Secondary Batteries for Mobile Applications: From Lead to Lithium

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Secondary batteries are rechargeable, unlike primary batteries, which must be disposed of when the electrodes have been consumed after discharge. Due to space limitations, this column focuses only on secondary batteries for mobile applications in portable electronics (PEs) and electric vehicles (EVs), namely batteries in which the electrodes host the energy conversion electrochemical reactions and also store energy in electrochemical form [1]. This column does not deal with stationary storage systems for grid services, which typically have higher power and energy ratings and involve a wider range of technologies, including flow batteries, which store energy in flowing electrolytic solutions rather than in the electrodes.

Introduction

Soon after the development of the voltaic battery in 1800 [2], very early observations of a rechargeable cell were made by Johann Wilhelm Ritter (Germany, 1776–1810) in 1803, building on the reversible electrolytic effect observed by Nicholas Gautherot (France, 1753–1803) in 1802. However, these early observations did not trigger further research since there was no interest in such batteries as long as the only known electrical power sources to charge them were primary cells. This situation changed in the 1850s when early practical dc generators appeared; being powered by steam machines or hydraulic turbines,

these devices were capable of producing much cheaper and virtually unlimited electrical energy, which could be used to profitably recharge secondary batteries [3].

Lead–Acid Batteries

In 1859, Gaston Planté (France, 1834–1889) developed the lead–acid (Pb-A) battery, which he presented the following year, consisting of a spongy lead negative electrode (the anode in discharge) and lead dioxide positive electrode (the cathode in discharge) immersed in sulfuric acid. In the early models, the two electrodes consisted of long strips with linen cloth or solid rubber separators and were rolled up to form a cylindrical shape that was placed into a glass vase, a common configuration of the time. This was the first practical rechargeable battery, capable of ~1 Wh kg^{-1}, and was first used in railway carriages. Today, the typical performance figures for Pb-A batteries based on Planté's concept are an operating voltage of 2.1 V; a specific energy of 30–40 Wh kg^{-1} (considering only active materials); a specific power of 180 W kg^{-1} (again, considering only active materials); a round-trip efficiency of 50–95%, a life of 350 cycles; and a self-discharge rate of 3–20% month^{-1}. Thanks to a very low internal resistance, they can produce remarkably large surge currents, meaning that they are still widely used in modern designs, particularly to start up internal combustion engine (ICE) vehicles and in uninterruptible power supplies.

1890s: The First Boom in Rechargeable Batteries

The design of the Pb-A cell was improved by the French chemical engineer Camille Alphonse Faure (1840–1898), who patented a method for permanently coating lead latticed plates with a paste of lead oxide in 1881. This design created a substantial increase in capacity compared with Planté's cell. Flat lead anodes and Faure's cathodes were used to form flat cells, which could be stacked in a trough arrangement into a prismatic container to form a battery. This design was suitable for industrial mass production at a competitive cost and remains very popular (Figure 1). Faure's battery was presented at the first Exposition Internationale d'Électricité, hosted at the Palais de l'Industrie of Paris in 1881, where early EVs powered by such secondary batteries were exhibited, notably an electric tricycle designed by electrician Gustave Trouvé (France, 1839–1902) and the first EV with a Gramme motor developed by engineer Charles Jeantaud (France, 1843–1906) [4].

Within a few years, a number of pioneers were producing commercial electrical cars that used the Pb-A rechargeable battery, and production boomed around the turn of century; at this time, 40% of the soaring U.S. market of motorized vehicles was made up of electric cars, and France was the largest automobile maker in the world, although it would be surpassed by the United States in 1904 [5]. These were city cars with ranges of a few tens of kilometers, which were limited by the

capacity of the Pb-A battery. The first boom in secondary batteries was driven by the expansion of the early market for EVs, although secondary batteries were also used to provide stabilization for dc grids, which were still competing with the emerging ac grids [6], [7].

It was within this period, in 1897, that the German scientist Wilhelm Peukert (1855–1932) put forward his eponymous law relating the change in the capacity of Pb-A batteries to the rate of discharge. Pb-A batteries underwent improvements in the following decades. In 1934, the German company Elektrotechnische Fabrik Sonneberg introduced the Pb-A gel battery, in which the liquid electrolyte was replaced by a gel electrolyte that was obtained by adding silica to a charged cell. These batteries were used in mobile vacuum-tube radios. The modern gel or valve-regulated Pb-A (VRLA) battery was invented by Otto Jache of the German company Sonnenschein in 1957 [8], while the first absorbent glass mat VRLA cell, dubbed *Cyclon*, was patented by an American company called Gates Rubber Corp. in 1972 and is now produced by EnerSys. Gel batteries became common in the 1970s since they could be used in different positions without failure or leakage [9].

