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Energy on demand:
A brief history of the development of the battery

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Abstract. Portable, readily available electrical energy provided by batteries is ubiquitous in modern society and can easily be taken for granted. From the early Voltaic piles to modern lithium ion cells, batteries have been powering scientific and technological advancement for over two centuries. A survey of select notable developments leading to modern batteries commercially available today are presented, with emphasis on early technologies and also including some of the advancements made within the last few decades. A brief discussion of the chemistry utilized by battery technology is also included.

Keywords. Battery, electrochemical cell, Voltaic pile, Daniell cell.

INTRODUCTION

In the modern industrialized world, it can be difficult to imagine life without ready access to on-demand electricity. Massive electrical infrastructures have been built allowing for safe, reliable, and constant delivery of electrical energy to households, businesses, and industrial complexes throughout much of the globe. By 1950, electric power consumption in the United States was reported at 291 billion kilowatt hours.[1] By the mid 1990's usage topped 3,000 billion kilowatt hours, and demand has continued to increase with consumption of 3,946 billion kilowatt hours reported for 2018, the bulk of which is split between residential (37%) and commercial (35%) usage.[1]

While this infrastructure effectively provides fixed access to electrical energy within relatively easy reach in homes, workplaces, and other locations, batteries are used as a source of power for a myriad of devices. From cell phones to flashlights, wall clocks to children's toys, more and more electronic devices utilize battery power. Medical devices, whether implanted such as a pacemaker or external like an insulin pump, also require lightweight mobile power sources, as do fully electric automobiles on an even larger scale.

With a ready supply of electrical energy ubiquitous in industrialized society, it can be easy to take this valuable resource for granted without consideration for the process by which the development of the battery occurred,

or the technological advancements that followed. A complete and exhaustive accounting of all these advances would be an undertaking beyond the scope of this work and may well be out-of-date prior to publication, as work currently continues to design and produce smaller, lighter, and longer lasting batteries for mobile electronics. As such, this work will focus on the earliest battery developments as well as the more significant general developments within the past several decades.
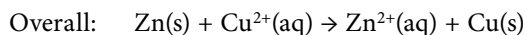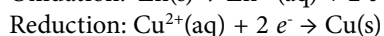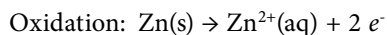
THE ELECTROCHEMICAL CELL

The term "battery" has several different meanings which may at first glance appear unrelated.[2] The common thread within these varied definitions is the reference to multiple parts working in concert, whether artillery pieces, a pitcher and a catcher in baseball, or a collection of electrochemical cells. Benjamin Franklin is attributed with one of the first uses of the term "Electrical Battery", included in a letter describing his work with static electricity using Leyden jars to English naturalist Peter Collinson in 1749:

> *Upon this We made what we call'd an Electric Battery, consisting of eleven Panes of large Sash Glass, arm'd with thin leaden Plates,…with Hooks of thick Leaden Wire one from each Side standing upright, distant from each other; and convenient Communications of Wire and Chain from the giving Side of one Pane to the receiving Side of the other; that so the whole might be charg'd together, and with the same Labour as one single Pane;…[3]*

Over time, the term "battery" has come to refer to both a collection of connected electrochemical cells and a single working cell, and will be generally used without specificity throughout this work.[4]

Batteries produce electrical energy through oxidation-reduction (redox) processes, wherein one substance loses electrons through oxidation while another substance gains electrons through reduction. It is sometimes convenient to examine the oxidation and reduction processes independently as half reactions, an example of which is shown below. However, it is important to note that oxidation cannot occur without a corresponding reduction process also occurring and vice versa, although the two processes do not necessarily need to occur at the same physical location.

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$
Reduction: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

In simple electrochemical cells (Figure 1), these processes occur at the surface of electronic conductors, termed electrodes. These electrodes may be composed of a redox-active material or more electrochemically inert materials such as platinum, mercury, gold, or graphite.[5] Oxidation occurs at the anode, while the reduction process occurs at the cathode. Between the electrodes is an electrolyte, an ionic conductor necessary to reduce polarization and allow current to flow. Wire or another electrically conducting material connects the two electrodes to a load, completing the circuit, allowing the battery to discharge and work to be done. The overall system must remain charge-neutral in order to continue functioning. If a build up of charge occurs, polarization results and the electric current is reduced and ultimately stopped completely.

Batteries are often classified as either primary or secondary batteries. In both cases, chemical potential energy is converted to electrical energy. For primary batteries, the chemical reactants are consumed in a process which is not easily reversible, resulting in a battery which can only be discharged a single time. Examples of primary batteries include common alkaline batteries, silver button cells and watch batteries, and the homemade "lemon battery" consisting of pieces of iron and copper stuck into the flesh of the acidic citrus fruit.

