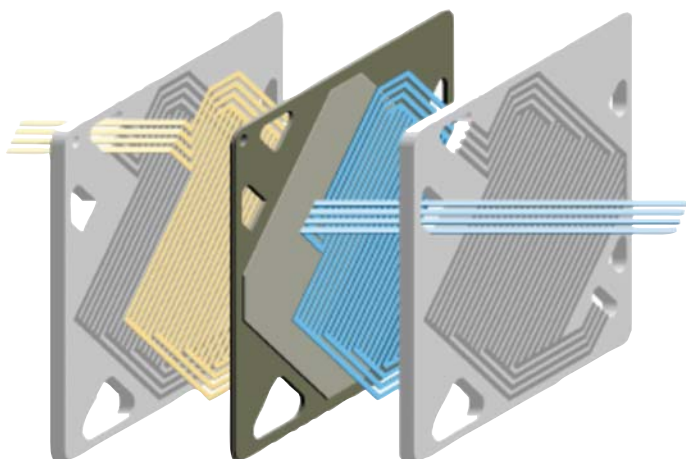


Toward a Sustainable Energy Future

Fuel cell research at Los Alamos

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“But in the end, my dear Cyrus, all this industrial and commercial development which you predict will continually grow, is it not in danger of coming to a halt sooner or later?... you can’t deny that one day all the coal will be used up... And what will they burn in the place of coal?”

“Water,” replied Cyrus Smith.

“Water!” exclaimed Pencroft. “Water to heat steamships and locomotives, water to heat water?”

“Yes, but water decomposed into its basic elements... Yes, my friends, I believe that water will one day serve as our fuel, that the hydrogen and oxygen which compose it, used alone or together, will supply an inexhaustible source of heat and light...”

—Jules Verne, *The Mysterious Island* (1874)

About 25 years ago, and more than 100 years after Jules Verne wrote *The Mysterious Island*, scientists and engineers at Los Alamos began an R&D program into fuel cells, a program that today leads our nation and the world toward a modern version of Jules Verne’s prophetic vision. In the “hydrogen economy,” hydrogen provides the means to carry the energy trapped in coal, uranium, or wind, to our homes, cars, or offices. Fuel cells provide a clean, efficient energy-conversion technology. Together, hydrogen and fuel cells offer the promise of a sustainable energy future.

Hydrogen was first isolated as a separate element by English chemist Henry Cavendish in 1766. Called

“inflammable air” upon discovery, the colorless, odorless gas was later named for its propensity to form water on combustion in air (*hydro-gen*). Sixty-five years later, in 1839, Sir William Grove, a British jurist and amateur physicist, invented the hydrogen-oxygen fuel cell, although Christian Friedrich Schonbein (who discovered ozone and invented guncotton) had demonstrated the basic electrochemistry a year earlier. The overall reaction combines hydrogen gas (H₂) with oxygen gas (O₂) to form water and generate heat:



The reaction proceeds through two steps, or half reactions, each con-

strained to take place on a different side of a reaction cell (the anode side and the cathode side). The two sides of the reaction cell are separated by an all-important electrolyte “barrier.” Hydrogen gas is fed to the anode, where a metal catalyst—typically, platinum—facilitates the breakdown of the hydrogen gas into hydrogen ions and electrons. The positively charged ions move through the electrolyte to the cathode, but the negatively charged electrons must take an external conducting path. Once at the cathode, the electrons combine with the ions and the oxygen gas—again with the help of a catalyst—to produce water (see Figure 1).

The flow of electrons through the external conduction path constitutes

an electric current that can do work. Thus, the fuel cell is a source of electric power that, like a battery, converts the chemical energy in the hydrogen fuel directly to electricity. Unlike a battery, the fuel cell has the reactants externally fed and will continue to provide full output as long as hydrogen and oxygen are supplied.

