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Overview of the Development of Battery Technologies Used in Electric Vehicles Over the Years.

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Summary: The discovery by Alessandro Volta at the turn of the 18th and 19th centuries significantly advanced battery technology. For over 200 years, new solutions have been developed to enhance energy storage parameters. Technologies such as lead-acid, nickel-based, and lithium-ion batteries have found applications across various industries, with lithium-ion batteries currently being the most advanced and widely used. Technological progress has expanded interest in battery technology, eventually creating a demand in the automotive sector as well. Ongoing efforts aim to refine existing solutions, exploring new ways to improve not only battery capacity and weight but also charging times through the addition of specialized components. Significant changes are also occurring in recycling and the development of a circular economy in this field. Established methods for material recovery are being enhanced, along with innovative approaches such as using bacteria for material decomposition.

Key words: battery technology, EV, recycling, battery construction, li-ion batteries

1. Introduction

Technologies used in the electric vehicle (EV) industry are continuously evolving. This is primarily driven by the ever-new challenges faced by electric vehicles, both in terms of the components used in these vehicles and improvements to the supporting infrastructure. The demands of society contribute to the intensification of work in this field. Additionally, the European Union closely monitors EV manufacturers, with a particular focus on environmental aspects. Over the years, these factors have led to significant changes in the planning, distribution, and use of electric vehicles and charging stations. Given their integral role in energy storage systems, the market is now inundated with a variety of battery chemistries. Notable types include nickel-based, lead-acid (LA), and lithium-ion (LI) batteries, each with distinct properties [32]. Currently, lithium-ion batteries are prevalent in power tools, electric bikes, electric motorbikes, electric cars, military equipment, aviation, and aerospace applications. For example, automotive brands like Tesla, BYD, and Changan utilize lithium batteries for energy storage. However, despite their benefits, lithium-ion batteries have several drawbacks that need addressing. These issues include cell material challenges, production process inefficiencies, high compaction of positive and negative electrodes, excessive moisture, and safety risks such as leaks and potential explosions [2].

2. The Beginnings of Battery Technology

The pioneer in battery technology was Alessandro Volta. In 1800, he conducted experiments in this field and ultimately developed the device known today as the Voltaic Pile (Fig. 1). The device was constructed using two metals: zinc and copper. Discs of these metals were stacked in the battery, with each disc separated by cardboard or fabric soaked in brine or vinegar (Fig. 2). The reaction occurring between the layers in each three-disc section created an electrical cell and generated a current. Connecting a wire to the end of the structure allowed for a continuous flow of electricity until the battery was depleted. Thus, it was a battery that stored chemical energy and, through appropriate electrochemical reactions, released it as electrical energy.

Fig. 1. The appearance of Volta's invention [3]

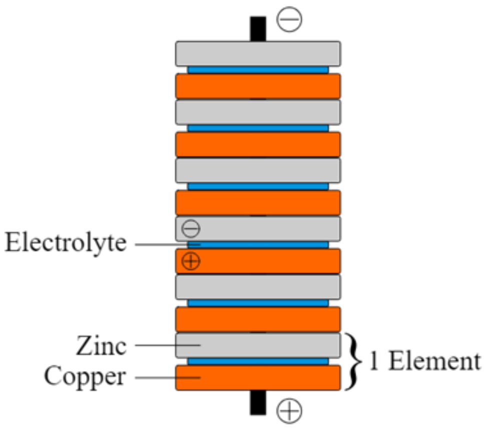

Fig. 2. The diagram of Volta's battery [4]

Volta's design, however, had its drawbacks, which quickly became apparent. Due to the substantial weight of the components, adding more cells was quite challenging, resulting in limited voltage output for devices. Additionally, the discs corroded rapidly, significantly shortening the battery's lifespan. While this invention was not perfect, it certainly laid the groundwork for further technological advancements [5]. Another key figure in the development of batteries was Michael Faraday. His research in electromagnetism led to the creation of new types of motors and batteries [6].

