The Electrochemical Engine for Vehicles

Fuel cells can power cleaner buses and cars, but key engineering and economic obstacles will delay widespread adoption of the technology

by A. John Appleby

s the number of cars, trucks and buses on the road increases, the need for alternatives to the internal-combustion engine becomes ever more apparent. The largest of the world's oil reserves are in the politically unstable Middle East and in any event cannot last indefinitely. The health hazards posed by nitrogen oxides and other compounds in vehicle exhausts are well known, and concerns about emissions of the greenhouse gas carbon dioxide are also growing. Although cars are becoming cleaner and more efficient, the gains are being offset by the rapid growth in the total number of vehicles, especially in Asian markets. In 1996 some 634 million vehicles were on the road worldwide, an increase of almost 30 percent from the figure a decade earlier; collectively, they emitted some 3.7 billion tons of carbon dioxide, according to the International Energy Agency.

Automakers are investigating a variety of ways to reduce emissions drastically. Electrochemical fuel cells producing power for electric drive motors are now widely seen as a promising possibility. Unlike familiar dry cell batteries, which store a fixed amount of energy in their electrodes, fuel cells can run as long as fuel and oxidant are supplied—or at least until components in the cells degrade.

Most major manufacturers now have programs for producing fuel cells for autos, and recent demonstrations have caught the public eye. DaimlerChrysler and General Motors both say they will make some passenger cars for the mass market by 2004; the London-based company Zevco is planning to build fuel cells for commercial vehicles in New York.

Although fuel-cell-powered vehicles have only recently emerged into the public spotlight, the use of fuel cells for traction actually goes back to the 1950s. And they have supplied power in all manned space missions since Project Gemini in 1965.

Chemical Choices

Vehicle fuel cells may employ various chemicals as their electrolyte, the material that electrically connects the electrodes inside the cell. Hydrogen supplied to the anode (the negative terminal, in this context) reacts there, liberating electrons. The resulting current flows through an external circuit to the cathode (the positive terminal), where electrons combine with oxygen. Ions flow through the electrolyte to complete the circuit. The only waste product is water. Fuels other than hydrogen can be used in principle, but then products from the reaction "poison" the catalyst, reducing output voltage and efficiency. Fuel cells that run at temperatures low enough for mobile use rely on a catalyst, generally platinum, to speed reactions to practical rates.

The direct chemical-to-electrical energy conversion accomplished in a fuel cell can theoretically reach a very high efficiency. In practice, the slow re-

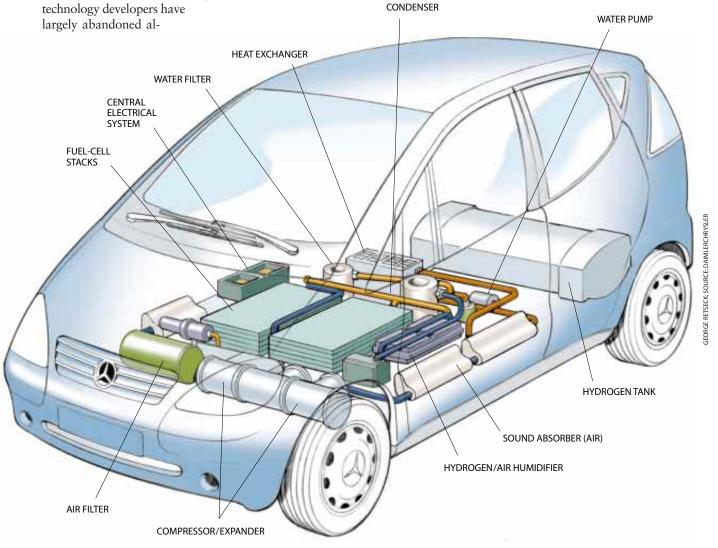
MODERN FUEL-CELL-POWERED CAR, DaimlerChrysler's Necar 4, uses fuel cells mounted under the floor to generate electricity. A compressor maintains them at pressure. Air and hydrogen fuel are conditioned by a humidifier and a heat exchanger; a condenser captures wastewater. Liquid-hydrogen fuel is stored in a cryogenic tank. An air-cooled radiator (*not shown*) eliminates waste heat.

action of oxygen at the cathode limits the achievable efficiency to 45 to 60 percent, even using the best platinum or platinum-alloy catalysts. But this is still better than the internal-combustion engines of today's autos, which might reach 35 percent efficiency under ideal conditions but actually average about 15 percent. One reason for the superior performance of fuel cells is that they do not have to idle when a vehicle is stationary.