Nickel-X and Alkaline Batteries

Motivated by the expansion of the electric car market, research into better rechargeable batteries progressed in the last decade of the 19th century. Ernst Waldemar Jungner (Sweden, 1869–1924) invented the nickel–iron (Ni-Fe) battery, for which he registered two patents in 1899. This cell had a nickel oxide hydroxide cathode, an iron anode, and a potassium hydroxide solution electrolyte, thus being the first rechargeable alkaline battery. An alkaline electrolyte, unlike an acid one, does not attack the metal components, meaning that the battery is more robust and can have a vast range of uses. Today, Ni-Fe cells provide 1.2 V, 19–25 Wh kg^{-1}, 100 W kg^{-1}, <65%, 20–30% $month^{-1}$.

In the same year, Jungner patented the nickel–cadmium (Ni-Cd) rechargeable alkaline battery, in which iron was substituted for cadmium at the anode, thus achieving improved performance (1.2 V, 40–60 Wh kg^{-1}, 150 W kg^{-1}, 70–90%, 10% $month^{-1}$). Since Ni-Fe batteries used cheap iron; had 1.5–2 times the specific energy of Pb-A batteries; and allowed high discharge rates and deep discharges (2,000 cycles at 80% depth of discharge), they also had strong market potential [10].

To exploit his inventions, Jungner started the firm Ackumulator Aktiebolaget Jungner in 1900 but became involved in a long patent dispute with Edison, who eventually won. The company had to change its name in 1904 to Nya Ackumulator Aktiebolaget Jungner and later became Ackumulator Aktiebolaget Jungner in 1910 [11]. The new company was finally able to profitably market the Ni-Fe and Ni-Cd batteries provided with further technological developments. Although Jungner

batteries were much more expensive than Pb-A batteries, they were robust and had significantly better energy density. After the crash of the airship *Italia* during Umberto Nobile's expedition to the North Pole in 1928, several batteries were dropped from an airplane to the nine surviving crew members awaiting rescue on the Arctic ice pack, of which only the Jungner Ni-Fe battery worked. During World War II, Jungner Ni-Fe batteries were used in German V1 flying bombs and V2 rockets.

The Ni-Cd battery arrived in the United States in 1946, where it was successfully used in the power systems of rockets and artificial satellites throughout the 1960s and 1970s as well as in terrestrial portable electrical devices well into the 2000s. Ni-Cd cells underwent continuous improvements, and by the 1990s, the very popular AA-type cell offered a fairly good capacity of 1,000 mAh, compared to 500 mAh of only few years before (Figure 2). The Ni-Cd battery is capable of very high discharge rates (10 min or less) and is tolerant of overdischarge and overcharge, resulting in high power and fast charge, which make it ideal for portable power tools. However, it is prone to high self-discharge rates and a "memory effect" that reduces its capacity if it undergoes repeated recharges after partial discharges. Due to the toxicity of cadmium, restrictions were introduced on the use of Ni-Cd in the 2000s, such as special procedures for disposal and compulsory recycling programs in the United States, while in the European Union (EU), its use has been limited to few special applications.

In 1901, Thomas Alva Edison (1847–1931) patented his version of the Ni-Fe battery in the United States and Europe. He believed that it would be the battery of choice for EVs as it surpassed Pb-A in terms of specific energy and recharge time [12], although it had lower performance at low temperatures and cost more. Edison thought that with this lightweight and durable battery, electric cars would become standard, and his factory would become the main manufacturer of car batteries. Some major U.S. carmakers (Detroit Electric and Baker Electric) adopted it, but Edison's first Ni-Fe model of 1903 was prone to leakage, leading to a short battery life, and it did not greatly outperform the Pb-A cell.

Edison was able to produce a more reliable and powerful model seven years later (Figure 3), but the use of EVs was declining at that time as cheap gasoline and the Ford Model T had entered the market. To Edison's disappointment, when the electric starter for the ICE engine was introduced, the Pb-A power supply was adopted. Nevertheless, the Ni-Fe battery had a market, being widely used for mine and railway locomotives; railroad signaling; forklifts; and standby power applications. Edison's batteries were
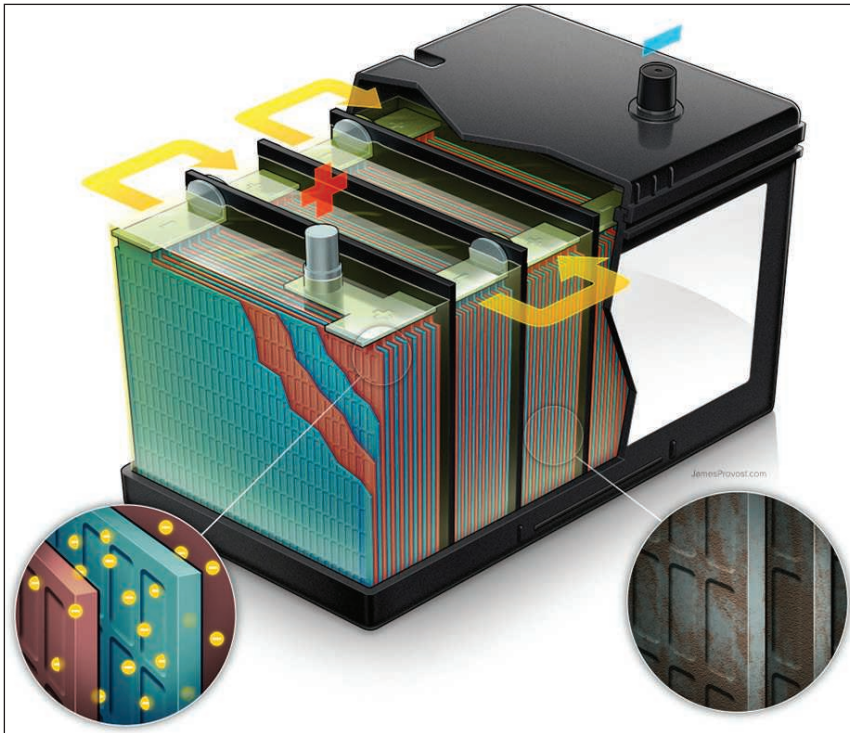

