# Swiss Rolls and Oreo Cookies

by Sossina M. Haile

> *"A simple chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car producing only water, not exhaust fumes. With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom so that the first car driven by a child born today could be powered by hydrogen, and pollution-free. Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy."*
> President George W. Bush, State of the Union Address, January 2003.

> *"The Stone Age didn't end because we ran out of stones."* Anon.

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**Above: Sir William Grove's 1839 gas battery, the first fuel cell, contrasts with Sossina Haile's miniature solid-acid fuel cell, aka "Oreo cookie," opposite.**

Fuel cells are taking the country by storm. Even the president of the United States is talking about them. While automobile makers compete to make the first mass-market cars running on hydrogen or methanol, fuel-cell-driven power plants have already been installed in commercial buildings, hospitals, and homes. And research departments—mine included—are developing miniature versions that can fit in your pocket and be refueled with a shot of methanol or lighter fluid. Invented in 1839 by Sir William Grove, a Welsh lawyer and amateur physicist, fuel cells were more or less forgotten until NASA developed them for the space program in the 1960s. Why so much interest now?

World energy consumption is rising dramatically, and most of this energy is generated by the combustion of fossil fuels. Although there are enough reserves of oil, gas, and coal to last well into the next century, there's a lot of geopolitical uncertainty surrounding their supply (a major issue at the moment), and they're causing an environmental catastrophe. The global increase in atmospheric carbon dioxide levels is truly very worrying. These levels were stable until the industrial revolution in the early 1800s, then began to rise rapidly. It's quite clear that there's an anthropogenic reason for this, in part because of our fossil-fuel consumption, but also in part because of the way we've consumed the forests that would otherwise have absorbed the carbon dioxide. The consequence in terms of global warming is that there's been a small but significant increase in atmospheric temperatures since 1880. What impact will this have? People are still debating that question, but do we want to do this experiment? I'm fairly certain I don't. Oil consumption per capita in the industrialized world is four times the global average, so it's really incumbent on us in the developed world to help solve this problem.

Are fuel cells a possible solution? They're certainly very attractive, because they are much more efficient than combustion engines. Even if they run on fossil fuels, the amount of carbon dioxide produced per action taken (such as per mile traveled or per unit of electricity generated) is much smaller. Fuel-cell efficiencies can be as high as 60 percent, even 80–90 percent if combined with hot-water cogeneration, while combustion engines have much lower efficiencies, on the order of 10–30 percent. And fuel-cell efficiency is entirely independent of size, unlike combustion engines, which become more efficient the larger they get. So fuel cells are suitable for all sorts of applications, ranging from big stationary power plants to portable electronics. In terms of the environment, not only are carbon-dioxide emissions lower, but chemical reactions are very carefully controlled so that there are zero toxic emissions. Best of all, fuel cells are very well-suited to a hydrogen economy. Run on hydrogen, they are a truly zero-emission energy device.

How do they work? Hydrogen and oxygen put together will inherently react to form water, with the release of a lot of energy:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + energy.$$
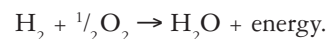
In the simple fuel cell shown on the following page, in which the fuel is hydrogen and the oxidant is oxygen, these two very reactive molecules are kept apart by an electrolyte, a material that lets only ions move through it. For the hydrogen to get to the oxygen, it has to turn into hydrogen ions, called protons ($H^+$). It does this by the reaction,
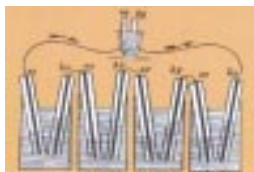
$$H_2 \rightarrow 2H^+ + 2e^-,$$

to give us two protons and two electrons. The protons travel through the electrolyte and react with the oxygen on the other side. There they pick up two electrons and give water as a by-product:
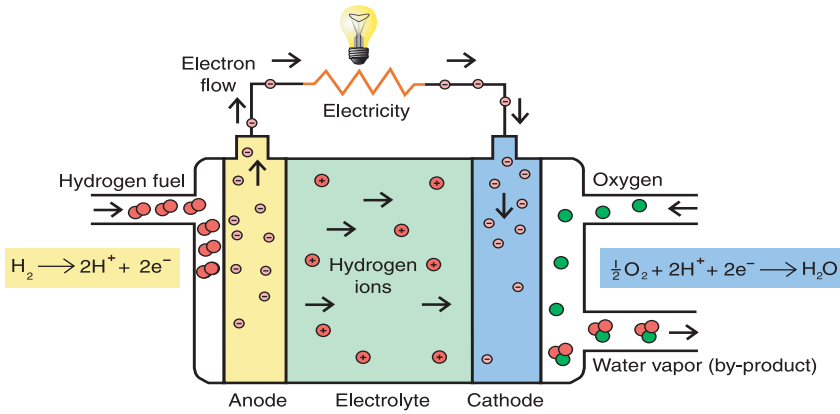
$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O.$$
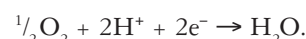
Electrons are produced on the hydrogen side (called the anode side, as in a battery) and consumed on