Other significant efficiency losses of fuel cells result from the electrical resistance of the electrolyte and from variations in its concentration from one microscopic site to another. These losses are minimized by employing strongly acidic or alkaline electrolytes. Alkaline fuel cells operating on compressed hydrogen and oxygen were the first type to power a vehicle, an Allis-Chalmers farm tractor, in 1959. Their disadvantage has been that they need to be supplied with hydrogen that contains no contaminating carbon dioxide, or it will react with the electrolyte to form a solid carbonate. Because many automotive concepts involve generating hydrogen on board from other fuels—a process that produces some carbon dioxide—the major

kaline fuel cells, although they have great promise where hydrogen of industrial purity is available. They can be made from inexpensive materials, and engineers learned in the 1980s how to make carbonate-insensitive cathodes, which lessen the susceptibility to carbon dioxide. Furthermore, alkaline cells can function with much less platinum than acid-based fuel cells can.

Acidic electrolytes are insensitive to carbon dioxide but have their own limitations. Typical acids require liquid water to conduct hydrogen ions, so cells must then operate below the boiling point of water. That requirement constrains efficiency. Concentrated phosphoric acid is an exception, however, and cells using it can operate at 200 degrees Celsius (390 degrees Fahrenheit). Some hospitals and hotels have used phosphoric acid cells operating on ambient air and hydrogen-rich fuel generated from natural gas since the early 1990s. Similar cells have also been used to power city buses, but the several-hour warm-up period that this type needs makes its use in consumer vehicles unlikely.



Because most aqueous acids are either volatile or unstable, chemists started to experiment in the 1960s with synthetic polymers as electrolytes. Modern versions, such as Du Pont's Nafion, contain sulfonic acid groups that allow protons to flow readily through them. The material is formed into a membrane that separates the electrodes. This design, the proton-exchange membrane fuel cell, runs at about 80 degrees C and is now seen as the leading technology for use in cars. Most recent fuel-cell demonstrators have employed this type.

Proton-exchange membrane fuel cells depend on platinum as their catalyst. Typically particles of the metal about 10 atoms in diameter—the smallest achievable size—are deposited on the surface of fine particles of carbon. Platinum's high cost has always been a major factor holding back commercial development of these devices. In 1986 the amount needed was about 16 grams per kilowatt of power produced (a kilowatt is equivalent to 1.3 horsepower). The 16 grams (0.6 ounce) would cost \$180 at today's prices, far too much for the mass market. An automobile needs to produce 50 kilowatts to accelerate, although a hybrid design could get by with a fuel cell providing perhaps 15 kilowatts and a battery to help out during periods of peak power demand.

Precious Platinum

Investigators at Los Alamos National Laboratory and at the research center that I direct at Texas A&M University made strides toward reducing the amount of platinum needed in proton-exchange membrane cells in the late 1980s and early 1990s, and more recently some commercial companies have made important contributions. The quantity typically used in modern cells corresponds to \$6 to \$8 per kilowatt—a 30-fold im-



AUSTIN A40 SEDAN was equipped with Union Carbide alkaline fuel cells in 1966 by Karl Kordesch. Though historically important, the vehicle was hardly practical: the cells occupied much of the interior of the passenger compartment. Tanks of compressed hydrogen are visible on the roof.

provement since 1986. Further improvements in the structure of electrodes and in the way platinum is used might reduce the amount of the metal needed by about half but barring unforeseen breakthroughs probably not more. Researchers have yet to find a substitute for platinum at either electrode.