2.1. Lead Acid Baterries

In 1859, French physicist Gaston Planté developed a new battery technology. His invention, the lead-acid battery, was the first to be used on a large scale. The operation of the battery is as follows: each cell consists of a cathode (lead peroxide) and an anode (pure lead) submerged in an electrolyte composed of sulfuric acid and water (in a 1:2 ratio). A reaction occurs between the cathode and the acid, producing positive hydrogen ions and negative sulfate ions. These ions further react to form lead sulfate and water. The negative sulfate ions then move toward the anode, where they release their extra electrons and react with lead sulfate to regenerate lead peroxide and sulfuric acid. The anode is connected to the battery's positive terminal, causing the released electrons to flow to the negative terminal connected to the cathode. This flow of electrons generates electric current, which can be used to power various components (see Fig. 3). The fact that water is produced during the reaction dilutes the sulfuric acid in the electrolyte, leading to gradual battery discharge, with each subsequent reaction being weaker than the last. However, this process is reversible; in cars, the alternator recharges the battery during operation [7],[8],[9].

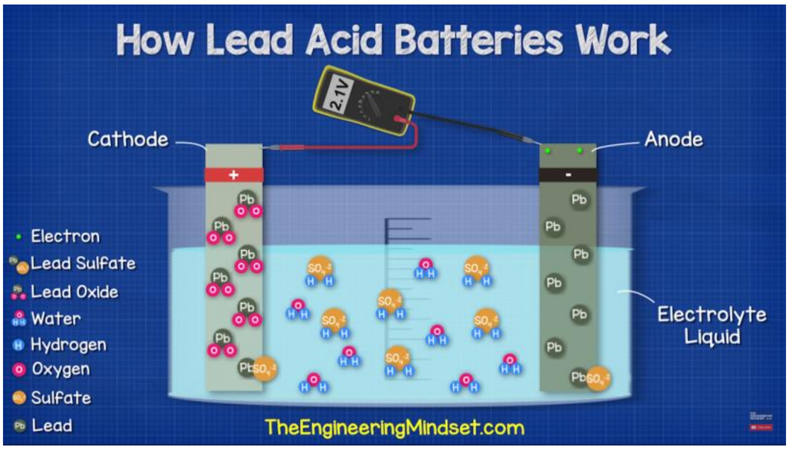

Fig. 3. The moment of current generation during the chemical reaction [8]

Lead acid batteries are characterized by a long charging time, typically ranging from 8 to 16 hours. Additionally, these batteries should be stored in a fully charged state, as leaving them discharged may prevent recharging or significantly affect their condition. The charging voltage is also crucial; charging the battery at too high a voltage can initially improve its condition but will significantly shorten its lifespan over time, while too low a voltage can damage the anode. It's also important to note that lead acid batteries do not perform well under full cycle usage, meaning frequent deep discharges can lead to damage. A good indicator of a battery's lifespan is the thickness of the cathode, which gets damaged during the battery's operation; in short, the thicker the plate, the longer the battery life [10].

2.2. Nickel Metal Hydride Batteries

Stanford Ovshinsky's nickel-metal hydride battery has found widespread use, particularly in hybrid vehicles. The cathode is made from nickel hydroxide, while the anode consists of a metal alloy that reacts with hydrogen. Both plates are submerged in potassium hydroxide. The separator is typically made of polyolefin. During discharge, the metal hydride in the anode reacts with negative hydroxide ions (OH-) from the potassium hydroxide, producing metal and water. The electrons released in this reaction are used to power the connected device, generating an electric current. At the same time, the water formed in the cathode reacts with nickel hydroxide (NiOOH), releasing negative hydroxide ions (OH-) and forming nickel hydroxide ($Ni(OH)_2$). During charging, the process reverses: water is produced in the cathode by reacting with OH- ions, which then reacts with the anode (see Fig. 4). Thus, the operation of the battery relies on the movement of OH- ions between the cathode and anode [11].

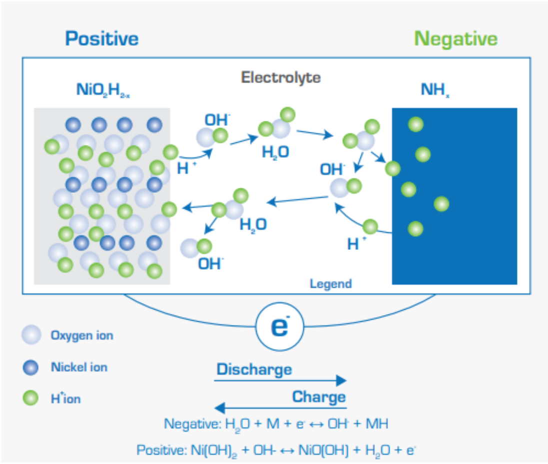

Fig. 4. Diagram of NiMH battery charging [12].

