# Emergence of fuel cell products

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2003 is a crucial period for the emergence of fuel cells in products that could have far-reaching effects on our lives. Fig. 1 shows the Citaro bus that will this year make its appearance in 10 European cities as a result of the CUTE project with funding from the European Community (www.fuel-cell-bus-club.com). It is a zero emission bus driven by pressurised hydrogen gas stored in the roof space, and recharged from hydrogen filling stations especially set up for the project. The hydrogen passes into the fuel cell over a stack of proton conducting membranes and loses its electrons as it meets the platinum coated carbon electrodes coated on the anode surfaces. The hydrogen ions diffuse through the polymer electrolyte and react with oxygen on the cathode electrode, picking up electrons, again catalysed by platinum/carbon particles.

◄ **Fig. 1:** Citaro fuel cell bus.

The electrical power generated by these electrochemical reactions, around 200 kWe, drives the electric drive train of the bus, which has excellent acceleration, speed and range. The only product of the reaction is steam that can be seen exhausting from the tailpipe as the bus runs through the city streets. The catalysts were made by Johnson-Matthey, the fuel cell stack by Ballard and the bus by Daimler Chrysler.

Two other fuel cell products making their commercial debut this year (Fig. 2) are the 2003 Honda FCX car that has gained the first certification for economy and emissions in the USA (www.hyweb.de 19/02/03) and the Daimler Fuel Cell A-Class model that just won approval in Japan to be run in 60 vehicles (hyweb 13/03/2003). These again will be fuelled by 5 hydrogen filling stations being installed in Japan at the moment.

▲ **Fig. 2:** Honda FCX and Daimler Chrysler fuel cell cars.

Although these products are unlikely to replace conventional buses and cars in full commercial operations before 2020, they represent a new step towards the low emission, high efficiency hydrogen economy of the future. In addition, laptop computers, mobile phones, portable power devices, emergency back-up systems and household water heaters are all likely to be powered by fuel cells in the near term. The purpose of this article is to describe the forces pushing fuel cells into applications, to review the recent advances in technology, then to look forward to the emerging issues such as hydrogen availability and storage.

## Forces driving fuel cells

First consider the major problems of our cities:-'Gloomy, noisy and dirty Birmingham' wrote Thomas de Quincy in 1849, when the city was 20 times smaller than its present dimension [1]. Although pollution was much reduced by the banning of smoky fuels in England in 1956, the emissions of barely visible NOX and particulates from cars and home heating are still substantial, while diseases like asthma, which may result from chronic exposure to irritants, are reaching epidemic proportions. It has always been necessary to legislate against technologies that emit dangerous pollutants because cleanup costs penalise the conscientious citizen. Perhaps the best example is the automobile exhaust emission legislation introduced in the US in 1969 that ultimately forced all new cars to carry exhaust catalysts, reducing CO, NOx and lead emissions considerably. This was an 'end of pipe solution' which did not fundamentally change the technical issues. But now legislation has been introduced in California to ensure that 10% of all new vehicles are 'zero emission vehicles', or ZEVs, starting in 2005 and gradually increasing to 2018. This will have a much more significant effect than the catalyst regulation because the drive train of the car must be altered in principle to accommodate this measure. Fuel cell driven cars seem to be the likeliest solution. Looking still further ahead to the end of the 21$^{st}$ century, it seems possible that all combustion and flame-based processes will be banned because of their harmful health consequences. Already, smoking is banned in New York public places, Hamburg has issued strong NOx limits, diesel generators are not allowed in certain locations, fires are banned in parks, etc, etc. The only logical end point is a flame-free society [2].

The second driving force for fuel cell introduction is efficiency. Although this concept is more difficult to define than pollution, because there are many different measures of efficiency, it is clear that more efficient technologies will use less fuel to achieve the same results, thus conserving our valuable fossil reserves, and utilising renewable energy more effectively. The fuel cell is the most efficient power-generating device invented so far. It converts the chemical energy of molecules like hydrogen, methane or alcohol directly into electrons at a potential near 1 Volt. Stacking a number of these cells together in series can give DC power at any desired voltage, rather like a battery of voltaic metal plates. The difference is that, unlike batteries, fuel cells do not need charging. Instead they provide power whenever fuel is pumped in. As a result, they do not need thick metal electrodes that make batteries too heavy for vehicle drives. But they share the two great advantages of batteries; high efficiencies and low emissions; advantages which our present power generation technologies do not possess.