FIGURE 1 – A cutaway drawing of a Faure's type Pb-A battery, made of several stacked flat cells. (Source: Illustration © James Provost; http://jamesprovost.com/portfolio/car-battery-cutaway; used with permission.)

FIGURE 2 – (a) Early Ni-Cd cells by Exide. (Source: https://en.wikipedia.org/wiki/File:Exide_NiCa_Battery.png.) (b) A number of standard Ni-Cd batteries from different producers. (Source: https://commons.wikimedia.org/wiki/File:%E3%83%8B%E3%83%83%E3%82%AB%E3%83%89%E9%9B%BB%E6%B1%A0.JPG.)

produced until 1972, when the battery company was sold to the Exide Battery Corp., which discontinued production in 1975. Currently, two companies are still manufacturing Ni-Fe cells, namely Kursk Accumulator in Russia and Changhong Battery in China.

In 1901, Thomas Alva Edison patented the rechargeable nickel–zinc (Ni-Zn) battery. Irish chemist James J. Drumm (1897–1974) developed it further, and in 1932–1949, he installed it in railcars servicing the Dublin–Bray line. This use revealed that Ni-Zn batteries were burdened with a very modest cycle life. In the 1960s, new Ni-Zn batteries were investigated as an alternative to silver–zinc batteries for military applications, and interest in them resurged for use in EVs in the 1970s. In particular, the American company Evercel Inc. patented several improvements to Ni-Zn batteries, which resulted in a longer cycle life, but withdrew them from use in EVs in 2004 when better cells became available. Ni-Zn batteries are capable of 1.65 V, 100 Wh kg^{-1}, 3,000 W kg^{-1}, 85%, and 500–600 cycles.

The rechargeable nickel–hydrogen (Ni-H$_2$) battery has a more recent history as it was initially developed at United States-based Comsat in 1970, and a patent was registered in the United States by Russian inventors Alexandr Ilich Kloss and Boris Ioselevich Tsenter in 1971. It uses a positive nickel electrode, as in the Ni-Cd cell; a negative electrode made of a catalyzed diffusion layer, as in a fuel cell; and a potassium hydroxide electrolyte. The hydrogen used to feed the negative electrode is stored at high pressure (82.7 bar) in the tank containing the cell. It is capable of 1.55 V, 55–75 Wh kg^{-1}, 220 W kg^{-1}, 85%, >20,000 cycles and this extremely long cycle life makes it ideal for powering satellites and space probes [13]; in fact, it was first used in a U.S. Navy satellite in 1977 and now equips space objects like the International Space Station, the Hubble Space Telescope, and commercial communication satellites (Figure 4). Currently, the major manufacturers of Ni-H$_2$ batteries are the American company EaglePicher Technologies and the American–Irish Johnson Controls International.

Early investigations at the Battelle–Geneva Research Center in 1967 with funding from Daimler–Benz and Volkswagen AG gave rise to the development of the rechargeable nickel–metal hydride (Ni-MH) battery in the 1970s as a variant of the Ni-H$_2$ battery, in which the bulky hydrogen storage is replaced by a complex alloy that absorbs hydrogen on charge and releases it on discharge, meaning that it is more viable for many applications [14]. A major challenge was the short cycle life due to alloy instability. This was overcome in 1987 by J.J.G. Willems and K.H.J. Buschow of Philips Research Laboratories (Eindhoven, The Netherlands), who demonstrated a successful battery based on an LaNi$_5$ compound (an alloy of nickel and rare earth lanthanum), in which six atoms of hydrogen could be inserted to form LaNi$_5$H$_6$ and which kept 84% of its charge capacity after 4,000 charge–discharge cycles [15]. This solution revolutionized the technology, and alloys made of rare earths and nickel were subsequently used in most small sealed cells, while complex alloys of titanium, vanadium, and nickel were preferred for EVs.