Nickel metal hydride batteries present significant challenges with charging. Their charging efficiency is around 150%, meaning that to fully charge a 100 Ah battery, 150 Ah of energy must be supplied. The efficiency worsens with faster charging. This issue arises because each battery cell has different resistance values, which, while similar, affect the smoothness of the charging process. To mitigate this problem, additional resistors are often used to regulate the current flow through the cells [13]. These batteries require periodic calibration, meaning they must be fully charged and discharged from time to time, which affects user convenience. They also suffer from overcharging and are sensitive to high temperatures, which can reduce their efficiency and lifespan [14].

2.3. Lithium – Ion Batteries

The lithium-ion battery technology was pioneered in the 1970s at Oxford University by chemist John Goodenough and his colleagues Phil Wiseman, Koichi Mizushima, and Phil Jones. Their concept was adopted in the 1990s when SONY began mass-producing these batteries. In 2019, John Goodenough received the Nobel Prize in Chemistry for his groundbreaking discovery [15]. The battery consists of a cathode (a cobalt oxide plate) and an anode (a plate made of lithium and carbon graphite), with a separator in between that acts as the electrolyte (lithium hexafluorophosphate). Lithium atoms release additional electrons that move towards the cathode. At the same time, positive lithium ions leave the anode and travel to the cathode. In the cathode, cobalt oxide breaks down into positive cobalt ions and negative oxygen ions. This process charges the anode positively and the cathode negatively. To prevent interruption of the reaction, lithium ions pass through the electrolyte to the cathode, neutralizing its negative charge. This allows the reaction to continue until all lithium ions leave the anode, indicating the battery is discharged (Fig. 5). During charging with a charger, the reverse reaction occurs—lithium ions return to the anode [16],[17].

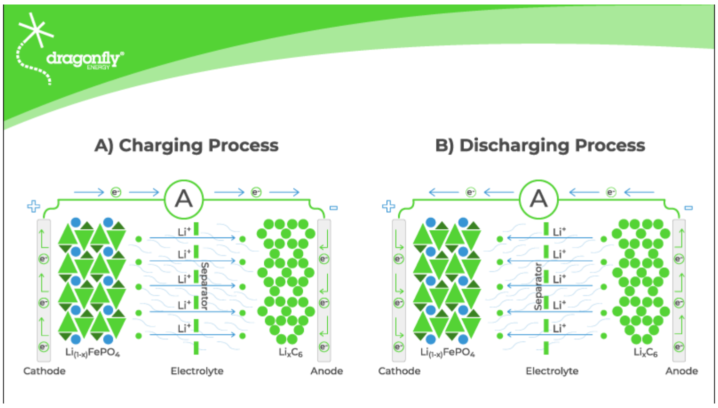

Fig. 5. Charging and discharging diagram for lithium-ion batteries [18]

Specific advantages of these batteries include high energy density with very low weight, long cycle life, and relatively short charging times. It is also worth noting that complete discharge does not affect their lifespan. Although lithium-ion batteries are safer than lead-acid batteries, they have their own issues that must be considered during use. Primarily, they can overheat, so they require a circuit to protect against excessive temperatures that could impact their lifespan. Low temperatures also negatively affect them, slowing down the charging process, especially at temperatures below 0°C [19].

2.4. Solid – State Batteries

In recent years, solid-state technology has been developed based on lithium-ion batteries. This advancement was significantly contributed to by a group of Japanese scientists who, in 2011, created the first electrolyte that was in a solid rather than a liquid phase [20],[21]. The principle of operation is similar, but the new solution uses a ceramic separator and eliminates the use of a solid anode (Fig. 6). During battery discharge, when lithium exits the cathode, an anode composed of lithium metal (lithium – metal anode) forms behind the separator [22].

