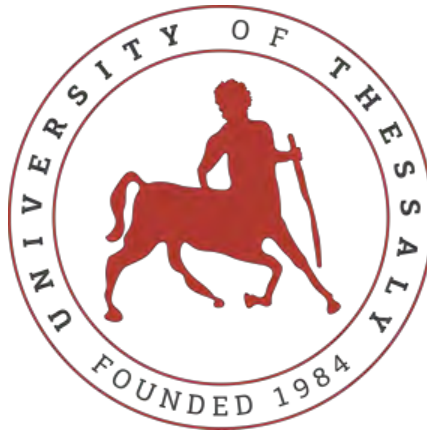




UNIVERSITY OF THESSALY
DEPARTMENT OF MECHANICAL ENGINEERING

LiFePO₄ BATTERIES: NEW MATERIALS, FAILURES AND RECYCLING

Diploma Thesis by :
Karavasileiou Alexandros

Supervisor: Panagiotis Tsiakaras

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Approved by the Committee on Final Examination:

Advisor Dr. Panagiotis Tsiakaras Professor
Department of Mechanical Engineering
University of Thessaly

Member Dr. Athanasios Papathanasiou Professor
Department of Mechanical Engineering
University of Thessaly

Member Dr. Angeliki Brouzgou Assistant Professor
Department of Energy Systems
University of Thessaly

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Abstract

Modern society is deeply invested and intricately tied to the use of energy, primarily derived from fossil fuels. However, the extraction and utilization of these fuels have given rise to health and environmental concerns. Though these concerns, the pursuit of alternative energy sources has risen. The most prominent one is the use of electrochemical devices, and among them, lithium-ion batteries stand out as one of the most promising options. From the lithium-ion batteries, we are going to talk about the LiFePO₄ batteries and how and why they matter. Nevertheless, there are notable uncertainties regarding the emergence and management of these batteries. With the increasing demand for lithium-ion batteries, there is a parallel rise in the volume of waste generated. In general, a lot of the materials that are used to make these batteries are considered hazardous and need to be dealt with after the use of the batteries and the direct disposal into the environment is not a viable solution. In light of these challenges, a new need has emerged for a better and more sufficient battery recycling circle.

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CHAPTER 1

Introduction

Among the overall rise in energy demand, electricity demand has seen the most significant increase in the latest years, and renewable energies accounted for half of the additional electricity production. Future projections forecast their increase at about 30 % of global power demand with the 70 % of that being covered by the global electricity generation through photovoltaics and wind power plants. According to **Figure 1**, in the stated policies scenario global electricity demand grows at 2.1% per year to 2040. This raises electricity's share in total final energy consumption from 19% in 2018 to 24% in 2040. Electricity demand growth is set to be particularly strong in developing economies.

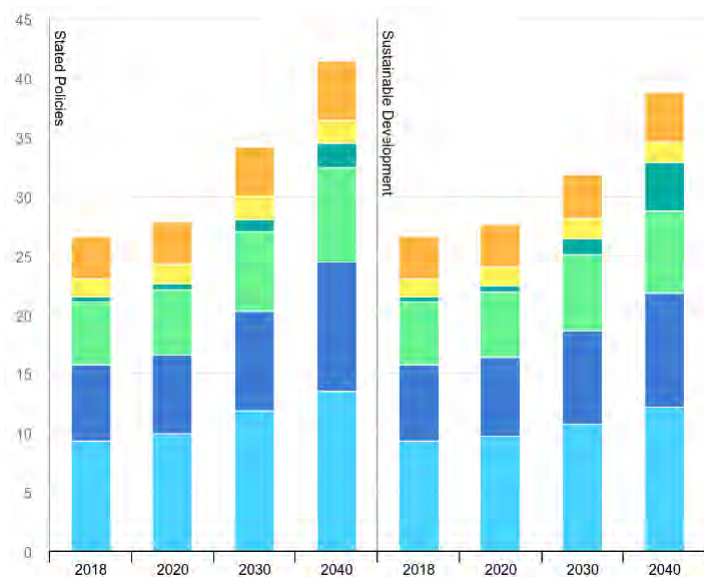


Figure 1 : Comparison of the renewable energy consumption in major markets worldwide [1].

This is also due to government policies, market conditions and available technologies collectively set a course for use of electricity as a way to combat climate change and lower carbon emissions. Also, according to the chart electricity will play an even larger role, reaching 31% of final energy consumption. As presented also in **Figure 2**, we can see a study growth in the need of the global battery supply and demand, with Asia (red) and Europe (blue) having the biggest growth of the regions.

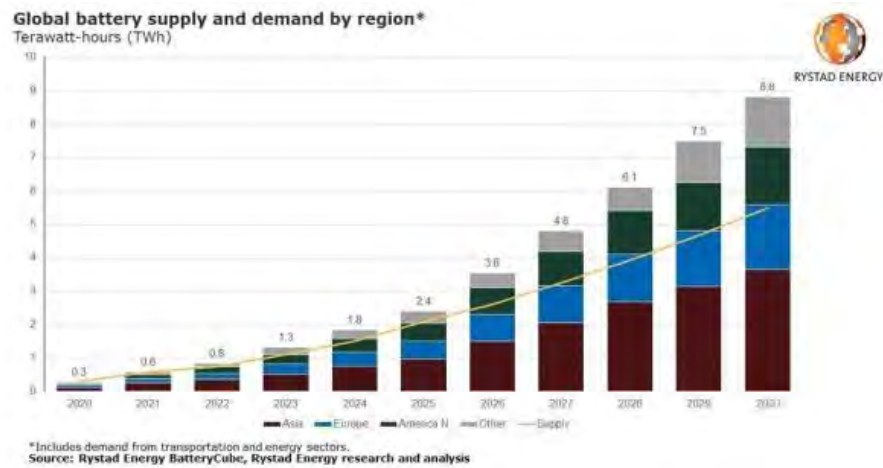


Figure 2 : This chart shows us the global battery supply and demand by region until the 2030 [2].

The increase in the battery demand could also be traced to the rapid electrification of the global transportation sector, with forecasts indicating a more substantial integration of electric vehicles into the market in the immediate future. The recent international agreement on climate change unequivocally illustrates that reducing internal combustion engine cars contributes to a decline in local air pollution, thereby positively impacting both the environment and human health. The shift toward electrification in the automotive sector is evident in the increasing sales of electric cars worldwide in recent years. China has played a significant role in this trend, doubling the number of electric cars in 2017 and accounting for nearly 40% of the global total. Conversely, Scandinavian nations boast the highest adoption of electric vehicles in their domestic markets, with Norway at the forefront, holding a remarkable 39% market share for electric cars [131].

In general batteries, serve as an alternative energy storage mechanism, that offers numerous advantages. There are types of batteries like the Zinc-air batteries that can enable people to hear because they are used in hearing aid devices [27]. Currently, traditional battery technologies like lead-acid and nickel-cadmium are gradually being replaced by lithium-ion (Li-ion) batteries, fuel-cell technologies, and nickel-metal hydride batteries. Among these, Li-ion battery technology emerges as the forefront and market leader. As presented in **Figure 3**, the Li-ion batteries have the best volumetric energy density to specific energy density demonstrating exceptionally high energy density. Lithium-ion batteries have demonstrated stability over 500 cycles, can be manufactured in various sizes, and demand minimal maintenance compared to alternative battery technologies. On going research endeavors focus on aspects such as cost reduction, enhancing cycling life, and improving safety. Already integrated into high-end electronics, Li-ion technology has recently entered the power tool markets and is making strides in the hybrid electric vehicle sector, positioning itself as a formidable candidate for powering future electric cars [1][2].

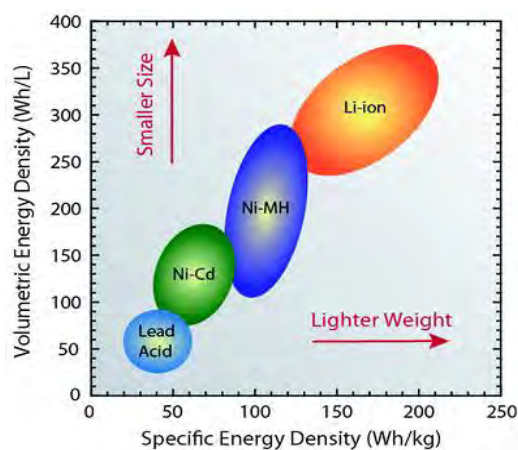


Figure 3: In this picture we can see a comparison between the various battery technologies in terms of energy density [3].

Nevertheless, due of the increase in demand of batteries and the sustainability of Lithium-ion Batteries (LIBs) for the future generations is it deemed necessary. The pivotal role of recycling in ensuring the overall sustainability of upcoming batteries is contingent upon battery features, encompassing environmental risks. Therefore, the incorporation of recycling considerations should be fundamental in the evolution of battery systems

Beginning this thesis in the second chapter we will be addressing the different electrochemical energy storage devices. These are one way to address the issues we face in shifting to a greener economy is through increased electrification of transportation and the ability to convert and store renewable energy. These include the metal-air cells, supercapacitors and the fuel cells.

In the upcoming third chapter, we will delve into the topic of lithium-ion batteries. These batteries have become widely utilized as a type of rechargeable battery. Over the past few decades, they have demonstrated their effectiveness as an energy storage technology, marked by inherent advantages like high efficiency, reliable performance, elevated energy density, impressive rate capability, and extended life cycles compared to other battery types. Recent advancements in LIB technology have further broadened their applications to encompass solar and wind stationary energy storage systems, power sources for electric vehicles, smart grids, and even space technologies.

In the fourth chapter, we will delve deeper into LiFePO₄ batteries. We will discuss their characteristics, structure, and electrochemical functions in greater detail. Additionally, we will explore common issues associated with this type of battery and examine new methods aimed at enhancing their performance.

In the fifth, several technological methods for reusing and recycling LiFePO₄ batteries will be introduced. Among others, pyrometallurgy and hydrometallurgy are some of the most critical recycling methods. Moreover, recent advances and key technologies will be mentioned.

In the concluding sixth chapter, there are final remarks and reflections on the potential advancements that could transpire in these field and current implementations will be pointed out.

CHAPTER 2

An Exploration of Electrochemical Devices and Energy Storage

2.1 Electrochemistry

Electrochemistry is the scientific exploration of the relationship between a measurable electrical potential and a discernible chemical change. In simpler terms, it is the branch of chemistry dedicated to understanding the electricity generated in spontaneous chemical reactions and the application of electrical energy to drive non-spontaneous chemical transformations. This area holds significance because electrochemical processes have the capability to produce diverse substances such as metals, chlorine, fluorine, sodium hydroxide, and other chemicals. Notably, electrochemical reactions are advantageous for their energy efficiency and environmentally friendly characteristics. Thus, delving into this field is crucial for the advancement of innovative and sustainable technologies. Furthermore, an electrochemical power source is a mechanism that produces electrical energy through chemical reactions. The main difference and benefit of the electrochemical power sources is that compared to other energy sources the conversion of energy happens only once. The conventional process uses multiple steps, like in the hydroelectric plants, but in electrochemical power sources is replaced by a single step. This single conversion of energy gives us a lot of benefits like better energy efficiency and lower cost of energy [29][30]. As we can see in the **Figure 4**, batteries and fuel cells that are two of the most fundamental electrochemical energy storage systems have good energy density.

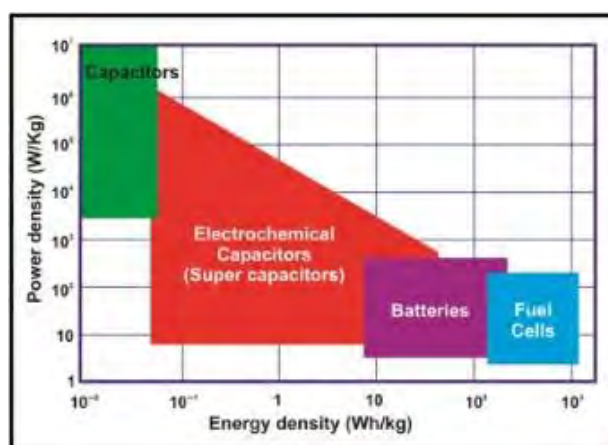


Figure 4 : A diagram of the most Fundamental electrochemical energy storage systems [9].

An electrochemical device consists of two electrodes, separated by an electrolyte. In its functioning, electrons are compelled to move from the negative electrode, known as the anode, to the positive electrode, referred to as the cathode. This typically takes place until the electrode is consumed. The electrodes can be made by metals or other chemical compounds. Also, the electrolyte can be solid or liquid [29]. In more detail electrochemistry involves the production or consumption of free electrons during reactions.

2.1.1 Reduction and oxidation processes

Reduction and oxidation are electrochemical processes that alter the oxidation state of a molecule or ion by either donating or accepting electrons. This reaction can happen when we apply external voltage is applied or when chemical energy is released. Typically, this process involves one component, identified as the reducing agent, undergoing oxidation, while another component, known as the oxidizing agent, experiences reduction. In this scenario, the first component is oxidized, while the second undergoes reduction [31].

2.2 Electrochemical Devices

Two highly important fields that have captured considerable interest from research communities are energy harvesting and storage. Moreover, renewable energy sources have experienced increased popularity in recent decades, while we try to distant our world from using fossil fuels, with new and innovative technologies that can improve their of energy generation not only for the people but also for industrial purposes. Over the years it was found that utilizing electrochemical energy production has been contemplated as an alternative energy source. Every year electrochemical energy technologies are increasingly being researched with the goals of optimizing their cost, longevity, and performance. Some examples of electrochemical energy storage and conversion systems are [32]:

- Batteries
- fuel cells
- electrochemical sensors
- and electrochemical capacitors

2.2.1 Fuel Cells

Fuel cells are devices that utilize fuel as an input and can produce electricity as an output. As long as a fuel cell continues to receive fuel as its raw material, it will consistently generate

electricity. This distinguishes fuel cells from batteries, as, even though both rely on electrochemistry for operation. Their biggest difference is that a fuel cell will not deplete during the process but a battery will do. Fuel cells have two electrodes and between them an electrolyte. To have a complete device we need also a flow path for the electrons such as a wire. We have a lot of types of Fuel cells. We can distinguish them by their electrolyte and the major types are:

- Phosphoric acid fuel cell (PAFC)
- Polymer electrolyte membrane fuel cell (PEMFC)
- Alkaline fuel cell (AFC)
- Molten carbonate fuel cell (MCFC)
- Solid-oxide fuel cell (SOFC)
- Direct methanol fuel cell (DMFC)
- Reversible fuel cell

The most common of the above are the PEMFC and SOFC fuel cells. Every type of fuel cell has different characteristics and benefits [33].

