Profile of Daniel G. Nocera

In a dim-lit laboratory in the chemistry department at the Massachusetts Institute of Technology, a postdoctoral researcher points out the parts of a handmade device that might be our best hope yet for harnessing solar energy. A chip the size of a microscopy slide, the device is an artificial leaf, the first of its kind made of relatively abundant and inexpensive materials that, if further refined, might help make the sun our main source of energy. The brainchild of National Academy of Sciences member and MIT chemistry professor Daniel Nocera, the leaf's stainless steel chip is coated with silicon, which can harvest sunlight, and catalysts that can use that light to split water into hydrogen and oxygen. When burned in a fuel cell, Nocera's postdoctoratal fellow Joep Pijpers explains, hydrogen generates electricity and water. The catalysts can help produce enough hydrogen from a liter of water to power an average home in the developing world. Someday, Nocera hopes, this technology might help personalize energy in the Western world, untethering its people from power grids based on energy sources that emit planet-warming gases.

Although he was born in Boston and returned to the city later in life, Nocera spent a childhood split between four states, as he moved with his father, who worked in retail sales. That peripatetic childhood came with a price. "When you move that much, you don't easily make friends. I became afraid to become attached to people," he says. The anxiety of separation spurred his interest in science as a place of refuge. Armed with an amateur microscope built from an educational kit, Nocera stoked his scientific curiosity, examining creatures unearthed from his back yard. "Science seemed like an individual's pursuit, something I could carry with me no matter where we moved," he recalls. Nocera soaked up the fundamentals of science at Bergenfield High School in New Jersey, motivated by physics and chemistry teachers. In 1974, he enrolled for a bachelor's degree in chemistry at Rutgers University, New Jersey, where as a plucky freshman, he volunteered to perform experiments with chemist Lester Morss, who studied lanthanides and actinides—periodic table residents that include radioactive and rare earth elements. For his undergraduate thesis under the guidance of Rutgers chemist Joseph Potenza, Nocera helped illuminate a physical phenomenon called dynamic nuclear polarization, which affects subatomic interactions between electrons and nuclei. Analyzing those interactions can help researchers determine high-resolution structures of biologically important molecules through methods such as NMR spectroscopy.

Daniel G. Nocera.

In 1979, Nocera began doctoral studies in inorganic chemistry in the laboratory of Caltech chemist Harry Gray. There, together with Caltech chemist Jay Winkler, Nocera fashioned a laser-based technique to measure the movement of an individual electron through proteins, a pursuit that had preoccupied Gray for nearly a decade and that could help unravel natural reactions like photosynthesis. Those findings, collectively called fixed-distance electron transfer, led to well-regarded reports in the *Journal of the American Chemical Society* (1, 2) and formed the basis of Nocera's then-novel interest in using light to generate energy. But it was his 1986 paper, which reported the observation of a chemically reactive intermediate named the delta star in reactions of quadruple-bonded metals, that Nocera remembers best. Although the report was published in the *Journal of the American Chemical Society* (3), the research also found an unlikely outlet; the delta star became a centerpiece of a bestselling work of detective fiction by the American writer Joseph Wambaugh (4) in which a band of chemistry professors help solve a mysterious murder. "The writer actually featured the abstract of the paper in the novel," Nocera recalls.

