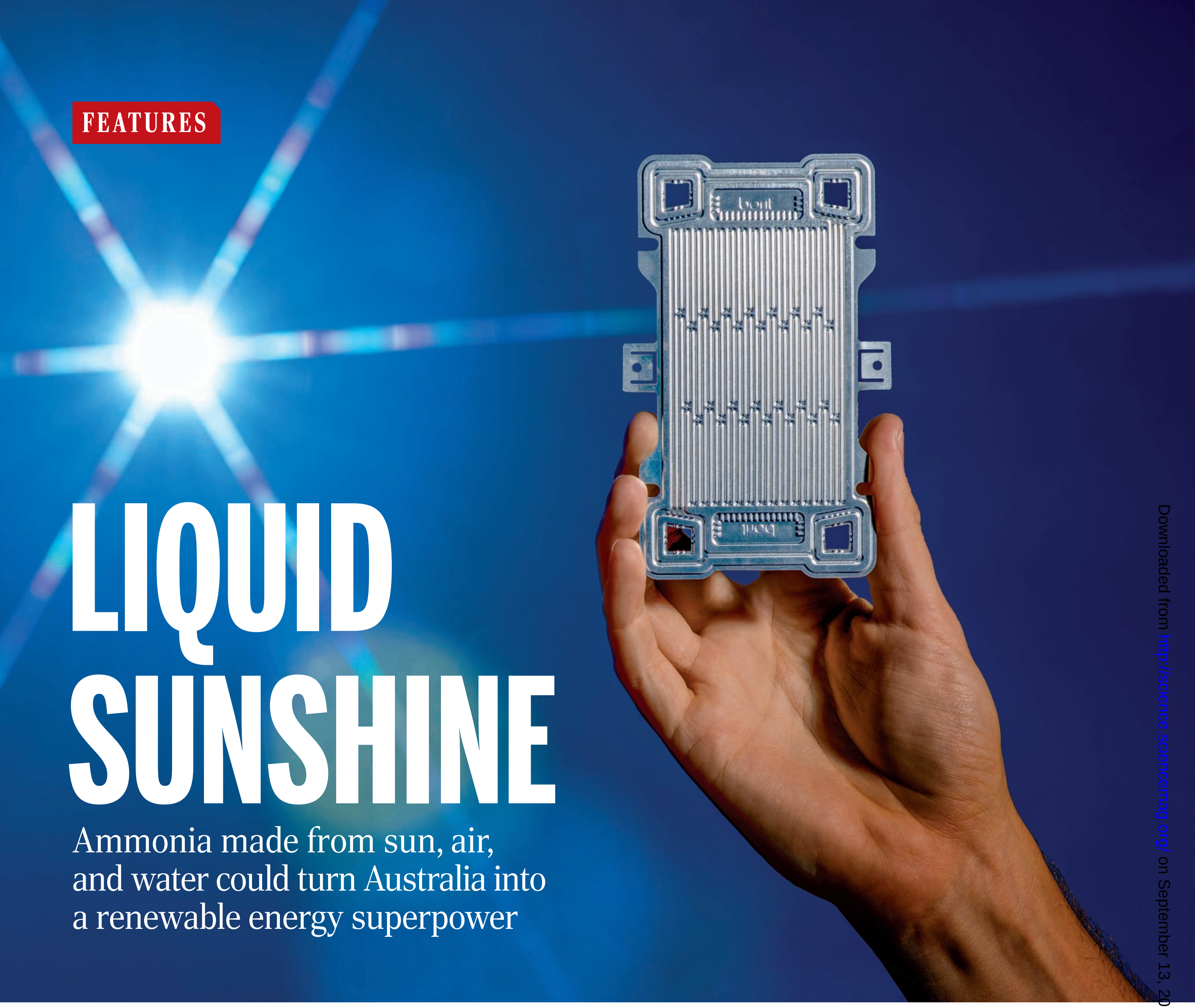


LIQUID SUNSHINE

Ammonia made from sun, air, and water could turn Australia into a renewable energy superpower

By **Robert F. Service**
in Sydney, Brisbane,
and Melbourne, Australia

The ancient, arid landscapes of Australia are fertile ground for new growth, says Douglas MacFarlane, a chemist at Monash University in suburban Melbourne: vast forests of windmills and solar panels. More sunlight per square meter strikes the country than just about any other, and powerful winds buffet its south and west coasts. All told, Australia boasts a renewable energy potential of 25,000 gigawatts, one of the highest in the world and about four times the planet's installed electricity production capacity. Yet with a small population and few ways to store or export the energy, its renewable bounty is largely untapped.