2.2.2 Types of fuel cells

Fuel cells are generally categorized according to the electrolyte type employed and their operational temperature. Various fuel cell technologies are currently under development for diverse applications, each employing distinct chemical processes.

- Proton Exchange Membrane fuel cell (PEMFC)

A Proton Exchange Membrane fuel cell (PEMFC) is a form of fuel cell that relies on electrochemical reactions to generate electricity. This type of fuel cell comprises a proton-conductive membrane, typically composed of a polymer electrolyte, which separates the anode and cathode sides. Known for their efficiency, high power density, and versatility, PEMFCs have found applications in various fields [45].

In the operation of a PEMFC, hydrogen gas is introduced to the anode side, while oxygen from the air is directed to the cathode side. At the anode, catalytic reactions take place, causing hydrogen molecules to undergo a process that releases protons (H^+) and electrons (e^-). The protons move through the proton-exchange membrane towards the cathode, while the electrons travel through an external circuit, generating an electric current. **Figure 5** shows us the movement of the hydrogen through a PEMFC giving us a better understanding in the operation of it.

One notable feature of PEMFCs is their ability to operate at relatively low temperatures, typically around 80°C. This characteristic allows for rapid start-up times and enhanced overall efficiency. The polymer electrolyte membrane plays a crucial role in enabling selective proton transport, facilitating the electrochemical reactions, preventing the passage of electrons, and inhibiting gas crossover between the anode and cathode [45].

PEMFCs have diverse applications, ranging from hydrogen fuel cell vehicles in transportation to stationary power generation and portable electronic devices. Their rapid response to changes in power demand, high energy efficiency, and minimal emissions make them an attractive choice for clean energy solutions.

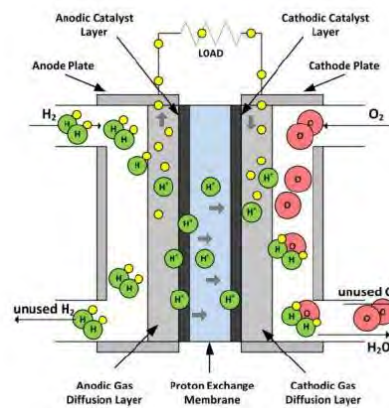


Figure 5 : Diagram of a PEMFC [32].

- Solid Oxide fuel cell (SOFC)

Solid Oxide Fuel Cell (SOFC) is a type of fuel cell that operates through the electrochemical conversion of fuel and oxygen into electricity. This category of fuel cell utilizes a solid oxide electrolyte to conduct ions between the anode and cathode, facilitating the electrochemical reactions involved in power generation. SOFCs are known for their high operating temperatures, making them suitable for various applications.

In the SOFC configuration, a solid oxide electrolyte, often made of ceramics like yttria-stabilized zirconia, serves as the medium for ion conduction. The anode and cathode sides of the cell are coated with catalysts that facilitate the oxidation and reduction reactions. At the anode, fuel, typically hydrogen or natural gas, undergoes catalytic oxidation, releasing electrons and oxygen ions (O^{2-}). The electrons travel through an external circuit, generating electric power, while the oxygen ions migrate through the solid oxide electrolyte to the cathode as we see in the **Figure 6** [46].

At the cathode, the oxygen ions combine with electrons and react with air to produce oxygen gas. This process completes the electrochemical cycle and sustains the fuel cell's operation. SOFCs are

recognized for their high efficiency, fuel flexibility, and capability to directly utilize hydrocarbon fuels without reforming.

One notable characteristic of SOFCs is their ability to operate at elevated temperatures, typically ranging from 500 to 1,000 degrees Celsius. This high-temperature operation contributes to their efficiency and makes them suitable for stationary power generation applications, such as combined heat and power systems [106]. SOFCs have seen applications in diverse sectors, including residential and commercial power generation, auxiliary power units for vehicles, and distributed energy systems. Ongoing research focuses on improving SOFC materials, lowering operating temperatures, and addressing durability concerns to enhance their commercial viability and widespread adoption as a clean and efficient energy technology [126].

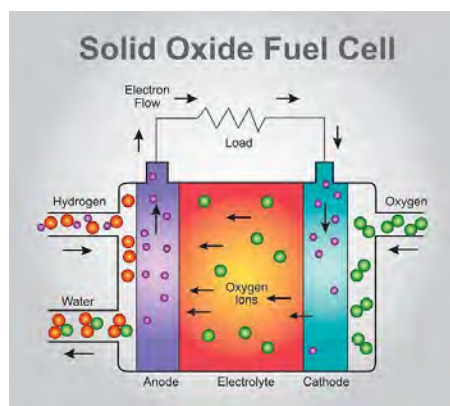


Figure 6 : Diagram of a SOFC [33].

- Alkaline fuel cell (AFC)

An Alkaline Fuel Cell (AFC) is a type of fuel cell that operates on the principle of electrochemical reactions to convert chemical energy into electrical energy. Unlike some other fuel cell types, AFCs use an alkaline electrolyte, typically a solution of potassium hydroxide (KOH) in water, to facilitate ion conduction and support the electrochemical processes involved in power generation [47].

In an AFC configuration, hydrogen gas is supplied to the anode, while oxygen or air is fed to the cathode. As presented also by the **Figure 7**, at the anode hydrogen undergoes a catalytic reaction, leading to the release of electrons and hydroxide ions (OH^-). The electrons follow an external circuit, creating an electric current, while the hydroxide ions migrate through the alkaline electrolyte to the cathode. At the cathode, oxygen or air combines with electrons and hydroxide ions to form water, completing the electrochemical cycle. This process produces electrical energy and water as byproducts, making AFCs an environmentally friendly option [127].

AFCs operate at relatively low temperatures compared to some other fuel cell types, typically between 60 and 80 degrees Celsius. This lower operating temperature simplifies materials and design requirements, contributing to the overall efficiency of AFCs. They are known for their simplicity, high efficiency, and potential for low-cost production.

AFCs have been used in various applications, including space exploration, where they were employed in the Apollo and Space Shuttle missions. They are also suitable for stationary power generation, as well as applications where the byproduct water is acceptable or even desirable, such as life support systems or medical devices [128].

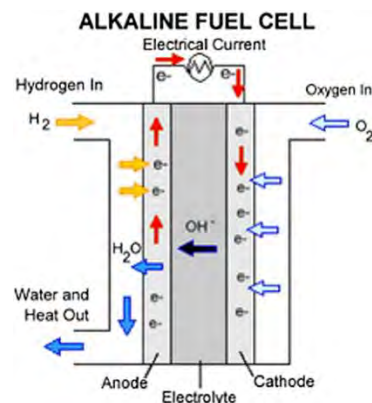


Figure 7 : Diagram of an AFC [34].

- Phosphoric Acid fuel cell (PAFC)

A Phosphoric Acid Fuel Cell (PAFC) is a type of fuel cell that operates on the principle of electrochemical reactions to convert chemical energy into electrical energy. PAFCs use a phosphoric acid-based electrolyte to facilitate ion conduction and support the electrochemical processes involved in power generation [48].

In a PAFC configuration, hydrogen gas is supplied to the anode, while oxygen or air is fed to the cathode. As presented by the **Figure 8**, at the anode, hydrogen undergoes a catalytic reaction, leading to the release of protons (H⁺) and electrons (e⁻). The protons migrate through the phosphoric acid electrolyte to the cathode, while the electrons follow an external circuit, creating an electric current. At the cathode, oxygen or air combines with electrons and protons to form water, completing the electrochemical cycle. This process produces electrical energy and water as byproducts, making PAFCs an environmentally friendly option [129].

PAFCs operate at higher temperatures compared to some other fuel cell types, typically between 150 and 200 degrees Celsius. The elevated operating temperature contributes to improved efficiency and allows for a faster electrochemical reaction [48].

PAFCs are known for their reliability, high efficiency, and suitability for stationary power generation. They have been utilized in various applications, including distributed power

generation for buildings and industrial facilities. PAFC systems can provide both electricity and useful heat through combined heat and power (CHP) configurations.

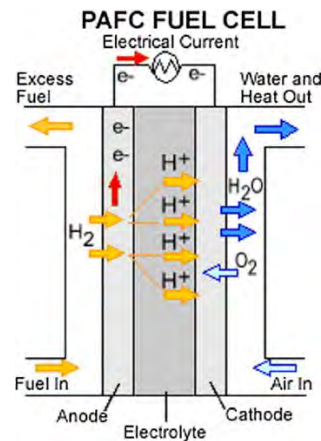


Figure 8 : Diagram of PAFC [34].

- Molten Carbonate fuel cell (MCFC)

A Molten Carbonate Fuel Cell (MCFC) is a type of fuel cell that operates based on electrochemical reactions to convert chemical energy into electrical energy. MCFCs use a molten carbonate electrolyte to facilitate ion conduction and support the electrochemical processes involved in power generation.

In the MCFC configuration, a mixture of lithium, sodium, and/or potassium carbonates serves as the electrolyte. Hydrogen gas is supplied to the anode, while oxygen or air is fed to the cathode. As presented also from the **Figure 9**, at the anode, hydrogen undergoes a catalytic reaction, leading to the release of electrons (e⁻) and carbonate ions. The carbonate ions migrate through the molten carbonate electrolyte to the cathode, while the electrons follow an external circuit, creating an electric current. At the cathode, oxygen or air reacts with electrons and carbonate ions to form water, carbon dioxide, and additional carbonate ions, completing the electrochemical cycle. This process generates electrical energy and produces water and carbon dioxide as byproducts.

MCFCs operate at elevated temperatures, typically between 600 and 700 degrees Celsius. The high operating temperature contributes to improved efficiency, allowing for a faster electrochemical reaction and increased tolerance to impurities in the fuel [110].

MCFCs are known for their potential for large-scale power generation and are suitable for stationary applications. They have been considered for stationary power generation and utility-scale power plants due to their ability to provide both electricity and useful heat through combined heat and power configurations [130].

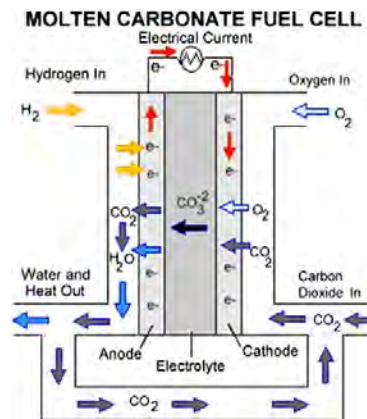


Figure 9 : Diagram of Molten Carbonate Fuel Cell [34].

Table 1 : Comparison of the different fuel cell types.

Fuel Cell	Fuel	Thermal operation range	Uses
Alkaline fuel cell (AFC)	H ₂	100–200°C	Space and Military
Molten Carbonate fuel cell (MCFC)	H ₂ και CO	650°C	Generation of power
Solid Oxide fuel cell (SOFC)	H ₂ και CO	750-1050°C	Generation of power
Phosphoric Acid fuel cell (PAFC)	H ₂	180-220°C	Space and Military
Proton Exchange Membrane fuel cell (PEMFC)	H ₂	60–80°C	Transportation and backup power plants

2.2.3 Advantages of Fuel Cells and Applications

Fuel cells often exhibit significantly greater efficiency compared to combustion engines as they directly generate electricity from chemical energy. This can lead to having efficiencies rates up to 60%. Because fuel cells don't have so many moving parts are less prone to mechanical failures and thus more reliable and durable. Additionally, fuel cells emit fewer or even no emissions at all. Fuel cells, unlike batteries, allow for independent scaling of power and capacity. Fuel cells operate efficiently for a wide range of applications. Fuel cells find applications in various fields, serving as power sources in transportation, industrial or residential structures, and even in long-term grid energy storage applications [34][107][155].

Transportation

- Automotives – Cars

Over the past decade, Proton Exchange Membrane (PEM) technology has emerged as the dominant fuel cell technology in the realm of transportation applications. These advancements,

along with other distinctive characteristics, position direct hydrogen fuel cells in electric vehicles (FCV) as a compelling alternative to internal combustion engine vehicles, whether running on gasoline (spark-ignition) or diesel. Fuel cells, by directly converting the chemical energy of the fuel into electrical energy, can achieve tank-to-wheel electric efficiencies of up to 60%. In contrast, conventional engines are constrained to efficiencies reaching up to 40% (diesel) or approximately 30% (gasoline) [125].

Fuel cell vehicles function by utilizing the chemical energy stored in hydrogen to generate electricity, which is then employed to drive an electric motor. This groundbreaking technology presents an eco-friendly and sustainable option in contrast to conventional internal combustion engine automobiles, with hydrogen fuel cells playing a pivotal role as the primary energy conversion system within these vehicles. The basic operational process of a fuel cell car encompasses various crucial components, comprising the fuel cell stack, hydrogen storage system, electric motor, and associated auxiliary systems. A detailed examination of the operational principles of fuel cell cars provides insight into the systematic process driving their functionality. Gaseous hydrogen, serving as the fuel for these vehicles, is stored in high-pressure tanks strategically positioned within the vehicle, typically in the chassis. This storage system is designed to ensure both safety and efficiency, maximizing the vehicle's hydrogen storage capacity. At the heart of a fuel cell vehicle lies the fuel cell stack, comprised of individual fuel cells. Each fuel cell consists of an anode and a cathode separated by an electrolyte membrane, often made of a proton-exchange membrane (PEM). When exposed to hydrogen gas, a chemical reaction occurs at the anode, breaking down hydrogen molecules into protons and electrons.

