Oesper Museum Booklets on
the History of Chemical Apparatus

No. 8

CLASSIC
VOLTAIC CELLS

William B. Jensen
University of Cincinnati

Photography by Jay Yocis

Oesper Collections
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SERIES INTRODUCTION

Like most museums, only about 25% of the holdings of the Oesper Collections in the History of Chemistry are on public display at a given time. In order to make the remaining 75% available in some form, it was decided to initiate a series of short museum booklets, each dedicated to a particular instrument or laboratory technique of historical importance to the science of chemistry. Each booklet would include not only photographs of both displayed and stored museum artifacts related to the subject at hand, but also a short discussion of the history of the instrument or technique and of its impact on the development of chemistry as a whole. Several of these booklets are expansions of short articles which have previously appeared in either the bimonthly series *Museum Notes*, which is posted on the Oesper website, or the series *Ask the Historian*, which appeared in the *Journal of Chemical Education* between 2003 and 2012.

William B. Jensen
Cincinnati, OH
April 2014

Some Preliminary Definitions

A voltaic or galvanic *cell* is a device for the conversion of chemical energy into electrical energy.[1] It generally consists of two solid *electrodes* (called the *cathode* and *anode*) in contact with a suitable ionically conducting liquid or *electrolyte*. In single-fluid cells the two electrodes share a common electrolyte, whereas in two-fluid cells each electrode has its own chemically distinct electrolyte and these are separated from one another by means of a suitable membrane or porous spacer in order to minimize their rate of mutual mixing.

Two or more cells wired in series are technically known as a *battery*. This use of the word battery to describe a collection or array of objects actually has broader application in everyday life. Thus, for example, a collection of cannons is also called a battery. Unhappily, in everyday usage the terms cell and battery have become hopelessly confused. Thus the size D, AA, and AAA cells used in such everyday devices as flashlights, portable radios, and TV remotes are often incorrectly called batteries, when in fact they are single cells. On the other hand, the larger rectangular 9 V snap cells actually contain six smaller 1.5 V disk cells wired in series and are therefore technically true batteries.

A second pertinent distinction is the difference between a primary voltaic cell and a secondary voltaic cell. A primary cell is irreversible. Once it has consumed its chemical “fuel” and “burned out,” it cannot be recharged and must be disposed of. In contrast, a secondary cell is reversible. Once it depletes its chemical fuel, it can be reversed or recharged again by pumping electricity into the cell so as to once more regenerate the initial starting chemicals. Thus, in a sense, it acts as a storage tank for electrical energy that can be repeatedly refilled when empty. For this reason such cells, when connected in series, are also called “storage batteries.” However, the recharging is never perfect and becomes less so with repeated rechargings until eventually these cells also burn out.

Before the Voltaic Cell

As we will shortly see, the voltaic cell is a child of the 19th century. As a result, the 18th-century chemist lacked a source of constant DC electrical energy and had to make do instead with various devices for the generation and storage static electrical charges. These included a variety of hand-cranked electrostatic machines or generators[2] (figure 1) and the so-called Leyden jar (figure 2) – a sort of macro-capacitor that allowed for the storage and transfer of static electrical charge. In the chemical laboratory, this latter device was used primarily in gas eudiometry to spark gas mixtures and especially those of hydrogen and oxygen.

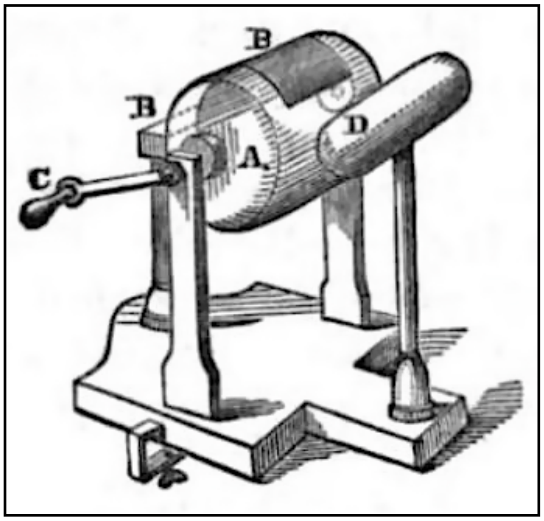


Figure 1. A typical early 19th-century electrostatic generator. A is a glass cylinder, B is a piece of silk attached to frame B, C is the handle to spin the glass cylinder, thus rubbing it continuously against the silk. D is a metallic cylinder to collect the resulting static charge by induction.

Though studied by a number of 18th-century chemists, the chemical effects of static electricity proved to be rather limited and often difficult to interpret. Thus in the 1770s both Priestley and Cavendish had noted the production of nitrogen oxides when sparks were discharged in air, and there were some preliminary investigations of the effects of electrical sparking on various chemicals by the Dutch scientist, Martin van Marum, in the 1780s. The most important result, however, was the successful electrostatic decomposition of water in 1789 by Adrien Paets van Troostwijk and J. R. Deimann.

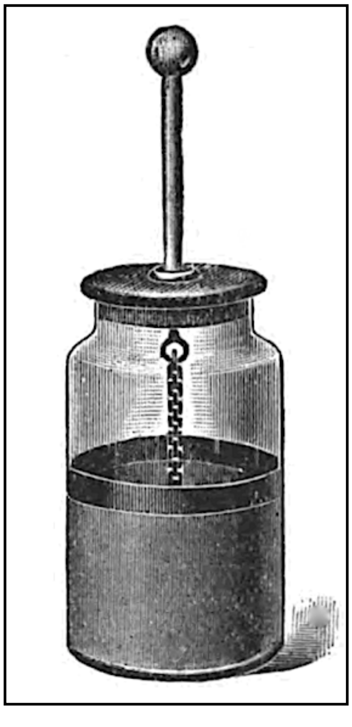


Figure 2. A typical 19th-century Leyden jar.

Unfortunately, while it is possible to generate high-voltage static charges, the actual quantity of charge involved is quite small and since, as Faraday's laws tells us, the amount of electrochemical change depends on this quantity rather than the voltage, the observed chemical effects are also quite small. In addition, the current during a spark discharge alternates, so that in the decomposition of water, for example, one obtains a mixture of oxygen and hydrogen rather than the spatially isolated gases obtained using direct current. Thus George Pearson, on repeating the electrostatic decomposition of water in 1799, found that he required 14,600 charging cycles of his Leyden jar in order to generate only 0.33 cubic inches of gas.

All of this would radically change with the accidental observation in 1791 by the Italian physician Luigi Galvani (figure 3) that, when two dissimilar metal strips were touched to the nerves of a severed frog's leg and to each other, the muscles of the leg would violently contract (figure 4).[3] The contractions of muscles when exposed to the static discharge of an electrostatic machine or a Leyden jar were well known before Galvani. Rather it was his discovery that the same phenomenon would occur in the absence of such devices, provided that the two dissimilar metal strips were used instead, that would prove deci-

Figure 3. Luigi Galvani
(1737-1798)

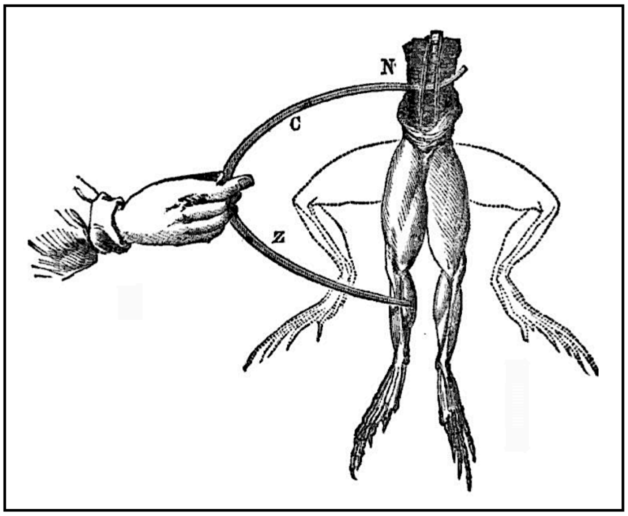


Figure 4. A 19th-century demonstration of Galvani's discovery using a strip of copper (c) and zinc (z) metal.

sive for the future of electrochemistry.

Enter the Voltaic Pile

There were two possible rationales for Galvani's discovery. Either the touching of the two metal strips in contact with the bodily fluids of the dead frog generated an electrical stimulus which caused the muscles of the frog legs to contract or else they functioned as conductors for a previously unknown form of "animal electricity" present in the nerves of both living and recently deceased animals.

Figure 5. Alessandro Volta (1745-1827)

Galvani chose the latter of these interpretations, whereas the Italian physicist, Alessandro Volta (figure 5), after reading of Galvani's discovery, chose the former. To prove his point that the resulting electrical phenomena were due to physical contact between dissimilar metals and had nothing to do with so-called animal electricity, Volta constructed a pile (figure 6) consisting of alternating zinc and copper disks, each copper/zinc pair being separated from the next by a piece of pasteboard soaked in salt solution. If a sufficient number of these bimetallic cells (20 or more) were used and the topmost zinc disk and the bottommost copper disk were connected to wires, the wires would give a spark on being brought near another, as

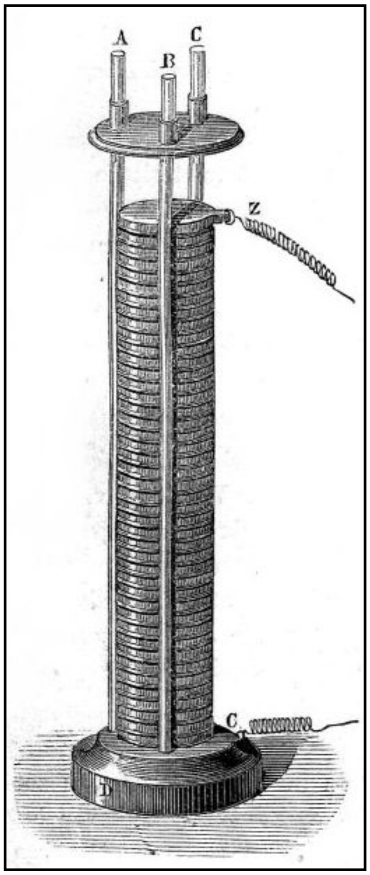


Figure 6. A typical early 19th-century voltaic pile.

well as a perceptible electric shock to any one bold enough to grab both wires simultaneously.

This device, now known as a *voltaic pile* in honor of its inventor, was first revealed to the scientific community in a famous letter to Sir Joseph Banks published in the *Philosophical Transactions of Royal Society* for 1800.[4, 5] Since the voltaic pile had nothing to do with living or dead organisms, Volta felt that he had conclusively proved his theory that contact between dissimilar metals was the source of the electric current and that the bodily fluids of the dead frog had merely acted as a conductor and the muscles as a detector of the resulting electrical current. However, Galvani remained unconvinced and for several years a debate over the nature of current electricity raged between the supporters of animal electricity, on the one hand, and the supporters of Volta's metallic contact theory, on the other.[6]

Ironically, with the passage of time, Volta's contact theory would in turn be attacked by chemists and physicists who claimed that the electrical current in a voltaic cell was the result of chemical reactions rather than simple metallic contact.[7] As events turned out, *contact potentials* or *volta potentials* really do exist and they were in fact eventually quantified as the century progressed.[8, 9] However, as we now know, they cannot possibly be the source of the continuous direct current provided by a voltaic cell without violating the law of conservation of energy. Though the proponents of the chemical theory of the voltaic cell were ultimately proven correct, I have never seen, in all of the historical and textbook accounts of the voltaic pile I have read, any indication of what specific chemical reactions are actually responsible for the pile's EMF and electrical current.

The source of the problem can most easily be seen by examining an alternative, but equivalent, arrangement of the pile's components also proposed by Volta and known as the *crown of cups*. As may be seen from figure 7, this consisted of a series of cups or glasses (up to 60) each filled with salt water and containing a strip of zinc and a strip of copper, that were connected together in series to form a multi-cell battery. Thus each cell of both the voltaic pile and the crown of cups is seen to consist of the arrangement Cu(s)/NaCl(aq)/Zn(s). Yet, based on this de-

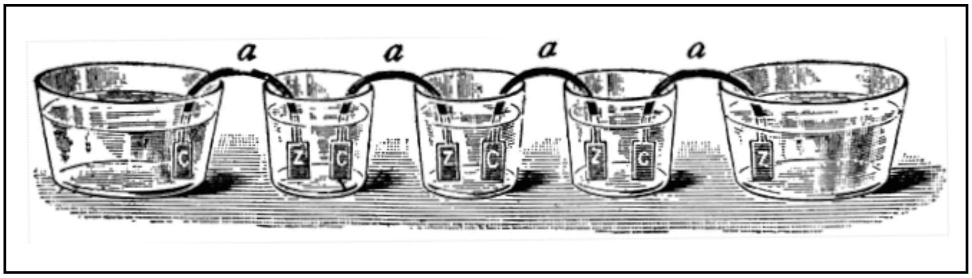


Figure 7. A later 19th-century depiction of Volta's "crown of cups" alternative to the voltaic pile, where *z* indicated zinc and *c* indicates copper.

scription, it is impossible to imagine an electron-transfer or redox reaction that could account for the source of the pile's electrical activity, even though it can easily be shown that such a cell gives a net EMF reading of 0.756 V.[10] Indeed, the only plausible rationale I have come across is that such a cell is actually a crude zinc-air cell based on the net cell reaction:

$$2Zn(s) + 2H_2O(l) + O_2(g) \rightarrow 2Zn(OH)_2(s)$$

in which O(0) is reduced to O(-II) at the Cu cathode:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH(aq)^-$$

and Zn(0) is oxidized to Zn(II) at the anode:

$$Zn(s) \rightarrow Zn(aq)^{2+} + 2e^-$$

Since Volta was unaware of this chemistry, his cell was not optimally designed to exploit it and indeed often had a workable lifetime of only two days or less. In modern zinc-air batteries the electrolyte is an aqueous solution or paste of sodium hydroxide, rather than salt, since this results in the formation of water soluble $Na_2[Zn(OH)_4]$ rather than insoluble $Zn(OH)_2$ and also gives a higher EMF for the cell. This would also explain Volta's passing observation that using soap "ley and other alkaline liquors" in place of salt improved the performance of the pile.