Secondary batteries also convert chemical potential energy to electrical energy, but do so through reversible chemical process which render the resulting battery rechargeable. Application of electrical energy from an external source such as a generator or another battery can regenerate the initial chemical reactants, restoring the battery's charge and allowing repeated charge/discharge cycles. Because of this ability to store energy, these types of cells are also known as "storage batteries". Common examples of storage batteries include lead-acid
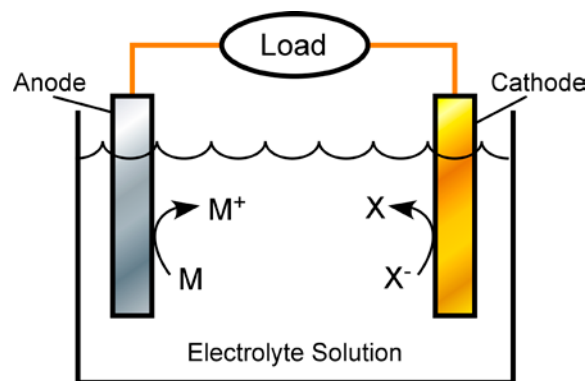

Figure 1. A simple electrochemical cell.

batteries used in most automobiles and lithium-ion batteries found in mobile consumer electronics.

THE VOLTAIC PILE

Prior to 1800, studies of electricity were limited to what could be achieved through collection and discharge of static electricity.[6–8] While arcs with rather large voltages could be achieved, their application was limited by the small current and extremely short duration of the discharge.[6] Despite this limitation, the study of electrical phenomenon spanned from attempts to split water through electrolysis, to studies with frogs predating Luigi Galvani's well-known work, to Franklin's famous lightning experiments.[9–13]

In March of 1800, Alessandro Volta (Figure 2), professor of natural philosophy at the University of Pavia in Lombardy, Italy, in a correspondence to Joseph Banks, President of the Royal Society of London, described a device which could provide a continuous supply of electrical power.[8,14] This apparatus (Figure 3), later known as the "Voltaic Pile" consisted of discs of tin or zinc paired with discs of copper, brass, or silver, with layers of water-soaked paper, fiber board, or leather between the disc pairs. Wire contacts with the discs on the top and bottom of the pile allowed the experimenter access to a constant electric current. Also included was a description of what Volta termed

a "crown of cups", a series of what would modernly be described as simple wet cells.[14]

Discharging Volta's pile resulted in visible corrosion occurring on the zinc (or tin) discs, the result of oxidation of the anode. A slight corrosion was also sometimes noted on the silver (or copper) cathode discs, but not to the same extent as seen on the anode. At the time this led him to believe the current was solely the result of the anodic reaction. Considering it is now known that oxidation cannot occur without reduction, and with Volta and others noting problematic polarization resulting from bubbles of hydrogen gas adhering to the electrode surfaces, it seems evident that the corresponding reduction process in Volta's pile was the reduction of hydrogen from water, as seen in the overall electrochemical reaction below.

$$Zn_{(s)} + 2H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)}$$
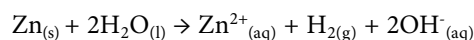
It should be noted that the reduction process is often incorrectly attributed to reduction of the cathode material (half reactions seen below for silver and copper). However, this would require ions of the cathode material to be already present in order to occur. While it is possible some advantageous oxidized cathode material may
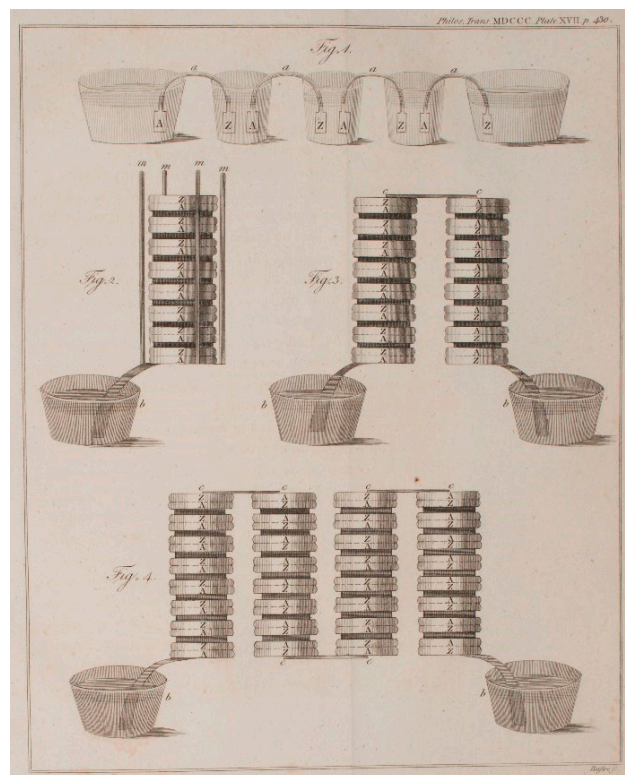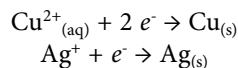

Figure 2. Alessandro Volta (1745-1827) (public domain).

