

From Bioelectricity to SPACE TRAVEL

PART 2

David Clark looks at the underlying principles behind electrochemical energy sources, from the 'voltaic pile' to the solid polymer fuel cell.

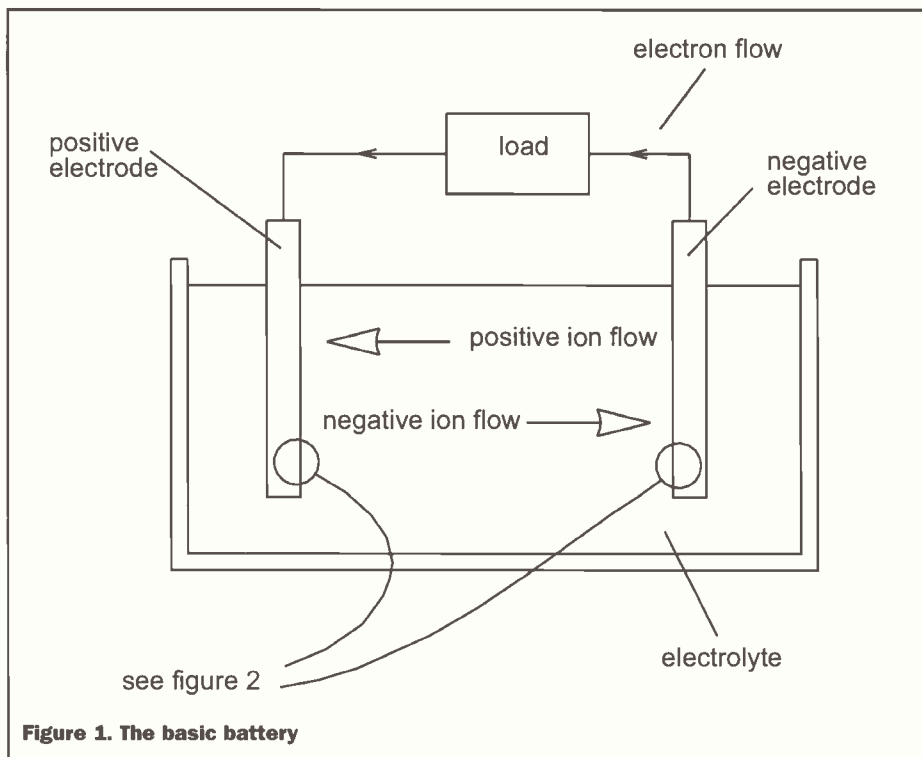


Figure 1. The basic battery

Although there are many different types of battery available, the variety is primarily based on trade-offs between cost and the primary requirement for a particular market. This might be voltage output, maximum current capability, total energy capacity, weight, volume, shape, range of temperature of operation, voltage stability, flatness of discharge curve, safety and environmental concerns, commercial demand, or shelf life. For secondary (rechargeable) cells additional factors might include charge method, charge time, memory effects, or the number of charge cycles the battery can survive and still be useable. The materials used in the manufacture of the battery are then chosen (or developed) accordingly. So what's going on inside a battery, determining these factors?

The Four Elements

The purpose of a battery is to provide energy to do some useful work, which it

does by producing free electrons that carry charge. The only materials where free electrons are available in large quantities (at normal temperatures) are metals. Furthermore the charge-carrying electrons must flow in a closed circuit to be able to do any significant work. Since a battery is a device that generates free electrons through chemical means, the electrons are 'produced' at a metal/chemical interface, and 'travel' through the chemical part of the battery by being 'carried' by atoms in the form of ions. (If an atom has more or less than the normal number of electrons associated with it then it becomes an ion that can carry charge, negative in the case of extra electrons and positive in the case of missing electrons). A substance that forms ions when dissolved in a solvent and takes part in chemical reactions associated with the transport of electrons is known as an electrolyte. Electrons are therefore effectively 'carried' by the electrolyte and so a closed system can exist that enables the

battery to do useful work. This circuit is summarised in Figure 1.