Trafficking Electrons and Protons

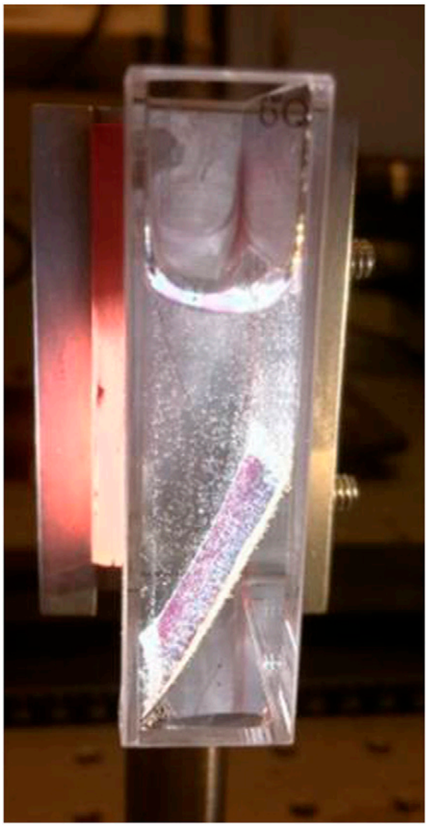
In 1983, just before graduation, Nocera accepted an offer of assistant professorship from Michigan State University in East Lansing, Michigan. There, he focused on the so-called energy problem, a cause that he has championed for most of his scientific career. Nocera brought his electron transfer expertise gained in Gray's laboratory to bear on the thorny problem of multiple electron transfer. At the heart of plants' ability to use sunlight for photosynthesis is their near-mystical knack for performing chemical reactions that involve the transfer of multiple electrons. Sunlight triggers the formation of excited electronic states in plant cells that, through a cascade of steps, lead to the coupling of protons and electrons, ultimately producing hydrogen and oxygen. It is a testament to the fiendish difficulty of replicating this chemical reaction—which plants carry out with casual ease—that a century after Italian chemist Giacomo Ciamician wrote in *Science* that "the photochemical processes that hitherto have been the guarded secret of the plants . . . will have been mastered by human industry," researchers are still trying to perfect artificial photosynthesis (5).

Long considered a hurdle to harnessing sunlight, the field of multielectron chemistry presented problems that Nocera addressed through kinetic studies using lasers. Among the first chemical reactions he addressed was the transfer of two electrons to an atom of hydrogen, a reaction catalyzed by hydrogenase enzymes, which help orchestrate anaerobic metabolism in organisms like algae. Understanding how algae carry out the reaction, for example, could help researchers generate hydrogen for use as a fuel. More importantly, multielectron chemistry turned out to be a gateway to a more complicated reaction called proton-coupled electron transfer (PCET), whose unraveling earned Nocera membership in the National Academy of Sciences years later. PCET pointed to a way to harness sunlight.

Such limber explorations of subatomic chemistry led to an assistant professorship in 1997 at MIT, where Nocera set about unifying the phenomena of multielectron chemistry and PCET as a path toward addressing the energy problem. Through nifty calculations that accounted for worldwide population, average gross

---

This is a Profile of a recently elected member of the National Academy of Sciences to accompany the member's Inaugural Article on page 10337 in issue 23 of volume 107.



An artificial leaf.

domestic product per capita (a measure of productivity), and energy consumed per unit of gross domestic product (a measure of energy conserved while achieving that productivity), Nocera estimated in a 2006 PNAS Perspective that, by the turn of the century, the global demand for energy would hover around a staggering 43 trillion watts (6). Although fossil fuels, like coal, oil, and natural gas, can together meet that demand handily, their use is forever pinned with an asterisk: climate change caused by the emission of greenhouse gases. Achieving the emissions reduction goals set by the Intergovernmental Panel on Climate Change, then, would call for a reliable source of carbon-neutral energy.

High Noon for Solar Energy

Nocera turned to an unfailing source: A benchmark for reliability, the sun provides more energy in an hour than people typically consume in a year. And there are two main ways to harness that energy, namely producing steam by using turbines or converting sunlight into electricity by using photovoltaic panels. But the challenge in harnessing solar energy lies in the ability to store the captured energy for use at night or when the sun is blanketed by clouds. A few ways to store solar energy at night have been developed, like entrapping the excess energy in molten salt or compressed air. But none are cost-effective enough to render solar energy an industrial option. In seeking a practicable solution to this seeming impasse, Nocera looked to nature. His unraveling of multielectron chemistry and PCET led to a quest to mimic photosynthesis. To that end, he sought an inexpensive catalyst that could use sunlight to split water into hydrogen and oxygen. The gases could then be combined in a fuel cell to generate electricity and water, thus creating a potentially bottomless, self-sufficient powerhouse. “Photosynthesis is a water-splitting reaction and involves four electrons and four protons. Plants store and move four electrons from water and produce an electric current. They also convert the electric current into chemical current conducted by protons, which are moved as atoms. Atoms are heavier and tougher to move than electrons. What we needed was a catalyst that could move atoms and assemble them,” Nocera explains.

