in which individuals recognize each other and share a high degree of genetic relatedness despite the maintenance of otherwise discrete social units."

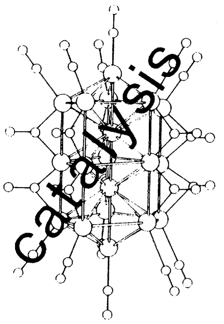
Social dynamics within and between groups are exceedingly complex, involving subtly shifting alliances and dominance hierarchies around kinship lines. The intellectual exigencies of coping with so complex a puzzle might explain why many nonhuman primates are able to play the demanding classification games that behavioral scientists love to challenge them with, suggest Cheney and Seyfarth. "It may well be that this ability derives from the selection pressure acting upon individuals to make complex hierarchical classifications of what is perhaps the most important feature of their environment—each other."—**Roger Lewin**

Additional Readings

1. *Am. Zool.* **22**, 519 (1982).
2. *Am. Nat.* **122**, 392 (1983).

Fuels from Solar Energy: How Soon?

Texas Instruments has the jump on a commercial photoelectrochemical system, but other systems under study could eventually be cheaper



"Now that good photoanodes and good photocathodes have been developed,"* says Mark S. Wrighton of the Massachusetts Institute of Technology, "the big problem is this: Are there in existence systems that would be durable and efficient and that can also be constructed on a large scale, in terms of area, and on a cost-competitive basis?" For now, the answer to that question is still no, he adds, but "people are making steps in that direction." In most cases, they are doing this with a unified system that contains both a photoanode and a photocathode. They are also attempting to carry out the photoconversions with materials that are much less expensive than those that have been used for research.

The impetus for this approach lies in the simple fact that most applications of photoelectrochemical cells will require voltages of at least 2 electron volts (eV). The optimum band gap for a semiconductor powered by sunlight, in contrast, is 1.3 eV. Says Wrighton: "Why not use two photoelectrodes whose combined potentials are great enough to carry out the desired reaction?" This is exactly what plants do; they have two photosystems of slightly different energies to develop sufficient potentials to split water. The process is inefficient, however, since plants use only about 1 percent of incident light. This low efficiency can be tolerated because the system is self-replicating.

There is some debate, however, about whether a solar cell should be used to split water. Investigators such as John O'M. Bockris of Texas A&M University argue that oxygen is an important chemical to produce because its cost determines the cost of many environmental controls. He also argues that a new generation of aircraft could use liquid hydrogen and oxygen as fuels.

In contrast, Adam Heller of Bell Laboratories argues that "Oxygen is cheap and abundant, and making it together with hydrogen wastes effort and money." A much better course, he argues, is to split a halogen acid. The half-reaction that converts halide ions into halogens at a photoanode requires less voltage than the oxidation of water to oxygen; it is also easier to accomplish because it is a one-electron process, whereas oxidation of water requires two electrons. Furthermore, the recombination of hydrogen and oxygen in a fuel cell to produce electricity is inefficient because of inherent problems at the oxygen electrode, whereas recombination of hydrogen and a halogen proceeds efficiently.

> "Why not use two electrodes whose combined potentials are great enough to carry out the desired reaction?"

The most straightforward way to employ two electrodes is to put individual photoanodes and photocathodes into each cell. This is how the Texas Instruments Solar Energy System (TISES) is constructed. TISES, conceived by Jack S. Kilby, who is now a consultant to TI, has more or less conventional photoelectrodes that have been reconfigured so that manufacture can be almost completely automated. "There are parallels for our semiconductor technology in research labs," says project leader E. L. "Pete" Johnson, but the way TI puts the cells together is "pretty damn unique." The company has been working on TISES since 1976 and, with the U.S. Department of Energy, has invested more than $20 million in its development. It is the only reported commercial program.

The system uses spherical silicon particles that average 10 to 16 mils (0.25 to 0.4 millimeters) in diameter. During most of the studies, the spheres were formed by dripping molten silicon from a capillary tube, allowing the silicon to cool while dropping through an inert gas atmosphere; this is the same process that is used to make lead shot in a shot tower. The process was not fast enough for full production, however, and TI now drops molten silicon onto a rapidly rotating disk which throws off small droplets that, again, cool in free fall.

These spheres are polycrystalline but are converted into mostly single crystals by annealing. In this process, the spheres are heated just to their melting point, then allowed to cool slowly. Surface tension draws the beads into spheres and the slow cooling allows single crystals to form. The spheres are then doped with boron to form n-type semiconductors or with phosphorus to form p-type. The surfaces of the spheres are then heavily doped with the opposite element to form n^+-p anodes and p^+-n cathodes. Each type of electrode is then embedded in a thin sheet of glass that acts as a support.