So there are four main elements to a battery. Firstly a metal/chemical interface that donates electrons (the negative electrode). Secondly a metal/chemical interface that receives electrons (the positive electrode). Thirdly an electrolyte that carries charge between the electrodes inside the battery. And additionally in a practical battery there is usually a means of reducing the electrochemical side effects that occur that decrease its ability to work effectively. But how does a metal/chemical interface release electrons?

The Electrode/Electrolyte Interface

When a piece of metal is dipped into a solution containing ions of the metal some of the metal dissolves to form metal ions, releasing electrons. At the same time some of the ions 'grab' an electron and become a metal atom again, thus becoming deposited on the electrode surface. See Figure 2.

Both processes occur at the same time and an equilibrium is set up. The free electrons can only occur in the metal and so a negative charge builds up on the metal. This negative charge attracts the positive end of water molecules (undissociated water molecules have a dipole moment, that is they have a slightly negative end and a slightly positive end - see box text, p64).

The water molecules therefore line up against the metal electrode, and for the same reason the negative end of the water molecules surround any positively charged ions. This arrangement effectively creates an 'atomic' capacitor with the metal surface acting as one plate, the 'layer' of ions acting as the other, and water molecules acting as the dielectric, as shown in Figure 4.

The voltage between the two 'plates' depends on the temperature and the concentration of the solution (since it is a chemical process), and also on how readily the metal releases electrons. For a given concentration of solution and temperature the voltage between the 'plates' is fixed and different for each metal. When the metal/metal ion voltage values are arranged in a decreasingly negative order they are called an electrochemical series (see Table 1).

Metal/Metal Ion	Voltage Generated
Lithium	-3.03
Aluminium	-2.87
Zinc	-0.76
Lead	-0.13
Platinum/Hydrogen	0.0
Copper	+0.34
Silver	+0.80

Table 1. Electrochemical Series (standard conditions of 25°C and ion concentration 6.023 x 10²³ ions [= 1 'mole'] per litre)

The reason for the differing voltages is that different metals 'hold onto' their outer electrons to different degrees depending on their atomic structure. This is due to differences in the charges on the nucleus of the atom, the size of the atom, and the number of electrons in the inner electron shells (which influence the electrical properties, but don't take part directly since only the outer electrons are free to leave the atom). See the box text on The Electrochemical Series.

An arrangement of one metal electrode in a solution of its ions is called a 'half cell'. If two different metals are placed in an ion solution the ions provide a conductive connection between the two 'atomic' plates of the 'atomic' capacitors since the ions can carry charge through the solution (how fast they can carry the charge depends upon other factors such as the rates of chemical reactions). There is therefore a voltage across the two metal electrodes equal to the difference between the voltages of the two half-cells. This is an electrochemical cell, or battery, and under fixed conditions these voltages are accurately known and can be used as laboratory references. For example the Clark cell uses a zinc-mercurous sulphate-mercury device to give 1.434 volts and the Weston cell uses a cadmium-mercurous sulphate-mercury arrangement to give 1.019 volts. The electrochemical cell is the device that Volta accidentally discovered 200 years ago.

Oxidisers and Transition Metals

The need for an aqueous solution means that hydrogen is released at the positive electrode and this reduces the effectiveness of the interface. It is also a problem for a practical battery since hydrogen gas is explosive, or if contained