**How a simple fuel cell works.**



Electron flow

Electricity

Hydrogen fuel

$H_2 \longrightarrow 2H^+ + 2e^-$

Hydrogen ions

Oxygen

$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

Water vapor (by-product)

Anode        Electrolyte        Cathode

the oxygen side (the cathode side). When we connect the two sides with a wire, these electrons travel through the circuit and produce an electrical current that can power a device. (Without electrical contact between the anode and the cathode, no current flows and the hydrogen and oxygen remain unreacted.) This is similar to the way that a battery works, but fuel cells combine the best of batteries with the best of combustion engines—the best of batteries in that they have very well-controlled electrochemical reactions, so there aren't any dirty side-reactions that release pollutants, and the best of combustion engines in that they can be refueled. One thing to keep in mind is that a fuel cell is an energy *conversion* device, not an energy *source*. There are no toxic

emissions, there's no pollution, but we still have to get the fuel from somewhere.

The electrolyte, often called the membrane, has to function as an efficient ion transporter, but it also has to block electrons—if any electrons were to move across the electrolyte instead of going through the circuit, there would be a drop in voltage between the anode and the cathode. The electrolyte also has to stop fuel and oxidant gases from coming into direct contact with one another, as any direct chemical reaction would reduce efficiency. At the electrodes, on the other hand, the ions, electrons, and gases all need to get together in order for a reaction to occur. So the electrodes are often composites that incorporate a catalyst, an ion conductor, an electron conductor, and something that will form pores at high temperatures so that gases can get to and from the electrolyte. The combination of electrolyte (or membrane) and two electrodes (which include the catalysts) is referred to as a membrane-electrode assembly. When this assembly is put inside a complete fuel-cell "engine," sealants are used to keep gases from leaking at the edges of the membrane.

A number of things can affect the efficiency of a fuel cell. In our simple hydrogen-oxygen cell, a theoretical voltage of 1.2 volts should be generated from the anode to the cathode in the open-circuit state, that is, when no device is attached. Once we put in some device that draws power, the voltage starts to go down, as shown in the graph on the left. This occurs for a number of reasons: (1) even in the open-circuit state, the fuel may be finding pores in the electrolyte and leaking across to the other side (crossover); (2) at small currents, the reaction kinetics at the anode and cathode may not be able to keep up with the rate at which electricity is being drawn; (3) the ions may meet resistance in the electrolyte as we try to step up the amount of current, and can't travel across it fast enough to keep up with the electrons; and (4) as we try to draw a lot of current, the gases can't diffuse in and out of the electrodes quickly enough. At this point the voltage really drops and eventually goes down to zero. The power that the fuel cell puts out is simply voltage times current, and it turns out that the cell doesn't generate the maximum amount of power at the point where it is working most efficiently. We use a voltage-current, or polarization, curve such as the one on the left to measure a fuel cell's performance. High-efficiency, high-power fuel cells have polarization curves in which the voltage stays high for very large currents.
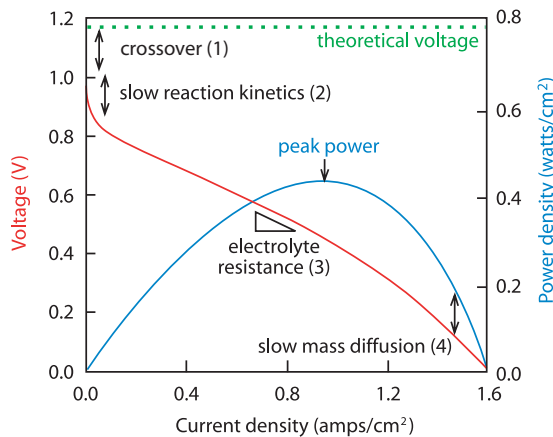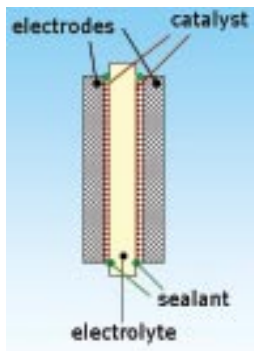
There are five main types of fuel cells, differentiated essentially by the type of electrolyte used. Different electrolytes transport ions with different effectiveness as a function of temperature, so that each of these types operates in a different temperature range. PEM fuel cells (PEM stands both for polymer electrolyte membrane and proton exchange membrane) operate at low temperatures of 90–110°C. These are the ones now being developed



electrodes    catalyst

sealant

electrolyte

Voltage (V)

Power density (watts/cm$^2$)

Current density (amps/cm$^2$)

crossover (1)

theoretical voltage

slow reaction kinetics (2)

peak power

electrolyte resistance (3)

slow mass diffusion (4)