One side of the glass and the semiconductor junction is etched away and replaced with a reflective coating and insulator; it is then coated with a thin layer of metal that acts as an electrical contact.

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*For a discussion of photoanodes and photocathodes, see *Science*, 30 September, p. 1358. Other articles in this series have 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.

The sheet is then flipped over and the glass etched away on the front to expose the silicon surface. The whole surface is plated with a noble metal and then partially etched so that the metal remains only on the silicon. The noble metal acts as a catalyst at both the anode and the cathode.

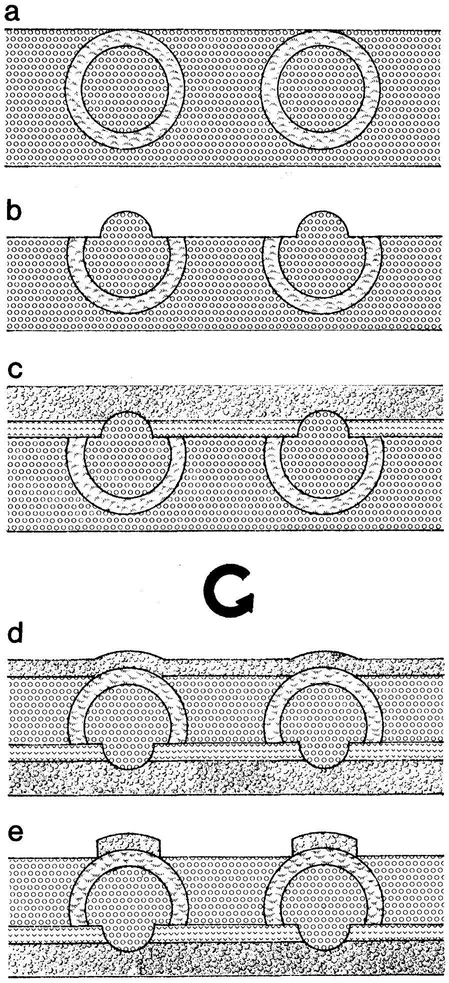
The whole system is designed for automated processing, says Johnson, and a key feature is that it is not important if a few of the individual electrodes are defective. Adjoining sheets of anodic and cathodic photoelectrodes can then be exposed to an electrolyte containing 48 percent (9*M*) hydrogen bromide. When illuminated, the cells produce hydrogen at the cathode and bromine at the anode (the sheets are separated by thin membranes that prevent reaction products from mixing). Cells with conversion efficiencies as high as 13 percent have been produced.

The photoelectrodes are part of a closed system in which hydrogen and bromine are stored, then recombined in a specially developed fuel cell to produce electricity as needed. The hydrogen is stored as a hydride in a calcium-nickel alloy; heat to remove the hydrogen from the hydride is provided by sun-warmed fluids. Importantly, Johnson says, the system also uses low-grade thermal energy for hot water and space heating. The overall efficiency (electrical and thermal) of the system is now about 7 percent, he adds, but TI hopes to have it up to 8 to 10 percent before the system is commercialized, possibly as soon as 1990. "The technical barriers are behind us," he notes, and the main problems now are scaling up and establishing reliability.

Johnson and his colleagues have modeled the performance of TISES in locales ranging from Boston to Dallas. They find that 30 to 40 4- by 8-foot panels could supply about 90 percent of a typical home's electricity needs. Over the projected 20- to 30-year life of the panels, Johnson says, the cost should be competitive with electricity purchased from a utility.

A related type of system, but one that is nowhere near commercialization, is being studied by Bockris and Oliver J. Murphy of Texas A&M. They use conventional *n-p* and *p-n* gallium arsenide photoelectrodes, but they coat the back of the anode with ruthenium oxide and the back of the cathode with platinum. The backs of both electrodes are then exposed to a sulfuric acid electrolyte while the front is illuminated; in this way, the anode is not exposed to the corrosive effects of the electrolyte. This system splits water with an efficiency of about 8 percent and without the need for an external power source. The best efficiency without an external power source previously had been about 2 percent, says Bockris. In essence, what both TI and the Texas A&M investigators have done is to combine a conventional photovoltaic cell and an electrolyzer into one unit. The efficiency of their unit is about the same as that of the separate components, but the cost should be lower and it would be easier to mount the flat apparatus on, say, the roof of a house. Gallium arsenide is too expensive for a commercial cell, however, and Murphy and Bockris are now working on a similar configuration using amorphous silicon. Amorphous silicon should be considerably cheaper, but so far the best efficiency they have achieved is 3 percent.

