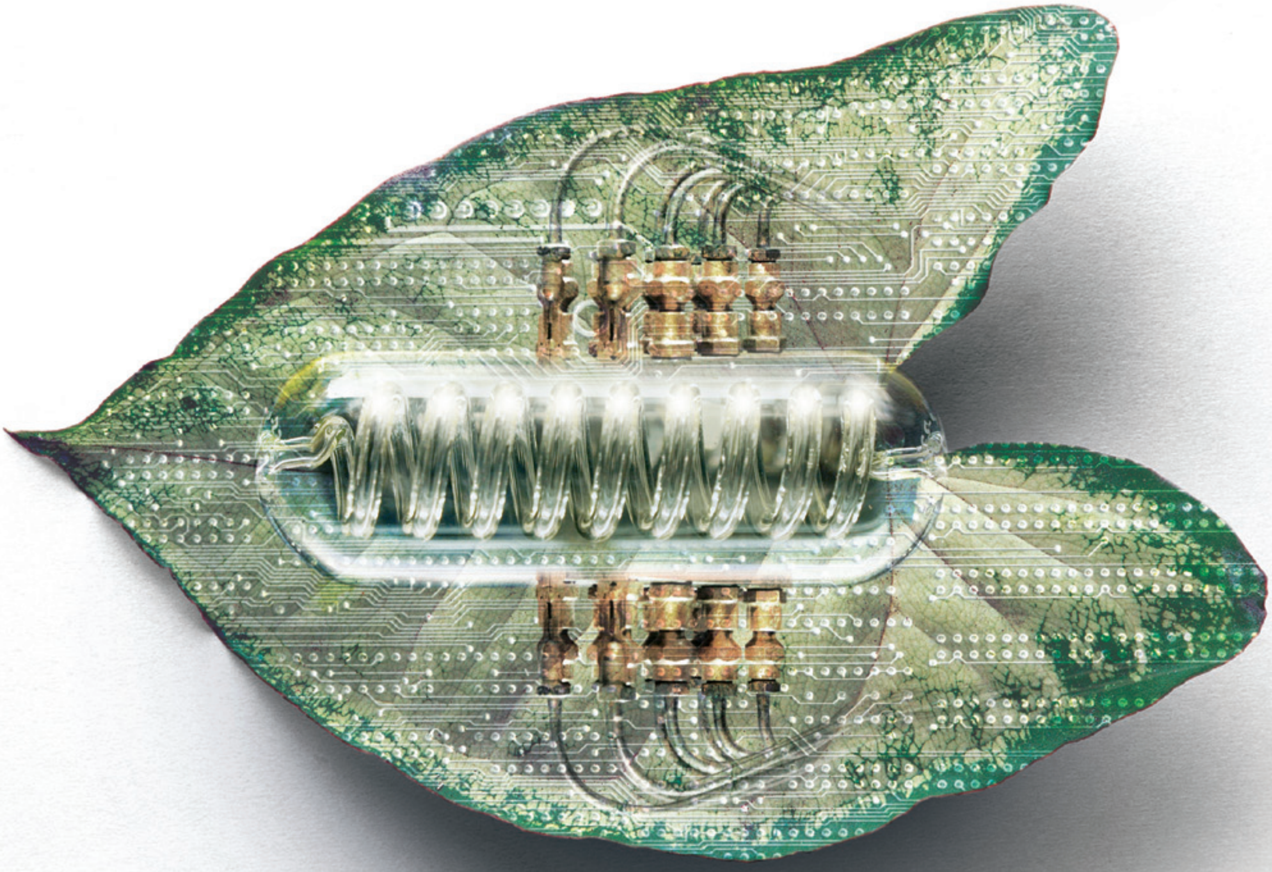

SPRINGTIME FOR THE ARTIFICIAL LEAF

Researchers make headway in turning photons into fuel.

BY JESSICA MARSHALL

On a bright spring morning in Pasadena, California, the air is rich with the smells of cut grass and flowers. Photosynthesis seems effortless here: the fronds and blooms that line the walkways of the California Institute of Technology (Caltech) bask in the sunlight, quietly using its energy to store sugars, stretch their leaves, deepen their roots and tend to their cellular processes.

Inside Caltech's Jorgensen Laboratory, however, more than 80 researchers are putting a lot of effort into doing the leaf's job using silicon, nickel, iron and any number of other materials that would be more at home inside a cell phone than a plant cell. Their gleaming new labs are the headquarters of the Joint Center for Artificial Photosynthesis (JCAP), a 190-person research programme funded by

ILLUSTRATION BY VIKTOR KOEN

the US Department of Energy (DOE) with US$116 million over five years. The centre's goal is to use sunlight to make hydrogen and other fuels much more efficiently than real leaves ever made biomass.

