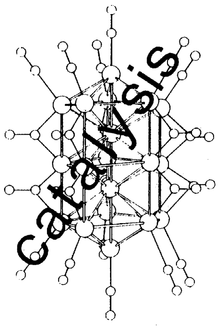
Catalysis in Solar Energy

Photoelectrochemical cells approach the efficiency of photovoltaics, but durability and cost are still major hurdles



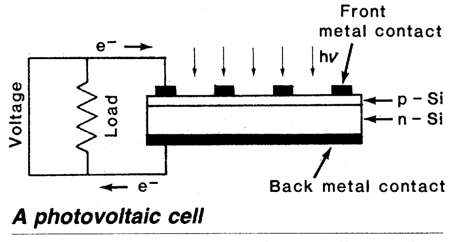
The vision is impressive: Energy From the Sun. The concept is both intellectually and emotionally appealing. Sunlight shines on everyone, rich or poor, industrial or agricultural, developed or developing. Large sections of the earth's surface are too parched for any other use but receive almost constant sunlight. It is necessary to collect only a fraction of the incident energy and convert it to electricity or synthetic fuels. The world would no longer be dependent on undependable supplies of petroleum, would not have to suffer the scars produced by strip-mining coal or oil shale, would not have to hazard the risks of nuclear fission. Major sources of pollution would be eliminated.

The vision is, indeed, impressive, but the reality is somewhat more pessimistic. Sunlight may be free, but technology is expensive and electrical energy from a power grid is still relatively cheap. In the United States, electrical energy from the national grid costs anywhere from 4 to 13 cents per kilowatt-hour. At noon on a clear day, says E. L. "Pete" Johnson of Texas Instruments, Inc., the sun's rays that reach the surface of the earth have an energy density of about 100 watts per square foot. If 10 percent of it—the minimum fraction most investigators believe will be necessary for economic viability—were collected and converted to electricity at today's prices, it would have a value of only 0.2 to 0.8 cent per day. The hard reality is that there is no commercial solar energy system today that can match that price. "There are no miracles in solar conversion," says Adam Heller of Bell Laboratories.

That is not to say that solar energy does not already have some uses beyond the space program. Passive solar energy systems are being installed in a small, but growing, number of new homes and offices, wind and ocean thermal energy systems (both of which ultimately derive their energy from the sun) are being actively explored, biomass is beginning to be converted into synthetic fuels in some land-rich countries such as Brazil, and salt gradient solar ponds (*Science*, 11 June 1982, p. 1213) are eliciting interest. But perhaps the greatest intellectual ferment involves the direct production of electricity and synthetic fuels from sunlight by means of photovoltaic devices. Within this category, one of the more active areas of research involves the catalytic production of fuels or electricity in a semiconductor-electrolyte or photoelectrochemical cell.*

The prospects for solar electricity and fuels production are still a matter of rather sharp debate. Many scientists, such as John O'M. Bockris of Texas A&M University, argue that solar energy will be "the single most important new energy source of the next 50 years." Some, such as T. Nejat Veziroglu of the University of Miami, even argue that hydrogen could replace electricity as a major carrier of energy. Many scientists are less sanguine, arguing that solar energy will have a more modest impact and that most applications will be small and localized.

About 55 percent of the world's population, notes Heller, is not connected to a power grid. When electricity is required, it is typically produced by small, diesel-powered generators at a cost from two to ten times as great as electricity from a grid. In many of these cases, particularly in remote areas, solar electricity is already competitive in cost and, Heller adds, "there is a clear trend of dropping costs and growing capacity of photovoltaics." In fact, production capacity throughout the world is growing at a rate of about 50 percent per year, and the industry is expected to gross more than $1 billion per year by 1990. In many places, electrical storage is not necessary. "A simple water-pumping solar generator could have wide use," he says; "we should set our sights at very, very modest goals."



A photovoltaic cell

In a p-n *silicon photovoltaic cell, incident light causes electrons to migrate to the back metal contact and holes to the front. They recombine after the electrons pass through the external circuit to produce electrical power.*

To understand the current high cost of solar energy, it is necessary to understand how it works. Unless solar energy is to serve merely as a heat source, its capture and use requires semiconductors. Semiconductors are insulators, such as silicon or germanium, that can be made conductive by doping with an impurity. In crystalline solids, the charge carriers, electrons (e^-) and holes (h^+), are accommodated in bands. Valence bands are formed by a merging of the bonding orbitals of molecules and are completely filled. Conduction bands are formed by a merging of antibonding orbitals and, at sufficiently low temperatures, are vacant. The energy difference between the valence band of highest energy and the conduction band of lowest energy is known as the band gap. This is the energy required to promote the most weakly bound electron into the conduction band.