[Bockris, it should be noted, created a stir last year (*Science*, 5 November 1982, p. 557) when he reported at a press conference that he had found a way to stabilize silicon electrodes so that insulating silicon dioxide does not interfere with the photoreaction. The process, which was not disclosed at the time, involved doping the oxide layer with noble metals to make it conductive. He has subsequently found that a cell produced by coupling such an anode with a *p*-silicon cathode still requires assistance from a battery, and he has largely abandoned that project in favor of the newer approach.]



Automated processing

Manufacture of solar cells for the TISES system begins with silicon spheres embedded in a glass matrix (a). The glass and the outer coating of silicon are etched away (b) and a glass reflective coating and a metal back are applied (c). The array is flipped over and the opposite side etched to expose the silicon, after which the entire surface is metalized (d). The metal is then selectively etched away to leave metal only on the surface of the spheres (e).

Many investigators argue that an economically viable solar energy system will require still cheaper construction techniques and less expensive semiconductor materials. One way to achieve the first requirement, and possibly the second, is to use small particles that contain both a photocathode and a photoanode short-circuited together; these are known as diodes.

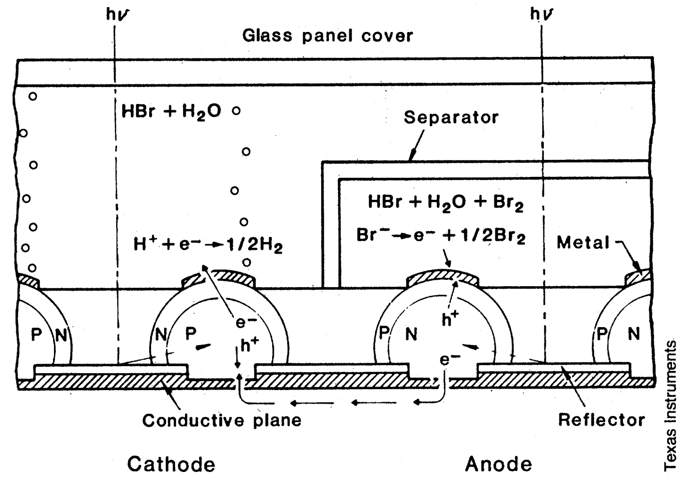
The first photoelectrochemical diodes were developed in 1977 by Arthur J. Nozik, who was then at Allied Chemical Corporation but is now at the Solar Energy Research Institute, and independently by Bockris and Ohashi Maccan. Nozik produced small particles that were half *p*-gallium phosphide and half *n*-titanium dioxide. When these particles were suspended in an electrolyte and illuminated, they evolved both hydrogen and oxygen. The efficiency was very low, however, because titanium dioxide has a band gap of about 3 eV and thus can use only a small fraction of incident sunlight. Bockris and Maccan used *p*-strontium titanate and *n*-cadmium telluride, and their system had much the same problems as Nozik's.

An operating particulate system does not have to be that complex, however. Allen J. Bard of the University of Texas has found that bare titanium dioxide particles, when illuminated, can catalyze the oxidation of cyanide:

$$CN^- + \tfrac{1}{2}O_2 \rightarrow OCN^-$$

This is an energetically favorable (downhill) reaction whose rate is simply accelerated by the photoassisted catalyst.

Kenichi Honda of the University of Tokyo has found that powders of titanium dioxide, cadmium sulfide, or gallium phosphide can, when illuminated, catalyze the conversion of carbon dioxide to methanol. This is an energetically unfavorable (uphill) reaction that does not occur without the added energy from light. John M. White of the University of Texas has found that, under certain conditions, titanium dioxide powders can even catalyze the electrolysis of water, also an uphill reaction. All of these processes have very low efficiencies. White argues that the mechanism by which the powders work is probably different from that of semiconductor-electrolyte junction cells. The particles, he argues, are too small to form the electric fields characteristic of the junctions. Instead, he thinks that the primary method of trapping holes involves formation of hydroxyl radicals on the surface, while electrons are trapped by formation of Ti(III).



The TISES array

A schematic diagram of fuels production by the solar cell in the TISES system.

Texas Instruments

Bard has found that titanium dioxide particles with some platinum on the surface (so that, in effect, the photoanode is shorted to the platinum counterelectrode) can catalyze the (downhill) oxidation of aqueous acetic acid:

$$CH_3COOH \rightarrow CH_4 + C_2H_6 + CO_2$$

He has also found that these microdiodes can catalyze the (downhill) production of amino acids (including glycine, alanine, serine, aspartic acid, and glutamic acid) from methane, ammonia, and water. Wrighton and others have found that platinized strontium titanate can electrolyze water (uphill). All of these reactions also have low efficiencies.