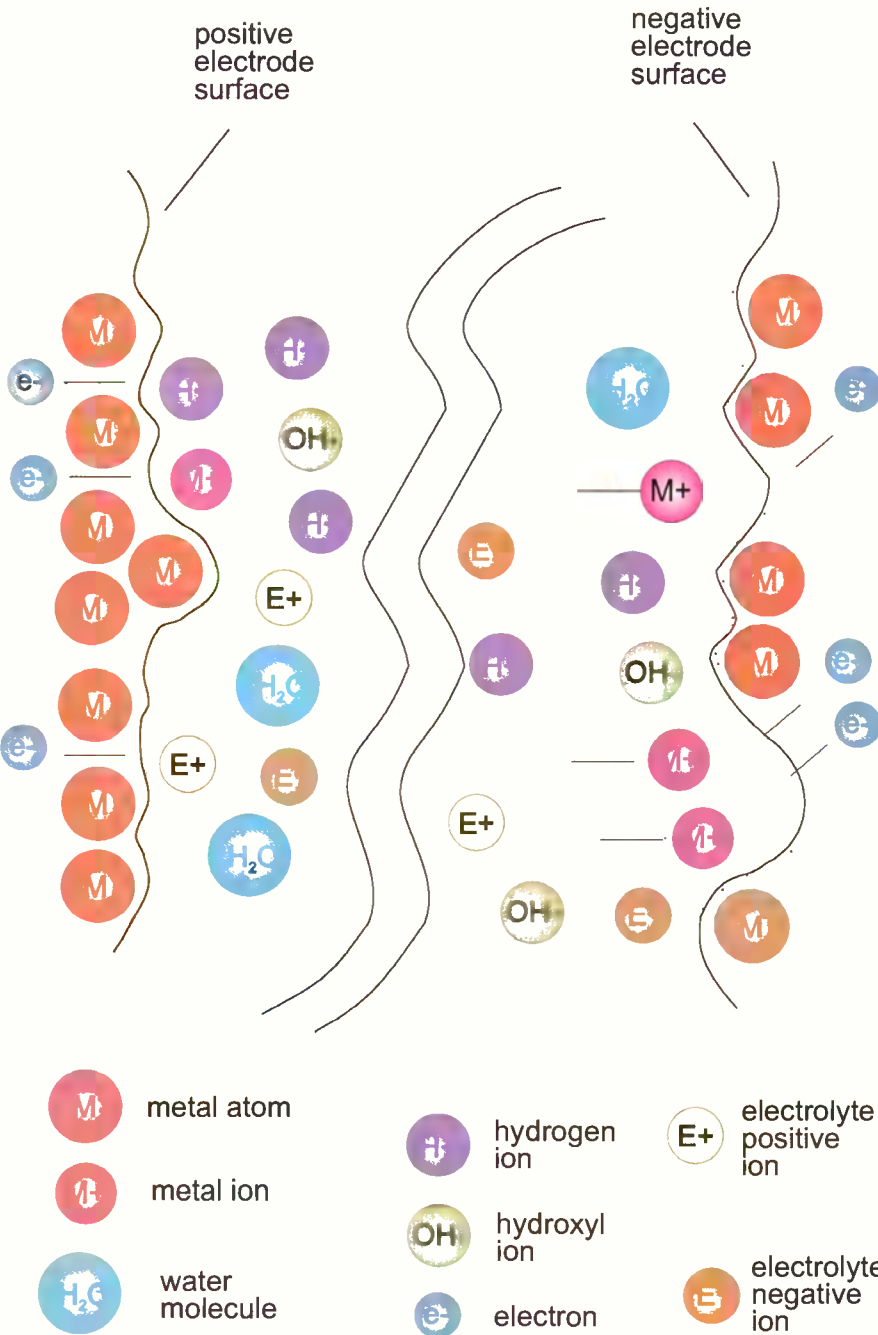


Figure 2.

builds up pressure. One solution as has been seen is to use nitric acid as an oxidising agent to oxidise the hydrogen to water. This is not a very practical method

for general use and the use of the manganese dioxide/carbon electrode has been adopted. This works because of the properties of a group of metals called the d-block or transition metals, of which manganese is one. Other important ones are nickel, silver and mercury. Metals conduct electricity because their atoms easily give up the electrons in their outermost electron shell. Zinc for example has two such electrons. But manganese can donate up to seven electrons, and in the form of manganese dioxide the manganese atom has given up four electrons, ie it is an ion with an overall positive charge of four. Its strength as an oxidising agent is that it can accept electrons singly and become a manganese ion with an overall positive charge of three. In 'grabbing' an electron at the electrode interface manganese dioxide