The protons migrate through the electrolyte membrane to the cathode, while the electrons are directed through an external pathway, generating an electric current. This electrochemical reaction stands as the fundamental process that converts the chemical energy of hydrogen into electrical energy. The generated electric current is then channeled to an electric motor, responsible for powering the vehicle's wheels. Functioning similarly to motors in battery electric vehicles (BEVs), this electric motor transforms electrical energy into mechanical energy to propel the car.

Crucially, fuel cell cars operate with emission-free functionality. Unlike traditional internal combustion engines that burn fossil fuels, fuel cells produce electricity through a clean electrochemical process, releasing only water vapor and heat as byproducts. This environmentally friendly approach contributes significantly to the reduction of greenhouse gas emissions and air pollutants. Additionally, fuel cell cars exhibit high energy efficiency due to

the direct conversion of chemical energy into electricity. Furthermore, these vehicles often incorporate regenerative braking systems, similar to electric vehicles. During braking, the electric motor operates in reverse, acting as a generator to convert kinetic energy back into electrical energy. This energy can be either stored for later use or utilized immediately, enhancing overall efficiency throughout the vehicle's operation. Altogether, the operational principles of fuel cell cars encompass a cohesive system that emphasizes clean energy generation, efficiency, and a positive environmental impact.

Fuel cell cars are gaining momentum as a sustainable transportation solution, offering zero-emission operation and efficient energy conversion. While challenges such as hydrogen infrastructure development still exist, ongoing advancements in fuel cell technology and increased investment in infrastructure are expected to further support the growth and adoption of fuel cell vehicles in the future [34]. As a disadvantage though the fuel cell cars are more mechanically complicated as we can see in the **Figure 10**.

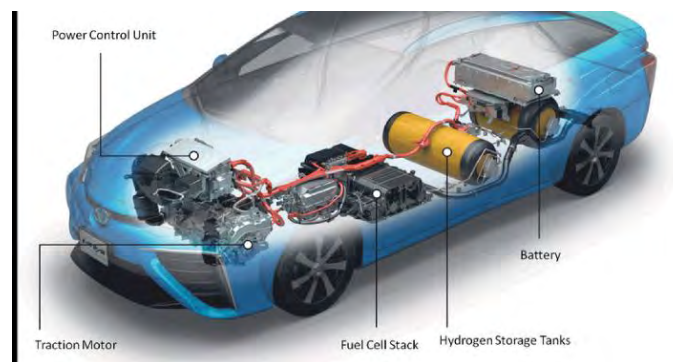


Figure 10 : Anatomy of a typical Fuel Cell car [10].

- Buses and Trucks

Fuel cell buses provide superior fuel efficiency when compared to diesel counterparts. With governments imposing stricter regulations on internal combustion engines, fuel cell buses are increasingly becoming the preferred choice for transit operators aiming to transition their fleets to lower-emission alternatives. Trucks constitute approximately 10% of the total vehicles on the road, yet they contribute to nearly half of carbon emissions. Their replacement with trucks power by fuel cells will lower carbon emissions dramatically [35]. The use of electric buses is a very new concept and it's not fully implemented yet in any country. In **Figure 11** we can see an example of a Bus with the corresponding hydrogen fuel station in the United Kingdom [111].



Figure 11 : Hydrogen fuel cell bus next to a refueling station [11].

- Planes

In 2020, Airbus unveiled conceptual designs for multiple hydrogen-powered planes with zero emissions and plans to conduct tests on a hydrogen engine installed on an A380 by 2026. Two startups, ZeroAvia and Universal Hydrogen, are actively working on hydrogen-powered aircraft, having recently conducted test flights with regional-sized planes and aiming to enter the market by 2025. In **Figure 12** we can see the size of the regional aircrafts that ZeroAvia uses in their test flights. However, substantial challenges, including obtaining regulatory approval and establishing the necessary hydrogen infrastructure, need to be addressed in the process [36].



Figure 12 : Hydrogen fuel cell airplane [12].

- Boats and Subs

We can use hydrogen fuel cells to power various naval applications. The biggest investor thought is the military. In the fall of 2016, the German military received the last of six submarines type U212-A. These submarines are manufactured by ThyssenKrupp Marine Systems and use a hybrid propulsion system that combines a diesel generator and a fuel cell. Fuel cell submarines also offer extended endurance and range compared to conventional submarines. The efficiency of fuel cells, coupled with the high energy density of hydrogen,

allows these submarines to operate for longer durations without the need for frequent refueling. [37]. A big market also is the making of unarmed and remote-controlled fuel cell submarines. A type of these submarines is presented in the **Figure 13**.

One notable advantage of fuel cell submarines is their enhanced stealth capabilities. The absence of noisy diesel engines and the quiet operation of electric motors powered by fuel cells contribute to reduced acoustic detectability, providing a tactical advantage for underwater missions. More and more navies around the world are exploring and adopting fuel cell technology for their submarine fleets as part of broader efforts to increase sustainability and reduce reliance on traditional fossil fuels. As technology advances, fuel cell submarines are likely to play a crucial role in the future of naval operations, providing a cleaner and more efficient solution for undersea warfare and surveillance.



Figure 13 : Unarmed and remote-controlled fuel cell submarine [13].

Power applications and generation

As technology progresses and need of electricity grows, we see new innovations all the time. One of these innovations is the usage of fuel cells as a storage of power. This is not actually a new innovation because NASA was using fuel cells in their space program from the late 60s to generate power. The innovations come more from the new uses that we find for the fuel cells and their implementation in real world scenarios.

- Mobile Power Generation

The origins of hydrogen's involvement in space exploration predate the formation of NASA itself. Back in 1957, nearly a year before NASA came into existence, the Air Force was actively engaged in evaluating a comprehensive proposal for creating a new space booster fueled by hydrogen. The objective of the proposal was to equip the U.S. with the capability to efficiently launch substantial payloads into orbit, with the aim of avoiding prolonged periods of research and development. The outcome of these efforts materialized in the form of the Centaur upper stage rocket, also recognized as America's primary workhorse in space.

The Centaur rocket played a pivotal role in propelling the United States ahead of the Soviet Union in the space race during the Cold War. Furthermore, the Apollo Command Module's primary source of electric power was from a set of three "fuel cells" housed in the Service Module. Each fuel cell combines hydrogen and oxygen to produce electricity and water. The water was used for drinking by the astronaut crew. Each of the fuel cell power plants contain 31 separate cells connected in series. Each cell has hydrogen and an oxygen compartments and electrodes and in combination produce 27 to 31 volts [38].

- Portable Power Applications

Fuel cells are employed in mobile power generation to provide a reliable and portable source of electricity. This application is particularly valuable in situations where traditional power sources may be unavailable or impractical. Mobile power generation using fuel cells is commonly used in outdoor events, construction sites, emergency situations, and recreational activities. The key advantage of fuel cells in mobile power generation lies in their ability to deliver electricity efficiently and quietly. Unlike traditional generators that rely on combustion engines, fuel cells operate electrochemically, resulting in lower noise levels and reduced emissions. This makes them an environmentally friendly and socially acceptable power solution, especially in noise-sensitive or densely populated areas.

One of the notable characteristics of fuel cells in mobile power generation is their scalability. They can be designed to suit various power requirements, from small portable devices to larger systems capable of providing electricity for multiple applications. The flexibility in sizing and power output makes fuel cells adaptable to different scenarios, ensuring that users can meet their specific energy needs without compromising on efficiency. In addition to scalability, fuel cells offer longer runtimes compared to some conventional power sources. This extended operational duration is particularly beneficial in situations where continuous and uninterrupted power supply is crucial. Mobile power generation with fuel cells ensures a reliable energy source for various applications, ranging from charging electronic devices to supporting critical operations in remote locations. Furthermore, the use of hydrogen as a fuel for mobile power generation adds to the appeal of fuel cells. Hydrogen is a clean and abundant energy carrier, and fuel cells that utilize hydrogen produce only water vapor as a byproduct. This makes them an environmentally sustainable choice, contributing to reduced greenhouse gas emissions and addressing concerns related to air quality.

Concluding, portable fuel cells are those which are built into, or charge up, products that are designed to be moved. These include military applications like a portable soldier power bank

for radios, skid mounted fuel cell generators. To power this range of products, portable fuel cells are being developed in a wide range of sizes ranging from less than 5 W up to 500 kW. Portable fuel cells typically replace or augment battery technology and exploit either PEM or DMFC technology. PEM fuel cells use direct hydrogen, with no point-of-use emissions, whereas DMFCS emit small quantities of CO₂ [39][40].

- Stationary Power Applications

Stationary fuel cells serve not only as a primary energy source but are frequently employed to offer additional electricity to homes situated off the grid. Within hybrid power setups, fuel cells can be integrated with batteries, photovoltaic systems, wind turbines, or capacitors, serving either as the main or backup power source. Numerous companies across the U.S.A. are incorporating fuel cells for both primary and secondary power, with notable examples including Adobe, Apple, AT&T, CBS, eBay, Google, Honda, and Microsoft. According to the tracking and surveys conducted by FCHEA [41], as of January 2020, over 550 megawatts (MW) of stationary fuel cells have been implemented in the United States, delivering dependable and environmentally friendly distributed power to clients throughout the country. Their small size compared to conventional stationary power applications, as presented by the **Figure 14**, make them ideal for limited space implementations. Additionally, due to the environmental advantages associated with fuel cells, federal facility managers are integrating them to achieve mandatory air pollution targets. Furthermore, utilities and companies striving to meet state-mandated renewable energy standards and emission criteria are progressively embracing fuel cell technologies [42].



Figure 14 : Fuel cell stationary power facility [14].

2.3.4 The impact of Fuel Cells in the environment

Fuel cells possess the potential to be environmentally friendly, but their overall environmental impact is contingent on various factors related to their production and utilization. However, their significant advantage over other energy conversion methods lies in

the potential for reduced environmental impact under appropriate circumstances. When not implemented with care, fuel cells may not offer substantial improvements over currently prevalent fossil energy conversion systems.

One crucial aspect is the production of hydrogen, a common fuel for fuel cells, which is typically carried out on an industrial scale through processes like hydrocarbon reforming. To truly harness the environmental benefits of fuel cells, there is a pressing need to transition towards alternative and sustainable methods for hydrogen production. Fortunately, several such approaches are already available or in the developmental stages. These include:

- Electrolysis

This method involves using electricity to split water into hydrogen and oxygen. If the electricity used comes from renewable sources, such as solar or wind power, electrolysis can be an eco-friendly means of hydrogen production.

- Renewable Liquid Reforming

This process involves the reforming of biofuels or other renewable liquid fuels to produce hydrogen. It offers a sustainable alternative to traditional hydrocarbon reforming.

- Water Splitting

Using renewable energy sources to power the electrolysis of water is another sustainable method for hydrogen production. This approach avoids the carbon emissions associated with conventional hydrogen production methods.

As technology advances and the focus on sustainability intensifies, the adoption of these alternative methods for hydrogen production is crucial to maximizing the environmental benefits of fuel cells. By integrating these sustainable approaches, fuel cells can play a more significant role in reducing the environmental footprint of energy conversion systems. So in general Fuel cells can be environmentally friendly but their environmental impact relies significantly on the specific circumstances of their production and use. This aspect may indeed represent their most noteworthy advantage compared to other methods of energy conversion. When not implemented appropriately, fuel cells may not offer substantial improvements over the currently prevalent fossil energy conversion systems. Presently, hydrogen is typically produced on an industrial scale through processes like reforming hydrocarbons. In general, there is a critical need to adopt alternative methods for hydrogen production. In fact, several sustainable approaches are already available or under development, including electrolysis, renewable liquid reforming, fermentation, and water splitting [43][44].

2.3.5 Hydrogen

Hydrogen, the most abundant element in the universe, is also the lightest and simplest element found in the periodic table. Predominantly found in water and organic compounds on Earth, hydrogen consists of a single electron and a solitary proton, existing as a colorless, odorless, and flammable gas. The extensive reliance on fossil fuels has given rise to significant environmental challenges and an energy crisis thus the utilization of hydrogen could prove to be a potential solution.

Hydrogen Production

Various methods for hydrogen production have garnered significant attention lately, aiming to streamline the shift from fossil fuels to a sustainable energy economy and enhance the integration of future energy systems. The efficiency, cost-effectiveness, and safety of any hydrogen production pathway hinge on the specific method employed in generating hydrogen. Three crucial aspects define a hydrogen production are:

- the material containing hydrogen (whether hydrocarbon or non-hydrocarbon)
- the energy sources
- the catalyst material.

These elements collectively determine the feasibility of the hydrogen manufacturing process. Factors such as the type of material used as a feedstock for hydrogen extraction, the scale of production, and the availability of energy resources play a pivotal role in selecting the appropriate hydrogen production pathway.

Steam Methane Reforming (SMR) stands out as the most widely employed method for hydrogen production, renowned for its high efficiency, favorable economics, and established technology, making it particularly well-suited for large-scale hydrogen production. In this process, methane undergoes treatment with high-temperature steam, resulting in a mixture comprising hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and various other impurities. The key reaction occurs within a reformer, featuring tubes filled with a nickel catalyst, and operates at temperatures ranging between 500–950°C, accompanied by a pressure of 30 bars. Excess steam is crucial for promoting the second step of the process, where the syngas (mixture of H_2 , CO, CO_2) is converted into the desired end product, hydrogen, through the water-gas shift reaction. The final step involves the separation of components, traditionally achieved through pressure swing adsorption (PSA). PSA is a method employed for the production of high-purity hydrogen, extracting it from the off-gas produced during steam methane reforming and refinery processes [123].