One way to dope a semiconductor is to substitute atoms of another element into its lattice. Silicon, for example, has four valence electrons while phosphorus has five. When a phosphorus atom is substituted into the silicon lattice, the extra valence electron will not be accommodated in the valence band and will become an itinerant electron in the conduction band. This produces an *n*-type semiconductor, so-named because conduction is by negatively charged electrons. Aluminum, in contrast, has only three valence electrons, and therefore its substitution in the silicon lattice creates electron vacancies or holes in the valence band. This is termed *p*-type doping because the current is formally considered to be carried by positively charged holes.

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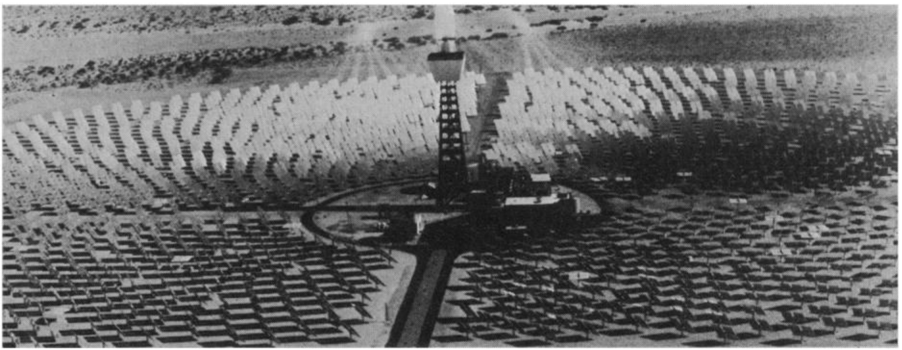
*Previous articles in this series appeared in the issues of 4 February, p. 474; 25 February, p. 944; 25 March, p. 1413; 6 May, p. 592; 3 June, p. 1032; 17 June, p. 1261; and 22 July, p. 351.

When light illuminates a semiconductor, incident photons of sufficient energy can boost electrons from the valence band to the conduction band; electrochemists call this separating an electron from a hole. The optimum band gap for utilizing solar energy is about 1.4 electron volts (eV). An ideal system with a band gap of 1.4 eV can have a maximum efficiency for conversion of sunlight to electricity of about 30 percent; if two absorbers are used, the maximum possible efficiency is 37 percent.

To perform useful work, however, a semiconductor alone is insufficient. Left to their own devices, electrons and holes recombine rapidly, releasing either heat or light. The ultimate goal of all solar electric research is to find a way to keep them separated long enough for them to carry out useful work before they recombine.

The classical silicon solar cell, invented in 1941 by Russell F. Ohl of Bell Laboratories and perfected in 1954 by D. M. Chapin, C. S. Fuller, and G. L. Pearson, also of Bell, accomplishes this by means of a *p-n* junction. A single silicon crystal is uniformly doped to form an *n*-type semiconductor; a thin layer on the surface is then counterdoped and made *p*-type. The *p-n* junction (or the *n-p* junction if the crystal is doped in the opposite manner) naturally creates a small electrical field or dipole moment that separates the electrons and holes. Electrons then flow through an external circuit from the *n* to the *p* region, performing work in the process. The best of these photovoltaic devices can convert sunlight into electricity with efficiencies as high as 20 percent.

Single crystals of silicon (or gallium arsenide or other semiconductors) are fairly expensive, however, which is one of the reasons why photovoltaic power is expensive. Devices made with less expensive polycrystalline semiconductors are less efficient—about 10 percent at best. They are also less stable because the dopant travels much faster through grain boundaries (the points where small crystallites come into contact) than through the body of the crystal, so that a nonuniform junction is formed or the device becomes electrically shorted during the doping process. Research at many laboratories is now directed toward circumventing these problems by continuous growth of nearly single-crystalline ribbons of silicon, by forming *p-n* junctions through light-flash or rapid thermal annealing in times too short to allow diffusion in grain boundaries, or by using amorphous silicon. While these show great promise, none is yet entirely satisfactory or sufficiently inexpensive.