The Daniel Cell

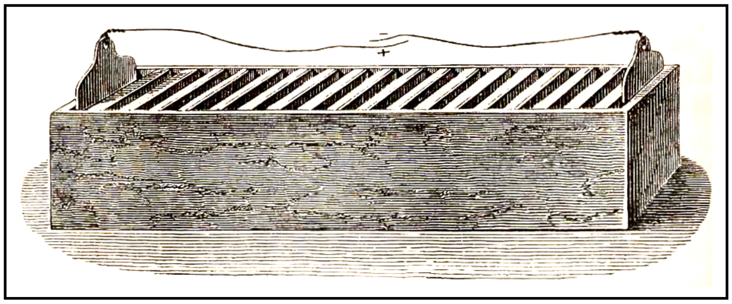


Figure 8. A typical early 19th-century trough battery with alternating plates of zinc and copper in a common electrolyte. The inside of the wood box or trough was painted with resin or tar to waterproof it.

The original voltaic pile was both awkward to work with and electrochemically inefficient as evidenced by the large number of cells required to give a workable current. Hence it is not surprising that chemists soon came up with more effective battery configurations and electrolytes, among the earliest of which were the various trough batteries used by such investigators as Cruickshank, Davy, and Wollaston (figure 8). Indeed, by the end of the century, as may be seen from such speciality monographs as Park Benjamin's 1893 tome, *The Voltaic Cell: Its Construction and Capacity*, an almost bewildering number of voltaic cells had been proposed, many of which were based less on modifications of the cell's chemistry than on changes in its physical configuration, usually with the intent of increasing the effective areas of the working electrodes.[11]

Figure 9. John Frederic Daniell (1790-1845)

One of the first successful cells based on a change in chemistry was the Daniell cell, named after its inventor – the British electrochemist, John Frederic Daniell (figure 9)[12] – who first described it in 1836.[13] This was a two-fluid, primary cell based on the cell configuration $Zn(s)/Zn(SO_4)(aq)//Cu(SO_4)(aq)/Cu(s)$ and the net cell reaction:

$$Zn(s) + Cu(SO_4)(aq) \rightarrow Zn(SO_4)(aq) + Cu(s) \quad [4]$$

in which Zn(0) is oxidized to Zn(II) at the anode, Cu(II) is reduced to Cu(0) at the cathode, and the net cell potential is about 1.1 V when the cell is fully charged. Unlike the voltaic pile and the trough battery, the Daniel cell is the first example of a commercially successful two-fluid cell.[14] In other words, rather than sharing a common electrolyte, each electrode has its own separate electrolyte: a saturated aqueous solution of $Cu(SO_4)(aq)$ in the case of the Cu cathode and a solution of $Zn(SO_4)(aq)$ and $H_2(SO_4)(aq)$ in the case of the Zn anode.

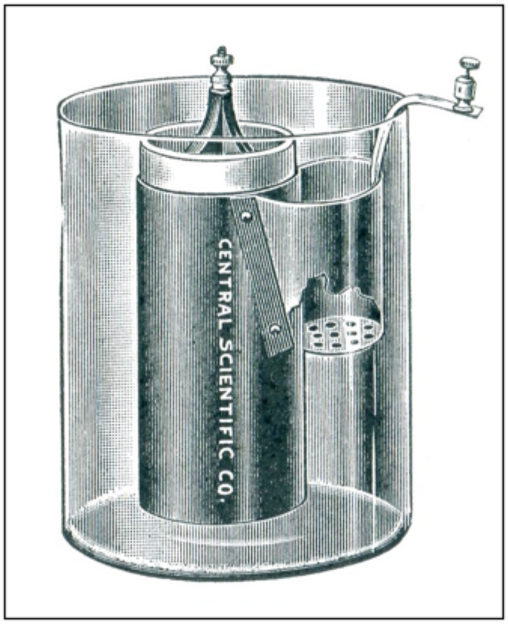


Figure 10. A late 19th-century example of the original Daniell cell with a ceramic spacer. The fluted Zn rod in the center compartment is the anode and the cylindrical wrap of sheet Cu on the outside of the spacer is the cathode. The bottom of the smaller Cu cylinder to the right is perforated and is intended to hold the solid $Cu(SO_4)$ crystals necessary to maintain saturation.

In the original form of the cell the cathode and anode compartments were separated by means of a porous ceramic cup or spacer (figure 10) with the anode and its accompanying electrolyte located inside the cup and the cathode and its accompanying electrolyte outside the cup. Both the fluting on the Zn anode and the large sheet of Cu used for the cathode were designed to maximize the surface areas of the electrodes and thus both the amount of reaction and the current generation.

Examination of the net cell reaction shows that not only is the Zn anode gradually consumed, so is the $Cu(SO_4)(aq)$ electrolyte, thus requiring that it be continuously replenished. In the form of the cell shown in figure 10, this was accomplished by means of the small Cu cylinder attached to the Cu cathode. This was filled with $Cu(SO_4)(s)$ crystals and these, in turn, were in direct contact with the cathode electrolyte via a series of holes punched in the bottom of the cylinder. Consequently, as the concentration of the $Cu(SO_4)(aq)$ in the cathode electrolyte diminished, the crystals would gradually dissolve and so maintain saturation.

The presence of the ceramic spacer in this cell meant that the cell had a relatively high internal resistance and therefore that a portion of its energy was consumed internally rather than being available for external work. Starting in the 1850s numerous attempts were made to eliminate the ceramic spacer by exploiting the large density difference between the saturated $Cu(SO_4)(aq)$ solution and the dilute $Zn(SO_4)(aq)$ solution. Indeed, Benjamin in his 1893 treatise on the voltaic cell described no less than 37 variations of the Daniell cell proposed between 1849 and 1890.[15]

Of these, one of the most important was the globe or so-called Meidinger cell (figure 11).[16] This consisted of an inverted round-bottom flask or globe whose neck terminated in a narrow tube. This tube extended almost to the bottom of a short glass cup containing the Cu cathode. This cup was placed inside a larger glass cylinder with the inverted globe or flask resting on top. The upper half of the larger cylinder had a diameter slightly bigger than the bottom half, thus creating a ledge which supported the Zn anode in the upper half. The inverted globe was filled with several pounds of $Cu(SO_4)(s)$ crystals and the cell with slightly acidified water to the top of the Zn anode. This level corresponded to about half of the globe also being filled with water, which soon dissolved some of the $Cu(SO_4)(s)$ crystals to create a dense saturated $Cu(SO_4)(aq)$ solution which then displaced the clear water from the small cup and surrounded the Cu cathode, while the slightly acidified water in the upper part of the large cylinder

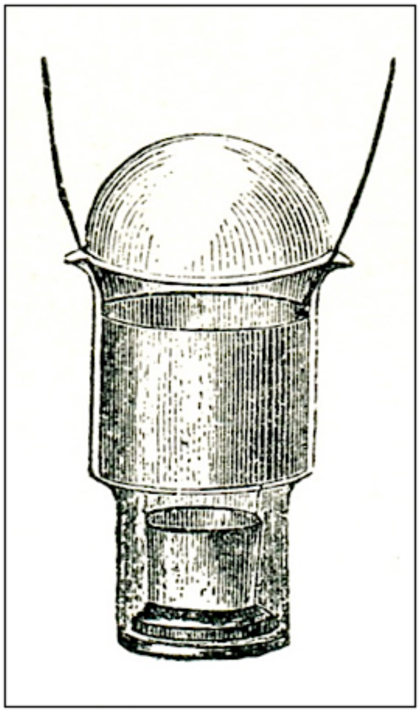


Figure 11. The globe or Meidinger form of the Daniell cell.

remained free of $Cu(SO_4)(aq)$ and now contained a very dilute $Zn(SO_4)(aq)$ solution instead.

But perhaps the most successful variation of the Daniel cell was the form shown in figure 12. Secondary sources are vague as to who deserves credit for this innovation,[17] but by the 1880s it seems to have largely displaced the more powerful Grove cell (see below) in most telegraph offices, in large part because it did not release obnoxious $NO_2(g)$ fumes when operating. An array of intersecting copper strips on the bottom of the cylindrical cell jar functioned as the cathode and a heavy cast Zn anode with radiating fingers hung on the the jar's upper lip. It was the supposed similarity between the shape of this anode and that of a crow's foot which gave the cell one of its characteristic names.

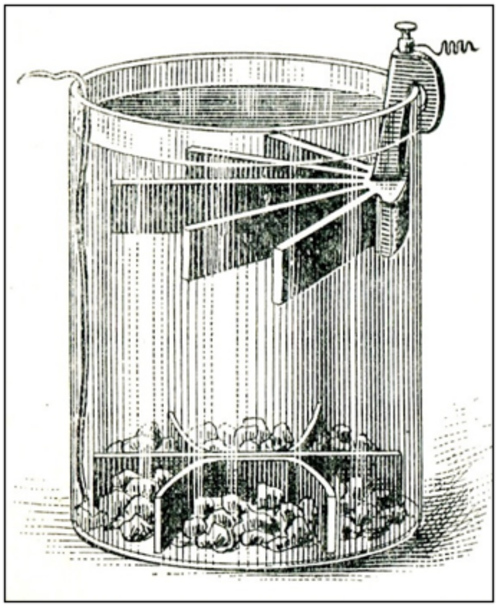


Figure 12. The crowfoot form of the Daniell gravity cell. The multiple branching of both the upper Zn anode and lower Cu cathode is intended to increase the area of active contact with the electrolyte. Not clearly shown is the concentration gradient between the lower layer of the saturated $Cu(SO_4)(aq)$ solution and the upper layer of the dilute $Zn(SO_4)(aq)$ solution.

To activate the cell, about three pounds of $Cu(SO_4)(s)$ crystals were placed on the bottom of the jar between the branches of the Cu cathode and slightly acidified water carefully added until it covered the Zn anode at the top. Once again, as the $Cu(SO_4)(s)$ dissolved it would form a dense, saturated $Cu(SO_4)(aq)$ solution at the bottom of the jar which only gradually merged into the less dense dilute $Zn(SO_4)(aq)$ solution at the top and thus eliminated the need for a ceramic spacer. As the $Cu(SO_4)(aq)$ solution became depleted, more of the excess crystals in the bottom of the jar would dissolve and thus maintain saturation. Since the cell's construction depended on the difference in the densities or specific gravities of the

$Cu(SO_4)(aq)$ versus the $Zn(SO_4)(aq)$ solutions, such cells were also called gravity cells.

If these cells were used for long periods of time, it was customary to float a thin layer of oil on top of the electrolyte to inhibit evaporation. However, starting around 1916, a sharp rise in the cost of $Cu(SO_4)(s)$ caused the cell to fall out of commercial favor and resulted in its displacement by the alkaline Edison-Lalande cell described below, which was not only less expensive but required far less maintenance.[18] At present the Daniel cell is essentially an artifact of the freshman chemistry course, where its continued popularity is largely a function of the simplicity of its underlying redox reaction.

The Grove and Bunsen Cells

First described by the British scientist and jurist, William Robert Grove (figure 13), in 1839, the Grove cell was based on the cell configuration $Zn(s)/H_2(SO_4)(aq)//H(NO_3)(aq)/Pt(s)$ and the net cell reaction (4):[19, 20]

$$Zn(s) + H_2(SO_4)(aq) + 2H(NO_3)(aq) \rightarrow Zn(SO_4)(aq) + 2NO_2(g) + 2H_2O(l)$$

in which Zn(0) is oxidized to Zn(II) at the anode, N(V) is reduced to N(IV) at the cathode, and the resulting net cell potential is roughly 1.9 V.

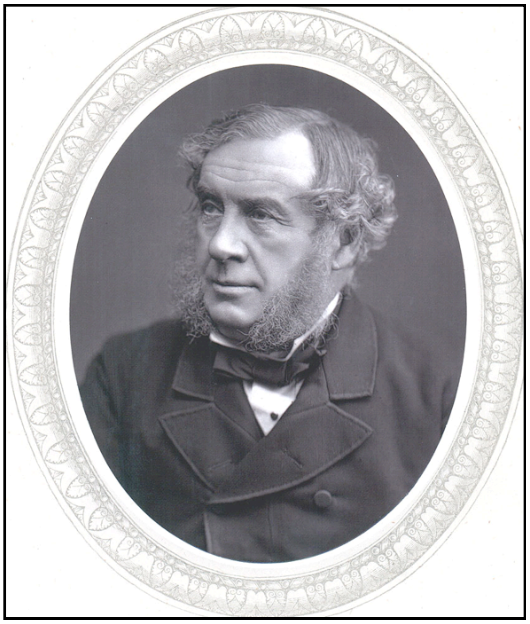


Figure 13. William Robert Grove (1811-1896).

Like the Daniel cell described in the previous section, the Grove nitric acid cell was a two-fluid system that employed separate electrolytes for the cathode and anode and a ceramic spacer. In his prototype Grove had employed the bowls from broken clay pipes as his spacers, with an inert platinum (Pt) cathode and the nitric acid [$H(NO_3)$] electrolyte inside the pipe bowl, and a Zn anode and dilute sulfuric

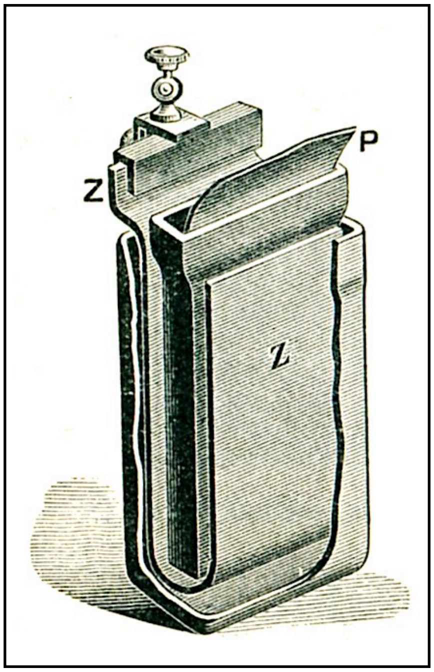


Figure 14. A period etching of a cutaway of a Grove nitric acid cell. Each rectangular 2"x 3"x 5" cell consisted of a sheet of zinc (Z) wrapped around a narrow porous ceramic separator with a flared lip, which contained, in turn, a sheet of platinum (P) as the cathode.

acid [$H_2(SO_4)$] electrolyte outside the pipe bowl.[21] In the final commercial version of the cell (figure 14), the pipe bowl was replaced by a narrow ceramic separator with a flared lip and the original rod-like electrodes with sheets of Zn and Pt in order to maximize electrode surface areas. Presumably, because of the expense of the Pt cathode, the first commercial cells were relatively small and usually corresponded to a 2"x 3"x 5" rectangular glazed ceramic or glass box.

