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### Fuel Cells - Green Power

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**Designed by Jim Cruz** 





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For more information: www.education.lanl.gov/resources/fuelcells

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Lamps, burning coal oil and coal gas, lit the living rooms of most homes of the early 1900's. But when electric light bulbs replaced those smoky, smelly sources of illumination, homes became brighter, cleaner, and safer. At first only the wealthy could afford electric lights. But as the demand went up and the cost went down, more and more of the population were able to afford electric lighting even though there was plenty of coal to continue lighting buildings in the usual way. The better technology won.

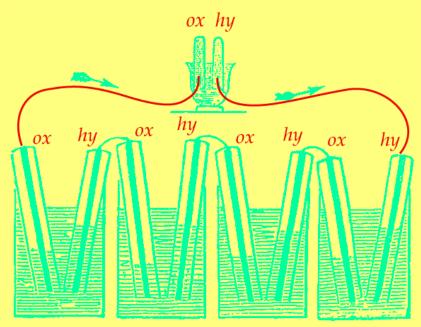
D.S. Scott and W. Hafele. "The Coming Hydrogen Age: Preventing World Climate Disruption." International Journal of Hydrogen Energy. Vol. 15, No. 10, 1990.

### "I cannot but regard the experiment as an important one..."

William Grove writing to Michael Faraday, October 22, 1842

#### **A Brief History**

A lthough fuel cells have been around since 1839, it took 120 years until NASA demonstrated some of their potential applications in providing power during space flight. As a result of these successes, in the 1960s, industry began to recognize the commercial potential of fuel cells, but encountered technical barriers and high investment costs — fuel cells were not economically competitive with existing energy technologies. Since 1984, the Office of Transportation Technologies at the U.S. Department of Energy has been supporting research and development of fuel cell technology, and as a result, hundreds of companies around the world are now working towards making fuel cell technology pay off. Just as in the commercialization of the electric light bulb nearly one hundred years ago, today's companies are being driven by technical, economic, and social forces such as high performance characteristics, reliability, durability, low cost, and environmental benefits.



In 1839, William Grove, a British jurist and amateur physicist, first discovered the principle of the fuel cell. Grove utilized four large cells, each containing hydrogen and oxygen, to produce electric power which was then used to split the water in the smaller upper cell into hydrogen and oxygen.



In March 1998, Chicago became the first city in the world to put pollution-free, hydrogen fuel cell powered buses in their public transit system. (Courtesy: Ballard Power Systems)



The first fuel cell powered bicycle to compete in the American Tour-de-Sol. (Courtesy: H-Power)



The FutureCar Challenge, sponsored by the U.S. Department of Energy, presents a unique assignment to students from North America's top engineering schools: convert a conventional midsize sedan into a super efficient vehicle without sacrificing performance, utility, and safety. In 1999, the Virginia Tech team entered the competition with a fuel cell vehicle.

**The automobile**, it is fair to say, changed the industrial and social fabric of the United States and most countries around the globe. Henry Ford epitomized "Yankee ingenuity" and the Model T helped create the open road, new horizons, abundant and inexpensive gasoline...and tailpipe exhaust. More people are driving more cars today than ever before — more than 200 million vehicles are on the road in the U.S. alone. But the car has contributed to our air and water pollution and forced us to rely on imported oil from the Middle East, helping to create a significant trade imbalance. Today many people think fuel cell technology will play a pivotal role in a new technological renaissance — just as the internal combustion engine vehicle revolutionized life at the beginning of the 20th century. Such innovation would have a global environmental and economic impact.

"In today's world, solving environmental problems is an investment, not an expense."

> William Clay Ford, Jr. Chairman and CEO, Ford Motor Company, September 1998

Fuel cells are not just laboratory curiosities. While there is much work that needs to be done to optimize the fuel cell system (remember, the gasoline internal combustion engine is nearly 120 years old and still being improved), hydrogen fuel cell vehicles are on the road — *now*. Commuters living in Chicago and Vancouver ride on fuel cell buses. You can take a ride around London in a fuel cell taxi and even compete in the American Tour de Sol on a fuel cell bicycle. Every major automobile manufacturer in the world is developing fuel cell vehicles. To understand why fuel cells have received such attention, we need to compare them to existing energy conversion technologies.

"The mission of our global fuel cell project center is nothing less than to make us the leader in commercially viable fuel cell powered vehicles."

> Harry J. Pearce, Vice Chairman, Board of Directors, General Motors. May 1998

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## Where the Action in Fuel Cells is Today

Allied Signal Volvo Ballard **DaimlerChrysler** Detroit Edison DuPont Shell Ford **General Motors** Honda Mazda **Georgetown University Case Western Reserve University** Los Alamos National Laboratory Motorola Penn State University **Princeton University Rolls-Royce** Argonne National Laboratory Sanyo DAIS Siemens **British Gas Plug Power** University of Michigan Texas A&M University ARCO Ерух **International Fuel Cells** H-Power **Energy Partners** Hydrogen Burner W.L. Gore A.D. Little Institute of Gas Technology Vairex Electrochem Giner Jet Propulsion Laboratory Toyota **University of California** Exxon Westinghouse Renault 3M Nissan BMW **PSA Peugeot Citroën** Texaco **University of Florida Tokyo Electric Power** 

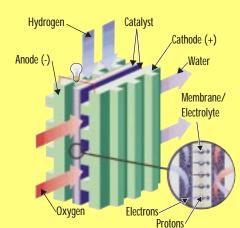
#### Carnot Cycle vs. Fuel Cells

T he theoretical thermodynamic derivation of Carnot Cycle shows that even under ideal conditions, a heat engine cannot convert all the heat energy supplied to it into mechanical energy; some of the heat energy is rejected. In an internal combustion engine, the engine accepts heat from a source at a high temperature  $(T_1)$ , converts part of the energy into mechanical work and rejects the remainder to a heat sink at a low temperature  $(T_2)$ . The greater the temperature difference between source and sink, the greater the efficiency,

Maximum Efficiency =  $(T_1 - T_2) / T_1$ 

where the temperatures  $T_1$  and  $T_2$  are given in degrees Kelvin. Because fuel cells convert chemical energy directly to electrical energy, this process does not involve conversion of heat to mechanical energy. Therefore, fuel cell efficiencies can exceed the Carnot limit even when operating at relatively low temperatures, for example, 80°C.

#### The Very Basics



- A fuel cell is an electrochemical energy conversion device. It is two to three times more efficient than an internal combustion engine in converting fuel to power.
- A fuel cell produces electricity, water, and heat using fuel and oxygen in the air.
- Water is the only emission when hydrogen is the fuel.

As hydrogen flows into the fuel cell on the anode side, a platinum catalyst facilitates the separation of the hydrogen gas

into electrons and protons (hydrogen ions). The hydrogen ions pass through the membrane (the center of the fuel cell) and, again with the help of a platinum catalyst, combine with oxygen and electrons on the cathode side, producing water. The electrons, which cannot pass through the membrane, flow from the anode to the cathode through an external circuit containing a motor or other electric load, which consumes the power generated by the cell.

The voltage from one single cell is about 0.7 volts – just about enough for a light bulb – much less a car. When the cells are stacked in series, the operating voltage increases to 0.7 volts multiplied by the number of cells stacked.

### How do Fuel Cells Compare to Internal Combustion Engines and Batteries?

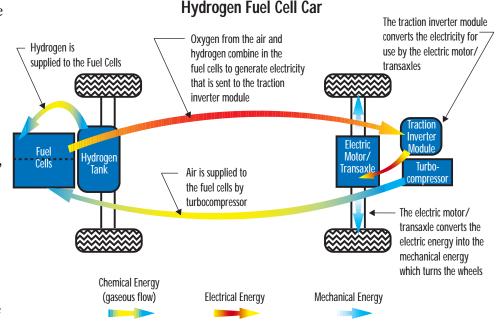
hat internal combustion engines, batteries, and fuel cells have in common is their purpose: all are devices that convert energy from one form to another. As a starting point, let's consider the internal combustion engine - used to power virtually all of the cars driven on U.S. highways today. These engines run on noisy, high temperature explosions resulting from the release of chemical energy by burning fuel with oxygen from the air. Internal combustion engines, as well as conventional utility power plants, change chemical energy of fuel to thermal energy to generate mechanical and, in the case of a power plant, electrical energy. Fuel cells and batteries are electrochemical devices, and by their very nature have a more efficient conversion process: chemical energy is converted directly to electrical energy. Internal combustion engines are less efficient because they include the conversion of thermal to mechanical energy, which is limited by the Carnot Cycle.

If cars were powered by electricity generated from direct hydrogen fuel cells, there would be no combustion involved. In an automotive fuel cell, hydrogen and oxygen undergo a relatively cool, electrochemical reaction that directly produces electrical energy. This electricity would be used by motors, including one or more connected to axles used to power the wheels of the vehicle. The direct hydrogen fuel cell vehicle will have no emissions even during idling — this is especially important during city rush hours. There are some similarities to an internal combustion engine, however. There is still a need for a fuel tank and oxygen is still supplied from the air.

Many people incorrectly assume that all electric vehicles (EVs) are powered by batteries. Actually, an EV is a vehicle with an electric drive train powered by either an on-board battery or fuel cell. Batteries and fuel cells are similar in that they both convert chemical energy into electricity very efficiently and they both require minimal maintenance because neither has any moving parts. However, unlike a fuel cell, the reactants in a battery are stored internally and, when used up, the battery must be either recharged or replaced. In a battery-powered EV, rechargeable batteries are used. With a fuel cell powered EV, the fuel is stored externally in the vehicle's

fuel tank and air is obtained from the atmosphere. As long as the vehicle's tank contains fuel, the fuel cell will produce energy in the form of electricity and heat. The choice of electrochemical device, battery or fuel cell, depends upon use. For larger scale applications, fuel cells have several advantages over batteries including smaller size, lighter weight, quick refueling, and longer range.

The polymer electrolyte membrane (PEM) fuel cell is one in a family of five distinct types of fuel cells. The PEM fuel cell, under consideration by vehicle manufacturers around the world as an alternative to the internal combustion engine, will be used to illustrate the science and technology of fuel cells.