The first consumer-grade Ni-MH cells for small appliances were put on the market in 1989. Improvements to the anodic alloy were introduced in 1998, and production reached 10% of that of Ni-Cd batteries by 1993, with a growth rate of 20% per year. At present, the performance of Ni-MH batteries can reach 1.2 V, 60–120 Wh kg^{-1}, 250–1,000 W kg^{-1}, 82–90%, 700–1,000 cycles, and AA-type cells with capacity up to 1,300–1,400 mAh are available. Compared to Ni-Cd, Ni-MH batteries have poorer self-discharge rates and temperature ranges; however, the
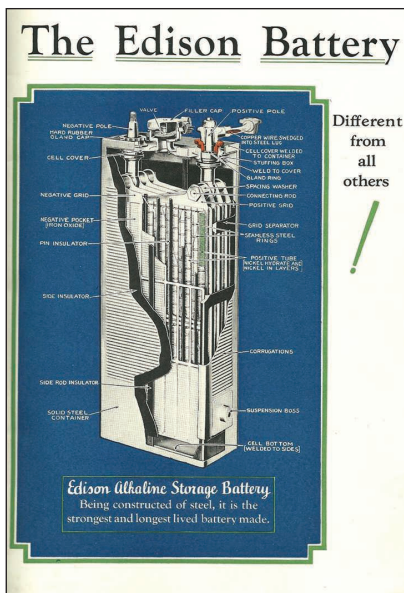

FIGURE 3 – A look inside each part of the nickel–iron cell marketed by Edison in 1917. This graphic is from a 1920s original Edison battery manual that described the use of these cells in EVs. (Source: https://en.wikipedia.org/wiki/File:Nickel_Iron_Battery_cut-away_drawing.jpeg.)

FIGURE 4 – The Hubble battery module assembly with lid removed, showing the Ni-H$_2$ cells and power isolation switches. (Source: https://en.wikipedia.org/wiki/File:218582main_Batt_FS_img1_lg.jpg.)

success of a battery also depends on nontechnical factors. In the EU, Ni-MH batteries mostly replaced Ni-Cd after the 2006/66/EC Battery Directive had dramatically restricted the latter's use due to cadmium toxicity [16]. Restrictions on Ni-Cd use were also introduced in other countries, and hence, the production of Ni-MH boomed outside the EU in the late 2000s, with this type becoming the workhorse for early chip-electronic devices such as computers and cell phones (Figure 5).

Ni-MH powered a number of early models of hybrid EVs (HEVs) that were put on the market at the turn of the century, such as the very successful first-generation Toyota Prius (1.78 kWh, 1997); the second-generation Toyota Prius (1.31 kWh, 2003); the Honda Civic IMA (0.8 kWh, 2003); and the first-generation Ford Fusion Hybrid (2008). By 2008, more than 2 million hybrid cars had been manufactured worldwide with Ni-MH batteries. Today, Ni-MH batteries have almost been totally displaced from the EV market by Li-ion batteries due to the latter's higher energy storage capability and lower cost.

The rechargeable alkaline–manganese (RAM) battery has a zinc anode; a cathode based on manganese dioxide (MnO_2); an electrolyte made of an alkaline compound; and a voltage of 1.5 V. Although MnO_2 cells were first conceived in the early 1900s, rechargeable models were introduced by the U.S. companies Union Carbide and Mallory in the 1970s after the success of disposable alkaline batteries. Second-generation RAMs were introduced to the market by Battery Technologies Inc. of Canada in 1986 and by Pure Energy in 1987. Mercury-free models were released after 1995, in the standard formats of AAA, AA, C, D, etc. In the 1990s, these batteries were produced and marketed under license by a number of companies as competitors to Ni-Cd and Ni-MH, with lower costs, self-discharge rates, and environmental impacts.

1980s–1990s: The Second Boom in Rechargeable Batteries

Secondary batteries based on the early concepts developed by Planté and Jungner satisfactorily met the requirements of the technology up to the 1960s, and Pb-A and Ni-Cd batteries remained the most common secondary batteries among the hundreds of electrochemical couples that were proposed during the late 19th and early 20th centuries. In the 1940s, the principal domestic uses for batteries were in flashlamps; ICE vehicles (for starting and other services); a few toys; and radios. At that time, radios used thermionic tubes, which required a low-voltage power source to heat the filaments and a high-voltage dc source to accelerate electrons between the valve cathode and anode. To achieve this without a grid supply, multiple cumbersome cell arrangements were required [17]. From the 1950s onwards, the development of transistors and solid-state electronics created a revolution in portable appliances, starting with consumer electronics (electronic watches, toys, controllers, and cameras); medical devices (implantable cardiac pacemakers and hearing aids); and military equipment [18]. To fulfill this demand, new types of small primary or rechargeable batteries were needed, and the former were more often preferred [1].

Throughout the 1980s and 1990s, the sensational expansion of PEs based on integrated circuits (chips, e.g., in cell phones, laptops, cameras, camcorders, and entertainment devices) [19] and portable power tools produced a dramatic growth in the demand for high-power portable energy, and additional requests emerged from an increasing number of other appliances, including household devices and entertainment gadgets. For most of these uses, alkaline–manganese and Pb-A batteries were no longer suitable, in terms of both Wh kg^{-1} and Wh cm^{-3}, and although small devices often still used primary batteries, there was a growing trend toward the adoption of more economical secondary batteries. New smaller rechargeable batteries with a greater capacity and reduced size and weight were needed. Initially, the chemistry that was predominantly used to meet this requirement was Ni-Cd; more than 1 million such batteries were produced in 1993, and the market then expanded further, with an annual growth rate of nearly 20% [20].

