

History

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20.1 EARLY BEGINNINGS

In Chapter 4 of the first English edition of the book *Portable Batteries* by K. Eberts you can read:

Our present knowledge of battery techniques traces back to times of four and a half thousand years ago. We can be sure that the copper vessels that were found from this time could only have been plated with gold by electrochemical means.

In 1936 there was an archeological sensation. Near to the present Baghdad in a Parther settlement that had flourished about from 250 B.C. to 225 A.D. an electrical element was found. A copper tube was placed in a clay vessel filled with an organic acid into which an iron rod insulated by asphalt was inserted. The element produced 5 volts and surely was not a battery of our understanding, but must be accepted as a base for this technology. It might have served galvanic purposes. [See [Figure 20.1](#).] For about 2000 years until 1799 the knowledge of these ancient cultures was obviously forgotten, as Volta based his research on more recent knowledge, on Galvanis' frog leg experiment. With his work the scientific side of our branch was introduced.

20.2 PRIMARY AND SECONDARY CELLS

The inventor of the first usable primary battery is with full right George Leclanché, whose 1868 invention used amalgamated zinc as negative electrode and a mixture of manganese dioxide and coal as positive electrode with a current collector of coal and as electrolyte a solution of ammonium chloride.

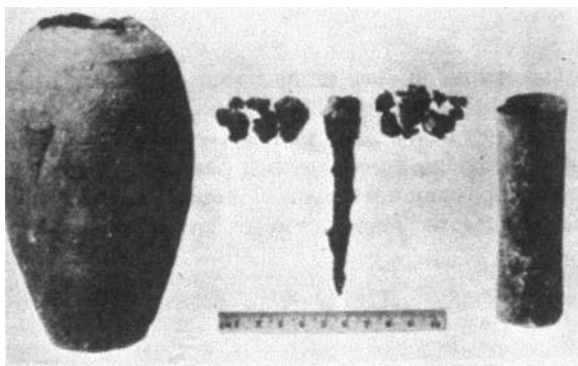


Figure 20.1 Prehistoric finds of the galvanic element from Khujut Rabuah close to Baghdad.

After Alessandro Volta (1800) presented the so-called Volta cell, practicable applications were wanted. First example of use of the Volta cell was the electrical telegraph invented by Sömmering in 1810. Here the voltage of the Volta cell was served for the transmission of letters of the alphabet through a four-line cable from one place to another. The hydrogen development observed on the positive electrode limited extremely the application. So scientists tried to eliminate the polarization originated by hydrogen with chemicals, e.g. with oxidizing agents.

One of the most popular cells in the beginning of the 19th century was the so-called *Grove* element with nitric acid as electrolyte. Bunsen improved the *Grove* element by introducing a carbon rod instead of a platinum rod (1841).

Many other elements and results of research could be named here, but many theories about the use of primary cells from that early time have been lost. Gassing elements, filled with fluid electrolytes with electrodes to be replaced after use offered no possibility for a wide application. By this we come back to the Leclanché cell, the first element that was made technically applicable. The first Leclanché cells were filled with a fluid electrolyte, so these cells could not be moved by transportation or used in just any position. Not before the end of the 19th century the Leclanché system was so far improved by using a zinc cup instead of a glass cup, i.e. the negative electrode was used as cell container.

The rise of production started with 20,000 Leclanché cells in 1868 to some million in 1918 to nowadays some thousand millions. In the course of time many steps of improvement could be watched. It was a long way from the soldered zinc cup to a dragged zinc cup, or from ground coal to graphite and later to soot, or from a clay cylinder to paper. Of extreme importance was the so-called immobilization of the electrolyte using a paste of ammonium chloride, zinc oxide, and gypsum, mixed with starch and flour. These so-called “pasted cells” dominated for decades the market for primary cells, especially for flashlights. Who later invented or improved the Leclanché system is difficult to describe and would need many pages; its development can be read in publications and patents or books on the history of electrochemistry. In many publications Gassner is called the inventor of the first “dry cell”. In his patent specification, published in 1887 (Deutsches Reichspatent 45,250),

he described a paste consisting of a solution of ammonium chloride mixed with zinc oxide and gypsum. This created the first dry cell, or pasted cell.

Until some years ago in dry cells amalgamated zinc was used, an effect already in 1870 described by Sturgeson was the elimination of the passivation. Today the same effect can be reached without using mercury, but by the choice of extremely pure materials. That manganese dioxide is not purely manganese dioxide has been known for a long time. Since the beginning of the last century in many research centers of the world intensive work was done to understand the chemical attributes of the different qualities of manganese dioxide. The aim was to produce cells with higher electrical performance and with a lower self-discharge rate. A great success in 1940 was the start of producing manganese dioxide by electrolysis.

