

by PETER LANKSHEAR



# The ancestors of today's batteries

Radio technology has always been very dependent on batteries. The history of batteries goes back 200 years, twice that of radio itself. During this long period, some very interesting ways of producing an electric current have evolved.

There is a common belief that the first practical battery was invented by Georges Leclanche in 1868, but in fact Leclanche's battery was a relative latecomer in a long line of developments – some successful, some bizarre, others dangerous, but most now forgotten.

The history of the battery actually starts in 1790, when Luigi Galvani of Bologna was experimenting with muscles from frog's legs. The story goes that he hung them on copper hooks, suspended from an iron railing. When the legs touched the iron, their muscles twitched from the stimulus of the electric current produced by contact with the dissimilar metals.

Another Italian, Alessandro Volta investigated the phenomenon further and in 1793, created the first battery – his 'Crown of Cups'. A row of glass cells filled with salt water was fitted with alternating series-connected copper and zinc plates. He discovered that the degree of muscle stimulus was proportional to the number of cells.

In 1800 Volta produced his 'Pile', a much more compact arrangement. Paired discs of copper and zinc were alternated with cardboard discs moistened with acidulated water. Initially, like the crown of cups, the pile used containers of dilute acid as terminals. It is worth noting that physically Volta's pile was identical to today's standard layer-built 9.0 volt carbon-zinc batteries — a space saving method of construction introduced to radio batteries about 60 years ago.

## Polarisation problem

Volta's battery had made possible research into 'current electricity' (as opposed to 'static electricity'), but it had a major weakness. Under load, hydrogen bubbles built up on the copper electrode until the current was cut off.

Operation could be restored by either removing the bubbles physically or resting the battery, but these remedies were both inconvenient.

The 19th century was the age of individual rather than corporate research, and experimenters were soon at work improving on Volta's pile. Various electrolytes and electrode materials were tried. Zinc was found to be the most satisfactory negative electrode and its use was universal. As acids will attack commercial grade zinc, in some instances the negative electrode was removed when the battery was idle, or it was coated with mercury as this was found to minimise wastage. Positive electrodes could be made from copper, silver, platinum or carbon and did not deteriorate.

One of the earliest developments was Wollaston's battery, an adaptation of the Crown of Cups using jars filled with dilute sulphuric acid. The electrodes were made as large as possible to lower the internal resistance and delay the onset of polarisation, and were mounted on a frame, so that they could be lifted out of the electrolyte when not in use.

Mechanical depolarisation was impractical, and experimenters concentrated on chemical methods which worked by persuading the hydrogen to combine with oxygen. This entailed surrounding the positive electrode with an oxidising material that reacted with hydrogen — but not at the expense of the normal operation of the electrolyte.

The first method was to use a liquid oxidiser with a porous container separating it from the acid electrolyte. In one popular variation, the bichromate cell, the electrolyte and depolariser were mixed together. A very important type used gravity to separate the liquids. Later, solid depolarisers surround-

ing the positive electrode were employed, as in the Leclanche and Edison cells.

#### Grove's cell

In 1839, Sir William Grove introduced a cell that performed excellently, but was expensive and produced a poisonous gas. Grove's cell consisted of a glass jar containing dilute sulphuric acid and a semicircular amalgamated zinc electrode, surrounding a porous earthenware pot. Inside the pot was a sheet platinum positive electrode and nitric acid. Hydrogen from the zinc and sulphuric acid reaction migrated through the walls of the porous pot to be oxidised by the nitric acid, producing water and nitric oxide fumes.

Platinum is not exactly cheap, and the German chemist Bunsen substituted a carbon positive electrode. Both the Grove and Bunsen cells were rated at 1.93 volts and the internal resistance of the 'quart' size (about 1 litre) was only 0.15 ohms, comparable to a small lead acid accumulator. These cells had ideal characteristics for experiments and were used well into the 20th century for laboratories and class room demonstrations.

Edison used a Bunsen battery in his development of the electric lamp. However, nitric acid is a dangerous material, and nitric oxide fumes require ventilating. Furthermore, when finished with, the cells had to be dismantled, the nitric acid and any free mercury bottled, and the electrodes and pots washed!