**Above left: A membrane-electrode assembly. Above right: The performance of a fuel cell is measured by a voltage-current curve that plots the drop in voltage (red) as more and more current is drawn. The blue curve is the amount of power put out by the fuel cell at a given current (or voltage). The higher the point of peak power, the better the fuel cell.**

for use in cars, so there's a lot of excitement surrounding them. The type developed by NASA for the space program are alkali fuel cells that use a potassium-hydroxide electrolyte, and they operate at 100–250°C. They also supply the astronauts with drinking water, which is fine because the water generated is very pure. If you watched the movie *Apollo 13*, you may remember that fuel cells played a prominent role. A third type, phosphoric-acid fuel cells, are commercially quite well developed, and work at 150–220°C. Molten-carbonate fuel cells operate at a high 500–700°C, topped only by solid-oxide fuel cells at 700–1,000°C. The three types running at lower temperatures are fueled by hydrogen or possibly methanol, while the two high-temperature ones use hydrocarbons. At lower temperatures, reaction kinetics are slow, so one has to use very active and expensive catalysts based on platinum or other precious metals in the electrodes. Each type of electrolyte transports different ions, but in all cases the oxidant is oxygen (typically from air), and water is always a by-product. In some cases, carbon dioxide is also a by-product.

With all these different types of fuel cells, how do we pick the right one for a particular application? Temperature of operation is an important criterion. The low-temperature cells have the advantage of a very rapid start-up, so they're great as a portable source of power and can handle many on-off cycles. They're also easy to run as small-sized devices. But the low temperatures of operation mean they

can only be run on hydrogen or methanol—the only fuels that react readily at or below the boiling point of water—and the catalysts in the electrodes are easily poisoned by impurities in the fuel stream. These impurities stick to the catalysts and stop the hydrogen or methanol from reaching them. Fuel cells running at higher temperatures have the advantage of being very fuel-flexible, because everything reacts more easily. The electrocatalysts also become very active when they're hotter, so the overall efficiency is significantly higher. Their disadvantage is a long start-up time. It takes quite a while for a fuel cell to get to 1,000°C, which isn't very useful in a portable power unit. (Imagine how long you'd have to wait to get your car started on a cold morning.) Not surprisingly, then, these high-temperature fuel cells are mainly used in stationary power systems where they can be left on all the time.

There are now many, many, demonstration power units and vehicles using fuel cells. Phosphoric-acid fuel-cell power plants generating 200 kilowatts of electricity have been used by the military in field operations since 1995, and many more currently provide power for buildings and homes—there's even an 11-megawatt power plant in Japan. And a stationary 100-kilowatt solid-oxide fuel cell put together by Siemens Westinghouse operated at a car plant in the Netherlands without measurable degradation for over 20,000 hours. So this is very much a demonstrated and commercially viable technology.

Both Toyota and Honda recently announced the first roadworthy PEM-based fuel-cell vehicles. UC Irvine and UC Davis are each leasing a Toyota FCHV (fuel-cell hybrid vehicle), and the city of Los Angeles is leasing a Honda FCX (fuel-cell experimental vehicle). There's a reason these first demonstration fuel-cell vehicles are in California—the state has a zero-emissions automotive standard that is really driving the technology. California also has a number of hydrogen-refueling stations, which other states don't have as yet (apart from

one in Las Vegas, Nevada). The biggest barrier to the production of these cars for the mass market is cost, in the sense that the precious-metal catalysts are expensive, fabrication is costly, and the whole fuel-cell system is very complex. Another key issue is that there's a big uncertainty about the fuel infrastructure. How long will we continue to use gasoline? Is hydrogen going to be a reality, or will it be methanol? The White House is proposing a lot more money to build up a hydrogen refueling infrastructure, but administrations come and go, so will this really happen? Uncertainties like these are preventing car manufacturers from moving forward.

All fuel cells operate best on hydrogen, but even though it's the cleanest fuel possible, using it is a real challenge. In terms of watt hours per gram (Wh/g), a unit that measures how much inherent

tank will be hydrogen, and the numbers don't get much better for the adsorbant materials. For an automobile that does the equivalent of 20 miles per gallon of gasoline (at 0.6 miles per kilowatt hour of hydrogen) to have a 350-mile range, you need to carry 18 kilograms (40 pounds) of hydrogen. Add to that the weight of the tank itself, and you're at a hefty 720 kilograms (1,600 pounds). Most of the fuel-cell vehicles today have a smaller range, and rely on having a much higher efficiency rather than carrying a large amount of hydrogen around. The Honda FCX, for example, stores 3.75 kilograms of hydrogen in high-pressure tanks and has a range of 220 miles. Another challenge with using hydrogen is that because it is such a small molecule, it easily diffuses through many materials and is lost, just as the helium in a child's floating balloon eventually diffuses away.