While the electrochemistry of the fuel cell was well understood years ago, enthusiasts discovered that engineering a practical device was difficult. The platinum catalyst is very expensive, and there are significant issues regarding the accessibility of gases to the electrodes, the purity of the gases, the electrolyte composition, the removal of water, and so on, all of which affect fuel-cell performance. Fuel-cell technology languished until World War II, when Francis Tom Bacon, an engineer at Cambridge University, refined the electrochemical cell and built a complete power system. Decades later, when the National Aeronautics and Space Administration (NASA) sought a compact, lightweight, reliable, and efficient power system for manned space flight, the technology really “took off.” What emerged from approximately 200 fuel-cell R&D contracts let by NASA during the Apollo program was the General Electric (GE) solid polymer electrolyte (SPETM) fuel cell, which was used in the Gemini space capsules. GE’s technology subsequently became known as the polymer electrolyte membrane (PEM) fuel cell, and it has been the main focus of fuel-cell work at Los Alamos National Laboratory since 1977.

The PEM Fuel Cell. The centerpiece of the PEM fuel cell is the solid, ion-conducting polymer membrane, which replaces the liquid electrolyte. Looking much like a thick sheet of plastic food wrap, the membrane is typically made from a tough, Teflon-

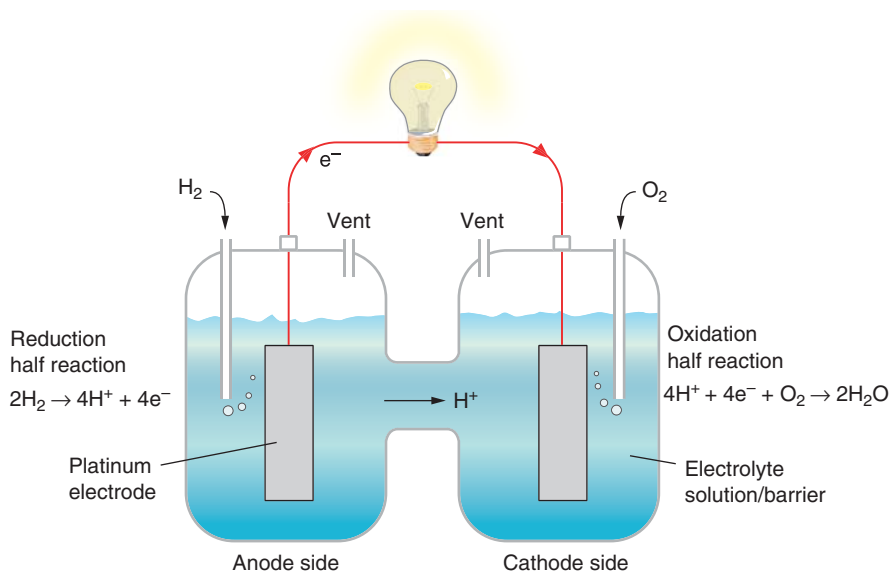


Figure 1. Fuel Cell Basics

A fuel cell takes hydrogen gas and combines it with oxygen gas to produce electricity. The only “waste” products are water and heat. As shown in this conceptual liquid-electrolyte cell, hydrogen gas is fed to the anode side of the cell, and oxygen gas is fed to the cathode side. The two electrodes are identical, each consisting of an electrical conductor studded with platinum. At the anode, the platinum catalyzes the breakdown of hydrogen gas into hydrogen ions and electrons (reduction half reaction). The ions are conducted to the cathode by the electrolyte solution, but the electrons, which do not move through the electrolyte, flow to the cathode along the connecting wire. The platinum catalyzes the water-forming reaction involving ions, electrons, and oxygen (oxidation half reaction). Because of the separation of charge, a voltage potential of about half a volt is established between the anode and cathode.

like material called NafionTM. This material is unusual in that, when saturated with water (hydrated), it conducts positive ions but not electrons—exactly the characteristics needed for an electrolyte barrier.

The membrane is sandwiched between the anode and cathode electrode structures—porous conducting films, about 50 micrometers thick, consisting of carbon particles that have nanometer-size-platinum particles bonded to them. Because the platinum particles have such a high surface area, the total catalytic activity of an electrode can be enormous. The electrodes are porous so that gases have ready access to the full surface area (see Figure 2).

In addition to having catalytic and electric conducting properties, the electrodes—and the backing material that supports them—are crucial to the

water management of the cell.

Ironically, even though water is a product of the fuel-cell reaction, both the hydrogen and oxygen gas streams must be humidified to keep the polymer membrane hydrated. If there is too little water, the membrane begins to lose the ability to conduct ions. However, if there is too much water, it floods the porous electrodes and prevents the gases from diffusing to the catalytically active sites. Thus, water produced at the cathode must continually be removed. Water management and the control of gas flows in and out of the cell are the keys to efficient cell operation.

