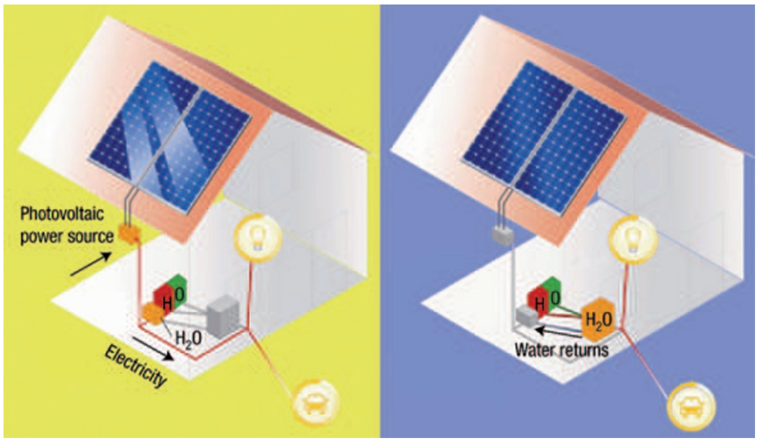
Chemistry for the climate

Chemists claim that by mimicking photosynthesis in the lab, they could revolutionize fuel production within five years. **Katharine Sanderson** reports.



PATRICK GILLOOLY, MIT

Diagram of the local power source Nocera envisions. In daytime, electricity from photovoltaic solar panels powers the home and is used to split water into hydrogen and oxygen. At night, these gases recombine in a fuel cell to produce more electricity, and the resulting water is recycled.

Dan Nocera, a chemist at the Massachusetts Institute of Technology (MIT), Cambridge, made a bold statement at the American Chemical Society's fall meeting in Philadelphia last month. He claimed that within five years he could build a device capable of producing locally sourced hydrogen gas, which could power all the world's houses, fill people's car batteries and revolutionize energy supply in the developing world. "I guarantee, in under five years, you'll see this," he said.

Nocera's innovation, reported in July this year, is a simple catalyst that can produce oxygen from water under benign conditions[1]. Nocera is one of scores of chemists worldwide racing to find ways to split water into hydrogen and oxygen using cheap materials, in a process ultimately powered by sunlight[2]. Such a system could boost solar power's contribution to the future mix of energy technologies, as the gases are produced using light during daytime and combined using a fuel cell to produce clean energy after dark.

But what nature finds so easy — water-splitting is a basic photosynthetic process — humans are having difficulty with. If the chemists can crack it, though, there might just be a long-term means of producing fuel that doesn't clog up the atmosphere with carbon dioxide.

"What we want to do is capture carbon dioxide and turn it back into fuel, just like a leaf does," says Jim Barber, a photosynthesis expert at Imperial College London.

MAKE LIKE A TREE

The process that Barber envisages would mimic photosynthesis. A light-driven chemical reaction would combine carbon dioxide with hydrogen to make sugars and other organic matter — fuel as we know it. There is an overabundance of carbon dioxide available, and sunlight is also plentiful. What we don't have a rich supply of is hydrogen. Never fear — chemists are working on that. "The source of hydrogen that we have on an enormous scale is water," says Barber. That water needs to be split into molecules of its component elements, oxygen and hydrogen. But replicating the photosynthetic processes of a tree involves some simple-sounding but thermodynamically difficult chemistry.

The hard part of water-splitting is making oxygen. Getting one molecule of oxygen from two molecules of water means moving four electrons around. That requires catalysts that can hold in place any reactive intermediate chemical species and also transfer the electrons between them.

But catalysts for splitting water are traditionally made from precious, rare metals such as platinum. To make a catalyst that is cheap and easily manufactured requires an abundant earth material.

Nocera's breakthrough came when he used a cobalt catalyst that deposited itself on the surface of an electrode sitting in a beaker of water when a small current was applied. The current changed the oxidation state of cobalt ions that were previously in solution — pushing the ions into an insoluble, catalytic form. This catalyst can help drag oxygen and electrons out of the water to leave behind hydrogen ions that move to another electrode. There, assisted by another catalyst, they combine in pairs with two electrons to form hydrogen molecules. The reaction is so effective that bubbles can be seen pouring out of the device. Since this finding was reported, Nocera has been working on figuring out the reaction mechanism and testing whether he can use his cobalt catalyst to get oxygen and hydrogen out of salt water, a far more bountiful resource than fresh water. He now thinks this is feasible[3].

At the moment, the electricity powering the system comes from a battery, but that could easily be replaced by a sun-powered photovoltaic cell, of which many cheap versions are in development. "This catalyst doesn't care where it's getting its electrons from," says Nocera. Another part of the system that needs work is the hydrogen-evolving catalyst that will ultimately be so important — at the moment, Nocera uses platinum.

But the chemistry for hydrogen production from water is slightly easier: it forms relatively readily from hydrogen ions and electrons, the byproducts of making oxygen.