Car engines, power station turbines and diesel generators that dominate our present culture are notoriously inefficient and dirty. Typically, only about 30% of the chemical energy in the fuel is converted into useful work by these devices because, as Carnot showed in 1824, these engines generate hot gas under pressure, and power cannot fully be extracted from a pressurised hot gas stream [3]. By contrast, a fuel cell extracts electrons directly from reacting molecules and can therefore be 100% efficient in principle. Indeed, a fuel cell can be more than 100% efficient if the reaction is endothermic and draws in extra heat energy from the surroundings, as methane does when it combines with steam. Of course, there must always be losses due to ohmic resistance and to mass transfer at the interfaces. Consequently, as more power is drawn from a fuel cell, its efficiency falls. When operating at maximum power, as in a battery, the fuel cell typically is 50% efficient since half the chemical energy is converted to external work and half to ohmic heating. Because this heat can also be converted to work



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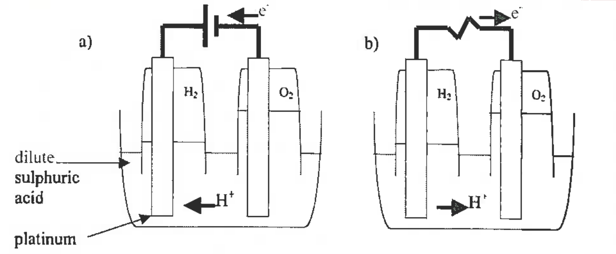



▲ **Fig. 3:** a) Grove's electrolysis experiment; b) Groves fuel cell demonstration.

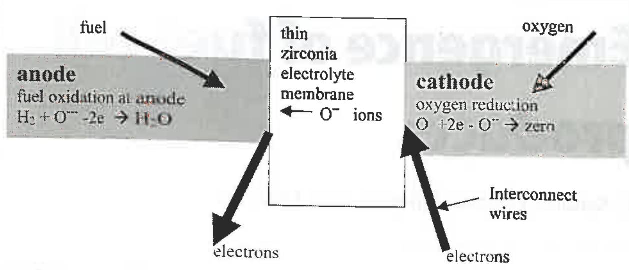
using a gas engine, a fuel cell combined with a turbine can give an overall efficiency of 75%, as demonstrated by Siemens Westinghouse [4]. This is significantly better than a combined cycle gas turbine generator that can typically attain 50% efficiency. And whilst such combined cycle engine systems may only operate effectively at hundreds of MWe capacity, in large centralised facilities that entail high distribution costs, a fuel cell system can operate down to 1 kWe quite easily, be small enough to fit in every room and every vehicle, leading to a fully distributed power network.

In order to understand these high efficiencies, it is worth reflecting on the principle of fuel cell operation, which was originally described by William Grove in 1839. Following Alessandro Volta's invention of the battery, Grove like many scientists of his time was electrolysing water using two platinum electrodes dipped in dilute sulphuric acid to promote ionic conductivity in the solution (Fig. 3a). By passing electric current through the water-acid electrolyte, Grove generated hydrogen bubbles on one of the platinum electrodes and oxygen bubbles on the other. The two gases were kept separate by positioning individual collector vessels over each electrode. Grove's pioneering insight was to realise that the reaction was reversible. The hydrogen and oxygen can recombine at their respective electrodes to drive current in the opposite direction (Fig. 3b). What Grove recognised was that a fuel cell is an electrolyser running backwards. Just as an electrolyser can be made almost 100% efficient by operating near the equilibrium voltage, so can a fuel cell, as long as low currents and good electrocatalysts are used. Under these conditions, there are no pollutant emissions either, water being the only reaction product. More usually, it is practical to operate the fuel cell near its maximum power output, roughly half the equilibrium voltage and around 50% efficiency. But as electrical demand reduces, ohmic losses fall and efficiency rises, unlike a combustion engine that gets less efficient as it is turned down because of frictional losses.

## Technology Push

So what has changed since Grove's time to make fuel cells more attractive than combustion engines? Obviously, legislation for zero emission has had the most significant effect, putting penalties in place for polluting companies. Another incentive is the climate change levy on fuels, introduced by the British Government in 2002, which has created a market for low carbon technologies [5]. Approximately 1 billion pounds will be raised by this novel tax this year, and some of that money will be used by the Carbon Trust to develop fuel cell technologies.