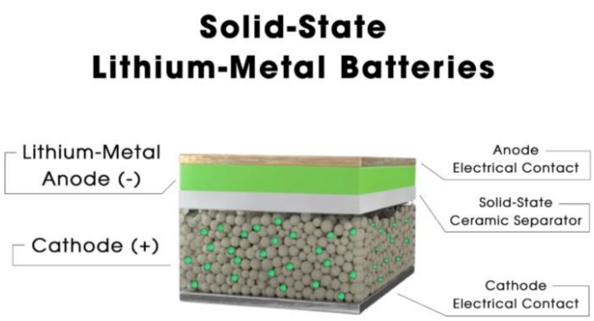

Fig. 6. Structure of solid-state batteries [23]

Solid-state batteries offer higher energy density compared to traditional lithium-ion batteries, which translates to greater range for electric vehicles and longer lifespan for portable devices. Faster charging is another advantage, making them more practical for electric vehicles. They are also safer, as the solid electrolyte is less prone to ignition compared to liquid electrolytes. One of the main challenges is the cost of production, as materials used for the solid electrolyte are more expensive and the manufacturing processes are more complex. Additionally, there are still safety challenges to address [23],[24].

3. Types of batteries in electric vehicles

Each type of battery finds its application in specific areas of electric vehicles, depending on their physicochemical properties, as well as cost and durability. The main types used are lead-acid, nickel-metal hydride, and lithium-ion batteries. The first type, lead-acid, is used less frequently now due to its poor resistance to low temperatures, which is crucial for electric cars. Nickel-metal hydride batteries are most commonly used in hybrid cars. This is primarily due to their ability to handle frequent use (many small cycles), which can be easily achieved in hybrid systems, ensuring long battery life. The last type, lithium-ion batteries, is widely used beyond the electric vehicle sector. Due to their performance characteristics, lithium-ion batteries have dominated the battery market across many sectors. They offer the best optimization of size and weight, a favorable mass-to-energy ratio, and a competitive price [25]. Several variations of lithium-ion batteries have been introduced to the market, mainly differing in the materials used for the cathode. In 2022, the nickel-manganese-cobalt (NMC) battery was the most popular type for electric cars worldwide, powering 60% of electric vehicles. Lithium iron phosphate (LFP) batteries were the second most common, with a market share of about 30%, while nickel-cobalt-aluminum (NCA) batteries accounted for 8%. Chinese manufacturers, particularly BYD, have favored LFP batteries, producing half of such batteries in China. Other companies are also increasing their use of LFP, with Tesla using LFP in 30% of its cars in 2022, up from 20% in 2021. LFP batteries have the advantage of slower degradation compared to other types, but they have a lower energy density, meaning they store less energy for the same weight. The most popular type, NMC, does not excel in either durability or energy density but optimally balances both properties [26]. Research and development of new solutions are ongoing. The primary objective of EV design is to maximize battery capacity while ensuring a high level of safety. A common strategy is to install the battery pack inside reinforced and stiffened compartments or other areas that are less likely to be damaged in crashes. This area is sometimes referred to as a passenger car's "safe zone." Typically, this zone is located between the wheelbase and the center of the chassis. By placing the lithium-ion battery (LIB) pack in this region, automakers aim to minimize the risk of battery damage in the event of a crash or impact [27].

4. Lithium-ion battery recycling technology

Recycling lithium-ion (Li-ion) batteries is crucial from an environmental protection and sustainable development perspective. The recycling process for these batteries involves several technologies aimed at recovering valuable materials and minimizing environmental impact.

The initial stage in recycling Li-ion batteries involves a pretreatment process. This stage focuses on separating the components and materials of spent LIBs based on various physical properties such as shape, density, conductivity, and magnetic characteristics. Effective pretreatment enables the segregation and enrichment of materials with similar physical attributes, enhancing recovery rates and reducing energy consumption in subsequent pyrometallurgical or hydrometallurgical processes [28]. A notable example of this process is the RECUPYL method, which is widely used in France on an industrial scale. Initially, used batteries are shredded using a rotary shredder operating at 11 rounds per minute, followed by further crushing with a rotor. Both processes are conducted in a sealed chamber filled with argon and carbon dioxide to prevent the lithium from reacting violently with air. The oxygen levels and pressure within the chamber are continuously monitored and controlled. After shredding, the resulting materials are sorted into several fractions: a fine fraction rich in carbon and metals, a magnetic fraction, an aluminum and copper fraction, and a low-density mixture of plastics and paper. The sorted fine materials are then placed into a specialized water bath, where lithium reacts with water to release hydrogen gas. The continuous mixing and controlled material dosing in the bath help minimize the risk of hydrogen buildup. Lithium is recovered from the solution containing lithium hydroxide by adding soda or phosphoric acid, while other metals are extracted using hydrometallurgical techniques [29].