Ni-Cd was later superseded by Ni-MH after restrictions on the former were applied in the 2000s. Although special sizes were designed and produced, the majority of production concentrated on the standard types (AA, AAA, C, D, etc.), sometimes assembled in customized packages. Progressively larger rechargeable batteries were used in electric and hybrid vehicles (cars; tugs and tractors; forklift trucks; electric mobility scooters; golf carts; milk fleets; and other road vehicles); space vehicles (satellites and space probes); off-grid solar energy storage (remote area power supplies and navigation beacons); and defense
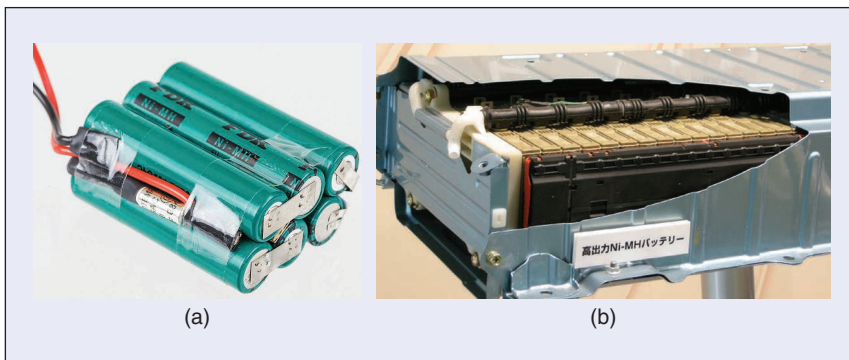

FIGURE 5 – Ni-MH cell packages. (a) A six-AA cell package for PEs. (Source: https://commons. wikimedia.org/wiki/File:Weinmann_WM_94051_-_FDK_Ni-MH_battery_pack-7410.jpg.) (b) A high-power Ni-MH package of a Toyota NHW20 Prius, second generation, 2003–2009 (14.4 V, 6.5 Ah, 37 kg; the total capacity was 1.31 kWh). (Source: https://commons.wikimedia.org/wiki/File:Ni-MH_Battery_02.JPG.)

(submarine traction batteries, torpedoes, missiles) [21].

Lithium Batteries

Lithium is the first metal in the periodic table; it has the lowest atomic number of all metals, with the smallest atomic weight (6.95) and the lowest density (0.534 g cm^{-3}). Located in the alkali group, lithium is also one of the most reactive metals. The fortuitous combination of a small atomic weight, extremely low reduction potential, and monovalent charge renders lithium unique as a material for batteries, with a theoretical specific capacity that is much higher than other metals (3,860 Ah kg^{-1}). However, the development of secondary batteries based on lithium was not straightforward [22]. A breakthrough arose from the development of new concepts for primary batteries in which lithium was used as one of the electrode materials. Since metallic lithium is not compatible with water, its use required replacing the common aqueous electrolytes with more electrochemically stable organic electrolytes, typically a solution of lithium salt in a carbonate organic solvent.

The lithium–iodine primary battery, made of a lithium metal anode and an iodine-based cathode, provided a practical specific energy of about 250 Wh kg^{-1}, a value almost five times higher than the best primary cells of the time, i.e., the zinc–mercury used in pacemakers. The primary lithium cell with a manganese dioxide cathode, made in a coin-type version, was similarly successful. These achievements stimulated an interest in rechargeable lithium cells [23]. Attention was initially focused on the more challenging cathode, for which materials capable of a long cyclability were needed. Building on the idea of solid solution electrodes, as reported by B.C.H. Steele, M.S. Whittingham, R. Huggins, and M.B. Armand in key chapters of a book edited by W. van Gool in 1973 [24], the breakthrough was achieved by Michael Stanley Whittingham (U.K.–United States, born 1941) in 1978, who developed the so-called *intercalation* electrodes,

made of compound lattices that can reversibly accept and release lithium ions in their open structure with no change except for a minor expansion or contraction [25].

Whittingham was the first to draw a clear demarcation between intercalation–reaction and conversion–reaction materials and to associate the cell reversibility with the minimum structural changes occurring in the host lattice [26]. This discovery triggered extensive research on rechargeable lithium batteries operating around room temperature [27]. At that time, it was discovered at the Exxon and Bell Laboratories (New Jersey) that these intercalation reactions could convey a lot of energy, which was of interest for energy storage. By exploiting this type of cathode, the first two commercial rechargeable lithium batteries were manufactured by Exxon Company in the United States (TiS$_2$ cathode) and by Moli Energy in Canada (MoS$_2$ cathode) in the late 1970s to early 1980s, both of which had liquid organic electrolytes.

