From Bioelectricity to SPACE TRAVEL

PART 1

In this 2-part feature David Clark looks at the invention and improvement of the first battery - Alessandro Volta's "voltaic pile".

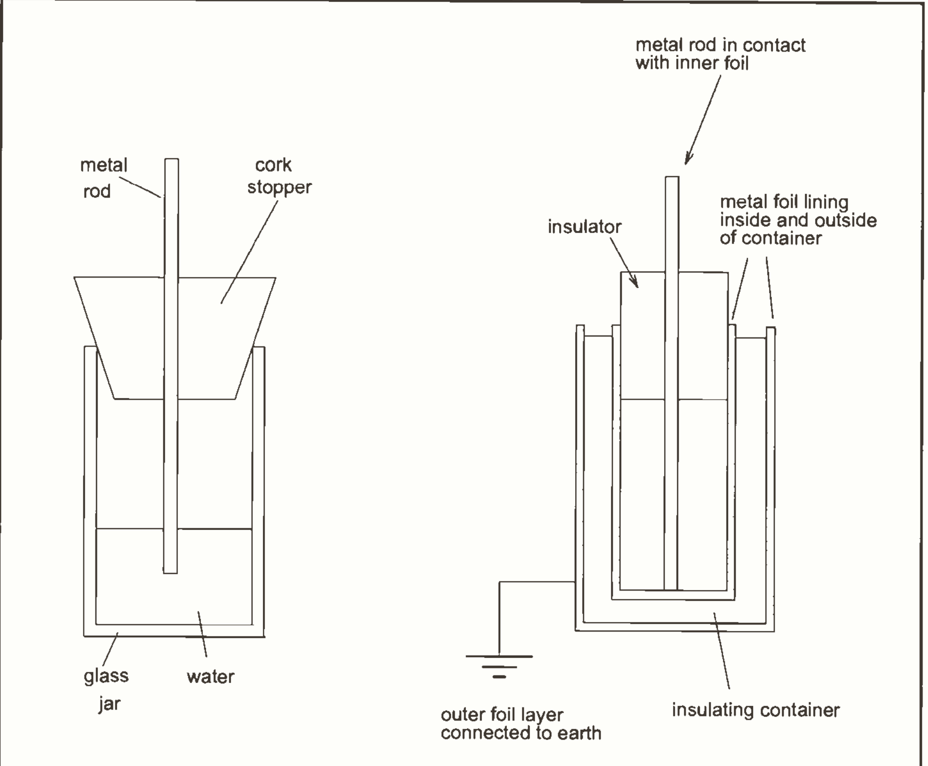

Figure 1.

With the ability to store charge and so do 'proper' experiments, theories about what electricity was began to develop. In France, in 1733, the chemist Charles François de Cisternay DuFay declared that electricity was composed of two fluids, which he called 'vitreous' and 'resinous' (words associated with the insulators used to generate the two types, glass and amber). Normally these two fluids were in balance in a substance and so matter was neutral, but friction could separate them and disturb the balance. The material would then attract or repel other substances. This was the 'two-fluid' theory. A later theory, supported by William Watson and Benjamin Franklin, was the 'single-fluid' theory. Knowledge of the composition of materials had not advanced much in the two millennia since the theories of the ancient Greek philosophers who held that all matter was composed of elements such as earth, air, fire and water. Adherents to the 'single-fluid' theory concluded that lightning electricity was also an element, a single fluid, which was evenly distributed throughout all other matter but particularly present in water and metals (which were therefore conductive). However if an object had too much of this fluid it would become positively charged, and if too little, negatively charged, and this explained the attraction and repulsion effects as the amount of 'electrical fire' tried to equalise between objects.

The 'single-fluid' theory fitted the facts well, although the 'two fluid' theory is perhaps closer to the concept of positive and negative charge. Nevertheless the idea that electricity, and also magnetism, heat and light were fluids, was one that would last until the late nineteenth century when electromagnetic radiation began to be understood. So when Joseph Priestley published his book 'The History And Present State Of Electricity' in 1767, he was stating the knowledge and beliefs of the majority of the scientific community of the time. However there was soon to be some major advances in the knowledge and use of this 'fluid'.