Electrolysis involves the utilization of electricity to break down water into diatomic molecules, H₂ and O₂. A cell with two electrodes is employed, immersed in a conducting medium, typically an alkaline electrolyte solution like an aqueous solution of potassium hydroxide (KOH) [52][53]. Electrons are absorbed and released at the electrodes, leading to the formation of hydrogen at the cathode and oxygen at the anode. The overall outcome of this process is the production of hydrogen and oxygen, utilizing only water and electricity [54]. The theoretical voltage required for decomposition at atmospheric pressure and 25°C is 1.23 volts. However, at this voltage, reaction rates are sluggish. Consequently, in practical applications, higher voltages are applied to expedite reaction rates. Nevertheless, this approach results in elevated heat losses to the surroundings, leading to reduced energy efficiency. To mitigate the need for higher applied voltages, catalysts or sophisticated electrode surfaces can be employed. Alternatively, increasing temperature and pressure may enhance efficiency, albeit at the expense of additional materials to withstand corrosion or higher pressures [123].

Water splitting is a technique employed to produce hydrogen by separating water into its constituent elements, hydrogen and oxygen, through the process of electrolysis. This approach is recognized as an eco-friendly and sustainable method for generating hydrogen, particularly when powered by renewable energy sources [154]. The fundamental principle of water splitting entails the application of an electric current to water, initiating a chemical reaction that leads to the release of hydrogen gas at the cathode and oxygen gas at the anode. The electric power essential for the water splitting process can be derived from renewable sources such as solar or wind power, enhancing the overall environmental sustainability of the procedure. By incorporating water splitting into hydrogen production methodologies, we can tap into hydrogen as a clean and adaptable energy carrier suitable for a variety of applications, including fuel cells and industrial processes. This integration contributes significantly to the promotion of a more sustainable and low-carbon energy future [124].

Hydrogen economy

Anticipation surrounds the potential of hydrogen-based energy and transportation, fueled by continuous advancements in the field. Hydrogen, emitting zero carbon at the point of use, presents an adaptable option for integration into existing energy and transportation networks, with the potential to significantly diminish air pollution. Despite being associated with environmental challenges such as oil spills and global warming, hydrogen is gaining prominence as a viable alternative. Policymakers are increasingly prioritizing price stability and securing the energy supply, steering the global shift from a fossil fuel-based economy towards a cleaner,

hydrogen-centric model known as the hydrogen economy. Originating in the 1970s, this concept has undergone thorough examination, marked by numerous reviews, case studies, and roadmap reports tracking developments and emphasizing hydrogen's potential in the energy sector. Recent research indicates a growing interest in comprehensively assessing the techno-economic, environmental, policy, and social implications of a hydrogen-based economy to gain a holistic understanding of the subject. Moreover, through **Figure 15** we can see the supply and demand of the Hydrogen economy where the fuel cells are depicted as a big part of the demand for Hydrogen. In response, various national and international organizations have been established to inform the public, industry professionals, and decision-makers, creating a foundation for preparing for the era of the hydrogen economy [49].

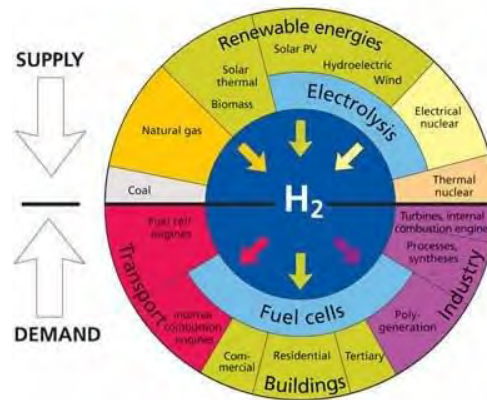


Figure 15 : Hydrogen economy diagram [35].

2.3.6 Electrochemical Sensors

A sensor is an instrument that responds to a physical stimulus such as heat, light, sound, pressure, magnetism, or movement by transmitting a measurable signal, as a means of measuring any intrinsic feature of the constituent material. In other words, it is a device used to detect signals from its surroundings and translates them into useful or quantifiable data. Chemical sensors are a category of sensors that receives signals as information from a chemical reaction [55]. Chemical sensors are categorized into optical, electrochemical, electrical, magnetic, mass-sensitive, and thermal sensors, or those based on other physical attributes such as radioactivity, depending on the operating principle of the transducer. Electrochemistry stands out due to its rapid, straightforward, and highly sensitive characteristics, providing superior properties compared to alternative measurement technologies. Specifically, electrochemical sensors are a subtype of chemical sensors that convert the impact of an electrochemical interaction occurring between the analyte and the electrode into a usable electrical signal, typically in the form of current or potential [56].

Contemporary electrochemical sensors employ various functionalities to identify chemical,

physical and biological elements in our everyday existence such as hazardous gas leakage. In **Figure 16** we can see examples of these types of electrochemical sensors. Examples encompass environmental monitoring, health and instrumentation sensors, as well as sensors associated with machinery such as automobiles, aircraft, mobile devices, and technology media. Advances in microelectronics and micro-engineering have significantly benefited modern sensing systems in recent decades, primarily by facilitating the creation of smaller sensors characterized by heightened sensitivity and selectivity, along with more cost-effective production and maintenance [57][58].



Figure 16 : Electrochemical Sensors for Hazardous Gas Detection [29].

2.3.6.1 Potentiometric Gas Electrochemical Sensors

A potentiometric sensor comprises an electrolyte, typically in the form of a closed tube with electrodes—one inside the electrolyte and the other external to it. During sensor operation, a balanced potential is generated at the sensing electrode, influenced by the concentration of the detected gas. The reference electrode establishes a reference potential to gauge the sensing electrode's potential. Noble metals like platinum often coat the electrodes as catalysts to enhance reaction speed and overall performance. Potentiometric sensors measure voltage in an open circuit, preventing electrical current flow through the sensor. On the opposite side of the sensor, forming a concentration cell, various chemical potentials of ionic species exist. An exemplary application of potentiometric sensors is the lambda sensor, employing a solid oxide electrolyte for detecting oxygen in exhaust gases [138].

Potentiometric sensors rely on the measurement of open circuit voltage for their operation. This approach involves creating an electrolyte that resembles a concentration cell, incorporating reversible electrodes and exposing it to varying chemical potentials of ionic species. Many potentiometric sensors operate on the fundamental principles of this straightforward concept.

2.3.6.2 Amperometric Gas Electrochemical Sensors

These sensors function by measuring the electrical current, which is associated with the diffusion flow of the gas being analyzed onto the working electrode. This diffusion can occur in an inner chamber or as part of the electrode, typically through a capillary or porous barrier. When exposed to the evaluated atmosphere, the ambient gas fills the chamber or porous electrode. The cathode initiates the reaction of the target gas once an external voltage charges the electrodes. The diffusion barrier, usually a porous layer or laser-drilled hole, is essential as it facilitates gas diffusion into the sensor's inner chamber from the surrounding atmosphere. The reaction rate increases with the applied voltage until it reaches a point where the concentration of the target gas inside the sensor becomes negligible. At this point, an additional increase in applied voltage does not affect the current response [139]. Amperometric sensors have an advantage over potentiometric ones as they can operate without a reference atmosphere. Hydrogen potentiometric sensors, in particular, require a stable reference environment, which can be challenging at their working temperature above 600 °C. On the contrary, potentiometric sensors are less sensitive at these concentrations due to the logarithmic relationship between the detecting signal and gas concentration. Amperometric sensors can detect various gases, such as O₂, H₂, CO, NO_x, CH₄, and NH₃, using different materials and geometries [140][141].

2.3.6.3 Electrical Biosensors

A biosensor typically consists of two key elements: a bioreceptor, often a biomolecule like an enzyme or antibody, responsible for capturing the target analyte (such as a virus), and a transducer that converts the signal generated by the bioreceptor into an electrical current, potential, or another signal form, depending on the type of transducer employed. Following signal amplification by a processing circuit, the results are displayed on a computer or smartphone after thorough evaluation. Electrochemical biosensors, whether the target analyte is labeled or not, offer portability, cost-effectiveness, ease of construction, high selectivity, and moderate sensitivity. These biosensors function by detecting the electrical signal produced when the bioreceptor interacts with the target analyte in a specific manner, with the signal's strength correlating with the analyte's concentration. Electrochemical biosensors can be divided into biocatalytic and affinity sensors based on their approach to identifying the target analyte. Biocatalytic electrochemical biosensors commonly utilize enzymes to identify the target analyte by generating electroactive species. In contrast, affinity electrochemical

biosensors selectively engage with a bioreceptor, such as an antibody, enzyme, nucleic acid, or other receptor, leading to the production of an electrical signal [142].

2.3.7 Electrochemical Sensors architecture

The functioning of an electrochemical sensor relies on the reaction of the target gas, generating an electrical signal proportional to the gas concentration. The sensor comprises a working (sensing) electrode, a counter electrode, and a thin electrolyte layer that separates them. The target gas traverses a small capillary, diffuses through a hydrophobic membrane, and reaches the surface of the sensing electrode, where it undergoes oxidation or reduction. Electrode materials, specifically chosen for the target gas, catalyze these electrochemical reactions. Once the appropriate amount of gas reacts at the sensing electrode, it generates a sufficient electrical signal. The hydrophobic barrier serves a dual purpose by preventing electrolyte leakage from the sensor. Connecting a resistor across the electrodes creates an external circuit, and a current proportional to the gas concentration flows between the anode and the cathode. Gas concentration is determined by measuring this current. Maintaining a stable and constant potential at the sensing electrode is crucial for sensors requiring an external driving voltage. To achieve this, a reference electrode is introduced within the electrolyte, positioned close to the sensing electrode. A fixed and stable constant potential is applied to the working electrode, with the reference electrode ensuring the maintenance of this fixed voltage at the sensing electrode. The reference electrode itself does not allow current passage. The current produced by the electrochemical reaction at the sensing electrode flows between the sensing and the counter electrode, is measured, and is typically correlated with the gas concentration using the Nernst equation. The voltage applied to the sensing electrode renders the sensor specific to the analyzed gas [122].

Figure 17 illustrates the arrangement of an electrochemical sensor, consisting of the sample (or analyte), a receptor responsible for binding the sample, and the transducer that converts the reaction into a measurable electrical signal. In the context of electrochemical sensors, the electrode serves as the transducer. In the majority of electrochemical sensors, the reaction occurs on the surface of an electrode. This electrode facilitates the oxidation or reduction of the analyte. The resulting current from this reaction is quantified and utilized to extract crucial information, such as sample concentrations. In various electrochemical sensors, adjustments to the electrode surface can be made using membranes, catalysts, or other metals to enhance the electrode's sensitivity or selectivity toward the analyte. [108]

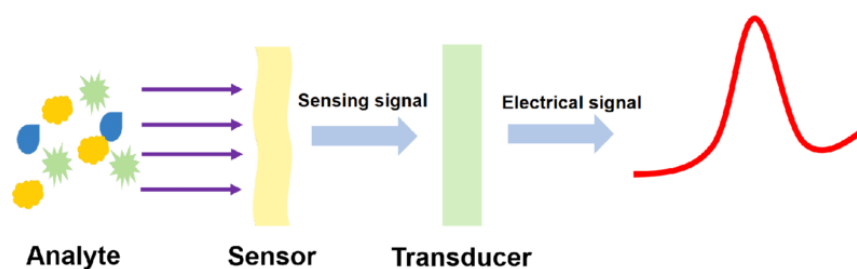


Figure 17 : Simple diagram of how a electrochemical sensor works [15].

2.3.8 Applications of Electrochemical Sensors

Electrochemical sensors serve a multitude of applications across diverse industries. In environmental monitoring, they play a crucial role in detecting water and air pollutants, ensuring adherence to environmental standards. In medical diagnostics, these sensors are integral to glucose meters for diabetes management and biosensing applications for detecting biomolecules. Industrial processes benefit from electrochemical sensors for monitoring parameters like pH, dissolved oxygen, and gas concentrations. They contribute to safety and security by detecting explosive and toxic gases, enhancing workplace safety. The food industry employs these sensors for spoilage detection and pathogen identification, ensuring food quality and safety. In the realm of energy, electrochemical sensors contribute to fuel cell technology for clean energy production and aid in monitoring battery health. Defense and security applications involve the detection of chemical warfare agents. Wearable devices integrate miniaturized electrochemical sensors for health and fitness tracking, while research laboratories utilize them in analytical chemistry for precise measurements. The adaptability and sensitivity of electrochemical sensors make them indispensable tools, continually advancing health, safety, and environmental monitoring across various sectors [132].

CHAPTER 3

An Introduction to lithium batteries

3.1 The History of lithium batteries

The research on rechargeable Li-ion batteries dates back to the 1960s. One of the earliest examples is a CuF_2/Li battery developed by NASA in 1965 [6]. In the early 1970s, a team of Exxon scientists embarked on developing an improved battery technology for greater efficiency and safety, surpassing the prevalent use of lead-acid batteries. During this period, M. Stanley Whittingham recognized the potential of a lithium intercalation compound, capable of storing lithium ions, as the foundation for a groundbreaking battery. Whittingham's endeavors culminated in the creation of the initial lithium-ion battery in 1976, representing a significant breakthrough [3]. He pioneered the development of the first lithium-ion battery using a titanium disulfide cathode and a lithium-aluminum anode, [4], as presented also in the **Figure 18**. A key feature of his invention was its high energy density, and the reversibility of lithium-ion diffusion into the titanium disulfide cathode rendered the battery rechargeable [5]. Exxon made attempts to bring this battery to the market in the late 70s. However, they encountered challenges with the costly and intricate synthesis process, primarily because titanium disulfide (TiS_2) is sensitive to moisture and emits toxic hydrogen sulfide (H_2S) gas upon contact with water. Additionally, the batteries had a significant drawback as they were prone to spontaneous combustion due to the inclusion of metallic lithium in the cells. So, because of various reasons, with the biggest being the safety concerns, Exxon decided to stop the development of Whittingham's lithium-titanium disulfide battery.