Figure 3. Volta's crown of cups and several piles (public domain).

have been present, it is unlikely there would be enough to support much electric current out of the device.

$$Cu^{2+}_{(aq)} + 2\,e^- \rightarrow Cu_{(s)}$$
$$Ag^+ + e^- \rightarrow Ag_{(s)}$$

Volta's description of his pile was quite complete and its design was elegant yet simple, allowing experimentalists to very quickly build replicas in their laboratories for application to their own work. Volta in this same letter described experiments where he applied the leads from his pile to his lips and tongue, describing the results:

In fact, once the circuit is closed in a convenient manner, one will excite simultaneously...a sensation of light in the eyes, a convulsion on the lips and even in the tongue, a painful prick at the point of the tongue, finally followed by a sensation of taste.[15]

IMPACT OF VOLTA'S PILE

This new development had an almost immediate impact on the study of electricity. Possibly due to hostilities between France and England at the time, Volta sent the first four pages of the letter to Banks in March, with the remainder sent several months later.[8] As a result, Volta's letter was not formally read into the Society until June 26, 1800.[14] However, Banks shared the contents of the first four pages with a number of the members of the Society, allowing them to build devices for their own work prior to the paper's reading. William Nicholson specifically mentions these circumstances in his accounts of this new "electrical or Galvanic apparatus" published in July, 1800, indicating he felt it proper to delay publication of his own work until Volta's entire paper had been read to the Society.[16]

In this same paper, Nicholson describes work he performed with Anthony Carlisle which included the electrolysis of water, with application of electric current for a period of 13 hours to produce 1.17 cubic inches of gas.[16] This was a significant improvement in both yield and efficiency from earlier works using static discharge. For comparison, George Pearson reported collecting one third of a cubic inch of gas utilizing over 14,600 static discharges.[9] While times for that specific experiment are not given by Pearson, based upon times given for other experiments in the same paper, the process likely took approximately 18 hours to complete. Later that same year, Humphry Davy produced isolated hydrogen and oxygen gases from samples of water in separate glasses using a Voltaic pile, completing the circuit through his own body by inserting a finger in each glass of water.[17]

Further advances rapidly followed. Electrodeposition of metals was reported by Nicholson and Carlisle along with William Cruickshank in England, and independently by J.W. Ritter in Bavaria in 1800.[18–20] In 1805, Ritter was reported to have developed a modified pile utilizing a single metal which could be charged, a precursor to the storage battery.[21] Humphry Davy confirmed that charcoal could substituted for the wires connected to the pile (a phenomenon originally reported by Volta), and is reported to have used charcoal to produce impressive sparks as early as 1802.[22] By 1808, Davy had used the Voltaic pile to discover and isolate several of the alkali and alkaline-earth elements, including sodium, potassium, barium, calcium, strontium, and magnesium.[23,24]

EARY IMPROVEMENTS TO THE BATTERY

While undoubtedly a monumental improvement over static discharge collecting devices of the time, the Voltaic pile was not without its imitations. The useful lifetime of the pile was limited, as corrosion of the metal discs, while a necessary result of the chemical processes driving the output, would occur quite rapidly and require the pile to be rebuilt.[25] In addition, polarization of the electrodes would result in a decrease in output over time. Within a year, numerous attempts to improve the Voltaic pile were made. One such modification was the trough battery developed by Cruickshank (Figure 4).[25] A grooved wooden trough was used, with soldered pairs of zinc and silver plates affixed in the grooves with rosin or wax to create a number of sealed chambers. These chambers were then filled with a solution of ammonium nitrate, effectively replacing the wetted paper discs of the pile with a fluid solution. This ensured a more ready supply of electrolyte at the surface of the plates, and allowed the plates to be more easily cleaned as corrosion occurred through treatment with hydrochloric acid solution.[25]

Charles Wilkinson modified Cruickshank's trough battery, using wooden partitions instead of metal plates, and attached wires to separated zinc and copper plates, allowing the plates to be removed at the conclusion of the battery's daily usage while leaving the electrolyte in the trough.[26] Wilkinson had previously noted the power of the device was not related to the contact area between the copper or silver plate and the zinc plate, and proposed an increase in available zinc surface area resulted in increased output.[27] With the zinc and copper plates completely separated, Wilkinson reported his plunge-type device with four inch plates was the equal of a Cruickshank-type trough battery with six inch plates.[26]
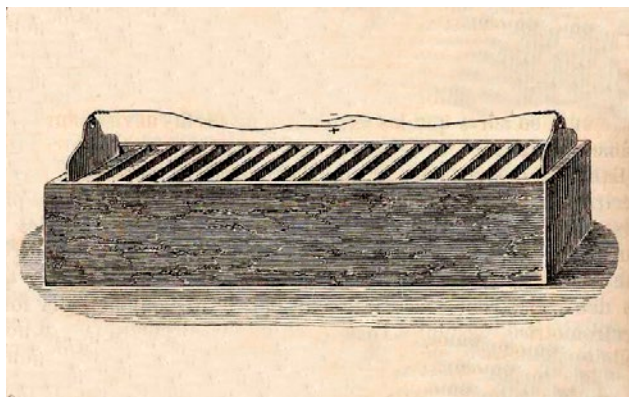
Figure 4. 19th Century illustration of a trough battery (public domain).