Because of their high net cell potential, these cells soon became a favorite of telegraph operators, electroplaters, and experimental electrochemists. However, both the expensive Pt cathode and the obnoxious $NO_2(g)$ fumes produced during cell operation continued to be serious drawbacks.

The first of these problems was finally eliminated in 1841 when the German chemist, Robert Bunsen (figure 13) – of both burner and spectroscope fame – proposed replacing the inert Pt cathode with an equally inert,

Figure 15. Robert Wilhelm Bunsen (1811-1899).

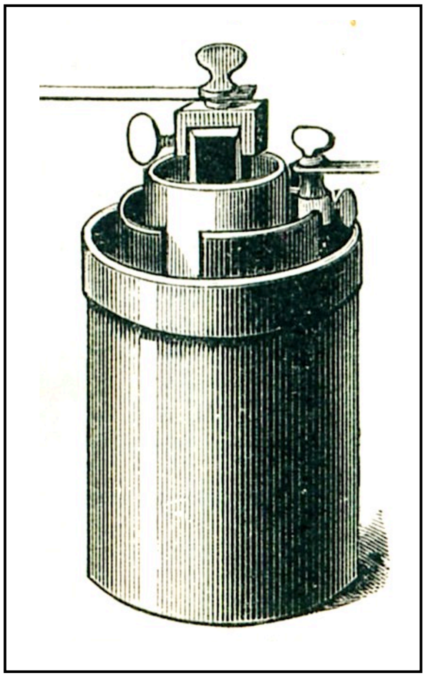


Figure 16. The original Bunsen cell with a rectangular carbon block for the cathode inside the ceramic spacer and a sheet of zinc for the anode wrapped around the outside.

but substantially cheaper, version made of baked coke or carbon.[22, 23] Precisely the same suggestion was made by the American chemist, Benjamin Silliman Jr, a year later.[24] Though Silliman's proposal was apparently made independently of Bunsen, as is usually the case in science, the winner takes all, and any claim to fame Silliman may have had for this innovation soon disappeared from the historical record.

In Bunsen's original modification of the Grove cell – usually referred to as a Bunsen carbon cell – he employed a cylindrical carbon cathode. This was placed in a cylindrical, rather than a rectangular, glazed ceramic cell container. Inside the cathode was a cylindrical ceramic spacer and the Zn anode. However, because of the expense of nitric acid, most later modifications of the cell reversed this design (figure 16). The inert carbon cathode (usually in the form of a rectangular block) and the nitric acid electrolyte were placed inside the ceramic spacer and the Zn anode and $H_2(SO_4)$ electrolyte on the outside. In early versions of this cell the anode was merely a large sheet of Zn, but in some

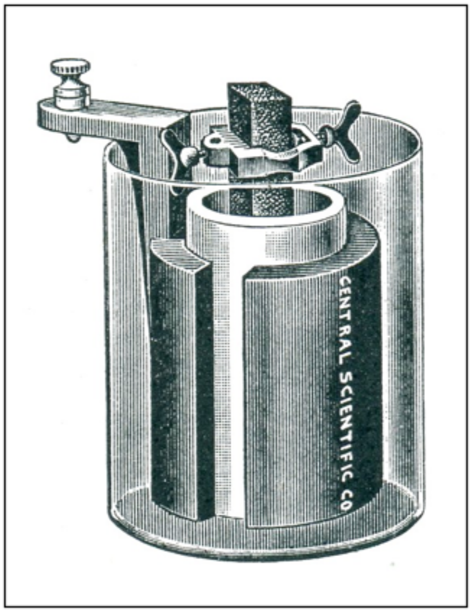


Figure 17. A modified Bunsen carbon cell but with a thick, heavy, cast Zn anode rather than a sheet of Zn on the outside of the ceramic spacer and a clear glass rather than a glazed ceramic container.

later modifications it corresponded to a thick, heavy Zn casting (figure 17).

With the introduction of the less expensive Bunsen cell, the original form of the Grove cell soon disappeared from both commerce and the chemical laboratory. Unfortunately, the Bunsen cell failed to eliminate the second of the above problems – the obnoxious $NO_2(g)$ fumes, and it was this problem which eventually led to the cell's commercial demise and its replacement, first by the crowfoot form of the Daniell gravity cell in the 1880s, and then by the Edison-Lalande alkaline cell in the 1920s.[25]

The Dichromate Cell

The dichromate cell (often called, in violation of current rules of chemical nomenclature, the bichromate cell). was first described in 1842 by both the English chemist, Robert Warington (figure 18),[26] and the German physicist, Johann Poggendorff (figure 19).[27] This primary cell is based on the cell configuration $Zn(s)/H_2(SO)_4(aq)//H_2(CrO_4)(aq)/Pt(C)(s)$ and the net cell reaction:

$$3Zn(s) + 6H_2(SO_4)(aq) + 2H_2(CrO_4)(aq) \rightarrow 3Zn(SO_4)(aq) + Cr_2(SO_4)_3(aq) + 8H_2O(l)$$

in which Zn(0) is oxidized to Zn(II) at the anode, Cr(VI) is reduced to Cr(III) at the cathode, and the resulting net cell potential is roughly 2 V.

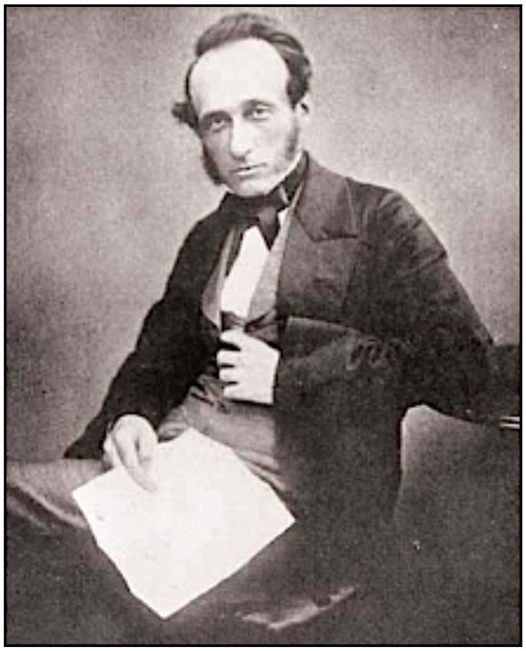


Figure 18. Robert Warington (1807-1867)

Though chromic acid [$H_2(CrO_4)$] is the actual oxidizing agent, rather than being added directly, it is instead made *in situ* within the cell using a mixture of sulfuric acid [$H_2(SO_4)$] and potassium dichromate [$K_2(Cr_2O_7)$]:[28]

Figure 19. Johann Christian Poggendorff (1796-1877)

$$H_2(SO_4)(aq) + K_2(Cr_2O_7)(aq) + H_2O(l) \rightarrow K_2(SO_4)(aq) + 2H_2(CrO_4)(aq)$$

whence the name dichromate cell instead of chromic acid cell. Warington simply substituted this mixture for the nitric acid in a standard Grove cell (see above), thus retaining both the expensive platinum cathode and the porous ceramic spacer,[29] whereas Poggendorff made use of Bunsen's recent discovery that baked carbon electrodes could be used in place of platinum in Grove's cell.[30]

However, by the last quarter of the 19th-century the most popular form of the dichromate cell was the so-called "Grenet" or bottle form, first patented by the French inventor Eugene Grenet in 1859,[31] in which the ceramic spacer was

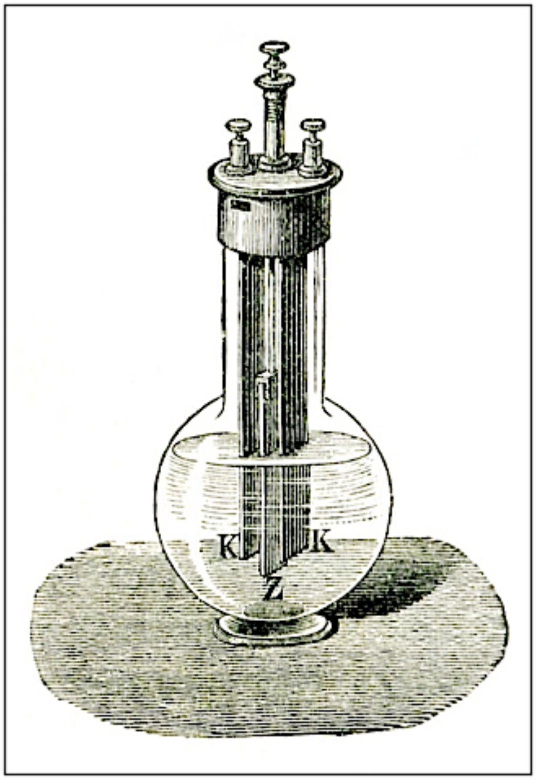


Figure 20. A 19th-century woodcut of the Grenet form of the dichromate cell. KK are the carbon cathode plates, Z is the zinc anode plate. The left electrical connection on the cap is for the cathode and the right is for the anode. What looks like a third electrical connection in the center is actually the device for raising and lowering the Zn anode plate.

eliminated and both electrodes directly immersed in the $H_2(SO_4)/K_2(Cr_2O_7)$ mixture, thereby lowering the internal resistance of the cell. As may be seen from figure 20, this cell consisted of a thick amalgamated Zn anode plate arranged between two carbon cathode plates and mounted in a special round flask or bottle. They were sold in sizes ranging from a fourth liter up to two liters.[31] The anode was connected by means of a rod to the top of the cell and could be raised out of the electrolyte when the cell wasn't in use (figure 21).[32]

Despite its large cell potential and its elimination of the objectionable $NO_2(g)$ fumes associated with the original Grove and Bunsen cells, the dichromate cell had the disadvantage that it gradually consumed its electrolyte as part of the net cell reaction and thus exhibited a progressively decreasing potential with continual use. It was most practical in situations requiring a short burst of high voltage, such as in detonating mines and other military applications, where detonation was achieved by rapidly plunging the Zn anode into the dichromate electrolyte.

In addition, secondary reactions led to accumulation of dihydrogen bubbles on the cathode surface and to a subsequent drop in cell efficiency – a phenomenon known as polarization. In later models there was an attempt to eliminate this problem by blowing air over the cathode to disrupt bubble accumulation. In the end, however, it was the relatively high cost of dichromate salts that limited the cell's commercial applications and by the 1940s it had largely dis-

Figure 21. A famous photo of Thomas Edison posing in 1888 with his improved phonograph. Note the two-liter Grenet cell on the far left. Also note that its anode is in the raised position, thus indicating that it is not in operation.

appeared from most laboratory supply catalogs.

The Planté Lead Storage Cell

All of the voltaic cells discussed so far have been irreversible primary cells. What would eventually prove to be the first practical reversible or secondary cell was first described by Gaston Planté (figure 22) in 1859 based on the cell configuration $Pb(s)/H_2(SO_4)(aq)/PbO_2(s)$ and the net cell reaction:[33]

$$Pb(s) + PbO_2(s) + 2H_2(SO_4)(aq) \leftrightarrow 2Pb(SO_4)(s) + 2H_2O(l)(s)$$

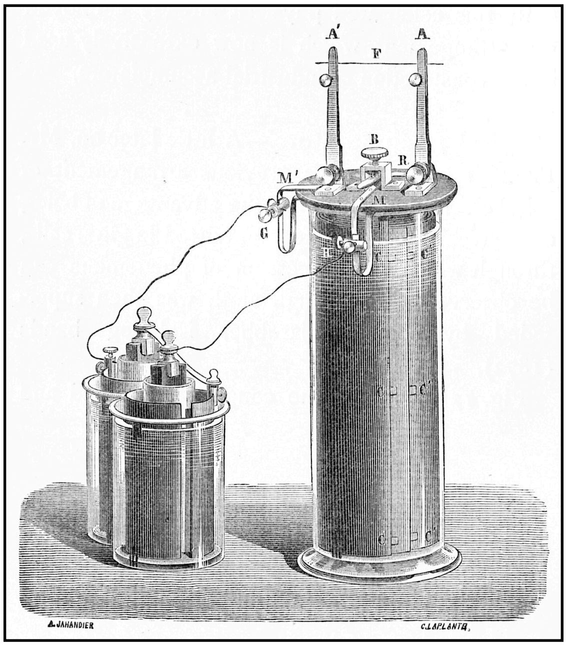


Figure 23. Charging an early Planté cylindrical cell (right) using two Bunsen cells (left).

Figure 22. Gaston Planté (1834-1889)

in which Pb(0) is oxidized to Pb(II) at the anode, Pb(IV) is reduced to Pb(II) at the cathode, and the net cell potential is 2.2 V at full charge.

To construct his original cell, Planté placed a spacer of either felt or canvas between two sheets of lead and rolled the resulting sandwich into a circular spiral which was then put into a cylinder containing an aqueous solution of sulfuric acid and lead sulfate. This was then connected to several Bunsen cells (figure 23) in order to plate, in

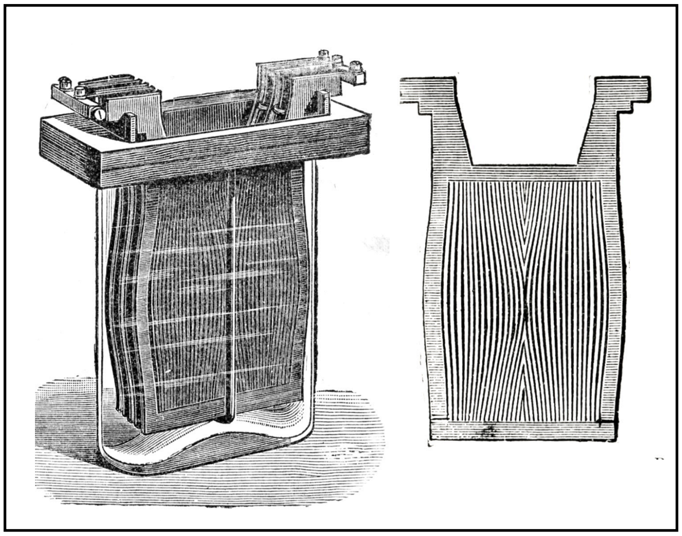


Figure 24. A circa 1889 five cell lead storage battery (left), also called a Reynier accumulator, employing grooved lead electrodes (right).

keeping with the reverse of the above equation, a layer of PbO_2 on the lead sheet that would ultimately serve as the cell's cathode and a layer of porous or spongy lead on the lead sheet that would serve as its anode. The cell was then allowed to discharge and the electrolysis step repeated once more. It required many cycles of charging and discharging, extending over a period of several months, before sufficient layers of PbO_2 and porous lead had accumulated on the electrodes to form a properly working storage cell.