**The Honda FCX, left, is a zero-emission four-seater with a 220-mile range; this one was the pace car in the recent L.A. Marathon. It's pretty standard inside, above, but there's a sleek electric motor under the hood (the fuel cell sits under the middle of the body), and the fill pipe looks different, right.**

energy is in the fuel, hydrogen at 33 Wh/g is much better than diesel fuel (12.7 Wh/g), gasoline (12.9 Wh/g), and methanol (6.2 Wh/g), but because it's a gas it takes up a lot more room. This is why methanol, even though it has less energy per gram than hydrogen, is considered by some a much better fuel choice for a fuel-cell vehicle. But let's say we did want to use hydrogen. How can the large volume needed to fuel a car be packed into a portable container like a car fuel tank? The choices are to use materials that adsorb large amounts of hydrogen—some metals and some forms of carbon—or to put it into a high-pressure tank, which is the way hydrogen is carried on most demonstration fuel-cell vehicles. Many people won't be comfortable with having a tank containing hydrogen compressed at 5,000 pounds per square inch in their automobile but, more importantly, the tank itself will weigh a lot because the walls have to be thick to hold this much pressure. Typically, only 2–3 percent of the weight of a full

And then there's the question of where to get the hydrogen from. It's possible to generate hydrogen by electrolysis:

$$\text{Electricity} + H_2O \rightarrow H_2 + {}^1/_2 O_2,$$
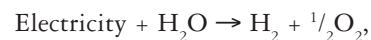
which is almost the reverse of what happens in a fuel cell, but it's an expensive procedure. And surely it defeats the whole purpose of a fuel cell if you have to use electricity, probably generated from fossil fuels, to make the fuel for it—though it could perhaps make sense if solar, wind, or water power were used. The other way to get hydrogen, and the way it's done commercially today, is to react some sort of hydrocarbon fuel with water using a process called the reforming reaction, which produces carbon dioxide and hydrogen:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2.$$
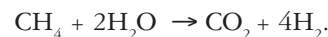
If the reaction does not go to completion, carbon monoxide is produced as well, and if the hydrocarbon fuel is not very clean, sulfur compounds

Most of the space inside one of those 200-kW power plants in Alaska on page 21 is taken up by auxiliary equipment. The blue-wrapped fuel-cell stack (unwrapped, left) is flanked on one side by fuel-processing, heat, and water-management systems, and on the other by power-conversion equipment.
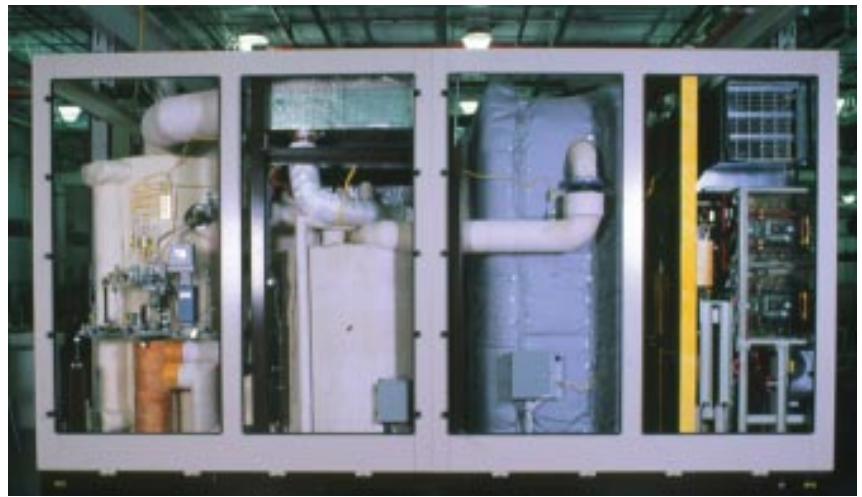
also are mixed with the hydrogen. Both carbon monoxide and sulfur compounds have to be removed before the fuel is introduced to the fuel cell.

All of this leads to a great deal of complexity. The basic fuel cell is a really simple, beautiful little electrolyte; but then we add electrodes to extract the electricity, catalysts to get the reactions to occur, and sealants to prevent contact between the fuel and oxidant. To produce more power we join several cells together in series to make a stack, and then we put the stack into a large system with numerous components that reform the hydrocarbon fuel; deliver the hydrogen in the right way; ensure the temperature and humidity are right; get rid of unwanted gases; and convert the electricity from direct to alternating current. And so we end up with a large and very complicated system. Fuel cells are not quite equivalent to batteries in their simplicity and ease of use—at least not yet.

The limitations of today's fuel-cell materials place severe design constraints on the overall system. If we can improve the materials, and come up with novel integrated designs to make everything much less complex, we can have a major impact on what the system looks like. That's what my group at Caltech is concentrating on.

Let me tell you first about our project to put a single-chamber, single-oxide fuel cell inside a

clever little heat exchanger to make a small, integrated micropower generator. We're collaborating on this DARPA-sponsored program with the Lawrence Berkeley National Laboratory, the University of Southern California (USC), and Northwestern University. Our goal is a portable box measuring about two centimeters per edge, and weighing as much as a golf ball, that can operate on propane or butane (the fuel used in Bic cigarette lighters) to give 200 milliwatts of power, enough to run a portable radio. Propane and butane have more energy per gram than methanol, are easier to handle than hydrogen, and have no storage difficulties.