The P2000, from Ford Motor Company, is a zero-emission vehicle that utilizes a direct hydrogen polymer electrolyte fuel cell. (Courtesy of Ford Motor Co.)

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#### **Resources:**

World Resources Institute http://www.wri.org **International Fuel Cells** http://www.hamiltonstandard.com/ifc-onsi **United Nations Framework Convention** on Climate Change http://www.unfccc.de/ Linkages http://www.iisd.ca/ linkages/ Environmental Protection Agency, **Alternative Fuels** http:// www.epa.gov/omswww U.S. Fuel Cell Council http://www.usfcc.com Fuel Cells 2000 http://fuelcells.org

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Chemical structure of membrane material; Nafion™ by DuPont

#### **Definitions:**

- Electrochemical reaction: A reaction involving the transfer of electrons from one chemical substance to another.
- Fuel cell: An electrochemical device that continuously converts the chemical energy of externally supplied fuel and oxidant directly to electrical energy.
- Oxidant: A chemical, such as oxygen, that consumes electrons in an electrochemical reaction.
- Electrolyte: A substance composed of positive and negative ions,
- Ion: An atom that has acquired an electrical charge by the loss or gain of electrons.
- 1 micron =  $10^{-6}$  m,  $10^{-4}$  cm,  $10^{-3}$  or 0.001 mm = 1 m
- Polymer: A substance made of giant molecules formed by the union of simple molecules (monomers). Thermal: Pertaining to heat

#### Structure of Polymer Electrolyte Membranes

The polymer electrolyte membrane is a solid, organic polymer, usually poly[perfluorosulfonic] acid. A typical membrane material, such as Nafion<sup>™</sup>, consists of three regions:

(1) the Teflon-like, fluorocarbon backbone, hundreds of repeating  $- CF_2 - CF - CF_2$  – units in length,

(2) the side chains,  $-O-CF_2 - CF - O-CF_2 - CF_2 -$ , which connect the molecular backbone to the third region,

(3) the ion clusters consisting of sulfonic acid ions, SO<sub>3</sub><sup>-</sup> H<sup>+</sup>.

The negative ions,  $SO_3^-$ , are permanently attached to the side chain and cannot move. However, when the membrane becomes hydrated by absorbing water, the hydrogen ions become mobile. Ion movement occurs by protons, bonded to water molecules, hopping from  $SO_3^-$  site to  $SO_3^-$  site within the membrane. Because of this mechanism, the solid hydrated electrolyte is an excellent conductor of hydrogen ions.

#### **Future Opportunities**

Polymer electrolyte membrane fuel cells are limited by the temperature range over which water is a liquid. The membrane must contain water so that the hydrogen ions can carry the charge within the membrane. Operating polymer electrolyte membrane fuel cells at temperatures exceeding 100°C is possible under pressurized conditions, required to keep the water in a liquid state, but shortens the life of the cell. Currently, polymer electrolyte membranes cost about \$100/square foot. Costs are expected to decrease significantly as the consumer demand for polymer electrolyte membrane fuel cells increases.

#### **Remaining Challenges:**

- producing membranes not limited by the temperature range of liquid water, possibly based on another mechanism for protonic conduction
- reducing membrane cost by developing different membrane chemistries

### The Polymer Electrolyte Membrane Fuel Cell

A s little as 10 years ago, vehicles powered by fuel cells seemed more science fiction than fact. Today, development of fuel cell technology for transportation is made possible due to the polymer electrolyte membrane fuel cell. This type of fuel cell is also known as the proton exchange membrane fuel cell, the solid polymer electrolyte (SPE<sup>™</sup>) fuel cell and simply, polymer electrolyte fuel cell. It is often referred to simply as the "PEM" fuel cell. The center of the fuel cell is the polymer electrolyte membrane. For all five families of fuel cells, it is the electrolyte that defines the type of fuel cell, so the discussion of the polymer electrolyte membrane fuel cell should logically begin with its electrolyte, the membrane.

#### The Polymer Electrolyte Membrane

An ordinary electrolyte is a substance that dissociates into positively charged and negatively charged ions in the presence of water, thereby making the water solution electrically conducting. The electrolyte in a polymer electrolyte membrane fuel cell is a type of plastic, a polymer, and is usually referred to as a membrane. The appearance of the electrolyte varies depending upon the manufacturer, but the most prevalent membrane, Nafion <sup>™</sup> produced by DuPont, resembles the plastic wrap used for sealing foods. Typically, the membrane material is more substantial than common plastic wrap, varying in thickness from 50 to 175 microns. To put this in perspective, consider that a piece of normal writing paper has a thickness of about 25 microns. Thus polymer electrolyte membranes have thicknesses comparable to that of 2 to 7 pieces of paper. In an operating fuel cell, the membrane is well humidified so that the electrolyte looks like a moist piece of thick plastic wrap.

Polymer electrolyte membranes are somewhat unusual electrolytes in that, in the presence of water, which the membrane readily absorbs, the negative ions are rigidly held within their structure. Only the positive ions contained within the membrane are mobile and are free to carry positive charge through the membrane. In polymer electrolyte membrane fuel cells these positive ions are hydrogen ions, or protons, hence the term – proton exchange membrane. Movement of the hydrogen ions through the membrane, in one direction only, from anode to cathode, is essential to fuel cell operation. Without this movement of ionic charge within the fuel cell, the circuit defined by cell, wires, and load remains open, and no current would flow.

Because their structure is based on a Teflon<sup>™</sup> backbone, polymer electrolyte membranes are relatively strong, stable substances. Although thin, a polymer electrolyte membrane is an effective gas separator. It can keep the hydrogen fuel separate from the oxidant air, a feature essential to the efficient operation of a fuel cell. Although ionic conductors, polymer electrolyte membranes do not conduct electrons. The organic nature of the polymer electrolyte membrane structure makes them electronic insulators, another feature essential to fuel cell operation. As electrons cannot move through the membrane, the electrons produced at one side of the cell must travel, through an external wire, to the other side of the cell to complete the circuit. It is in their route through the circuitry external to the fuel cell that the electrons provide electrical power to run a car or a power plant.

#### **The Electrodes**

All electrochemical reactions consist of two separate reactions: an oxidation half-reaction occurring at the anode and a reduction half-reaction occurring at the cathode. The anode and the cathode are separated from each other by the electrolyte, the membrane.

In the oxidation half-reaction, gaseous hydrogen produces hydrogen ions, which travel through the ionically conducting membrane to the cathode, and electrons which travel through an external circuit to the cathode. In the reduction half-reaction, oxygen, supplied from air flowing past the cathode, combines with these hydrogen ions and electrons to form water and excess heat. These two half-reactions would normally occur very slowly at the low operating temperature, typically 80°C, of the polymer electrolyte membrane fuel cell. Thus, catalysts are used on both the anode and cathode to increase the rates of each half-reaction. The catalyst that works the best on each electrode is platinum, a very expensive material.

The final products of the overall cell reaction are electric power, water, and excess heat. Cooling is required, in fact, to maintain the temperature of a fuel cell stack at about 80°C. At this temperature, the product water produced at the cathode is both liquid and vapor. This product water is carried out of the fuel cell by the air flow.

#### **Definitions:**

Catalyst: A substance that participates in a reaction, increasing its rate, but is not consumed in the reaction. Current: The flow of electric charge through a circuit. **Electrode:** An electronic conductor through which electrons are exchanged with the chemical reactants in an electrochemical cell. Electron: An elementary particle having a negative charge. 1 nanometer: =  $10^{-9}$  m =  $10^{-7}$  cm  $= 10^{-6} \text{ mm} = 10^{-3} \mu \text{m} = 1 \text{ nm}$ Oxidation half reaction: A process in which a chemical species changes to another species with a more positive charge due to the release of one or more electrons. It can occur only when combined with a reduction half reaction. Reduction half reaction: A process in

which a chemical species changes to another species with a less positive charge due to the addition of one or more electrons. It can occur only when combined with an oxidation half reaction.

#### **Electrochemistry of Fuel Cells**

Oxidation half reaction Reduction half reaction	<u> </u>	→ $4H^+ + 4e^-$ → $2H_2O$
Cell reaction	$2H_2 + O_2$	→2H <sub>2</sub> 0

The physical and electrochemical processes that occur at each electrode are quite complex. At the anode, hydrogen gas  $(H_2)$  must diffuse through tortuous pathways until a platinum (Pt) particle is encountered. The Pt catalyzes the dissociation of the  $H_2$  molecule into two hydrogen atoms (H) bonded to two neighboring Pt atoms. Only then can each H atom release an electron to form a hydrogen ion (H<sup>+</sup>). Current flows in the circuit as these H<sup>+</sup> ions are conducted through the membrane to the cathode while the electrons pass from the anode to the outer circuit and then to the cathode.

The reaction of one oxygen  $(O_2)$  molecule at the cathode is a 4 electron reduction process (see above equation) which occurs in a multi-step sequence. Expensive Pt based catalysts seem to be the only catalysts capable of generating high rates of  $O_2$  reduction at the relatively low temperatures (~ 80°C) at which polymer electrolyte membrane fuel cells operate. There is still uncertainty regarding the mechanism of this complex process. The performance of the polymer electrolyte membrane fuel cells is limited primarily by the slow rate of the  $O_2$  reduction half reaction which is more than 100 times slower than the H<sub>2</sub> oxidation half reaction.

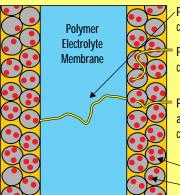
#### Why a Fuel Cell Goes "Platinum"

Water and Fuel Cell Performance

The half reactions occurring at each electrode can only occur at a high rate at the surface of the Pt catalyst. Platinum is unique because it is sufficiently reactive in bonding H and O intermediates as required to facilitate the electrode processes, and also capable of effectively releasing the intermediate to form the final product. For example, the anode process requires Pt sites to bond H atoms when the H<sub>2</sub> molecule reacts, and these Pt sites next release the H atoms, as H<sup>+</sup> + e<sup>-</sup>

 $H_2 + 2Pt \rightarrow 2Pt-H$ 2 Pt − H → 2 Pt + 2 H<sup>+</sup> + 2e<sup>-</sup>

This requires optimized bonding to H atoms — not too weak and not too strong — and this is the unique feature of a good catalyst. Realizing that the best catalyst for the polymer electrolyte membrane fuel cell is expensive, lowering Pt catalyst levels is an on-going effort. One of the best ways to accomplish this is to construct the catalyst layer with the highest possible surface area. Each electrode consists of porous carbon (C) to which very small Pt particles are bonded. The electrode is somewhat porous so that the gases can diffuse through each electrode to reach the catalyst. Both Pt and C conduct electrons well, so electrons are able to move freely through the electrode. The small size of the Pt particles, about 2 nanometers in diameter, results in an enormously large total surface area of Pt that is accessible to gas molecules. The total surface presented by this huge number of small particles is very large even when the total mass of Pt used is small. This large Pt surface area allows the electrode reactions to proceed at many Pt surface sites simultaneously. This high dispersion of the catalyst is one key to generating significant electron flow, i.e. current, in a fuel cell.