Bioelectricity

The eighteenth century physician Luigi Galvani was possibly the first to witness the phenomenon of a lifeless frog's leg twitching due to electricity. When Priestley's book was published Galvani was well on his way to becoming President of the Bologna Academy of Science, a post which he took in 1772. Like William Watson he too was a physician; Galvani's interests were anatomy and physiology, the sciences of the structure and the functions of living organisms. This became an enthusiasm for electrophysiology when he obtained an electrostatic generator and a Leyden jar, and his enthusiasm soon turned the subject into his primary area of study. A basic tool of anatomy is dissection, and frogs' legs were frequently used as subjects of examination. He is believed to have first observed the kicking of the lifeless frog leg in the late 1780s, the effect being seen both while his electrostatic machine was operating and also during thunderstorms. He went on to prove to his own satisfaction in further experiments that this movement was due to an electrical phenomenon. Galvani decided that a living frog must therefore produce its own electricity in order to move its muscles. He believed he had discovered a 'vital' force, which he named 'animal' electricity. According to Galvani this 'animal' electrical fluid was secreted by the brain and was conducted to the muscles by the nerves. He announced his results in 1791. He thought this was a third form of electricity, 'animal' electricity, to go with 'natural' electricity like lightning and 'artificial' electricity like static electricity. Although his belief in a 'vital force' was incorrect, as was the belief that electricity was some kind of fluidic element, Galvani was correct in his theory that nerve conduction is an electrical effect. In frogs, as in all animals, biological molecules and ions conduct nerve impulses throughout the body.

Metallic Electricity

Alessandro Volta, a physicist of the nearby northern Italian University of Pavia, was not so sure about Galvani's 'animal' electricity. Galvani himself had found that the dead frog's leg would also twitch when its spinal cord was simultaneously touched with a copper wire and an iron wire. Volta believed that the twitching might be a consequence of the electricity produced by the copper and iron metals and that the frog only responded to the electricity; it did not

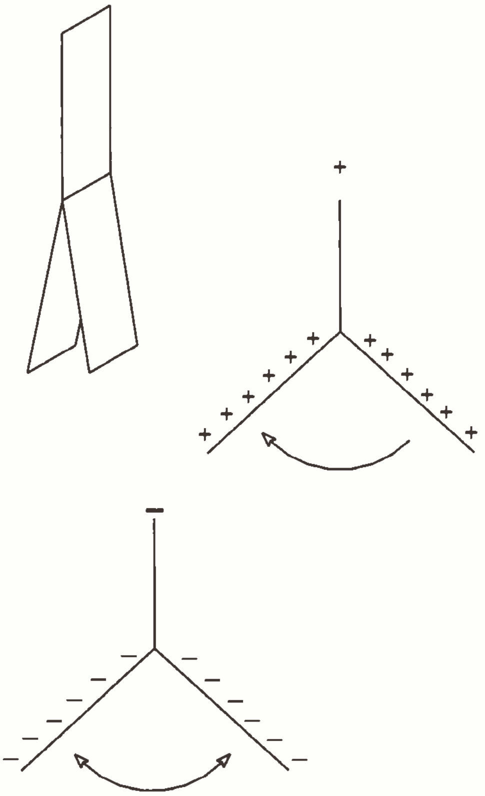

Figure 2.

The Electroscope

Two thin 'leaves' of gold foil are each attached by one end to a fixed conductor. If there is no charge on the conductor the gold leaves fall vertically. If either a positive or a negative charge is connected to the fixed contact both leaves will take the same charge and move apart (since like charges repel). This is a sensitive method of detecting charge but it does not differentiate between positive and negative types.

generate electricity. The frog's legs were merely acting like an electroscope, the device used to show the presence of charge. (See the box text on the electroscope.)

This he called 'metallic' electricity. As part of his investigations Volta had placed two coins of different metals, one on top of and one beneath his tongue. He noticed an unusual sensation or 'taste', not present when the coins were the same. He thought this might be a similar phenomenon to Galvani's 'animal' electricity, until in 1796 he found he could miraculously generate electricity without needing any 'animal' effects by using a piece of cardboard soaked in salty water instead of his tongue. Electricity could be generated simply with metals and salt water! Building on this simple cell (see Figure 3) he made the first battery, or voltaic pile, in 1800. This consisted of multiple layers of silver, moist cardboard and zinc, ie several cells in series.