How can we make a small box containing a stack of single-oxide fuel cells running at very high temperatures that is cool to the touch? That's where the heat exchanger comes in. In a linear counter-flow heat exchanger, the products leaving a combustion chamber exchange heat with the incoming reactants by flowing through a tube-like device so that the reactants are warmed up while the products are cooled down. If we roll up a linear heat exchanger into a coil, we get what we call a Swiss roll. We can even roll it up again and get a toroidal Swiss roll. This concept has been exploited by Paul Ronney at USC to make all sorts of microcombustors. It's quite easy to maintain a
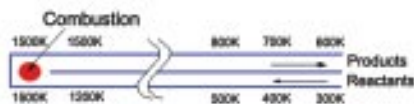


By rolling up a linear heat exchanger, we get a Swiss roll (center), which could be further rolled into a toroid, like the one on the right designed by Paul Ronney at USC.
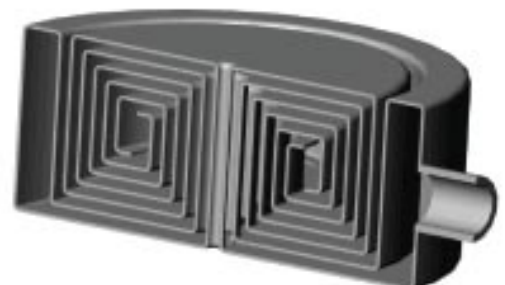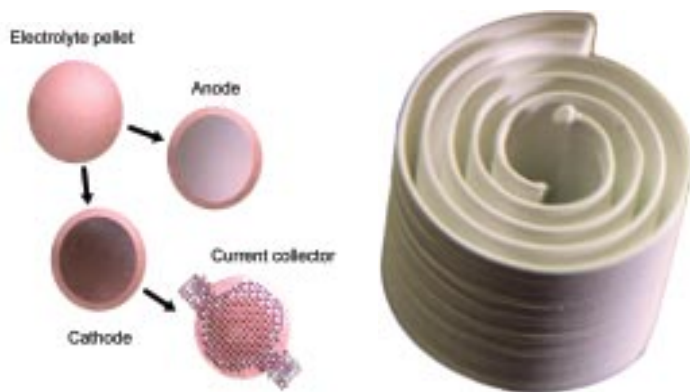
Above left: To make one of our single-chamber, solid-oxide fuel cells, a dime-sized electrolyte pellet, 500 microns thick, has anode and cathode materials deposited on each face before silver current collectors are attached. We're going to squeeze a stack of these fuel cells into the center of one of Robert Shepherd's Swiss rolls, above right. In the scanning electron micrograph on the right you can see that we've achieved an electrolyte that's only 20–30 microns thick. We did this by using a mechanically strong anode material and depositing the electrolyte and cathode materials onto it.

temperature of 500°C in the center of one of these while leaving the exterior close to room temperature. This is exactly what we need for operating a micro single-oxide fuel cell. A catalytic afterburner next to the fuel cell to burn off any unused fuel will also make sure the temperature in the center remains what we'd like it to be.

Now how about that single-chamber, single-oxide fuel cell? You'll remember that in a conventional fuel cell, fuel and oxidant have to be kept separate. But by using very well-designed catalysts at the electrodes, it has now become possible for them to be mixed together in the same chamber, which makes the design much less complex and eliminates the need for sealants to separate fuel and oxidant.
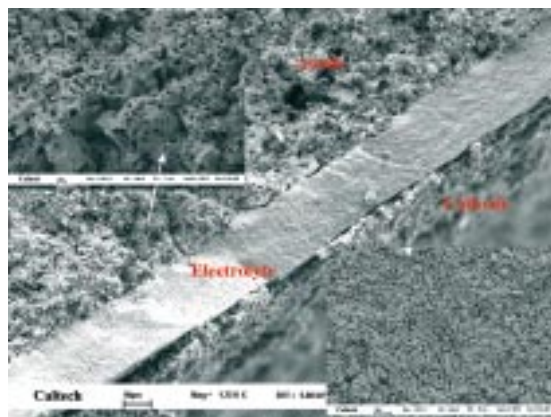


Sealants are very problematic in fuel cells that get turned on and off frequently, because they can't handle the changes in thermal expansion and contraction, and tend to crack. My group can't take the credit for the single-chamber innovation, but we're working on adapting it for our integrated micropower generator. The way it works is that at the anode, the fuel (in this example, methane) reacts with oxygen to give carbon monoxide and hydrogen, a process known as partial oxidation:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2.$$
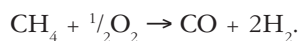
A high concentration of carbon monoxide and

hydrogen builds up at the anode side and, in principal, none builds up at the cathode side. The anode can continue to do its conventional electro-chemical reactions that generate electrons,

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad \text{and}$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^-,$$

while at the cathode, through the conventional electrochemical reduction reaction, electrons are consumed:

$$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-}.$$
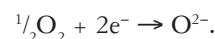
The fuel and oxidant can only be together in the same chamber as long as the temperature is low enough to prevent any gas-phase reaction. Hydrogen and oxygen as gases react explosively, so we have to be careful that we don't cause the experiment to explode by letting it get too hot. We also have to make sure all the reactions occur at the surface of the catalyst.