All of this changed in 1881 when Camille Faure discovered that he could achieve the same result in a much shorter time by coating the lead sheets with a paste of sulfuric acid, lead dioxide, and lead sulfate.[34] This coincided with an increasing interest in the 1880s in the use of arrays of such cells – also called accumulators[35] – for electrical power storage in connection the electrical lighting systems that were being installed in many cities and towns.[36] In response to this growing interest, dozens of proposals appeared for increas-

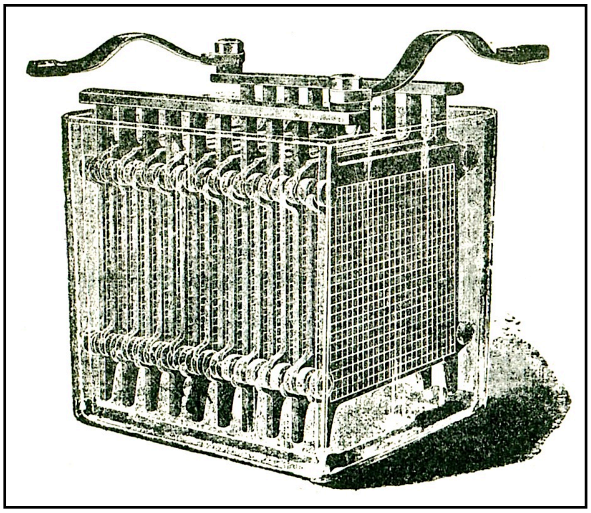


Figure 25. A circa 1893 mult-cell lead storage battery (right) with grid electrodes that is a recognizable precursor of the modern car battery.

ing the efficiency of the lead storage battery by increasing the working area of its electrodes, either by grooving the lead sheets (figure 24) or by using various open grid systems (figure 25). As a result of these changes, by the 1890s the lead storage battery had begun to assume a form that is a recognizable precursor of our modern day automobile battery.

Figure 26. A portrait medallion commemorating Georges Leclanché (1838-1882).

The Leclanché Cell

First described by the French scientist, Georges Leclanché, (figure 26) in 1866,[37, 38] this cell is based on the cell configuration $Zn(s)/(NH_4)Cl(aq)/MnO_2(s)$ and the net cell reaction:

$$Zn(s) + 2MnO_2(s) + 2(NH_4)Cl(aq) + 2H_2O(l) \rightarrow Zn(NH_3)_2Cl_2(aq) + 2Mn(OH)_3$$

in which Zn(0) is oxidized to Zn(II) at the anode, Mn(IV) is reduced to Mn(III) at the cathode, and the resulting net cell potential is roughly 1.5 V.

Unlike the previous cells, the Leclanché cell was a single-fluid system that employed a saturated aqueous solution of ammonium chloride [$(NH_4)Cl$] as the electrolyte. As originally conceived, the $MnO_2(s)$ and an inert rectangular carbon cathode came sealed in a

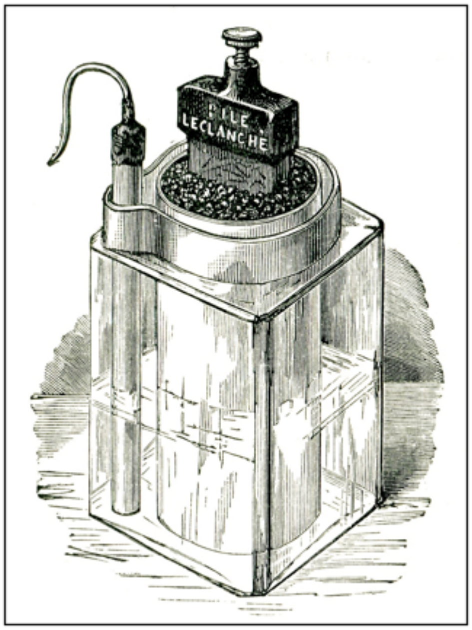


Figure 27. The "wet" Leclanché cell as depicted in Benjamin's 1893 treatise on the voltaic cell.

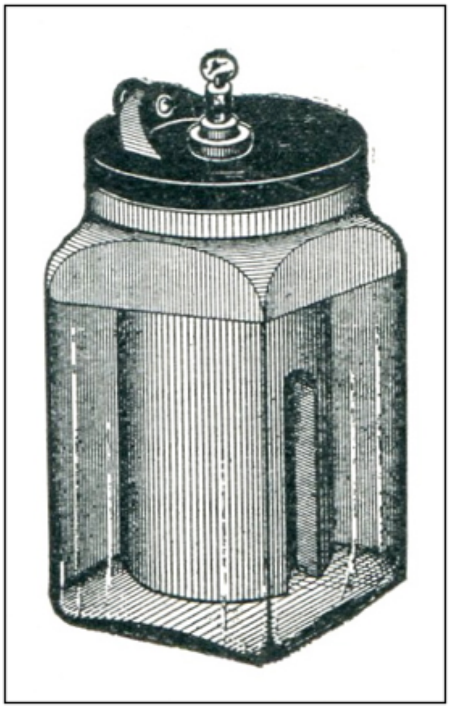


Figure 28. A circa 1909 jar form of the Leclanché cell in which the MnO_2/C cathode has been shaped into a hollow cylinder with a Zn rod anode in the center.

large porous ceramic spacer (figure 27) and the Zn anode as a separate rod. Both of these were placed in a large rectangular glass battery jar and the jar half-filled with the $(NH_4)Cl(aq)$ electrolyte. To increase the conductivity of the $MnO_2(s)$, it was intermixed with an equal quantity of powdered carbon.

Later several alternative forms of the wet cell were developed in which the ceramic spacer was eliminated. Rather than using loosely powdered $MnO_2(s)$ in a ceramic cup, the $MnO_2(s)$ and $C(s)$ were instead mixed with a resin binder and pressed into various electrode configurations. In the form shown in figure 28, they were shaped into a hollow cylinder that surrounded the Zn rod used as the anode.

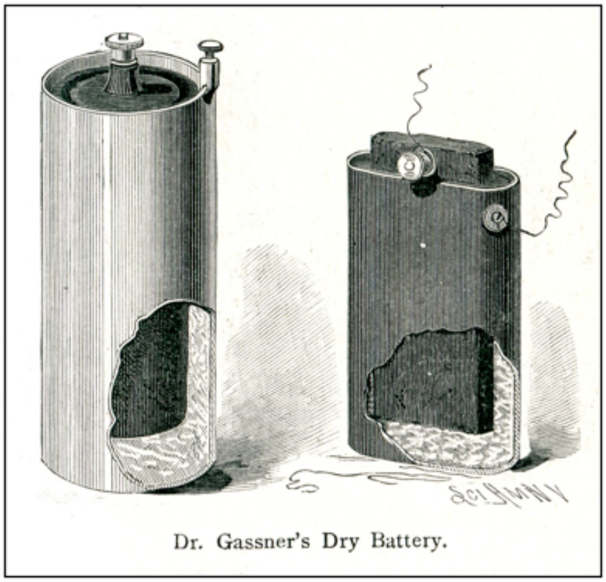


Figure 29. A circa 1890 etching of two of Gassner's early dry cells. The gap between the outer Zn case and the central MnO_2/C cathode containing the electrolyte paste is clearly visible in each case.

Starting around the last decade of the 19th century, the so-called "wet form" of the Leclanché cell was gradually transformed into the modern "dry cell" (figure 29), which is the version most commonly used today. Generally attributed to the German, Carl Gassner, around 1888, this transformation involved two major structural changes (figure 29). Firstly, the Zn rod anode was replaced with a Zn can which also acted as the cell container. Secondly, the MnO_2/C mixture was formed into a cylinder surrounding a central carbon rod cathode, and the space between it and the Zn can filled with a starch and flour-based electrolyte paste containing $(NH_4)Cl(s)$ and a small amount of $ZnCl_2(s)$. In later versions, the MnO_2/C mixture and electrode paste were mixed together and the Zn anode can furthered encased in an outer steel can and sealed at the top (figure 30) in order to help contain any leaks due to chemical corrosion of the Zn liner. According to Vinal, these changes also altered the net cell reaction to:[39]

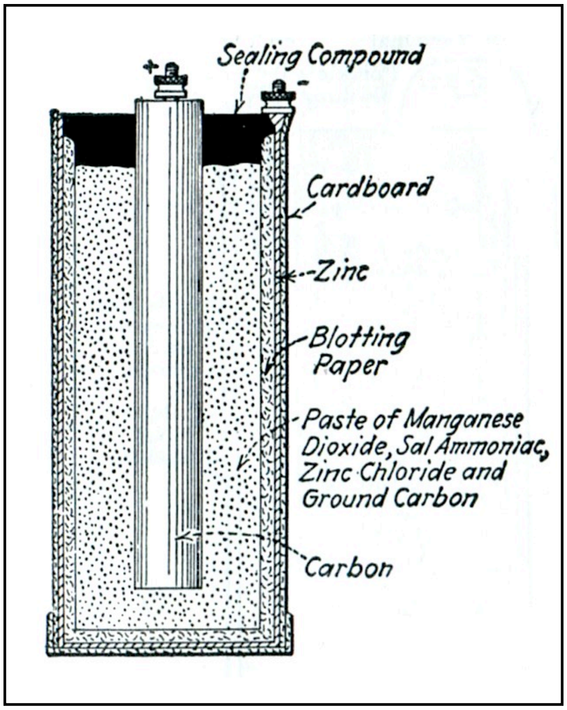


Figure 30. Cross section of a typical modern day dry cell.

$$Zn(s) + 2MnO_2(s) \rightarrow ZnMn_2O_4(s)$$

in which Zn(0) is once again oxidized to Zn(II) at the anode, Mn(IV) to Mn(III) at the cathode, but the net cell potential remains at 1.5 V

Dry cells began to appear in laboratory supply catalogs around 1900[40] and came in various sizes, ranging from the size D-cells still used in flashlights to the larger pint-size A cells once widely used in laboratory apparatus and by electrical hobbyists.

A second fundamental change in the Leclanché cell occurred in the late 1950s when the Canadian engineer, Lewis Urry, replaced the slightly acidic $(NH_4)Cl$-$ZnCl_2$ mixture in the electrolyte paste with K(OH). Now known as the alkaline battery, this modification was finally patented by Union carbide in 1960 and is supposedly based on the net cell reaction:

$$Zn(s) + 2MnO_2(s) \leftrightarrow ZnO(s) + Mn_2O_3(s)$$

in which Zn(0) is still oxidized to Zn(II) at the anode, Mn(IV) is still reduced to Mn(III) at the cathode, and the net cell potential remains at 1.5 V. However, it is not apparent whether this reaction is really all that different from the one given earlier by Vinal for the original $(NH_4)Cl(aq)$ dry cell, since:

$$ZnO(s) + Mn_2O_3(s) \rightarrow ZnMn_2O_4(s)$$

or why, in the presence of K(OH), the ZnO does not end up as K_2ZnO_2 instead:

$$ZnO(s) + 2K(OH)(aq) \rightarrow K_2ZnO_2(s) + H_2O(l)$$

To further minimize leakage due to corrosion of the Zn liner, the mechanical arrangement of the cell's contents was also reversed in the alkaline cell (figure 31). A hollow cylindrical MnO_2/C cathode was now placed next to the outer steel casing and powdered Zn and a Zn rod anode placed in the center, all of these components being intermixed with the K(OH)(aq) paste electrolyte. Your everyday AA and AAA sized cells are now all of this alkaline variety.

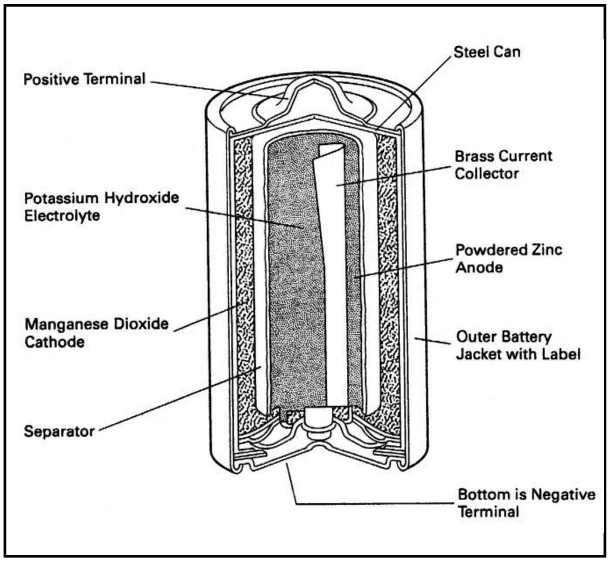


Figure 31. A cutaway diagram of a typical alkaline dry cell.

The Lelande Cell

The modern day alkaline battery is

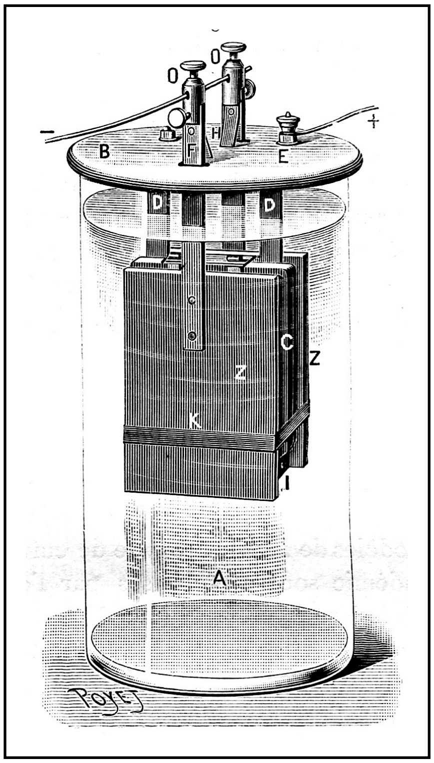


Figure 32. Lalande's improved cell of 1891. C is the CuO cathode and ZZ are the plates of the Zn anode.

hardly the first known example of an alkaline-based voltaic cell. An early commercially successful example (figure 32) was the alkaline cell first described by Felix de Lalande and Georges Chaperon in 1883 and in improved form in 1891.[41] This was based on the cell configuration $Zn(s)/Na(OH)(aq)/CuO(s)$ and the net cell reaction:

$$Zn(s) + CuO(s) + 2Na(OH)(aq) \rightarrow Na_2ZnO_2(s) + Cu(s) + H_2O(l)$$

in which Zn(0) is oxidized to Zn(II) at the anode, Cu(II) is reduced to Cu(0) at the cathode, and the net cell potential is roughly 0.8 V when fully charged.