Each PEM fuel cell develops a potential of about 0.4 to 0.8 volts between the anode and cathode, depending on temperature, gas pressure, flow, and other operating conditions. Higher voltage is obtained when

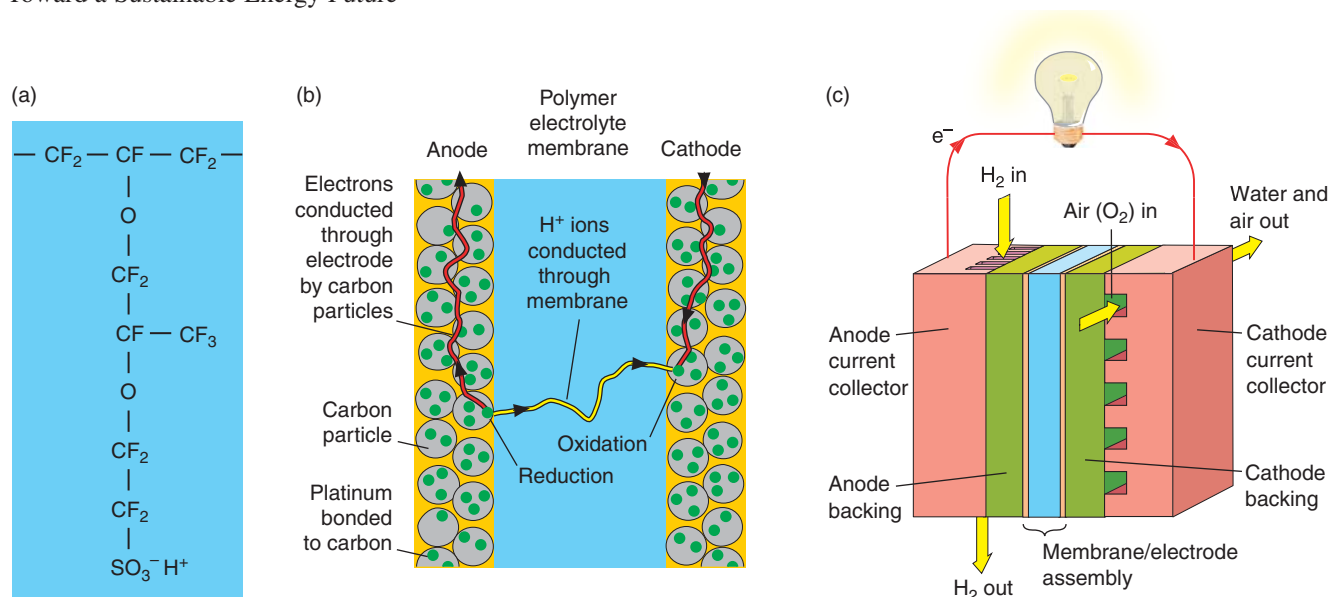


Figure 2. The PEM Fuel Cell

(a) The side chains of the NafionTM polymer making up the membrane contain a sulfonic acid ion cluster, SO_3^-H^+ . The negative SO_3^- ions are permanently attached to the side chain, but when the membrane becomes hydrated, the H^+ ions can attach to water molecules and form H_3O^+ ions. These ions are free to migrate from SO_3^- site to SO_3^- site, making the hydrated membrane an effective conductor of H^+ ions. (b) The electrodes on each side of the membrane consist of sootlike carbon particles with nanometer-size platinum particles bonded to them. Running between the carbon particles are NafionTM polymers to aid in ion

conductivity. The porous electrodes are pressed against the PEM. (c) The membrane and electrode assembly is sandwiched between backing layers and end plates. The porous, electrically conducting backing layers provide a way for incoming gases to diffuse uniformly to the electrodes and help in water management. The conducting end plates channel electrons to external circuits. Channels cut into the plates create a circuitous flow field for the gases and provide a way to remove water on the cathode side (see the opening graphic). This cell can be linked in series with other cells to make a higher-voltage fuel cell stack.

a number of cells are placed in series to create a “fuel-cell stack.” Because the electrochemically active cross-sectional area of each cell has a characteristic current density (typically several hundred to more than a thousand milliamperes per square centimeter, depending on operating conditions), the desired electrical current for a specific application can be achieved by changing the cross-sectional area of the stack. Through proper design and selection of operating conditions, stacks producing as much as 100 kilowatts have been achieved.