But the most important technical advance has been the invention of solid electrolytes to replace the nasty and messy liquids, such as sulphuric acid, used by Grove. Liquid electrolytes have a number of drawbacks; they leak, evaporate and corrode; whereas solid electrolytes are stable, non-corroding and self-supporting. Two materials are leading this advance. One is a polymer made from sulphonated fluoropolymer, while the other is a ceramic made from yttria stabilised zirconia.




▲ **Fig. 4:** Operation of a solid oxide fuel cell.

The mode of operation is illustrated in Fig. 4 that shows that the central component of a solid electrolyte fuel cell is a thin membrane of the solid electrolyte, typically 10 to 100 μm in thickness. This allows ions to pass through but stops the flow of both gas molecules and electrons. Yttria stabilised zirconia is the simplest solid electrolyte because it only conducts oxygen ions $O^-$. These ions are formed by reduction of oxygen atoms that pick up electrons at the catalytic oxygen electrode (cathode) which is usually a porous lanthanum manganite semiconductor. The electrons enter the electrode through a metal wire, the 'interconnect' which connects the cell to the external circuit. The oxygen ions can then diffuse through the electrolyte membrane to the fuel electrode (anode) which is normally made of fine nickel particles supported on a porous zirconia lattice. This requires red-hot conditions, typically 800°C, for a good diffusion rate. The electrons are released from the oxygen ions and can then flow out through the interconnect wire while the oxygen reacts with the fuel, hydrogen in Fig.1, which is continually fed to the anode compartment.

The overall reaction is the sum of the two reactions occurring on the two electrodes as shown below in reaction scheme 1 for hydrogen reacting with oxygen, the simplest reaction.

| | |
|---|---|
| Fuel electrode (anode) | $H_2 + O^- - 2e \rightarrow H_2O$ |
| Oxygen electrode (cathode) | $O - O^- + 2e \rightarrow$ zero |
| Resultant overall reaction | $H_2 + O \rightarrow H_2O$ |

▲ **Scheme 1:** Two electrode reactions adding to give the complete reaction.

From this scheme it is clear that there is no product formed in the cathode compartment and only water is produced at the anode. Thus, this fuel cell is 'zero emission' as defined by US regulations. The equilibrium voltage for this reversible reaction depends on both temperature and reactant concentrations. Typically it is 1 V at 800°C. Current flow of about 1 A for each square centimetre of membrane surface is possible, and the voltage then drops because of ohmic losses to around 0.5 V. For high power, it is therefore obvious that the area of membrane needs to be as large as possible, 1 $m^2$ providing typically 1 kWe. Consequently, the fuel cell design must be a stack of plates or tubular cells, similar to that of a heat exchanger or a filter, devices that also depend on high membrane area for their operation.

The conclusion is that a solid state device made up of 5 layers (electrolyte + 2 electrodes + 2 interconnects) can produce DC power directly without moving parts. This is almost magical in its simplicity and lends credence to the new idea that small, reliable, efficient, zero-emission power generators may develop commercially for a number of applications in the next decade.

## Applications

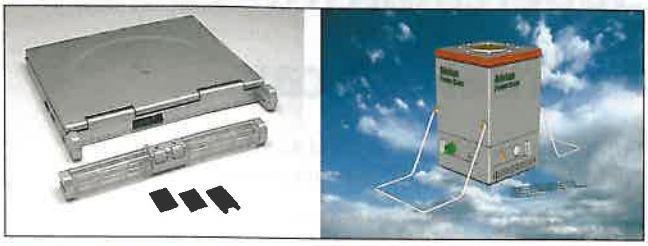
Already, every new car has a fuel cell built in, to control the catalyst clean-up system. This is a single cell, like that in Fig 4, comprising an yttria stabilised zirconia membrane with two electrodes and two interconnect wires, inserted in the exhaust manifold where it reaches 600 to 700°C. On one side of the membrane is air, and on the other side is the engine exhaust stream that is deficient in oxygen. The difference in oxygen concentration across the membrane creates a voltage that depends on the oxygen level. The fuel cell therefore acts as a sensor that can be used to control the engine management system for emission catalyst performance. Only a small power is required for this task, but it is envisaged in future that the whole electrical system of the car, ie the radio, electric windows, air conditioner, etc, will be powered by a stack of such cells. In the USA there is a large development project on this theme, the SECA project, supported by Siemens, Honeywell etc [6].