Southern California Edison

Solar One

The world's largest solar thermal electric power plant is undergoing tests in the Mojave desert near Daggett, California.

Many investigators are thus studying an alternative approach known as the semiconductor-electrolyte junction. The physics of these junctions was worked out in 1955 by Walter H. Brattain and Charles G. B. Garrett of Bell Laboratories, and in 1964 Richard Williams of RCA Corporation made the first cells resembling current ones. In 1972, Kenichi Honda and Akira Fujishima of the University of Tokyo made the first photoanode for electrolysis of water, and in 1975 Heinz Gerischer of the Fritz Haber Institute in West Germany began a series of what have been described as "key experiments" in this field. All of the first cells were either very inefficient or very unstable, but they did suggest that semiconductor-electrolyte junction devices could be made. Since then, investigators have succeeded in making cells with efficiencies of more than 13 percent,† but there are still problems to be worked out, particularly those of cost and durability. Says Allen J. Bard of the University of Texas: "We've only just learned the rules of the game."

The operation of a semiconductor-electrolyte junction is not unlike that of the *p-n* junction photovoltaic cell. When an *n*- or *p*-type semiconductor is immersed in an electrolyte, a small electric field is created at the interface because of the difference in the tendencies of the two phases to gain or lose electrons—that is, the difference in the electrochemical potential of the two phases. This electrical field will help separate the electrons and holes produced by sunlight.

If the semiconductor is *n*-type, electrons move toward the bulk of the semiconductor and holes move toward the surface; because holes can oxidize the electrolyte, this is a photoanode. If the semiconductor is *p*-type, holes move toward the bulk and electrons toward the surface; because the electrons can reduce the electrolyte, this is a photocathode. Thus, light promotes photoreductions at *p*-type materials and photooxidations at *n*-type materials.

The primary difference between a photovoltaic cell and a photoelectrochemical cell is that current flow is completely electronic in the former and is partially ionic in the latter. That is, electrical contact between the electrodes in a photoelectrochemical cell must be carried out chemically. This can be done by what is known as a redox couple, a combination of the oxidized and reduced forms of an ion, such as S^{2-}/S_n^{2-}, I^-/I_3^-, or, more generally, D/D^+. An oxidation ($D + h^+ \rightarrow D^+$) occurs at one electrode, while the corresponding reduction ($D^+ + e^- \rightarrow D$) occurs at the counterelectrode. In this case, there is no net chemical change in the cell, but current is driven through the external circuit, effecting conversion of sunlight to electricity.

Alternatively, in the absence of a reversible redox couple, the solvent or a solute can be oxidized or reduced simultaneously to generate a fuel that can be stored. In acids, protons can be reduced at a photocathode to produce hydrogen; water or halide ions can be oxidized at a photoanode to produce oxygen or halogens. When an external potential is required to supplement the energy of the incident photons, the process is termed "photoassisted electrolysis." The choice between use of a reversible redox couple to generate electricity or oxidizable and reducible substrates to produce fuels depends primarily on whether energy is

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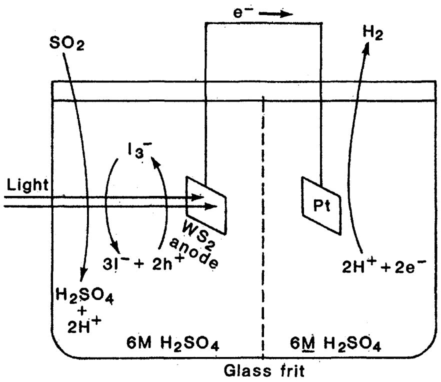
†There are several different ways to compute efficiencies. The computation is straightforward when electricity is produced: the efficiency is simply the electrical power produced divided by the energy of the incident sunlight, times 100. When fuels are produced, the situation is more complicated. The best way is to divide the Gibbs free energy of the fuels by the energy of the incident sunlight; this is the way that is normally used in this article. An alternative is to use the value of the energy that would be produced by recombination of the fuels in an ideal fuel cell, divided by incident energy; this generally gives a lower value. Efficiencies reported with monochromatic light are generally much higher than efficiencies that can be obtained with sunlight.

needed immediately or is to be stored for future use. Whether one form is inherently superior to the other, says Mark S. Wrighton of the Massachusetts Institute of Technology, "is a question that has not yet been answered."