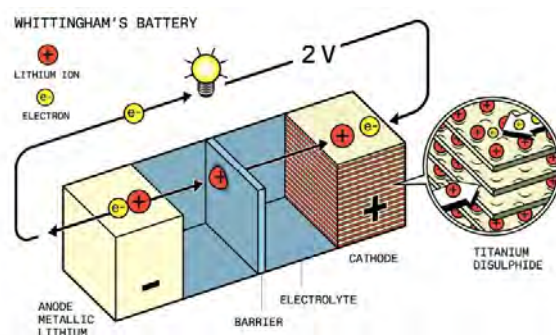


Figure 18 : Whittingham's battery, developed at Exxon using titanium disulfide for the cathode and metallic lithium for the anode [4].

In 1980, Ned A. Godshall, Koichi Mizushima and John B. Goodenough, started to find and test a range of alternative materials and replaced titanium disulfide (TiS_2) with lithium cobalt oxide (LiCoO_2). This material has a similar layered structure but offers a higher voltage and is much more stable in air [7][8]. In the diagram presented by the **Figure 19** we can see that we have an increased voltage compared to the diagram of the **Figure 18**.

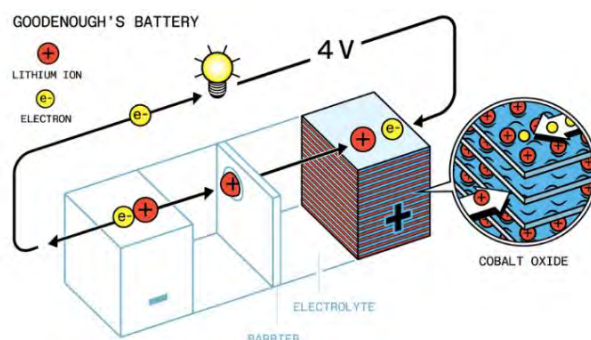


Figure 19 : Goodenough's battery using lithium cobalt oxide in the cathode [4].

In 1983, Rachid Yazami published an article highlighting the reversible electrochemical intercalation of lithium in graphite, leading to the invention of the lithium graphite electrode, specifically serving as the anode. Yazami's research was constrained using polyethylene oxide, a solid electrolyte [9]. In 1987, Akira Yoshino secured a patent for the initial commercial lithium-ion battery, employing a "soft carbon" anode (a charcoal-like material), in combination with Goodenough's previously documented LiCoO_2 cathode and a carbonate ester-based electrolyte. In **Figure 20** we can see the use of Goodenough's Cobalt oxide cathode but with the addition of the Petroleum coke, a carbon-rich solid material that derives from oil refining. The most interesting aspect of this battery is that it is assembled in a discharged state, thus improving its safety during the manufacturing process.

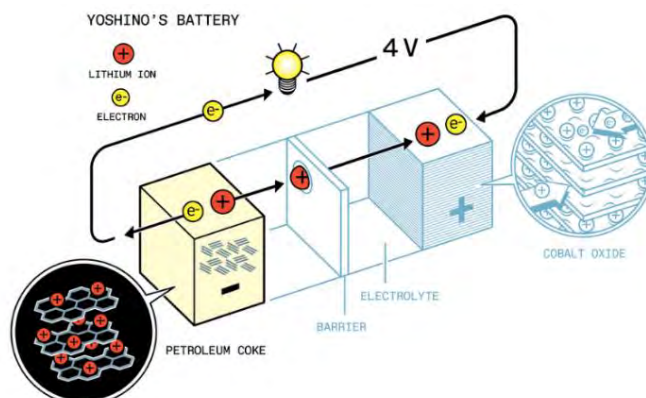


Figure 20 : Yoshino's battery, developed at Asahi Chemical in 1987 [4].

Following his discovery, Sony in 1991 started the production and sale of the first rechargeable lithium-ion batteries worldwide, based on Yoshino's design. In 1992 Toshiba and Asahi Kasei Co. introduced their own lithium-ion battery to the market [10]. Significant improvements in energy density were achieved in the 1990s by replacing the soft carbon anode first with hard carbon and later with graphite. In 1990, Jeff Dahn and two more associates documented the reversible intercalation of lithium ions into graphite using an ethylene carbonate solvent. This solvent, which solidifies at room temperature and is blended with other solvents to form a liquid, represented the crucial missing element that completed the puzzle for the development of the contemporary lithium-ion battery [11]. In 2019, Whittingham shared the Nobel Prize in Chemistry with John Goodenough and Akira Yoshino for their work on developing lithium-ion batteries.

3.2 Lithium batteries and their anatomy

Lithium batteries power many electronic devices, featuring three main parts: the anode, cathode, and electrolyte. During use, lithium ions move between the anode and cathode, generating electrical energy. This design ensures efficient, rechargeable power for various applications, from gadgets to electric vehicles.

3.2.1 General features of batteries

A battery is an electrochemical power source, functioning as a device capable of converting chemical energy into electrical energy and vice versa. It consists of multiple fundamental units known as cells, each comprising three main components: the positive electrode (cathode), the negative electrode (anode) and the electrolyte system. The two electrodes house the electroactive materials, while the electrolyte typically consists of a liquid solution containing a dissociated salt, serving as a source of ions. The chemical energy is stored in the electroactive species within the two electrodes, and it undergoes conversion into electric current through electrochemical reduction-oxidation reactions. Furthermore, according to their ability of being recharged, batteries can be classified in two categories. First is the single use category where is a battery that converts the chemical energy into electricity only once and then its discarded. Secondly, we have rechargeable batteries where they can be recharged thanks to an external power supply that forces a reaction during which the cathode active material oxidizes, and the anode active material reduces [12].

3.3 Types of cell construction of batteries

The performance of the overall cell is significantly influenced by both the energy storage materials and the cell chemistry. Lithium-ion cells, despite their varied form factors, are subject to the influence of cell engineering, which plays a crucial role in shaping the overall cell and, consequently, the performance of the battery in its final application. For effective integration into battery packs, energy storage cells require engineered supports and retention systems that facilitate their connection and secure retention within the battery pack structure. The most common types are cylindrical, prismatic and pouch [60][61].

- Cylindrical

The cylindrical cell design remains widely employed for both primary and secondary batteries due to its manufacturing simplicity and robust mechanical stability, capable of withstanding elevated internal pressures without deformation. Many cylindrical cells, especially those utilizing lithium and nickel-based chemistries, incorporate a positive thermal coefficient switch. As it can be seen in the **Figure 21** as a PTC switch, this component is made out of a conductive polymer and reacts to excessive current by heating up and transitioning to a resistive state. This way its effectively interrupting the current flow and providing short circuit protection. Once the short circuit is resolved, the positive thermal coefficient switch cools down, returning to its conductive state.

Additionally, most cylindrical cells are equipped with a pressure relief mechanism. In **Figure 21** we can see it being marked as a Gas release vent. The basic design often involves a membrane seal that ruptures under high pressure, potentially leading to leakage and dry-out after the rupture.

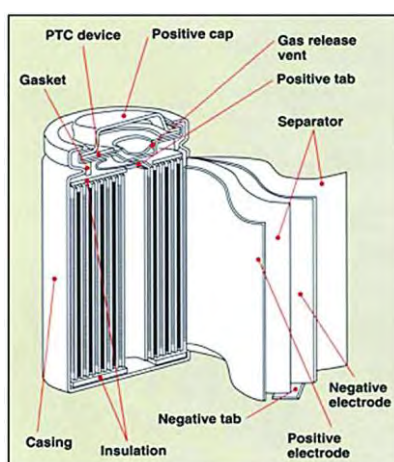


Figure 21 : Cross section of a cylindrical battery [37].

More advanced designs opt for re-sealable vents featuring a spring-loaded valve, which is preferable to mitigate issues related to membrane breakage. Certain consumer lithium-ion cells also integrate a charge interrupt device designed to disconnect the cell irreversibly when activated due to the buildup of unsafe pressure.

The most well know of the cylindrical batteries' family is the 18650 formats. This type finds widespread application in various consumer products, including laptops, power tools, and E-Bikes. Additionally, these cells may incorporate internal safety features, such as over-temperature and pressure cut-off mechanisms.

Alternative cylindrical Li-ion formats, such as the 20700, 21700, and 22700, offer diverse options in the battery market. Industry leaders like Tesla, Panasonic, and Samsung have chosen the 21700 formats for its manufacturing simplicity, optimal capacity, and various advantages. In comparison to the 18650, which has a volume of approximately 16 cm³ (16 ml) and a capacity of around 3000mAh, the 21700 cell boasts a larger volume of approximately 24 cm³ (24 ml) with a reported capacity of up to 6000mAh. The difference in the size can be spotted with the help of the **Figure 22**. This represents a significant improvement, doubling the capacity with a 50% increase in volume. Tesla Motor, in particular, emphasizes their 21700 as the "highest energy density cell that is also the cheapest." It's worth noting that while Tesla refers to it as a 2170, the correct model designation adheres to the IEC standard with the last zero in 21700 signifying its cylindrical nature.



Figure 22 : Cylindrical cells. In the left we have the 18650, in the middle the 21700 and in the right the 4680 [36].

Even though the cylindrical cell does not fully utilize the space by creating air cavities on side-by-side placement, the 18650 has a higher energy density than a prismatic/pouch Li-ion cell. The higher energy density of the cylindrical cell compensates for its less ideal stacking abilities and the empty space can always be used for cooling to improve thermal management.

- Button cell

The button cell, commonly referred to as a coin cell, played a crucial role in enabling compact designs for portable devices during the 1980s. Achieving higher voltages involved stacking these cells into a tube, making them suitable for applications like cordless telephones, medical devices, and security wands at airports. Despite their small size and cost-effectiveness, the stacked button cell eventually lost popularity and was replaced by more conventional battery formats. Today, most button cells in use are non-rechargeable and are commonly found in medical implants, watches, hearing aids, car keys, and memory backup devices. In **Figure 23** we can see the cross section of this type of battery.

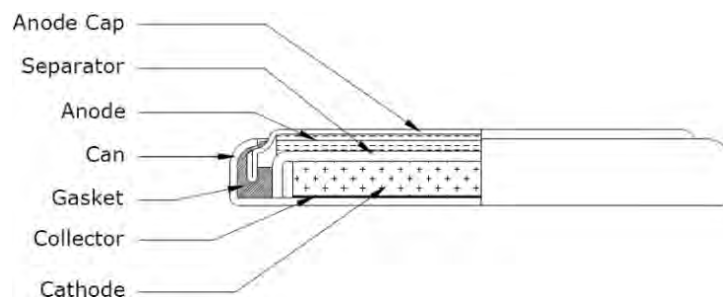


Figure 23 : Cross section of a button cell more specifically type CR 2032 [38].

- Prismatic

Introduced in the early 1990s, the contemporary prismatic cell meets the demand for slimmer sizes. Encased in sleek packaging reminiscent of a box of chewing gum or a small chocolate bar, prismatic cells maximize space utilization through a layered approach. Alternatively, certain designs involve winding and flattening into a pseudo-prismatic jelly roll. These cells are predominantly utilized in mobile phones, tablets, and low-profile laptops with capacities ranging from 800mAh to 4,000mAh. Notably, there is no universal format, and each manufacturer devises its own. Prismatic cells are also available in larger formats. Housed in welded aluminum casings, these cells offer capacities of 20–50Ah and are primarily employed in electric powertrains for hybrid and electric vehicles. **Figure 24** illustrates an exploded view of a prismatic cell.

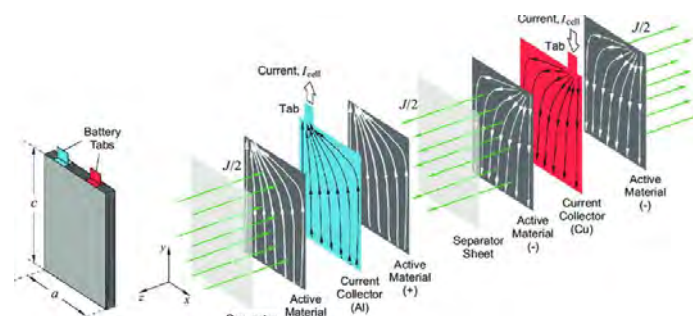


Figure 24 : Exploded view of a prismatic cell [39].

While the prismatic cell enhances space utilization and allows for flexible design, it may be more expensive to manufacture, less efficient in thermal management, and exhibit a shorter life cycle compared to the cylindrical design [133].

- Pouch

In 1995, the pouch cell revolutionized the battery industry with its innovative design. Unlike traditional batteries using metallic cylinders and glass-to-metal electrical feed-throughs, the pouch cell introduced conductive foil-tabs welded to the electrodes and sealed in a fully enclosed manner. Figure 6 depicts a pouch cell. Offering a straightforward, flexible, and lightweight solution to battery design, the pouch cell requires some stack pressure, but provisions must be made for swelling. While it can deliver high load currents, its optimal performance is achieved under light loading conditions and with moderate charging.

Commonly employed in Li-polymer configurations, small pouch cells are popular for portable applications demanding high load currents, such as drones and hobby gadgets. Despite being easily stackable, precautions must be taken for swelling. Extreme swelling is a significant concern. The pressure generated can lead to the cracking of the battery cover and, in some cases, damage the display and electronic circuit boards. In the event of an inflated battery, it is crucial to discontinue use and avoid puncturing the bloated cell near heat or fire, as the escaping gases can ignite. **Figure 25** showcases a swelled pouch cell.



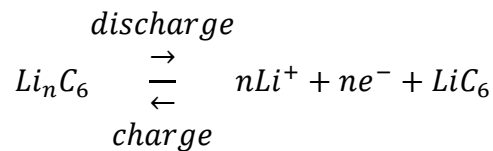
Figure 25 : In the picture it is depicted the same pouch cell but on the right side it is swelled significantly [17].

