FUEL CELLS: ENERGY CONVERSION FOR THE NEXT CENTURY

What the world needs now is an environmentally benign way to generate electric power efficiently. The emerging technology of fuel cells is rising to meet the challenge.

Sivan Kartha and Patrick Grimes

Fossil fuel combustion, the technology on which the world relies most heavily for power generation, heating and transportation, was adopted long before its environmental burdens had been fully recognized. The results of our recent efforts to mitigate these environmental costs are perceptible, but still modest and very costly. Despite the use of sulfur scrubbers, acid rain remains a serious regional threat, especially with the increased use of low-quality coals. Catalytic converters have reduced nitrogen oxide and carbon monoxide emissions from automobiles in some countries, but the poor air quality of many of the world's urban areas nonetheless constitutes a severe health threat. New, more efficient power plants and automobiles generate less carbon dioxide per unit of useful energy than did their predecessors, but atmospheric carbon dioxide concentrations continue to rise, intensifying the threat of global warming. Despite our diligent efforts, a major strategic shift in energy production may be required to achieve more than incremental and perhaps inadequate advances. What is needed is an energy conversion technology that is inherently clean, efficient and compatible with renewable energy sources.

A timely technology

A technology that meets these environmental criteria, and indeed advances beyond combustion altogether, is the fuel cell.[1] Figure 1 shows the basic design of a typical fuel cell. The key components are an anode, to which the fuel is supplied, a cathode, to which the oxidant is supplied, and an electrolyte, which permits the flow of ions (but not electrons or reactants) between the anode and the cathode. The net chemical reaction is exactly the same as if the fuel were burned, but by spatially separating the reactants, the fuel cell intercepts the stream of electrons that flow spontaneously from the reducer (the fuel) to the oxidant (say, oxygen) and diverts it for use in an external circuit. The main distinction between a fuel cell and a conventional battery is that the fuel and oxidant are not integral parts of a fuel cell, but instead are supplied as needed to provide power to an external load, while the waste products are continuously removed. In the case shown in figure 1, hydrogen is supplied to the anode and oxygen to the cathode, and water is produced.

Different types of fuel cells rely on different ions to

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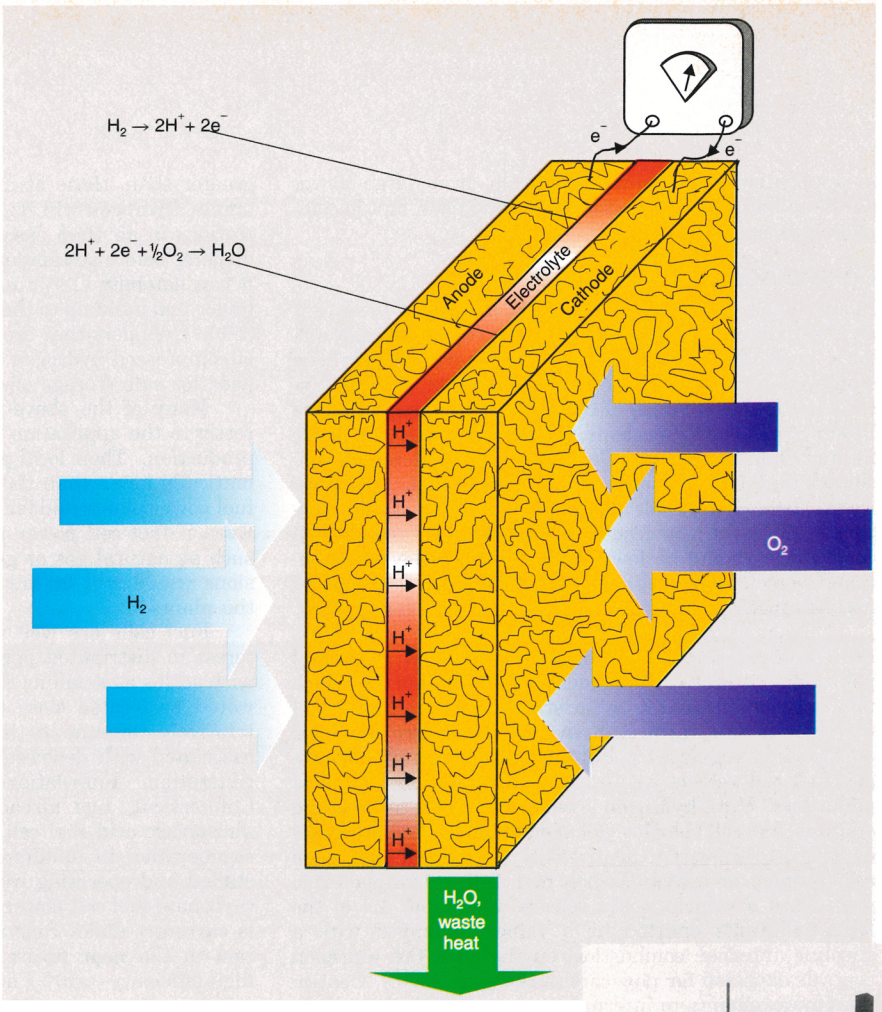
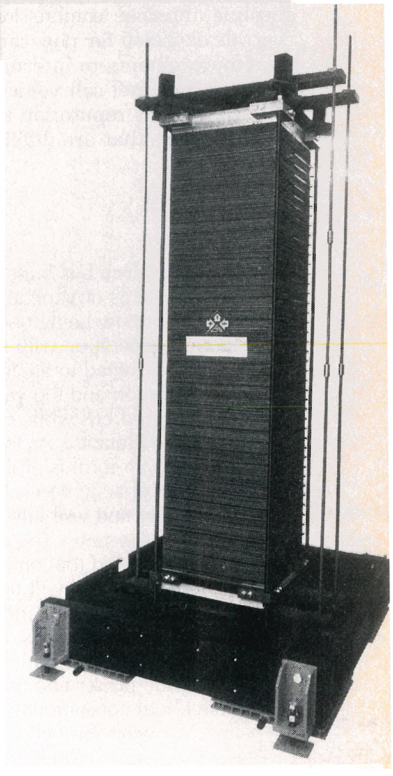