Our development effort is to come up with anodes that catalyze partial oxidation and electro-oxidation, and cathodes that catalyze electrochemical reduction but don't allow any oxidation reactions to occur. It's quite a challenge. We're also trying to make the electrolyte as thin as possible, between 5 and 50 microns, to minimize the resistance losses I mentioned earlier. The paper this is printed on is about 75 microns thick, so our membranes will be thinner. They will be made of a ceramic material similar to the electrolyte used in a conventional single-oxide fuel cell, and will be supported on one side by a thick but porous anode to provide mechanical strength and let the gases in and out, and on the other side by a very thin and porous cathode. In terms of performance, the fuel cell needs to provide about 75 milliwatts per square centimeter in order for us to meet our target of 200 milliwatts for the overall device. It will have an operational temperature of about 500°C.

So far we've optimized the composition of the various components, the fabrication routes, and the gas flow and composition, and our fuel cell can reproducibly reach close to the target power output, so we're happy with that. In terms of making a functional device, we also have to get this fuel cell to work inside the Swiss roll. As you can imagine, we've had a bit of a tough time getting the wires in and out without shorting the device. Once we learn how to properly wire things up, we plan on using the beautiful Swiss-roll structures being made by Robert Shepherd, a graduate student working with Professor Jennifer Lewis at the University of Illinois, Urbana-Champaign. All in all, it won't be very long before we have a micro single-oxide fuel cell for portable power.

My research group is also working on alternative electrolytes for low-temperature PEM fuel cells. The state-of-the-art membrane polymers used in these fuel cells, such as Nafion from DuPont, work because they're full of water regions. Water

molecules can pass through the electrolyte by moving from one water region to another, and protons hitch a ride by forming what we call hydronium ions:

$$H_2O + H^+ \rightarrow H_3O^+.$$
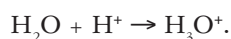
Once the hydronium ions get over to the cathode side, the protons jump off:

$$H_3O^+ \rightarrow H_2O + H^+.$$

The advantages of this material are that it has very high conductivity, flexibility, and strength. But water has to be recycled from the cathode back to the anode in such a way that the cathode isn't
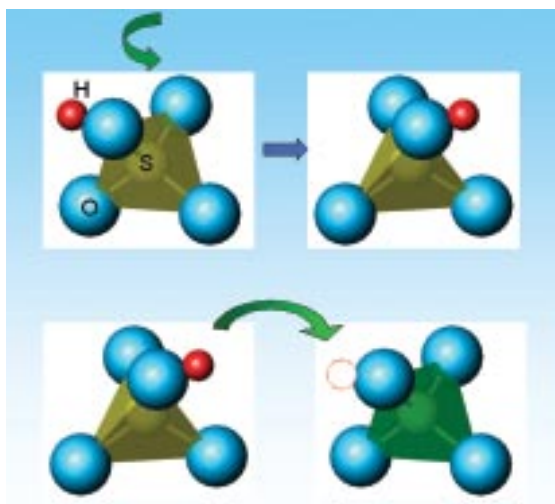


When solid acids are warmed, their bisulfate groups reorient, changing the spatial position of the red hydrogen atom so that it gets the chance to jump over to the next sulfate group.

flooded or the anode dried out, which really adds to the overall complexity. Moreover, the fuel cell has to be operated at temperatures below the boiling point of water so that it doesn't dry out, which means you can't take advantage of the fact that catalysts are more effective at slightly higher temperatures. There's also a higher likelihood the catalysts will be poisoned by impurities in the fuel stream at this low temperature: poisons like carbon monoxide desorb quite easily if the temperature is just a little bit higher. Another disadvantage of a



Polymer electrolyte membranes (PEMs) like Nafion, the cellophane-like material in the photo, have sulfonic acid side-groups that form interconnected watery regions within a Teflon-like matrix, through which protons can move from anode to cathode as hydronium ions ($H_3O^+$). The membrane-electrode assembly in the photo is the working heart of all PEM-based fuel-cell stacks.

polymer with a lot of water in it is that methanol can diffuse right through, which is a very serious problem if you want to use methanol instead of hydrogen as the fuel.

For the above reasons, and also because it would be advantageous for automotive applications, we'd like to operate at slightly higher temperatures. We're looking at inorganic proton conductors called solid acids, which are chemical intermediates between normal salts and normal acids. If we take a normal acid such as sulfuric acid and react it with a normal salt such as cesium sulfate, we end up with cesium hydrogen sulfate (cesium bisulfate):

$$\tfrac{1}{2}Cs_2SO_4 + \tfrac{1}{2}H_2SO_4 \rightarrow CsHSO_4.$$

This is our prototype solid-acid compound, one that has protons in the structure even though it's a solid. Physically, it's similar to a salt, and at low temperatures it has a very normal structure without any disorder in it. But at warm temperatures it undergoes a structural disordering that causes the conductivity to increase dramatically. The advantages of these solid acids are that they transport "bare" protons (not ones hitching a ride on water molecules), they're inherently impermeable if you can manufacture them without any pores, and their conductivity is humidity insensitive. By operating at warm temperatures we don't have to make sure that absolutely no carbon monoxide is left in our hydrogen fuel, which simplifies the system tremendously and makes the fuel cell much less costly. One disadvantage of solid acids is that they're brittle. Another is that they're water soluble—and as water is a by-product of the fuel-cell reaction, we've had to devise a way to get around this.