That's where MacFarlane comes in. For the past 4 years, he has been working on a fuel cell that can convert renewable electricity into a carbon-free fuel: ammonia. Fuel cells typically use the energy stored in chemical bonds to make electricity; MacFarlane's operates in reverse. In his third-floor laboratory, he shows off one of the devices, about the size of a hockey puck and clad in stainless steel. Two plastic tubes on its backside feed it nitrogen gas and water, and a power cord supplies electricity. Through a third tube on its front, it silently exhales gaseous ammonia, all without the heat, pressure, and carbon emissions normally needed to make the chemical. "This is breathing nitrogen in and breathing ammonia out," MacFarlane says, beaming like a proud father.

Companies around the world already produce $60 billion worth of ammonia every year, primarily as fertilizer, and MacFarlane's gizmo may allow them to make it more efficiently and cleanly. But he has ambitions to do much more than help farmers. By converting renewable electricity into an energy-rich gas that can easily be cooled and squeezed into a liquid fuel, MacFarlane's fuel cell effectively bottles sunshine and wind, turning them into a commodity that can be shipped anywhere in the world and converted back into electricity or hydrogen gas to power fuel cell vehicles. The gas bubbling out of the fuel cell is colorless, but environmentally,

PHOTO: STEVEN MORTON/FELLOW OF THE ROYAL PHOTOGRAPHIC SOCIETY

A component in a reverse fuel cell uses renewable power to knit together water and nitrogen to make ammonia.

MacFarlane says, ammonia is as green as can be. "Liquid ammonia is liquid energy," he says. "It's the sustainable technology we need."

Ammonia—one nitrogen atom bonded to three hydrogen atoms—may not seem like an ideal fuel: The chemical, used in household cleaners, smells foul and is toxic. But its energy density by volume is nearly double that of liquid hydrogen—its primary competitor as a green alternative fuel—and it is easier to ship and distribute. "You can store it, ship it, burn it, and convert it back into hydrogen and nitrogen," says Tim Hughes, an energy storage researcher with manufacturing giant Siemens in Oxford, U.K. "In many ways, it's ideal."

Researchers around the globe are chasing the same vision of an "ammonia economy," and Australia is positioning itself to lead it. "It's just beginning," says Alan Finkel, Australia's chief scientist who is based in Canberra. Federal politicians have yet to offer any major legislation in support of renewable ammonia, Finkel says, perhaps understandable in a country long wedded to exporting coal and natural gas. But last year, the Australian Renewable Energy Agency declared that creating an export economy for renewables is one of its priorities. This year, the agency announced AU$20 million in initial funds to support renewable export technologies, including shipping ammonia.

In Australia's states, politicians see renewable ammonia as a potential source of local jobs and tax revenues, says Brett Cooper, chairman of Renewable Hydrogen, a renewable fuels consulting firm in Sydney. In Queensland, officials are discussing creating an ammonia export terminal in the port city of Gladstone, already a hub for shipping liquefied natural gas to Asia. In February, the state of South Australia awarded AU$12 million in grants and loans to a renewable ammonia project. And last year, an international consortium announced plans to build a US$10 billion combined wind and solar plant known as the Asian Renewable Energy Hub in Western Australia state. Although most of the project's 9000 megawatts of electricity would flow through an undersea cable to power millions of homes in Indonesia, some of that power could be used to generate ammonia for long-distance export. "Ammonia is the key enabler for exporting renewables," says David Harris, research director for low-emissions technologies at Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO) Energy in Pullenvale. "It's the bridge to a whole new world."

First, however, the evangelists for renewable ammonia will have to displace one of the modern world's biggest, dirtiest, and most time-honored industrial processes: something called Haber–Bosch.