The membrane-electrode assembly of a modern cell is as little as 2.5 millimeters (0.1 inch) thick. The cathode of one cell and the anode of an adjacent one are physically separated by a plate that connects them electrically in series. On each side of this plate are either gas distribution channels or porous materials that allow hydrogen and oxygen to reach the electrodes easily. The plates may also contain channels for circulating cooling water.

To make a practical power source, a series of assemblies and plates are bolted together in a "stack." In 1989 Ballard Power Systems in Vancouver, B.C., developed a 45-kilogram stack with a volume of about 30 liters (7.9 gallons) that produced five kilowatts of power from stored hydrogen gas and pressurized air. Though impressive, the design still had impractically high platinum loadings, corresponding to about \$80 per kilowatt. In 1995 Ballard announced a much improved stack that could compete in performance with the internal-combustion engine. This design had the same weight and volume but generated 32.3 kilowatts and achieved an efficiency of 54 percent. Various generations of Ballard's stacks are now powering buses in Vancouver and Chicago as well as several experimental DaimlerChrysler vehicles.

Automobiles demand higher performance than buses do. But U.S. automakers cooperating in a federal initiative, the Partnership for a New Generation of Vehicles, have selected proton-exchange membrane fuel cells as one of two promising technologies that could help achieve the project's goal of developing an ultralow-emission passenger car. (The other is a hybrid concept that employs a highefficiency internal-combustion engine coupled with batteries.) Received wisdom in the auto world is that an "electrochemical engine"—a fuel-cell stack powering electric motors—could compete economically with an internal-combustion engine if the cost could be brought down to \$50 per kilowatt.

That might be possible in time. There are two competing approaches. One, as indicated above, is to combine a fuel cell with a battery that would provide supplementary power when necessary. This combination makes it possible to employ regenerative braking: when the vehicle is slowing down, the traction motors serve as brakes that generate power to recharge the battery. The battery can also provide power at start-up if the vehicle has a hydrogen-production system that needs time to warm up. Such a system can achieve an overall efficiency of about 40 percent. It has been used in several vehicles, including buses powered by experimental phosphoric-acid fuel cells.

The other approach is to use an electrochemical engine with no supplementary battery and no regenerative braking. Ballard followed this strategy in its buses powered by proton-exchange membrane fuel cells. This approach can reach 50 percent efficiency with an average load. But because the fuel cell must be more powerful, it is more expensive. Furthermore, the world supply of platinum is limited, and the metal is in demand for many other applications. If two million cars with 50-kilowatt electrochemical engines were made every year-about 5 percent of current auto production—they would use 50 metric tons of platinum, about one third of the current global production of the metal. This consideration suggests that pure proton-exchange membrane fuelcell vehicles will not dominate the future world market. Hybrid vehicles combining a battery and a smaller fuel cell could be made in much larger numbers, especially if the fuel cell were alkaline, because this type needs only one fifth as much platinum as proton-exchange membrane models. Zevco is pursuing this option.

Achieving Peak Performance

A July 1998 report to the California Air Resources Board estimated that carmakers will have spent \$1 billion to \$1.5 billion on the proton-exchange membrane fuel cell by July 2000. Yet to achieve widespread acceptance in coming years, a fuel-cell vehicle must have clear economic advantages over hybrid internal-combustion engine/battery systems that are likely to be developed: merely having negligible emissions is not enough.

In an effort to boost efficiency and thereby help the economics, developers have experimented with pressurizing cells to a few atmospheres, which increases the rate at which hydrogen and oxygen diffuse and react. This maneuver can reduce the amount of platinum needed, although the gains are modest and the heavier containment necessary to operate at pressure adds to a stack's weight. Moreover, efficient operation requires oxygen to be supplied in excess of requirements, so the amount of air that has to be compressed is much more than the amount consumed. Because compressors are noisy and inefficient, pressurization is, all in all, of questionable value.