Much of the work on semiconductor-electrolyte junctions has been devoted to photoanodes, primarily because the first stable semiconductors that were available for this purpose were *n*-type materials such as titanium dioxide. Unfortunately, titanium dioxide has a band gap of about 3.0 eV, and thus responds only to ultraviolet light. Some investigators have tried to overcome this problem by using sensitizers, dye molecules that capture incident sunlight to produce an excited state that injects a charge carrier into the conduction band of the semiconductor. Michael Grätzel of the Swiss Federal Polytechnic Institute, for example, has used acridine dyes and Jean-Marie Lehn of the Louis Pasteur University in France has used a $[Ru(2,2'\text{-bipyridine})_3]^{3+}$ complex. The best results with this approach have been obtained by Hiroshita Tsubomura of Osaka University, who used *n*-type zinc oxide sensitized with the dye rose bengal, but the efficiency was still less than 1 percent.

Greater efficiencies can obviously be obtained with semiconductors having smaller band gaps, but this introduces a new, more serious problem. As the band gap decreases, the photoanodes become more susceptible to photocorrosion. This occurs because the holes that arrive at the surface are strong oxidants; if they cannot react with the redox couple fast enough, they will oxidize the anode itself. A silicon anode will be oxidized to silicon dioxide, for instance, and cadmium sulfide will be oxidized to Cd^{2+} and elemental sulfur. Both silicon dioxide and sulfur are insulators that block transport of charge carriers; their presence on the anode destroys the cell's efficiency. A naked silicon photoanode loses more than 90 percent of its efficiency in less than 5 minutes.

There are several ways to minimize this problem, although no one has eliminated it completely. One of the first solutions, adopted independently by Barry Miller and Heller, by Wrighton, and by Gary Hodes and his colleagues at the Weizmann Institute in Israel, was to use moderate to high concentrations of S^{2-}/S_n^{2-} in the electrolyte to stabilize cadmium sulfide and cadmium selenide electrodes. The sulfide created a minor problem with the cadmium selenide anode because ion exchange produced a surface layer of $CdSe_xS_{1-x}$ that acts as a barrier to transport of holes to the surface. Miller and Heller found that addition of small quantities of elemental selenium to the electrolyte repressed this ion exchange and "led to the first efficient (that is, 7 percent) cell that operated for months without change in its electrical characteristics."



Photoelectrochemical fuels

In a photoelectrochemical cell designed for fuel production, an oxidation of one substrate occurs at the photoanode and the reduction of a second substrate occurs at the counterelectrode. In this case, the redox couple (I^-/I_3^-) mediates the oxidation of sulfur dioxide to sulfuric acid while platinum catalyzes the reduction of protons to hydrogen.

A few materials have inherent resistance to photocorrosion. The most important of these are metal dichalcogenides such as MoS_2, WS_2, $MoSe_2$, and WSe_2, which have been extensively studied by Gerischer and by Helmut Tributsch of the Hahn-Meitner Institute in West Germany. These semiconductors have layered geometrical structures like that of graphite. The metal-chalcogenide bonds are very strong and tend to lie in planes, while the sulfur-sulfur or selenium-selenium bonds are much weaker and merely hold the cleavage planes together. Bruce A. Parkinson of the Solar Energy Research Institute was the first to show that high efficiencies and stabilities could be obtained if only the cleavage planes are exposed to the electrolyte; he found that halides could be oxidized at layered photoanodes at efficiencies better than 10 percent. If the edges of the planes are exposed or if the surface is scratched, however, the efficiencies fall below 1 percent and the cells are much less durable.

The layered metal dichalcogenide semiconductors "seem to be closest to ideal" of the photoanodes studied so far, says Wrighton, and their interactions with chalcogenide or halide ions "are very likely the sorts of situations that will lead to the first applications of semiconductor photoelectrochemical devices for photochemical synthesis of redox products." One good example of the many possibilities is the oxidation of sulfur dioxide mediated by a tungsten disulfide photoanode:

$$SO_2 + H_2O \xrightarrow{h\nu} H_2SO_4 + H_2$$

The oxidation of sulfur dioxide in 50 percent sulfuric acid has very poor kinetics, says Wrighton, and it does not compete with decomposition of the electrode; in the presence of the redox couple I^-/I_3^-, however, the reaction proceeds smoothly and becomes "one of the most efficient optical-to-chemical-energy conversions (up to about 14 percent from 632.8-nanometer light) known."