Typical fuel cell (right) consumes reactants and generates a current. The reactants (hydrogen and oxygen in this case) move to the electrolyte through rough-surfaced, porous, electrically conductive electrodes. Electrons are produced at the anode–electrolyte interface, pass through an external circuit and are then consumed at the cathode–electrolyte interface. Besides electrical power, water and potentially useful heat are generated. The meter represents the external load, which could be a lightbulb, an automobile engine or a city's power grid. A typical fuel cell voltage is about one volt; practical systems have a stack of fuel cells, with the anode of one cell in electrical contact with the cathode of the next. The photo (below) shows a stack of 240 molten-carbonate fuel cells, each two feet square. This stack consumes natural gas and is an example of the 100-kW class of stacks developed by Energy Research Corporation for the Santa Clara demonstration power plant mentioned in the text. **Figure 1**



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carry charge from one electrode to the other and are therefore generally distinguished by their electrolytes. The fuel cell depicted in figure 1 (above) has an acidic electrolyte (such as phosphoric acid or a proton-exchange membrane), and it relies on H^+ ions to carry charge from anode to cathode. In various other fuel cells, charge moves from cathode to anode via $O^=$ ions (solid oxide ceramic fuel cells), OH^- ions (alkaline fuel cells) or $CO_3^=$ ions (molten-carbonate fuel cells). Table 1 gives some of the distinguishing features of these major types of fuel cells.

The value of deriving electric current directly from fuels was recognized well before electricity became a commodity sold by power utilities. The first investigations go back to 1839 and Sir William Grove, whose enthusiastic experimentation yielded a current large enough that "a shock was given which could be felt by five persons joining hands, and which when taken by a single person was painful."[2] In more recent times, research continued in many national, academic and industrial laboratories, and technical experience accumulated as prototypes and novelty applications were developed. It wasn't until the 1960s, however, that fuel cells were employed in a practical capacity. After several years of intensive research, NASA used them to provide electric power on board the Gemini space mission and the Apollo missions to the Moon. Steady progress over the next 30 years has made it possible for fuel cells to start displacing combustion from its central technological role. In recent years many advances have occurred so quickly that the fuel cell's potential is still largely unappreciated beyond the fairly small community involved with its development.

Not only is fuel cell research and development proceeding in many countries, but industry is now taking the first steps toward commercializing fuel cell products. One of the most appealing aspects of the fuel cell is its inherent modularity: Both its efficiency and its cost per unit power are relatively insensitive to its size. This suggests its effective use

in applications of wide-ranging scale, from large power plants to portable power generators and even laptop computer power supplies.