Beginning in the early 1890s, the Edison company arranged to manufacture the improved version of this cell in the United States and, as noted earlier, by the early 20th century it had largely displaced both the Daniell gravity cell and the Bunsen cell in most everyday applications. Though Lalande and Chaperon originally claimed that this cell was reversible and so could function, like the Planté cell, as a storage battery, Reynier, in his 1889 monograph on voltaic accumulators, claimed that this was not the case in actual practice.[35] Nevertheless, as we will see in the next section, this cell would serve as an important stepping stone to the invention of a true alkaline storage battery.

The Edison Nickel-Iron Alkaline Storage Cell

Published biographies of Thomas Edison (figure 33) are literally legion and dif-

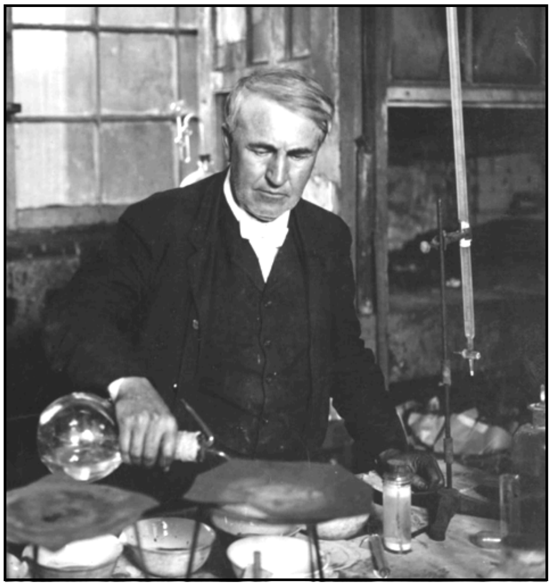


Figure 33. Publicity photo of a middle-age Thomas Edison (1847-1931) posing at the chemical bench.

fer widely in their emphasis and sophistication. However, a little-known 1971 study by Byron Vanderbilt, which focuses exclusively on the chemical aspects of Edison's work, is of particular value when it comes to understanding the basics of Edison's alkaline storage cell.[42] According to this author, the first commercial electric car, known as the "Electobat" was produced in 1894 by Henry Morris and Pedro Salom of Philadelphia, and by 1899 ninety percent of the motorized cabs operating in New York City were electrical. The power source for these early vehicles was the Planté lead storage battery described above and they are still used in modern automobiles, but for purposes of powering the electric starter and running the lights and radio when the motor is turned off, rather than as the vehicle's primary source of motive power.

By 1900 the trend in electric vehicles had caught Edison's attention and he was determined to cash in on this growing market by developing a superior storage battery for electric vehicles. Lead storage batteries had several disadvantages. The dense lead electrodes meant that the battery was quite heavy and thus had a low energy to mass ratio. This is a critical parameter for an electric car. Since part of a battery's output must be consumed in transporting the battery itself rather than the vehicle and its passengers, the lighter the battery the better. This disadvantage alone restricted the average driving range to about 25 miles before recharging was required.[43] Likewise the sulfuric acid [$H_2(SO_4)$] electrolyte was not only highly corrosive and dangerous to work with, it had to be continually monitored, since it was consumed in the course of the battery's cell reaction and thus caused the cell voltage to gradually decrease with use.

In response to these limitations, Edison decided to develop a cell employing electrodes made from materials much less dense than lead and an alkaline rather than an acidic electrolyte. These choices were almost certainly prompted by the fact that for more than a decade Edison had been successfully manufacturing the Lalande primary alkaline cell described in the previous section. As usual, Edison proceeded empirically. Inspired by the low-density CuO cathode in the Lalande cell, he first prepared a series of test-tube sized cathode half-cells using K(OH)(aq) as the electrolyte and various oxides deposited on porous carbon strips as the electrodes. These were coupled to a standard anode half-cell to determine which cathode best optimized the net cell potential. The winner proved to be nickel oxide hydroxide, NiO(OH). Using this cathode half-cell, he then varied the anode half-cell in the same manner and discovered that the optimal electrode choice was cadmium metal, thus giving the net cell reaction:

$$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \leftrightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$$

in which Cd(0) is oxidized to Cd(II) at the anode, Ni(III) is reduced to Ni(II) at the cathode, and the net cell potential is 1.5 V. However, at the time, Cd metal was too expensive for the market Edison had in mind. In addition – apparently unknown to Edison – this cell had already been patented in 1899 by the Swedish chemist, Waldemar Jungner, who began commercial production in Sweden in 1904, though the cell would not impact on the American market until the 1940s.

Searching for a more practical and less expensive replacement for Cd, Edison eventually settled upon iron as the best alternative, giving the net cell reaction:

$$3Fe(s) + 8NiO(OH)(s) + 4H_2O(l) \leftrightarrow Fe_3O_4(s) + 8Ni(OH)_2(s)$$

in which Fe(0) is oxidized to a 1:1 mixture of Fe(II) and Fe(III) at the anode, Ni (III) is reduced to Ni(II) at the cathode, and the net cell potential is 1.6 V.

On the chemical side, commercial production of the cell required the development of entirely new industrial processes for the preparation and purification of

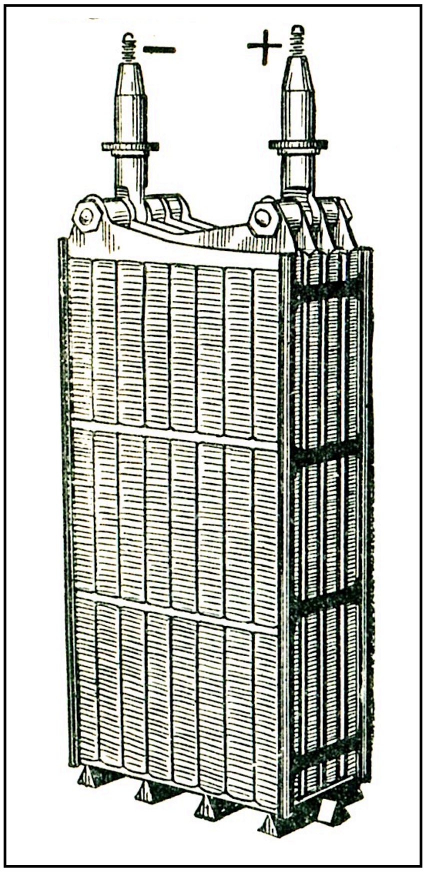


Figure 34. The interior of a cell for the final commercial version of Edison's nickel-iron alkaline storage battery showing the interleaved electrodes and the hundreds of pockets containing the active oxides.

the necessary chemicals, and for this purpose Edison built a chemical plant at Silver Lake, New Jersey. On the mechanical side, the production problems proved to be even more challenging. The end product (figure 34) was encased in a nickel-plated steel container and was composed of an elaborate array of between 9 and 17 interleaved nickel-plated steel electrode plates in order to optimize the active surface area of each electrode. Each plate, in turn, contained an array of either punched pockets or perforated metal tubes containing the appropriate chemically active oxide.

Unfortunately, pure NiO(OH) proved to be a poor electrical conductor and to correct this problem Edison initially tried intermixing it with graphite. The resulting cell was put on the market in 1904 but proved to be unreliable and had to be recalled. Edison eventually tried intermixing the NiO(OH) with feather-light flakes of Ni metal (for which he also had to develop an elaborate manufacturing process) and enhancing the K(OH)(aq) electrolyte

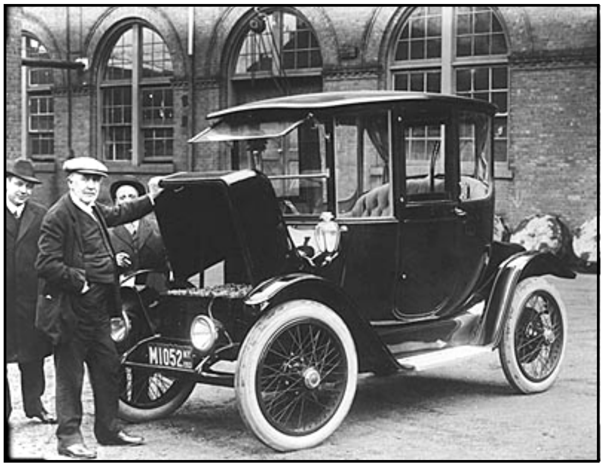
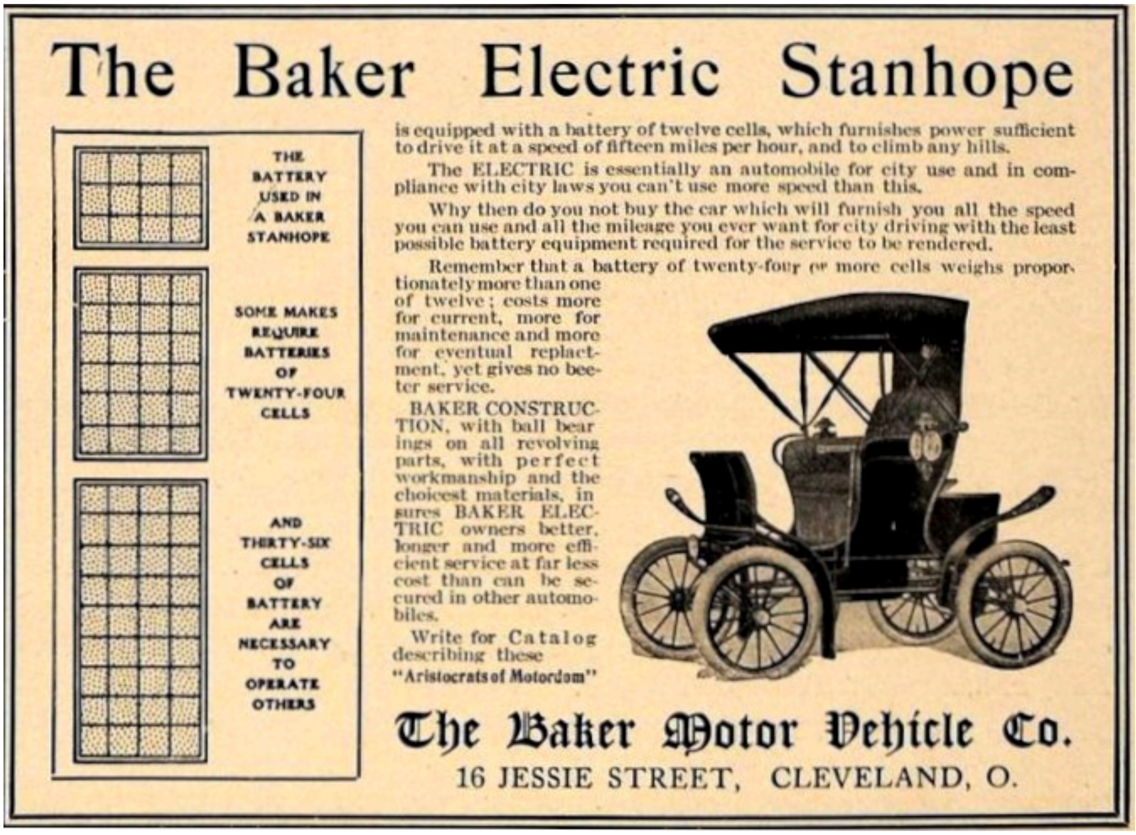


Figure 35. Edison posing with an electric car. The hood has been raised in order to display the array of nickel-iron storage batteries inside.



The Baker Electric Stanhope

THE BATTERY USED IN A BAKER STANHOPE

SOME MAKES REQUIRE BATTERIES OF TWENTY-FOUR CELLS

AND THIRTY-SIX CELLS OF BATTERY ARE NECESSARY TO OPERATE OTHERS

is equipped with a battery of twelve cells, which furnishes power sufficient to drive it at a speed of fifteen miles per hour, and to climb any hills.

The ELECTRIC is essentially an automobile for city use and in compliance with city laws you can't use more speed than this.

Why then do you not buy the car which will furnish you all the speed you can use and all the mileage you ever want for city driving with the least possible battery equipment required for the service to be rendered.

Remember that a battery of twenty-four or more cells weighs proportionately more than one of twelve; costs more for current, more for maintenance and more for eventual replactment, yet gives no beeter service.

BAKER CONSTRUCTION, with ball bearings on all revolving parts, with perfect workmanship and the choicest materials, insures BAKER ELECTRIC owners better, longer and more efficient service at far less cost than can be secured in other automobiles.

Write for Catalog describing these "Aristocrats of Motordom"

The Baker Motor Vehicle Co.
16 JESSIE STREET, CLEVELAND, O.

Figure 36. Period advertisement for one of several electric cars made by the Baker Motor Vehicle Co. of Cleveland.

by adding some Li(OH). This revised cell, unlike the original, proved reliable and was put on the market in 1909. The cells were wired in groups of three or five in steel cases with carrying handles and up to a dozen or more of these batteries, depending on vehicle size, were then installed under the hoods (figure 35) of such popular electric cars of the period as the Studebaker, Anderson, and Baker Runabout (figure 36).

Though its net cell potential was less than that of the lead storage battery and it was far more expensive, the Edison nickel-iron cell also had numerous advantages. It had a higher energy to mass ratio, could be recharged almost indefinitely without deterioration, and allowed vehicles to travel 50-75 miles between rechargings rather than the 25 miles obtainable from early models of the lead storage battery. In addition, the lead storage battery was sensitive to mechanical shocks – a serious problem in this era of cobblestone city streets and unpaved country roads. Edison cells, on the other hand, with their steel-clad cases, were quite resilient, as Edison flamboyantly demonstrated by having his assistants throw them from the second- and third-floor windows of his West Orange laboratory.

But even before Edison began marketing his revised battery, several events occurred that would spell the eventual demise of the original electric car.[44] These include the introduction of Henry Ford's popular and inexpensive gasoline-powered Model T in 1908 and the introduction of the electric starter by Charles Kettering in 1911, which eliminated the most objectionable and dangerous aspect of gasoline engines – hand cranking – and which would also ensure the future of the lead storage battery in automobile design.

Edison tried to carve out an alternative market for his creation through advocacy of battery-powered electric street cars, but without notable success. Eventually it found use as a power source for the small trucks used to handle baggage and freight at airports, shipyards, railway stations, and bus depots, as well as to move materials in factories. It was also used to power forklift trucks, mine and switch locomotives, and for railway signaling and communications equipment. One further advantage of the cell, not mentioned earlier, is its long shelf life (30-50 years) which has also made it a favorite for emergency electrical backup systems.