The researchers are pursuing this goal with a certain urgency. Roughly 13% of greenhouse-gas emissions worldwide come from transportation, so phasing out polluting fuels is a key environmental target. One approach is to replace cars and light trucks with electric vehicles charged by solar cells or wind — but that cannot tackle the whole problem. Nathan Lewis, an inorganic chemist at Caltech and JCAP's scientific director, says that some 40% of current global transportation cannot be electrified. For example, barring a major breakthrough, there will never be a plug-in hybrid plane: no craft could hold enough batteries. Liquid fuels are unbeatable when it comes to convenience combined with compact energy storage.

That is why funding agencies around the world — and at least a few private companies — are putting unprecedented resources into making fuels using power from the Sun, which is not only carbon-free but effectively inexhaustible. JCAP stands out not only for its scale, but also for its ambition. It is one of five Energy Innovation Hubs created by the DOE beginning in 2010 to focus on specific problems using basic research, applied research and engineering. JCAP has promised to deliver a working prototype of an artificial leaf by the time its initial grant runs out in 2015.

Although the centre has taken some important steps in that direction — including one reported just last week[1] — it is still a long way from delivering on that promise, "This is a really, really difficult, challenging problem," says electrochemist John Turner of the US National Renewable Energy Laboratory in Golden, Colorado. "The payback would be huge, but it's not as simple as everyone wanted it to be when we started playing in this area 40 years ago."

Still, the surge of funding and attention has given many researchers reason to hope for long-term success. "If you could sustain this type of effort for the next ten years," says Michael Wasielewski, a chemist at Northwestern University in Evanston, Illinois, "it's conceivable you could have a practical solution."

CATCHING RAYS

The concept of artificial photosynthesis goes back to 1912, but the push to achieve it did not start until 1972, when Japanese researchers outlined what a device would need to take in sunlight and use it to split water into oxygen and hydrogen fuel[2]. Progress was slow. In 1998, Turner reported[3] a complete system that showed a major advance — it stored 12% of the incoming solar energy as fuel, compared with 1% of energy stored as biomass in real leaves. But it cost more than 25 times too much to be competitive, and its performance dropped off after 20 hours of sunshine.

There are three things you want from an artificial leaf, says Lewis: "You want it to be efficient, cheap and robust. I can give you any two today, but not the third at the same time."

JCAP's mission is to fix that problem — and in the process, to create a system that is much cheaper than just splitting water with electricity from a solar panel. At the heart of JCAP's artificial-leaf design are two electrodes immersed in an aqueous solution. Typically, each electrode is made of a semiconductor material chosen to capture light energy from a particular part of the solar spectrum, and coated with a catalyst that will help to generate hydrogen or oxygen at useful speeds (see 'Splitting water'). Like many other artificial-photosynthesis devices, JCAP's system is divided by a membrane to keep the resulting gases apart and reduce the risk of an explosive reaction.

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Once the water has been split, the hydrogen is harvested. It can be used as a fuel by itself — perhaps in hydrogen-powered cars such as those already making their way into showrooms in California — or be reacted with carbon monoxide to make liquid-hydrocarbon fuels.

Making any one of the artificial leaf's components work well is a challenge; combining all of them into a complete system is even harder. "This is exactly like building a plane," says Lewis. "You've got to not just have an engine, you have to have a design with wings and the fuselage and the engine and the avionics — and the plane, in the end, has to fly."

Much of the difficulty comes down to finding the right materials. Silicon, for instance, makes a good photocathode — the electrode that produces hydrogen gas — but is stable only when the solution around it is acidic. Unfortunately, the situation is reversed with photoanodes, which produce oxygen: the good ones are stable only when the solution is basic, not acidic. And the best catalyst for the oxygen-producing electrode, iridium, is both rare and expensive, which makes it unsuitable for commercial-scale devices.

JCAP's High Throughput Experimentation lab is tackling the materials problem with inkjet printers modified to churn out spots of alloys on glass plates for testing as catalysts and photoabsorbers. Together, the printers are able to produce up to one million spots of varying composition per day.