Pathway(s) allowing conduction of hydrogen ions

Pathway(s) allowing conduction of electrons

 Pathway(s) allowing access of gas to catalyst surface

> <sup>—</sup> Carbon — Platinum

Polymer electrolyte membrane with porous electrodes that are composed of platinum particles uniformly supported on carbon particles. **WW** ater management" is key to effective operation of a polymer electrolyte membrane fuel cell. Although water is a product of the fuel cell reaction, and is carried out of the cell during its operation, it is interesting that both the fuel and air entering the fuel cell must still be humidified. This additional water keeps the polymer electrolyte membrane hydrated. The humidity of the gases must be carefully controlled. Too little water prevents the membrane from conducting the H<sup>+</sup> ions well and the cell current drops.

If the air flow past the cathode is too slow, the air can't carry all the water produced at the cathode out of the fuel cell, and the cathode "floods." Cell performance is hurt because not enough oxygen is able to penetrate the excess liquid water to reach the cathode catalyst sites.

#### **Future Opportunities**

- Impurities often present in the H<sub>2</sub> fuel feed stream bind to the Pt catalyst surface in the anode, preventing H<sub>2</sub> oxidation by blocking Pt catalyst sites. Alternative catalysts which can oxidize H<sub>2</sub> while remaining unaffected by impurities are needed to improve cell performance.
- The rate of the oxygen reduction process at the air electrode is quite low even at the best Pt catalysts developed to date, resulting in significant performance loss. Alternative catalysts that promote a high rate of oxygen reduction are needed to further enhance fuel cell performance.
- Future alternative catalysts must be less expensive than Pt to lower the cost of the cell.

#### Making a Membrane/Electrode Assembly

embrane/electrode assembly construction varies greatly, but the following procedure is one of several used at Los Alamos National Laboratory where fuel cell research is actively pursued. The catalyst material is first prepared in liquid "ink" form by thoroughly mixing together appropriate amounts of catalyst (a powder of Pt dispersed on carbon) and a solution of the membrane material dissolved in alcohols. Once the ink is prepared, it is applied to the surface of the solid membrane in a number of different ways. The simplest method involves painting the catalyst "ink" directly onto a dry, solid piece of membrane. The wet catalyst layer and the membrane are heated until the catalyst layer is dry. The membrane is then turned over and the procedure is repeated on the other side. Catalyst layers are now on both sides of the membrane. The dry membrane/electrode assembly is next rehydrated by immersing in lightly boiling dilute acid solution to also ensure that the membrane is in the H<sup>+</sup> form needed for fuel cell operation. The final step is a thorough rinsing in distilled water. The membrane/electrode assembly is now ready for insertion into the fuel cell hardware.

#### **Future Opportunities**

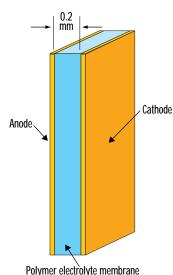
Optimization of membrane/electrode assembly (MEA) construction is on-going. Fundamental research into the catalyst layer/ membrane interface is needed to further understand the processes involved in current generation. New MEA designs which will increase fuel cell performance are needed. As always, the science and technology of MEAs are interconnected; whether improved understanding will lead to better MEA design or a different design will lead to improved understanding remains to be seen.

### The Membrane/Electrode Assembly

T he combination of anode/membrane/cathode is referred to as the membrane/electrode assembly. The evolution of membrane/electrode assemblies in polymer electrolyte membrane fuel cells has passed through several generations. The original membrane/ electrode assemblies were constructed in the 1960s for the Gemini space program and used 4 milligrams of platinum per square centimeter of membrane area  $(4 \text{ mg/cm}^2)$ . Current technology varies with the manufacturer, but total platinum loading has decreased from the original 4 mg/cm<sup>2</sup> to about 0.5 mg/cm<sup>2</sup>. Laboratory research now uses platinum loadings of 0.15mg/cm<sup>2</sup>. This corresponds to an improvement in fuel cell performance since the Gemini program, as measured by amperes of current produced, from about 0.5 amperes per milligram of platinum to 15 amperes per milligram of platinum.

The thickness of the membrane in a membrane/electrode assembly can vary with the type of membrane. The thickness of the catalyst layers depends upon how much platinum is used in each electrode. For catalyst layers containing about 0.15 mg Pt/cm<sup>2</sup>, the thickness of the catalyst layer is close to 10 microns, less than half the thickness of a sheet of paper. It is amazing that this

membrane/electrode assembly, with a total thickness of about 200 microns or 0.2 millimeters, can generate more than half an ampere of current for every square centimeter of membrane/electrode assembly at a voltage between the cathode and anode of 0.7 volts, but only when encased in well engineered components — backing layers, flow fields, and current collectors.



Membrane/electrode assembly

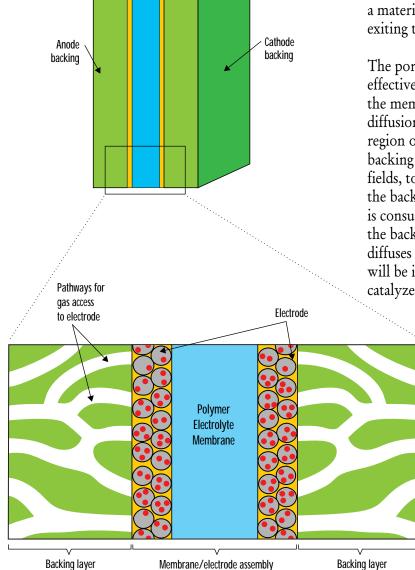
### The Backing Layers

The hardware of the fuel cell, backing layers, flow fields and current collectors, is designed to maximize the current that can be obtained from a membrane/electrode assembly. The so-called backing layers, one next to the anode, the other next to the cathode, are usually made of a porous carbon paper or carbon cloth, typically 100 to 300 microns thick (4 to 12 sheets of paper). The backing layers have to be made of a material, such as carbon, that can conduct the electrons exiting the anode and entering the cathode.

The porous nature of the backing material ensures effective diffusion of each reactant gas to the catalyst on the membrane/electrode assembly. In this context, diffusion refers to the flow of gas molecules from a region of high concentration, the outer side of the backing layer where the gas is flowing by in the flow fields, to a region of low concentration, the inner side of the backing layer next to the catalyst layer where the gas is consumed by the reaction. The porous structure of the backing layers allows the gas to spread out as it diffuses so that when it penetrates the backing, the gas will be in contact with the entire surface area of the catalyzed membrane.

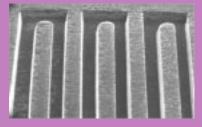
> The backing layers also assist in water management during the operation of the fuel cell; too little or too much water can cause the cell to cease operation. The correct backing material allows the right amount of water vapor to reach the membrane/electrode assembly to keep the membrane humidified. The backing material also allows the liquid water produced at the cathode to leave the cell so it doesn't "flood". The backing layers are often wet-proofed with Teflon<sup>™</sup> to ensure that at least some, and hopefully most, of the pores in the carbon cloth (or carbon paper) don't become clogged with water, which would prevent rapid gas diffusion necessary for a good rate of reaction to occur at the electrodes.

Membrane/electrode assembly with backing layers.

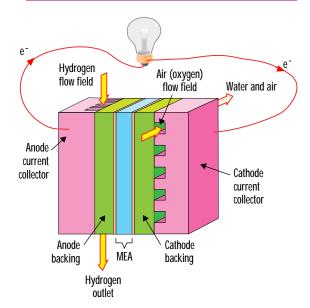


Enlarged cross-section of a membrane/electrode assembly showing structural details.

Photographs of stainless steel flow fields/current collectors



Micrograph of a milled carbon-fiber composite flow-field. Height, width and spacing of channels = 0.8mm (0.032 inch)



### The Flow Fields / Current Collectors

**P** ressed against the outer surface of each backing layer is a piece of hardware, called a plate, which often serves the dual role of flow field and current collector. In a single fuel cell, these two plates are the last of the components making up the cell. The plates are made of a light-weight, strong, gas-impermeable, electron-conducting material; graphite or metals are commonly used although composite plates are now being developed.

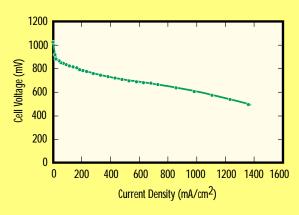
The first task served by each plate is to provide a gas "flow field." The side of the plate next to the backing layer contains channels machined into the plate. The channels are used to carry the reactant gas from the point at which it enters the fuel cell to the point at which the gas exits. The pattern of the flow field in the plate as well as the width and depth of the channels have a large impact on the effectiveness of the distribution of the reactant gases evenly across the active area of the membrane/electrode assembly. Flow field design also affects water supply to the membrane and water removal from the cathode.

The second purpose served by each plate is that of current collector. Electrons produced by the oxidation of hydrogen must be conducted through the anode, through the backing layer and through the plate before they can exit the cell, travel through an external circuit and re-enter the cell at the cathode plate.

With the addition of the flow fields and current collectors, the polymer electrolyte membrane fuel cell is now complete. Only a load-containing external circuit, such as an electric motor, is required for electric current to flow, the power having been generated by passing hydrogen and air on either side of what looks like a piece of food wrap painted black.

A single polymer electrolyte membrane fuel cell.