THE AMMONIA FACTORY, a metallic metropolis of pipes and tanks, sits where the red rocks of Western Australia's Pilbara Desert meet the ocean. Owned by Yara, the world's biggest producer of ammonia, and completed in 2006, the plant is still gleaming. It is at the technological vanguard and is one of the largest ammonia plants in the world. Yet at its core are steel reactors that still use a century-old recipe for making ammonia.

Until 1909, nitrogen-fixing bacteria made most of the ammonia on the planet. But that year, German scientist Fritz Haber found a reaction that, with the aid of iron catalysts, could split the tough chemical bond that holds together molecules of nitrogen, N_2, and combine the atoms with hydrogen to make ammonia. The reaction takes brute force—up to 250 atmospheres of pressure in the tall, narrow steel reactors—a process first industrialized by German chemist Carl Bosch. The process is fairly efficient; about 60% of the energy put into the plant ends up being stored in the ammonia's bonds. Scaled up to factories the size of Yara's, the process can produce vast amounts of ammonia. Today, the facility makes and ships 850,000 metric tons of ammonia per year—more than double the weight of the Empire State Building.

Most is used as fertilizer. Plants crave nitrogen, used in building proteins and DNA, and ammonia delivers it in a biologically available form. Haber–Bosch reactors can churn out ammonia much faster than natural processes can, and in recent decades the technology has enabled farmers to feed the world's exploding population. It's estimated that at least half the nitrogen in the human body today comes from a synthetic ammonia plant.

Haber–Bosch led to the Green Revolution, but the process is anything but green. It requires a source of hydrogen gas (H_2), which is stripped away from natural gas or coal in a reaction using pressurized, superheated steam. Carbon dioxide (CO_2) is left behind, accounting for about half the emissions from the overall process. The second feedstock, N_2, is easily separated from air, which is 78% nitrogen. But generating the pressure needed to meld hydrogen and nitrogen in the reactors consumes more fossil fuels, which means more CO_2. The emissions add up: Ammonia production consumes about 2% of the world's energy and generates 1% of its CO_2.

Yara is taking a first step toward greening that process with a pilot plant, set to open in 2019, that will sit next to the existing Pilbara factory. Instead of relying on natural gas to make H_2, the new add-on will feed power from a 2.5-megawatt solar array into a bank of electrolyzers, which split water into H_2 and O_2. The facility will still rely on the Haber–Bosch reaction to combine the hydrogen with nitrogen to make ammonia. But the solar-powered hydrogen source


Australia's windy coasts offer a bounty of energy, which it might one day export as a carbon-free fuel.

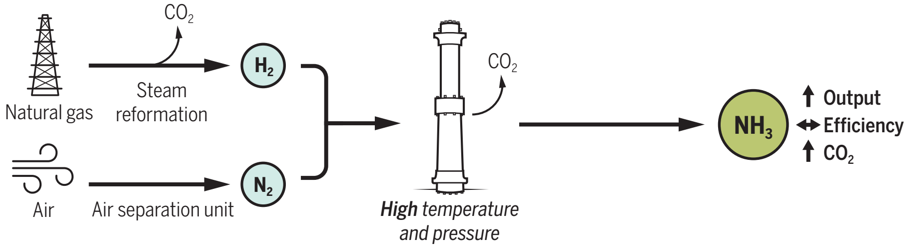
PHOTO: COAST PROTECTION BOARD, SOUTH AUSTRALIA

A green way to make ammonia

Reverse fuel cells can use renewable power to make ammonia from air and water, a far more environmentally friendly technique than the industrial Haber–Bosch process. Renewable ammonia could serve as fertilizer—ammonia's traditional role—or as an energy-dense fuel.