This revolutionised the study of electricity because, although it produced a smaller voltage than the Leyden jar, it could provide a continuous current. The next year he demonstrated his battery to the Emperor Napoleon, who was so impressed he made him a count and a senator of the kingdom of Lombardy. Volta's battery was a source of power in more ways than one!

The Age of Electricity

The nineteenth century is often called the age of electricity, seeing an explosion of scientific knowledge directly made possible by Volta's invention. Literally within weeks of Volta announcing his source of 'metallic' electricity two English scientists, William Nicholson and Anthony Carlisle had used his battery to break down water into hydrogen and oxygen. Within a few years the battery had been used to isolate many more true elements from their compounds, elements such as sodium and potassium, calcium and magnesium. Two of the best known workers in this field were Humphrey Davy and his assistant at the time Michael Faraday. Davy was instrumental in work on the connection between electricity and chemistry, and in using electricity to establish new theories on the nature of materials and to correct many previously held misconceptions. Faraday's work led to his two laws of electrolysis, laws fundamental to battery operation, which relate quantities of substance, ie number of atoms or ions, to quantities of electricity and the charge on the ions involved. By the mid to late 1800s enough had been learned about elements and their properties for Dmitri Mendeleev to produce an early Periodic Table. The position of an element in the Periodic Table enables its properties to be predicted and so is an important starting point for the 'design' and engineering of materials with specific desired properties.

The Better Battery

Development of materials, then as now, was the key to improvements in the basic battery. Volta himself of course did not see most of the development; he died in 1827, long before he would be honoured by having the unit of electromotive force named after him in 1881. Out of Faraday's work on the relationship between power

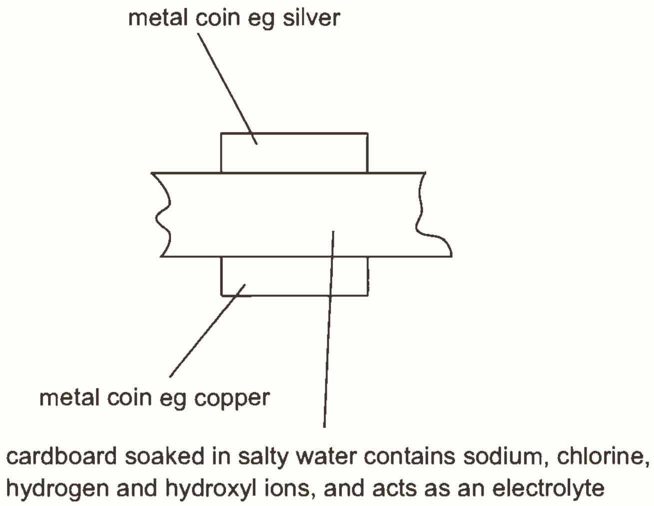

Figure 3.

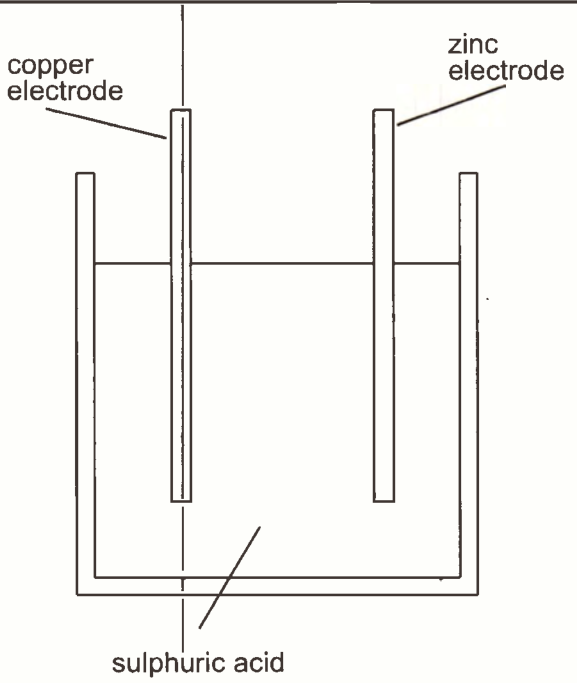

Figure 4. The Daniell Cell. With electrodes of zinc and copper, and sulphuric acid as the aqueous medium giving half cells of zinc/zinc sulphate and copper/copper sulphate, Daniell's cell could give larger continuous currents than Volta's cell.