Another approach is to reduce the concentration or the activity of water in the electrolyte. Metal dichalcogenides are not inherently durable in aqueous 0.1*M* KCl, an electrolyte that might be used for the oxidation of chloride ion to chlorine. Wrighton has found, however, that the oxidation proceeds efficiently and the anode is durable in aqueous 15*M* LiCl; the high activity of the chloride ion at this concentration allows it to compete effectively for the photogenerated holes, while the lowered activity of water reduces corrosion significantly.

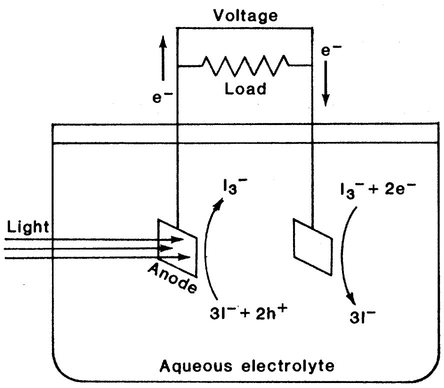
This approach can be carried to an extreme by using cells with a nonaqueous electrolyte, but cells produced in this fashion have generally not been successful. A major problem is the internal resistance of the cells; the low conductivity of the electrolyte means that voltage must be sacrificed to get current or vice versa. Other problems include rapid recombination of electrons and holes and limitations on photovoltage produced by a process known as "pinning." The voltage that can be produced at a photoelectrode is controlled by the difference in potential between the semiconductor and the redox couple in the electrolyte. But for most of the materials that have been used for photocathodes, such as gallium phosphide or gallium arsenide, the surface of the semiconductor is so rich in trapped charge carriers that the junction is formed between the semiconductor and its surface rather than between the semiconductor and the electrolyte. The cell thus produces the voltage characteristic of that junction no matter what the redox couple is; the voltage is said to be pinned at this characteristic level. Since this voltage is usually less than the voltage that could be obtained with the redox couple, cells that are pinned have low efficiencies. Several photoanodes, including *n*-gallium arsenide, also suffer from this problem when in contact with nonaqueous electrolytes.

Recently, however, Chris M. Gronet and Nathan S. Lewis of Stanford University reported that they had made photoanodes that would lead to 13 percent efficiency if the problem of the high internal resistance were solved. Their cell had an acetonitrile electrolyte and a ferrocene/ferricenium redox couple. They used heavily doped (n^+) gallium arsenide or gallium phosphide photoanodes covered with a relatively thick layer of gallium arsenophosphides, the best of which had the composition $GaAs_{0.72}P_{0.28}$. Gallium arsenide or gallium phosphide photoanodes under the same conditions give conversion efficiencies of less than 3 percent. Gronet and Lewis speculate that substitution of phosphorus for arsenic in the gallium arsenide lattice "eliminates most of the sources of inefficiency in the acetonitrile solvent." Their work, Heller says, "destroys the myth that gallium arsenide electrodes have to be pinned in nonaqueous solvents."

The ability to reduce photocorrosion with high concentrations of redox reagents, says Wrighton, "led to the conclusion that redox reagents covalently anchored to the photoelectrode might prove useful." Wrighton found, for example, that ferrocene could be linked to silicon, polymerized, and attached to the electrode surface to protect against photocorrosion. In essence, the surface agent captures holes and retains them until some species in the electrolyte can be oxidized. It also makes the surface more hydrophobic.

More recently, Wrighton, Bard, Arthur J. Nozik of the Solar Energy Research Institute, and others have been working with films of polypyrrole, often over a thin layer of gold or platinum. Unlike the ferrocene polymer, polypyrrole is an electrical conductor. This is important, Wrighton says, because "the rate of ion transport of redox polymers may be too slow" to achieve useful currents. Bard and Tsubomura have also used films of phthalocyanine, and Bard has used polybenzyl viologen.