Standard Cells

All of the above voltaic cells were "working" cells that were valued as much for their ability to provide a significant electrical current for use in the laboratory and industry as for their EMF values. However, in the last quarter of the 19th century a second class of voltaic cells – called standard cells – came into existence that were valued more for their ability to maintain a constant EMF value than for their current output and which would play an important role in the emerging fields of physical and electroanalytical chemistry and in establishing electrical standards.[45]

The earliest of these was a standard cell first proposed by Latimer Clark in

1872 based on the cell configuration $Zn(Hg)/Zn(SO_4)*7H_2O(s)/Zn(SO_4)(sataq)/Hg_2(SO_4)(s)/Hg(l)$ and the net cell reaction:[46]

$$Zn(s) + Hg_2(SO_4)(s) + 7H_2O(l) \rightarrow Zn(SO_4)*7H_2O(s) + Hg(l)$$

in which Zn(0) is oxidized to Zn(II) at the anode, Hg(I) is reduced to Hg(0) at the cathode, and the net cell potential is 1.43302 V at 15°C.

In 1892 Edward Weston patented a closely related standard cell based on the cell configuration $Cd(Hg)/Cd(SO_4)*2.67H_2O(s)/Cd(SO_4)(sataq)/Hg_2(SO_4)(s)/Hg(l)$ and the net cell reaction:[47]

$$Cd(s) + Hg_2(SO_4)(s) + 2.67H_2O(l) \rightarrow Cd(SO_4)*2.67H_2O(s) + Hg(l)$$

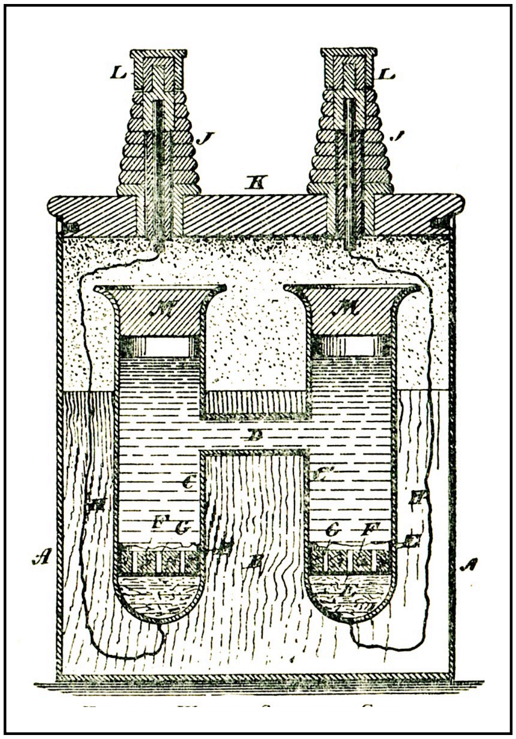


Figure 37. A cross section of the original Weston cell enclosed in a protective wooden box.

in which Cd(0) is oxidized to Cd(II) at the anode, Hg(I) is reduced to Hg(0) at the cathode, and the net cell potential is 1.01864 V at 20°C. The Weston cell proved to be superior to the Clark cell in several respects, most of which were traceable to the differences in the thermal behavior of hydrated zinc sulfate versus hydrated cadmium sulfate, and by the 1920s had largely displaced it.[48]

The Weston cell is usually constructed using a hermetically sealed H-shaped glass container and, to prevent breakage, this is often enclosed, in turn, in a protective box, initially made of wood, but later of Bakelite (figures 37-38). By 1920 such cells had become a standard feature of most laboratory supply catalogs, and in the United States most were being manufactured by Eppley Laboratory Inc. of Newport RI.[49]

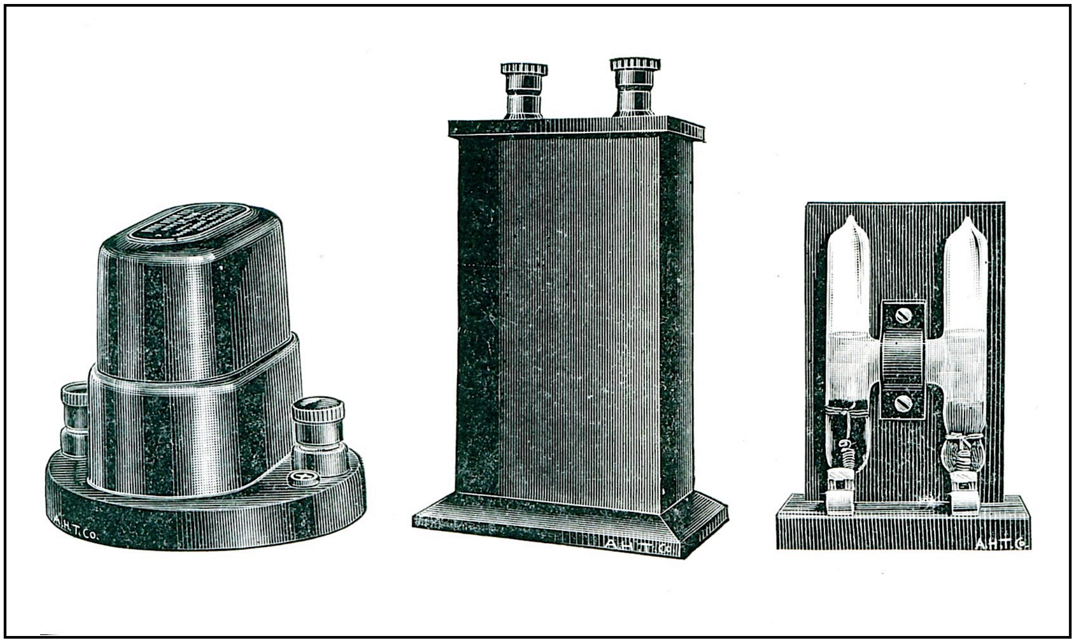


Figure 38. Typical Weston cells, both exposed (far right) and encased, as shown in the 1921 catalog for the Arthur Thomas Company of Philadelphia.

Museum Holdings

The vast majority of the voltaic cells in the museum's collections were donated by the Chemistry Department of Oberlin College, where they had been used for many years for display and demonstration purposes in the teaching of freshman chemistry but were no longer needed once the curriculum, like that at all American colleges and universities, shifted away from descriptive chemistry and became increasingly theoretical in its emphasis.

Jensen-Thomas Apparatus Collection

Figure 39. A 19th-century (5” x 14”), half-gallon Leyden jar and a handheld (7.5” x 10”) discharger (foreground). Compare with figure 2.

Jensen-Thomas Apparatus Collection

Figure 40. A 19th-century (13.5” x 20” x 20”) “battery” of four interconnected half-gallon Leyden jars. Chains, rather than wires, were traditionally used to establish electrical contact.

Jensen-Thomas Apparatus Collection

Figure 41. A modern (4.75” x 15”) reproduction of a small voltaic pile. Compare with figure 6.

Jensen-Thomas Apparatus Collection

Figure 42. A typical (5.25” x 6.5” x 9”) late-19th century Daniell’s cell. Note the fluted Zn anode inside the porous ceramic spacer and the compartment for the $Cu(SO_4)(s)$ supply connected, on the right, to the sheet of Cu serving as the cathode. Compare with figure 10.

Jensen-Thomas Apparatus Collection

Figure 43. A late 19th-century (4” x 9”) example of the globe or Meidinger form of the Daniell gravity cell. Compare with figure 11.

Jensen-Thomas Apparatus Collection

Figure 44. A disassembled Meidinger cell. From left to right: the outer cylinder and Zn anode, the globe or $Cu(SO_4)(s)$ reservoir, and the inner cup and Cu cathode.

Jensen-Thomas Apparatus Collection

Figure 45. An early 20th-century (6” x 9.75”) example of the crowfoot form of the Daniell gravity cell. The cast Zn crowfoot anode hangs from the edge of the jar and the star shaped Cu cathode rests on the bottom. Compare with figure 12.

Jensen-Thomas Apparatus Collection

Figure 46. A 19th-century (2.5” x 3.5” x 7”) example of a Grove nitric acid cell. The Zn anode is wrapped around the outside of the porous ceramic spacer and the Pt cathode is inside. A spare (0.5” x 3.25” x 4.5”) ceramic spacer is shown on the right. Compare with figure 14.

Jensen-Thomas Apparatus Collection

Figure 47. A 19th-century (3.5" x 7.5") example of a Bunsen carbon cell. The Zn anode is wrapped around the outside of the porous ceramic spacer and the carbon block cathode is inside. Compare with figure 16.

Jensen-Thomas Apparatus Collection

Figure 48. A late 19th-century (4” x 5” x 7”) example of a Bunsen carbon cell. The Zn anode is arranged around the outside of the porous ceramic spacer and the carbon block cathode is inside. However, instead of a Zn sheet, the anode – despite its blackened appearance – is actually a thick casting of Zn metal. Compare with figure 17.

Jensen-Thomas Apparatus Collection

Figure 49. Two (4” x 8.25”) 19th-century, half-liter Grenet dichromate cells. The Zn anode for the cell on the right is in the raised position. Compare with figure 20.

Jensen-Thomas Apparatus Collection

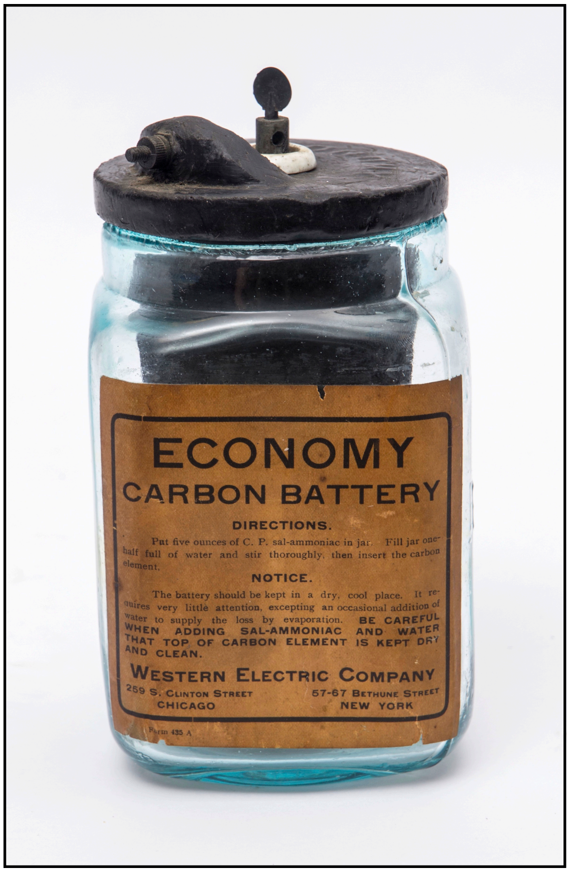
Figure 50. A circa 1920 handcrafted (5.75” x 6.75” x 7.5”) Planté lead-acid cell with grooved electrodes made for use as a demonstration in the freshman chemistry course at Oberlin College.

Jensen-Thomas Apparatus Collection

Figure 51. A circa 1960 (4.5” x 8” x 12.5”) four cell lead storage battery that is an obvious descendent of the 1889 cell shown in figure 24. The name “Hyray” is molded into the side of the glass container.

Jensen-Thomas Apparatus Collection

Figure 52. An early (4” x 4” x 7”) wet Leclanché cell. The porous ceramic cylinder containing the graphite-MnO_2 mixture and the carbon block cathode is in the center and the Zn rod anode is on the far left. Compare with figure 27.



ECONOMY
CARBON BATTERY

DIRECTIONS.

Put five ounces of C. P. sal-ammoniac in jar. Fill jar one-half full of water and stir thoroughly, then insert the carbon element.

NOTICE.

The battery should be kept in a dry, cool place. It requires very little attention, excepting an occasional addition of water to supply the loss by evaporation. BE CAREFUL WHEN ADDING SAL-AMMONIAC AND WATER THAT TOP OF CARBON ELEMENT IS KEPT DRY AND CLEAN.

WESTERN ELECTRIC COMPANY
259 S. CLINTON STREET
CHICAGO
57-67 BETHUNE STREET
NEW YORK

Form 435 A

Jensen-Thomas Apparatus Collection

Figure 53. A circa 1909 (4" x 4" x 7") jar form of the wet Leclanché cell made by Western Electric of Chicago. Compare with figure 28. The choice of the name "Economy Carbon Battery" invites confusion with the better known Bunsen carbon cell.

Figure 54. The cell in figure 53 shown from the back so as to reveal the hollow molded cylindrical MnO_2/C cathode with the Zn rod anode in the center.

Jensen-Thomas Apparatus Collection

Jensen-Thomas Apparatus Collection

Figure 55. A circa 1960 (2.5” x 2.5” x 3.75”) EVEREADY 1.5 V *Radio “A” Battery*, though it is technically not a battery at all since it is composed of a single Leclanché dry cell.

Figure 56. Two circa 1960 (1.25” x 2.75” x 3.5”) 67.5 V EVERREADY battery packs each composed of forty-five small 1.5 V “flat” Leclanché dry cells.

Jensen-Thomas Apparatus Collection

Jensen-Thomas Apparatus Collection

Figure 57. A circa 1960 (1.75” x 3” x 4.75”) RCA 45 V battery pack composed of thirty small 1.5 V Leclanché “flat” dry cells.

Jensen-Thomas Apparatus Collection

Figure 58. A cylindrical (6” x 12.5”), half gallon, ceramic Edison-Lalande cell. The embossed printing on the ceramic lid reads “Edison Lalande Battery, Patented June 17, 1890. Other Patents Applied For.” The central plate is the Cu/CuO cathode and those on either side are the Zn anodes. Compare with figure 32.

Jensen-Thomas Apparatus Collection

Figure 59. The final commercial version of a single (2.5” x 5” x 8.5”) cell for Edison’s nickel-iron alkaline storage battery with the case partially cut away to reveal the interior. The nine interleaved plates are not separate cells but are rather a way of increasing electrode surface area. Compare with figure 34.