#### Efficiency, Power and Energy of Polymer Electrolyte Membrane Fuel Cell



Graph of voltage vs. current density of a hydrogen/air polymer electrolyte membrane fuel cell.

Energy conversion of a fuel cell can be summarized in the following equation:

#### Chemical energy of fuel = Electric energy + Heat energy

A single, ideal H<sub>2</sub>/air fuel cell should provide 1.16 volts at zero current ("open circuit" conditions), 80°C and 1 atm gas pressure. A good measure of energy conversion efficiency for a fuel cell is the ratio of the actual cell voltage to the theoretical maximum voltage for the H<sub>2</sub>/air reaction. Thus a fuel cell operating at 0.7 V is generating about 60% of the maximum useful energy available from the fuel in the form of electric power. If the same fuel cell is operated at 0.9 V, about 77.5% of the maximum useful energy (40% or 22.5%) will appear as heat. The characteristic performance curve for a fuel cell represents the DC voltage delivered at the cell terminals as a function of the current density, total current divided by area of membrane, being drawn from the fuel cell by the load in the external circuit

The power (P), expressed in units of watts, delivered by a cell is the product of the current (I) drawn and the terminal voltage (V) at that current (P = IV). Power is also the rate at which energy (E) is made available (P = E/t) or conversely, energy, expressed in units of watt-hours, is the power available over a time period (t) (E = Pt). As the mass and volume of a fuel cell system are so important, additional terms are also used. Specific power is the ratio of the power produced by a cell to the mass of the cell; power density is the ratio of the power produced by a cell to the volume of the cell. High specific power and power density are important for transportation applications, to minimize the weight and volume of the fuel cell as well as to minimize cost.

#### **Derivation of Ideal Fuel Cell Voltage**

Λ

 $\Delta E$ 

Prediction of the maximum available voltage from a fuel cell process involves evaluation of energy differences between the initial state of reactants in the process ( $H_2 + 1/2 O_2$ ) and the final state ( $H_2O$ ). Such evaluation relies on thermodynamic functions of state in a chemical process, primarily the Gibbs free energy. The maximum cell voltage ( $\Delta E$ ) for the hydrogen/air fuel cell reaction ( $H_2 + 1/2 O_2 \Rightarrow H_2O$ ) at a specific temperature and pressure is calculated [ $\Delta E = -\Delta G/nF$ ], where  $\Delta G$  is the Gibbs free energy change for the reaction, n is the number of moles of electrons involved in the reaction per mole of  $H_2$ , and F is Faraday's constant, 96, 487 coulombs (joules/volt), the charge transferred per mole of electrons.

At a constant pressure of 1 atmosphere, the Gibbs free energy change in the fuel cell process (per mole of H<sub>2</sub>) is calculated from the reaction temperature (T), and from changes in the reaction enthalpy ( $\Delta$ H) and entropy ( $\Delta$ S)

$$\Delta G = \Delta H - T \Delta S$$
  
= - 285,800 J - (298 K)(-163.2 J/K)

For the hydrogen/air fuel cell at 1 atmosphere pressure and 25°C (298 K), the cell voltage is 1.23 V.

As temperature rises from room temperature to that of an operating fuel cell (80°C or 353 K), the values of  $\Delta$ H and  $\Delta$ S change only slightly, but T changes by 55°. Thus the absolute value of  $\Delta$ G decreases. For a good estimation, assuming no change in the values of  $\Delta$ H and  $\Delta$ S

$$\Delta G = -285,800 \text{ J/mol} - (353 \text{ K})(-163.2 \text{ J/mol} \text{ K})$$
  
= -228,200 J/mol

Thus, the maximum cell voltage decreases as well (for the standard case of 1 atm), from 1.23 V at 25°C to 1.18 V at 80°C

An additional correction for air, instead of pure oxygen, and using humidified air and hydrogen, instead of dry gases, further reduces the maximum voltage obtainable from the hydrogen/air fuel cell to 1.16 V at 80°C and 1 atmosphere pressure.

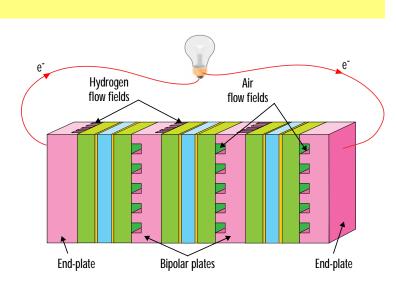
#### **Rate of Heat Generation in an Operating Fuel Cell**

A ssume a 100 cm<sup>2</sup> fuel cell is operating, under typical conditions of 1 atmosphere pressure and 80°C, at 0.7 V and generating 0.6 A/cm<sup>2</sup> of current, for a total current of 60 A. The excess heat generated by this cell can be estimated as follows:

Power due to heat = Total power generated – Electrical power  $P_{heat} = P_{total} - P_{electrical}$ 

- $= (V_{ideal} \times I_{cell}) (V_{cell} \times I_{cell})$
- = (V<sub>ideal</sub> V<sub>cell</sub>) x I<sub>cell</sub>
- = (1.16 V 0.7 V) x 60 A
- = 0.46 V x 60 coulombs/sec. x 60 seconds/min.
- = 1650 J/min

This cell is generating about 1.7 kJ of excess heat every minute it operates, while generating about 2.5 kJ of electric energy per minute.



A 3 cell fuel cell stack with two bipolar plates and two end plates.



### The Polymer Electrolyte Membrane Fuel Cell Stack

**S** ince fuel cells operate at less than 100% efficiency, the voltage output of one cell is less than 1.16 volt. As most applications require much higher voltages than this, (for example, effective commercial electric motors typically operate at 200 – 300 volts), the required voltage is obtained by connecting individual fuel cells in series to form a fuel cell "stack." If fuel cells were simply lined-up next to each other, the anode and cathode current collectors would be side by side. To decrease the overall volume and weight of the stack, instead of two current collectors, only one plate is used with a flow field cut into each side of the plate. This type of plate, called a "bipolar plate," separates one cell from the next, with this single plate serving to carry hydrogen gas on one side and air on the other. It is important that the bipolar plate is made of gas-impermeable material. Otherwise the two gases would intermix, leading to direct oxidation of fuel. Without separation of the gases, electrons pass directly from the hydrogen to the oxygen and these electrons are essentially "wasted" as they cannot be routed through an external circuit to do useful electrical work. The bipolar plate must also be electronically conductive because the electrons produced at the anode on one side of the bipolar plate are conducted through the plate where they enter the cathode on the other side of the bipolar plate. Two end-plates, one at each end of the complete stack of cells, are connected via the external circuit.

In the near term, different manufacturers will provide a variety of sizes of fuel cell stacks for diverse applications. The area of a single fuel cell can vary from a few square centimeters to a thousand square centimeters. A stack can consist of a few cells to a hundred or more cells connected in series using bipolar plates. For applications that require large amounts of power, many stacks can be used in series or parallel combinations.

**Polymer electrolyte membrane fuel cell stack.** (Courtesy: Energy Partners)



Computer model of 50kW fuel cell stack with reformer. (Courtesy: International Fuel Cells)

#### Processing Hydrocarbon Fuels into Hydrogen

A s long as hydrogen is difficult to store on a vehicle, on-board fuel processors will be needed to convert a hydrocarbon fuel, such as methanol or gasoline, to a  $H_2$  rich gas for use in the fuel cell stack. Currently, steam reforming of methanol to  $H_2$  is the conventional technology, although partial oxidation of gasoline to  $H_2$  is attractive because of the gasoline infrastructure already in place in most countries. Both types of fuel processors are complex systems.

The steam reforming of methanol involves the reaction of steam and pre-vaporized methanol at 200°C (gasoline requires temperatures over 800°C) to produce a mixture of H<sub>2</sub>, carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and excess steam. This mixture passes through another reactor, called a shift reactor, which uses catalysts and water to convert nearly all of the CO to CO<sub>2</sub> as well as additional H<sub>2</sub>. There can be a third stage in which air is injected into the mixture in a third type of reactor, the preferential oxidation reactor. Oxygen in the air reacts with the remaining CO over a Pt-containing catalyst to convert CO to CO<sub>2</sub>. The final gas mixture contains about 70% H<sub>2</sub>, 24% CO<sub>2</sub>, 6% nitrogen (N<sub>2</sub>) and traces of CO.

With the partial oxidation reformer system, liquid fuel is first vaporized into a gas. The gas is then ignited in a partial oxidation reactor which limits the amount of air so that primarily  $H_2$ , CO and  $CO_2$  are produced from the combustion. This mixture is passed through a shift reactor to convert the CO to  $CO_2$  and then through a preferential oxidation reactor to convert any remaining CO to  $CO_2$ . Conventional partial oxidation takes place at ~1000°C and catalytic partial oxidation takes place at ~700°C. The final reformate composition is about 42%  $N_2$ , 38%  $H_2$ , 18%  $CO_2$ , less than 2%  $CH_4$  and traces of CO.

### Other Types of Polymer Electrolyte Membrane Fuel Cell Systems

There are several other types of polymer electrolyte membrane fuel cells for transportation applications, although none have reached the same stage of development and simplicity as the hydrogen/air.

#### **Reformate/Air Fuel Cell**

In addition to the direct hydrogen fuel cell, research is currently underway to develop a fuel cell system that can operate on various types of hydrocarbon fuels including gasoline, and alternative fuels such as methanol, natural gas, and ethanol. Initially, this fuel-flexible fuel strategy will enable reformate/air fuel cell systems to use the exisiting fuels infrastructure. A hydrogen/air polymer electrolyte membrane fuel cell would be fueled from an onboard reformer that can convert these fuels into hydrogen-rich gas mixtures. Processing hydrocarbon fuels to generate hydrogen is a technical challenge and a relatively demanding operation.

Hydrocarbon fuels require processing temperatures of 700°C - 1000°C. Sulfur, found in all carbon-based fuels, and carbon monoxide generated in the fuel processor, must be removed to avoid poisoning the fuel cell catalyst. Although the reformate/air fuel cell lacks the zero emission characteristic of the direct hydrogen fuel cell, it has the potential of lowering emissions significantly vs. the gasoline internal combustion engine. The near-term introduction of reformate/air fuel cells is expected to increase market acceptance of fuel cell technology and help pave the way for the widespread use of direct hydrogen systems in the future.