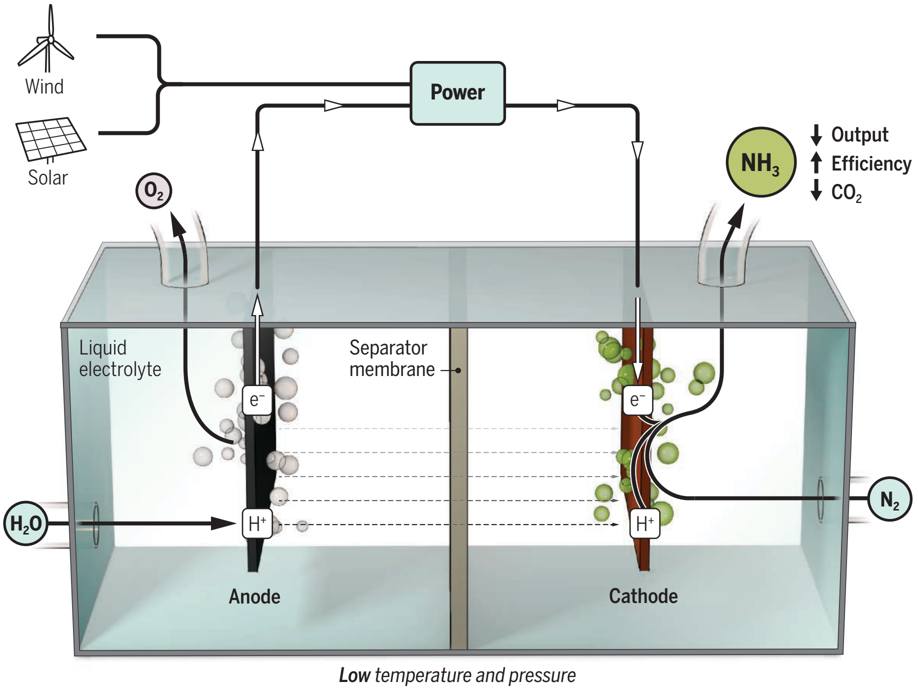
Industrial ammonia

Most of the world's ammonia is synthesized using Haber–Bosch, a century-old process that is fast and fairly efficient. But the factories emit vast amounts of carbon dioxide (CO_2).



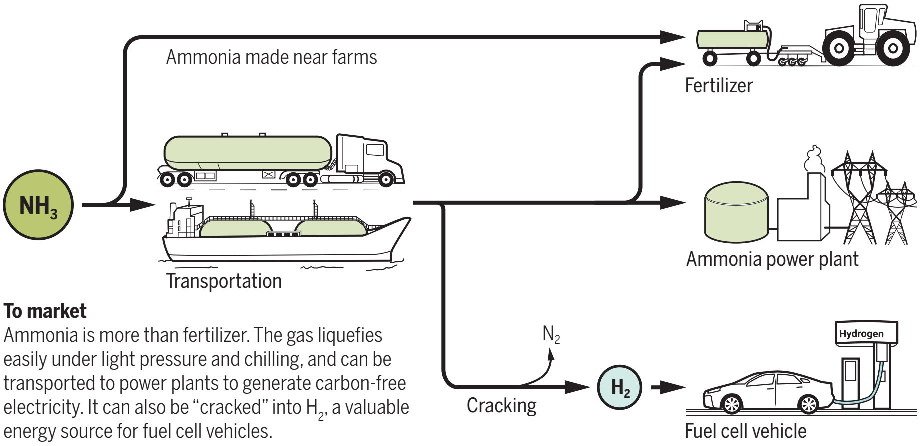
Gentler reactions

A reverse fuel cell uses renewable electricity to drive a chemical reaction that makes ammonia. Water reacts at the anode to make hydrogen ions (H^+), which migrate to the cathode where they react with nitrogen (N_2) to form ammonia. The reaction is efficient, but slow.



To market

Ammonia is more than fertilizer. The gas liquefies easily under light pressure and chilling, and can be transported to power plants to generate carbon-free electricity. It can also be "cracked" into H_2, a valuable energy source for fuel cell vehicles.



GRAPHIC: V. ALTOUNIAN/*SCIENCE*

cuts total CO_2 emissions from the process roughly in half.

Other projects are following suit. The state of South Australia announced plans in February to build a AU$180 million ammonia plant, again relying on electrolyzers powered by renewable energy. Slated to open in 2020, the plant would be a regional source of fertilizer and liquid ammonia, which can be burned in a turbine or run through a fuel cell to make electricity. The supply of liquid energy will help stabilize the grid in South Australia, which suffered a debilitating blackout in 2016.