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In one experiment[4] to find the best proportions of nickel, iron, cobalt and cerium oxides to generate oxygen from water, the team screened nearly 5,500 combinations for stability and function using a miniaturized chemical lab that glided over the glass plates tirelessly. The best-performing combination is not the most effective catalyst ever found for this reaction, but it is transparent, allowing light to pass through to the photoabsorber, and it has good chemical compatibility with that material.

One of the toughest challenges for artificial photosynthesis has always been getting a good material for the photoanode, says Carl Koval, an electrochemist and JCAP's director. "Those things were always horribly unstable, often not even stable for minutes." Many researchers have focused their search on materials known to be cheap and stable — certain metal oxides, for example — and tried to make them into good light absorbers. Others feel that it is better to start with materials that are known to be efficient light harvesters, and to work at making them stable and cheap.

Just last week, a JCAP team reported[1] success with the latter approach. By putting a protective coating of titanium dioxide on high-performing photoabsorbers such as silicon, the researchers achieved big gains in stability. "That's basically the last piece of the puzzle to create the first-generation prototype," says Koval, who predicts that JCAP will have an artificial leaf running in the next few months.

Publication of a preliminary system including the titanium dioxide coating is in the works, says Lewis. "That's going to be a double-digit-efficiency, stable system." The threshold for commercial viability is thought to be in the 10–20% range. The photoabsorbers will not be cheap enough to bring to market, concedes Lewis, because their cores are made from expensive single-crystal silicon. But if subsequent research shows that cheaper fabrication methods work, the system could be cost-effective.

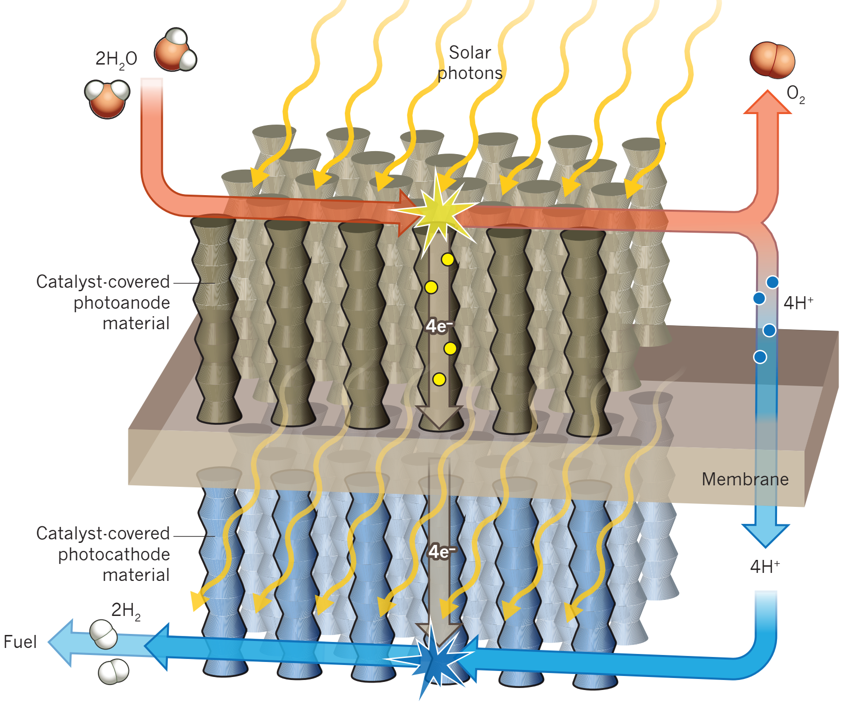
SPECTRUM OF IDEAS

JCAP will soon complete its fourth year of operations. It got off to a slow start as new labs were built, but researchers both in and outside the centre praise its systematic focus on producing a practical system, and its progress so far. Even Turner, whose lab bid to become the solar-fuels hub but lost out to Lewis's team, is encouraged by JCAP's latest direction.

Still, says Koval, the centre has its critics. Some take issue with its emphasis on engineering and prototype development. But if JCAP were to focus on basic science, he says, it would not be "doing what the DOE created the hub for in the first place". Other critics object to how JCAP concentrates on just one of several

SPLITTING WATER

Artificial photosynthesis uses photons from sunlight to split water molecules into oxygen and hydrogen, which can be used to make fuel. Every two molecules of water yield one oxygen molecule (O_2), as well as four pairs of protons (H^+) and electrons (e^-). The protons and electrons migrate across a membrane, where a photocathode recombines them into hydrogen using a catalyst plus sunlight.