Cars, buses and power plants

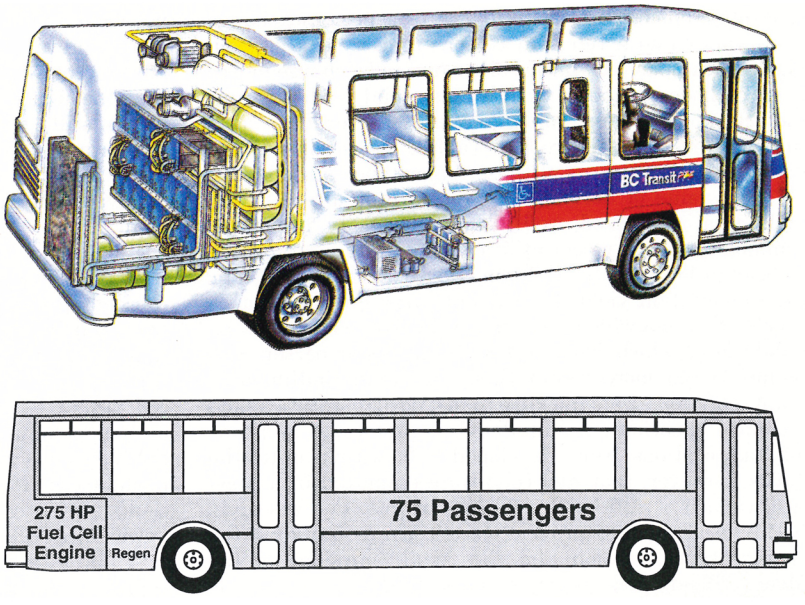
Early in the next decade, fuel cells may start to appear as alternatives to internal combustion engines in automobiles, buses and other vehicles. They have already been employed in several vehicle demonstration projects, including those of H Power of Belleville, New Jersey; Ballard Power Systems of Vancouver, British Columbia (see figure 2); and Daimler–Benz of Germany. A recent report concluded that fuel cell cars, if mass produced, may have initial costs comparable to those for internal combustion cars.[3] Moreover, the cost of owning and operating a fuel cell vehicle should be lower than that of today's conventional vehicle, due to greater fuel efficiency and ease of maintenance.[4] A fuel cell, after all, has no moving parts.

Currently, the great interest in fuel cell vehicles arises from their extremely low emissions of local environmental pollutants. A recently adopted California mandate (which may soon be adopted in other states) requires that 2% of the vehicles sold in the state in 1998 must have zero local emissions of regulated pollutants. Operation of a hydrogen fuel cell vehicle would emit only water and *no* local pollutants. Until hydrogen is widely available at refueling stations, fuel cell vehicles will need to have a fuel processor on board to convert a more easily distributed fuel, such as methanol or a hydrocarbon fuel, into a hydrogen-rich gas. Such a vehicle would release only about 1% of the local pollutants emitted by a vehicle equipped with a gasoline internal combustion engine and the emission controls expected for new cars in the year 2000.[5] Continued improvements to internal combustion vehicles can be expected, but fuel cell vehicles will be difficult to match.

[Despite its reputation as being hazardous, hydrogen poses dangers that are different from, but not necessarily greater than, those of more widely used fuels.[6] For example, hydrogen will ignite over a wider range of concentrations in air than gasoline, but its buoyancy helps it to disperse before accumulating to the concentration at which it can detonate (18%), unlike gasoline vapors, which can linger and build up to their lower detonation concentration (1%). Cylinders that are now being developed for storage of compressed hydrogen would be similar to those widely used for safe storage of compressed natural gas.]

Many of the above-mentioned benefits translate directly to the application of fuel cells for stationary power production. Their local pollutant emissions would be dramatically lower than those of conventional thermal fossil fuel power plants and far below regulated emissions limits. Even if fuel cell power plants were fed with fossil fuels such as natural gas or gasified coal, carbon dioxide emissions would still be low, owing to the high efficiency of the plants.

Fuel cells are well matched to utilities' growing interest in distributed power generation facilities[7]—plants with scales as small as tens or hundreds of kilowatts that would be located close to consumers. Such plants are relatively immune to the cost and efficiency penalties associated with downscaling conventional thermal power generation. International Fuel Cells of South Windsor, Connecticut, has already commercialized 200-kilowatt phosphoric acid fuel cell systems for heat and electricity cogeneration in buildings, with more than 50 units installed and operating worldwide. A 2-megawatt molten-carbonate fuel cell power plant in Santa Clara, California, is currently under construction and scheduled for operation in the near future. This is the pilot plant for a high-efficiency (>50%), natural-gas-fueled, small-scale distributed power generation system that Energy Research Corporation of Danbury, Connecticut, plans to begin marketing in the next few years. Industry and government labs in North America, Europe and Japan are conducting



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Fuel-cell-powered bus built by Ballard Power Systems of Vancouver, British Columbia, is now being operated and tested in cooperation with BC Transit. It is designed to attain the same acceleration and top velocity as a diesel-powered bus while emitting no local pollutants. As the cutaway diagram for this project shows, passenger capacity was sacrificed for accessibility and visibility of the fuel cell system. The anticipated commercial design (bottom) has much more room and will use the next generation of fuel cell and hydrogen storage technology. Advanced batteries, charged by the fuel cells, will help provide power and may be used to reduce fuel consumption and brake wear through regenerative braking. **Figure 2**

Table 1. Major types of fuel cells

Electrolyte	Temperature	Advantages	Drawbacks	Status
Alkaline	70–200 °C	High current and power densities, high efficiency	CO_2 intolerance	Extensive field testing
Proton-exchange membrane	80–110 °C	High current and power densities, long operating life	CO intolerance, water management, noble catalyst	Field testing (kilowatt scale) including prototype vehicles
Phosphoric acid	150–210 °C	Technologically well advanced	Relatively low efficiency, limited lifetime, noble catalyst	Commercially available
Molten carbonate	550–650 °C	High efficiency, internal fuel processing, high-grade waste heat	Electrolyte instability, short operating life	Field testing (2-megawatt scale)
Solid oxide ceramic	1000–1100 °C	Internal fuel processing, high-grade waste heat, long operating life, potentially inexpensive	High operating temperature, limited thermodynamic efficiency, relatively low ionic conductivity	Laboratory testing (kilowatt scale)

other programs to advance fuel cell power generation.

