# From Solar Fuel Back to Electricity

By Marcus Woo


**Burning clean hydrogen, Honda's new FCX Clarity is now available for a three-month lease running at about $600 a month. But before you rush out to get one, note that the car is only available to those living near hydrogen-fuel stations in the Southern Californian cities of Torrance, Santa Monica, and Irvine.**

This summer, a new fuel-cell car will be hitting the streets of Los Angeles. Instead of belching out carbon dioxide and toxic fumes, this car—running on hydrogen gas—releases nothing but water. Honda's FCX Clarity is now being leased to a limited number of people who live in those parts of Los Angeles equipped with hydrogen-fuel stations. California has approximately two dozen hydrogen-fuel stations, about half of which are in Los Angeles. Boasting an equivalent gas mileage of 68 miles per gallon and a 270-mile range, the car is part of the nation's push toward fuel-cell technology to reduce foreign-oil dependence and to combat climate change. In his 2003 State of the Union speech, President George W. Bush introduced the Department of Energy's Hydrogen Fuel Initiative. With a 2007 budget of $274 million, the program aims to develop the production, storage, and delivery of hydrogen, as well as fuel-cell technology for vehicles and stationary uses.

While the buzz surrounding fuel cells has centered on fancy new cars, transportation is not the only thing fuel cells are good for. Fuel cells are not an energy source, but rather an efficient and, most importantly, clean way to convert chemical energy—in the form of hydrogen, methanol, or methane, for instance—into electricity. "It's a direct competitor to any other kind of power plant," says Sossina Haile, professor of materials science and chemical engineering. Haile's lab is among the leaders in fuel-cell technology. Recently, the lab has made several major advances, developing materials for record-breaking and potentially revolutionary fuel cells that, one day, may help power the world.

When a fuel cell runs on carbon-based fuels, it converts the energy stored in chemical bonds into electricity in a much cleaner and more efficient way than combustion does, reducing the amount of carbon dioxide emitted per unit energy. Thus fuel cells could serve as an important intermediate in the transition toward an alternative-energy economy.

But the ultimate goal, of course, is to use only clean fuels. Haile envisions putting a fuel-cell plant next to a solar power facility that would produce hydrogen fuel. In addition to producing electricity, solar power splits water into oxygen and hydrogen. The hydrogen, then, would be put into the fuel cells, which recombine it with oxygen to recover the stored energy. So at night, when photons are lacking, the fuel cells would provide clean power. "It's like having the sun in your back pocket," Haile says. "You use it when you need it."

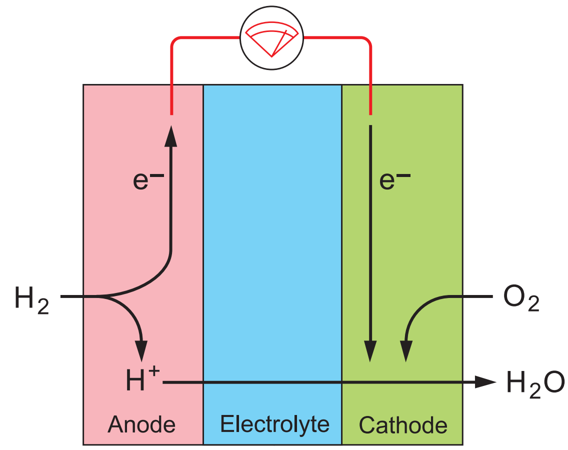
## Which Fuel Cell Would Goldilocks Choose?

"Fuel cells combine the best of batteries and the best of combustion engines," Haile says. Like a battery, fuel cells operate via a clean, well-controlled reaction. But like a combustion engine, fuel cells are easily refueled—you don't have to wait hours for one to recharge. Even better, a tiny fuel cell is just as efficient as a giant one. A coal-fired power plant, on the other hand, has to reach a certain size before it attains a decent efficiency. Since a small and therefore cheap fuel cell is just as good as a big and therefore expensive one, you don't have to invest a lot of money to get an efficient power plant. "You can buy whatever your capital allows you to," Haile says. "In that regard, it's very useful for the developing world, which is in desperate need of electricity, but does not have the capital to invest in large power plants."

