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Sun + Water = Fuel

With catalysts created by an MIT chemist, sunlight can turn water into hydrogen. If the process can scale up, it could make solar power a dominant source of energy.

By Kevin Bullis

"I'm going to show you something I haven't showed anybody yet," said Daniel Nocera, a professor of chemistry at MIT, speaking this May to an auditorium filled with scientists and U.S. government energy officials. He asked the house manager to lower the lights. Then he started a video. "Can you see that?" he asked excitedly, pointing to the bubbles rising from a strip of material immersed in water. "Oxygen is pouring off of this electrode." Then he added, somewhat cryptically, "This is the future. We've got the leaf."

What Nocera was demonstrating was a reaction that generates oxygen from water much as green plants do during photosynthesis--an achievement that could have profound implications for the energy debate. Carried out with the help of a catalyst he developed, the reaction is the first and most difficult step in splitting water to make hydrogen gas. And efficiently generating hydrogen from water, Nocera believes, will help surmount one of the main obstacles preventing solar power from becoming a dominant source of electricity: there's no cost-effective way to store the energy collected by solar panels so that it can be used at night or during cloudy days.

Solar power has a unique potential to generate vast amounts of clean energy that doesn't contribute to global warming. But without a cheap means to store this energy, solar power can't replace fossil fuels on a large scale. In Nocera's scenario, sunlight would split water to produce versatile, easy-to-store hydrogen fuel that could later be burned in an internal-combustion generator or recombined with oxygen in a fuel cell. Even more ambitious, the reaction could be used to split seawater; in that case, running the hydrogen through a fuel cell would yield fresh water as well as electricity.

Storing energy from the sun by mimicking photosynthesis is something scientists have been trying to do since the early 1970s. In particular, they have tried to replicate the way green plants break down water. Chemists, of course, can already split water. But the process has required high temperatures, harsh alkaline solutions, or rare and expensive catalysts such as platinum. What Nocera has devised is an inexpensive catalyst that produces oxygen from water at room temperature and without caustic chemicals--the same benign conditions found in plants. Several other promising catalysts, including another that Nocera developed, could be used to complete the process and produce hydrogen gas.

Nocera sees two ways to take advantage of his breakthrough. In the first, a conventional solar panel would capture sunlight to produce electricity; in turn, that electricity would power a device called an electrolyzer, which would use his catalysts to split water. The second approach would employ a system that more closely mimics the structure of a leaf. The catalysts would be deployed side by side with special dye molecules designed to absorb sunlight; the energy captured by the dyes would drive the water-splitting reaction.

Either way, solar energy would be converted into hydrogen fuel that could be easily stored and used at night--or whenever it's needed.

Nocera's audacious claims for the importance of his advance are the kind that academic chemists are usually loath to make in front of their peers. Indeed, a number of experts have questioned how well his system can be scaled up and how economical it will be. But Nocera shows no signs of backing down. "With this discovery, I totally change the dialogue," he told the audience in May. "All of the old arguments go out the window."

The Dark Side of Solar

Sunlight is the world's largest potential source of renewable energy, but that potential could easily go unrealized. Not only do solar panels not work at night, but daytime production waxes and wanes as clouds pass overhead. That's why today most solar panels--both those in solar farms built by utilities and those mounted on the roofs of houses and businesses--are connected to the electrical grid. During sunny days, when solar panels are operating at peak capacity, homeowners and companies can sell their excess power to utilities. But they generally have to rely on the grid at night, or when clouds shade the panels.

This system works only because solar power makes such a tiny contribution to overall electricity production: it meets a small fraction of 1 percent of total demand in the United States. As the contribution of solar power grows, its unreliability will become an increasingly serious problem.

If solar power grows enough to provide as little as 10 percent of total electricity, utilities will need to decide what to do when clouds move in during times of peak demand, says Ryan Wiser, a research scientist who studies electricity markets at Lawrence Berkeley National Laboratory in Berkeley, CA. Either utilities will need to operate extra natural-gas plants that can quickly ramp up to compensate for the lost power, or they'll need to invest in energy storage. The first option is currently cheaper, Wiser says: "Electrical storage is just too expensive."

But if we count on solar energy for more than about 20 percent of total electricity, he says, it will start to contribute to what's called base load power, the amount of power necessary to meet minimum demand. And base load power (which is now supplied mostly by coal-fired plants) must be provided at a relatively constant rate. Solar energy can't be harnessed for this purpose unless it can be stored on a large scale for use 24 hours a day, in good weather and bad.

