in photocatalytic performance over the base perylene diimide has not been observed.

Co-catalyst Voltammetry

The ability of catalytic substances to work in synergy with the light-absorbing material to accelerate the reaction of interest is well known. One mechanism by which this occurs would be enhanced

rates of charge transfer with the redox mediator, or in our case, I/IO_3^- . We sought to investigate this idea via cyclic voltammetry using the co-catalyst as bulk electrode material. The electrolyte is alkaline iodate/iodide solution, just as in the dual bed system. As shown in Figure 2, the iodine couple does not exhibit reversible behavior, i.e., the voltammetric waves for oxidations and reductions do not occur within a narrow (a few 100 millivolts) range of each other. The iodine species are apparently adsorbed to the electrode surface throughout the electrochemical cycle.

The noble metal co-catalysts nevertheless continue to demonstrate their important role in facilitating the water-splitting process. Ir only exhibited two waves in the cathodic region (2a): one is IO_3^- reduction, while the other is due to O_2 that was generated during the anodic voltage excursion. There was no voltammetric activity that could be ascribed to iodide oxidation. Therefore, one might conclude that the reason Ir is a better co-catalyst than Pt for photocatalytic O_2 evolution is that it is resistance toward the back reaction, i.e., I^- oxidation.

The pair of waves in the Pt voltammogram (2b) correspond to I^- oxidation and IO_3^- reduction. With only I^- or only IO_3^- initially present, essentially the same voltammogram was obtained, although the proportional size of the two peaks was altered somewhat. In the absence of iodine species, the voltammogram was featureless out to the solvent limits. The hysteresis or current crossover effect seen in the negative potential regime, plus the steepness of the current decay for the oxidative wave once again indicates that iodine species are strongly adsorbed to the electrode surface throughout the applied potential range. The peak potentials are nearly 1.0 V apart, demonstrating rather poor reversibility for the iodine couple.

The Ni wire voltammogram (2c) showed most of its activity in the anodic region. In the absence of iodine species, a nearly reversible oxide formation and reduction wave was observed in the +250 mV potential region (SCE ref). Adding IO_3^- had little effect; however, I^- substantially interfered with the oxide formation reaction and subsequent O_2 evolution. Iodine species had little effect in the negative voltage region. The intent is that Ni may be a cheap co-catalyst substitute for Pt in the H_2 -evolving module.

The activity series for O_2 evolution continues to be $Ir > Pt > Ni$, as was derived for M/TiO_2 systems. While iodine adsorption bodes poorly in terms of electrolyte recirculation, it may have catalytic effect for O_2 evolution. Ultimately, it was found that the ferro/ferricyanide couple, $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$, exhibited considerable more reversibility on the co-catalyst materials tested, and so was used in the systems development work described below.

Systems Development

While identification of effective photocatalysts and co-catalysts is an ongoing task, it is also intended that we deduce the optimized configuration of the various components. In the current contract period, we wanted to simulate a dual bed system under mass transport limitation conditions, i.e., a system where the rate of reaction on the photoparticle surface is so great that the redox mediator is depleted as it passes through each module. This question has an impact on what the ultimate solar energy conversion efficiency of the apparatus will be.

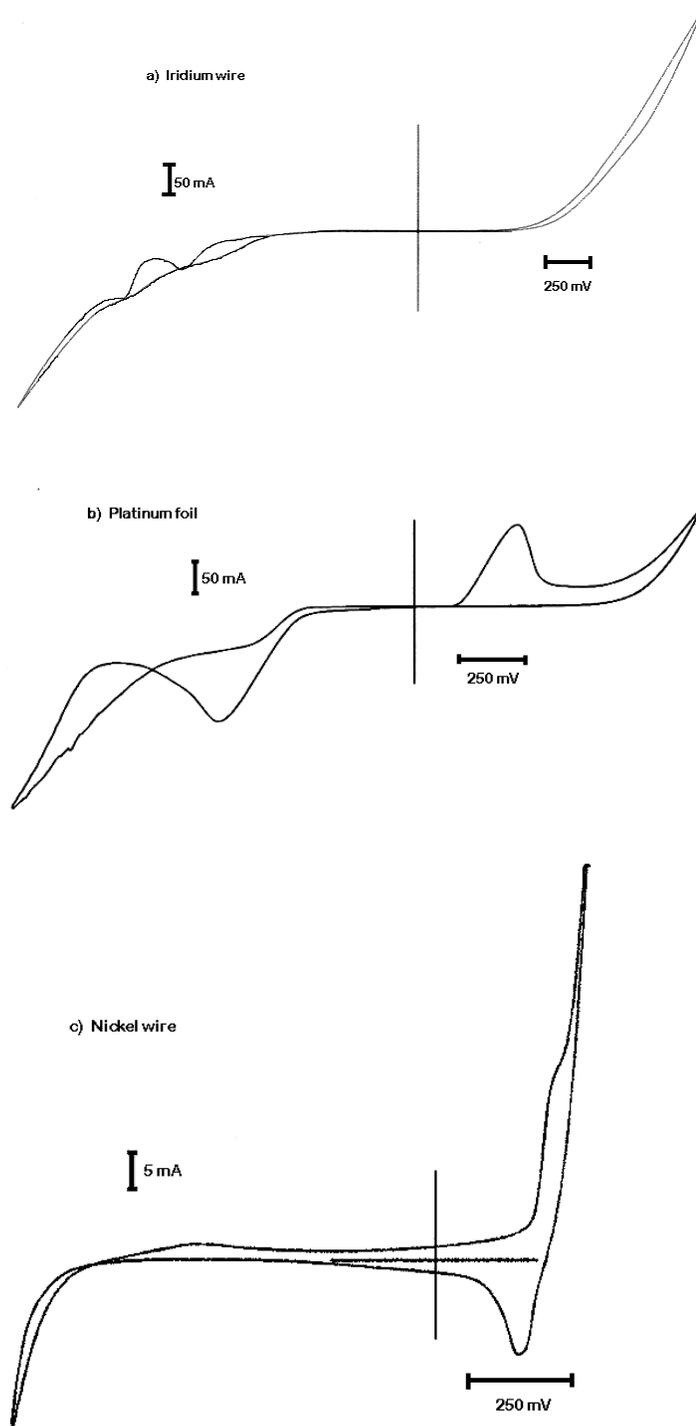


Figure 2. Cyclic voltammograms of co-catalyst materials in iodide/iodate alkaline electrolyte. 1.0 M NaOH, $[KIO_3] = [KI] = 0.1$ M, 50 mV/s, Ar purged solution, SCE reference.