3.4 The operational principles of Li-ion batteries

A lithium battery typically comprises porous electrodes, which are called anode and cathode, an electrically insulating separator in-between and an ionically conducting medium, that is called electrolyte. Both electrodes are typically an electroactive material mixed with electrically conducting additives which are coated to an aluminum current collector, as the cathode, or a copper current collector, as the anode. The active material within the electrode acts as a host substance capable of either accepting mobile lithium ions from the electrolyte

through intercalation or releasing them. The electrolyte consists of a salt dissociated in an organic mixture of carbonates. Inside the electrolyte we immerse the anode, cathode and the separator. This separator between anode and cathode prevents electron transport between the electrodes through the inside of the cell, while allowing lithium-ions to permeate. When fully charged, a maximum amount of lithium is intercalated inside the anode. As presented by the **Figure 26**, during discharge lithium leaves the anode and is each oxidized to an electron and a lithium-ion in an electrochemical reaction at the electrolyte interface. For better understanding here is an example that describes the oxidation reaction at a carbon anode C₆ and states that n lithium stored (intercalated) in the anode electrode (LiC₆) participate in an electrochemical reaction, such that yielding n lithium-ions Li⁺, n electrons e⁻ and remaining active host material LiC₆.

Equation 1 : This equation describes the above example.



The lithium-ions are released into the electrolyte, while the porous separator, which serves as an electronic insulator between anode and cathode, forces the electrons to follow a deferent path to the lithium-ions through an external circuit via the current collectors. The lithium-ions travels through the electrolyte phase by diffusion due to concentration gradients to the cathode and react each with an electron from the external circuit. This reduction reaction at the cathode electrode interface where lithium-ions and electrons are reduced to intercalated lithium is formally expressed for a metal oxide MO₂ electrode as upon which the intercalated lithium diffuses from the surface of the electrode to its bulk. As a consequence of the reaction direction during discharge, the negative electrode where the oxidation reaction is occurring is commonly referred to as the anode, while the electrode where the reduction reaction takes place is called the cathode.

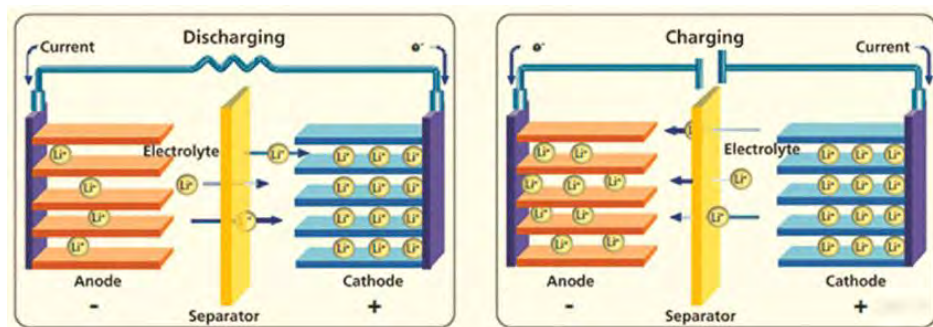


Figure 26 : This picture shows the operation of a typical Li-ion battery during charge and discharge [5].

This convention is maintained during charge, although the reduction (cathodic) reaction is now actually occurring at the anode and the oxidation (anodic) reaction is now actually taking place at the cathode. To have charge we need to apply a voltage greater than the open circuit voltage. Charging a cell causes electrons to flow from the cathode to the anode. This results in a corresponding ionic-flux inside the cell from cathode to anode; intercalated lithium are oxidized at the cathode, travel through the electrolyte to the anode where they are reduced with the electrons from the external circuit [13].

3.5 Materials of Lithium-Ion batteries

In this part of the thesis, we will briefly illustrate the development in electrode and electrolyte materials. In general, all applications of Lithium-Ion Batteries (LIBs) demand high energy and power densities, but specific sectors may prioritize different key properties based on the device the battery powers [2]. For instance, safety and extended operational lifespan are crucial considerations in the emerging electric vehicles and hybrid electric vehicles. Other sectors can emphasize design flexibility and compactness. Regardless of the battery technology and application, it's essential to note that the power and energy supplied by the battery system are directly tied to its capacity and voltage, which are inherently linked to the active materials constituting the electrodes [14]. Additional factors that depend on the nature and stability of the electrode is the life cycle, longevity and safety. It's easy to understand that the requirements of any battery technology are connected to the intrinsic properties of the materials forming the cells making any new innovation or advancement in the active chemistry governing the exchange of lithium ions pivotal for the future development of the battery systems.

3.5.1 Anodes

In lithium-ion batteries, the anode is a crucial component responsible for storing and releasing lithium ions during the charging and discharging cycles. Typically composed of materials like graphite, the anode undergoes a reversible electrochemical process, allowing it to intercalate and deintercalate lithium ions. As the battery discharges, lithium ions move from the anode to the cathode, generating electrical energy. Graphite anodes are widely used, but ongoing research explores alternative materials like silicon to enhance energy density. However, challenges such as volume expansion in silicon anodes must be addressed. The stability, efficiency, and cycling performance of the anode significantly impact the overall battery performance, influencing factors like safety, charging rates, and longevity.

Ongoing advancements in anode materials, nanotechnology, and engineering aim to overcome limitations and improve the overall efficiency and capabilities of lithium-ion batteries, essential power sources for applications ranging from portable electronics to electric vehicles. The main active materials for anodes encompass a variety of substances, including carbonaceous materials, alloys containing elements such as Si (silicon), Al (aluminum), Sn (tin), Ge (germanium), Ga (gallium), Sb (antimony), Pb (lead), and metal oxides. Among these, carbonaceous materials, like graphite or carbon nanotubes, emerge as the most widely adopted active anode materials. They are favored due to their cost-effectiveness, reversibility, low volume variation, and a high number of charge/discharge cycles. Despite these advantages, certain challenges persist. For example, when graphite is used as an anode material, it tends to form a solid electrolyte interface (SEI) layer, presenting a drawback. Researchers are actively exploring newer technologies on a daily basis to address such challenges and enhance the overall performance of anodes [59].

3.5.2 Cathodes

The cathode in a lithium-ion battery is a critical component responsible for the storage and release of lithium ions during the battery's charge and discharge cycles. Typically, cathodes in Li-ion batteries are made from various materials, and different formulations offer distinct advantages and disadvantages. One common type of cathode material is Lithium Cobalt Oxide (LiCoO_2), which has been widely used in early generations of Li-ion batteries. However, due to concerns about cobalt's cost, environmental impact, and ethical mining practices, researchers have explored alternative cathode materials.

One such alternative is Lithium Iron Phosphate (LiFePO_4), known for its safety, thermal stability, and relatively low cost. LiFePO_4 cathodes have found applications in electric vehicles and energy storage systems, particularly where safety and longevity are paramount. Another notable cathode material is Lithium Nickel Manganese Cobalt Oxide (LiNiMnCoO_2 or NMC), which strikes a balance between energy density, power output, and cost. NMC cathodes are prevalent in a wide range of applications, from consumer electronics to electric vehicles [148].

Additionally, Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO_2 or NCA) is employed in some Li-ion batteries, offering high energy density and extended cycle life. However, NCA cathodes can be more expensive due to the cost of cobalt. Continuous research aims to discover new cathode materials that enhance performance, energy density, and sustainability while addressing concerns related to material scarcity and environmental impact [147].

3.5.3 Electrolyte

Electrolytes can take several different forms and phases. They can be liquid, polymer, solid, or ionic liquid. Liquid electrolytes have low viscosity, high ionic conductivity, and are extremely flammable. Polymer electrolytes have a significantly higher viscosity and lower ionic conductivity and are also extremely flammable. Certain ceramic structures are capable of li-ion conduction and can serve as an electrolyte. The problem with the ceramic ones is that they operate at a higher temperature, and they cannot be used easy on LIB [20]. Ionic liquids (molten salts) have the highest conductivity but must be maintained at a high temperature to remain in the liquid state to be an ionically-conducting electrolyte. The most common organic carbonate solvents that are being used include:

- ethylene carbonate (EC)
- dimethyl carbonate (DMC)
- ethyl methyl carbonate (EMC)
- and diethyl carbonate (DEC)

All of them though are extremely flammable. Ethylene carbonate (EC) can be found in almost every liquid electrolyte. This is because its capable of forming and maintaining interfacial stability on both the anode and cathode [19]. The most common inorganic lithium salt is lithium hexafluorophosphate. Structure of LiPF₆ can be seen in the **Figure 27**. LiPF₆ has been the LIB industry standard for lithium salt due to its high ionic conductivity and stability with a variety of cathode and anode chemistries. The main disadvantage with LiPF₆ is that it has very poor thermal stability and can readily form hydrofluoric acid when exposed to water. Other notable inorganic lithium salts include lithium perchlorate (LiClO₄) and lithium tetrafluoroborate (LiBF₄), but are not common in commercial products due to their poor compatibility with the cathode aluminum current collector at high potentials

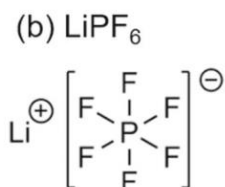


Figure 27 : Chemical structures and acronyms for the carbonate solvents, fluorinated carbonate solvents, ether solvents, additives, and lithium salts [27].

3.5.4 Separator

The separator in a lithium-ion (Li-ion) battery plays a crucial role in preventing short circuits and ensuring the safe and efficient operation of the battery. Positioned between the positive and negative electrodes, the separator acts as a physical barrier that allows ions to pass through while inhibiting the direct contact of the electrodes. It is typically made of a porous and insulating material. Also, the separator facilitates the flow of lithium ions between the cathode and anode during the battery's charge and discharge cycles. The porous structure, and this can be seen in the **Figure 28**, enables the movement of ions while maintaining an effective barrier against the passage of electrons, preventing internal short circuits that could lead to thermal runaway or even a battery fire. The separator's properties, such as thickness, porosity, and mechanical strength, are critical factors influencing the battery's performance and safety. Thinner separators can enhance the battery's energy density but may compromise safety, while thicker separators provide better protection but may limit the battery's performance. In addition to its primary function as a physical barrier, the separator also helps manage the electrolyte flow within the battery. It retains the electrolyte, a conductive solution containing lithium salts, ensuring proper ion transport and maintaining the electrochemical reactions necessary for the battery's operation [134].

The most common used separators are primarily made out of the polymeric membrane (polyethylene or polypropylene) or glass fiber composites [18]. Separators for LIBs must be electrically insulating, allow for lithium-ion migration, and provide enough mechanical strength to withstand cell manufacturing processes. Microporous polyolefins such as polypropylene (PP) and polyethylene (PE) are commonly used. In the use case of solid electrolytes, we can use glass-ceramic separators like the $\text{Li}_2\text{S-P}_2\text{S}_5$ which is capable of lithium-ion conduction and electrical insulation [21].

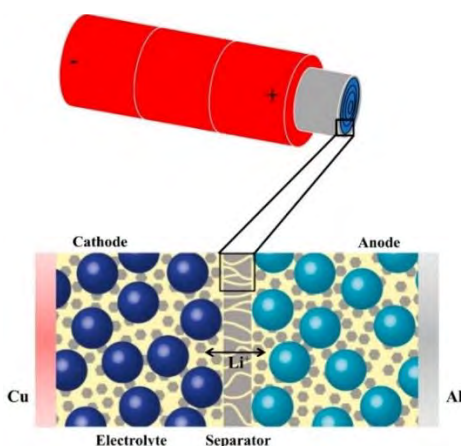


Figure 28 : Example of a separator in a cylindrical Li-ion battery cell [8].

3.6 Battery production

The initial aspect to consider is the production of batteries. To achieve a battery with superior performance and extended lifespan, it is essential to advance production technologies and systematically optimize manufacturing processes. While the fundamental procedures are generally similar, specific batteries may necessitate distinctive manufacturing processes owing to differences in their chemistry, structure, and shape. In **Figure 29** we can see the manufacturing processes for Li-ion batteries, encompassing mixing, coating, drying, calendaring, cutting, stacking, welding, sealing, as well as electrolyte filling and additional processes such as testing and sorting.

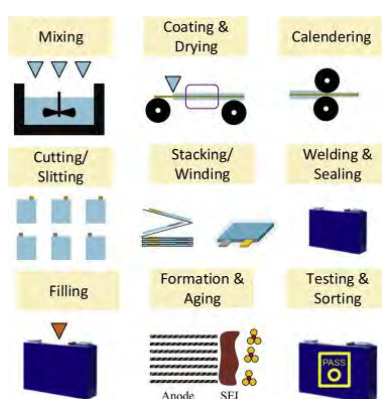


Figure 29 : Manufacturing processes of Li-ion batteries [150].

- Mixing

The dispersion apparatus plays a crucial role in blending the powders of active substances, conductive additives, binder, and solvent in the slurry preparation phase. This mixing step is vital for defining the particle size distribution of the active material and ensuring the even distribution of materials that conduct electricity throughout the battery [149].

- Coating

In the coating and drying stage, the slurry is administered onto the current collector and then dried to eliminate the organic solvent present in the slurry. Throughout the manufacturing process, the movement of conductive additives and binders within the electrode can be influenced by solvent evaporation and the settling of active material particles [149].

- Calendering

The calendering or pressing process is employed to compress the battery electrodes, influencing crucial electrode parameters such as thickness, porosity, and compaction density. Careful selection of key operational parameters like roller speed and rolling force is essential.

Inadequate homogeneity in the distribution of anode or cathode active materials may lead to uneven distribution in certain areas, resulting in either excess or insufficient material in those regions [149]. Uneven electrode thickness can cause deformations and wrinkles, negatively impacting battery performance and leading to local lithium deposition in the wrinkled areas. Inadequate local anode materials may also contribute to localized lithium deposition, potentially diminishing battery lifespan [151].