Fuel cells may play a vital role in the transition to renewable energy sources. Fuel cells for transportation could use hydrogen or methanol produced through thermochemical gasification of biomass resources such as agricultural residues and dedicated plantations. Eventually, hydrogen may be produced electrolytically using wind or solar electricity. For stationary power applications, fuel cells coupled to thermochemical gasifiers could be competitive at much smaller scales than biomass combustion technologies. By avoiding the cost of transporting the feedstock over long distances, this possibility greatly expands the potential for economically generating electricity from biomass.

Theory of fuel cells

Most fuel cells being developed consume either hydrogen or fuels that have been preprocessed into a suitable hydrogen-rich form. Some fuel cells can directly consume sufficiently reactive fuels such as methane, methanol, carbon monoxide or ammonia, or can process such fuels internally; this substantially reduces the amount of auxiliary equipment required. At the anode of a hydrogen-consuming fuel cell such as the one illustrated in figure 1, the hydrogen molecules disassociate into H^+ ions, which are free to migrate through the electrolyte toward the cathode, and electrons, which can pass through the external load. This dissociation, $H_2 \rightarrow 2H^+ + 2e^-$, occurs spontaneously simply because there is an equilibrium ratio of hydrogen ions to hydrogen molecules at any finite temperature. At the cathode, oxygen molecules similarly dissociate into atoms, which combine with electrons and the migrating H^+ ions to form water: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$. An electric potential appears between the electrodes because of the excess of electrons at the anode (where they are generated) compared with the cathode (where they are consumed). It is this potential difference that drives current through the external load, making the fuel cell a source of power.

To derive the magnitude of the electric potential appearing across the fuel cell electrodes, consider the schematic in figure 1: With an open circuit, no current is flowing, and the partial reactions occurring at the anode and cathode are at equilibrium. By definition, equilibrium exists when the chemical potential of the products equals that of the reactants, so

$$\mu^a(H_2) = 2\mu^a(H^+) + 2\mu^a(e^-)$$

and

$$\mu^c(H_2O) = 2\mu^c(H^+) + 2\mu^c(e^-) + \tfrac{1}{2}\mu^c(O_2)$$

where μ^a and μ^c refer to the chemical potentials at the anode and cathode, respectively. Since the ionic charge carriers can migrate freely through the electrolyte, the chemical potentials of the ions at the two electrodes are also at equilibrium: $\mu^a(H^+) = \mu^c(H^+)$. The voltage difference that appears between the two electrodes simply reflects their different electrochemical potentials:

$$V \equiv [\mu^c(e^-) - \mu^a(e^-)]/q_e$$

where $-q_e$ is the electron's charge. The above three equilibrium conditions yield the total work provided by the fuel cell:

$$W = -2q_eV = -[\mu^c(H_2O) - \tfrac{1}{2}\mu^c(O_2) - \mu^a(H_2)] = -\Delta G$$

where $-\Delta G$ is the change in Gibbs free energy for the formation of a water molecule. (Note that the factor $2q_e$ arises because two electrons are transferred per water molecule formed.) The first and second laws of thermodynamics can also be used to derive this result for the maximum work available from a fuel cell (see the box on page 58), but they do not explain how a voltage appears across the electrodes.

In this particular case, the potential difference is 1.23 V, and the work done per molecule of water produced is 2.46 eV. Practical systems use a stack of many fuel cells, with the anode of each cell in electrical contact with the cathode of the next. The resulting voltage is then the sum of the constituent cells' voltages.

High efficiency

The efficiency of a fuel cell, $\eta = \Delta G/\Delta H = qE_{th}/\Delta H$, is clearly unconstrained by the Carnot limitation, which

applies to heat engines. (See the box below and table 2.) Fundamentally, the reason why it is difficult to convert heat efficiently to work lies in the second law of thermodynamics: The entropy of a closed system cannot decrease. Heat emanating from a combustion chamber is a high-entropy form of energy, and when we convert it into a low-entropy form, such as electrical or mechanical energy, the second law mandates that we also generate entropy elsewhere. To do this, we are forced to discard some energy as waste heat with a sufficiently high entropy content—that is, at a sufficiently low temperature.

Fuel cells can substantially improve the efficiency with which power is generated from fuels by reacting fuel and oxidant in a controlled "electrochemical combustion" process, which altogether avoids the intermediate generation of heat and the inefficient conversion of heat into electrical energy. We are familiar with this shortcut in the case of batteries: While electricity could conceivably be produced by grinding up a household battery, mixing together its various chemical ingredients and then harnessing the resulting heat, it is much more efficient to keep the battery intact and produce electricity directly.

