Two New Routes to Solar Hydrogen

Controversial new photocatalytic electrodes may make it possible to produce hydrogen from sunlight inexpensively

Two new systems in which sunlight provides the energy for splitting water into hydrogen and oxygen have been reported within the past month. Both systems are based on new semiconductor electrodes that appear to be both stable and inexpensive. Either system might make photochemically produced hydrogen much more cheaply than other proposed systems.

Interest in hydrogen has grown because of its potential for storage of solar energy. When sunlight is converted into electricity by photovoltaic cells, it must be used immediately or stored in batteries, which are only moderately efficient and can store the energy for only relatively short periods. Hydrogen, in contrast, can be stored virtually indefinitely, yet still be converted into electricity at high efficiency in a fuel cell. Hydrogen can also replace many liquid fuels. Automobiles, for example, can be converted to run on hydrogen with only minor modifications to the engine—plus, of course, the addition of a special tank to store the hydrogen.

"The first electrochemical cell that uses only sunlight and inexpensive chemicals" to produce hydrogen from water was reported at the recent American Chemical Society meeting* by Christofer Leygraf of the Lawrence Berkeley Laboratory. The work, performed by Leygraf, Monica Hendewerk, and Gabor Somorjai in Somorjai's laboratory, is also reported in the September *Proceedings of the National Academy of Sciences* (volume 79, page 5739). The key feature of the device is a pair of electrodes composed of iron oxide.

Previous investigators, including Somorjai, have used rare and expensive elements to produce electrodes, including platinum, strontium titanate, and gallium phosphide. Most of these require external energy in addition to sunlight, either as an applied potential between the electrodes or for heating the cell to operating temperature. These materials, in general, are sensitive primarily to ultraviolet radiation, and most are unstable in the electrochemical cell.

In place of these, the Berkeley group used iron oxide powder fabricated into small disks. For each cell, one disk was doped with silicon dioxide (an electron donor) and one with magnesium oxide (an electron acceptor). The two disks were cemented together with a conducting silver epoxy to form a diode, which was suspended in a solution of sodium sulfate or sodium hydroxide at a *p*H between 6 and 14.

When illuminated with visible light, the device produces about 10^{15} molecules of hydrogen per minute from a surface area of about 0.6 square centimeter, giving an overall energy conversion efficiency of 0.05 percent. At this rate, a similar disk with an area of about 1 square meter would produce about 4 liters of hydrogen per hour—a relatively high chemical yield despite the low efficiency, says Somorjai. After about 8 hours, hydrogen production slows as the magnesium electrode becomes reduced, but it can be restored by bubbling air through the system for about 10 minutes. The electrodes are stable indefinitely.

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Their study proves that the system will work, Somorjai says, and improving the efficiency is now "an engineering question" rather than a chemical one. In particular, improvement in the architecture of the cell, changes of the iron oxide stoichiometry and doping levels, and modification of the experimental conditions all seem likely to improve hydrogen production. Because of the low cost of the raw materials, Somorjai says, an improvement to only 1 percent efficiency "would be very intriguing" with respect to commercialization.

Much less is known about the second system, which was revealed on 7 October in a press conference called by John O'M. Bockris of Texas A & M University. Bockris frankly conceded that the announcement was timed to take advantage of the public interest generated by Somorjai's announcement, but he refused to disclose substantive detail about his system pending the filing of a patent application. The credibility of his claims thus rests solely on his scientific reputation, which is generally acknowledged to be good. Details of the system are, however, scheduled to be published in about 2 months in the *Journal of the Electrochemical Society*.

The device developed by Bockris, Marek Szklarczyk, and A. Q. Contractor is based on silicon. Silicon is, of course, the primary component of most photovoltaic cells but, when immersed in water, it rapidly becomes coated with a nonconductive film of silicon dioxide. This problem is partially overcome by doping such electrodes with phosphorus and boron to make them semiconducting anodes and cathodes, respectively, but this alone is inadequate for efficient photolysis of water. The Texas group further dopes the anode with an unspecified substance, while the cathode is coated with a catalyst, such as platinum.

When the semiconductor electrodes thus produced are suspended in dilute sulfuric acid and illuminated with visible light, the resultant electrical current splits water into hydrogen and oxygen—but only when a potential is applied across the two electrodes with an external battery. The overall efficiency of the system, Bockris says, is about 13 percent, a very high yield for a photoelectric process. The high efficiency of the cell and the relatively low cost of the electrodes, Bockris argues, should make it possible to produce hydrogen at a cost equivalent to gasoline at $1 per gallon.

Independent assessment of the two projects is difficult to obtain. Most investigators agree that Somorjai's results are real: Somorjai has been able to repeat his results reliably since March and he has an excellent track record in the study of heterogeneous catalysis. Some investigators are concerned, however, about the need to regenerate the system continually, suggesting that the process may not be catalytic. Others are skeptical that it will be possible to improve the efficiency enough to make the process economically feasible.

Bockris also has a good track record, but his system has been operating at high efficiency for only 3 weeks and no one knows what materials he is using or has seen any of his results—a situation which makes any speculation futile. His system's efficiency seems remarkably high, however, since good photovoltaic cells have an efficiency of only about 10 percent. Other investigators are thus eagerly awaiting publication of his results.—THOMAS H. MAUGH II

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