In short, for solar to become a primary source of electricity, vast amounts of affordable storage will be needed. And today's options for storing electricity just aren't practical on a large enough scale, says Nathan Lewis, a professor of chemistry at Caltech. Take one of the least expensive methods: using electricity to pump water uphill and then running the water through a turbine to generate electricity later on. One kilogram of water pumped up 100 meters stores about a kilojoule of energy. In comparison, a kilogram of gasoline stores about 45,000 kilojoules. Storing enough energy this way would require massive dams and huge reservoirs that would be emptied and filled every day. And try finding enough water for that in places such as Arizona and Nevada, where sunlight is particularly abundant.

Batteries, meanwhile, are expensive: they could add $10,000 to the cost of a typical home solar system. And although they're improving, they still store far less energy than fuels such as gasoline and hydrogen store in the form of chemical bonds. The best batteries store about 300 watt-hours of energy per kilogram, Lewis says, while gasoline stores 13,000 watt-hours per kilogram. "The numbers make it obvious that chemical fuels are the only energy-dense way to obtain massive energy storage," Lewis says. Of those fuels, not only is hydrogen potentially cleaner than gasoline, but by weight it stores much more energy--about three times as much, though it takes up more space because it's a gas.

The challenge lies in using energy from the sun to make such fuels cheaply and efficiently. This is where Nocera's efforts to mimic photosynthesis come in.

Imitating Plants

In real photosynthesis, green plants use chlorophyll to capture energy from sunlight and then use that energy to drive a series of complex chemical reactions that turn water and carbon dioxide into energy-rich carbohydrates such as starch and sugar. But what primarily interests many researchers is an early step in the process, in which a combination of proteins and inorganic catalysts helps break water efficiently into oxygen and hydrogen ions.

The field of artificial photosynthesis got off to a quick start. In the early 1970s, a graduate student at the University of Tokyo, Akira Fujishima, and his thesis advisor, Kenichi Honda, showed that electrodes made from titanium dioxide--a component of white paint--would slowly split water when exposed to light from a bright, 500-watt xenon lamp. The finding established that light could be used to split water outside of plants. In 1974, Thomas Meyer, a professor of chemistry at the University of North Carolina, Chapel Hill, showed that a ruthenium-based dye, when exposed to light, underwent chemical changes that gave it the potential to oxidize water, or pull electrons from it--the key first step in water splitting.

Ultimately, neither technique proved practical. The titanium dioxide couldn't absorb enough sunlight, and the light-induced chemical state in Meyer's dye was too transient to be useful. But the advances stimulated the imaginations of scientists. "You could look ahead and see where to go and, at least in principle, put the pieces together," Meyer says.

Over the next few decades, scientists studied the structures and materials in plants that absorb sunlight and store its energy. They found that plants carefully choreograph the movement of water molecules, electrons, and hydrogen ions--that is, protons. But much about the precise mechanisms involved remained unknown. Then, in 2004, researchers at Imperial College London identified the structure of a group of proteins and metals that is crucial for freeing oxygen from water in plants. They showed that the heart of this catalytic complex was a collection of proteins, oxygen atoms, and manganese and calcium ions that interact in specific ways.

"As soon as we saw this, we could start designing systems," says Nocera, who had been trying to fully understand the chemistry behind photosynthesis since 1984. Reading this "road map," he says, his group set out to manage protons and electrons somewhat the way plants do--but using only inorganic materials, which are more robust and stable than proteins.

Initially, Nocera didn't tackle the biggest challenge, pulling oxygen out from water. Rather, "to get our training wheels," he began with the reverse reaction: combining oxygen with protons and electrons to form water. He found that certain complex compounds based on cobalt were good catalysts for this reaction. So when it came time to try splitting water, he decided to use similar cobalt compounds.

Nocera knew that working with these compounds in water could be a problem, since cobalt can dissolve. Not surprisingly, he says, "within days we realized that cobalt was falling out of this elaborate compound that we made." With his initial attempts foiled, he decided to take a different approach. Instead of using a complex compound, he tested the catalytic activity of dissolved cobalt, with some phosphate added to the water to help the reaction. "We said, let's forget all the elaborate stuff and just use cobalt directly," he says.

The experiment worked better than Nocera and his colleagues had expected. When a current was applied to an electrode immersed in the solution, cobalt and phosphate accumulated on it in a thin film, and a dense layer of bubbles started forming in just a few minutes. Further tests confirmed that the bubbles were oxygen released by splitting the water. "Here's the luck," Nocera says. "There was no reason for us to expect that just plain cobalt with phosphate, versus cobalt being tied up in one of our complexes, would work this well. I couldn't have predicted it. The stuff that was falling out of the compounds turned out to be what we needed.