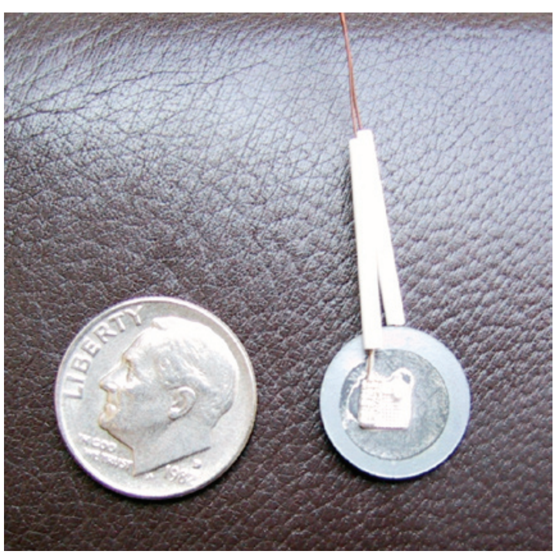
A fuel cell is based on a reaction in which a fuel, such as hydrogen, and oxygen produce water and energy. Left alone, hydrogen and oxygen "want" to join together as water and acquire a lower overall energy state—always nature's preference. A fuel cell controls this reaction and channels the energy into electric current. There are zero emissions—neither greenhouse-causing carbon dioxide (when the fuel is hydrogen) nor toxic by-products like nitrous oxide or sulfuric oxide.

The cell separates the hydrogen from the oxygen with an electrolyte, a material that allows only ions to pass through. The hydrogen still wants to react with oxygen, but the only way it can do so is to lose its electrons and become ionized. The electrolyte acts as a gatekeeper of sorts, preventing molecular hydrogen from going straight to the oxygen and reacting. Instead, the electrolyte only allows the hydrogen ions—protons—to pass. Meanwhile, the electrons flow out through a circuit, creating the desired electrical current, and continue to the other side of the cell where the oxygen is. Called the cathode, this is where the protons, electrons, and oxygen react to form water vapor.

When using fuels other than pure hydrogen, the reactions are more complicated, but the principle of combining hydrogen with oxygen to create water and energy is the same. In a methanol-based fuel cell, for example, methanol reacts with water




**How a simple hydrogen fuel cell works. In the anode, hydrogen gas is split into protons and electrons. The protons cross the electrolyte membrane while the electrons generate electrical current. At the cathode, the electrons rejoin the protons, and along with oxygen, react to form water.**




**At just over a centimeter in diameter, this prototype fuel cell is made with a nickel and cerium-oxide anode, cerium-oxide electrolyte, and a barium-strontium-cesium-colbalt-iron-oxide cathode. The cathode is made from a new solid-oxide material that enables the fuel cell to give record power outputs for operation at intermediate temperatures.**

at the anode, producing carbon dioxide, hydrogen ions, and electrons.

The key part of the fuel cell is the electrolyte, which determines the fuel cell's operating temperature. Temperature, in turn, determines how fast the reaction happens. The higher the temperature, the more the molecules and ions scurry about, and the faster the reaction and the more efficient the fuel cell. The operating temperature can be lowered, however, by using catalysts to speed up the reactions.