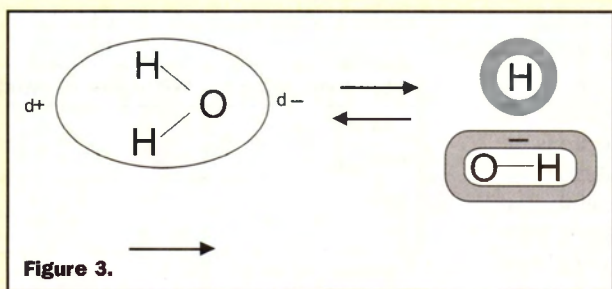
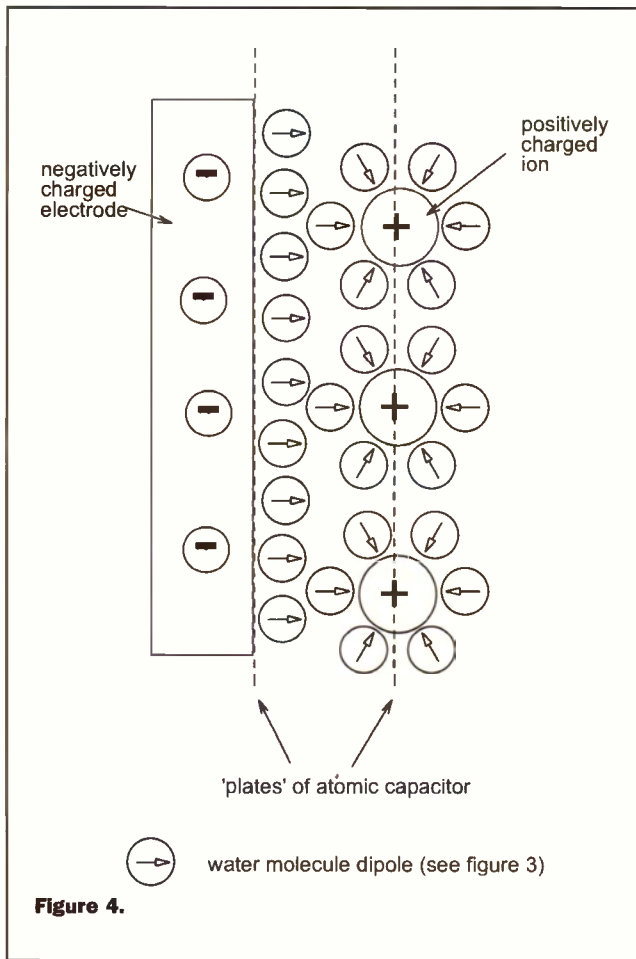


Figure 3.

Water Dipole Moment

The water molecule tends to dissociate slightly into hydrogen and hydroxyl ions, which are strongly positively and negatively charged. Because of the strongly negative oxygen ion however the water

molecule also tends to have a slightly positive and a slightly negative end, and will therefore 'surround' other charged ions, including the hydrogen and hydroxyl ions themselves. A molecule with opposite small charges at either end is said to have a dipole moment and this can be represented by a small arrow (as in Figure 4).



reactions occurring which again depends on factors such as chemical concentrations, surface area available for reactions and temperature. The total amount of energy that the battery can provide depends on the voltage generated across the electrode/electrolyte interfaces and is the familiar volts times ampere-hours formula. So it can be seen how all batteries are ruled by these basic principles and that the choice of materials and configuration is the best compromise that can be achieved for the required performance specification. So what are the different options?

Battery Variations

The most basic general-purpose battery available is the one that has been around for over a century, the one based on the

the battery was 'used up'.

The next development was the familiar alkali battery, which replaced the zinc chloride electrolyte with the alkali substance potassium hydroxide. This gives the highest power to size ratio of the manganese dioxide and zinc type batteries.

A more specialised variation of this type is the manganese dioxide and magnesium battery, which is used where light weight is important. Other specialised alkali cells are the mercuric oxide-zinc and silver oxide-zinc cells, commonly used as watch batteries.

Lithium is a relative new material for commercially available batteries. Its use was initially prevented because it reacts aggressively with aqueous solutions and so non-aqueous electrolytes needed to be developed; electrolytes such as lithium tetrafluoroborate in a carbon based solvent. The advantage of a lithium half-cell is its high voltage (refer to Table 1). One cell using lithium is of the lithium-manganese dioxide type. Another is the lithium-iron sulphide cell. A commercially successful type is the lithium-carbon monofluoride battery. Yet another lithium type that demonstrates a further technological advance is the lithium-thionyl fluoride cell. This uses the liquid thionyl chloride not only as the electrolyte solvent but also as the material of one of the electrodes. A film of lithium chloride automatically forms to provide the barrier between the two half-cells. This type of cell provides the greatest commercially available energy and power density, and furthermore will operate at down to -54°C . It is used for providing backup power in aerospace systems.

effectively prevents the hydrogen being released as a gas. Manganese has the largest number of possible different stable states of electrons free to take part in interactions with other atoms, but all the transition metals can do this to varying degrees.