I find the proton transport mechanism in these solid acids quite fascinating. The bisulfate ($HSO_4^-$) group forms a tetrahedron with an oxygen atom at each corner and a hydrogen atom sitting on one of the oxygens. At room temperature, all the sulfate groups have a fixed orientation. When we raise the temperature, disorder sets in and the sulfate groups reorient, changing the positions of the hydrogen atoms as they do so. The time frame for this reorientation is about $10^{-11}$ seconds. Every once in a while, a proton from one sulfate group transfers over to the next. This transfer is on the order of $10^{-9}$ seconds. Essentially, these sulfate groups rotate almost freely—and every 100 reorientations or so, they're in exactly the right position for a proton transfer to happen. As the material goes through this transition, there's a sudden increase in conductivity of several orders of magnitude. Conductivity values for the acid salts are comparable to the conductivity of Nafion and other electrolyte polymers, but at slightly higher temperatures. A number of different solid-acid compounds with such behavior have been discovered, quite a few of which have come out of our laboratory. We're searching for others, and I'll tell you more about that further on.

The potential of fuel-cell technologies for reducing our reliance on fossil fuels, and the environmental damage of our energy consumption, is tremendous.



The little fuel cell that could: to show that our "Oreo cookies" (above) generate electricity, we put them into a stack (right) wired up to an LED display (bottom). It worked!
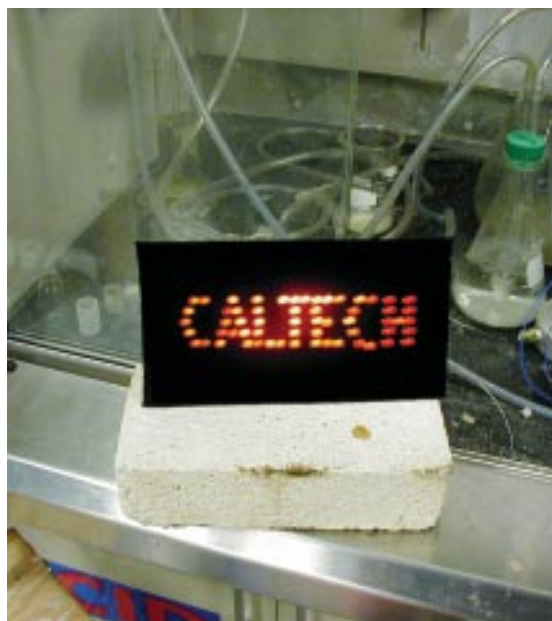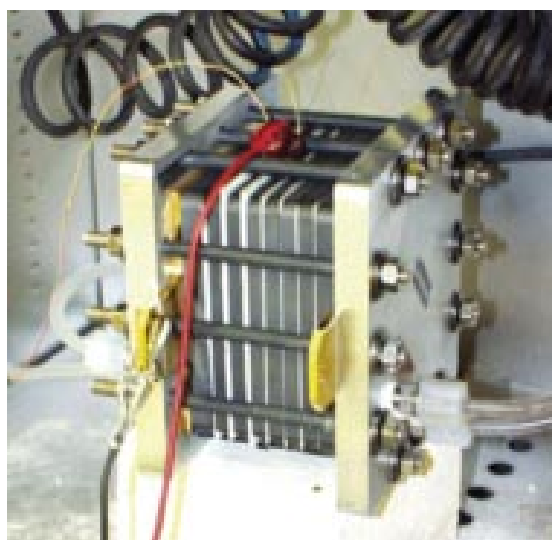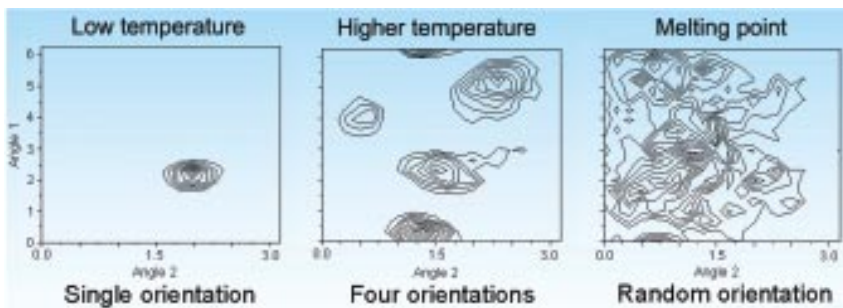




We've made a fuel cell using cesium hydrogen sulfate—the white central layer in the close-up of the pellet on the left. The current collector, which is graphite paper, is the dark outer part. In between are the electrocatalysts, but they're too thin to see. My students sometimes like to call these fuel cells Oreo cookies, hoping they'll get sponsorship from Nabisco (which hasn't happened quite yet). Although these electrolytes are water soluble, we can get them to work if the cell is operated above 100°C. We've achieved a very high open-circuit voltage with this fuel cell—much better than with PEM fuel cells. But overall, the power we're getting is quite low, only 10 to 15 milliwatts per square centimeter, so we still have to make our electrolytes much thinner (the one in the photo is 1,400 microns thick, and we'd like to get down to 20 microns) and find better ways to put the catalysts on.