The PEM cells operate at relatively low temperatures (about 80° Celsius), a feature that makes them attractive for applications requiring multiple start-stop cycles, such as passenger vehicles. Because a fuel-cell-based electric propulsion system offers two to three times the energy efficiency of an internal combustion engine and associated drive train, the transporta-

tion sector is a driving force accelerating fuel-cell R&D. Besides energy efficiency, fuel cells offer low emissions (approaching zero if the hydrogen is made cleanly), and they help with energy and economic security because hydrogen can be made from a diverse array of domestic energy resources.

In the near term, hydrogen can be produced from natural gas, fossil fuels, biomass, or through electrolysis of water (separating H_2O into hydrogen and oxygen in a process akin to running a fuel cell in reverse). The electricity needed to run these processes would come from fossil-fuel and nuclear power plants, or from renewable resources such as the sun and the wind. In the longer term, hydrogen can be produced by use of heat from nuclear reactors and a thermochemical process to do the water electrolysis. In another concept, zero-emission coal systems could sequester

carbon in the process of separating hydrogen. Hydrogen, therefore, provides a means to carry the energy contained in coal or nuclear fuels to an end user. It is also possible to produce the hydrogen entirely from renewable resources and thus enable a truly sustainable energy future.

Los Alamos R&D

Work at Los Alamos in the last 25 years has been enabling for the emerging fuel-cell industry, and the Laboratory holds several seminal patents required by would-be product developers. Arguably, the breakthrough that brought the PEM fuel cell out of the space program and made possible its consideration as a ubiquitous power-conversion technology was our development in the late 1980s and early 1990s of the low-platinum PEM electrodes described earlier.

Before these developments, state-of-the-art PEM “electrodes” had relatively large platinum particles embedded (basically, rammed) directly into the membrane. To maintain electron conductivity, those electrodes required very large amounts of platinum. The cost of platinum was not an issue for NASA, but it stifled any commercial applications.

Low-platinum porous electrodes had already been developed for liquid electrolyte systems, but their initial application to the dry PEM cell was unsuccessful. The sootlike carbon particles did not conduct ions very well, and in the absence of a liquid electrolyte, most ions had no conducting path to the membrane.

The Los Alamos breakthrough came when Ian Raistrick applied a solution that contained dissolved Nafion™ material to the surface of the porous electrode. Once the solution dried and the electrodes were pressed to the membrane, the Nafion™ material provided an ion-conducting path from the PEM to the platinum particles. Mahlon S. Wilson later invented methods for fabricating repeatable thin-film electrodes bonded to the PEM membrane—the so-called membrane electrode assembly (MEA). In combination, these techniques have dramatically lowered the required precious-metal catalyst loadings by a factor of more than 20 while simultaneously improving performance. They are now used by fuel-cell manufacturers and researchers worldwide.

Another Los Alamos innovation dramatically improves cell tolerance to hydrogen impurities and performance in the presence of impurities, enabling low-temperature PEM fuel cells to operate not only with pure hydrogen, but also with hydrogen-rich gas streams derived from hydrocarbon fuels (such as gasoline, methanol, propane, or natural gas). Such gas streams invariably contain trace amounts of carbon monoxide (CO), a



Figure 3. Equipment and Testing Brent Faulkner is pictured (photo taken around 1994) with the 10-kW electrochemical engine, a complete PEM fuel-cell power system, developed through a joint collaboration between the Laboratory and GM. The insulated components to the right are part of the methanol steam reformer that produced, on demand, hydrogen-rich gas from a liquid fuel. The two 5-kW PEM fuel cell stacks (made by Ballard) have blue endplates and can be seen at left. Additional equipment required to complete the power system is out of the photo frame.

species that poisons the catalyst by getting adsorbed and lowering the active surface area. The Los Alamos technique, invented by Shimshon Gottesfeld, injects small amounts of oxygen-containing air into the fuel stream before it enters the fuel cell. Even at PEM operating temperatures, the oxygen can oxidatively remove the CO from the catalyst surface, thus maintaining electrode surface area for the hydrogen oxidation reaction.