A car needs a fuel cell that works at a relatively low temperature. It would take too long to warm up your engine to 1,000°C every time you go to the store to pick up a loaf of bread. The latest fuel-cell cars, such as the FCX Clarity, use a cell made with polymer electrolyte membranes—also called proton exchange membranes, or PEMs—which operate at temperatures of 70°C to 90°C. The membrane works by allowing water molecules to ferry protons from the hydrogen side, called the anode, to the oxygen side, the cathode. Embedded in the membrane are pockets of water, and when a water molecule acquires a proton, it becomes an ion called hydronium, which crosses the membrane into the cathode and delivers the proton. What's difficult is to maintain a balance of water between the anode and cathode, ensuring that the water molecules return to the anode side after the protons are delivered. Another downside is that the membrane is permeable to methanol, requiring major feats of engineering to get this fuel to work with PEM fuel cells. If the methanol goes directly to the oxygen, electrons aren't stripped and no electric current is made. Instead, the methanol just burns—sometimes quite vigorously. And finally, because a PEM cell has to run at low temperatures—otherwise the water would evaporate—it's less efficient, even with catalysts.

Current technology demands that the catalyst be made from precious metals like platinum. If all the vehicles in the United States ran on PEM fuel cells as they're currently configured, 25 million kilograms of platinum would be needed. This is a problem, as the estimated supply of all the world's platinum is only 32 million kilograms. "We might free ourselves from having to import petroleum," Haile says, "but then we would simply become a platinum-importing nation."

The highest-temperature fuel cells, on the other hand, don't need catalysts at all. But, they cost a lot more to make because materials that can withstand high temperatures during operation require high temperatures—and therefore lots of energy—to process. If some fuel cells are too cold and others too hot, would something in the middle be just right? Fortunately, there are fuel cells that operate at in-between temperatures, including phosphoric-acid and alkali fuel cells. Phosphoric-acid fuel cells were promoted in the 1990s, Haile says, but they were never able to produce enough power. The electrolyte was corrosive, and the platinum catalyst would become caked in phosphoric acid. Alkali fuel cells are very efficient, but they react quickly with carbon dioxide and make solid potassium carbonate, which kills the cell. This not only ruled out carbon-containing fuels, such as methane or methanol, but keeping a fuel cell protected from carbon dioxide in the atmosphere is expensive. Alkali fuel cells have found their niche, though. They power NASA's spacecraft, since there's no carbon dioxide in space.

A few years ago, Haile's group came up with a completely new kind of fuel cell—one that even Goldilocks might like. Using electrolytes made from materials called solid acids, the researchers have built fuel cells that operate at a "warm" 250°C. This is not hot enough to be expensive, but still warm enough to be efficient without needing a lot of catalysts. At first, they used a compound called cesium hydrogen sulfate, which is physically similar to table salt. But when they tried their new fuel cells, they got something no one would want on any dinner table.

At first, they used a compound called cesium hydrogen sulfate, which is physically similar to salt. But when they tried their new fuel cells, they got something no one would want on any dinner table.

### A Radical Idea, Rotten Eggs, and a Start-Up

After reaching a certain temperature, solid acids become conductive, enabling protons to travel through the material. In cesium hydrogen sulfate ($CsHSO_4$), the bisulfate group ($HSO_4^{-2}$), made from a sulfate and a hydrogen ion, forms a tetrahedron, or four-sided pyramid. At ambient temperatures, the pyramids are aligned, like soldiers at attention. But when you crank up the heat, they start to fidget, and eventually become completely disordered. They twitch fast—reorienting themselves every $10^{-11}$ seconds or so—and when they do, they can pass a hydrogen ion to an adjacent bisulfate group. Protons are handed off from one group to another as they make their way through the electrolyte. They don't need an intermediary like hydronium ($H_3O^+$) to give them a lift. "Perhaps it's because I'm originally from Ethiopia that I like to say that our protons run across the electrolyte on their own two legs—they're marathon runners," Haile says. "They don't need to have a big limo, the water molecule, to carry them around."