Jensen-Thomas Apparatus Collection

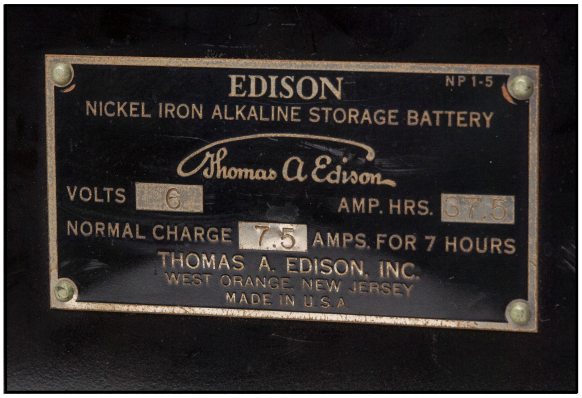


Figure 60. (Above): An almost pristine (6.5” x 10” x 17”) five-cell battery pack of Edison nickel-iron storage cells ready for installation in an electric car. (Right): A closeup of the plate on the battery pack. This indicates a total EMF of only 6 V, suggesting that each cell provides only 1.2 V under load instead of the optimal value of 1.6 V reported earlier.

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Figure 61. Circa 1920 (3” x 3.5” x 5”) exposed Weston cells. The Hg cathode is on the right and the Cd amalgam anode on the left. Compare with figure 38.

Jensen-Thomas Apparatus Collection

Figure 62. A circa 1920 (2.75” x 4.25” x 7.25”) Weston cell in a Bakelite case made by the Eppley Laboratory of Newport RI. Compare with figure 38.

Jensen-Thomas Apparatus Collection

Figure 63. Circa 1940 “student” grade (1.25” x 3” x 5.25”) Weston cells in Bakelite cases made by the Eppley Laboratory of Newport RI.

Jensen-Thomas Apparatus Collection

Figure 64. Circa 1940 precision grade (4” x 4” x 5”) Weston cells in Bakelite cases made by the Eppley Laboratory of Newport RI.

The Voltaic Cell's Significance in the History of Chemistry

The practical everyday impact of the voltaic cell is apparent to anyone familiar with today's plethora of battery-driven devices, be they laptop computers and tablets, CD players and cell phones, or cordless drills and weed whackers. Our intent here, however, is not to describe this ever-escalating technological aspect, but rather to briefly outline the impact of the voltaic cell on the internal conceptual development of chemistry itself.[50]

As we have seen, Volta, whose invention of the pile had shown that living tissue was not required for the generation of electricity, believed instead that it was due to the contact of the dissimilar metals used in its construction. Indeed, he had studied the phenomenon of contact potentials for sometime before constructing his pile and had succeeded in qualitatively arranging the common metals on a linear scale, such that the further apart two metals were on the scale, the greater the contact potential when they were made to touch to one another. Volta's contact theory precluded a chemical rationale of the pile's EMF. However, as early as 1798, the German chemist, Johann Wilhelm Ritter, (figure 65), had observed that there was a correlation between the positions of various metals on Volta's contact potential scale and their relative chemical affinities for oxygen:[51]

The [galvanic] actions produced by two different metals are proportional to their affinity for oxygen.

and he even hinted, albeit rather obliquely, that chemical change and galvanism might well be one and the same:[51]

Yes – and here I dare to say something about which I eventually hope to convince

Figure 65. Johann Wilhelm Ritter (1776-1810).

my readers completely during the course of my observations – the phenomena of galvanism might very well belong to the same class as those of chemistry.

Figure 66. Sir Humphry Davy (1778-1829).

In 1800, shortly after Volta's announcement of his discovery of the voltaic pile, William Nicholson and Anthony Carlisle reported on its ability to decompose water,[52] and William Cruckshank on its ability to decompose aqueous solutions of various salts, acids, and alkalis.[53] In addition to the question of the origin of the pile's electromotive force, these results now raised the further question of the underlying mechanism by which the pile's electric current was able to chemically decompose or *electrolyze* various liquids and solutions.

Not unexpectedly, these results initiated a flurry of electrochemical experimentation and speculation among British and European chemists during the first two decades of the century, and at least a half dozen different chemists proposed their own speculative theories of electrolysis and the relationship between electricity and chemical affinity – the most influential of which were those of Sir Humphry Davy in England (figure 66) and of Jöns Jacob Berzelius in Sweden (figure 67). Though both men accepted Ritter's hint that the driving force of the pile was the result of a chemical reaction between its various components, and also assumed that there was a correlation between the chemical affinities of the various solution components and their ease of electrolysis, there were significant differences in how they viewed the underlying molecular mechanisms.

Davy, who threw out alternative hypotheses in rapid succession and whose true position is often difficult to determine, can be interpreted in some cases (1807,

Figure 67. Jöns Jacob Berzelius (1779-1848).

1812) as having suggested that chemical affinity was the result of electrical attractions between opposite charges induced on the atoms when they came into physical contact, and that electrolytic decomposition was the result of the charged atoms or particles being more strongly attracted to the charged poles of the electrolysis cell than to each other:[54, 55]

In the present state of our knowledge, it would be useless to speculate on the remote cause of the electrical energy, or the reason why different bodies after being brought into contact should be found differently electrified; its relation to chemical affinity is, however, sufficiently evident. May it not be identical with it, and an essential property of matter? The coated glass plates of Beccaria strongly adhere to each other when oppositely charged, and retain their charges on being separated. This fact affords a distinct analogy to the subject; different particles on combining must still be supposed to preserve their particular states of energy [i.e. their electrical charges].

Berzelius, on the other hand, assumed that the atoms and molecules of matter already contained unequal amounts of positive and negative electrical fluid prior to combining and that these were concentrated at opposite poles on their particles. Particles attracted to the negative wire during electrolysis had an excess of positive over negative fluid whereas those attracted to the positive wire had an excess of negative over positive fluid. When atoms combined to form molecules, their oppositely charged electrical fluids reacted with one another to form free caloric (i.e. heat) and the residual unneutralized electrical fluids then redistributed themselves at opposite poles of the product molecules:[56]

> *... in all chemical combinations there is a neutralization of opposing electricities, and this neutralization produces fire in the same manner that it produces it in the discharge of the electric jar, the electric pile, and thunder, without being accompanied in these latter phenomena, by chemical combination.*

In other words, the electrical charges, which were destroyed on combination, accounted not for the bonding between the particles, as in Davy's theory, but rather for the heat that was evolved when they reacted. Electrolysis reversed compound formation by restoring the electrical fluids to the levels found in the atoms prior to combination.[57] Thus, in contrast to the summary accounts appearing in many histories of chemistry, Berzelius' dualistic theory was neither an electrical theory of chemical bonding nor an imperfect anticipation of the later ionic theory, but rather an electrical theory of heats of reaction.

Berzelius took the excess of negative over positive fluid to be a measure of a given atom's "unipolarity" or "electronegativity" (1811) and, following the earlier work of Avogadro (1809), attempted to arrange all of the then known chemical elements in a continuous "electrochemical" series, with the most electronegative (oxygen) at the top and the most electropositive (potassium) at the bottom. This was in many ways a relic of the affinity tables popular in the 18th century, since the resulting electronegativity scale was, in effect, measuring the relative affinities of the various atoms for the two electrical fluids. According to Berzelius, the greater the difference in the electronegativities of the reacting atoms, the greater their chemical affinity and the greater the heat evolution produced when their oppositely charged fluids combined. Though these assumptions implied a direct correlation between affinity and heats of reaction, Berzelius never quantitatively followed up their thermochemical implications. Instead, he applied his theory to the classification and naming of chemical compounds and to establishing restrictions on what atoms and groups could displace one another in chemical reactions.

Figure 68. Michael Faraday (1791-1867). Note the trough battery to his immediate right.

Our modern electrochemical vocabulary (ion, cation, anion, electrode, cathode, anode, electrolyte, etc.) is largely due to Michael Faraday (figure 68), whose extensive electrochemical studies in the period 1833-1840 uncovered the first quantitative laws of electrochemical action and did much to disentangle which chemical effects were dependent on the current and which were dependent on the voltage – issues that were thoroughly confused by Berzelius.

First stated nonmathematically by Faraday in 1834, and independently by the Italian chemist, Carlo Matteucci, in 1835, his "law of definite electrochemical action" has traditionally been broken into two separate verbal laws:[58]

a. The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.

b. The masses of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights.

but is (assuming the current to be constant), usually written today in the form of a single equation:

$it = zFN$

in which i is the electrical current, t is the time, N is the moles of product formed or reactant consumed, z is the moles of electrons required per mole or product or reactant, and F is the number of coulombs per mole of electrons. Often referred to incorrectly as Faraday's law(s) of electrolysis, it is important to realize that the above equation applies to voltaic cells as well as electrolysis cells, in which case i is the current produced rather than consumed during operation.

The increasing inability of Berzelius' theory to account for the facts of organic chemistry led to a decline in electrochemical speculations among chemists in the period 1840-1880, and much of the work in the field during this period was done instead by physicists – most notably by the Germans, Wilhelm Hittorf and Friedrich Kohlrausch, who developed and refined the measurement of ionic conductivities. Despite these advances, however, two major questions continued to haunt 19th-century electrochemistry:

a. What did the ions responsible for electrolyte conductivity correspond to at the molecular level and were they created by the applied voltage in the electrolysis cell or did they preexist in the electrolyte before the voltage was applied?

b. What was the mechanism by which the electrodes were provided with a continuous supply of ions during the operation of a voltaic cell or during course of the electrolysis?

The answer to the first of these questions changed with time. During the first half of the century it was generally assumed that the cation and anion corresponded to the electropositive and electronegative oxides of the dualistic system, in which copper sulfate, for example, was represented as CuO^+, SO_3^-. However, in the period 1839-1844 the English chemist, John Daniell,[59] presented electrochemical evidence suggesting that Cu^{2+} and SO_4^{2-} were the true ionic components and, after the rise of type theory and structure theory in the period 1855-1865, this became the common mode of representation. Though assumed to preexist within the electrolyte molecules prior to electrolysis, in neither case were the ions assumed to be free or dissociated prior to the application of the cell voltage.

During the first half of the century, the answer to the second of these questions was based on the so-called "chain theory" of electrolysis, first proposed by the German chemist, Theodore von Grotthuss, in 1805 – a theory which illustrates how difficult it was to imagine a viable molecular reaction mechanism within the context of the static Newtonian model of solids, liquids, and gases popular at the time in which heat was an imponderable fluid rather than an intrinsic molecular motion and matter moved only when the static equilibrium of contenting forces was disrupted and then only far enough to reestablish that equilibrium.[60]

According to Grotthuss, the molecules of the solute (AB) were polarized into positive and negative parts (A^+B^-) by the applied voltage of the electrolysis cell. This applied voltage also caused the polarized molecules to aligned themselves in a continuous chain between the positive and negative electrodes, with the positive ends of the molecules pointing toward the negative electrode and the negative ends of the molecules pointing towards the positive electrode:

(-) electrode: A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- :(+) electrode

The (+) end of the molecule closest to the negative electrode and the (-) end of the molecule closest to the positive electrode then gave up their electrical fluids to the electrodes in question thereby forming neutral reaction products which escaped from the solution:

(-) electrode: A B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+B^- A^+ B :(+) electrode

The remaining halves of these molecules than reacted with the adjacent molecules in the chain causing an exchange of the (+) and (-) parts which propagated down the chain, thus creating a new chain in which the (+) and (-) parts were reversed with regard to the wires:

(-) electrode: B^-A^+ B^-A^+ B^-A^+ B^-A^+ B^-A^+ B^-A^+ :(+) electrode

Figure 69. Svante Arrhenius (1859-1927).

These new molecules then rotated in order to realign their (+) and (-) ends with the oppositely charged electrodes and the entire process repeated itself. Presumably the continuous insertion into the chain of fresh molecules from the surrounding solution allowed it to maintain the proper length as the electrolysis proceeded.

It was not until 1857 that Clausius finally replaced this intrinsically implausible mechanism by applying the new kinetic theory of matter to the phenomenon of electrolysis.[61] He pointed out that the fluctuations in the kinetic energies of the randomly colliding electrolyte molecules would occasionally result in their dissociation into free ions, and that collision of these free ions with other neutral electrolyte molecules would lead to ion displacement and thus to a net random movement of the ions through the solution. Eventually, however, oppositely charged ions would collide with one another and recombine to once again form a neutral electrolyte molecule. In other words, in an electrolyte solution at a given temperature there was a dynamic equilibrium which maintained a small but characteristic population of free ions. Application of a voltage to an electrolysis cell did not create the free ions, rather it caused a net drift of the randomly colliding ions in the direction of the oppositely charged electrodes.

The work of Svante Arrhenius (figure 69) in 1887 revealed that the molar conductivities of most electrolyte solutions increased with dilution, suggesting that the degree of ionic dissociation (defined as the molar conductivity at the concentration in question, divided by the molar conductivity at infinite dilution) also increased – a result in keeping with Clausius' dynamic model of free ion formation, but one that led to the shocking conclusion that, in very dilute solutions, not just a few, but virtually all of the electrolyte molecules were dissociated into free ions. Arrhenius showed that the degrees of ionic dissociation calculated from his conductivity studies correlated with both those calculated from van't Hoff's recently proposed theory of osmotic pressure and those calculated from Raoult's law for freezing point depression.[62, 63] Yet additional evidence for free ions was provided by the additive nature of the heats of neutralization, specific volumes, conductivities, and molar refractivities of salt solutions. The full implications of the resulting "theory of ionic dissociation," as it came to be called, for the law of mass action and for the traditional methods of wet chemical analysis were worked out by Ostwald in his 1894 textbook, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, where he explicitly pointed out the necessity, in the writing of rate laws and equilibrium constants for electrolyte systems, of treating each ion as an independent species.

With the discovery of the law of conservation of energy in the 1840s it became apparent that voltaic cells and electrolysis cells were devices for the mutual interconversion of chemical energy and electrical energy:

chemical energy ↔ *electrical energy*

and by the 1850s the flawed molecular models of Davy and Berzelius had been replaced by the proposition that the chemical affinity of the reaction in an electrochemical cell correlated in some manner with the cell's electrical potential. Thermodynamic treatments of cell potentials by Helmholtz (1847)[64] and Lord Kelvin (1851),[65] based on the first law of thermodynamics, further suggested that this potential difference ($\mathcal{E}$) should also correlate with the heat or enthalpy (ΔH) of the cell reaction:

$$\mathcal{E} = f(\Delta H)$$

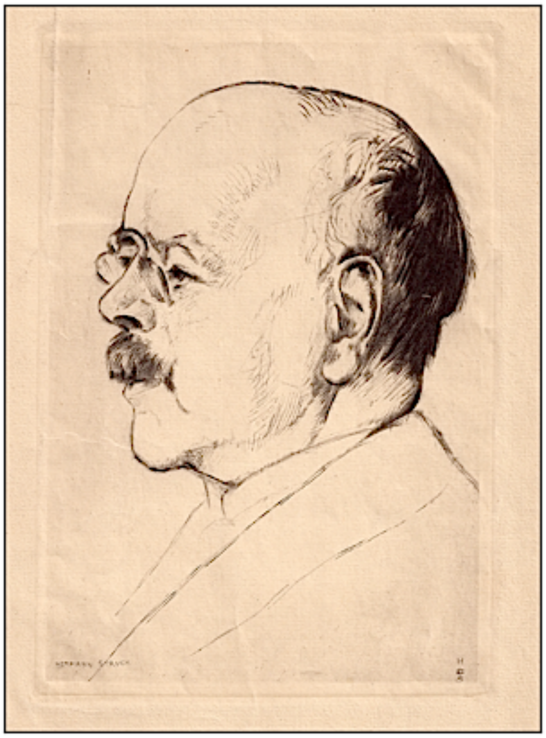

Figure 70. Walther Nernst (1864-1941).