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- www.eren.doe.gov

#### The Fuel Cell Engine

F uel cell stacks need to be integrated into a complete fuel cell engine. A fuel cell engine must be of appropriate weight and volume to fit into the space typically available for car engines. Importantly, the operation of the entire engine must maintain the near zero emissions and high efficiency of fuel cells. Finally, all these requirements must be met with components that are both inexpensive and designed for low cost, high volume manufacturing.

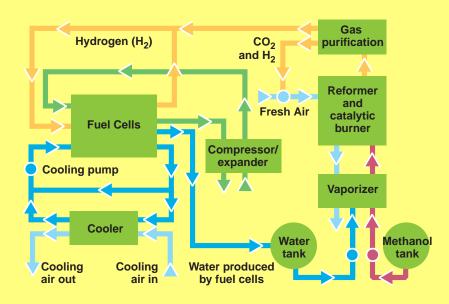


Diagram of reformate/air fuel cell "engine" utilizing liquid methanol as fuel.

Hydrogen & Fuel Cell Letter http://mhv.net/~hfcletter Hydrogen and the Materials of a Sustainable Energy Future http://education.lanl.gov/ RESOURCES/h2 Karl Kordesh and Gunter Sinander. Fuel Cells and Their Applications. VCH Publishers, New York, 1996. **DOE Office of Transportation** Technologies http:// www.ott.doe.gov United States Council For Automotive Research http://www.uscar.org/ Arthur D. Little http://www.arthurdlittle.com





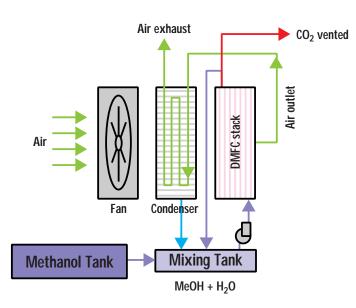
The Opel Zafira, by General Motors, reforms methanol to operate a polymer electrolyte membrane fuel cell. This vehicle has nearly zero emissions of sulfur dioxide and nitrogen oxides and the carbon dioxide output is expected to be 50% less than a comparable internal combustion engine vehicle. (Courtesy: General Motors)

#### **Emissions from Fuel Cell Engines**

The potential of fuel cells to provide zero or near zero emissions has been a significant force in the development of the technology over the past 30 years. Direct hydrogen/air systems (utilizing on-board hydrogen storage) are the only fuel cells having zero emissions from the tailpipe. On-board processing of gasoline, methanol and other carbon-based fuels into hydrogen rich gas can be done with minute amounts of tailpipe emissions and water and  $CO_2$  as the major by-products. Over the next few years, near-zero emissions and performance will continue to improve.

#### **Direct Methanol Fuel Cell**

As its name implies, methanol fuel is directly used in this fuel cell. In the direct methanol fuel cell, as in the hydrogen/air fuel cell, oxygen from the surrounding air is the oxidant, however, there is no oxidation of hydrogen. Liquid methanol is the fuel being oxidized directly at the anode.



**Schematic of direct methanol fuel cell system.** (Courtesy: Los Alamos National Laboratory)

Electrochemistry	of a Direct	t Methanol Fu	iel Cell

he electroch in a direct n			
Anode Cathode	$CH_3OH + H_2O$ 3/2 $O_2 + 6H^+ + 6e^-$		$CO_2 + 6H^+ + 6e^-$ $3H_2O$
Cell reaction	CH <sub>3</sub> OH + 3/2 O <sub>2</sub>	+	$CO_2 + 2H_2O$

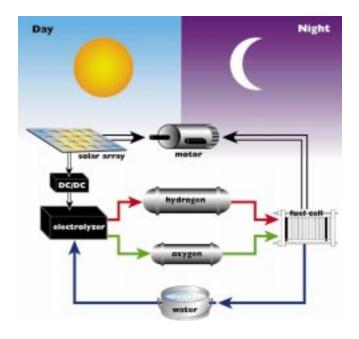
Direct methanol fuel cell technology, unique as a low temperature fuel cell system not utilizing hydrogen, is still relatively new compared to hydrogen/air polymer electrolyte fuel cell technology, with several challenges remaining. Recent advances in direct methanol fuel cell research and development have been substantial, with the direct methanol fuel cell achieving a significant fraction of the performance of direct hydrogen/air fuel cells. However, there are critical obstacles to be overcome. To achieve high current, the necessary amount of expensive platinum catalyst is still much greater than the amount used in hydrogen/air polymer electrolyte fuel cells. Methanol fuel crosses through the membrane from the anode to the cathode; this undesired methanol "crossover" decreases the performance of the air cathode and wastes fuel.

The advantages of supplying methanol directly to the fuel cell are significant — with consumer acceptance of a liquid fuel being high on the list. While a new or modified infrastructure would be required to supply large quantities of methanol, there are some methanol pumps already available. Importantly, a direct methanol fuel cell system does not require a bulky and heavy hydrogen storage system or a reforming subsystem. This advantage, in terms of simplicity and cost, means the direct methanol fuel cell system presents an attractive alternative to hydrogen or reformate-fed systems. In addition, a direct methanol fuel cell is considered a zero emission vehicle.

#### **Regenerative Fuel Cell**

A regenerative fuel cell, currently being developed for utility applications, uses hydrogen and oxygen or air to produce electricity, water, and waste heat as a conventional fuel cell does. However, the regenerative fuel cell also performs the reverse of the fuel cell reaction, using electricity and water to form hydrogen and oxygen. In the reverse mode of the regenerative fuel cell, known as electrolysis, electricity is applied to the electrodes of the cell to force the dissociation of water into its components.

The "closed" system of a regenerative fuel cell could have a significant advantage because it could enable the operation of a fuel cell power system without requiring a new hydrogen infrastructure. There are two concerns to be addressed in the development of regenerative fuel cells. The first is the extra cost that would be incurred in making the fuel cell reversible.



Renewable regenerative fuel cell utilizing the energy source of the sun to produce power (Courtesy: Aerovironment)

The second drawback to the operation of the regenerative fuel cell is the use of grid electricity to produce the hydrogen. In the United States, most electricity comes from burning fossil fuels. The fossil fuel 
+ electricity 
+ hydrogen energy route generates significantly more greenhouse gases than simply burning gasoline in an internal combustion engine. Although the concept of a regenerative fuel cell is attractive, until renewable electricity, e.g. electricity from solar or wind sources, is readily available, this technology will not reduce greenhouse gas emissions.



Unmanned solar plane powered by a renewable regenerative fuel cell (Courtesy: Aerovironment)

In the near term, fuel availability could be an important reason for operating fuel cell vehicles on gasoline. Today, oil refiners in the U.S. are spending over \$10 billion to comply with reformulated gasoline regulations to help lower tailpipe emissions. Fuel cell vehicles operating on alternative fuels will require new and expensive fueling infrastructures. However. alternative fuels will provide superior environmental performance. In the long term, incremental investments in a new domestic fuel infrastructure will be necessary for the 21<sup>st</sup> century.

RFG :
Reformulated
Gasoline
M 100 :
Methanol
E 100 :
Ethanol
H <sub>2</sub> :
Hydrogen
CNG :
Compressed
Natural Gas

#### **Characteristics of Potential Fuel Cell Fuels**

	Production	Storago	Cost est./	Safaty	Distribution	Environmental	
RFG	ProductionLarge existing production operationUses imported feedstockNo energy security or trade balance benefitsAbundant domestic/imported natural gas feedstockCan be manufactured renewably from domestic biomass - not currently being	Storage Conventional storage tanks	gal. eq \$.0515 more than gasoline \$.90	Safety         Low flashpoint         Narrow flammability         limits         Potentially         carcinogenic when         inhaled         Toxic and can be         absorbed through the         skin         No visible flame         Adequate training         required to operate	Infrastructure and distribution system Infrastructure needs to be expanded	AttributesReduction in greenhouse gasesMuch lower reactive hydrocarbon and sulfur oxide emissions than gasolineHigh greenhouse gas emissions when manufactured from coalZero emissions when made renewably	
E 100	done Made from domestic renewable resources: corn, wood, rice, straw, waste, switchgrass. Many technologies still experimental Production from feedstocks are energy intensive	Requires special storage because fuel can be corrosive to rubber, plastic and some metals	\$1.10- \$1.15	safely Wide flammability limit Adequate training required to operate safely Less toxic than methanol and gasoline	Nearly no infrastructure currently available Food/fuel competition at high productions levels	Zero carbon dioxide emissions as a fuel Significant emissions in production	
H <sub>2</sub>	Domestic manufacturing: Steam reforming of coal, natural gas or methane Renewable solar	Compressed gas cylinders Cryogenic fuel tanks Metal hydrides Carbon nanofibers Currently storage systems are heavy and bulky	\$.79- \$1.91	Low flammability limit Disperses quickly when released Nearly invisible flame Odorless and colorless Non-toxic Adequate training required to operate safely	Needs new infrastructure	High emissions when manufactured from electrolysis Lower emissions from natural gas Zero emissions when manufactured renewably	
CNG	Abundant domestic/imported feedstock Can be made from coal	CNG needs to be compressed during refueling and requires special nozzles to avoid evaporative emissions Stored in compressed gas cylinders		Low flashpoint Non-carcinogenic Dissipates into the air in open areas High thermal efficiency Adequate training required to operate safely	Limited infrastructure	Non-renewable Possible increase in nitrogen oxide emissions	
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#### **Definitions:**

Quad: A unit of heat energy, equal to 10<sup>15</sup> British thermal units.



The world's first prototype polymer electrolyte membrane fuel cell (on the right) used to provide all residential power needs for a home in Latham, New York. This 7kW unit is attached to a power conditioner/storage unit that stores excess electricity. (Courtesy: Plug Power)



A laptop computer using a fuel cell power source can operate for up to 20 hours on a single charge of fuel. (Courtesy: Ballard Power Systems)



4 Times Square in New York City is one of the first office buildings in the U.S. to be powered by a 200 kW phosphoric acid fuel cell system (Courtesy: International Fuel Cells)

# Fuel cells are becoming an alternative choice for rural energy needs

- In places where there are no existing power grids
- Where power supply is often unreliable
- In remote locations that are not accessible to power lines

### Potential Applications for Fuel Cells

**F** uel cells were developed for and have long been used in the space program to provide electricity and drinking water for the astronauts. Terrestrial applications can be classified into categories of transportation, stationary or portable power uses.