Conventional thermal power generation technology has progressed far toward minimizing the second law penalty; today's power plants have efficiencies of 35–40%, compared with 2–3% at the turn of the century. (Efficiencies can be defined with respect to either the higher heating value or lower heating value of fuel, depending on whether liquid water or water vapor is produced. The HHV exceeds the LHV by the latent heat of vaporization of the water produced, and the difference between the two will be larger for hydrogen than for, say, coal, which doesn't produce much water when burned. Efficiencies in this article are based on HHVs.)

Advanced materials and turbine technology inherited from military jet engine research have pushed power plant efficiencies to 50% for gas and steam turbine combined-cycle plants with capacities of hundreds of megawatts, and combined-cycle efficiencies are expected to rise further. Depending on such issues as their emissions, total efficiencies and costs relative to fuel cell power plants, these gas-turbine-based systems may continue to be appealing for power generation at large central plants. However, these systems are less suited to the small scale of many of society's most pressing applications, such as transportation (which requires a capacity of about 50–100 kilowatts) and small, distributed power generation (at scales as small as kilowatts). Such small-scale applications are ideal for the highly efficient, cleanly operating fuel cell.

Table 2 shows some typical values for the change in enthalpy and the change in Gibbs free energy for a number

Thermodynamics of Heat Engines and Fuel Cells

In a heat engine, a quantity of heat energy Q_{in}, supplied at temperature T_{in} is converted partially to work W, while the remainder is rejected as heat Q_{out} at temperature T_{out}. The first law of thermodynamics requires that energy be conserved ($W = Q_{in} - Q_{out}$) but does not prohibit a perfect heat engine, with $W = Q_{in}$ and $Q_{out} = 0$. The second law, however, demands that entropy does not decrease; in the case of ideal reversible operation, this translates to the requirement that the entropy in, $S_{in} = Q_{in} / T_{in}$, is not greater than the entropy out, $S_{out} = Q_{out} / T_{out}$. For given T_{in} and T_{out}, the heat engine's efficiency, $\eta \equiv W / Q_{in}$ is limited by $\eta_c = (T_{in} - T_{out}) / T_{in}$, the Carnot efficiency.

There are practical constraints on the upper and lower temperatures that can be attained. In a working system, the cool reservoir is at ambient temperature, so $T_{out} \geq 300$ K. The maximum temperature that can be attained by combustion is fairly high (typically about 2100 K or higher), but the maximum practical operating temperature for materials in industrial settings is much lower, so the Carnot limit becomes significant. Conventional coal- or oil-fired power generating plants using steam cycles operate at maximum temperatures of only about 800 K. Modern gas turbines rely on materials and processes capable of enduring temperatures up to 1600 K, and ongoing R&D is aimed at achieving still higher temperatures.

Since it bypasses the intermediate generation of heat, the fuel cell avoids the Carnot limitation altogether; there is no need for higher and higher temperatures. Its efficiency will depend, of course, on the reaction taking place in the fuel cell. For the case illustrated in figure 1, the net reaction is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \Delta H$, where $\Delta H = 2.97$ eV, the difference in enthalpy between the reactants and the products at constant pressure and temperature. (It is the change in enthalpy, not the change in internal energy, that is relevant here. Some energy is exchanged with the atmosphere via $p\Delta V$ work, due to the change in volume of the reactants as they transform into products. The enthalpy change, $\Delta H \equiv \Delta U + p\Delta V$, can be slightly larger or slightly smaller than the internal energy change ΔU, but in any case these quantities will typically differ by less than 1%.)

The fuel cell, like the heat engine, must pay dues to the second law and will be constrained by the need to reject heat to the environment, to ensure that the total entropy does not decrease. As a fuel cell isothermally consumes fuel and generates waste products, it causes a change in the universe's entropy, owing to the difference in entropy ΔS between the reactants it consumes and the products it creates. This change in entropy will therefore be compensated by the generation of an amount of heat Q at temperature T (the operating temperature of the fuel cell) such that $Q / T = -\Delta S$ (under ideal reversible operation). As a result, the theoretical maximum available work is given by

$$W = -\Delta H - Q = -(\Delta H - T\Delta S) = -\Delta G$$

where ΔG is the Gibbs free energy.

When fuel is consumed to produce power, the efficiency is conventionally defined as the ratio of the useful energy produced to the change in enthalpy (sometimes called the "heating value") of the consumed fuel, given by $\eta = \Delta G / \Delta H$. This is clearly unconstrained by the Carnot limitation. Table 2 shows some typical values for the change in enthalpy and the change in Gibbs free energy for a number of reactions, as well as the comparatively high theoretical efficiencies of fuel cells powered by these reactions.