Ballard appears committed to the idea, however, which enables the company to exploit the high pressure in its cells to expel water that tends to clog the cathode gas channels. In contrast, International Fuel Cells in South Windsor, Conn., a venture of United Technologies and Toshiba, has shown that unpressurized operation can lead to a more efficient and lighter cell. It utilizes permeable graphite containing microscopic pores to control water movement. Manufacturers have successfully tested the tolerance of membrane electrode assemblies for being frozen and thawed down to –40 degrees C, although the pure water used for cooling and keep-

ing the membrane moist must be drained out first.

To reduce costs, manufacturers are looking at using lighter-weight molded graphite-polymer composites and corrosion-resistant metal foams in the plates connecting electrodes. The cost of membranes, \$95 per kilowatt in a typical atmospheric-pressure stack, is still a significant obstacle. Du Pont states that prices should fall almost 10-fold if it can sell enough for 250,000 autos a year. That is still likely to be too expensive, so developers are looking at different electrolyte chemistries, though with no notable success to date.

If fuel cells are ever to be widely used in vehicles, improvements will also be needed in the onboard systems for either storing hydrogen or manufacturing it. If the gas is to be delivered to vehicles in its elemental form, an entirely new network of hydrogen refueling stations would have to be established.

It is easy to make hydrogen from natural gas. Hydrogen with an energy content equal to a gallon of gasoline might cost \$1.20 to \$1.50, which—because a fuel-cell vehicle can operate more than twice as efficiently as today's autos—could provide very low fuel costs per kilometer. More challenging are the systems that would be required for a car to carry three kilograms of hydrogen, the amount necessary to drive a small car 500 kilometers. Three kilograms may not sound like very much, but at atmospheric pressure it would occupy 36,000 liters—the volume of several entire cars.

A pressure vessel could carry compressed hydrogen gas, but it would occupy 180 liters, a lot of space in a car. Some designs proposed by Ford, which incorporate advanced composite materials, might, however, weigh only 25 kilograms.

An alternative would be to develop a nationwide liquid-hydrogen delivery system. A cryogenic vessel storing three kilograms would weigh 45 kilograms and occupy 100 liters, more than a gasoline fuel tank but manageable. Yet liquefaction wastes 30 percent of the energy of the fuel, and liquid hydro-



OPERATIONAL BUS built by Ballard Power Systems in Vancouver, B.C., is powered by proton-exchange membrane fuel cells (*visible at right*). The bus carries compressed hydrogen fuel and emits no pollutants.

RDHUNT	
RICHA	

Eugl Dange

Date	Developer	Vehicle	Technology	Fuel, Range (where available)
1966	Karl Kordesch	Austin A40 sedan	6 kilowatts, Union Carbide, alkaline*	Compressed hydrogen, 320 km
1990 (Operational April '94)	H Power, Georgetown University, U.S. government	Three 9.1-meter buses	50 kW, Fuji Electric, phosphoric acid*	Reformed methanol supplies hydrogen
1991 (Operational Feb. '93)	Ballard Power Systems	9.8-meter bus	120 kW, Ballard Mk 5, p/proton- exchange membrane	CH
Oct. 1993	Energy Partners	"Green Car" sports car	15 kW, p/PEM	CH, 100 km
April 1994	Daimler-Benz	Necar (Mercedes-Benz 180 goods van)	60 kW, Ballard Mk 5, p/PEM	CH
May 1996	Daimler-Benz	Necar 2 (V-class Mercedes-Benz minivan)	50 kW net, Ballard Mk 7, p/PEM	CH, 250 km
Sept. 1997	Daimler-Benz	Necar 3 (Mercedes-Benz A-class subcompact)	(as above)	RM, 400 km
July 1998	Daimler Chrysler	Necar 4 (as above)	(as above)	Liquid hydrogen, 400 km
1994–97	Ballard	Six 12.2-meter buses	205 kW net, Ballard Mk 6, p/PEM	CH
Nov. 1996	Toyota	RAV4 sport-utility	10 kW, p/PEM*	Metal hydride stores hydrogen, 250 km
Sept. 1997	Toyota	RAV4 sport-utility	25 kW, p/PEM*	RM,500 km
May 1997	Daimler-Benz	Nebus 12-meter O405 N bus	190 kW net, Ballard, p/PEM	CH,250 km
Aug. 1997	Renault	Laguna station wagon	30 kW, De Nora (Milan), p/PEM	LH, 500 km
Dec. 1997	Mazda	Demio FCEV station wagon	25 kW, p/PEM*	MH, 170 km
May 1998	Georgetown University, Nova BUS, U.S. Department of Transportation	12-meter bus	100 kW net, International Fuel Cells, phosphoric acid*	RM, 550 km
July 1998	Zevco	Millennium London taxi	5 kW, alkaline*	CH, 150 km
Oct. 1998	General Motors (Opel)	Zafira minivan	50 kW, p/PEM*	RM