Nevertheless, the proof of principle is there, so we've gone ahead and made a stack out of these cells. We purchased a commercial stack, put our own membranes inside, and connected them to an LED to demonstrate that the cells were generating a current. We also ran the stack in direct-methanol mode, and again got a substantial open-circuit voltage compared to PEM fuel cells running on this fuel. Solid-acid electrolytes don't have any problems with methanol permeability, so we can use quite a high methanol concentration, which is one of the reasons we can achieve such a good voltage.

Now for the fly in the ointment. After we operated our fuel cell for some time, the performance started to degrade. It turned out that the cesium hydrogen sulfate electrolyte was being reduced by hydrogen to produce hydrogen sulfide, a terrific poison not only for human beings but also for the platinum catalyst. So now we're engaged in a search for solid acids that are stable in hydrogen. Many of the solid-acid compounds known to have a high conductivity when heated are sulfates and selenates, but this phenomenon has also recently been found in phosphates and arsenates. Phosphorus and arsenic are one group to the left of sulfur and selenium in the periodic table. If we go one more group to the left, we find silicon and germanium. Do silicates and germanates also have high conductivity? We're looking at the many possible chemical analogs of cesium hydrogen sulfate, such as barium hydrogen phosphate, strontium dihydrogen germanate, lanthanum hydrogen silicate, and so on, to see if their conductivity also rises when heated. These alternatives are all stable in hydrogen, which is what we're looking for. Moreover, many are water insoluble, which is great for the application, but makes them much more challenging to synthesize.

To guide our synthesis efforts, we're doing computational studies in collaboration with Bill Goddard, the Ferkel Professor of Chemistry, Materials Science, and Applied Physics, that allow us to predict the properties in advance before we go through the very difficult exercise of synthesizing

Low temperature — Single orientation
Higher temperature — Four orientations
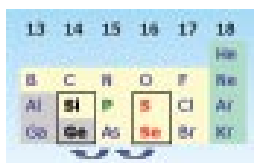Melting point — Random orientation

them. We started our computation exercise with cesium hydrogen sulfate, to show that we could do it. Basically, we were trying to work out theoretically—with no experimental input—how the positions of the cesium, hydrogen, sulfur, and oxygen atoms in the solid acid change as we change the temperature. We put these atoms in an imaginary box, worked out the forces acting between them using quantum-chemistry calculations, and simulated the way they would interact with one another. The diagram above shows the computed orientation of a single sulfur-oxygen bond, relative to the edge of the box, at different temperatures. At low temperature, the sulfur-oxygen bond always points in the same direction, meaning the sulfate group has only one orientation. At a higher temperature, there are four different directions, meaning four different orientations, which is exactly what we see experimentally. This is a terrific result because it means we can correctly predict the disordered, high-proton-conductivity state, and we now have a handle on determining which materials are going to give us this behavior. We hope to answer a lot of scientific questions: What types of compounds exhibit this transition to a disordered state? Do silicates and germanates have it? Can it be predicted? Can we manipulate the transition temperature and even the conductivity? And ultimately, we're heading toward a water-insoluble, stable electrolyte that will revolutionize portable, low-temperature fuel cells.

I'm hopeful that the novel power devices we're currently developing will be widely adopted in the not-so-distant future. The potential of fuel-cell technologies for reducing our reliance on fossil fuels, and the environmental damage of our energy consumption, is tremendous. It is essential that our work succeed: we have a moral obligation to deliver a sustainable world to the next generation and beyond. □



**This area of the periodic table will hopefully yield more candidates for solid-acid electrolytes.**

*Associate Professor of Materials Science and Chemical Engineering Sossina Haile gained her BS (1986) and PhD (1992) from MIT, and her MS (1988) from UC Berkeley. A 1991 Fulbright fellowship took her to the Max Planck Institute for Solid State Research in Stuttgart, Germany, where she continued as a post-doctoral student and Humboldt Research Fellow until a faculty position at the University of Washington brought her back across the Atlantic in 1993. She moved to Caltech in 1996. Although still at an early stage in her career, her research has already garnered prestigious awards such as the National Young Investigator Award of the National Science Foundation, the Robert Lansing Hardy Award of the Minerals, Metals, and Materials Society, the American Ceramic Society's Robert L. Coble Award for Young Scholars, and the J. B. Wagner Award of the Electrochemical Society's High Temperature Materials Division. The Watson Lecture can be viewed on http://atcaltech.caltech.edu/theater/.*



**Will the fuel cells being developed at Caltech today be everyday objects for Alemayouh Haile Snyder by the time he drives his first car (hydrogen-powered, of course)?**