TOTAL INTEGRATION

"You still need to get a totally integrated system," says Nocera. Since the news of his discovery broke in July, Nocera has become increasingly convinced that the hurdles to get to that system will be overcome in just a few years, not least because he has been contacted by many individuals and companies working hard on other parts of the puzzle. And he has been surprised by how much is "sitting on people's shelves."

Taking on board other scientists' developments makes sense, says Barber. "There's a lot of knowledge there already," he says, especially about cheap photovoltaics. "To piggy back on that with a chemical system would seem the right thing to do."

A collaborative science project called Powering the Planet, funded by the US National Science Foundation, is now looking at the technologies needed to make an integrated device. Headed up by Harry Gray at the California Institute of Technology, the project also includes Nocera. Three basic parts of the problem — how to make a hydrogen catalyst, a cheap photovoltaic membrane and an oxygen catalyst — are being tackled by different research teams.

Nocera's vision is of what he calls 'personalized energy'. "There's no reason to expect your house can't be a power station," he says. Houses could use sunlight and water to produce hydrogen on demand, either to go into a fuel-cell battery or, as Barber suggests, to be reacted with nearby carbon dioxide molecules, producing a liquid fuel. But to do the latter, other discoveries have to be made, probably by chemists. "We're going to need chemists to come up with ways of taking CO_2 and hydrogen to make a liquid fuel," says Nocera. The idea has caught the public's imagination, he says: "I have hundreds of emails from people saying 'please try it out on my house first.'"

Barber would rather see a system that doesn't need a photovoltaic cell to capture the electricity and drive an electrochemical reaction. His ideal is to have the sunlight act directly on a catalyst. This is closer to nature's way, and an oxygen-making catalyst that is activated directly by light has recently been developed by Leone Spiccia from Monash University, Victoria, Australia, and colleagues[4].

Their catalyst is based on the heart of a leaf's photosynthetic power: the oxygen-evolving complex of the photosystem II


DONNA COVENEY

Dan Nocera.

protein. As in photosystem II, Spiccia used a system of four manganese atoms. This cluster is doped into proton-conducting films, made from Nafion, and the films are then coated onto a conducting electrode. "To our surprise, when we applied a bias of 1.2 volts and light was shone on the electrode a reproducible photocurrent was generated," says Spiccia. He saw small amounts of oxygen gas being produced, as well as the hydrogen ions and electrons that balance the chemical equations. Spiccia is now working on a light-gathering antenna so he can do away with the applied electrical bias.

> "I am not sure if Dan Nocera will have a cheap and efficient water-splitting device within five years. But I admire him for setting that goal."
> Tom Mallouk

So far these breakthroughs are a long way from a realistic working system. Nocera's claim for a useful device within five years is bullish, but he stands by it. "We went to the moon," he says. "There is no reason why we can't put the pieces together to power a house with sunlight." Spiccia is more cautious — both about his own system and Nocera's. "Both approaches have their merit in my view, and it is difficult or unwise to speculate which will reach a practical device sooner. From the proof of concept stage, such discoveries can take at least 10–15 years before they become a commercial reality," notes Spiccia.

Tom Mallouk at Pennsylvania State University is another researcher active in the water-splitting field. He has built an entire water-splitting system, as yet unpublished. The device is based on more rare and expensive metals but is slightly more active than Nocera's system, Mallouk says. Nocera argues that with personalized energy, efficiencies are less important. "For a home you don't need to have the hydrogen made in three minutes," says Nocera. "You can start relaxing about how fast you make it — you can put simpler constraints on the chemistry."

"I am not sure if Dan Nocera will have a cheap and efficient water-splitting device within five years. But I admire him for setting that goal and for trying," says Mallouk.

At MIT, Nocera has been able to get involved with the Masdar Initiative. The programme, which kicked off in Abu Dhabi, the United Arab Emirates, in 2006, aims to build a city by 2015 that produces no emissions and is run completely on solar or other renewable energy sources. The MIT–Masdar relationship will allow Nocera to test his ideas.

Future energy hinges on advances in chemistry, whether they lead to a direct water-splitting device or not. Battery technologies still need a lot of work, and identifying catalysts to make liquid fuels will require chemists, as will carbon-sequestration technology. "The contribution of chemists will be on many fronts," says Spiccia. "It is difficult to say which will have the biggest impact in the long term." Scientists and engineers will need to focus on both energy generation and reducing energy use, he says.

"Chemistry is going to be at the heart of solving this climate change problem," says Nocera. Adds Mallouk: "We'll see if any new findings on water splitting will deliver systems for real world solar energy. If they do, it will certainly be a victory for chemistry."

Published online: 18 September 2008

doi:10.1038/climate.2008.96

References

1. Sanderson, K. *Nature News* doi:10.1038/news.2008.996 (2008).
2. Sanderson, K. *Nature* **452,** 400–402 (2008).
3. Kanan, M. W. & Nocera, D. G. *Science* **321,** 1072–1075 (2008).
4. Brimblecome, R. *et al. Angewandte Chemie* international edn **47,** 7335–7338 (2008).

Katharine Sanderson is a reporter for Nature *based in London.*