As previously mentioned, corrosion of the anode material was recognized to occur during discharge of a battery. However, corrosion would also occur, albeit more slowly, even when the battery was left idle or stored for a period of time. While removal of the anode metal from the electrolyte solution as seen in plunge-type batteries was an effective means to halt this secondary corrosion, the two-fluid cell would prove to be another approach with historical significance.[6]

THE DANIELL CELL

While aspects of a two-fluid cell had previously been described independently by Becquerel and Wach, the successful invention is generally credited to J. Frederic Daniell.[6,28] In letters to Michael Faraday, Daniell describes a cell composed of a copper cylinder with a membrane tube "formed of a part of the gullet of an ox" suspended by collars inside (Figure 5).[29–31] Within the membrane was contained a zinc rod as well as a solution of either sulfuric acid or zinc sulfate, with the copper cylinder filled with a copper(II) sulfate solution. Additionally, a siphon tube was included to allow removal of saturated zinc sulfate solution from the bottom of the membrane tube. Thus, fresh acid and copper(II) sulfate could be added as needed. Later other materials such as paper dividers or porous ceramic were used to separate the two solutions.[6,32,33] The presence of copper ions in the outer solution, and the need to occasionally add copper(II) sulfate to the cell, indicate the reduction reaction for the Daniell cell was not hydrogen reduction as seen in the Voltaic pile and the trough battery, but rather the reduction of copper ion, resulting in the following overall reaction.
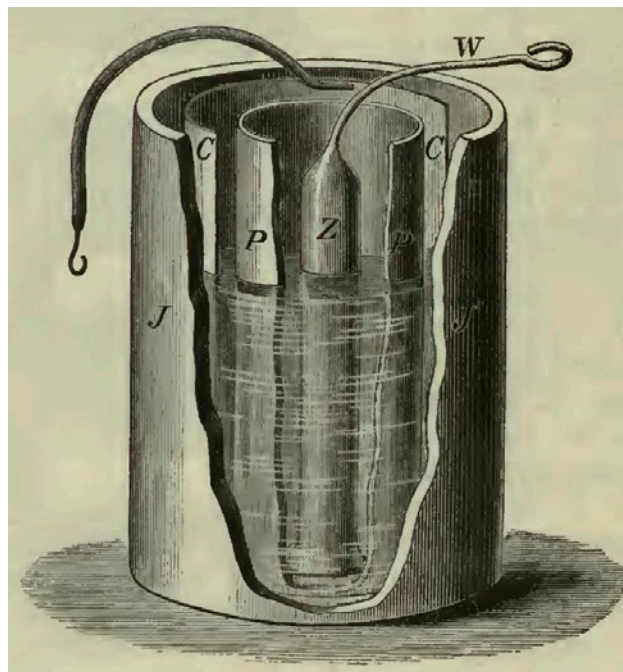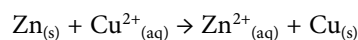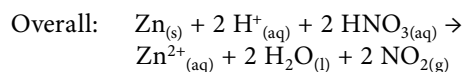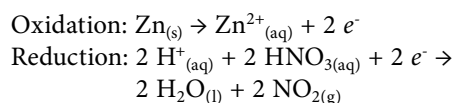
$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Figure 5. A drawing of a Daniell Cell. This later design utilizes a ceramic cell container and paper divider, with copper sheet and zinc rod electrodes.

One particularly noteworthy modification of the Daniell cell was developed by William Grove.[34,35] While investigating the action of a mixture of nitric and hydrochloric (muriatic) acids on gold foil, he discovered connecting the gold foil to an isolated pool of nitric acid via a wire resulted in the dissolution of the gold foil.[34] He also proposed that using nitric acid and an inactive cathode such as platinum in one chamber of a Daniell cell, with a zinc anode in the other, should produce a greater electric current than the standard configuration.[34] While nitric acid had been used as an electrolyte previously, this is believed to be the first time nitric acid was recognized as a cathodic reactant.[6] The half reactions, as well as the combined overall redox reaction, can be seen below.

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^-$
Reduction: $2\ H^+_{(aq)} + 2\ HNO_{3(aq)} + 2\ e^- \rightarrow$
    $2\ H_2O_{(l)} + 2\ NO_{2(g)}$

Overall: $Zn_{(s)} + 2\ H^+_{(aq)} + 2\ HNO_{3(aq)} \rightarrow$
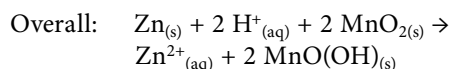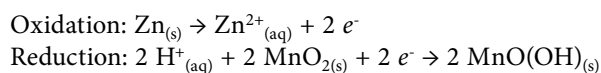 $Zn^{2+}_{(aq)} + 2\ H_2O_{(l)} + 2\ NO_{2(g)}$

Further improvement of the Grove cell occurred through the inclusion of carbon as an inert electrode material.[6] While many investigators, including Volta and Davy, had already explored charcoal and graph-

ite for charge collection or as electrical conductors, it is Robert Bunsen who is commonly credited with initiating its widespread use in batteries.[6] The replacement of the expensive platinum cathode with carbon helped reduce the cost of Grove-type batteries, which undoubtedly increased their usage. However, the disadvantages inherent to the use of nitric acid were still present, particularly the production of noxious nitrogen oxides (NO, N_2O_4). Eventually oxidants other than nitric acid were explored, including chromic acid, permanganate, and chlorates, and modified Grove cells were used for the next several decades for certain applications.[6] However, the greatest value in both the Daniell and Grove cells may have been in laying the groundwork for what would eventually become the modern dry cell battery.