"Now we want to understand it," he continues. "I want to know why the hell cobalt in this thin film is so active. I may be able to improve it or use a different metal that's better." At the same time, he wants to start working with engineers to optimize the process and make an efficient water-splitting cell, one that incorporates catalysts for generating both oxygen and hydrogen. "We were really interested in the basic science. Can we make a catalyst that works efficiently under the conditions of photosynthesis?" he says. "The answer now is yes, we can do that. Now we've really got to get to the technology of designing a cell."

Catalyzing a Debate

Nocera's discovery has garnered a lot of attention, and not all of it has been flattering. Many chemists find his claims overstated; they don't dispute his findings, but they doubt that they will have the consequences he imagines. "The claim that this is the answer for artificial photosynthesis is crazy," says Thomas Meyer, who has been a mentor to Nocera. He says that while Nocera's catalysts "could prove technologically important," the advance is "a research finding," and there's "no guarantee that it can be scaled up or even made practical."

Many critics' objections revolve around the inability of Nocera's lab setup to split water nearly as rapidly as commercial electrolyzers do. The faster the system, the smaller a commercial unit that produced a given amount of hydrogen and oxygen would be. And smaller systems, in general, are cheaper.

The way to compare different catalysts is to look at their "current density"--that is, electrical current per square centimeter--when they're at their most efficient. The higher the current, the faster the catalyst can produce oxygen. Nocera reported results of 1 milliamp per square centimeter, although he says he's achieved 10 milliamps since then. Commercial electrolyzers typically run at about 1,000 milliamps per square centimeter. "At least what he's published so far would never work for a commercial electrolyzer, where the current density is 800 times to 2,000 times greater," says John Turner, a research fellow at the National Renewable Energy Laboratory in Golden, CO.

Other experts question the whole principle of converting sunlight into electricity, then into a chemical fuel, and then back into electricity again. They suggest that while batteries store far less energy than chemical fuels, they are nevertheless far more efficient, because using electricity to make fuels and then using the fuels to generate electricity wastes energy at every step. It would be better, they say, to focus on improving battery technology or other similar forms of electrical storage, rather than on developing water splitters and fuel cells. As Ryan Wiser puts it, "Electrolysis is [currently] inefficient, so why would you do it?"

The Artificial Leaf

Michael Grätzel, however, may have a clever way to turn Nocera's discovery to practical use. A professor of chemistry and chemical engineering at the École Polytechnique Fédérale in Lausanne, Switzerland, he was one of the first people Nocera told about his new catalyst. "He was so excited," Grätzel says. "He took me to a restaurant and bought a tremendously expensive bottle of wine."

In 1991, Grätzel invented a promising new type of solar cell. It uses a dye containing ruthenium, which acts much like the chlorophyll in a plant, absorbing light and releasing electrons. In Grätzel's solar cell, however, the electrons don't set off a water-splitting reaction. Instead, they're collected by a film of titanium dioxide and directed through an external circuit, generating electricity. Grätzel now thinks that he can integrate his solar cell and Nocera's catalyst into a single device that captures the energy from sunlight and uses it to split water.

If he's right, it would be a significant step toward making a device that, in many ways, truly resembles a leaf. The idea is that Grätzel's dye would take the place of the electrode on which the catalyst forms in Nocera's system. The dye itself, when exposed to light, can generate the voltage needed to assemble the catalyst. "The dye acts like a molecular wire that conducts charges away," Grätzel says. The catalyst then assembles where it's needed, right on the dye. Once the catalyst is formed, the sunlight absorbed by the dye drives the reactions that split water. Grätzel says that the device could be more efficient and cheaper than using a separate solar panel and electrolyzer.

Another possibility that Nocera is investigating is whether his catalyst can be used to split seawater. In initial tests, it performs well in the presence of salt, and he is now testing it to see how it handles other compounds found in the sea. If it works, Nocera's system could address more than just the energy crisis; it could help solve the world's growing shortage of fresh water as well.

Artificial leaves and fuel-producing desalination systems might sound like grandiose promises. But to many scientists, such possibilities seem maddeningly close; chemists seeking new energy technologies have been taunted for decades by the fact that plants easily use sunlight to turn abundant materials into energy-rich molecules. "We see it going on all around us, but it's something we can't really do," says Paul Alivisatos, a professor of chemistry and materials science at the University of California, Berkeley, who is leading an effort at Lawrence Berkeley National Laboratory to imitate photosynthesis by chemical means.

But soon, using nature's own blueprint, human beings could be using the sun "to make fuels from a glass of water," as Nocera puts it. That idea has an elegance that any chemist can appreciate--and possibilities that everyone should find hopeful.

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