By 2002, Nocera had developed a rhodium-based catalyst to generate hydrogen gas from a chemical solution using light energy to make hydrogen atoms from protons and electrons wrested from the solvent. Meanwhile, other researchers at the US National Renewable Energy Laboratory in Golden, Colorado, had uncovered ways to use semiconductors to split water. But rhodium and semiconductors are too expensive for large-scale use. Also, there was still no reasonable means to generate oxygen from water. “Reading the book of nature helped us move closer to an inexpensive catalyst for oxygen,” Nocera says. A revealing chapter in the book came to light when London’s Imperial College biochemist James Barber published the high-resolution crystal structure of the enzymatic machinery that helps plants carry out photosynthesis. Known as the oxygen-evolving complex, this macromolecular structure was found to be the secret behind plants’ photosynthetic prowess. “When we saw what the plant’s catalytic machinery looked like, we set out to design a synthetic catalyst to split water,” he adds. Thanks to a National Science Foundation grant to explore renewable energy sources and a private, philanthropic gift, Nocera set up an energy research program at MIT called the Solar Revolution Project, one of whose goals was to develop such a catalyst.

Bolstered by the influx of research dollars, Nocera and his then-postdoctoral fellow Matthew Kanan fashioned a process that could produce hydrogen and oxygen from water. The process involves an electrode made of indium tin oxide, which when subjected to a voltage in a catalytic solution of cobalt, potassium phosphate, and water, generates oxygen gas and hydrogen ions. At a different electrode coated with a platinum catalyst, the hydrogen ions recombine into hydrogen gas. As the reaction proceeds, the cobalt catalyst breaks down—but reassembles over time, regenerating itself for prolonged use. Published in a 2008 *Science* report, Nocera’s process was hailed as a breakthrough (7). Over the course of a day, the catalyst could use electricity generated by a photovoltaic panel to split water and produce energy to power an average American home. The strength of the catalyst, Nocera explains, was in its ability for near-continuous self-repair, not to mention the relative safety, abundance, and affordability of raw materials such as cobalt and phosphate. “The real scientific discovery was its self-healing property, which resembles that of the oxygen-evolving catalyst of photosynthesis,” Nocera says. Yet Nocera’s catalyst had a number of shortcomings that needed to be addressed. First, the catalyst needed a good deal of electricity to start splitting water, affecting its overall efficiency. Complicating the matter further, it could only accept low levels of current. Further still, the platinum used to generate hydrogen was prohibitively expensive for Nocera’s purpose. In the next two years, Nocera and his team surmounted some of those problems, publishing in a 2010 PNAS inaugural article, an improved oxygen-evolving catalyst based on nickel borate (8). At a pH of 9.2, thin films of the catalyst, the paper reported, could be electrodeposited from dilute solutions of nickel borate electrolyte, allowing researchers to control the thickness of the films and the electric potential at which the catalyst operates. “Structurally, the nickel–borate catalyst is similar to the cobalt catalyst, but it runs faster and better in certain pH regimes. It also shows that our original discovery isn’t an isolated curiosity,” Nocera says. “Our focus is now on this nickel–borate catalyst,” he adds.

No Mere Pie in the Sky

To help commercialize the water-splitting catalyst, Nocera cofounded Sun Catalytix, a Massachusetts-based technology firm that hopes to put his basic research advances to work for people. The company’s long term goal is to personalize energy by producing it at its point of use instead of relying on traditional methods of distribution along grids from a centralized source. In a tidily imagined scenario, Nocera envisions turning surplus light energy harvested by rooftop photovoltaic panels into electricity with the help of his water splitter, a pair of underground tanks to store hydrogen and oxygen, and a fuel cell to burn the hydrogen. “Thus, your home becomes its own solar power station," Nocera explains with his characteristic can-do spirit. In September 2009, *National Geographic* featured a snapshot of Nocera cradling little more than a gallon of water in his hands—the amount that he estimates is needed to power an average American home. A vision of pharaonic scope that Nocera hopes to someday pull off, personalized energy must first overcome several hurdles, not least of which are the still-prohibitive cost of fuel cells and the political inertia facing alternative energy. "Over the years, we've been getting greener in thinking about the future of our energy, but it's still largely carbon-based. The slow pace of greening is disappointing, mainly because of the lack of policies to implement carbon pricing," he says.