Moli Energy developed a first-generation AA cell in 1985 and later significantly improved its capacity. By 1988, they were marketing an AA cell that could store more than 2 Wh under the brand name Molicel, although these cells, which were used in cell phones, were subject to a number of fire incidents in 1989. The rechargeable lithium batteries from Exxon were also unsuccessful. These failures caused a shift toward safer intercalation electrode materials [28]. In fact, the anode of the early batteries, which was made of pure lithium metal, reacted easily with the electrolyte to form a passivation layer on its surface called a *solid electrolyte interface* (*SEI*). Irregularities in the SEI can lead to uneven lithium deposition upon charging, with the formation of "dendrites" (crystalline masses with a branching treelike structure) that grow to eventually short-circuit the cell. In addition, the high chemical reactivity of pure metallic lithium resulted in poor battery characteristics; low durability; and the inherent danger of a thermal

runaway reaction and consequent fire risk.

Supported by significant interest and investment from petroleum corporations, a series of intercalation materials with layered structures was developed between 1974 and 1979, with the seminal work of Whittingham being particularly notable [29]. The winning approach relied on a new concept consisting of the combination of two intercalation electrodes: one that was capable of accepting lithium ions, operating as the anode, and the other that was capable of releasing lithium ions, operating as the cathode. In these cells, lithium ions "rock" back and forth between the electrodes, creating a new type of system that was initially called the *lithium rocking chair battery*. This concept was studied by Michel Armand (France, born 1946), who proposed an early mathematical model based on intercalation cells with two different hosts [30]. The concept was demonstrated in practice in the early 1980s by Bruno Scrosati (Italy, born 1937), who presented the first actual asymmetrical intercalation cell that shuttled Li$^+$ back and forth [31].

Independently, Akira Yoshino (Japan, born 1948) of Asahi Chemical conceived a battery based on these concepts in the early 1980s; he completed a practical prototype in 1986, for which he had filed a priority patent in 1985, in which graphite was used as the "lithium sink" anode and lithium in cobalt oxide was used as the "lithium source" cathode [32]. In Yoshino's words, this was a "nonaqueous secondary battery using transition-metal oxides containing lithium ion such as LiCoO$_2$ as a positive electrode and carbonaceous materials as a negative electrode" [33]. LiCoO$_2$, which had been put forward by John B. Goodenough (United States, born 1922) while at Oxford University in 1980, was crucial in providing cathode reversibility [34], while anodic graphite reacted with lithium to form the intercalation compound LiC$_6$ very readily at room temperature, as reported by Rachid Yazami (Morocco, 1953) in 1983.

After years of persistent research, Sony succeeded in commercializing the first practical battery based on these concepts in 1991, and the "lithium rocking chair battery" was renamed the lithium-ion (Li-ion) battery (LIB). The production process was simple and efficient, requiring no special atmosphere since $LiCoO_2$ carbonaceous materials are stable. Many other producers followed Sony (Asahi Kasei and Toshiba in 1992), and the initial production went into camcorders, laptops, and cellular phones. Interestingly, the successful commercialization of the lithium secondary battery took fewer than 17 years, compared to the more than 30 years needed for Ni-MH. Today, the underlying technology has not changed in more than 40 years. All commercial secondary lithium batteries use intercalation reactions at both electrodes as the basis for storing energy, and a carbon-based anode is widely used.

In 1997, Sony and Asahi Kasei released the lithium–polymer battery, which holds its electrolyte in a solid polymer composite rather than in a liquid solvent, with the electrodes and separators laminated to each other. This design allows the battery to be wound in a flexible wrapping, meaning that that these batteries could be produced in any shape to fit a specific device and meet the space limitations in mobile devices and laptops. These batteries can provide a specific energy of 100–265 Wh kg^{-1} and have a self-discharge rate as low as 5% $month^{-1}$.

By the 2000s, some issues had emerged regarding cost and safety. The former was mainly related to raw materials, and the latter was related to thermal runaway in the electrolyte, due to the propensity of the cathode to lose its oxygen so that the coexistence of combustible materials and oxidizing agents involved a risk of runaway reactions resulting in fires or explosions. Improvements in monitoring and management became essential to safely allow LIBs to fulfill their potential in PEs and the automotive market [35]. Since 2005, most Li-ion applications have used "smart charger" chips to control the operation of the battery and predict the remaining capacity. New energy policies and the trends in the automobile market led most developed countries in North America, Europe, and Asia to make very large financial investments in expanding and advancing battery performance, thus allowing development to continue.

The arrival of nanomaterials gave LIBs a new lease on life and provided benefits in terms of capacity, power, cost, and material sustainability that have not yet been fully exploited [36]. Since the 2010s, worldwide efforts have been directed to replace current battery components with materials with higher performance in terms of energy, power, cost, reliability, lifetime, and safety. The major targets are the replacement of the organic carbonate liquid electrolyte solutions with safer and more reliable alternatives and the replacement of graphite and lithium cobalt oxide with materials with higher capacity and lower costs [37]. In particular, cobalt is ranked as a critical raw material in several nations (United States, EU, U.K., Japan, and Korea) due to its rarity, which makes it increasingly expensive as demand grows. In addition, it is mined mostly in the Democratic Republic of Congo under conditions that raise major ethical concerns, such as child labor.