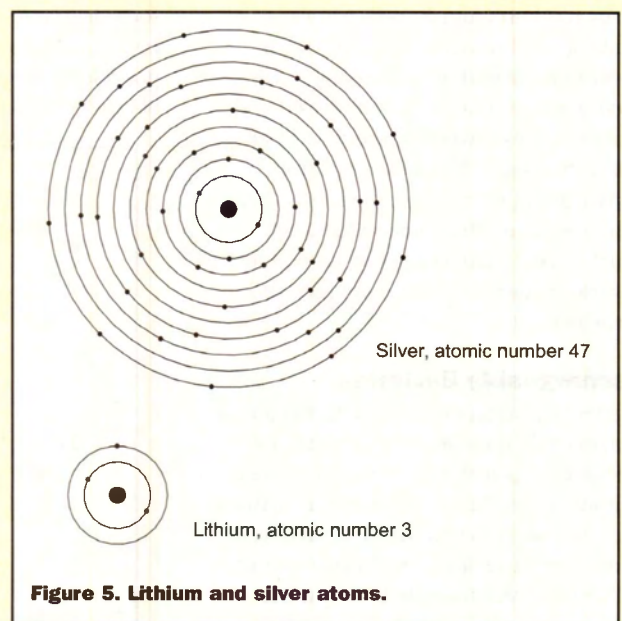
Battery Capacity

Michael Faraday established in 1834 the other main principle behind battery operation, relating the amount of material in the battery to the amount of electricity it can produce. For example for every two electrons flowing in the circuit one atom of zinc is dissolved in the electrolyte in the form of its ion. At the same time two atoms of manganese four plus are converted to manganese three plus. The electrolyte must be able to carry the equivalent charge through the electrolyte by means of ions carrying one negative charge (or positive charge for ions moving the opposite direction) for each electron. So the amount of charge a battery can produce is governed by the amount of material present and its purity. Within the electrolyte itself the concentration can be increased to give more ions per volume, but the less solvent there is the less of the electrolyte is in the form of ions, which is essential for battery operation. So there is a fundamental limit to the total amount of charge a battery can produce. The rate at which this charge can be produced ie charge per unit time, or current, is ruled by the rate of the chemical

Leclanché cell and consisting of graphite/manganese dioxide and zinc electrodes with an ammonium chloride/zinc chloride electrolyte. The main development of this was the replacement of the electrolyte mixture with zinc chloride alone, the ammonium chloride tending to 'leak' though the zinc electrode/container when

Electrochemical Series

The degree to which the outer electrons of materials are held depends on the charge on the atom. Metals with large nuclei contain more protons and have more positive charge, which tends to attract electrons. But atoms with more protons also have more electrons in the inner shells (a neutral atom has the same total number of electrons as protons). These inner shells therefore shield the outer electrons from the positive nucleus and the outer electrons are less firmly held. Additionally the atoms with more protons and electrons are larger and so many of the electrons are much further away from the nucleus and so feel the attraction of the positive charge even less strongly. The interaction of these effects determines the metal's electrode voltage.