Further remarkable steps in the development of the Leclanché cells was the introduction of the so called “paper-lined” construction in 1950, followed in 1962 by the so-called “segment cell” for high loads. The steel sheet-protected cell was invented in 1940 (still today known as the “leak-proof” type), but was not introduced into the market before 1957. In the 1960s Huber in the German Pertrix manufacturing lines introduced the zinc-chloride technique. This was a great step toward extreme high-leakage-proof manganese dioxide cells.

Until now the Leclanché cell has had a great share of the market, efficiently completed by the “alkaline manganese dioxide cell” introduced in 1945. The alkaline cells could be established on the market not earlier than 1960. The difference between both principles of construction are shown in [Figure 20.2](#). The secret of the high performance of the alkaline cell is the fine zinc powder (which was originally amalgamated) as active material. The large surface area of the powder allows higher

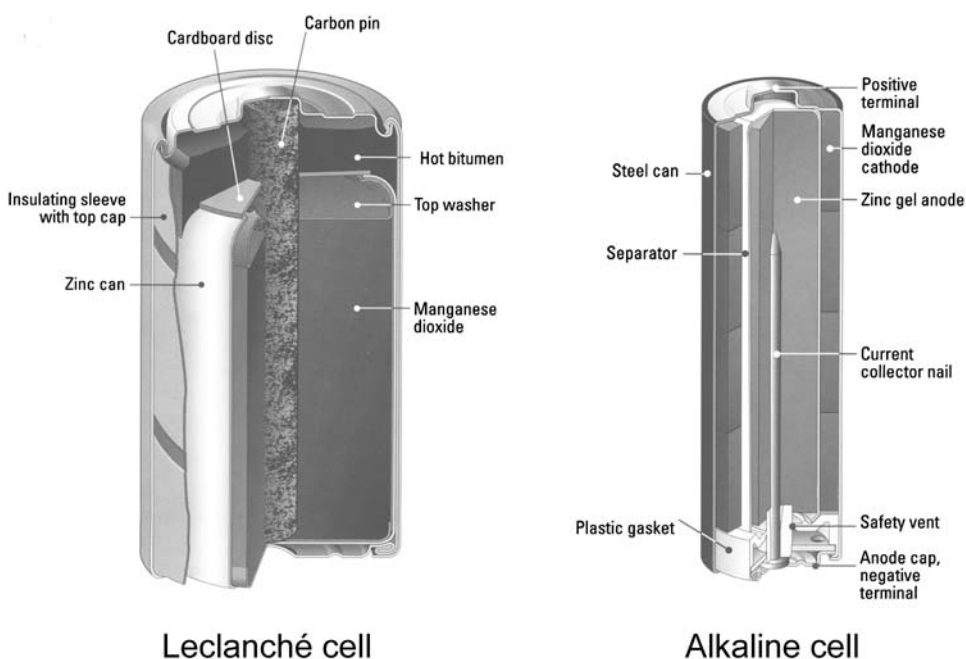


Figure 20.2 Construction of the Leclanché cell and the alkaline cell.

current densities, an absolute necessity for the newer portable and cordless electric devices with high current demand, e.g. recorders, cameras, etc.

From year to year improvements were made, either in the sealing and compound technology, in the use of better plastic materials, or by better exploitation of the active materials. Last but not least it has to be mentioned that today alkaline cells are free of mercury, a result of effective but expensive research and development. A pollution problem has been solved (see Chapter 19, Sec. 19.1.2.7).

Besides the family of manganese dioxide cells with zinc as negative electrode during the last decades manifold other battery systems have been developed and produced for the market. More capacity and higher load ability were the motivation for research. Here can be named the mercury zinc cell, produced in millions of button cells each year for hearing aids, calculators, watches, cameras, etc. Never was it possible to create one “universal cell” doing the job for all kinds of applications. Always it has to be noticed that primary cells are specialists, exactly designed for a special application. So in 1980 the smallest button cell of the world was made by Varta with a diameter of 6.8 mm and a thickness of 0.7 mm for wristwatches.

Very early in the beginning of the 19th century the polarization effect of air on the positive electrode was known. So Grove described a first, so-called “gas battery” by giving the fundamentals for today’s well-known zinc-air cells in button cell design, e.g. for hearing aids and many other applications. Bigger sizes are in use for the illumination of roadwork or for electric fences around cattle pastures. The high energy output of zinc-air cells is given by the principle of the “reaction electrode” using oxygen from the air coming into the cell through small holes in the cell surface, while oxidizing substances as active material are not needed, giving space for more zinc in the counter-electrode.