The problem with organic films, Bard says, is that they are subject to chemical degradation that is not necessarily connected to the anodic process. To overcome this problem, he has begun using thin layers of platinum silicide or iridium silicide, either pure or modified with ruthenium dioxide. He has found that these electrodes can photogenerate iodine, bromine, chlorine, and even oxygen with high stabilities and with efficiencies greater than 5 percent. He attributes the excellent stability to a rapid transport of holes from the silicon substrate through silicides.



Photoelectrochemical power

In a photoelectrochemical cell designed for production of electricity, a redox couple provides the electrical link between the photoanode and the counterelectrode.

A related approach has been adopted by Jay A. Switzer of the Union Oil Company of California. He coated an n-silicon photoanode with a thin layer of thallic oxide that both protects the surface from corrosion and catalyzes the oxidation of a ferrocyanide/ferricyanide redox couple. He reported at the recent meeting of the American Chemical Society that the cell has an efficiency of electricity production of 14.3 percent when illuminated with a xenon arc. The photocurrent decayed less than 10 percent after 5 days of illumination, suggesting that the electrode is fairly stable.

One of the main reasons for working with semiconductor-electrolyte junctions was the difficulty of constructing photovoltaic cells with polycrystalline semiconductors. Most of the research on photoelectrochemical cells, however, has also involved single-crystal electrodes, for much the same reasons. The grain boundaries and surface defects tend to trap holes and allow electron-hole recombinations before useful work can be accomplished. This recombination results from the weaker, stressed, or broken bonds present at defects and boundaries. These weak bonds have the effect of introducing new states between the valence and conduction bands in which recombination of electrons and holes occurs more readily. The boundaries may also cause pinning and reduce photovoltages.

Most investigators had assumed that impurities on the surface of the photoelectrode would only aggravate this problem, and they thus stressed the importance of keeping the surface clean. Heller reasoned that strongly adsorbed impurities can be used to strengthen the surface bonds; this redistributes surface states and results in reduced recombination. He found that strongly chemisorbed ions such as Ru^{3+} and Pb^{2+} could improve the performance of single-crystal gallium arsenide photoanodes. More important, the ions quadrupled the efficiency of polycrystalline anodes so that they retained as much as 70 percent of the efficiency of single-crystal electrodes. Similar results with polycrystalline cadmium chalcogenide anodes were attained by Hodes and with amorphous silicon anodes by Wrighton.

Photocathodes are not susceptible to corrosion by oxidation because of the flux of electrons to their surface under illumination. Corrosion by reduction of the electrode, moreover, occurs much more slowly than oxidative corrosion. Heller and his colleagues have been able to achieve 11.5 percent efficiency for conversion of sunlight to electricity with a p-indium phosphide photocathode. They used a V^{3+}/V^{2+} redox couple in hydrochloric acid. If a group VIII metal such as platinum or rhodium is included in the electrode surface as a catalyst, the redox couple is not required and the photocathode evolves hydrogen. With a rhodium catalyst, Heller's group produced hydrogen with an efficiency of 13.3 percent. Heller argues that hydrogen saturates the catalyst, increasing the photovoltage of the cell. Bockris has obtained similar results with nonnoble metal catalysts and he argues that the increased efficiency results from a change in the rate-determining step of the reduction.

In some photocathodes, pinning has also been a problem. Heller says a thin (6 to 10 angstroms) layer of indium oxide on the surface of the gallium phosphide prevents pinning, as well as suppressing recombination of electrons and holes and protecting the surface from contaminants in the electrolyte. Others argue, however, that this layer simply pins the cathode at a higher photovoltage.

For both photoanodes and photocathodes, says Wrighton, "the efficiencies are now sufficiently high that you can't rule out photoconversion as a long-term prospect. That doesn't mean that it will be a good prospect, but it's good enough that you wouldn't want to stop research on it." But it is a long way from an isolated electrode to an integrated system, and some of the problems involved will be discussed in a subsequent article.—**THOMAS H. MAUGH II**

Additional Reading

1. M. S. Wrighton, in *Inorganic Chemistry: Toward the 21st Century*, M. H. Chisholm, Ed. (American Chemical Society, Washington, D.C., 1983), p. 59.
2. A. J. Bard, *J. Phys. Chem.* **86**, 172 (1982).
3. M. Gratzel, *Acc. Chem. Res.* **14**, 376 (1981).
4. H. B. Gray and A. W. Maverick, *Science* **214**, 1201 (1981).
5. A. Heller, *Acc. Chem. Res.* **14**, 154 (1981).