and electrode material came the cell of the Briton John Frederic Daniell in 1836, followed by a two-fluid cell invented by Welshman William Robert Grove in 1839. Daniell's cell (see Figure 4) used copper and zinc in sulphuric acid, which gave a much improved performance over Volta's cell. Grove's cell (see Figure 5), which used zinc in sulphuric acid and platinum in nitric acid, the two being separated by a porous pot (which allowed electrical continuity), gave even further improvement in performance.

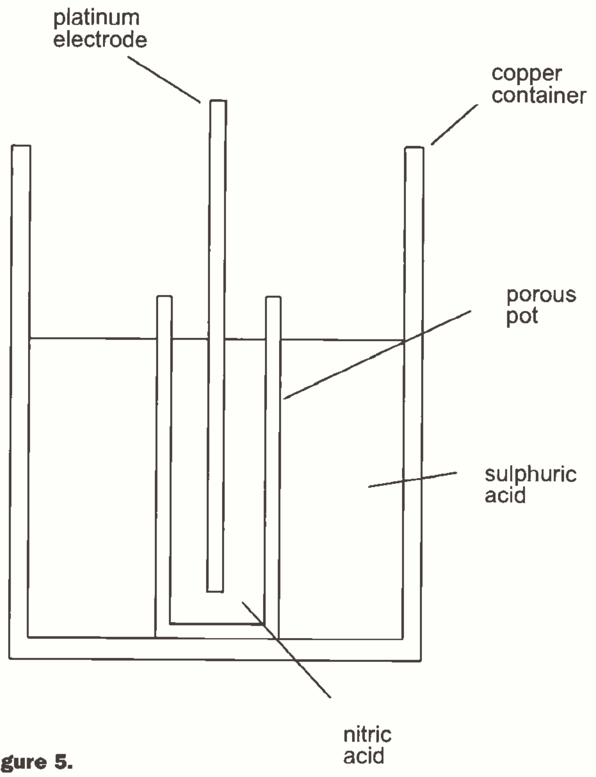

Figure 5.

The German Robert Wilhelm Bunsen made a commercial improvement on Grove's cell when he substituted cheap carbon for expensive platinum. The first lead-acid battery, produced in France in 1859 by Gaston Planté, gave a greatly increased energy capacity and power capability. This same type of battery is still in widespread use today in motor vehicles because of its cost-effectiveness, despite the disadvantage of its weight. Another significant point about this battery is of course that it was the first practical rechargeable battery.

The next major breakthrough was the cell developed by Georges Leclanché in 1866, the forerunner of the first 'dry' cell. This was the first cell to provide a practical solution to the problems of the need for strongly acidic fluids in batteries, which was a great limitation in terms of portability, safety and the size of the unit, and the outgassing of hydrogen, a safety and efficiency problem.

The Hydrogen Problem

The outgassing of hydrogen in the earlier cells was a consequence of the fact that in an aqueous solution the water molecules tend to dissociate into hydrogen and hydroxyl ions.

The hydrogen ion tends to attract electrons strongly, so electrons returning to the positive electrode combine with hydrogen ions. In doing so the hydrogen ions in solution are converted to hydrogen gas which is not soluble to any significant degree. The hydrogen gas accumulates on the electrode and causes loss of voltage. Using a half-cell consisting of a platinum electrode in a nitric acid solution was an attempt to solve this. Nitric acid is a strong oxidising agent, and oxidising agents strongly attract electrons. Electrons returning to the cell electrode are therefore in effect 'absorbed' by the nitric acid, in fact by the nitrogen atom in the nitric acid molecule which in the process changes its 'oxidation state'. This releases oxygen from the nitric acid, which 'oxidises' the hydrogen to water and so hydrogen gas is no longer released from solution.