In 1997, Goodenough presented a new cathode based on the olivine class of compounds, with the formula $LiMPO_4$ (where M can be Fe, Ni, Co, or Mn) [38], and LIBs with these new cathodes were soon used commercially. In particular, $LiFePO_4$ found successful application in larger vehicles such as buses, watercraft, and grid systems. $LiFePO_4$ has a capacity 25% lower than other lithium batteries due to its operational voltage of 3.2 V (compared to 3.7 V for Co-based Li-ion), but the need for cobalt is eliminated. In addition, $LiFePO_4$ batteries are less prone to thermal runaway and the consequent risks of fire and explosion.

In the 2000s, the lithium–titanate or lithium–titanium–oxide (LTO) battery attracted increasing attention. It uses lithium–titanate nanocrystals instead of carbon anode, which provide faster recharging than other LIBs (for example, 80% in 15 min, even at –50 °C) with good cyclability, but it has a lower voltage and specific energy (2.4 V, 30–170 kWh kg^{-1}, 4,500 cycles) [39]. At present, LTO is exploited in batteries for plug-in HEVs (PHEVs).

By 2011, the production of LIBs had reached several billion units per year, and they were used to power very popular portable devices such as smartphones, cellular phones, laptops, notebooks, camcorders, and MP3 players. By then, the large majority of hybrid, plug-in hybrid, and battery electric cars (HEVs, PHEVs, and BEVs) had adopted LIBs instead of Ni-Cd or Ni-MH (Figure 6). The specific energy of the early commercial $LiCoO_2$ batteries was 68 Wh kg^{-1} in 1991, twice that of Ni-Cd or Ni-MH; it more than tripled between its introduction and 2012 and now reaches 406 Wh kg^{-1}. At the same time, prices have dropped from above US$5,000 kWh^{-1} to below US$200 kWh^{-1} [40] (Figure 7). In 2011, a medium-sized electric car using 200 kg of available LIBs (~150 Wh kg^{-1}) offered

FIGURE 6 – Li-ion cell packages. (a) A hexagonal lithium–polymer cell for underwater vehicles. (Source: https://en.wikipedia.org/wiki/File:Custom_Cells_Itzehoe_GmbH_free_form_factor_battery_for_Unmanned_Underwater_Vehicle_(UUV_AUV).png.) (b) A LIB of a Nissan Leaf, first generation (2009 model: 7.6 V 24 kWh; 2023 models are provided with batteries rated 350 V, 40–62 kWh). (Source: https://en.wikipedia.org/wiki/File:Nissan_Leaf_012.JPG.)

a nominal driving range of 250 km, whereas in 2022, the same number of new LIBs (~260 Wh kg^{-1}) extended this range to 430 km.

The global production capacity of LIBs rose from 20 GWh in 2010 to 767 GWh in 2020, and 75% of these were made in China. Nearly 30 years after their commercialization, LIBs have become one of the landmark technologies that have profoundly changed our lives. It was the commercialization of LIBs that hatched a new era that has not only seen the increasing quality and success of countless portable devices but also marks the beginning of the energy transition toward mass vehicle electrification and grid storage for stationary applications [41].

Beyond Lithium

A number of other chemistries are being studied as a result of energy decarbonization programs and the need for the further expansion of rechargeable batteries. Promising options include solid lithium anode cells; secondary zinc–manganese dioxide cells; secondary zinc–air; solid-state microbatteries; and metal–air batteries.

In the 1960s, Herbert Danuta and Ulam Juliusz of Electric Tech Corp. patented a primary lithium–sulfur (Li-S) battery that employed lithium or lithium alloys at the anode; sulfur at the cathode; and an electrolyte composed of aliphatic saturated amines. A rechargeable Li-S battery was demonstrated in 1980. While development is still ongoing to prevent the formation of dendrites, to extend the cycle life and to improve the safety of operation, several companies are engaged in the early commercialization of Li-S batteries. The reasons for this interest are the low cost of sulfur, which makes Li-S cheaper than Li-ion; its high specific energy of 450–550 Wh kg^{-1}; and its lightness, thanks to the low atomic weight of lithium and the moderate atomic weight of sulfur [42], [43].

The principle of operation of the sodium-ion battery (NIB or SIB) is very similar to that of the LIB except that it uses sodium ions (Na$^+$) as the charge carriers. In addition, it operates at low temperatures, unlike other sodium batteries (sodium–sulfur and sodium–nickel chloride). Development was carried out side by side with Li-ion technology in the 1970s and early 1980s. By the 1990s, interest had declined in favor of better-performing LIBs, but in the early 2010s, there was a resurgence in interest in NIB batteries, largely driven by the increasing demand for batteries and the cost of raw materials for LIBs. NIBs provide 3.3–3.7 V with 75–165 Wh kg^{-1} [44].