- Size control

Maintaining control over size is imperative during the cutting and slitting processes. It is advisable for the active components of the anode to be notably larger than the cathode active materials to prevent lithium deposition at the anode's edge and the formation of burrs during the cutting process. Cracks in the materials can result in internal short circuits or a higher self-discharge rate, both of which can significantly reduce the battery's lifespan and compromise its safety [149]. The battery's longevity and safety may be at risk if there is metal debris on the electrode surface after cutting, potentially leading to localized metal deposition, dendrite growth, and penetration of the separator [149].

- Filling and Forming

The primary stages in battery production encompass filling and forming, with the main objective being the establishment of a reliable solid electrolyte interface (SEI) film [150]. The filling process, also known as electrolyte injection, determines the quantity of electrolyte within the battery. Excessive electrolyte usage may result in wastage, diminished battery energy density, and compromised seal integrity. Conversely, insufficient electrolyte can lead to inadequate wetting of the separator and internal active elements, resulting in increased internal resistance, an unstable SEI film, and a heightened risk of lithium plating. In cases of inadequate electrolyte, the battery's capacity may rapidly decline due to continuous electrolyte consumption. Following electrolyte injection, the electrode and separator absorb the electrolyte. Incomplete wetting of the entire electrode by the electrolyte may impact battery performance, causing certain areas of the active materials to be inactive during the charging and discharging process, leading to lithium deposition and reducing battery life. Techniques such as ultrasonic or neutron imaging can be employed to observe and monitor the wetting process, ensuring battery longevity. The formation process is pivotal in guaranteeing the durability and efficiency of the battery. During the initial charging and discharging cycles post-electrolyte injection, the electrolyte and lithium ions combine on the anode particles' surface to generate the SEI layer [149].

- Testing and Sorting

The concluding phases in battery manufacturing involve testing and sorting, where specific indicators and threshold values are established to filter out unqualified cells and classify qualified ones. Implementing an effective sorting system is critical for identifying cells with inferior quality, ensuring the overall longevity of the battery. Key determinants of battery durability include impedance, capacity, and self-discharge rate. Setting appropriate thresholds for these parameters becomes vital in guaranteeing cell longevity [149].

3.7 Sourcing the Materials of Lithium-Ion batteries

In the present, lithium transcends its role as a merely another metal utilized in various sectors. It is now recognized as a crucial material in the transition away from fossil fuels, playing a role in addressing the significant challenge of climate change. The integration of Lithium-Ion Batteries (LIBs) in electric vehicles and other renewable energy storage systems is expected to reduce reliance on fossil fuels. The end-use consumption of lithium has experienced a substantial increase in recent years [16]. As presented in the **Figure 30** batteries have the 80% of global distribution of lithium and it is estimated to be increased considerable in the next years.

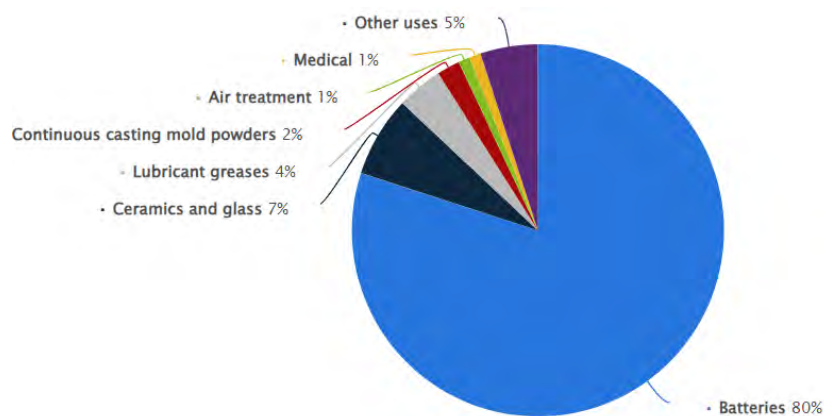


Figure 30 : Worldwide distribution of lithium [7].

To framework this increase in the use of lithium in energy applications, note that the global energy market is estimated to be worth 250 billion € by 2025. Also, the surge of consumer electronics is driving an increasing demand for lithium in the form of LIBs. According to studies this increase in demand resulted in a 61% price rise for battery-grade carbonate between 2016-2017. So, it's not surprising at all that there is a big demand for it and thus the price of it

might go up every year. This is good for the countries that mine lithium but not good for the planet because lithium has many problems with its production [17].

3.7.1 Raw materials

Present and future approaches to energy production, storage, and distribution extend well beyond the essential technological challenges. This insures the making of political and economic implications. To accomplish the goal of decarbonization and to build real sustainable development the modern environmental and energy policies have to develop evaluations of critical raw materials concurrently to the projections of renewable power generations and additions of storage energy capacities. To make batteries we need raw materials that are critical for their production. These materials can be described with having natural scarcity and their supplies are concentrated in few countries, sometimes these supplies are located in politically instable regions. Especially, two elements are nowadays considered critical or nearly-critical: cobalt and lithium itself. Nevertheless, when taking into account toxicity and environmental consequences, there are also apprehensions regarding the environmental harm associated with vanadium-based materials. Although cobalt counts on a higher natural abundance compared to lithium, its low concentration in the soil leads to much lower reserves. As presented in world map from the **Figure 31** we can see that the majority of cobalt reservoirs are located in Congo, USA, Canada, Russia and Australia. Moreover, Congo supplies the 54 % of the global demand, while Australia, Russia, Canada and China count for the 20%. The last decade the public debates for the unrulied mining activity in Congo, which operates under low or even no safety standards [15].

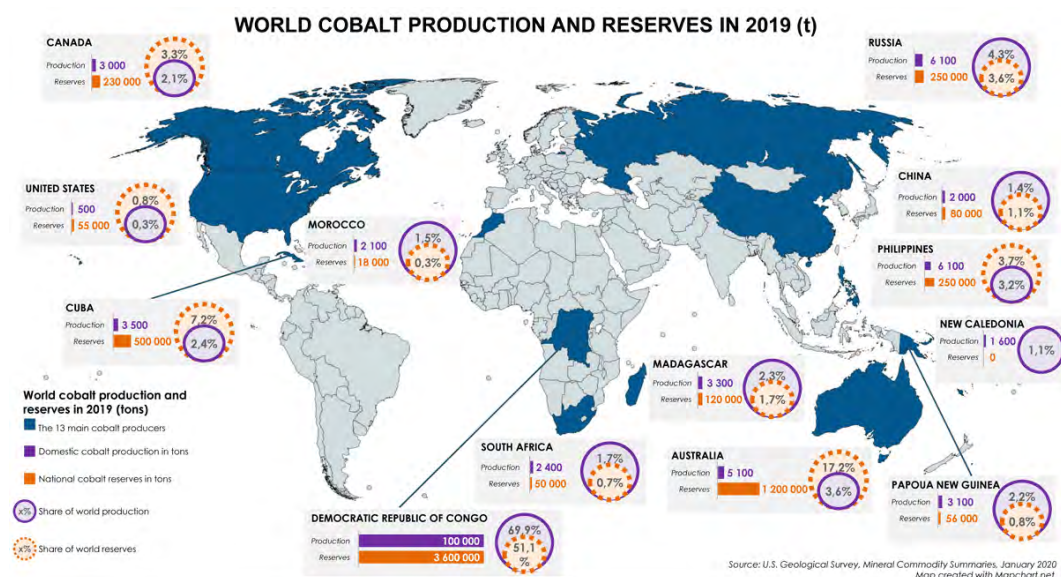


Figure 31 : World map showing the cobalt production and reserves according to 2019 data [6].

Regrettably, the question remains today. With the anticipated surge in Electric Vehicles (EVs) and Hybrid Electric Vehicles (HEVs) production, there is a likelihood of a significant rise in the price of lithium. This could trigger competition among developed nations to secure control over its reserves, primarily situated in concentrated regions susceptible to political instability. According to studies done by the USGS (United State Geological Survey), world lithium resources have been revised to approximately 47 million tons in 2018, while the Global Lithium Reserves are calculated to be 16 million tons and are primarily located in China, Australia, Canada and Russia [16]. Moreover, the collective Li-ion market is projected to reach 2.5 TWh during the 2020-2030 period, indicating a cumulative demand for approximately 400,000 tons of lithium. This corresponds to around 2.5% of the global lithium reserves, based on the current material intensity of 0.16 kg kWh⁻¹.

The transition towards cleaner energy involves the shift from pollutant fossil fuel-based vehicles to electric vehicles, with lithium-ion batteries being the preferred technology for power delivery systems. The global outlook regarding lithium depletion and expenses becomes more alarming when considering the desired growth in electricity production from renewable sources. Cobalt-free lithium-ion batteries meet the technological and environmental criteria for an effective storage system for electricity generated by intermittent renewable sources, positioning them as the preferred technology for upcoming smart grid-connected energy storage systems. However, their current challenge lies in cost competitiveness, and the outlined projections in the large-scale production market do not alleviate this concern. As was already described, lithium is a critical raw material and therefore it is not safe to strongly depend on lithium supplies. In this direction, recycling policies and diversification of electrochemical storage solutions are highly recommended.

Table 2 : Lithium reserves and production [18].

COUNTRY	Production in 2019 (tones)	Estimated reserves (tones)
Australia	42.000	2.800.000
China	7.500	1.000.000
Argentina	6.400	1.700.000
Brazil	300	95.000
Chile	18.000	8.600.000
World	77.000	15.115.000

Australia is the leading overall producer, with 42.000 tons of lithium mined in 2019. This is roughly 55% of the world's total mining. Looking more on the table we can see thought that Chile holds the largest lithium reserves, containing 8.6 million tons. Analyzing the total global reserves and taking into account current production and anticipated demand growth, it appears

that there is an abundance of lithium for the next century. Nevertheless, predictions suggest that the demand for lithium might surpass its supply soon, even in a scenario where recycling processes fail to halt this trend [16][17].

3.8 Types of Lithium-Ion batteries

Lithium-ion batteries are a widely used class of rechargeable batteries, characterized by the necessity of an anode, a cathode, and an electrolyte for their operation. The anode typically consists of porous carbon, while the cathode is made from metal oxide. The essential mechanism involves the flow of ions from the cathode to the anode during charging and, conversely, from the anode to the cathode during discharge, facilitated by the electrolyte and separator. This electrochemical process is fundamental to the functioning of lithium-ion batteries. Several types of lithium-ion batteries exist, each with unique characteristics. Common variants include those featuring lithium cobalt oxide (LiCoO₂) as the cathode material, known for its high energy density and prevalent use in consumer electronics. Lithium manganese oxide (LiMn₂O₄) batteries offer enhanced safety and thermal stability. Lithium iron phosphate (LiFePO₄) batteries, recognized for their longevity and stability, are frequently employed in electric vehicles. The diversity of lithium-ion batteries allows for tailored solutions across various applications, meeting specific requirements for energy density, safety, and overall performance.

3.8.1 Lithium Cobalt Oxide (LiCoO₂)

In the 1980s, a team of researchers from Oxford and Tokyo University identified the utility of lithium cobalt oxide as an intercalation electrode. In the charging process, cobalt undergoes partial oxidation, accompanied by the movement of certain lithium ions to the electrolyte. While LiCoO₂ batteries exhibit consistently stable capacities, it's worth noting that their capacities are lower compared to those based on nickel-cobalt-aluminum. The researchers concluded that, in relation to thermal stability, LiCoO₂ exhibits slightly better characteristics compared to other nickel-rich chemistries. However, this renders the batteries vulnerable to thermal runaway in situations exceeding 130°C or overcharging. Elevated temperatures can lead to LiCoO₂ decomposition, releasing oxygen that reacts with the cell's electrolyte, posing a potential issue due to the significant exothermic reaction. Presently, batteries of this type are commonly found in mobile phones, tablets, laptops, and cameras [22][25].

Moreover, the choice of lithium cobalt oxide (LiCoO_2) in consumer electronics is influenced by its relatively high energy density, providing a balance between performance and size. Despite the thermal challenges, LiCoO_2 batteries have been a staple in portable electronic devices due to their ability to deliver reliable power in a compact form. Manufacturers have employed various safety mechanisms and thermal management systems to mitigate potential risks associated with LiCoO_2 batteries. Continuous research and development in battery technology aim to address the limitations of LiCoO_2 batteries, and newer generations with enhanced safety features and improved performance are continually being introduced to meet the evolving demands of electronic devices [135].

3.8.2 Lithium Manganese Oxide (LiMn_2O_4)

In 1983, the Li-ion battery with manganese spinel was published in the Materials Research Bulletin, and by 1996, Moli Energy had commercialized a Li-ion cell featuring lithium manganese oxide as the cathode material. LiMn_2O_4 , a manganese oxide-based cathode, has been extensively studied due to its incorporation of cost-effective materials. Its molecular structure facilitates high-rate capability during the charge and discharge cycles of the battery, providing a well-connected framework for the insertion and de-insertion of Li^+ ions. Additionally, it offers enhanced safety and high thermal stability but the battery's cycle and life is more limited. This type of battery is commonly used in power tools, medical devices, and powertrains [22].

3.8.3 Lithium Nickel Manganese Cobalt Oxide (LiNiMnCoO_2)

The Lithium Nickel Manganese Cobalt Oxide battery, abbreviated as NMC, was identified in 2008, and the nickel-manganese-cobalt cathode combination has proven to be highly successful in Li-ion systems. This cathode configuration can be customized to function as either energy cells or power cells, similar to Li-manganese. NMC batteries find applications in power tools, e-bikes, and various electric powertrains. Typically, the cathode composition consists of one-third nickel, one-third manganese, and one-third cobalt, a distribution that lowers the raw material costs by reducing the cobalt content [22][24].

3.8.4 Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO_2)

Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO_2), or NCA, is a widely used cathode material in lithium-ion batteries due to its desirable properties. NCA batteries are known for

their high energy density, making them suitable for applications that require a lightweight and compact power source. This includes electric vehicles (EVs), where maximizing the range on a single charge is crucial. The composition of NCA includes nickel, cobalt, and aluminum, with lithium ions moving between layers in the crystal structure during charge and discharge cycles. The layered structure contributes to the high energy density of NCA batteries. Manufacturers can adjust the specific ratios of nickel, cobalt, and aluminum to tailor the performance of the cathode based on specific requirements.