TOWARD THE MODERN DRY CELL

One significant downside to the Cruickshank, Daniell, and Grove batteries, as well as their derivatives, was the need for liquid electrolytes, often times corrosive acid solutions. These solutions resulted in batteries that were quite heavy, prone to spillage if moved, and susceptible to messy leaks. This combination of factors was especially problematic for applications requiring a mobile source of power, such as on railroads, street cars, or eventually for carriage lighting.

A significant step toward a solution to this problem occurred with the design of a cell by Georges Leclanché, patented in France in 1866.[36] The Leclanché cell continued to utilize a zinc rod as the anode, but made use of a porous ceramic pot filled with a mixture of manganese(IV) oxide and carbon with a carbon rod current collector as the cathode (Figure 6). Reduction of the manganese from +4 to +3 occurred at the cathode, and can be seen below.[7] A solution of saturated ammonium chloride was used as the electrolyte.[6]

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^-$
Reduction: $2\ H^+_{(aq)} + 2\ MnO_{2(s)} + 2\ e^- \rightarrow 2\ MnO(OH)_{(s)}$

Overall: $Zn_{(s)} + 2\ H^+_{(aq)} + 2\ MnO_{2(s)} \rightarrow$
$Zn^{2+}_{(aq)} + 2\ MnO(OH)_{(s)}$

While still a wet cell, and thus still suffering from some of the same limitations of its predecessors, the elimination of acid served to improve the stability of the cell, and reduced the hazards associated with leaks and spills. Unfortunately, current outputs were limited under prolonged use, with only a slight improvement over the Daniell cell, possibly due to the limited redox availability of the MnO_2 residing in microdomains within the

carbon matrix.[6] As with the Daniell and Grove cells, the Leclanché cell also served as an important stepping stone toward the eventual development of the dry cell battery.

Numerous attempts were made through the years to immobilize the electrolyte and create a "dry cell", thus reducing or eliminating risk of leaking or spillage. Volta's original pile immobilized the electrolyte by absorbing it in paper or leather.[14] Attempts with other materials were reported, including starch pastes, sand, asbestos, wool, and gelatin.[6,36] In 1887, Carl Gassner, Jr. filed a patent in the United States outlining the use of zinc oxide mixed with plaster surrounding a MnO_2/C cathode inside a zinc cylinder, which served as both anode and cell container for a battery.[37] While this approach was not particularly successful, likely due to extremely limited ion mobility within the solid plaster, it does bear a striking resemblance to the modern dry cell configuration.

Alkaline electrolytes were reported in a French patent in 1881, followed by a U.S. patent in 1883, by Felix de Lalande and Georges Chaperon, although it is likely the use of alkaline solutions was investigated far earlier.[38] Lalande and Chaperon used caustic potash or caustic soda with zinc anodes and copper oxide as the cathode material to good effect, and in 1889 a manufacturing plant was producing alkaline zinc and copper oxide cells in the United States.[38,39]
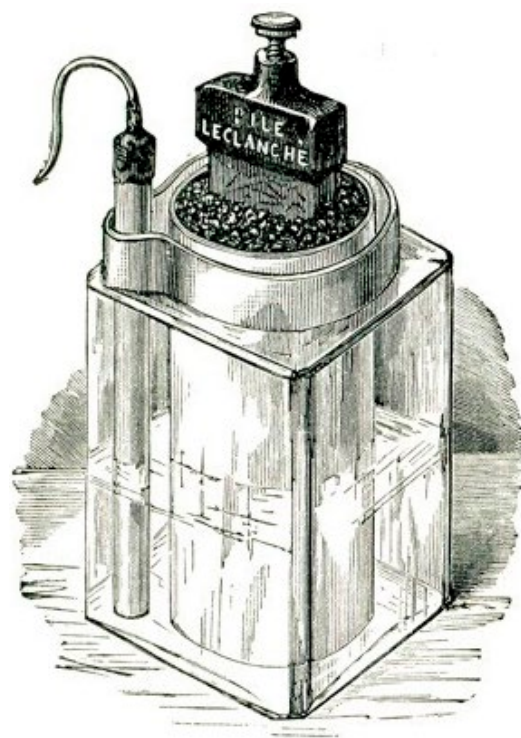

Figure 6. Leclanché wet cell (public domain).

The modern alkaline battery can be considered a culmination of many of the advances described above, although 50 years would pass before its invention. A zinc casing serves as the anode as used by Gassner. Contained within the cell is a cathode composed of the carbon rod collector made popular by Bunsen surrounded by a MnO_2/C paste similar to that found in the Leclanché cell. A caustic soda paste serves as the electrolyte as described by de Lalande and Chaperon. The alkaline electrolyte and the cathode materials are separated with a layer of paper, reminiscent of the separators used in Volta's original pile. Patents were granted for this configuration to Lewis Urry, Paul Marsal, and Karl Kordesch in 1947 in Great Britain, and in the United States over a decade later in 1960.[40] One additional development to improve safety was the use of small amounts of mercury to suppress hydrogen gas production inside the cell which could cause the cell to rupture.[41] Due to the toxicity of mercury, its use eventually fell out of favor, and there is now a worldwide ban on the use of mercury in commercial batteries.