Two former graduate students, Calum Chisholm (MS '01, PhD '03) and Dane Boysen (MS '01, PhD '04) played key roles in developing the cesium-hydrogen-sulfate fuel cell. The cells reached reasonable power densities, Haile says, but then after about a day—or sometimes just a few hours—they would die. This was a puzzle until the researchers smelled something rotten. "It took a long time to figure out that the sulfur in the sulfate was turning into $H_2S$, which is hydrogen sulfide, a fantastic poison. Fortunately, your nose is very sensitive to it, and that was how—once we pulled the test station out of the fume hood—we realized we were making it." (Hydrogen sulfide is also responsible for the smell of rotten eggs.) "It's bad, bad news for the fuel-cell catalyst. So we had to go back to the drawing board."

Haile and Boysen knew, from a separate study, that cesium hydrogen phosphate, another solid acid with similar structure, became conductive at a similar temperature. But some other researchers argued that the conductivity was due to dehydration: heating the material squeezed out water molecules in the form of hydronium and hydroxide ($OH^-$) ions, they said, making the material conductive. The debate raged in the literature for 20 years over whether cesium hydrogen phosphate undergoes a "superprotonic" transition the way cesium hydrogen sulfate does.

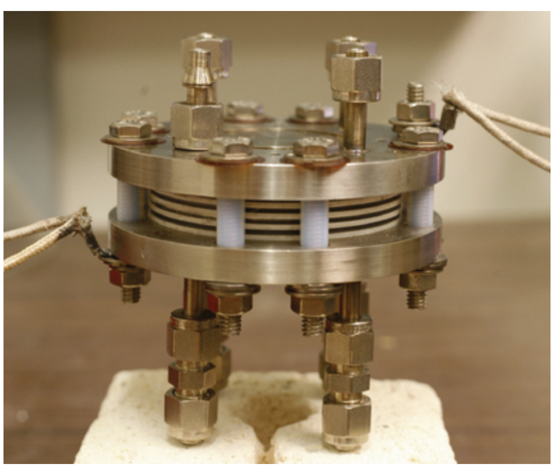
Haile's group reasoned that if conductivity were not due to dehydration—and instead was an inherent property of the material—keeping the humidity high while heating the material would still cause a transition to high conductivity. And indeed, when they heated their samples in a high-water-vapor atmosphere, they saw the transition. Varied groups came up with varied results because they didn't keep well-controlled conditions, Haile says. Experimental results in humid Moscow, which favored

the "superprotonic" explanation, for instance, differed from those in the drier climate of Pasadena, which initially favored the dehydration explanation. Haile says that over the last few years they've laid the debate to rest, showing that cesium hydrogen phosphate becomes superprotonic upon reaching 230°C.

Now that they knew the material behaved properly, the next step was to build a fuel cell. Unlike the sulfate cell that lasted for a day, the new one lasted for more than 100 hours. "In academic timescales, this is basically a lifetime," Haile notes. They got a power density of 50 milliwatts for every square centimeter of material—a scientific achievement, but too low for practical use. The PEM technology used for fuel-cell cars, for example, has power densities of one watt per square centimeter (watt/cm$^2$).

Fortunately, increasing power densities is relatively simple. All they had to do was make a thinner electrolyte to minimize the electrical resistance within the cell. Their prototype in 2004 had an electrolyte membrane that was 250 microns thick. They've now reduced the thickness to only 25 microns, and got 0.4 watts/cm$^2$, within a factor of two of the best fuel cells—which operate at much higher temperatures or use a lot of precious-metal catalysts.

**Top and bottom: Superprotonic's solid-acid fuel cell, based on technology developed in Haile's lab. This design requires 2.5 grams of platinum catalyst, costing about $126, to run a 60-watt lightbulb.**



Former postdoc Tetsuya Uda, who is now a professor at Kyoto University, then tested the device with different fuels. One of the problems with PEM cells is that they're permeable to methanol. But because solid acids are, well, solid, methanol can't penetrate the electrolyte. After the researchers added a so-called reformer catalyst, which extracts hydrogen from potential fuels without needing any precious metals, their solid-acid fuel cell performed with methanol about as well as it did with pure hydrogen, and much better than PEM fuel cells did with methanol. The fuel cell also worked with ethanol—popular these days as a biofuel—and a related potent potable, vodka.