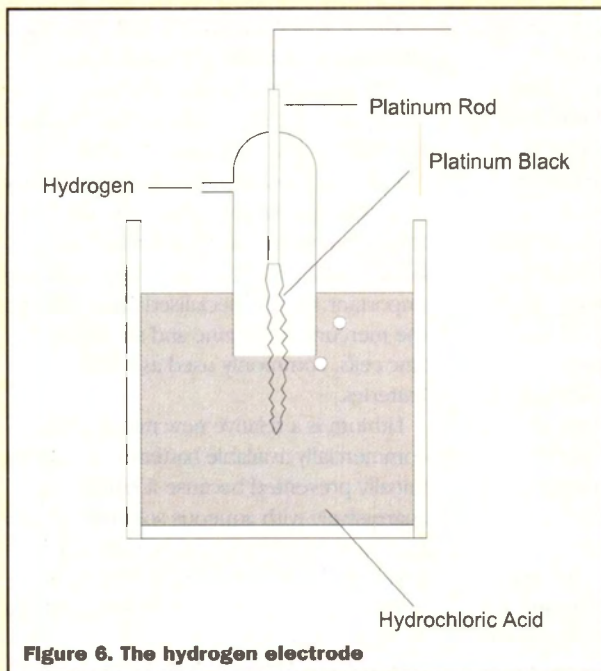


Figure 6. The hydrogen electrode

Hydrogen electrode

Instead of an electrode rod of hydrogen (obviously impossible) a rod of inert platinum coated with platinum black (a finely divided platinum layer that provides a large surface area on which reactions can occur) is dipped into a solution containing hydrogen ions (such as hydrochloric acid). Hydrogen is passed over the electrode, the reactive area of the platinum rod being partly in the ionic solution and partly in the hydrogen gas.

Gas and Air Electrode Cells

A similar cell to the lithium-thionyl fluoride type is the lithium-sulphur dioxide cell, which uses sulphur dioxide gas under pressure as one electrode. One practical problem is the need for the gas to be under pressure but there is another class of cells that use the oxygen in air as an electrode. It may seem strange to consider a gas as an electrode but in fact the hydrogen electrode is used as the reference against which all other half-cell voltages are measured (see the box text for the hydrogen electrode).

Zinc-air systems are commercially available but are difficult to make. If oxygen reaches the other electrode it will attack it. Aluminium-air cells are also available, and research is underway to develop a cell of this type in which the used reaction products are removed and replaced. This is where battery and fuel cell technology start to overlap. The particular appeal of these devices is their light weight and high energy density, which makes them of special interest for electric powered transport vehicles and aerospace use.

Rechargeable Batteries

The technological differences between non-rechargeable (primary) and rechargeable (secondary) batteries is no longer as great as it was when the comparison was between zinc chloride cells and lead-acid batteries. Apart from in vehicles, probably the most widely used rechargeable battery is the nickel cadmium battery. This is an alkali electrolyte battery and the electrons flow between nickel and cadmium compounds as they change oxidation state according to whether they are charging or discharging.

Cadmium is unfortunately a highly toxic

pollutant and hopefully the nickel metal hydride battery will eventually replace it. The part of cadmium is taken by a metal hydride, a molecule that consists of atoms of a metal and hydrogen, the hydrogen being of the form where it gains an additional electron rather than the usual situation where it loses the electron from its outer, reacting, shell.

New Cells

Perhaps the most exciting technological advances in battery manufacture are in the use of plastics, or polymers. Normally of course plastics are insulators and this is due to the fact that they are composed of chains of carbon and hydrogen atoms, the bonds between the atoms of the molecules being such that there are no free electrons to conduct electricity. However it is now possible to 'dope' the polymers with atoms of other materials such as sulphur and

lithium, and this frees some electrons giving the polymers useful electrical properties. Most important of these properties for battery manufacturers is the ability of the material to act as an electrolyte and hence allow for a completely solid, light, very thin battery. Some polymers may soon replace metal electrodes, allowing for a completely plastic battery!

Fuel Cells

Fuel cells have existed for nearly as long as batteries. When the first batteries were found to break down water into hydrogen and oxygen it wasn't long before the reverse effect, generating electricity from hydrogen and oxygen was discovered. William Grove established this in 1839. It was the need for small highly efficient and stable power supplies for satellites and spacecraft in the 1950s and 60s however that prompted the development of these devices. A fuel cell is essentially two different gas 'half' cells connected together as a single cell (see Figure 8). A practical cell uses porous electrodes and an incorporated catalyst to maximise gas/electrolyte/electrode contact and hence improve efficiency. Pumps and control systems are needed to regulate pressures and temperatures, but once these have been designed to operate reliably the cell will produce electricity for as long as there are gases supplied.