An aluminum–ion battery is a rechargeable battery in which aluminum ions (Al^{3+}) move back and forth between the positive and negative electrodes, exchanging three electrons (rather than one as for Li$^+$), which allows for specific energies as high as 1,060 Wh kg^{-1} with a specific power of 200 W kg^{-1} at 2.65 V. In addition, aluminum is abundant, meaning that rechargeable aluminum-based batteries have a low cost, and they also have low flammability, which makes these batteries appealing candidates for replacing LIBs. However, they also give rise to electrochemical issues that have not yet been fully addressed (e.g., electrode corrosion), so that, at present, they are limited to niche (e.g., military) applications [45].

Conclusion

The development of secondary batteries over the last decades has been astonishing and has made them a keystone in the success of PEs and electric mobility. Further plans for development in these fields, fostered by the transition to decarbonized energy, are very ambitious, and important research programs have been funded that aspire to ambitious goals over the next decades compared to the results achieved today.

Nevertheless, every technological domain has its own internal laws and constraints. Fewer than two dozen battery systems, including both primary and rechargeable, have been successfully commercialized since Alessandro Volta built the very first battery more than two centuries ago, which indicates
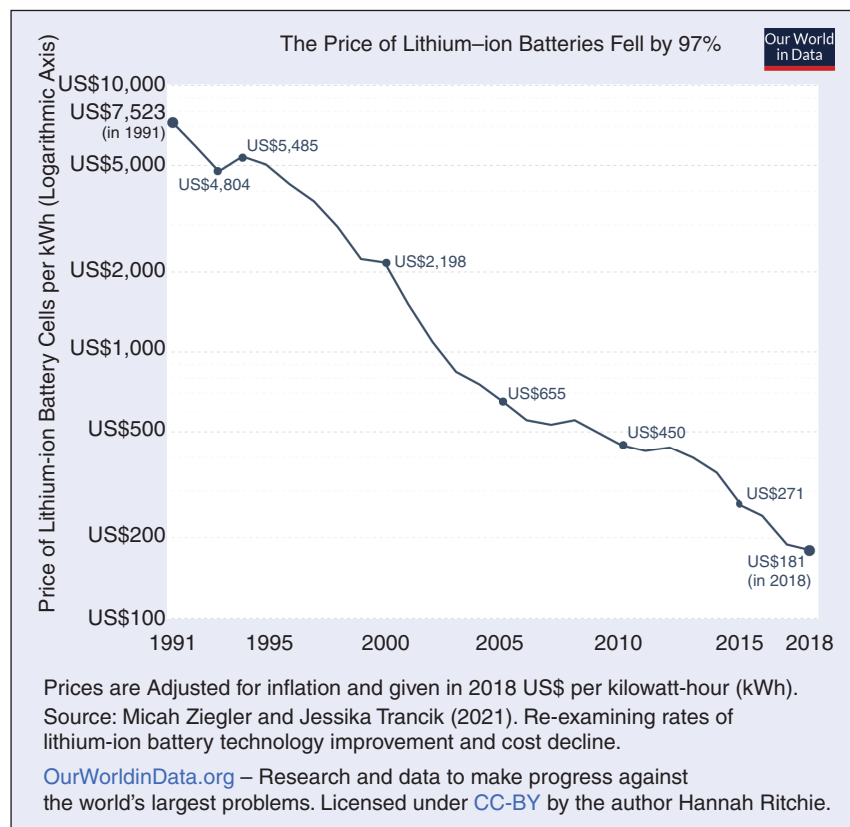

FIGURE 7 – The decline of LIB prices in the period 1991–2018. (Source: Taken from [40]; available at https://ourworldindata.org/battery-price-decline.)

the arduous nature of progress in this sector [41]. A comparison with the evolution of semiconductors and electronics, as governed by Moore's law, is illuminating [19]. If we take the first rechargeable Pb-A battery, developed by Planté in 1860 and capable of ~1 Wh kg^{-1}, as our starting point and assume that the evolution of specific energy is governed by Moore's law, then by 1928, the energy stored in a 1-kg battery would equal the energy released in the detonation of the first atomic bomb (~10^{11} Wh), and a battery pack used in a Tesla semitruck (~3,000 kg) would provide an energy comparable to that released from the explosion of a Type IA supernova (~10^{41} Wh kg^{-1}). In reality, the highest energy density achieved presently (2018) remains around 400 Wh kg^{-1} [41].

The epochal importance of the invention of the LIB was recognized with the assignment of the Nobel Prize in Chemistry to Goodenough, Whittingham, and Yoshino in 2019 for their outstanding contributions to this revolutionary battery. As I have tried to show in this column, other researchers also played fundamental roles in progress toward the LIB, including Armand, Yazami, and Scrosati, to mention only a few. As often happens, science and technology are moved by a kind of internal force and evolve when the conditions are mature. In this process, the role played by a single discoverer and/or inventor is often a question of who is first to achieve a result that is persistently worked toward by several others.

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