The Fuller cell substituted a mixture of sulphuric and chromic acids for the nitric acid of the Bunsen cell, to produce a more docile but still very useful source of current. It had the further advantage that it did not require dismantling.

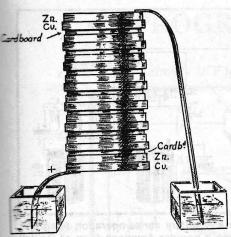


Fig.1: Volta's 'Pile', first made in 1800. Zinc/copper pairs of discs were alternated with cardboard discs moistened with dilute acid.

#### **Bichromate cell**

It was found that Fuller's cell could be simplified by eliminating the porous pot and separate sulphuric acid solution. By immersing carbon and zinc electrodes directly in a mixture of dilute sulphuric acid and either chromic acid or potassium bichromate, results were comparable to those from a Bunsen cell. The only precaution to be observed

Fig.2: Bunsen's was a powerful but noxious cell. The carbon electrode inside the central unglazed earthenware pot was surrounded by strong nitric acid.

was that the zinc electrode had to be removed from the liquid 'electrolyte' when the cell was not in use.

Known generally as the *Bichromate* battery, in its original form each cell consisted of a shapely flask with a long wide neck supporting the electrodes. A rod enabled the position of the zinc to be adjusted to give some degree of current control, or for its complete removal from the electrolyte.

The Bichromate battery was used in early radio experiments. Producing about 2 volts per cell, and capable of supplying several amps, it was an inexpensive and reliable source of power for spark coils used for transmission. Other applications were for powering small electric motors and electroplating.

Apart from its aesthetic appeal, there was no particular merit in the fancy bottle and satisfactory home made versions were more mundane. Harmsworth's 1923 Radio Encyclopedia gives detailed instructions for making a three-cell Bichromate battery in jam jars.

The electrolyte in a freshly charged cell was a most attractive orange colour, and I well remember as a youth making a Bichromate cell to provide the 2-volt filament power for a radio. It was most successful until an accident tipped the electrolyte down the wall. Somehow the orange-stained wallpaper was not so appealing to my parents!

#### Daniell's cell

We now go back to 1836 and Professor Daniell of King's College, London. In that year he invented the principle of electroplating — and, at the same time, what was to be commercially the most important primary battery of all, until the close of the 19th century.

Daniell's was unique among the 19th century cells in that the chemical makeup of the electrolytes did not change during operation, and provided that the consumables were replaced and liquid volumes adjusted, output was maintained indefinitely. Furthermore, as no free hydrogen was involved in the reaction, it never polarised. It also used inexpensive materials. Why then, if this was such a paragon of cells, were other types bothered with?

Nothing is perfect, and the Daniell cell had limitations. Even in large sizes it had a high internal resistance, something like 50 times that of a bichromate cell of the same size, severely limiting its current capability. The voltage was only a fraction over 1.0 volt and if it was not kept working, the electrolytes would diffuse. However, as we shall

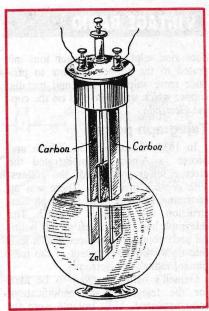


Fig.3: Grenet's Flask or Bottle Bichromate Cell. When idle, the zinc was withdrawn from the solution by means of the rod.

see, in its chief application, these were not significant problems.

In its original form, Daniell's cell consisted of a copper jar that was also the positive electrode, containing a saturated solution of copper sulphate – the 'bluestone' used in garden sprays. Inside a porous central container was the zinc negative electrode and a dilute sulphuric acid, zinc sulphate or magnesium sulphate solution. During operation, this solution reacted with the zinc to pro-

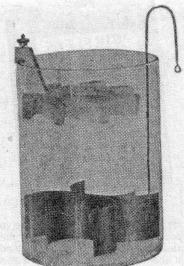


Fig.4: The shape of the zinc upper electrode suggested the name of the 'Crowfoot' Daniell gravity cell. It used saturated solutions of copper sulphate and zinc sulphate of different specific gravities.