A major advantage of fuel cells is their efficiency in converting fuel to electricity. This is because the fuel is converted to energy directly, rather than by for example burning fuel in a first stage and then using a second process to create the electricity. This might involve the use of steam to turn a turbine, or an internal combustion engine to drive a generator. This is obviously of major environmental importance for reducing fossil fuel consumption and in generating fewer waste products, whether greenhouse gases or toxic materials. The ideal system could use combined fuel cell and battery technology. Fuel

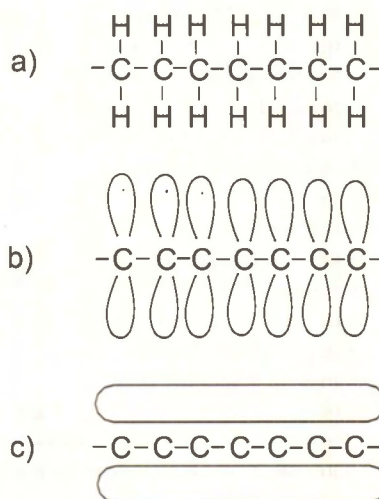


Figure 7.

Ion polymers

- a) Polymers are made by linking small carbon and hydrogen based molecules to form long chains.
- b) The electrons associated with the bonds between the atoms are normally fixed in orbitals.
- c) By adding other atoms such as lithium into the structure the electron 'clouds' can be made to overlap. This gives polymers with properties that enable them to be used as conductors and electrolytes since the electrons can then move through the material.

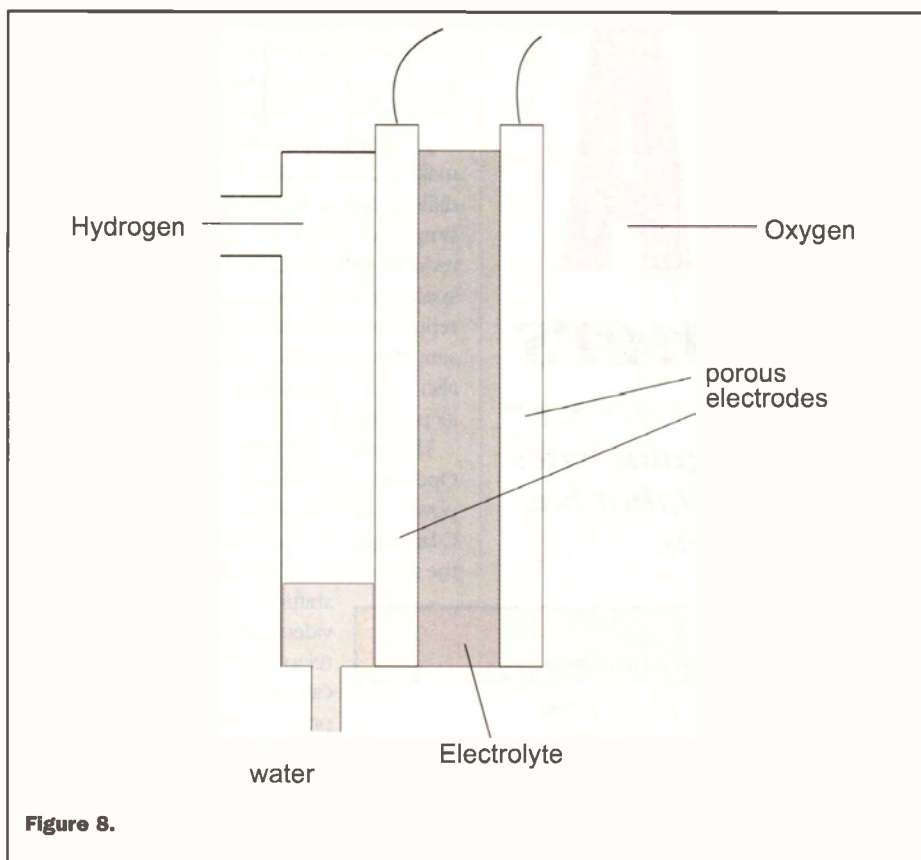


Figure 8.

cells would generate the electricity for charging lightweight high energy density batteries to be used in electric powered vehicles, removing the need for the most widespread generator of pollution and environmental damage. Some fuel cells can convert energy at efficiencies of around 80%; the internal combustion engine is less than 40% efficient.