Intertwined with this vision to wean the Western world from its dependence on fossil fuels is Nocera's goal to make solar energy a predominant resource in developing countries, which remain relatively independent from large power grids. But most photovoltaic panels are made of semiconductors like silicon, whose high cost would rapidly scupper plans to commercialize personalized energy in poor countries. Which is why Nocera developed a workaround by further improving his water-splitting catalyst.

"There's a lot of cost going into the fabrication of the photovoltaic panel. If I could show there was a way to integrate the silicon directly on the catalyst, I wouldn't need a panel," he says. That is precisely what he showed to a room full of scientists and engineers at a March 2011 meeting of the American Chemical Society in Anaheim, California. The demonstration doubled as a preview to a 2011 PNAS paper describing his version of an artificial leaf (9). Based on the oxygen-evolving complex of leaves, Nocera's device is composed of a slender film the size of a business card that bears crystalline silicon cells covered with a layer of indium tin oxide and containing his catalysts. As sunlight hits a beaker of water into which the leaf is immersed, oxygen and hydrogen bubble up from separate sides of the leaf. By directly placing his catalysts on the silicon, Nocera obviated the need for a photovoltaic panel. "This is really what I started out to do in Gray's lab—to make an unsupported device that could split water with nothing else but sunlight," Nocera says. In laboratory settings, Nocera showed, the artificial leaf worked continuously for three days. Nocera has struck a partnership with Indian businessman Ratan Tata to help harness solar energy in parts of rural India, and he hopes that a prototype artificial leaf might be ready for use in people's homes within a few years.

Nocera's efforts to harness solar energy earned him a place in *Time* magazine's 2009 list of the 100 most influential people, an honor that he shared with US Secretary of Energy Steven Chu. "The recognition was noteworthy, because we were among the few scientists who made the list that year," Nocera recalls. His commitment to solving the energy crisis runs beyond the often-closeted world of academia. To help demystify scientific efforts to use solar energy to solve the energy crisis, Nocera has partnered with the MIT Museum and the Boston Museum of Science, mounting exhibits that have enthralled visitors. "People often think that cool discoveries are made by technocrats. What they don't get is that they are enabled by basic science," Nocera says. "My goal is to help people see the road between basic science at places like MIT and technology in the real world."

Prashant Nair, *Science Writer*

1. Winkler JR, Nocera DG, Yocom KM, Bordignon E, Gray HB (1982) Electron-transfer kinetics of pentaammineruthenium(III)(histidine-33)-ferricytochrome c. Measurement of the rate of intramolecular electron transfer between redox centers separated by 15 Å in a protein. *J Am Chem Soc* 104:5798–5800.
2. Nocera DG, Winkler JR, Yocom KM, Bordignon E, Gray HB (1984) Kinetics of intermolecular and intramolecular electron transfer from ruthenium (II) complexes to ferricytochrome c. *J Am Chem Soc* 106:5145–5150.
3. Nocera DG, Gray HB (1981) Electron transfer chemistry of the luminescent excited state of octachlorodirhenate (III). *J Am Chem Soc* 103:7349–7350.
4. Wambaugh J (1983) *The Delta Star* (Bantam Publishers, New York).
5. Ciamician G (1912) The photochemistry of the future. *Science* 36:385–394.
6. Lewis NS, Nocera DG (2006) Powering the planet: Chemical challenges in solar energy utilization. *Proc Natl Acad Sci USA* 103:15729–15735.
7. Kanan MW, Nocera DG (2008) In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co2+. *Science* 321:1072–1075.
8. Dincă M, Surendranath Y, Nocera DG (2010) Nickel-borate oxygen-evolving catalyst that functions under benign conditions. *Proc Natl Acad Sci USA* 107:10337–10341.
9. Pijpers JJ, Winkler MT, Surendranath Y, Buonassisi T, Nocera DG (2011) Light-induced water oxidation at silicon electrodes functionalized with a cobalt oxygen-evolving catalyst. *Proc Natl Acad Sci USA* 108:10056–10061.