*Hybrid system including battery or other storage device; p/ = pressurized

NUMEROUS FUEL-CELL-POWERED VEHICLES based on various engineering strategies have been built in recent years. The table shows some of the more notable vehicles licensed for use on the highway, including some buses now in service. Many other projects are in progress.

gen has a high boil-off rate; you might return to your car after leaving it at the airport for a week to find all the fuel had boiled away. Moreover, accumulations of hydrogen gas pose a risk of explosion.

Another option is to combine hydrogen with alloys of compounds called metal hydrides, which can reversibly store up to 2 percent of the gas by weight. These materials are expensive and heavy but compact: they could pack the required three kilograms into a reasonable volume of 50 liters. Researchers at Northeastern University announced last year a storage method that involves reversibly absorbing hydrogen inside carbon nanofibers at ambient temperature. Their results require confirmation, but if the amount stored is within a factor of two of the amount claimed, this technique could reduce the volume needed to hold three kilograms of hydrogen dramatically—to 35 liters.

Fill 'Er Up

R ather than building cars that require hydrogen fuel, automakers might opt instead to design vehicles that make hydrogen on board from a carrier fuel, such as methanol or even gasoline. Cars with such processing systems will be ultralow-

emission, not zero-emission, vehicles because onboard processors will inevitably create some pollutants. DaimlerChrysler and General Motors agree that a methanol-based fuel system is the best technical alternative to hydrogen. But like hydrogen, methanol would require expensive new tanks and pumps at service stations. The onboard "reforming" to make hydrogen from methanol is accomplished by reacting it with steam at 280 degrees C in the presence of a catalyst. Phosphoric-acid fuel cells work particularly well with a methanol reformer because their relatively high operating temperature allows them to supply "free" steam for the conversion. The elevated temperature also makes them resistant to poisoning by small amounts of carbon monoxide produced as a contaminant.

For typical phosphoric-acid cells, a respectable methanol-to-electricity efficiency of approximately 50 percent is possible. During the 1990s, H Power in Belleville, N.J., developed several experimental buses of this type. They ran quietly and were twice as efficient as diesel buses, yet they emitted only 1.5 percent of the carbon monoxide and 0.25 percent of the nitrogen oxides allowed by federal law.

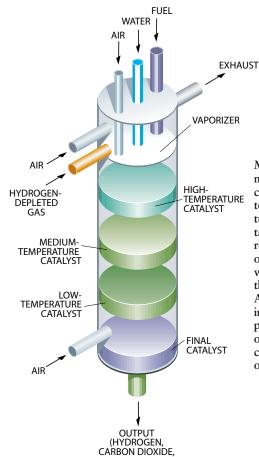
Methanol reforming is less easily combined with a proton-exchange membrane fuel cell because a catalytic conversion step is needed to reduce levels of carbon monoxide in the product, and even so the fuel cell needs a lot of platinum-ruthenium alloy catalyst at the anode to prevent poisoning. In addition, some of the hydrogen produced in the process has to be burned to produce steam for the reformer. A system built by Toyota achieved an average overall efficiency of only 37 percent. Some would question whether this is a goal worth pursuing, because that level of efficiency can be achieved by a hybrid internal-combustion engine, and methanol costs about twice what gasoline does for the same energy content. Moreover, a methanol reformer is large and heavy.