LEAD-ACID BATTERY

While Ritter's "charging pile" should be recognized as the first storage battery, its application did not gain traction at the time.[21] The first widely utilized secondary battery was the lead-acid battery. The use of lead plates to store electrical charge was first described by W.J. Sinsteden in 1854.[42] However, it was Gaston Planté several years later who would develop a version which would be viable on a useful scale, although its usefulness was still limited and it could be considered to be ahead of its time.[43]

Sinsteden, for unknown reasons, used lead plates to connect batteries to a voltammeter instead of using silver, platinum, or copper wires as was commonly done.[42,43] He noted a small secondary current that could be measured, which increased with subsequent charge/discharge cycles. He also noted the formation of lead oxides on one of the plates. Planté looked at this phenomenon more closely, comparing the results of a number of different metals including aluminum, silver, copper, lead, iron, and gold.[43] He also compared electrolyte acidified with sulfuric acid to other options.

The modern lead-acid battery utilizes a series of cells, each containing a lead-alloy grid as one electrode, and a lead(IV) oxide-coated lead plate or grid as the other electrode (Figure 7). The overall redox process results in both oxidation and reduction of lead, as seen below.
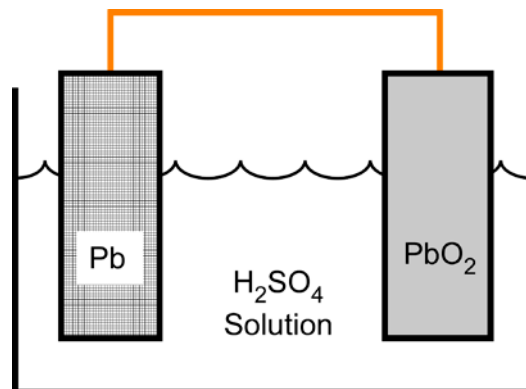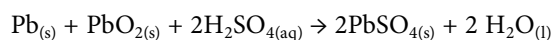
$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2\,H_2O_{(l)}$$

Figure 7. Diagram of a lead-acid battery.

The increased surface area of the lead grid allows for a greater current output than could be achieved using similar sized plates. A solution of 20-30% aqueous sulfuric acid serves as the electrolyte.

Although the battery was capable of being recharged, the technology needed to generate the current to efficiently charge it had not yet been developed, and as such the only way to recharge a lead acid battery was to exhaust a number of primary batteries such as Daniell or Grove cells. It wasn't until the 1880's when large scale electrical power production allowed storage batteries to flourish.[6] Even today, the lead-acid battery holds a worldwide market share of over $35 billion USD annually, with automotive batteries as the primary market.[44]

NICKEL STORAGE BATTERIES

While the lead-acid battery was (and continues to be) quite serviceable for many static applications, its weight and acidic electrolyte made it less-than-ideal for more portable purposes. The first secondary battery to successfully compete with the lead-acid battery was developed by E.W. Jungner. In a patent filed in his native Sweden, Jungner first described a nickel-iron cell in 1897, followed in 1901 by a patent replacing iron with cadmium.[45,46] In 1901, Thomas Edison also obtained a United States patent for a nickel-iron secondary battery.[47] It is unclear if Edison was aware of the work of Jungner at the time.

Owning to the lower density of nickel and cadmium (7.81 and 8.00 g/cm^3, respectively) versus that of lead (10.66 g/cm^3), these cells showed a significant decrease in weight when compared to their lead-acid counterparts.[48] Jungner also utilized an alkaline electrolyte rather than acid, which would eventually allow for dry cell development. However, mass production of NiCd (sometimes

termed "nicad") batteries did not occur until the middle of the 20th century, upon development of a means of dealing with gases that can be produced during the redox processes, allowing for creation of a completely sealed battery.[49]

While quite popular in the second half of the 20th century, NiCd cells had several downsides. First, they were prone to memory effects, requiring a full discharge prior to recharging to avoid loss of charge capacity. Additionally, the toxic nature of the cadmium cathode was a disposal concern, and in 2009 the European Union prohibited their use in most applications.[7]

Improvements to NiCd batteries were investigated as early as the 1960's. Efforts to improve the capacity of the nickel hydroxide electrode through inclusion of didymium hydrate (a mixture of rare-earth oxides, primarily lanthanum and neodymium) were granted a United States patent in 1967.[50] Development of what would become known as nickel-metal hydride batteries occurred in the 1990's, when Stanford Ovshinsky and coworkers expanded the scope of additives to include many rare-earth and transition metals.[51,52] These additives allowed the cadmium cathode to be replaced with a nickel-metal alloy. These cathodes allowed for the storage and discharge of hydrogen (as hydride) through charge/discharge cycles, increasing the charge capacity and greatly reducing memory effects compared to standard NiCd batteries.[7] Having led the work that directly allowed commercialization of nickel-metal hydride batteries, Ovshinsky, a prolific inventor, is often referred to as the inventor of the nickel-metal hydride battery.[53]

THE RISE OF LITHIUM

While zinc was the predominant anode material for almost two centuries, potential was seen for lithium as a replacement. Lithium has a higher activity and a lower density than zinc, which would allow for lighter batteries with increased voltage output than zinc cells. Gilbert Lewis and Frederick Keys successfully measured the potential of the lithium electrode as early as 1913.[54] Unfortunately lithium, like the rest of the alkali metals, reacts with water, rendering it unusable with aqueous electrolytes. Additionally, lithium metal reacts readily with atmospheric nitrogen at ambient temperatures to produce a surface coating of lithium nitride, generally with some amount of lithium oxide as well, thereby requires inconvenient inert atmosphere conditions to successfully work with lithium metal.