Consequently, we constructed an electrochemical equivalent of a dual bed cell. The idea was to have microelectrode arrays in close proximity to each other that would perform their respective electrode reactions: either O_2 evolution and mediator reduction, or H_2 evolution and mediator oxidation. This was done by stringing Ni wire back and forth across a piece of “perf board” between the holes in such a way that alternate parallel wires belonged to an electrically isolated system. The result was an “interdigitated” array of Ni metal wire that would function as an electrochemical equivalent of a dual bed cell.

A photograph of the electrochemical set-up is shown in Figure 3. A pair of Ni wire arrays were placed into respective modules and sealed. A dual channel power supply was utilized to independently vary the applied voltage (or simulated photopotential) to each cell. A pump circulated an alkaline solution of ferro/ferricyanide ion. The headspace above the working fluid in each compartment was connected to a gas volume measurement apparatus (inverted graduated cylinders). Adding this feature created some difficulty in maintaining a constant solution volume inside each module, however.



Figure 3. Electrochemical equivalent of dual bed cell using interdigitated arrays.

Using an analytical concentration of 0.1 M Fe complex ($[Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-} = 0.1$), we found that we could sustain the respective gas evolution reaction at the 5-10 mA/cm^2 level. Observing the electrode arrays under an optical microscope, one could observe gas evolution off of alternate wires as shown in Figure 4. If we attempted to further increase the current density of the system, the power supply, operating in the current limiting mode, would raise the voltage into the 1.5 V+ range, whereupon we would observe gas evolution from all the wires in the array, i.e., regular water electrolysis.

If the initial mediator concentration was either all Ox or all Red, mediator-driven gas evolution was easily observed. If, however, we operated the cells under nearly equal concentrations of Ox

and Red, the effect was quite difficult to achieve. This means that as gas evolution proceeds across the module in the direction of fluid flow, Ox is being converted to Red, or vice versa. The product of the mediator conversion reaction builds up, until the back reaction rate nulls out the forward one. Consequently, it may be necessary to include a redox flow cell between the modules with a voltage assist that will condition the mediator concentration for its respective module. With a mediator as reversible as ferro/ferricyanide, an external voltage of only a couple tenths of a volt may be all that is necessary to sustain the net photochemical water-splitting reaction.

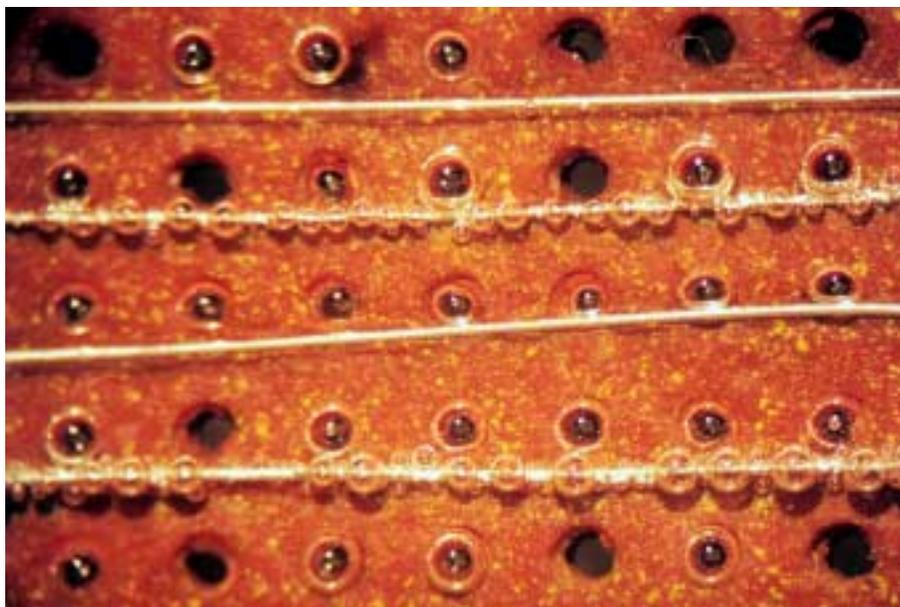


Figure 4. Microscope image of H₂ evolution from cathode array.

Future Work

In terms of photocatalyst development, it is important to understand mechanisms of excitonic charge carrier production. The organic pigments are doing a good job in terms of absorbing large amounts of solar photons, but their conversion into charge carriers that can perform oxidations or reductions needs work. In the area of systems studies, we intend on building and demonstrating a mediator regeneration cell in conjunction with photochemical modules. We will also develop mathematical models that will lay out mediator concentration gradients and gas evolution rates, which can be related to conversion efficiency. As efficiencies improve, we will construct and demonstrate larger photocatalytic modules. We are currently at the 6" square size; we see no limitations in building up to the 48" square size. Whether it makes sense to ever build a module larger than that (at least for the shorter dimension) is open to debate, since that would take it into the custom building materials realm where nonstandard sizes substantially increase module cost.

References

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