Another major advantage is that the processes occurring in these kinds of system are reversible. A fuel cell using hydrogen and oxygen as fuel produces electricity and water. Using electricity the water can be broken back down into hydrogen and oxygen for re-use. If the electricity used to regain the hydrogen and oxygen fuel were to be obtained from solar energy a highly efficient system would be in place. The problem at the moment is the level of technology needed for the materials making up a fuel cell. As will be seen in the next section, fuel cell materials need some special properties.

Types Of Fuel Cells

There are several different types of fuel cell in existence, but a problem common to most of them is the complexity of the requirements for the electrode structure. Electricity is only produced at the surface of the electrode so careful design is needed to maximise the interaction between metal, fuel and electrolyte. This also has safety implications. If too much or too little electrolyte reaches the reacting surface the reaction will be slowed. If fuel reaches the electrolyte compartment there is danger of

explosion through pressure and/or ignition. A catalyst is needed to speed up the rate of reaction especially for those fuel cells operating at lower temperatures. To fulfil all these requirements an electrode assembly must typically consist of a conducting supporting structure capable of carrying the current generated, a thin gas-permeable waterproof membrane such as polytetrafluoroethylene to separate the fuel and the electrolyte and a catalytic layer of platinum or an organometallic compound (consisting of molecules of a metal linked to a carbon based material). Not an easy or cheap device to design and manufacture to perform with high levels of efficiency and safety, particularly at the temperatures employed in some types of fuel cell!

Alkaline fuel cells, like alkaline batteries, have an aqueous solution of potassium hydroxide as the electrolyte. Electrodes are typically of carbon and nickel, and the device usually operates at less than 100 °C, although even at this relatively low temperature special care must be taken over construction, as the hot electrolyte tends to attack joints and seams. The water by-product is removed by evaporation, and can be recovered by condensation. The cell can be up to 80% efficient. This is the type used in space vehicles, in particular the United States Space Shuttle.

High Temperature Fuel Cells

Another type of fuel cell named after the material used as the electrolyte is the phosphoric acid fuel cell. This cell operates at up to 200 °C and can use hydrogen that is

contaminated with some carbon dioxide, so the fuel need not be purified to such a high degree thus reducing costs. Two other types of fuel cell are expected eventually to be used as electricity generators in power stations. These are the molten carbonate and the solid oxide fuel cells, and these use a mixture of hydrogen and carbon monoxide for fuel, usually obtained from fossil fuels. (The advantage over conventional power stations is efficiency.) The electrolytes are respectively molten potassium lithium carbonate and a conductive oxide such as yttria treated zirconium. They operate at around 650 °C and 1000 °C respectively, and are expected to provide around 45% and 55% efficiency. Important issues for the use of these types include design and safety factors because of the nature of the materials and the temperatures involved. However the costs of the materials needed are less than with other types because the electrodes are metal based and simpler in construction - the fuel is deliberately mixed with the electrolyte as part of the reaction process, so separation of fuel and electrolyte is not necessary.

Solid Polymer Fuel Cells

In the same way that polymers are making inroads into commercially available batteries following a period of being restricted to use in specialised applications, solid polymer electrolytes are beginning to be used in fuel cells though currently at high cost. The electrolyte is based on an ion-conducting membrane such as perfluorosulphonic acid. An early version of this fuel cell was used on the Gemini spacecraft that flew in the 1960s as part of the programme to develop the docking techniques that would be needed for the Moon landings at the end of that decade.

Conclusion

The use of hydrogen and oxygen to generate electricity and water for use in spacecraft is a reversal of exactly the same process that nearly two hundred years earlier had been used to break down water into hydrogen and oxygen. This was the process that began the understanding of the elemental composition of substances, and enabled the prediction of their properties, knowledge that has enabled the development of yet more powerful and efficient batteries. From the simple bioelectricity experiments of Galvani and Volta to the power sources of the Space Shuttle the battery has undergone many changes but in some ways has hardly altered. However with the new polymers coming into general use a dramatic new phase of battery evolution could be underway.

Acknowledgements: Encyclopaedia Britannica CD ROM.