Other significant Los Alamos technology advances include development of processes to generate hydrogen-rich gas streams on demand from gaseous and liquid hydrocarbon fuels, significant improvement of direct methanol fuel cells (cells that run on methanol instead of hydrogen), development of fuel-cell test procedures and performance characterization methodologies, and fundamental data-supported modeling of fuel cell per-

formance. Technology transfer has been facilitated by publishing, licensing, student programs, direct training of industrial personnel, cooperative R&D agreements, and migration of our technical staff and students to industry.

The Electrochemical Engine

Our researchers have worked closely with industry from the beginning of the Los Alamos fuel-cell program. One key example was the establishment of the Los Alamos–General Motors (GM) Joint Development Center (JDC) at the Laboratory in 1991, funded by GM and the Department of Energy (DOE). The JDC effort was focused on development of the electrochemical engine, a complete PEM fuel-cell power system fueled by methanol (shown in Figure 3), which was converted on demand to a hydrogen-rich gas by a steam-reformation process. At that time, liquid fuel was considered crucial to the acceptance of fuel-cell-powered vehicles because using liquid fuel would allow exploitation of the transportation sector’s mature fuel-distribution infrastructure.

In the steam-reforming process, methanol (CH_3OH) reacts with water vapor in a series of controlled catalytic reactors to form a mixture of hydrogen and carbon dioxide. The carbon dioxide flows through the PEM cell with little effect, and the hydrogen is consumed in the fuel-cell reaction. The JDC team worked on all aspects of the power system: from optimizing the membrane electrode assembly to providing system integration, modeling, and testing. At the same time, a DOE-funded core research activity, in what is now the Electronic and Electrochemical Materials and Devices Group, was making enabling breakthroughs that

were soon incorporated into the electrochemical engine. Phase I of the project developed and demonstrated the complete 10-kilowatt (gross electric) electrochemical engine shown in Figure 3. Phase II extended this work to a stand-alone, 30-kilowatt (net electric) engine.

As Phase II neared its end, GM took the knowledge and expertise gained at the JDC and established a corporate fuel-cell R&D center in upstate New York. In a recent letter to the Laboratory director, the GM director of fuel-cell activities noted, "General Motors and Los Alamos have a long and successful history working together to research and develop fuel cells for automobiles. This collaboration, supported by the Department of Energy, serves as the technical foundation for the intensive development effort in fuel cells at General Motors today."

After the electrochemical engine project, the engineering research effort shifted away from methanol and toward making "stack-quality gas" from gasoline. This work was done in an effort to further reduce the fuel infrastructure barrier to commercialization of fuel-cell-powered vehicles. The fundamental fuel-cell research and development also put an increased emphasis on optimizing fuel-cell performance and on achieving durability in "gasoline reformat," the product of gasoline processing typically consisting of 40 percent hydrogen, 18 percent carbon dioxide, 30 percent nitrogen, 12 percent water, less than 10 parts per million carbon monoxide, and unspecified "other impurities." Gasoline reforming is typically accomplished by partial oxidation of gasoline to provide the endothermic heat of reaction required for subsequent process steps, including steam reforming of the remaining hydrocarbons and conversion of the residual carbon monoxide to carbon dioxide and hydrogen by reaction



Figure 4. The Consumer Market President George W. Bush tries out a cellular telephone powered by a DMFC, while Bill Acker of MTI MicroFuel Cells looks on. The fuel cell is in the President's hand and is connected to the phone by wire. The methanol fuel is stored in a small plastic capsule that is inserted into the cell. MTI MicroFuel Cells is commercializing Los Alamos technology under license. (White House photo by Paul Morse.)

with water (the "water-gas shift").

In 1997, a team from the Engineering Sciences and Applications' Energy and Process Engineering Group sent 2200 pounds of equipment to Cambridge, Massachusetts, by air freight to integrate a Los Alamos fuel-product cleanup system with a gasoline reformer developed by Arthur D. Little and a PEM fuel-cell stack developed by Plug Power. (Los Alamos also took a precommercial Ballard stack for testing.) To great acclaim, the "integrated" system generated the world's first electrical power from a low-temperature fuel cell operating on gasoline reformat. The Laboratory-industry team received the Partnership for a New Generation of Vehicles Medal in a 1998 ceremony at the White House.