Table 2. Thermodynamic parameters for sample fuel cell reactions

Fuel	Reaction	Δn^*	ΔH^{**} (eV)	ΔG^{***} (eV)	$q^\dagger$ (qe)	$E_{th}^{\dagger\dagger}$ (V)	$\eta^{\dagger\dagger\dagger}$ (%)
Hydrogen	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$-\frac{3}{2}$	2.97	2.46	2	1.23	83.0
Methane	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	−2	9.25	8.50	8	1.06	91.9
Methanol	$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$	$-\frac{1}{2}$	7.55	7.29	6	1.21	96.7
Ethane	$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$	$-\frac{5}{2}$	16.2	15.2	14	1.09	94.1
Ethanol	$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$	−1	14.2	13.7	12	1.14	96.5
Formic acid	$HCOOH + \frac{1}{2}O_2 \rightarrow CO_2 + H_2O$	$\frac{1}{2}$	2.81	2.96	2	1.48	105.6
Ammonia	$NH_3 + \frac{3}{4}O_2 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O$	$-\frac{5}{4}$	3.97	3.51	3	1.17	88.4
Hydrazine	$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$	−1	6.46	6.25	4	1.56	96.8
Carbon	$C + O_2 \rightarrow CO_2$	0	4.09	4.10	4	1.02	100.2
Carbon	$C + \frac{1}{2}O_2 \rightarrow CO$	$\frac{1}{2}$	1.15	1.43	2	0.71	124.1
Carbon monoxide	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$-\frac{1}{2}$	2.94	2.67	2	1.34	90.9

*Change in number of gaseous constituents
**Change in enthalpy per atom of fuel
***Change in Gibbs free energy per atom of fuel
†Charge transferred per atom of fuel
††Theoretical voltage
†††Theoretical efficiency

of reactions, along with the theoretical efficiencies of fuel cells powered by these reactions. In all cases, the efficiency is high, rarely falling lower than 90%, because the heat exchanged with the surroundings, $T\Delta S$, tends to be small relative to the change in enthalpy. Note that for some reactions, the efficiency exceeds 100%! If the entropy of the products is *greater* than the entropy of the reactants, then as the reaction reversibly proceeds, the system will *absorb* heat from the environment and convert it into electrical power.

Since the leading contribution to the change in a system's entropy arises from the translational degrees of freedom of its particles, a reaction with more gaseous products than gaseous reactants will tend to have a positive change in entropy. In general then, the ideal efficiency of a reaction will increase as the ratio of moles of gaseous products to gaseous reactants increases, as seen in table 2.

An efficiency exceeding 100%, though odd, is entirely consistent with the thermodynamic laws: The efficiency of such a fuel cell operating reversibly exceeds 100% only because energy (considered "free") is drawn from the environment (so the first law is not violated), and the entropy that seems to disappear when heat is converted to work is actually transferred to the higher-entropy reaction products of the fuel cell (so the second law is not violated). Still, it is counterintuitive that heat will be absorbed by a reaction that is, ultimately, highly exothermic. This simply highlights the main virtue of a fuel cell: In a fuel cell's energy-producing reaction, it liberates electrical energy, not thermal energy. Perhaps the term exo*energetic* would be more appropriate than exo*thermic* when describing the processes at work in a fuel cell.

Fuel cells in operation

The previous discussion of fuel cell performance refers to the ideal thermodynamic efficiency. Needless to say, parasitic losses bring the efficiency below these theoretical values: Auxiliary equipment requires energy, power conditioning (such as dc-to-ac conversion) is less than 100% efficient, and fuel processing generally consumes some of the energy content of the fuel. Most important, a fuel cell does not operate under ideal, thermodynamically reversible conditions. Reaction rates cannot be infinitesimally slow, because nonzero current must be provided to generate power. The fuel cell must be perturbed away from its equilibrium, causing thermodynamically irreversible processes that diminish performance to less than the theoretical limit. The greater the current provided by a fuel cell, the further it must be perturbed from equilibrium, and the further the operating voltage will sink below the ideal theoretical voltage. For a given fuel energy content, the electrical output decreases while heat output increases. The efficiency of a fuel cell relative to its ideal efficiency—given by the ratio of the operating voltage at a given current density, $V(i)$, to the ideal theoretical voltage—can be inferred from its current density-vs-voltage curve, as shown in figure 3.

The power density of a fuel cell (the product of the current density and the voltage) will increase with current density to some peak value, at which the voltage has dropped low enough that more current does not provide more power.

A major objective of current research is to reduce the rate at which a fuel cell's potential drops as current increases and thereby to increase its efficiency and the current densities it can sustain. For example, since proton-exchange membrane fuel cells were first used in the aerospace program, the practical current density of PEM cells has increased by more than an order of magnitude. (See figure 3.) Doubtless, current densities will continue to increase as the mechanisms limiting fuel cell performance are further understood.

Three overpotentials

With fuel cells, there are three main sources of "overpotential" (the name historically given to the deviation of potential from the theoretical value). The relative importance of each varies with the magnitude of the current.