The Dry Cell

In the Leclanché cell (see Figure 7) the copper negative electrode of early versions of the battery is replaced by a zinc can, and the sulphuric acid electrolyte is replaced by an aqueous paste of ammonium chloride, or an ammonium chloride/zinc chloride mixture. This paste is more easily contained and can be more concentrated than sulphuric acid. The solution to the hydrogen gas problem in this cell is dealt with by the use of manganese dioxide, an oxidising agent in solid form and the substance used in the majority of today's commercially successful batteries. The former platinum rod electrode and nitric acid oxidising agent are replaced by an electrode of powdered carbon (graphite) mixed with manganese dioxide. The electrode surrounds a carbon rod which 'collects' electrons.

The hydrogen released is safely oxidised by the manganese dioxide to water, and the ammonia produced as a by-product of the reactions in the cell dissolves in the paste.

This then is the zinc carbon (also called zinc manganese dioxide) standard battery. The zinc chloride battery is the same as this

The lead acid battery

The lead-acid battery has one lead plate and one plate coated in lead dioxide, both surrounded by sulphuric acid.

At the lead plate the lead reacts with sulphuric acid to give lead sulphate and two electrons, which do work in the battery circuit, and then return to the other plate. At this plate the lead dioxide reacts with the sulphuric acid and takes the two electrons to give lead sulphate and water.

As the battery discharges the sulphuric acid is effectively used up as electricity is generated.

The reactions are reversible however and by charging the battery the sulphuric acid is replenished and so the battery is ready to do more work.

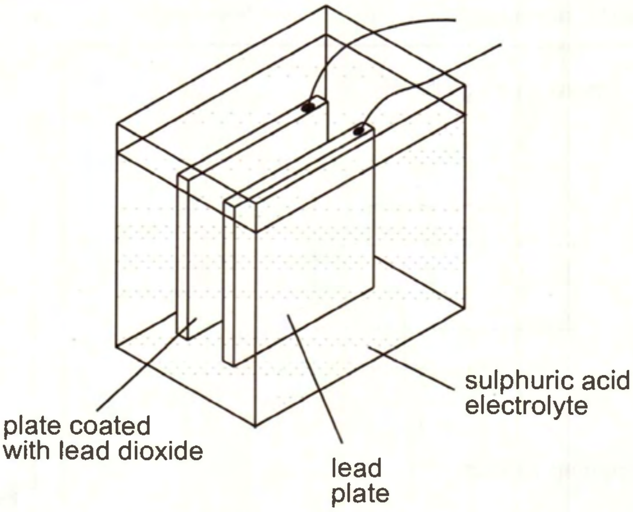

Figure 6.

but uses zinc chloride instead of the ammonium chloride or ammonium chloride/zinc chloride mix as electrolyte.

Alkaline batteries are so called because in this case the electrolyte is the alkaline substance potassium hydroxide. The positive electrode is the same carbon/manganese dioxide combination, but here the negative electrode is powdered zinc contained in a steel case; this gives a much more reactive surface area for yet more power. Hydrogen is oxidised to water as usual, which is readily absorbed by the potassium hydroxide.

Other batteries using alkali electrolyte and a zinc electrode but with different materials for the other electrode are the silver oxide and mercuric oxide types. The common factor in all these electrodes is that they are all metals that can have different 'oxidation states' and so accept electrons. (See the box text on oxidation states).

Further variations use sulphur compounds rather than oxygen compounds – sulphur is similar to oxygen in its chemical reactions as can be predicted from their relative positions in the Periodic Table. Using these different materials however is really 'fine tuning', even though there can be big performance improvements. Despite using varied and modified materials to give specifically engineered improvements the basic battery principle remains the same as in Volta's cell.