In was not until 1965 when a patent for a secondary battery utilizing lithium (as well as sodium, potassium,
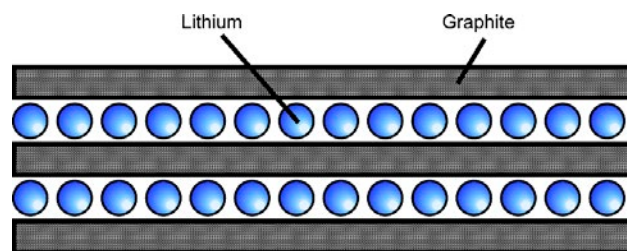

Figure 8. Intercalation of lithium ions.

magnesium, beryllium, and aluminum) was obtained, although the patent application was filed in 1961.[55] An organic solvent with salts of the anode material is specified, avoiding the problems associated with aqueous electrolyte solutions. Also mentioned are cathodes composed of redox-active organic polymers including polymers of quinones, sulfoxides, hydroxylamines, and azo compounds. Another approach was described by D.A.J. Swinkels in 1966, wherein a molten lithium chloride electrolyte was used.[56] Unfortunately, this system required a minimum operating temperature of 650 °C, making it impractical for widespread use.

One practical application of lithium metal anodes was the lithium-iodine battery.[57] Its development had a significant positive impact in medicine, improving the performance of pacemakers implanted in cardiac patients by decreasing the weight and increasing the battery life compared to previous battery options of the time.[58] While not necessarily a problem for pacemaker applications, the lithium-iodine battery was a primary battery, and could not be effectively recharged. With pure metal anodes, ions produced through oxidation upon discharge must be reduced and redeposited onto the anode when the cell is recharged. Unfortunately, for several reasons, lithium often does not redeposit evenly on the electrode surface but instead can form dendrites which can grow to sufficient length to short circuit the cell.[58]

In the mid 1970's, intercalation of ions, including lithium ions, into a host framework had been recognized and described.[59] Rather than relying upon a pure lithium metal electrode with the inherent risks associated with it, electrodes composed of materials capable of accepting lithium ion insertion within its solid structure (Figure 8) were explored. Attempts to develop cells based upon intercalating electrodes proceeded through the 1980's.[58] The most successful of these, which would form the basis for the lithium ion batteries now common, utilized a lithium cobalt oxide ($LiCoO_2$) material developed by J.B. Goodenough and coworkers in 1981.[60] Other materials were also found to support lithium ion insertion, including TiS_2, V_4O_{10}, and graphite.[61] Intercalating elec-

trodes are now commonly used for both the anode and the cathode in lithium ion batteries, with lithium ions shuttled between them during charge or discharge processes.[62]

CONCLUSIONS

As society relies more and more on portable electric power, there is little doubt that significant effort will be expended to further improve battery technology. The desire for increased charge capacity, better thermal stability, longer functional lifetimes with more charge/discharge cycles, faster recharge rates, and decreased size and mass will continue to drive exploration and innovation. For example, efforts are currently underway to improve the performance of gel electrolytes in lithium ion batteries for mobile electronics and electric automobiles. It seems likely that increased efforts to develop ultra-high capacity, large scale stationary batteries to store renewable energy sources such as wind and solar to stabilize a greener energy grid is also on the horizon. One can only guess at what Alessandro Volta would think if he were to see the impact his device ultimately had on the world.