### **VINTAGE RADIO**

duce zinc sulphate. Hydrogen ions migrated to the copper sulphate to produce more sulphuric acid and metallic copper which was deposited on the copper electrode.

#### Telegraph power

In 1838, Wheatstone in Britain and Morse in America demonstrated the electric telegraph, one of the greatest 19th century inventions. There was an enormous investment in telegraph construction, with revenues to match. The telegraph had tremendous social, political and economic influences, and it lead directly to the development of the telephone, radio and electronics.

Daniell's battery proved to be ideal for the telegraph, and modifications soon appeared. Most notable were the 'gravity' batteries. A solution of zinc sulphate will float on a copper sulphate solution. By putting the copper electrode and copper sulphate at the bottom of the jar, and suspending the zinc from the top, it was possible to eliminate the porous pot. The best known version was the *crowfoot*, named from the shape of the zinc electrode.

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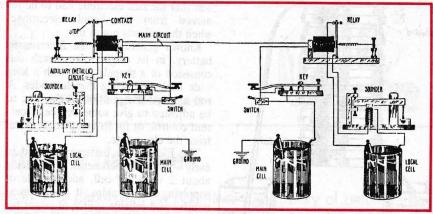


Fig.5: This 19th century sketch of an elementary series-operation telegraph illustrates that the Crowfoot Gravity was a popular American form of Daniell battery. In practice the local cells would have been the larger.

Unlike many other types, it was possible to tell at a glance the condition of a Daniell gravity battery and it could be maintained during operation. This entailed adding copper sulphate crystals, drawing off excess zinc sulphate solution and topping up with water — and from time to time, renewing the zinc electrodes.

By 1875, there was a worldwide network of electric telegraphs. The total number of cells powering them must have been astronomic. Some interesting statistics about one circuit come from Frank Clune's most readable book Overland Telegraph, describing the epic South Australian enterprise connecting Port Augusta with Darwin, the Australian terminal of the undersea cable to Asia and Europe.

Completed in 1872, the 1800 miles of 8-gauge iron wire was split into 11 sections with 10 intermediate stations, all connected in series. Each station had 120 'Meidinger' gravity Daniell line cells. Including terminals, there would have been 1,440 line cells producing a total of 1.5kV, and several dozen larger local instrument cells.

Daniell's batteries were not very suitable for domestic radios. Apart from the need for a continuous load, there was the problem of their size. Even the 'small' line cells had a good half gallon capacity! One unlikely domestic use was found in accumulator charging. Three Daniell cells could effectively 'float charge' a lead-acid cell used for intermittent lighting service.

#### Edison's battery

The last major development in 19th century primary batteries came from Thomas Edison, whose 'Improved Phonograph' of 1888 used an electric motor. Something more docile than

Bunsen or bichromate cells were necessary for Victorian living rooms. Like Edison's better known secondary battery, it used a caustic potash solution for an electrolyte.

With an EMF of 0.75 volt per cell, Edison's battery used a depolariser of copper oxide. It was a low maintenance, low internal resistance battery with a high ampere-hour rating. A cell 175mm (7") in diameter and 450mm (18") high had a rating of 600Ah. The Edison was primarily an industrial battery used for telephone exchanges, fire alarms and railway signalling — applications now left to secondary batteries.

#### Leclanche at last

Finally, we come to the Leclanche battery, described by Peter Phillips in the March 1990 issue of *Electronics Australia*.

Compared with many of its contemporaries, Leclanche's cell was an indifferent performer. It had neither the staying power of the Daniell nor the 'grunt' of the Bunsen and Bichromate types, and its voltage sagged long before it was worn out — a problem that persists with its modern descendant, today's common dry cell.

The Leclanche's success resulted from its compact size, low cost, minimal maintenance requirements, suitability for intermittent service and — especially—the fact that there was no local action when it was 'resting'. Most importantly, there were no dangerous acids. It was very suitable for domestic service such as bells and telephones.

But the real merit of the Leclanche cell was that it was the parent of the zinc-carbon dry cell, without which portable battery power and the development of radio would have been very different.