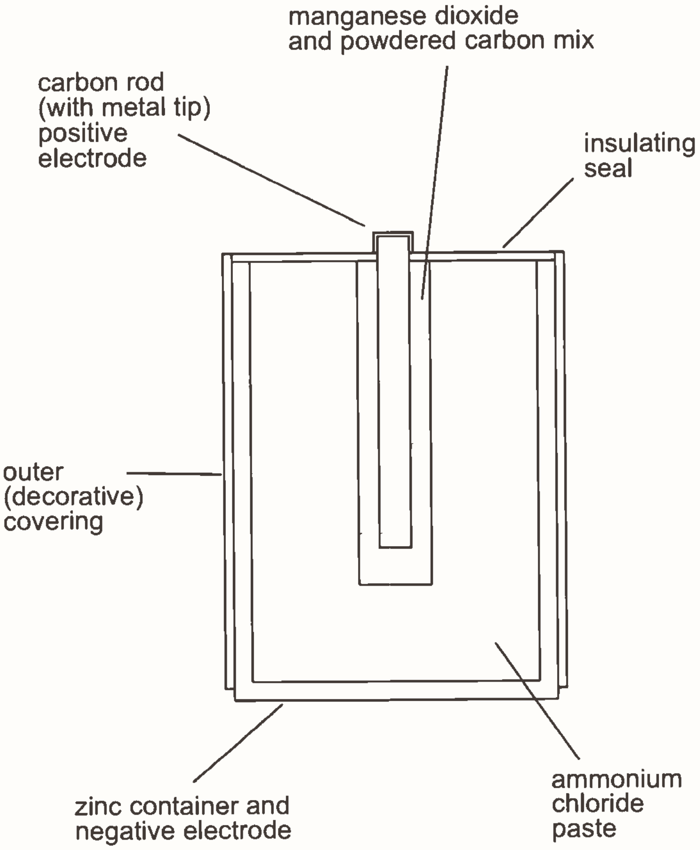

Figure 7.

Conclusion - The Even Better Battery

With contributions from scientists of many nationalities then, the development of the battery seems to have been one of the first dry cell, based on the Leclanché cell and the most successful battery since the 1880s, is the basis of all the general-purpose primary cells that have been used during the twentieth century. It has now been joined by a multitude of options, each with different qualities and so best suited to a different purpose. One major advance in development though is due to the progress being made with polymer (plastic) materials. Before long a completely plastic battery might be available in the local newsagent's shop!

Join us in Part 2 where we take a present day look at batteries.

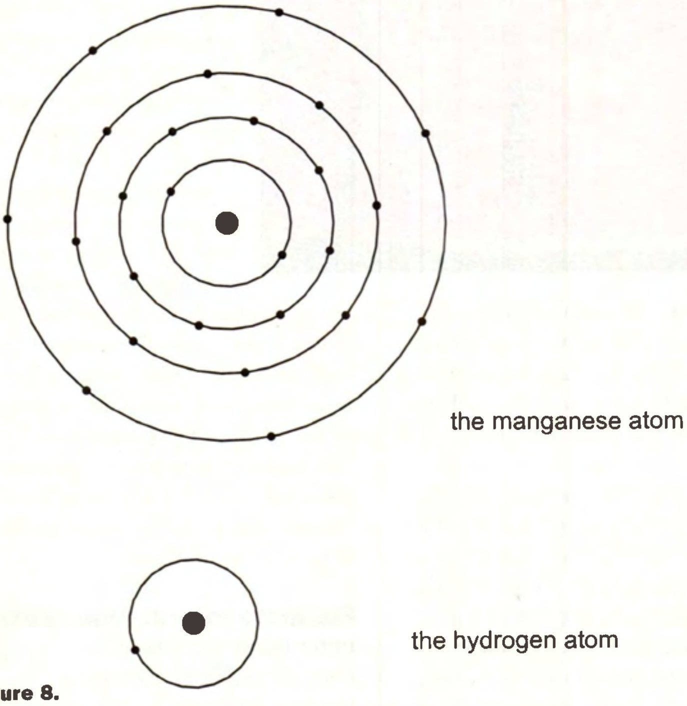

Figure 8.

Hydrogen and manganese atoms

The hydrogen atom has a nucleus with only one positive charge, and so has only one (negatively charged) electron in its normal atomic state. So in solution a hydrogen ion, which is the atom with the electron missing, only needs to gain one electron to become its normal gaseous form. Its oxidation state is said to have gone from one plus to zero.

Manganese however has a nucleus with twenty-five positive charges and so an atom of manganese has twenty-five electrons, seven of these being in the outer shell. In the form of solid manganese dioxide the manganese atom has lost four of the outer electrons and is said to have an oxidation state of four plus. Since the outer shell is not full it can gain another electron and thus be three missing from the full set of seven, and is then said to have an oxidation state of three plus. In this way the manganese, by taking an electron and changing its oxidation state, releases an oxygen atom from the metal oxide that then combines with hydrogen to give water and prevent the release of hydrogen gas.