However, experimental work by, among others, Raoult in 1865 and Favre in the period 1866-1871 showed that this was incorrect and, in the last quarter of the century, fresh thermodynamic treatments (Gibbs 1878,[66] Helmholtz 1882,[67] van't Hoff 1884[68]) based on the second law, rather than the first law, revealed that cell potentials should instead correlate with the free-energy change (ΔG) or *Arbeit* of the chemical reaction, a result now written as:

$$-zF\mathcal{E} = \Delta G$$

Since ΔG would soon become the accepted thermodynamic measure of chemical affinity, we see in this equation the quantitative fulfillment of the correlation between cell potentials, on the one hand, and chemical affinities, on the other, that had been assumed by most electrochemists since the work of Ritter at the end of the 18th century. In keeping with this, the above equation, as well as the corresponding equation for the temperature dependence of the cell potential which allows calculation of the corresponding entropy change (ΔS) for the cell reaction:

$$zF(d\mathcal{E}/dT) = \Delta S$$

were extensively used by G. N. Lewis and his associates in the early decades of the 20th century to calculate the first tables of free energy and entropy values.[69, 70]

A final refinement was provided by Walther Nernst (figure 70) in the period 1888-1889 when he related the cell potential to the osmotic pressures of the cell reactants and ultimately to the equilibrium constant of the cell reaction itself, a result now written as:[71, 72]

$$\mathcal{E} = -\Delta G/zF = \mathcal{E}^\circ - (RT/zF)\ln Q$$

The quantification of redox potentials based on half-cell reactions at inert electrodes was first undertaken by the American physical chemist, Wilder D. Bancroft, in 1892,[73] though he failed to find the concentration dependency predicted by Nernst. In 1897 Nernst further suggested the use of the hydrogen electrode as the zero-point standard for reporting cell potentials.[74] This proposal was experimentally implemented by Wilsmore in 1900,[75] who determined the hydrogen-scale half-cell potentials for 31 elements, and was also adopted by the first reference work dealing with the tabulation of cell potentials, the 1911 publication, *Messungen elektromotorischer Kräfte galvanischer Ketter mit wässerigen Elektrolyten*, edited by Abegg, Auerbach and Luther.

Thus we see that, by the end of the 19th century, chemists had discovered both the fundamental law governing the relation between current consumption and/or production and the amount of chemical reaction in an electrochemical cell, as well as the law governing the correlation between cell potential and thermodynamic chemical affinity. Though beyond the period covered in this booklet, the 20th century would also see the development of a kinetic theory of electrode processes, as well as many advances in the design of new voltaic cells, including mercury cells, cadmium cells, and lithium cells.[76]

References and Notes

1. Given the fact that Galvani, in contrast to Volta, never constructed a true physical device for the generation of DC current, it is rather ahistorical to name such devices after him and we have consequently chosen to use the term voltaic cell rather than galvanic cell. The historically neutral term “electrochemical cell” is also often used but, strictly speaking, this term should also include electrolysis cells as well as voltaic cells.

2. For drawings of typical late 18th-century electrostatic generators, see the plates to J. Priestley, *The History and Present State of Electricity, with Original Experiments*, 2 Vols., Bathurst et al: London, 1775.

3. L. Galvani, *De viribus electricitatis in motu musculari commentarius*, Instituti Scientiarum: Bologna, 1791. English translation available as L. Galvani, *Commentary on the Effect of Electricity on Muscular Motion*, Licht: Cambridge, MA, 1953.

4. A. Volta, "On the Electricity Excited by Mere Contact of Conducting Substances of Different Kinds," *Phil. Trans. Roy. Soc.*, **1800**, *90(2)*, 403-431. Though the title is in English, the original text was in French. An English translation is given in B. Dibner, *Alessandro Volta and the Electric Battery*, Watts: New York, NY, 1964, Appendix A.

5. J. L. Heilbron, "Volta's Path to the Battery," in G. Dubpernall, J. H. Westbrook, Eds., *Selected Topics in the History of Electrochemistry*, Electrochemical Society: Princeton, NY, 1978, pp. 39-67.

6. For a revisionist account of the Galvani-Volta debate see M. Pera, *The Ambiguous Frog: The Galvani-Volta Controversy on Animal Electricity*, Princeton University Press: Princeton, NJ, 1992.

7. For the history of the debate between the proponents of the contact theory of the voltaic cell and the proponents of the chemical theory, see reference 50, Vol. 1, Chapter 12.

8. L. H. Fisher, R. N. Varney, "Contact Potentials Between Metals: History, Concepts, and Persistent Misconceptions," *Am. J. Phys.*, **1976**, *44*, 461-475.

9. S. Ross, "The Story of the Volta Potential," in G. Dubpernell, J. H. Westbrook, Eds., *Selected Topics in the History of Electrochemistry*, Electrochemical Society: Princeton, NJ, 1978, pp. 257-278.

10. For an example of a modern zinc-air battery based on a Zn(s)/NaCl(aq)/Cu(s) cell, see the website: http://sci-toys.com/scitoys/scitoys/echem/batteries/batteries.html

11. P. Benjamin, *The Voltaic Cell: Its Construction and Capacity*, Wiley: New York, NY, 1893.

12. For biographical background on Daniell, see A. Thackray, "John Frederic Daniell," in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Vol. 3, Schribners: New York, NY, 1970-1990, pp. 556-558.

13. J. F. Daniell, "On Voltaic Combinations," *Phil. Trans. Roy. Soc.*, **1836**, *126*, 107-124.

14. An earlier two-fluid cell was described by Becquerel but was not commercially viable. Interestingly this cell was described by Jules Verne in his 1874 novel, *The Mysterious Island*. See "Captain Nemo's Battery and the Science Fiction of Jules Verne," in W. B. Jensen, *Captain Nemo's Battery: Assorted Chemical Annotations on Science Fiction and Literature*, The Epicurean Press, Cincinnati, OH, 2013, pp. 10-19.

15. Reference 11, pp. 195-226.

16. H. Meidinger, "Ueber eine völlig constante galvanische Batterie," *Pogg. Ann. Physik*, **1859**, *184*, 602-610.

17. Thus the historical account in G. W. Vinal, *Primary Batteries*, Wiley: New York, NY, 1950 mentions the names of Varley, Callaud, and Meidinger in this regard but with insufficient information to evaluate the accuracy of the claims.

18. Reference 17, p. 235. See also R. F. Schallenberg, "Batteries Used for Power Generation During the Nineteenth Century," in G. Dubpernell, J. H. Westbrook, Eds., *Selected Topics in the History of Electrochemistry*, Electrochemical Society: Princeton, NJ, 1978, pp. 341-359.

19. For biographical background on Grove see J. G. Crowther, *Statesmen of Science*, Cresset Press: London, 1965, pp. 77-101, and E. L. Scott, "William Robert Grove," in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Vol. 5, Schribners: New York, NY, 1970-1990, pp. 559-561.

20. W. R. Grove, "On a New Voltaic Combination," *Phil. Mag.*, **1839**, *14 (3rd series)*, 388-390; "On a Small Voltaic Battery of Great Energy," *Ibid.,* **1839**, *15 (3rd series)*, 287-293.

21. W. B. Jensen, "The Chemical Uses of Clay Tobacco Pipes," *Museum Notes*, September/October 2011, Oesper Website.

22. For biographical background on Bunsen, see G. Lockemann, *Robert Wilhelm Bunsen*, Wissenschaftliche Verlagsgesellschaft: Stuttgart, 1949.

23. R. W. Bunsen, "Ueber die Anwendung der Kohle zu Volta'schen Batterien," *Pogg. Ann. Physik*, **1841**, *54 (2nd series)*, 417-430; "Ueber Bereitung einer das Platin in der Grove'schen Kette ersetzenden Kohle," *Ibid.*, **1842**, *55 (2nd series)*, 265-276.

24. B. Silliman, Jr., "On the Use of Carbon in Grove's Battery," *Am. J. Sci.*, **1842**, *43*, 393; "Description of a Carbon Voltaic Battery," *Ibid.*, **1843**, *44*, 180-186.

25. J. Stock, "Bunsen's Batteries and the Electric Arc," *J. Chem. Educ.*, **1995**, *72*, 99-102. Also reference 18.

26. For biographical background on Warington, see C. Hamlin, "Robert Warington (1807-1867)," *Oxford Dictionary of National Biograph*y, Oxford University Press: New York, NY, 2004.

27. For biographical background on Poggendorff, see F. Klemm, "Johann Christian Poggendorff" in C. C. Gillispie, Ed., *Dictionary of Scientific Biography,* Vol. 11, Schribners: New York, NY, 1970-1990, pp. 49-51.

28. The chemistry of the sulfuric acid/potassium dichromate mixture is actually quite complex. In addition to $H_2(CrO_4)$, it may contain such chromium species as $H_2(Cr_2O_7)$ and CrO_3. In all three of these species, however, Cr maintains an oxidation state of VI.

29. R. Warrington, "On the Employment of Chromic Acid as an Agent in Voltaic Arrangements," *Phil. Mag.*, **1842**, *20 (3rd series)*, 393-395.

30. J. Poggendorff, "Ueber die mit Chromsäure construirten galvanischen Ketten," *Pogg. Ann. Physik*, **1842**, *57 (2nd series)*, 101-111.

31. E. Grenet Jr. "Improved Galvanic Battery," United States Patent No. 25503, 20 September, 1859. Though a chromic acid battery, the device described in this patent is not the table-top bottle form of the Grenet cell and calls into question the 1859 date often cited for its invention.

32. *Catalogue of Chemical & Scientific Apparatus*, Townson & Mercer: London, 1901, p. 572..

33. G. Planté, "Nouvelle pile secondaire d'une grande puissance," *Compt. rend.*, **1860**, *50*, 640-642. Also G. Planté, *The Storage of Electrical Energy*, Whittaker: London, 1887.

34. I have been unable to locate a citation of Faure's original 1881 patent.

35. E. Reynier, *The Voltaic Accumulato*r, Spon: London, 1889.

36. For a detailed history of the development of the storage battery, see R. H. Schallenberg, *Bottled Energy: Electrical Engineering and the Evolution of Chemical Energy Storage*, American Philosophical Society: Philadelphia, PA, 1982.

37. I have been unable to locate a detailed biographical account for Leclanché.

38. G. Leclanché, "Une pile à oxyde insoluble," *Brevet d'invention*, No. 71865, 8 June 1866. I would like to thank Dr. Bastian Rapp of the Karlsruhe Institute of Technology for bringing this document to my attention.

39. Reference 17, pp. 32-33.

40. Thus the 1901 edition of *Catalogue of Chemical & Scientific Apparatus*, Townson & Mercer: London, 1901 lists seven brands of dry cells for sale, in as many different sizes and varieties, whereas the 1894 edition lists none.

41. F. de Lalande, G. Chaperon, "Nouvelle pile à oxyde de cuivre," *Compt. rend.*, **1883**, *97*, 164-166; F. de Lalande, "Nouveaux modèles de pile à oxyde de cuivre," *Ibid.*, **1891**, *112*, 1253-1256.

42 B. Vanderbilt, *Thomas Edison, Chemist*, American Chemical Society: Washington, DC, 1971, Chapter 7.

43. In the case of commercial electric vehicles, the battery array did not remain in the vehicle itself while it was being recharged. Rather the array was exchanged for a fully charged array so the vehicle could be quickly put back into service and the depleted array set on the shelf for overnight recharging.

44. For an excellent study of the economic and social factors contributing to the demise of the original electric car, see M. B. Schiffer, C. T. Butts, K. K. Grimm, *Taking Charge: The Electric Automobile in America*, Smithsonian Institution Press: Washington, DC, 1994.

45. W. J. Hamer, "The History and Uniqueness of Standard Cells," in G. Dubpernall, J. H. Westbrook, Eds., *Selected Topics in the History of Electrochemistry*, Electrochemical Society: Princeton, NY, 1978, pp. 279-293.

46. L. Clark, "On a Voltaic Standard of Electromotive Force," *Proc. Roy. Soc.*, **1872**, *20*, 444-448. Also L. Clark, "On a Standard Voltaic Battery," *Phil. Trans. Roy. Soc.*, **1874**, *164*, 1-14.

47. E. Weston, German Patent 75,194, 08 June, 1892; British Patent 22,482,06 February 1892; United States Patent 494,827, 04 April 1893.

48. Reference 17, pp. 168-169.

49. *Laboratory Apparatus and Reagents*, Arthur H. Thomas Co: Philadelphia, PA, 1921, p. 247.

50. The most thorough history of 18th- and 19th-century academic electrochemistry is still W. Ostwald, *Elektrochemie: Ihre Geschichte und Lehre*, Veit: Leipzig, 1896. This is available in English translation as W. Ostwald, *Electrochemistry: History and Theory*, 2 Vols., Smithsonian: Washington, DC, 1980. For much more concise and up to date accounts, see L. Dunsch, *Geschichte der Elekrochemie: Ein Abriss*, VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1985 and P. Bianco, *De la pile du Volta à la conquete de l'espace: Deux siècles d'électrochimie (1799-1999)*, Université de Provence: Provence, 1998.

51. J. W. Ritter, *Beweis dass ein beständiger Galvanismus den Lebenprocess den Tierreich begeite*, Weimar: 1798, pp. 70, 81. See also W. D. Wetzels, "J. W. Ritter: The Beginnings of Electrochemistry in Germany," in G. Dubpernall, J. H. Westbrook, Eds., *Selected Topics in the History of Electrochemistry*, Electrochemical Society: Princeton, NY, 1978, pp. 68-73.

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