Of course, it is also possible to replace the whole engine of the car with a fuel cell stack, and this has now been demonstrated by many car manufacturers using the Polymer Electrolyte Membrane (PEM) fuel cell that has been much developed by Ballard in Vancouver [7]. The PEM fuel cell uses a sulphonated fluoropolymer swollen in water to conduct proton species. Carbon electrodes with platinum catalyst are pasted on each side and graphite interconnects are generally used. Humidified hydrogen is the fuel, fed to the anode compartment and air is the oxidant, which also flushes out the product water from the cathode compartment. The temperature of operation is around 100 °C. Thus this fuel cell gives zero emissions and could provide a solution to the ZEV (zero emission vehicle) legislation. Problems of hydrogen supply are still to be overcome, as are the costs of the components compared to a standard combustion engine. However, it is estimated that a significant penetration of such ZEV fuel cells will be achieved by 2020.

An alternative possibility has been demonstrated by BMW, who have used hydrogen as the vehicle fuel instead of gasoline. The hydrogen drives an almost standard internal combustion engine and also powers a fuel cell for auxiliary electricity. This satisfies ultra low emission regulations, although some nitrogen oxides are produced under combustion conditions. BMW also adopted liquid hydrogen storage, using cryostatic tanks in the trunk of the car, while proving that that these tanks could be topped up at robotic filling stations [8]. However, the practicality of such fuel storage is still in doubt.

The hydrogen storage issue is one of the most challenging problems in the fuel cell field. If the storage density is defined as the mass of hydrogen stored divided by the total mass of the storage system, then present methods, including hydrogen bottles and liquid hydrogen only give storage density of a few per cent, whereas gasoline is near 20%. Hydrides like lithium hydride (12.7% density) offer a possibility of improving over the present standard of pressurised bottles (about 5%). Carbon nanotubes have been suggested as storage media, but early reports of 50% density have not been repeatable. The currently accepted value is 0.5%. In order to evaluate the possibilities, a large European project, FUCHSIA has been started [9]. Hydrocarbons are still the best bet, if the carbon could be dealt with.

The most fundamental issue is the source of the hydrogen, which now is manufactured mainly from natural gas, but could be generated on board the vehicle from gasoline by means of a steam reformer. In this steam reacts with hydrocarbon to give hydrogen and CO. Unfortunately, such fuel processors are bulky, slow and expensive, and do not appear viable in the near future. A new approach to the hydrogen economy is needed where hydrogen is generated from renewable sources such as biogas, wind energy or photovoltaics. One possibility is methanol, derived from biomass, which can be used with a polymer fuel cell [10] to produce power for a laptop as shown in Fig. 5a. Also, natural gas is available in homes and could be used directly in the solid oxide fuel cell device [11] shown in Fig. 5b to provide both heat and power. This device was made using 1000 tubular zirconia fuel cells to replace the conventional metal burner in a water heater. In future, this could be augmented with biogas or renewable hydrogen to give a sustainable energy economy.



▲ Fig. 5: a) Casio lap-top computer powered by a PEM fuel cell fuelled by methanol; b) A solid oxide fuel cell system driven by natural gas for combined heat and power.

One exciting prospect is to generate power using such devices locally in homes. This is not yet possible with combustion engines because of their lubrication, wear, emission and ignition problems. But a small solid state fuel cell could give the reliability and lifetime needed for this application. Consider a vision of the future where each home has a fuel cell within its central heating boiler. This could run on natural gas, but also on biogas and hydrogen. Because the fuel cell is a catalytic device, without a flame, it can run on a variety of molecules, and actually runs better on diluted fuel such as biogas, whereas engines stop under these circumstances. Under base-load conditions, the fuel cell would operate at high efficiency and would also generate heat for the home. Excess power could be exported through the grid if restrictive regulations were removed. The system would be totally secure. Also, the nation's carbon dioxide emissions would be halved in the domestic and business sectors and our fuel imports reduced substantially. Totally distributed power could be achieved through fuel cells in the future. With a fuel cell in every home, there would be sufficient electricity generated without the need for large power stations.



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