The hydrometallurgical approach is the primary method for recycling spent lithium-ion batteries (LIBs), representing over half of all recycling activities. This technique encompasses various processes such as leaching and recovery, including solvent extraction, chemical precipitation, and electrochemical deposition [28]. Hydrometallurgy is effective in extracting metals from used LIBs, offering several advantages: it produces high-purity materials, recovers a majority of LIB components, operates at lower temperatures, and generates less CO2 compared to pyrometallurgical methods. However, it also has some limitations, such as the necessity for sorting, which can drive up costs, and difficulties in separating elements with similar properties in the solution [1]. In the United States, the TOXCO hydrometallurgical process is utilized. This process starts with cryogenically cooling the batteries using liquid nitrogen at -196°C. After cooling, the batteries are shredded and then immersed in water. This causes metal ions to react with water, forming hydroxides and releasing hydrogen gas. Notably, the TOXCO process also achieves a lithium recovery rate of 15-26%, distinguishing it from other industrial methods [29].

Pyrometallurgy is a thermal treatment method that encompasses processes such as pyrolysis, smelting, distillation, and refining. Initially, batteries are shredded and then subjected to gradual heating. During pyrolysis, plastics and solvents are combusted, leading to the breakdown of organic materials. This process facilitates the separation of materials into metallic fractions and slag, which includes lithium and manganese. [1], Although pyrometallurgy offers some benefits, it also has significant drawbacks, including material losses, high energy consumption, and the release of harmful gases such as dioxins and furans [28]. A notable example of pyrometallurgical processing is UMICORE's method, which involves melting used lithium-ion batteries. "The resulting metal alloy, which includes cobalt, nickel, copper, and iron, is then further processed using hydrometallurgical techniques, specifically acid leaching, to extract these metals [29]". In this context, pyrometallurgical processes are focused on recovering cobalt, which means that the estimated economic efficiency of the process also significantly depends on the cobalt price [28].

In recent years, biological methods for material recovery have emerged as an eco-friendly alternative, though they are less efficient compared to chemical and thermal processes. These methods utilize acidophilic bacteria, such as *Acidithiobacillus ferrooxidans*, which are essential for bioleaching. These bacteria facilitate the transfer of metals from solid to liquid phases. The process works through mineral bio-oxidation, where microorganisms oxidize metal sulfides – insoluble in water – into soluble sulfates, using electrons sourced directly from the material itself [29].

5. Conclusion

Due to the rapid development of the battery industry, there is an ongoing search for new technologies or improvements to existing solutions. Currently, in addition to advancements in solid-state batteries and efforts to create better energy management systems in energy storage, several interesting trends are emerging. In China, the company CATL is progressively introducing sodium-ion batteries to the market. These batteries operate on a principle similar to lithium-ion batteries but use a different material for the cathode. The advantage of this solution is not an improvement in battery efficiency but a significant reduction in cost. In response to this trend, where price plays a crucial role, efforts have been made to develop cathodes made from cheaper materials. Current NMC (nickel manganese cobalt) cathodes, which are among the most expensive on the market, are being replaced by LFP (lithium iron phosphate) cathodes. These are a more affordable alternative, and recent advancements have improved their performance to an acceptable level, leading to a market share increase from 10% to 40% between 2018 and 2022. This technology has particularly caught the interest of Tesla, which is already incorporating it into some of its vehicles, and companies like Ford and Volkswagen have also expressed interest in similar actions. While manufacturers are currently focused on improving cathodes, there is also significant potential for enhancement in the area of anodes. Research in this area is expected to begin in the near future. Most anodes used in lithium-ion batteries contain graphite, but other materials, such as silicon, could be used to improve battery performance (e.g., to accelerate charging) [30],[31]. There are many ideas, with the goals being the same: improving performance, reducing costs, and minimizing environmental impact.

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