Polymer electrolyte membrane fuel cells are well suited to transportation applications because they provide a continuous electrical energy supply from fuel at high levels of efficiency and power density. They also offer the advantage of minimal maintenance because there are no moving parts in the power generating stacks of the fuel cell system.

The utility sector is expected to be an early arena where fuel cells will be widely commercialized. Today, only about one-third of the energy consumed reaches the actual user because of the low energy conversion efficiencies of power plants. In fact, fossil and nuclear plants in the U.S vent 21 quads of heat into the atmosphere - more heat than all the homes and commercial buildings in the country use in one year! Using fuel cells for utility applications can improve energy efficiency by as much as 60% while reducing environmental emissions. Phosphoric acid fuel cells have been generally used in the initial commercialization of stationary fuel cell systems. These environmentally friendly systems are simple, reliable, and quiet. They require minimal servicing and attention. Natural gas is the primary fuel, however, other fuels can be used — including gas from local landfills, propane, or fuels with high methane content. All such fuels are reformed to hydrogen-rich gas mixtures before feeding to the fuel cell stack. Over 200 (phosphoric acid fuel cells) units, 200 kilowatts each, are currently in operation around the world. Fuel cell manufacturers are now developing small scale polymer electrolyte fuel cell technology for individual home utility and heating applications at the power level of 2-5 kilowatts because the potential for lower materials and manufacturing costs could make these systems commercially viable. Like the larger fuel cell utility plants, smaller systems will also be connected directly to natural gas pipe lines — not the utility grid. In addition to these small scale uses, polymer electrolyte fuel cell technology is also being developed for large scale building applications.

"Distributed power" is a new approach utility companies are beginning to implement — locating small, energy-saving power generators closer to where the need is. Because fuel cells are modular in design and highly efficient, these small units can be placed on-site. Installation is less of a financial risk for utility planners and modules can be added as demand increases. Utility systems are currently being designed to use regenerative fuel cell technology and renewable sources of electricity.

### **Other Fuel Cell Technologies**

he electrolyte defines the key properties, particularly operating temperature, of the fuel cell. For this reason, fuel cell technologies are named by their electrolyte. Four other distinct types of fuel cells have been developed in addition to the polymer electrolyte membrane fuel cell:

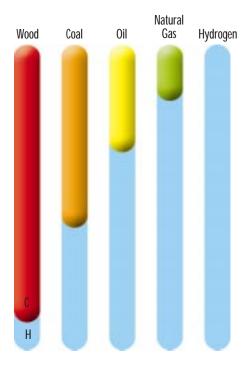
- alkaline fuel cells
- phosphoric acid fuel cells
- molten carbonate fuel cells
- solid oxide fuel cells

These fuel cells operate at different temperatures and each is best suited to particular applications. The main features of the five types of fuel cells are summarized in chart form.

### **Comparison of Five Fuel Cell Technologies**

-		-	
Fuel Cell	Electrolyte	Operating Temperature (°C)	Electrochemical Reactions
Polymer Electrolyte/ Membrane (PEM)	Solid organic polymer poly-perfluorosulfonic acid	60 - 100	Anode: $H_2 \Rightarrow 2H^+ + 2e^-$ Cathode: $1/2 O_2 + 2H^+ + 2e^- \Rightarrow H_2 O$ Cell: $H_2 + 1/2 O_2 \Rightarrow H_2 O$
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100	Anode: $H_2 + 2(0H)^2 \rightarrow 2H_20 + 2e^2$ Cathode: $1/2 0_2 + H_20 + 2e^2 \rightarrow 2(0H)^2$ Cell: $H_2 + 1/2 0_2 \rightarrow H_20$
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	175 - 200	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2 O$ Cell: $H_2 + 1/2 O_2 \rightarrow H_2 O$
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium and/ or potassium carbon- ates, soaked in a matrix	600 - 1000	Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^{-1}$ Cathode: $1/2 O_2 + CO_2 + 2e^{-1} \rightarrow CO_3^{2-1}$ Cell: $H_2 + 1/2 O_2 + CO_2 \rightarrow H_2O + CO_2$ (CO <sub>2</sub> is consumed at cathode and produced at anode)
Solid Oxide (SOFC)	Solid zirconium oxide to which a small amount of ytrria is added	600 - 1000	Anode: $H_2 + 0^{2^-} \Rightarrow H_2 0 + 2e^-$ Cathode: $1/2 0_2 + 2e^- \Rightarrow 0^{2^-}$ Cell: $H_2 + 1/2 0_2 \Rightarrow H_2 0$

Applications	Advantages	Disadvantages
electric utility portable power transportation	<ul> <li>Solid electrolyte reduces corrosion &amp; management problems</li> <li>Low temperature</li> <li>Quick start-up</li> </ul>	<ul> <li>Low temperature requires expensive catalysts</li> <li>High sensitivity to fuel impurities</li> </ul>
military space	• Cathode reaction faster in alkaline electrolyte — so high performance	<ul> <li>Expensive removal of CO<sub>2</sub> from fuel and air streams required</li> </ul>
electric utility transportation	<ul> <li>Up to 85 % efficiency in co-generation of electricity and heat</li> <li>Impure H<sub>2</sub> as fuel</li> </ul>	<ul> <li>Pt catalyst</li> <li>Low current and power</li> <li>Large size/weight</li> </ul>
electric utility	<ul> <li>High temperature advantages*</li> </ul>	High temperature enhances corrosion and breakdown of cell components
	*High temperature advantages include higher efficiency, and the fle reactions involving breaking of carbon to carbon bonds in larger hy	xibility to use more types of fuels and inexpensive catalysts as the drocarbon fuels occur much faster as the temperature is increased.
electric utility	<ul> <li>High temperature advantages*</li> <li>Solid electrolyte advantages (see PEM)</li> </ul>	High temperature enhances     breakdown of cell components
		22



C=Carbon H=Hydrogen

Trends in energy use: Hydrogen-to-Carbon ratio increases as we become less dependent on carbon-based fuels. (Courtesy: "Wired" 10/97)

This document, and

### Hydrogen As a Fuel

ydrogen is the most attractive fuel for fuel cells — having excellent electrochemical reactivity, providing adequate levels of power density in a hydrogen/air system for automobile propulsion, as well as having zero emissions characteristics.

Historically, the trend in energy use indicates a slow transition from fuels with high carbon content, beginning with wood, to fuels with more hydrogen. Fossil fuels release varying quantities of carbon dioxide into the atmosphere — coal having the highest carbon content, then petroleum, and finally natural gas — the lowest carbon dioxide emitter per thermal unit. Hydrogen obviously releases no carbon dioxide emissions when burned.

Hydrogen (H<sub>2</sub>) is the most abundant element in the universe, although practically all of it is found in combination with other elements, for example, water (H<sub>2</sub>O), or fossil fuels such as natural gas (CH<sub>4</sub>). Therefore, hydrogen must be manufactured from either fossil fuels or water before it can be used as a fuel. Today, approximately 95% of all hydrogen is produced by "steam reforming" of natural gas, the most energy-efficient, large-scale method of production. Carbon dioxide (CO<sub>2</sub>) is a by-product of this reaction.

#### $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

Hydrogen can also be produced by gasification of carbon containing materials such as coal — although this method also produces large amounts of carbon dioxide as a by-product. Electrolysis of water generates hydrogen and oxygen.

#### $H_20 \rightarrow H_2 + 1/20_2$

The electricity required to electrolyze the water could be generated from either fossil fuel combustion or from renewable sources such as hydropower, solar energy or wind energy. In the longer term, hydrogen generation could be based on photobiological or photochemical methods.

While there is an existing manufacturing, distribution, and storage infrastructure of hydrogen, it is limited. An expanded system would be required if hydrogen fuel were to be used for automotive and utility applications.

> In 1809, an amateur inventor submitted a patent for this hydrogen car.

nore, is available for download at Martin's Marine Engineering Page - www.dieselduck.net

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#### **Resources:**

HyWeb http://www.HyWeb.de Hydrogen InfoNet http://www.eren.doe.gov/ hydrogen/infonet.html

- The New Sunshine Program http://www.aist.go.jp/nss/ text/wenet.htm
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While a single hydrogen production/distribution/ storage system may not be appropriate for the diverse applications of fuel cells, it is certainly possible that a combination of technologies could be employed to meet future needs. All of the system components are currently available — but cost effective delivery and dispensing of hydrogen fuel is essential. If hydrogen were to become available and affordable, this would reduce the complexity and cost of fuel cell vehicles enhancing the success of the technology.

"Hydrogen Economy" is an energy system based upon hydrogen for energy storage, distribution, and utilization. The term, coined at General Motors in 1970, caught the imagination of the popular press. During the oil crisis in the early 70's, the price of crude oil sharply increased, concern over stability of petroleum reserves and the potential lack of a secure energy source grew, and government and industry together developed plans and implementation strategies for the introduction of hydrogen into a world energy system. However, the lessening of tensions in the Middle East led to a lowering of crude oil prices and the resumption of business as usual. Petroleum has continued to be the fuel of choice for the transportation sector worldwide.

Hydrogen fuel has the reputation of being unsafe. However, all fuels are inherently dangerous — how much thought do you give to the potential dangers of gasoline when you drive your car? Proper engineering, education, and common sense reduce the risk in any potentially explosive situation. A hydrogen vehicle and supporting infrastructure can be engineered to be as safe as existing gasoline systems. Dealing with the perception and reality of safety will be critical to the successful wide introduction of hydrogen into our energy economy.

"Shell has established a Hydrogen Economy team dedicated to investigate opportunities in hydrogen manufacturing and new fuel cell technologies..."