Ammonia made this way should attract buyers in places such as the European Union and California, which have created incentives to buy greener fuels. And as the market grows, so will the distribution routes for importing ammonia and the technologies for using it, Harris says. By then, fuel cells like MacFarlane's could be ready to displace Haber–Bosch itself—and the half-green approach to ammonia production could become fully green.

INSTEAD OF APPLYING fearsome heat and pressure, reverse fuel cells make ammonia by deftly wrangling ions and electrons. As in a battery being charged, charged ions flow between two electrodes supplied with electricity. The anode, covered with a catalyst, splits water molecules into O_2, hydrogen ions, and electrons. The protons flow through an electrolyte and a proton-permeable membrane to the cathode, while the electrons make the journey through a wire. At the cathode, catalysts split N_2 molecules and prompt the hydrogen ions and electrons to react with nitrogen and make ammonia.

At present, the yields are modest. At room temperature and pressure, the fuel cell reactions generally have efficiencies of between 1% and 15%, and the throughput is a trickle. But MacFarlane has found a way to boost efficiencies by changing the electrolyte. In the water-based electrolyte that many groups use, water molecules sometimes react with electrons at the cathode, stealing electrons that would otherwise go into making ammonia. "We're constantly fighting having the electrons going into hydrogen," MacFarlane says.

To minimize that competition, he opted for what's called an ionic liquid electrolyte. That approach allows more N_2 and less water to sit near the catalysts on the cathode, boosting the ammonia production. As a result, the efficiency of the fuel cell skyrocketed from below 15% to 60%, he and his colleagues reported last year in *Energy & Environmental Science*. The result has since improved to 70%, MacFarlane says—but with a tradeoff. The ionic liquid in his fuel cell is goopy, 10 times more viscous than water. Protons have to slog their way to the cathode, slowing the rate of ammonia production. "That hurts us," MacFarlane says.

To speed things up, MacFarlane and his colleagues are toying with their ionic liquids. In a study published in April in *ACS Energy Letters*, they report devising one rich in fluorine, which helps protons pass more easily and speeds ammonia production by a factor of 10. But the production rate still needs to rise by orders of magnitude before his cells can meet targets, set for the field by the U.S. Department of Energy (DOE), that would begin to challenge Haber–Bosch.

Next to Monash University, Sarb Giddey and his colleagues at the Clayton offices of CSIRO Energy are making ammonia with their "membrane reactor." It relies on high temperatures and modest pressures—far less than those in a Haber-Bosch reactor—that, compared to MacFarlane's cell, boost throughput while sacrificing efficiency. The reactor designs call for a pair of concentric long metallic tubes, heated to 450°C. Into the narrow gap between the tubes flows H_2, which could be made by a solar- or wind-powered electrolyzer. Catalysts lining the gap split the H_2 molecules into individual hydrogen atoms, which modest pressures then force through the atomic lattice of the inner tube wall to its hollow core, where piped-in N_2 molecules await. A catalytically active metal such as palladium lines the inner surface, splitting the N_2 and coaxing the hydrogen and nitrogen to combine into ammonia—much faster than in MacFarlane's cell. So far only a small fraction of the input H_2 reacts in any given pass—another knock to the reactor's efficiency.

Other approaches are in the works. At the Colorado School of Mines in Golden, researchers led by Ryan O'Hayre are developing button-size reverse fuel cells. Made from ceramics to withstand high operating temperatures, the cell can synthesize ammonia at record rates—about 500 times faster than MacFarlane's fuel cell. Like Giddey's membrane reactors, the ceramic fuel cells sacrifice some efficiency for output. Even so, O'Hayre says, they still need to improve production rates by another factor of 70 to meet the DOE targets. "We have a lot of ideas," O'Hayre says.

Whether any of those approaches will wind up being both efficient and fast is still unknown. "The community is still trying to figure out what direction to go," says Lauren Greenlee, a chemical engineer at the University of Arkansas in Fayetteville. Grigorii Soloveichik, a manager in Washington, D.C., for the DOE's Advanced Research Projects Agency-Energy program on making renewable fuels, agrees. "To make [green] ammonia is not hard," he says. "Making it economically on a large scale is hard."