Perhaps the greatest amount of work has been carried out by Michael Grätzel and his colleagues at the Swiss Federal Polytechnic Institute. His group has worked with two different systems. The simplest of these uses colloidal cadmium sulfide loaded with ultrafine ruthenium dioxide at a concentration of 0.1 to 0.5 percent. When these particles are dispersed in aqueous hydrogen sulfide and illuminated with visible light, says Grätzel, "hydrogen is generated at an astonishingly high rate." Free sulfur is also formed.

The key to this system, Grätzel says, is that ruthenium oxide promotes the oxidation of sulfide by free holes so that it occurs fast enough to compete with photocorrosion. This makes the photoanode durable. Other investigators, however, have not yet been able to achieve the stability reported by Grätzel. If the system could be perfected, he argues, it would be potentially useful for producing fuels from the hydrogen sulfide extracted from many fossil fuels.

Grätzel has developed a more complicated system for electrolysis of water. In this case, colloidal particles of titanium dioxide carry both ruthenium dioxide and platinum on the surface. A ruthenium complex, $[Ru(4\text{-methyl-}4'\text{-decyl-}2,2'\text{-pyridine})(2,2'\text{-bipyridine})_2]^{2+}$, is used as a sensitizer and *N*-methyl-*N'*-tetradecylviologen as an electron relay. Upon illumination, the sensitizer is excited and reduces the electron relay while it is itself oxidized. The electron relay injects an electron into the conduction band of platinum, where it is used to evolve hydrogen. The sensitizer gives up a hole to ruthenium dioxide, where it is used to evolve oxygen.

With this system, Grätzel has observed efficiencies of about 1 percent—low, but promising. The colloidal titanium dioxide also plays another vital role, he adds. Oxygen generated at its surface is reduced to O_2^- by electrons in the conduction band; this species becomes firmly bound to the colloidal particle. This provides, Grätzel argues, the first practical way to separate the hydrogen and oxygen produced in colloidal systems. Hydrogen would be evolved during the day while the system is illuminated, and oxygen could be released at night by several methods, such as exposing the colloidal particles to sodium phosphate. This would, of course, require additional energy input.

Jean-Marie Lehn and his colleagues at the Louis Pasteur University in France have been working with strontium titanate particles loaded with rhodium. Suspended in water and illuminated, this system also evolves hydrogen and oxygen. The rhodium catalyst, Lehn says, is far superior to the ruthenium, platinum, and cobalt catalysts that have been used in similar systems. Nonetheless, the system responds only to ultraviolet light, and Lehn is working on ways to get around this problem.

A somewhat different approach has been adopted by Gabor Somorjai and his colleagues at the University of California, Berkeley. They reported last year (*Science*, 5 November 1982, p. 557) that they had used inexpensive iron oxide to fabricate photoelectrodes. The powder was pressed into small disks and doped with silicon dioxide to make anodes or magnesium dioxide to make cathodes. Anodes and cathodes were cemented back to back with a conducting epoxy to form diodes. Suspended in sodium hydroxide or sodium sulfate and illuminated, the diodes evolved hydrogen and oxygen, although with an efficiency of only 0.05 percent. Somorjai's group also reported that the diodes had to be regenerated every 8 hours by bubbling air through the electrolyte.

The latter problem was most easily solved, says Somorjai. They found that stopcock grease was being dissolved by the electrolyte and coating the electrode; bubbling air through the system oxidized the residual carbon. This problem was eliminated by ensuring that the system did not contact the grease, and a new cell has been running for 10 weeks with no loss of efficiency. The efficiency has also been improved, primarily by increasing the doping levels and improving the contact between the two electrodes, and is now about 0.1 percent. An overall efficiency of 14 percent is possible, says Somorjai, and he is "pretty confident that we can reach 1 to 5 percent in the near future." Further increases in efficiency, he adds, may require using single crystals of iron oxide or colloidal particles. Furthermore, little is known about the electronic structure of iron oxide, and additional improvements may be possible once that is better understood.

Despite these successes, concludes Wrighton, there is still a lot to be done. The reduction of oxygen in a fuel cell, for example, is a related problem where a good solution would give substantial increases in efficiency. A great deal of work is also required on other multielectron processes, particularly the reduction of nitrogen to ammonia and the reduction of carbon dioxide. "If we could carry out one of these efficiently in a photocell," he says, "we would really have something."

—THOMAS H. MAUGH II