Although technology development over the last two decades has been dramatic, PEM fuel cells are still too expensive and do not have the power density, durability, or reliability to be economically and functionally competitive with conventional power-conversion devices. Today's development

program is oriented toward reducing costs through materials substitutions, performance improvement, and system simplification and increasing durability through understanding performance degradation and life-limiting effects.

In 2003, the program direction shifted. There is now a significant focus on PEM fuel cells running on pure hydrogen stored onboard the vehicle. This change in emphasis, embodied in the president's Freedom Cooperative Automotive Research and Fuel initiatives, resulted from the desire to reduce system complexity, thereby reducing cost and improving reliability, and the desire to minimize the country's dependence on imported oil while maximizing environmental benefits. However, storing enough hydrogen onboard to enable a 350-mile driving range is challenging and is still the subject of research. Because of this change in direction, our fuel-processing effort is shifting to offboard stationary processors that would reform natural gas, propane, or liquid hydrocarbon fuels to gaseous hydrogen. There is also a growing emphasis on reforming "difficult" fuels such as diesel and Jet A (a common aviation fuel) for use in auxiliary power units for both civilian and military applications.

The Future

Although the bulk of our funding has come from transportation programs, fuel cells are inherently scalable, and one of the earliest market introductions is likely to occur in distributed power systems. A fuel cell sitting beside a home, using reformed natural gas or propane, would provide not only electricity but also "waste" heat that could be captured and exploited for space heating and hot-water production. Such heat and power systems could convert fuel

chemical energy into useful products with close to 75 percent efficiency, far exceeding what a utility power plant can achieve. Furthermore, by placing the generating asset near the end use, we would avoid electrical transmission losses. The resulting distributed power system would be much more robust.

Still, the first large-scale commercialization of fuel cells is likely to occur in the portable electronics market, because fuel-cell power systems offer greater energy densities than batteries. The miniature fuel cells developed for this application rely on a Los Alamos development that adapted and optimized the basic PEM technology to use dilute methanol as the fuel. The methanol molecule (CH_3OH) can be considered a high-energy-density hydrogen carrier. The methanol is directly oxidized at the anode in a multistep process, and protons are transported across the polymer electrolyte membrane just as they are in a hydrogen fuel cell. Although direct methanol fuel cells (DMFCs) are less efficient than hydrogen fuel cells and require more expensive catalysts, they seem a good match for hand-held electronics and small portable applications, in which a 1-watt, state-of-the-art battery can cost \$100 (or \$100,000 per kilowatt)—refer to Figure 4.

The Laboratory has also assembled an impressive intellectual-property portfolio in DMFC technology. Licensing and royalty revenues from hydrogen fuel-cell and DMFC portfolios generate about one quarter of the annual intellectual-property revenue for the Laboratory.

Citizen awareness of the concepts of energy security, economic security, and sustainability are growing. Because of increasing bipartisan political support and the continuing innovation and commitment of our world-class research scientists, engineers, and technicians, we expect that the Laboratory's contributions to solving

these complex national and global problems will only increase in the future. President Bush's budget request for fiscal year 2003 contained language to establish a fuel-cell National Resource Center at Los Alamos to address "... technical barriers to polymer electrolyte membrane fuel-cell commercialization."

While the designation of this National Resource Center and details of the center's work scope, operations, and funding requirements are subject to further discussion, we believe the center, if established, will focus on close collaboration with industry, universities, and other national laboratories, and will perform fundamental research to enable development of the next generation of fuel cells and related technologies, which will feature reduced cost, higher performance, and increased durability. The center will also provide resources in the form of access to the existing knowledge base, experts in the field, and state-of-the-art experimental and analytical capabilities and could provide a magnet for regional economic development. ■

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Further Reading

Gottesfeld, S. May 1990. "Preventing CO Poisoning in Fuel Cells," U.S. Patent No. 4,910,099.

Raistrick, I. October 1989. "Electrode Assembly for Use in a Solid Polymer Electrolyte Fuel Cell," U.S. Patent No. 4,876,115.

Wilson, M. S. May 1993 "Membrane Catalyst Layer for Fuel Cells," U.S. Patent No. 5,211,984.

———, August 1993. "Membrane Catalyst Layer for Fuel Cells," U.S. Patent No. 5,234,777.

For more information, including references, a fuel-cell primer, and an animation showing how a PEM fuel cell works, visit our website at <http://www.lanl.gov/mst/fuelcells/>.

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