The 2001 sulfate-based prototypes could power a 60-watt lightbulb for $2,000, Haile says. It's now down to $125, which still isn't exactly a bargain. The high cost is primarily due to the platinum catalyst, but Haile says they can further reduce the amount of platinum they need. One way to do this is to use platinum nanoparticles. Because of their tiny sizes, the surface area where the reaction occurs goes way up, and a smaller amount of platinum is just as effective.

Solid-acid fuel cells are immune to another problem that plagues their liquid and wet-polymer-electrolyte brethren. The platinum particles don't get coarse. The liquid causes the smaller particles to dissolve and the bigger ones to grow, reducing their total surface area and thus the effectiveness of the catalyst.

Haile hopes to eliminate the need for platinum completely. By pushing the operating temperature up to 250°C and beyond, one could, in principle, build a fuel cell that runs efficiently enough that a catalyst isn't needed at all.

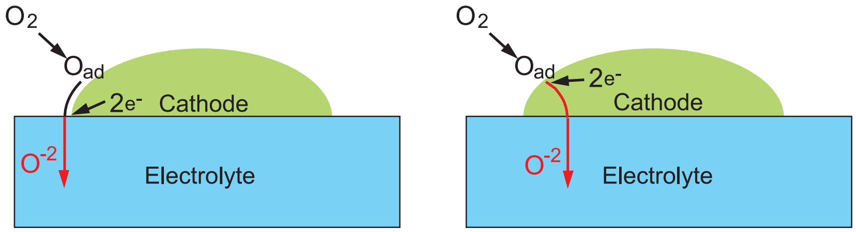
Other than a couple of groups in Japan and Russia who have dabbled in solid-acid fuel cells, Haile's lab is the only one doing significant work, she says, since this technology is such a major departure from the norm. "We're a little too far ahead for anyone else to try to get into the game." But the novelty of the technology also means they have a lot of learning to do. While dozens of labs around the world have been studying other fuel-cell technologies for decades, no one knows much about solid acids. "We're starting out from complete scratch, with no knowledge base whatsoever," Haile remarks. "That means there's huge potential, but very little to build upon."

In 2003 Chisholm, Boysen, and Uda founded a company called Superprotonic Inc. (SPI) to develop solid-acid fuel cells. They're looking at how to scale up the cells made in the laboratory to fuel-cell stacks that can power real devices. Early this year, the company delivered pre-commercial prototypes to customers for testing. The company is making fuel cells for a variety of applications, including auxiliary power units for long-haul diesel trucks and power units that generate heat and electricity for homes.

Meanwhile, if anyone else is looking to start a company, Haile's lab has yet another fuel cell that's ready for commercial development.

## Send in the Oxygen

Solid-oxide fuel cells (SOFCs) operate at the highest temperatures, up to 1,000°C. Along with low-temperature fuel cells such as the PEMs, SOFCs have enjoyed high levels of investment and development in the last few years, Haile says. Because high temperatures render catalysts unnecessary and spark fast reactions, they're the most efficient, although high temperatures also hike up




**In a solid-oxide fuel cell, oxygen is captured by adsorption on the cathode surface. The adsorbed oxygen ($O_{ad}$), however, can only join with the electrons in places where the resulting oxygen ions have somewhere to go. (Eventually, of course, they want to pass through the electrolyte and react with the hydrogen). In previous fuel-cell designs (left), oxygen ions could travel through the electrolyte but not through the cathode, so adsorbed oxygen had to diffuse along the surface toward the intersection of the cathode, electrolyte, and air. But the new cathode material (right) does allow oxygen ions to pass through, so the adsorbed oxygen can combine with the electrons anywhere on the cathode surface, increasing the fuel cell's power output.**

the manufacturing cost. Well over a decade ago, the Department of Energy determined that the SOFCs at the time, which ran at 800 to 1,000 degrees, were too expensive, and said that the operating temperatures had to be brought down to 500 to 800 degrees.