DaimlerChrysler and Shell are considering gasoline itself as a fuel-cell feedstock because it would make use of the existing \$200-billion gasoline distribution system. Vehicles would carry a multifuel steam processor that could make hydrogen from methanol or gasoline, burning some of the fuel to provide the steam required. A two-stage process would be needed to clean up the hydrogen. Argonne National Laboratory has tested a system that can convert pump gasoline to hydrogen with an efficiency of 78 percent. Yet after factoring in fair allowances for the energy needed to generate steam and the efficiency of the fuel cell, the efficiency of a vehicle using this system with gasoline would be an unimpressive 33 percent. And start-up of the fuel processor at low temperature still needs improvement, although a battery can supply power temporarily.

What is more, the sulfur present in all gasoline (and in hydrogen made from it) will poison the catalyst in a proton-exchange membrane cell. In stationary phosphoric-acid fuel-cell systems, fuel is desulfurized before being transformed to hydrogenrich gas. But gasoline cannot at present be cost-effectively desulfurized on board a vehicle.

Solutions might be developed. One possibility is to let hydrogen diffuse at high temperature and pressure through a membrane of palladium. Another idea is for manufacturers to produce a special sulfur-free synthetic fuel for use both in fuel-cell vehicles and in high-efficiency internal-combustion engines. But this proposal again raises questions about the needed infrastructure and its cost.

Not all major carmakers are committed to fuel cells. In June 1998 BMW announced that it preferred to move toward hydrogen-fueled internal-



MULTIFUEL PROCESSOR may be used in vehicles to convert gasoline or methanol to a hydrogen-rich gas mixture for fuel cells. Gas containing residual hydrogen, returned from fuel-cell anodes, is burned to heat fuel, water and air, which react on the high-temperature catalyst. Additional catalysts operating at successively lower temperatures reduce the amount of carbon monoxide and increase the hydrogen in the output stream.

GEORGE RETSECK

combustion engines, with liquid natural gas as an intermediate fuel. Yet a dedicated hydrogen-fueled internal-combustion engine would be less efficient than an optimized fuel cell and would produce some nitrogen oxides. Furthermore, until hydrogen produced from renewable energy sources such as solar power becomes widely available, it will be manufactured from natural gas and so cannot compete against the latter as a fuel.

NITROGEN)

In time, we are likely to see an infrastructure for delivering hydrogen for fuel-cell-powered vehicles. The result will be a more efficient, clean transportation sector, a reduction in imported oil and lower carbon dioxide emissions. A hydrogen delivery system will be built when it is technically feasible, affordable and necessary. But that point is still some years in the future.

The Author

A. JOHN APPLEBY trained as a metallurgist and electrochemist at the University of Cambridge. He has studied electrochemical aspects of all the common types of fuel cells, including bioelectrochemical systems, for more than 30 years. Appleby worked on fuel cells and advanced batteries at the Marcoussis research center of the Compagnie Générale d'Électricité in France in the 1970s before joining the Electric Power Research Institute in Palo Alto, Calif., in 1978 to manage advanced fuel-cell technology. He was also consulting professor of chemical engineering at Stanford University. Since 1987 he has been professor of applied electrochemistry and director of the Center for Electrochemical Systems and Hydrogen Research at Texas A&M University.

Further Reading

FUEL CELL HANDBOOK. A. John Appleby and Frank R. Foulkes, Van Nostrand Reinhold, 1989.

Fuel Cell Systems. Leo J.M.J. Blomen and Michael N. Mugerwa. Plenum Press, 1993.

FUEL CELLS AND THEIR APPLICATIONS. Karl Kordesch and Günter Simader. John Wiley & Sons, 1996.

FUEL CELL COMMERCIALIZATION ISSUES FOR LIGHT-DUTY VEHICLE APPLICATIONS. Christopher E. Borroni-Bird in *Journal of Power Sources*, Vol. 61, Nos. 1–2, pages 33–48; 1996.