Chris Fay, Chief Executive, Shell UK

### "Don't paint your ship with rocket fuel"

At 7:30, on the evening of May 6, 1937, the Hindenburg dirigible was destroyed by fire and explosions as it was about to land in Lakehurst, New Jersey. 62 passengers survived and 35 lost their lives. The Hindenburg was nearing its landing site during an electric storm. According to observers on the ground, the dirigible began to drift past its landing position, and after a brief delay, the ship started to valve hydrogen into what was highly charged outside air. This combination of factors could prompt severe corona activity on any airship. In fact, an eyewitness reported seeing a blue glow of electrical activity atop the ill-fated Hindenburg before the fire started, which is indicative of the extremely high temperatures typical of a corona discharge. As the crew attempted to bring it back on course, the ship lost its balance, the tail touched the ground, and the stern burst into flames. Passengers who were afraid the ship might explode, jumped to their deaths. The burns and other injuries were a result of the diesel fuel



fire, not from hydrogen. Most of the passengers, who waited for the airship to land, walked safely away from the accident.

Until recently, this tragedy was thought to be caused by hydrogen, the highly flammable gas used to inflate the skin of the ship. However, historical photographs show red-hot flames, and hydrogen burns invisibly. Also, no one smelled garlic, the scent which had been added to the hydrogen to help detect a leak. The mystery of the Hindenburg was solved by Addison Bain, a former manager of the hydrogen programs for NASA. Using infrared spectrographs and a scanning electron microscope, Bain, working with other NASA scientists, was able to discover the chemical makeup of the organic compounds and elements present in the fabric of the dirigible's skin. The Hindenburg was covered with a cotton fabric that had been treated with a doping compound to protect and strengthen it — however, this compound contained a cellulose acetate or nitrate (gunpowder). Aluminum powder (which is used in rocket fuel) was also identified. The outside structure was wooden and the inside skeleton was duralumin coated with lacquer. The combination was flammable and deadly.

Front page of The New York Times, May 7, 1937, the day after the explosion of the Hindenberg. (Enhanced color photograph courtesy: National Hydrogen Association)

#### The Evolution of the Zero Emission Vehicle (in the 1990's)

The 1990 Clean Air Act Amendments along with the National Energy Policy Act of 1992 paved the way for less polluting gasoline vehicles and the introduction of alternative fuel vehicles on the roads in the U.S. Also in 1990, the California Air Resources Board recognized that even the cleanest gasoline powered vehicles wouldn't reduce pollution enough to satisfy the state's goals for healthful air. Meeting state and federal air standards in seriously polluted areas such as Los Angeles would require either restrictions on driving or a large-scale switch to vehicles that don't pollute. California adopted the Low Emission Vehicle Act that mandated the seven largest auto manufacturers begin immediately to reduce all tailpipe emissions and to introduce zero emission vehicles (ZEVs) by 1998.

In March 1996, the California Air Resources Board modified their zero emission vehicle program to encourage a market based introduction in the near-term and to promote future advances in electric vehicle (including fuel cells) technology. Beginning in 2003, 10% of the new vehicles will be required to be zero emission vehicles or nearly zero emission vehicles — also knows as equivalent ZEVs.

Because of the legislative initiative taken by California and subsequent similar regulations imposed by a number of states in the Northeast, every major automobile manufacturer has made significant progress toward the development of ultra-low and zero emission vehicles.

The remarkable developments of fuel-cell engines will help California in its war on smog as well as provide new consumers choices for transportation.

### Getting To Cleaner Transportation

he success story of the past three decades in the transportation sector has been the dramatic reduction of air-polluting emissions from new vehicles. Emission rates of gasoline vehicles have fallen by 70 - 90%, and the costs for cleaner cars have also fallen. Under real driving conditions, actual reductions are about 70% for nitrogen oxides and 90% for hydrocarbon and carbon monoxide emissions. With a near zero emission gasoline car on the horizon, and legislation in California and the Northeast states mandating 10% of the new vehicle market to be zero emission vehicles by 2003, even greater reductions in emissions are imminent. These are important improvements in the U.S. - but still, one in four Americans breathes unhealthy air. It's worse in the rest of the world. Cities such as Mexico City, Athens, and Shanghai don't have the same stringent emissions standards found at home and transportation remains the largest contributor to urban pollution. Worldwide, over one billion people living in urban areas are suffering from severe air pollution, and according to the World Bank, over 700,000 deaths result each year.

### Estimates from the EPA indicate that motor vehicles in the U.S. still account for

- 78% of all Carbon Monoxide emissions
- 45% of Nitrogen Oxide emissions
- 37% of Volatile Organic Compounds

The impact of lower emission gasoline vehicles is being offset by the growth in the number and size of vehicles on the road as well as an increase in the number of miles each vehicle travels. Americans pay around \$.36 per gallon in fuel tax as opposed to our European counterparts who spend an average of \$2.50 per gallon in taxes. Low gasoline prices don't encourage fuel efficiency or conservation. Rather, the sport utility vehicle market share continues to rise, now surpassing passenger vehicles. Even as these larger vehicles have cleaner tailpipe emissions, energy use and carbon dioxide emissions will continue to increase. If recent growth trends continue, Americans will be driving twice as many miles in 2015 as we do today. Along with continuing research on cleaner transportation options, it will be critical to develop policies that decrease the number of cars on the road, minimize congestion, encourage public transportation as well as telecommuting.

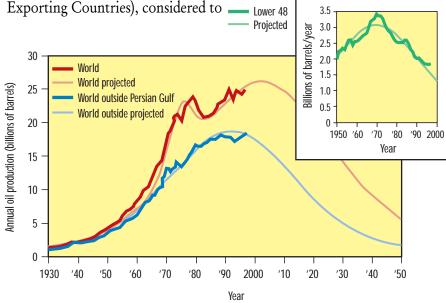
California Air Resources Board, August, 1998

### Oil Reserves, Transportation, and Fuel Cells

N o one can preserve in the oil prices o one can predict what will or global oil demand. The world's production of oil reached a record level of 65 million barrels a day in 1997, and global demand is rising more than 2% a year. Americans spend roughly \$100,000 per minute to purchase foreign oil, and the U.S. transportation sector uses over 10% of the world's oil. Consumption of oil by passenger vehicles, which include automobiles and light duty trucks, exceeds all of the United States' domestic production. Reserves of fossil fuels are large but finite, and there is growing evidence to suggest that world production of crude oil will peak early in the 21st century. The Energy Information Agency forecasts that worldwide demand for oil will increase 60% by 2020. By 2010, Middle East OPEC states (Organization of Petroleum

be unpredictable and often unstable, will have over 50% of the world oil business, and the switch from growth to decline in oil production could cause economic and political tension. As excess oil production capacity begins to decline over the coming decades, oil prices can be expected to rise, and the transportation sector is likely to be most heavily affected by these fluctuations. World wide, transportation relies almost totally on oil, and there are few viable short-term fuel options.

Every gallon of gasoline manufactured, distributed, and then consumed in a vehicle releases roughly 25 pounds of carbon dioxide.



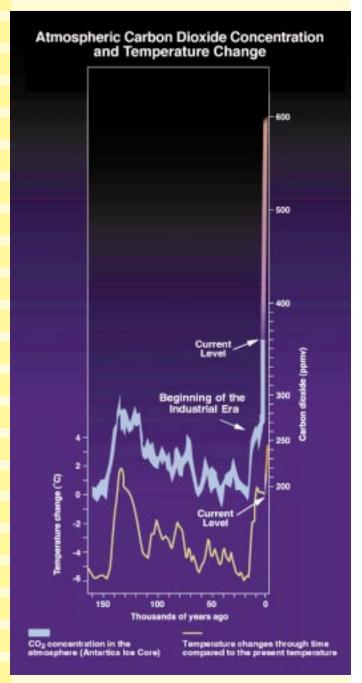
U.S. oil production in the lower 48 states (upper right) peaked in 1970 as predicted by a bell shaped curve. World oil production is expected to follow suit. (Courtesy: Science, vol. 281, Aug. 21,1998, p.1128; C. Campbell & J. Laherrere)

#### Since 1985, energy use is up

- 40% in Latin America
- 40% In Africa
- 50% in Asia

About 25% of all human-generated greenhouse gases come from transportation — more than half of that from light-duty vehicles. Unlike air pollutants (carbon monoxide, nitrogen oxides, hydrocarbons, and particulates - soot, smoke, etc.), greenhouse gas emissions (primarily carbon dioxide, methane, nitrous oxide, water vapor, etc.) from vehicles cannot be easily or inexpensively reduced by using add-on control devices such as a catalytic converter. In addition, unlike air pollutants, greenhouse gas emissions are not regulated by the Environmental Protection Agency. The relationship between gasoline consumption and carbon dioxide emissions is fixed. Today, increasing fuel economy, reducing vehicle miles traveled, and switching to lower or non-carbon fuels will begin to decrease carbon dioxide emissions.

The introduction of fuel cells into the transportation sector will increase fuel efficiency, decrease foreign oil dependency, and become an important strategy/technology to mitigate climate change. As fuel cell vehicles begin to operate on fuels from natural gas or gasoline, greenhouse gas emissions will be reduced by 50%. In the future, the combination of high efficiency fuel cells and fuels from renewable energy sources would nearly eliminate greenhouse gas emissions. The early transition to lower carbon-based fuels will begin to create cleaner air and a stronger national energy security.



The  $CO_2$  level has increased sharply since the beginning of the Industrial Era and is already outside the bounds of natural variability seen in the climate record of the last 160,000 years. Continuation of current levels of emissions are predicted to raise concentrations to over 600 ppm by 2100. (Courtesy: Office of Science and Technology Policy)

### Climate Change, Greenhouse Gases, and Fuel Cells: What is the Link?

here is a growing scientific consensus that increasing levels of greenhouse gas emissions are changing the earth's climate. The natural greenhouse gases include carbon dioxide (CO<sub>3</sub>), water vapor (H<sub>2</sub>O), nitrous oxide  $(N_2O)$ , methane  $(CH_1)$  and ozone  $(O_2)$ , and are essential if the Earth is to support life. With the exception of water vapor, carbon dioxide is the most plentiful. Since the beginning of the Industrial Revolution in 1765, burning fossil fuels and the increased energy needs of a growing world population have added man-made, or anthropogenic, greenhouse gas emissions into the environment. Carbon dioxide constitutes a tiny fraction of the earth's atmosphere — about one molecule in three thousand — but is the single largest waste product of modern industrial society. The concentration of carbon dioxide in the atmosphere has risen from about 280 parts per million by volume to the current level of over 360 parts per million by volume and anthropogenically caused atmospheric concentration of methane has doubled. In the past 100 years, levels of nitrous oxide have risen about 15%. Increasing concentrations of greenhouse gases trap more terrestrial radiation in the lower atmosphere (troposphere), artificially enhancing the natural greenhouse effect. The average temperature of the Earth has warmed about 1°C since the mid-19th century when measurements began, and fragmentary records suggest the Earth is warmer than it has been in nearly 2,000 years.