Lower temperatures slow the ions trying to cross the electrolyte membrane, but even when thinner membranes were developed to solve this problem, the power output of the fuel cell was too low. What was needed was a new cathode material.

On the cathode side, oxygen has to react with electrons to become oxygen ions. The problem is that the reaction can only happen where the oxygen ions have a place to go: the corner where the cathode joins the electrolyte (see figure above). The fuel cell has a small number of these sites, so the reaction proceeds slowly. Researchers in Haile's lab thought they could speed things up if they found a new cathode material that allowed oxygen ions to pass through, which would make the cathode's entire surface available. In 2003, they eventually found that barium strontium cobalt iron oxide (written as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$), which Haile's graduate students call alphabet soup, did just that.

The exact details as to why this material works so well aren't fully understood, but the reason has to do with inherent defects in the crystal structure. "What's quite phenomenal about this material is that normally you would expect three oxygen atoms in each crystal unit," Haile explains. "As far as we can measure, one out of six oxygen atoms are missing, and yet it stays together. I find this exceptionally fascinating." These missing oxygen atoms, called oxygen vacancies, allow other oxygen ions to travel through, boosting the fuel cell's reaction rates.

The new fuel cell produced one watt/cm$^2$ at only 600°C, a record at this intermediate temperature. This technology, Haile adds, is ready to leave the lab and become a commercial enterprise. Unlike the solid-acid fuel cells, whose uniqueness required a start-up company to develop it, solid-oxide fuel-cell technology is established enough that many other companies could easily pick it up. This hasn't happened yet, but Haile's hopeful that someone will license it and work with them to develop commercial fuel cells. As with many other alternative-energy technologies, the key with fuel cells is making them cost effective. "They're viable today," Haile says. "It's just, at what price?"

Both solid-acid and solid-oxide fuel cells are technologies for stationary power. Fuel-cell cars may get more press, but the reality is that portable fuel cells pose the most engineering hurdles, Haile says. Not only are stationary fuel cells closer to commercial viability, they are more important for solving the energy and climate crises. While cars contribute a large fraction of the world's carbon emissions, they're not the biggest problem. Stationary fuel-cell technology has the best chance of changing the future of the planet. "That's where you have the biggest environmental impact in terms of global warming," she says.

The researchers develop their fuel cells without any particular fuel in mind. "I like to say we're fuel agnostic," Haile says. Since the question of fuels quickly enters into the messy realm of policy, and no one knows which fuel will turn out to be the best choice, her lab focuses on the engineering. In any case, fuel cells are not an energy source, as we saw earlier. Instead, they're a way to harness chemical energy, and if that energy isn't produced cleanly, you're not solving the problem—just shifting it to another place. No technology is a solution by itself because each type only tackles one aspect of the energy and climate problem, she says. "Fuel cells are not an energy solution—they're just part of it."

Haile says fuel cells will eventually reach wide, commercial use—the question is just when. But when asked to speculate, she laughs and demurs. "I've been asked that for the past decade, so I better not answer." □

*Professor of Materials Science and Chemical Engineering Sossina Haile earned her BS (1986) and PhD (1992) from MIT, and her MS (1988) from the University of California, Berkeley. Prior to joining Caltech in 1996, she was an assistant professor at the University of Washington, Seattle. From 1991 to 1993, Humboldt and Fulbright Fellowships took her to the Max Planck Institute for Solid State Research in Stuttgart, Germany. She has received numerous awards, including the NSF National Young Investigator Award, the J. B. Wagner Award of the High Temperature Materials Division of the Electrochemical Society, the Coble Award from the American Ceramics Society, and the Robert Lansing Harding Award of the Minerals, Metals, and Materials Society.*

PICTURE CREDITS: 32 — Honda; 33, 36-39 — Doug Cummings; 33, 35 — Haile lab