Research and development teams tested in the last century nearly all theoretically possible combinations of electrodes and electrolytes. The scientists were highly interested on lithium as a light metal for use as the negative electrode. From the beginning of their research the scientists knew about the difficulties in processing the non-precious lithium, despite of its high availability; lithium reacts with humid air, especially with water very intensively. The melting point is low, 180 °C.

For laymen the area of lithium cells is difficult to overlook. Consider that since 1960 more than 100 systems have been patented, but only few could establish a market share. Advantages of the lithium cells are the high voltage (1.7 to 3.6 V) and the very high energy density, a multitude of the so-called “classic” systems described above. Lithium cells furthermore can be used in a wider temperature range and the self-discharge rate p.a. is, at less than 1%, extremely low. (For more about lithium systems, see Chapter 16, Sec. 16.2.2.12, and Chapter 18.)

Since the beginning of primary cells it was tried again and again to make secondary cells from primary cells. By definition secondary cells are such cells which firstly have to be charged before electrical energy can be discharged. This is contrary to primary cells, which can be discharged immediately when they have left the production lines. Thanks to the research efforts on alkaline cells by Kordesch, who was responsible for remarkable progress; nevertheless the alkaline cells are no genuine secondary cells, because after a few discharge/charge cycles (10 to 20) a maximum 50% of the original capacity is available. Therefore the cost/performance ratio is poor for the user. (Some consumer associations defined them as expensive

nonsense.) The risk that some users think that now all primary cells are rechargeable may not be ignored; therefore safety standards do not allow the charge of primary cells as such, except where the manufacturer declares its cells as secondary cells.

But the problem can be solved, as has been shown by the development groups of rechargeable lithium-ion batteries. Nickel/metal hydride cells (having 50% more capacity and no cadmium content) had just started to penetrate the market to the debit of nickel/cadmium cells, and are being pushed away now by rechargeable lithium-ion batteries. Main applications are cellular phones, mobile phones, and video cameras. It cannot yet be foreseen whether nickel/cadmium will disappear from the market, because they cannot be substituted for in the use in tools. Never in the past has a new battery system eliminated an established system totally.

Development on primary cells shows no standstill, because new applications with new demands require adoption of the existing “battery specialist”.

Rechargeable elements trace back to Johann Wilhelm Ritter, while the invention of the lead-acid battery is attached to such famous names as Gaston Planté, Camille Faure, Henry Tudor, and Volkmar. The industrial production began over 100 years ago and it demonstrates the difficulty implemented in electrochemical elements that even today sometimes the behavior of a battery can’t be foreseen or explained totally. On the field of maintenance-free lead-acid batteries Otto Jache made a break-through in 1957 after extensive preparatory work by many others.

Rechargeable secondary alkaline cells are connected with two famous names: Thomas A. Edison and Valdemar Jungner. While Edison was the inventor of the nickeliron battery, Jungner tried to improve the secondary alkaline battery by using cadmium for the negative electrode. The different constructions are described in detail in Chapter 1, Sec. 1.8.2, and Chapter 7, Sec. 7.3.

In the field of well-established rechargeable systems, lead-acid and nickel/cadmium for traction and stationary use, much progress was made. Higher performance, longer service life, less maintenance, and lower cost may be listed here. Let us wait and see what in the future can be realized; the only limit is Faraday’s law.

20.3 FUEL CELLS AND HIGH TEMPERATURE CELLS

New Developments and state-of-the-art technologies are described in detail in Chapter 10, secs. 10.2, 10.3, 10.4, and 10.6.

REFERENCES

1. G Leclanché. French patent 71,865, 1866.
2. Gassner. Deutsches Reichspatent 45,250.
3. RH Schallenberg. Bottled Energy: Electrical Engineering and the Evolution of Chemical Energy Storage. Philadelphia: American Philosophical Society, Volume 148, 1982.
4. AJ Salkind, ed., Proceedings of the Symposium on History of Battery Technology. The Electrochemical Society Proceedings, Vol. 87-14, 1987.
5. KJ Euler. Geschichte der Elektrotechnik: Sinsteden—Planté—Tudor (Zur Geschichte des Bleiakкумуляtors). VDE-Verlag, 1982.
6. D Berndt. Die Geschichte des Akkumulators. Varta.
7. K Jäger, ed. Geschichte der Elektrotechnik 13. Gespeicherte Energie, VDE-Verlag, 1994.