Activation overpotential is the most interesting from the standpoint of the physics underlying fuel cell operation. If one is to extract a sustained nonzero current from a fuel cell, the reactions at the electrodes must be perturbed from equilibrium and driven in the forward direction at a rate sufficient to yield the desired current. At equilibrium, although there is no net current, the forward reaction at each electrode proceeds at a nonzero rate that is precisely balanced at that electrode by the corresponding reverse reaction. These reactions generate balancing "exchange currents" of ions across each electrode–electrolyte interface. The exchange current magnitude is determined by the rate of thermal activation from the initial state (H_2, in the case of the forward reaction at the anode), over some intermediate configuration of

higher free energy, to a final state ($2H^+ + 2e^-$).

The key to driving the reaction in the forward direction lies in biasing the potentials of the electrodes away from their equilibrium values. Because the electrode processes are thermally activated, these potential shifts will cause exponential increases in the forward reaction rates at each electrode (and exponential suppression of the reverse reactions), and the electric current will increase correspondingly.

Activation overpotential is the reduction in the external potential that results from biasing the electrodes; the potential of the anode is raised, and the potential of the cathode is lowered. The activation overpotential develops naturally as soon as the electrodes are connected through an external load, and electrons then start to be depleted from the anode and to accumulate on the cathode. This change in charge at each electrode immediately shifts the electrode potentials and induces the required activation overpotential.

The exchange current densities of different electrode reactions span many orders of magnitude, varying from 10^{-16} amps/cm^2 to 10^{-2} amps/cm^2. A PEM fuel cell, for example, has an exchange current density of 10^{-6} amps/cm^2. (The current in a typical household appliance wire can exceed 100 amps/cm^2.) To obtain a high exchange current, a fuel cell may use a catalyst (an acid-resistant noble metal such as platinum for the phosphoric acid and PEM fuel cells, or nickel for alkaline fuel cells) to accelerate the electrode reactions. Alternatively, a fuel cell can be designed to operate at a sufficiently high temperature that thermal activation facilitates the electrode reactions and no catalysts are needed. Despite the very small value of the exchange current, a fuel cell of a reasonable size can still produce a practical flow of current: An increase in activation potential of only about 50–100 mV will raise the net current by a factor of ten—a relatively large increase that is characteristic of Arrhenius behavior. Also, the convoluted interface between a porous electrode and an electrolyte has an area much greater than the apparent geometrical surface area. The initial few hundred millivolts of overpotential shown in figure 3 indicate the logarithmic regime characterizing activation overpotential.

Ohmic overpotential accompanies the passage of current through the various components of the fuel cell (electrodes, electrolyte, conducting leads and so on) and is due simply to inherent electrical resistance. Ohmic overpotential increases linearly with current density and is responsible for the wide region of figure 3 (shown in red).

Concentration overpotential results from the complex hydrodynamic flow of fuel and oxidant within the fuel cell and from limits to ion diffusion in the electrolyte. As the external current increases, reactants are consumed and products accumulated in amounts that may begin to exceed the rates at which reactants can be supplied or products removed. This third type of overpotential develops as the electrode reactions become limited by the availability of reactants at the active electrode–electrolyte interfaces. As the concentration of reactants at the electrode surfaces drops toward zero, so will the external potential, and a maximum limiting current will eventually be reached. At this point, the fuel cell is providing no power, despite the large current produced and the prodigious consumption of fuel; all the energy is being converted to heat. This effect is seen in the green portion of figure 3, where the voltage quickly diminishes toward zero.

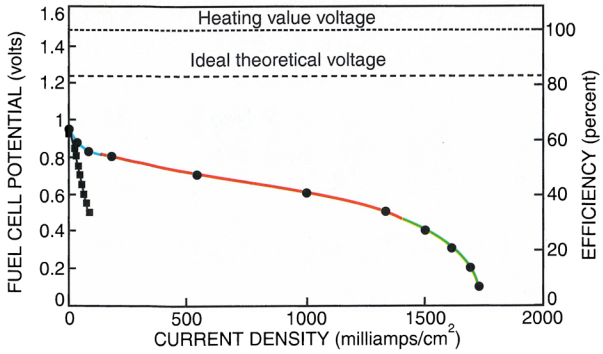
Prospects for advancement

Because the fuel cell is an immature technology, advances in fundamental scientific understanding can still rapidly translate into engineering advances that enhance commercial prospects.[8] Fuel cell research is one of many fields now expanding in response to growing environmental concerns, and there is considerable room for basic research to propel the technology forward.