SOURCE: JCAP; ART: NIK SPENCER/NATURE

possible ways to tackle artificial photosynthesis. "A lot of people would have been happier if the DOE had spread the funding around all these different ways of doing this," says Koval. But that kind of dilution of effort would be risky in its own way, he argues: "Then you'd have progress on none of them."

Besides, many of the alternative approaches are being pursued elsewhere. Up the coast in Santa Barbara, California, for example, a start-up firm called HyperSolar is testing a system in which coated nano- or micro-particles combining a photoabsorber and a catalyst are placed in a transparent, water-filled plastic bag. The bag will inflate as it is exposed to sunlight, and hydrogen and oxygen gas form inside. Such units could be deployed in sunny regions such as deserts. A 2009 DOE report[5] estimated that, if it uses cheap materials, this 'baggie' approach could produce hydrogen economically with 10% efficiency, stable for 10 years.

But the system is risky, says Turner, because it produces oxygen along with the hydrogen. "If you're talking about 100 square miles of baggies in the desert with this explosive mixture," he says, "one lightning bolt and you have a disaster." HyperSolar researchers are exploring several ways to eliminate that danger. One is to use a system that separates the gases into two bags, says Syed Mubeen, a postdoc at the University of California, Santa Barbara, and lead scientist at the company. Another is to run the system using waste water rather than pure water, so that the oxygen reacts with organic impurities and degrades them into valuable chemicals. This approach "completely removes oxygen out of the equation", says Mubeen. As with JCAP's stable photoanode, HyperSolar's photoabsorber is protected by a coating.

LIGHT INDUSTRY

Another entrant in the artificial-photosynthesis field is the Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), a consortium of universities and companies that has government funding comparable to JCAP's grant — although over ten years rather than five — to develop a bag-based approach. Kazunari Domen, a chemist at the University of Tokyo and leader of ARPChem's water-splitting group, says that one of the companies in the consortium has been working on a membrane to separate the hydrogen and oxygen products.

Other projects are making photoabsorbers from organic molecules, rather than semiconductors. Some are building molecular assemblies inspired directly by the photosynthetic apparatus of plants. And in the past few years, a class of materials called perovskites has drawn the attention of the solar-photovoltaic community for its high energy-conversion efficiency; some researchers think that the materials also have potential in artificial photosynthesis.

Daniel Nocera, a chemist at Harvard University in Cambridge, Massachusetts, launched Sun Catalytix to develop his work on a low-cost catalyst. But the company announced last year that it has put that research on hold to pursue a less challenging product with prospects of turning a profit for investors sooner. The decision underscores the challenges of bringing a commercially viable artificial-photosynthesis system to market.

BERKELEY BUBBLES

On a spring day in the arty–industrial district of Berkeley, California, researchers demonstrate a prototype system inside the temporary lab space that houses JCAP's northern site. As a sunlamp shines on a CD-sized plastic box, fine streams of hydrogen bubbles rise between blue strips of catalyst-coated silicon and exit through tubes in the box's top. This prototype system is not the team's best: it won't last and it is not very efficient. But it is still encouraging to see champagne-like bubbles triggered simply by light.

Then Karl Walczak, a postdoc in JCAP's prototyping group, slides a second plastic box in front of the lamp. Inside is a small black square: a new titanium dioxide-coated photocathode. This second system immediately begins to generate bubbles much faster than the first. "This is where the field is going," says Walczak.

JCAP researchers hope that such prototypes will ultimately lead to industrial hydrogen-production plants. They predict arrays of cells kilometres long, with a tower supplying water and pipes drawing the hydrogen to a storage tank. Some researchers propose that domestic units may also be part of the future, but Lewis warns that the small amount of sunlight that falls on a rooftop cannot make enough hydrogen to supply a family's energy needs. Others say that the technology could be useful in areas of the developing world that lack an energy infrastructure, offering distributed fuel generation where it is needed.

In the meantime, researchers at JCAP and elsewhere are moving forward on all fronts. Devens Gust, a chemist at Arizona State University in Tempe, echoes a near-universal sentiment. "The bottom line," he says, "is that nobody really knows yet what's going to win out, what's going to be practical."

But whatever technology prevails, says Lewis, the logic behind artificial photosynthesis is inexorable. "The biggest energy source we have by far is the Sun," he says. "The best way to store energy other than in the nucleus of an atom is in chemical fuels. It's inevitable someone is going to take the biggest source and store it in the most dense way." ■ SEE EDITORIAL P.7

Jessica Marshall *is a freelance writer in St Paul, Minnesota.*

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