#### "The balance of evidence suggests that there is a discernible human influence on global climate."

#### United Nations Intergovernmental Panel on Climate Change, 1995

Under the most optimistic scenarios proposed by the United Nations Intergovernmental Panel on Climate Change, carbon dioxide is expected to rise to approximately 600 parts per million by volume during the next century — more than double the level held for 10,000 years since the end of the last ice age.

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#### **Resources:**

President's Council on Sustainable Development http:// www.whitehouse.gov/PCSD/ Rocky Mountain Institute http:// www.rmi.org California Air Resources Board http://www.arb.ca.gov/ homepage.htm

#### The Science of Global Climate Change

he regulating factor for global climate change depends on a fundamental principle, the First Law of Thermodynamics, also known as the Law of Conservation of Energy. Mathematically this can be represented as follows:

dQ = dU - dW

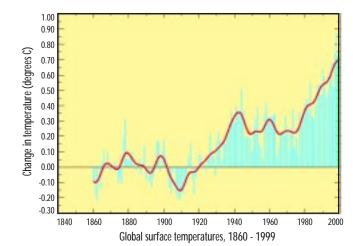
where dQ = heat added to the system, dU = change in the internal energy of the system, and dW = work extracted. Energy cannot be gained or lost in a stable system; it can only change forms. Such a system is said to follow an "Energy Balance Model." To maintain stability, the Earth-ocean-atmosphere system absorbs energy from the Sun, radiates it in the form of infrared (heat) energy, and transports it in the form of both latent heat and sensible heat flux. Several natural events (volcanic eruptions, forest fires, fluctuating intensity of solar radiation, varying cloud cover, and others) and human activities (fuel combustion, aerosol production, and industrial and land use practices that release or remove heat-trapping greenhouse gases, and others) can affect the balance between absorption and emission of radiation.

Based on these scenarios, the Intergovernmental Panel on Climate Change has concluded that the increase in greenhouse gases may be expected to cause a rise in the global average temperature of between 1°C and 3.5°C in the 21st century.

### In 1997, global carbon emissions amounted to more than six billion tons — more than a ton for every human being on the planet.

1998 was the warmest year on record, and no one is absolutely certain what these temperature increases will do — changes in precipitation, extreme weather, and sea level rise are all possible. The climate modeling and resulting scientific conclusions are not universally accepted because climate codes have difficulties simulating such events. The picture is far from clear, but it appears that climate is driven by a variety of forcing mechanisms and anthropogenic forcing must be placed within the total context that includes the long-term variations of the earth's orbit, solar variability, and the natural cycles of nature. However, as all of these data are taken into account, evidence is increasing that the climate model predictions cannot be too far wrong and that we are warming the Earth. Compelling societal implications place even more significance on prudent policy directions.

Instrumental Temperature Record from 1860 – 1999 indicates a global warming over the past century, with many peaks and valleys suggesting the natural year-to-year variability of climate. (Courtesy: Hadley Centre for Climate Prediction & Research)



#### The Climate Change Debate

The Road to Kyoto: How the Global Climate Treaty Fosters Economic Impoverishment and Endangers U.S. Security. Angela Antonelli, et.al. The Heritage Foundation, Roe Backgrounder No.1143, October 6, 1997.

The Forgiving Air – Understanding Environmental Change. Richard C.J. Sommerville. University of California Press, 1996.

Global Warming: The High Cost of the Kyoto Protocol – National and State Implications. WEFA, Inc. 1998.

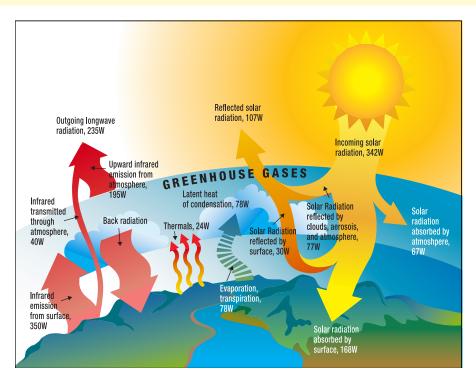
Kyoto Protocol: A Useless Appendage to an Irrelevant Treaty. Testimony of Patrick Michaels, Cato Institute, Committee on Small Business, U.S. House of Representatives, July 29, 1998.

CLIMATE: Making Sense and Making Money. Amory B. Lovins and L.Hunter Lovins, Rocky Mountain Institute, November 13, 1997.

The Costs of Climate Protection: A Guide for the Perplexed. Robert Repetto and Duncan Austin, World Resources Institute, 1997.

While the link between climate and ecology remains uncertain, decisions made during the next ten years could affect generations to come. Given the current levels of uncertainty, the complexity of our environment, and the potential for "surprises" or unanticipated events, prudent action appears to win out over a "business as usual" scenario. Given the long time lags between cause and effect, and between effect and remedy, we are challenged to use technology wisely to enhance our investment in the future. The world's governments have signed a climate convention and are negotiating implementation strategies. It is not unreasonable to suggest that the introduction of fuel cells into the transportation and energy sectors will have global implications. Energy efficiency, reducing world use of petroleum, the transition to renewable fuels, and continued support for research are important and responsible steps.

While the link between climate and ecology remains uncertain, decisions made during the next ten years could affect generations to come.



The Greenhouse Effect: Essentially, all energy that enters the Earth's atmosphere comes from the sun. The incoming radiation is partly absorbed, partly scattered, and partly reflected back into space by the various gases of the atmosphere, clouds, and aerosols — tiny particles suspended in the atmosphere. The sun emits solar radiation mainly in the form of visible and ultraviolet radiation. As this radiation travels toward Earth, approximately 25% of it is absorbed by the atmosphere and 25% is reflected by the clouds back into space. The remaining radiation travels to the Earth and heats its surface. Because the Earth is much cooler than the sun, energy reflected from the Earth's surface is lower in intensity than that emitted from the sun, i.e. in the form of invisible infrared radiation. About 90% of the infrared radiation reflected by the earth's surface is absorbed by atmospheric trace gases, also known as "greenhouse gases," before it can escape to space. These gases, as well as clouds, re-emit this radiation — sending it back toward ground. The atmosphere acts like the glass in a greenhouse, allowing short-wavelength radiation to travel through, but trapping some of the long wavelength infrared radiation which is trying to escape. This process makes the temperature of the atmosphere rise just as it does in the greenhouse. This is the Earth's natural greenhouse effect and keeps our planet about 60°F warmer than it might otherwise be. (Courtesy: National Oceanic and Atmospheric Administration)

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Ridge National Laboratory http://cdiac.esd.ornl.gov Intergovernmental Panel on Climate Change http:// www.usgcrp.gov/usgcrp/ IPCCINFO.html

### A Once-In-A-Lifetime Opportunity

**S** ustainable development is one of those often used, but seldom defined, phrases. According to the United Nations, it is "meeting the needs of the present without compromising the ability of future generations to meet their own needs." Attaining sustainable development doesn't mean that growth must stop; it does mean that environmental limits do exist because of the limited ability of the biosphere to deal with the wastes from human activities. This is one of the greatest challenges we face today — a challenge that can only be met by responsibly developing and using technologies that will protect our environment for everyone.

Today's innovations in fuel cell technology are addressing local, national, and global environmental needs. The decision to become involved with bringing these innovations into our daily lives is a strategic career opportunity and a smart thing to do. The winners will be those people who are ahead of the crowd.

Innovative solutions can be an important competitive plus. Over half of the threat to our climate disappears if we use energy in ways that save money. In general, it's far cheaper to be efficient and save fuel than burn fuel. Fuel cells offer an opportunity for innovation. Helping to make fuel cells be a part of the solution might be a challenge that's too exciting to ignore.

"Developing countries face a fundamental choice. They can mimic the industrial countries, and go through a development phase that is dirty and wasteful and creates an enormous legacy of pollution. Or they can leapfrog over some of the steps followed by industrial countries and incorporate modern efficient technologies."

> "The Human Development Report." The United Nations. Oxford University Press, September, 1998.

The U.S. Department of Energy through its Office of Transportation Technologies is pursuing critical technological advances that can help to create new and improved national transportation systems. The Office of Transportation Technologies supports research that is often too financially risky for private industry to develop on its own. Partnerships are developed with industry, working with national laboratories, as a way to strengthen resources.

#### The mission of the Office of Transportation Technologies is to reduce U.S. dependence on petroleum.

Within the Office of Transportation Technologies, the Office of Advanced Automotive Technologies focuses its efforts on developing cleaner and more energy-efficient technologies for automobiles of the future. The *Transportation Fuel Cell Program* is just one of many exciting research activities.

The Partnership for a New Generation of Vehicles (PNGV) Program is a partnership between 11 government agencies and the United States Council for Automotive Research, a cooperative research effort among DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation, to develop commercially-viable vehicle technology that, over the long-term, can preserve personal mobility, reduce the impact of cars and light trucks on the environment and reduce U.S. dependency on foreign oil.

*The Alternative Fuels Research and Development Program* has been developing alternative fuels technologies in partnership with industry for more than 20 years.

The CARAT Program (Cooperative Automotive Research for Advanced Technology) supports universities and small businesses to accelerate the development and production of innovative technologies that address barriers to producing ultra-efficient vehicles including the design and development of advanced, energy-efficient automotive components and systems.

*The Graduate Automotive Technology Education Program* (GATE) is a multidisciplinary automotive engineering program for graduate students that focuses on technologies critical to the development and production of future automobiles.

Benefits of Office of Transportation Technologies Program

- Reducing dependence upon foreign oil
- Increasing energy savings
- Improving air quality by reducing destructive air pollution and greenhouse gases

To learn more about the Office of Transportation Technologies:

#### www.ott.doe.gov