Consider the fundamental science underlying the three sources of inefficiency outlined in the last section. Reducing activation overpotential, for example, requires increasing the exchange current, which in turn requires substantially improving our understanding of the "heart" of the fuel cell, the electrode–electrolyte interfaces where the chemical reactions occur. Thankfully, the recent boom in surface and interface physics offers powerful tools for the type of study needed. Advanced probes such as scanning tunneling electron microscopy, optical reflection spectroscopy, synchrotron radiation scattering and second-harmonic generation are evolving into *in situ* probes that will ultimately help reveal in detail the complex structure of the charged interface. Various electromodulation probes are well suited for investigating the high electric field generated at the interface; for example, impedance spectroscopy measurements reveal details regarding the fractal nature of the convoluted electrode surface.

Making optimal use of the available electrode surface area requires understanding the structures of surface catalysts and how those structures evolve with time. The amount of expensive platinum catalyst required for the early PEM fuel cells used in aerospace applications was so large as to preclude their use in automobiles, but recent advances in electrode design and catalyst application have dramatically increased the effectiveness with which platinum is used. The need for platinum is now reduced to a level where it would contribute only a couple of hundred dollars, rather than a few thousand, to the cost of a new fuel cell car (assuming the laboratory advances can be carried over to commercial fuel cells and sustained over the cells' operating lives).[9,10] Controlling the aging process in a fuel cell will depend in part on understanding the migration and aggregation of surface catalyst particles. Even more subtle is the reaction process itself, involving not only the quantum chemistry that describes any set of interacting atoms, but also the interaction between adsorbates and charge-carrying lattice excitations (polarons) occurring at the electrode–electrolyte interface.

Ohmic overpotential is governed predominantly by ionic conduction within the electrolyte, a process whose basic characteristics are by no means fully understood. In the liquid electrolytes used in alkaline, acid and molten-carbonate fuel cells, ions interact with the surrounding molecules and migrate as ion complexes, exhibiting important screening effects. The structure of such liquids is now being investigated by increasingly sophisticated



Performance curves for proton-exchange membrane fuel cells show the potential difference across the electrodes as a function of the current drawn by the external load per unit fuel cell area. The squares are for a PEM fuel cell used in 1966; the circles are for a PEM fuel cell of today using 200 times less platinum catalyst. The regimes of three sources of inefficiency are indicated for the modern fuel cell: activation overpotential (blue), ohmic overpotential (red) and concentration overpotential (green). These regimes are not apparent in the steep curve for the early fuel cell. The heating value voltage is determined by the total energy output, including both heat and current. Impurities prevent a fuel cell from achieving its ideal theoretical voltage, even at very low current densities. **Figure 3**

molecular dynamics calculations and analytical statistical mechanics models. To demystify the conduction mechanism, detailed *ab initio* calculations and density functional approaches are providing information about structural properties (such as density correlation functions) and thermodynamic properties (such as possible phase transitions in the structure of the ionic complexes). Similarly, the detailed mechanism responsible for ionic conductivity in the solid-electrolyte fuel cells remains largely unexplained: The role of water molecules in PEM fuel cells is of critical importance but poorly understood, as is the mechanism of vacancy migration in solid oxide ceramic fuel cells. Understanding these processes will lead to electrolytes with substantially increased conductivities and decreased ohmic overpotentials and to fuel cells with improved efficiencies and power densities.

Concentration overpotential, which is largely responsible for limiting the maximum operating current density and the peak power density of a fuel cell, is determined in part by the extent of laminar vs turbulent flows for the fuel and oxidant and by the concentration profiles of these reactants at the electrode surfaces. Since the local reactant concentration determines the electrode potential, a method for characterizing the spatial and temporal correlations of the turbulent velocity field is to measure current densities or voltages over a spatially distributed array of microelectrodes. This technique not only can provide information about the processes of importance to electrode kinetics but also can help to advance our basic scientific understanding of turbulence.

With continued advances in both the theoretical understanding of fuel cells and the experimental sophistication with which they are studied, fuel cells will become increasingly competitive with conventional combustion-based technologies. The cost of fuel cells will decrease as their lifetimes lengthen, power densities increase (allowing the stacks to shrink), tolerance to fuel stream impurities improves and overall reliability rises.

Fuel cell system technology is at a steep part of its learning curve. Rapid progress is being made as auxiliary equipment is developed and integrated with fuel cells, as fuel processing technology is improved, as system designs are optimized and as mass production processes are established.

Though fuel cell commercialization is under way, the rate of market growth will depend on the rate of technological improvement. Basic and applied research can play large roles in solving questions about fuel cell science, thereby helping to improve the technology and expand its market opportunities. But despite the promise offered by fuel cells, government R&D support has been modest. Government funding for fuel cell research through the 1980s in North America, Japan and the European community collectively amounted to less than 1% of total spending for energy research and development. Funding for fuel cells is growing, however, driven largely by environmental concerns.

Because fuel cell technology historically has been targeted for military and aerospace applications, most of the related research and development has been carried out in government and industry laboratories. But with the end of the cold war and the shift to civilian applications, there will be major roles for university research as well. This is especially true because the best prospects for reaching the demanding cost targets of commercial markets are offered by technological improvements based on increased understanding of the fundamentals.

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