HOWEVER DISTANT, the prospect of Asia-bound tankers, full of green Australian ammonia, raises the next question. "Once you get ammonia to market, how do you get the energy out of it?" asks Michael Dolan, a chemist at CSIRO Energy in Brisbane.

The simplest option, Dolan says, is to use the green ammonia as fertilizer, like today's ammonia but without the carbon penalty. Beyond that, ammonia could be converted into electricity in a power plant customized to burn ammonia, or in a traditional fuel cell, as the South Australia plant plans to do. But currently, ammonia's highest value is as a rich source of hydrogen, used to power fuel cell vehicles. Whereas ammonia fertilizer sells for about $750 a ton, hydrogen for fuel cell vehicles can go for more than 10 times that amount.

In the United States, fuel cell cars seem all but dead, vanquished by battery-powered vehicles. But Japan is still backing fuel cells heavily. The country has spent more than US$12 billion on hydrogen technology as part of its strategy to reduce fossil fuel imports and meet its commitment to reduce CO_2 emissions under the Paris climate accord. Today the country has only about 2500 fuel cell vehicles on the road. But by 2030 Japanese officials expect 800,000. And the nation is eyeing ammonia as a way to fuel them.

> *"It looks like there's enough interest to get this industry started."*
> **David Harris**, CSIRO Energy

Converting hydrogen into ammonia only to convert it back again might seem strange. But hydrogen is hard to ship: It has to be liquefied by chilling it to temperatures below –253°C, using up a third of its energy content. Ammonia, by contrast, liquefies at –10°C under a bit of pressure. The energy penalty of converting the hydrogen to ammonia and back is roughly the same as chilling hydrogen, Dolan says—and because far more infrastructure already exists for handling and transporting ammonia, he says, ammonia is the safer bet.

That last step—stripping hydrogen off ammonia molecules—is what Dolan and his colleagues are working on. In a cavernous metal warehouse on the CSIRO campus that has long been used to study coal combustion, two of Dolan's colleagues are assembling a 2-meter-tall reactor that is dwarfed by a nearby coal reactor. When switched on, the reactor will "crack" ammonia into its two constituents: H_2, to be gathered up for sale, and N_2, to waft back into the air.

That reactor is basically a larger version of Giddey's membrane reactor, operating in reverse. Only here, gaseous ammonia is piped into the space between two concentric metal tubes. Heat, pressure, and metal catalysts break apart ammonia molecules and push hydrogen atoms toward the tube's hollow core, where they combine to make H_2 that's sucked out and stored.

Ultimately, Dolan says, the reactor will produce 15 kilograms per day of 99.9999% pure hydrogen, enough to power a few fuel cell cars. Next month, he plans to demonstrate the reactor to automakers, using it to fill tanks in a Toyota Mirai and Hyundai Nexo, two fuel cell cars. He says his team is in late-stage discussions with a company to build a commercial pilot plant around the technology. "This is a very important piece of the jigsaw puzzle," Cooper says.

Beyond 2030, Japan will likely import between $10 billion and $20 billion of hydrogen each year, according to a renewable energy roadmap recently published by Japan's Ministry of Economy, Trade and Industry. Japan, Singapore, and South Korea have all begun discussions with Australian officials about setting up ports for importing renewably produced hydrogen or ammonia. "How it all comes together economically, I don't know," Harris says. "But it looks like there's enough interest to get this industry started."

Cooper knows how he wants it to end. Over coffee on a rainy morning in Sydney, he describes his futuristic vision for renewable ammonia. When he squints, he can see, maybe 30 years down the road, Australia's coast dotted with supertankers, docked at offshore rigs. But they wouldn't be filling up with oil. Seafloor powerlines would carry renewable electricity to the rigs from wind and solar farms on shore. On board, one device would use the electricity to desalinate seawater and pass the fresh water to electrolyzers to produce hydrogen. Another device would filter nitrogen from the sky. Reverse fuel cells would knit the two together into ammonia for loading on the tankers—a bounty of energy from the sun, air, and sea.

It's the dream that nuclear fusion never reached, he says: inexhaustible carbon-free power, only this time from ammonia. "It can never run out, and there is no carbon in the system." ■

Science

Liquid sunshine

Robert F. Service

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