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REFERENCES

1. U.S. Energy Information Administration, *Monthly Energy Review,* U.S. DOE, Washington, DC, **April 2019**.
2. *New Oxford American Dictionary*, 3rd ed. (Eds.: A. Stevenson, C.A. Lindberg), Oxford University Press, New York, **2010**.
3. B. Franklin, *Franklin Papers* **1749**, *3*, 352.
4. K.B. Oldham, J.C. Myland, *Fundamentals of Electrochemical Science,* Academic Press, San Diego, CA, **1994**.
5. A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, *2nd ed.*, John Wiley & Sons, Hoboken, NJ, **2001**.
6. G. W. Heise in *The Primary Battery,* Vol 1 (Eds. G.W. Heise, N.C. Cahoon), John Wiley & Sons, New York, **1971**, 1-58.
7. M. Nentwich, B. Störr, J. Hanzig in *Electrochemical Storage Materials: From Crystallography to Manufacturing Technology* (T. Leisegang, M. Zschornak, H. Stöcker), De Gruyter, Boston, MA, **2018**, 41-74.
8. B. Dibner, *Alessandro Volta and the Electric Battery,* Franklin Watts, New York, **1964**.
9. G. Pearson, *Philos. Trans. R. Soc. London* **1779**, *87*, 142.
10. A. P. van Troostwijk, J. R. Deiman, *Obs. sur la Phys.* **1789**, *35*, 369.
11. H.A.M. Snelders, *Ambix* **1979**, *26*, 116.
12. A. Stuart *Philos. Trans. R. Soc. London* **1732**, *37*, 327.
13. B. Franklin, *Franklin Papers* **1752**, *4*, 360.
14. A. Volta, *Philos Trans. R. Soc. London* **1800**, *90*, 403.
15. P.A. Abetti, *Electr. Eng.* **1952**, *71*, 773.
16. W. Nicholson, *J. Nat. Philos. Chem. Arts* **1800**, *4*, 179.
17. H. Davy, *J. Nat. Philos. Chem. Arts* **1800**, *5*, 275.
18. W. Nicholson, A. Carlisle, W. Cruickshank, *Philos. Mag.* **1800**, *7*, 337.
19. D. Gilbert, *Ann. Phys.* **1800**, *6*, 470.
20. W.M. Sudduth, The Electrical Decomposition of Water: A Case Study in Chemical and Electrical Science, University of Oklahoma, United States, **1977**.
21. J.W. Ritter, *Philos. Mag.* **1805**, *23*, 51.
22. H. Davy, *J. Nat. Philos. Chem. Arts* **1800**, *5*, 326.
23. H. Davy, *Philos. Trans. R. Soc. London* **1808**, *98*, 1.
24. H. Davy, *Phil. Trans. R. Soc. London* **1808**, *98*, 333.
25. W. Cruickshank, *J. Nat. Philos. Chem. Arts* **1800**, *4*, 254.
26. C.H. Wilkinson, *Philos. Mag.* **1807**, *29*, 243.
27. C.H. Wilkinson, *J. Nat. Philos. Chem. Arts* **1804**, *8*, 1.
28. D. Owen, *Ambix* **2001**, *48*, 25.
29. J.F. Daniell, *Philos. Trans. R. Soc. London* **1836**, *126*, 107.
30. J.F. Daniell, *Philos. Trans. R. Soc. London* **1836**, *126*, 125.
31. J.F. Daniell, *Philos. Trans. R. Soc. London* **1837**, *127*, 141.
32. J.P. Gassiot, *Philos. Mag. III* **1838**, *13*, 436.
33. W. R. Grove, *Philos. Mag. III* **1838**, *13*, 430.
34. W. R. Grove, *Philos. Mag. III* **1839**, *14*, 388.
35. W. R. Grove, *Philos. Mag. III* **1839**, *15*, 287.
36. G. LeClanché, 71865, **1866**.
37. C.J. Gassner, 373064, **1887**.
38. F. de Lalande, G. Chaperon, 274110, **1883**.
39. E.A. Schumacher in *The Primary Battery*, Vol 1 (Eds. G.W. Heise, N.C. Cahoon), John Wiley & Sons, New York, **1971**, 1-58.
40. P.A. Marsal, K. Kordesch, L.F. Urry, 2960558, **1960**.
41. S. Ruben, 2422046, **1947**.

42. W.J. Sinsteden, *Ann. Der Phys. und Chemie* **1854**, *92*, 1.
43. G. Planté, *The Storage of Electrical Energy, Whittaker*, London, **1887**.
44. G.J. May, A. Davidson, B. Monahov, *J. Energy Storage* **2018**, *15*, 145.
45. E.W. Jungner, 8558, **1897**.
46. E.W. Jungner, 15567, **1901**.
47. T.A. Edison, 678722, **1901**.
48. *Handbook of Chemistry and Physics,* 79th ed (Ed. D.R. Lide), CRC Press, New York, **1998**.
49. G. Neumann, U. Gottesmann, 2571927, **1951**.
50. W.N.J. Carson, 3311502, **1967**.
51. S.R. Ovshinsky, M.A. Fetcenko, C. Fierro, P.R. Gifford, D.A. Corrigan, P. Benson, F.J. Martin, 5523182, **1996**.
52. S.R. Ovshinsky, B. Aladjov, S. Venkatesan, B. Tekkanat, M. Vijan, H. Wang, S.K. Dhar, 2004/0175615A1, **2004**.
53. Available online, last accessed on 05/31/2019.
54. G.N. Lewis, F.G. Keyes, *J. Am. Chem. Soc.* **1913**, *35*, 340.
55. S.W. Mayer, D.E. McKenzie, 3185590, **1965**.
56. D.A. Swinkels, *J. Electrochem. Soc.* **1966**, *113*, 6.
57. J.B. Phipps, T.G. Hayes, P.M. Skarstad, D.F. Unereker, *Solid State Ionics* **1986**, *18-19*, 1073.
58. B. Scrosati, *J. Solid State Electrochem* **2011**, *15*, 1623.
59. M.S. Whittingham, *Prog. Solid State Chem.* **1978**, *12*, 41.
60. K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Solid State Ionics* **1981**, *3-4*, 171.
61. M.S. Whittingham, *Proc. IEEE* **2012**, *100*, 1518.
62. M.S. Whittingham, *J. Electrochem. Soc.* **1976**, *123*, 315.