One significant advantage of NCA batteries is their high voltage output. This characteristic makes them well-suited for applications demanding high power, such as electric vehicles. However, challenges exist, particularly related to safety and longevity. NCA batteries are sensitive to high temperatures, and excessive heat can lead to safety concerns and reduced battery life [22].

Despite these challenges, ongoing research aims to enhance the safety and performance of NCA batteries. Engineers and researchers are exploring new materials and designs to mitigate heat-related issues and improve the overall reliability of lithium-ion batteries, ensuring their continued use in a variety of applications. The development of advanced cooling systems and thermal management strategies is one avenue being explored to address temperature-related challenges in NCA batteries [23].

3.8.5 Lithium Titanate Oxide (Li_2TiO_3)

Lithium Titanate Oxide (Li_2TiO_3) batteries, commonly referred to as LTO batteries, represent a distinct category within the lithium-ion family. These batteries employ lithium titanate as the anode material, which sets them apart from traditional lithium-ion batteries that typically use graphite-based anodes. The choice of lithium titanate offers notable advantages, including excellent thermal stability, a longer cycle life, and rapid charging capabilities.

In LTO batteries, lithium ions shuttle between the cathode and the lithium titanate anode during charge and discharge cycles. The lithium titanate structure allows for faster ion diffusion, enabling quick charge and discharge rates. One of the prominent features of LTO batteries is their impressive cycle life, often exceeding tens of thousands of cycles without significant degradation [22].

However, LTO batteries are characterized by their higher cost and a lower capacity and voltage compared to conventional lithium-ion batteries. Currently, these batteries are utilized in electric vehicles and solar street lighting systems [26].

3.8.6 Lithium Iron Phosphate (LiFePO₄)

In 1996 a research group from the University of Texas published the use of LiFePO₄ as a battery electrode. It has gained considerable market acceptance due to its low cost, its thermal stability, non-toxicity, the abundance of iron, safety characteristics and specific capacity. For the commercialization LiFePO₄ particles were coated with conductive materials because its intrinsically low electrical conductivity was a barrier. That idea was developed by, Michel Armand and his co-workers but there were others approach that consisted of doping LFP with cations of materials like aluminums, zirconium and niobium [28]. The Massachusetts Institute of Technology (MIT) has unveiled a novel coating that enhances the movement of ions within the battery. This battery incorporates a bypass system, enabling lithium ions to swiftly enter and exit the electrodes, facilitating a complete charge in less than a minute. This type of battery is particularly suited for devices requiring high currents and prolonged endurance [22].

Characteristics table of the lithium-ion batteries

Table 3 : Different types of lithium-ion batteries and their specification [23].

Chemistry	Licoo2	Limn2o4	Linimnco o2	Linicoal o2	Li2tio3	Lifepo4
Voltage	3.6 V	3.7 V	3.6 V	3.6 V	2.4 V	3.2 V
Cycle life	Acceptable	Acceptable	Acceptable	Very Good	Good	Excellent
Maintenance	Keep cool, store partially charged, prevent full charge cycles, use moderate charge and discharge currents.					
Cost	High	Acceptable	Acceptable	High	High	Economic
Stability	Acceptable	Not stable	Not stable	Acceptable	Acceptable	Stable
Applications	Mobile phones, tablets, laptops	Power tools, medical devices	E-bikes, medical devices	Medical, industrial, Ev	Ups, Ev, solar street lighting	Stationary with high currents

3.9 Different kinds of batteries

New types of batteries are developed every year through large investments from big technological companies that are trying to open new opportunities to develop new types of batteries or simply, energy storage systems. Some of them are known and others are innovative and new products.

3.9.1 Metal-air

Metal-air batteries (MABs) represent a promising technology applicable across various domains, from portable devices to large-scale energy storage. They offer enhanced safety features along with a superior energy density compared to alternative technologies. MABs have garnered significant attention due to their ability to operate in an open-air atmosphere, utilizing not only metal components, as seen in traditional batteries, but also incorporating the abundant oxygen present in the environment. This system comprises three fundamental components: a metal anode, a permeable air cathode, and an electrolyte that serves as a separator between the two electrodes [121]. The anode material in a metal-air battery consists of metals such as lithium (Li), sodium (Na), iron (Fe), zinc (Zn), and various other elements. Electrolytes are available in diverse formulations, including aqueous electrolytes, non-aqueous (aprotic) electrolytes, solid-state electrolytes, and hybrid electrolytes. Non-aqueous electrolytes find application in the anodes of lithium-air, sodium-air, and potassium-air batteries, demonstrating a pronounced sensitivity to water. Conversely, aqueous electrolytes are utilized in anodes composed of magnesium, aluminum, iron, or zinc. These aqueous systems necessitate a hydrophobic protective layer to mitigate the risk of electrolyte leakage. Within the anodic electrode of Metal-Air Batteries (MABs), metals undergo transformation into ions, while on the cathodic electrode, oxygen undergoes conversion into hydroxide ions. This stands in contrast to conventional ionic batteries, where metallic ions migrate from the anode to the cathode. The gas diffusion layer allows oxygen to diffuse into the MAB and consequently the metal-air battery requires minimal space for the positive electrode's active material, with only a thin catalyst layer necessary, allowing for maximum utilization of the negative electrode's active mater [50]. As can be shown by the **Figure 33**, in an aqueous electrolyte system, the behavior of oxygen differs from that in a non-aqueous electrolyte medium.

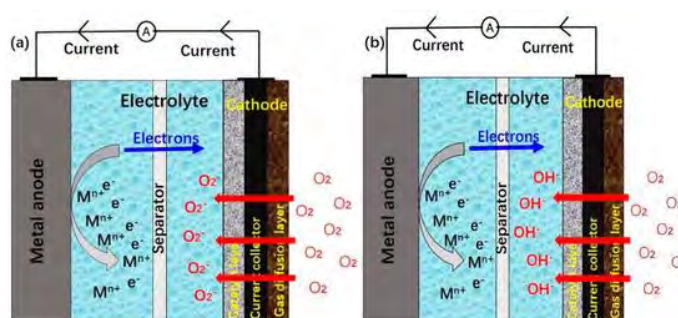


Figure 32 : Diagrams of MABs principles (a) non-aqueous, and (b) aqueous electrolyte [31].

Despite the remarkable theoretical characteristics of Metal-Air Batteries (MABs), their commercialization faces noteworthy technical challenges, classified based on the impacted components. Initiating with the anode, corrosion, passivation, and dendritic formation pose major hurdles. Metallic anodes undergo corrosion in the presence of an aqueous electrolyte, negatively impacting battery performance, reducing columbic efficiency, and potentially leading to explosions. Passivation occurs when a coating forms on the electrode surface, obstructing the passage of discharge products. Dendritic formation alters the metal electrode's shape, causing uneven roughness and risking an unstable battery or short circuit. In aqueous electrolytes, CO₂ dissolution from the air, reacting with OH⁻ to generate CO₃²⁻, is a primary concern. To counteract this, MABs can employ a CO₂ filter, though this solution may increase costs. Hydrogen evolution, insoluble by-products, and moisture absorption from the air present significant challenges for the electrolyte. Effective cell design and humidity balance calculation are essential for overcoming these issues. For the cathode, the key challenge is the heightened precipitation of solid Li₂O₂, leading to the formation of a thick insulating layer that impedes electron and air flow [137]. Addressing these challenges through innovative design and strategic humidity management holds the potential for the success of MABs.

3.9.2 Solid-state Lithium

The solid-state battery represents a progression from the conventional lithium-ion battery, with its primary advancement credited to John B. Goodenough, acknowledged as a key proponent of this battery type. Functioning on the same principles as lithium-ion batteries, the notable distinction lies in the electrolyte, where the former employs a liquid, and the latter utilizes a solid material. Goodenough's team employs a solid crystal electrolyte as the replacement for the liquid counterpart. This crystal electrolyte allows for the use of an alkaline metal anode, enhancing the battery's charge density, enabling it to store more energy compared to a lithium-ion battery of similar size, and preventing the formation of dendrites. Also, the battery is capable of functioning even in extreme ambient temperatures (-20°C). Solid-state batteries offer increased autonomy, swift recharge times, and enhanced safety features. According to Goodenough's team, a solid-state battery can store three times more energy than a lithium-ion battery and recharge in less than an hour. Importantly, in the event of an accident, it is not prone to catching fire, a safety concern associated with lithium-ion batteries. The crystal-based electrolyte also facilitates cost-effective mass production of these batteries, potentially reducing their overall cost [51].

3.9.3 Lithium-sulfur

Lithium-Sulfur batteries are considered a potential future battery technology due to their significantly high specific energy (three times that of Li-ion) and commendable specific power. These batteries utilize a main ingredient that is abundantly available and demonstrate favorable cold temperature discharge characteristics, allowing recharging even at -60°C. Additionally, they are environmentally friendly. However, a notable drawback is the limited charging cycles these batteries can endure, leading to a relatively short lifespan. Recent breakthroughs, particularly at the University of Monash in Australia, have resulted in patented innovations that address this issue. Through extensive testing, they have developed a system that mitigates stress on the batteries, enabling them to achieve more than 1,500 charge cycles. The key lies in the incorporation of a polymeric material into the carbon matrix responsible for electron transfer to the insulating sulfur. This polymer serves to hold the sulfur and carbon together, preventing the rapid deterioration in battery performance caused by stress during charging. The focus of the research has been on this material, aiming to separate the sulfur particles. Among the advantages of this innovation are increased charge capacity, leading to greater autonomy in various applications such as smartphones, cars, or other devices relying on rechargeable batteries. Additionally, the enhanced charging capacity translates into more powerful batteries, which can be advantageous in certain devices. However, despite these promising developments, commercialization is still in the early stages as further testing is underway to understand their performance better. Additionally, the current high cost of these batteries poses a potential disadvantage that needs to be addressed before widespread adoption.

3.10 Battery's ageing Influence Factors

Battery aging can manifest as capacity fading, power fading, or a combination of both, and various influencing factors contribute to these phenomena. The production process and operational conditions significantly impact a battery's aging process. Factors such as elevated cycling rates, extreme temperatures (either high or low), operating at high or low states of charge (SOC), instances of overcharging or over-discharging, high depth of discharge (DOD), and exposure to moisture are key contributors to battery aging [75].

3.10.1 Working Conditions

The degradation of lithium-ion batteries is influenced by various working conditions, impacting their overall performance and lifespan. Factors such as high temperatures can

accelerate degradation by promoting internal reactions, while low temperatures affect the reduction of metal ions, lithium plating, and the crystal structure of materials, making them more susceptible to damage. High State of Charge (SOC) or overcharging can lead to negative consequences, including lithium plating, electrolyte breakdown, and adverse interactions with the cathode. Conversely, low SOC or over-discharge may result in the corrosion of the anode copper current collector and the collapse of the crystal structure in the active material. High charge and discharge rates can induce fatigue in the crystal structure of the active material, and elevated rates can lead to temperature increases, accelerating internal negative effects. To maintain optimal battery performance and extend its lifespan, it is crucial to operate within a reasonable range, avoiding both extreme conditions and the associated risks of degradation [152]. As we can see from the **Figure 34**, batteries have typically a reasonable operational range. The primary goal is to ensure the battery operates within the range of optimal efficiency and extended lifespan, while also steering clear of the danger zone, prompting immediate action and necessary precautions.

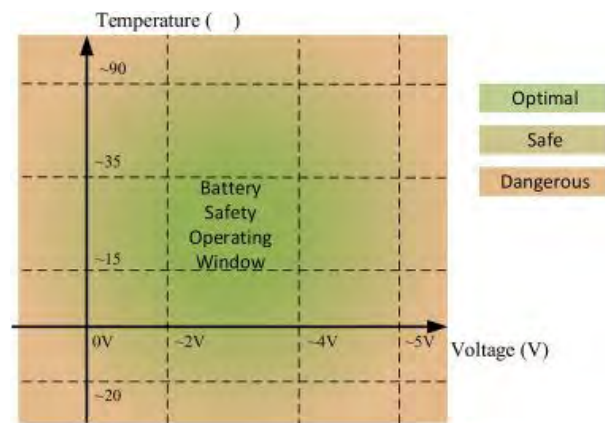


Figure 33 : Battery operational window. With green is depicted the optimal range [40].

3.10.2 Temperature

Temperature significantly affects a battery's lifespan, with both high and low temperatures accelerating its degradation. Understanding this impact is crucial. Most commercial lithium-ion batteries operate optimally between 15 and 35 degrees Celsius. Temperature is a critical factor influencing various processes within the battery, affecting primary and secondary reactions. Higher temperatures speed up side reactions and can lead to self-heating, causing thermal runaway. Lower temperatures increase internal resistance, resulting in greater polarization. Charging at low temperatures may induce lithium deposition, accelerating deterioration and posing safety risks. Material embrittlement caused by low temperatures also impacts battery life. Therefore, maintaining the battery within the appropriate temperature

range is vital for longevity. Factors influencing temperature include ambient temperature, the battery's heat capacity, thermal conductivity, heat generation, and the presence of heating and cooling systems [152]. Each variable significantly affects the battery's temperature.

Temperature plays a significant role in determining a battery's lifespan, and both high and low temperatures can expedite its deterioration. It's crucial to comprehend this impact, especially since most commercial lithium-ion batteries function optimally between 15 and 35 degrees Celsius [152]. Temperature affects various processes within the battery, influencing primary and secondary reactions. Elevated temperatures accelerate side reactions and can trigger self-heating, leading to thermal runaway. Conversely, lower temperatures increase internal resistance, causing greater polarization. Charging at low temperatures may induce lithium deposition, speeding up deterioration and posing safety risks. Material embrittlement due to low temperatures also affects battery life. Therefore, maintaining the battery within the appropriate temperature range is crucial for its longevity.

The lifespan of a battery is notably affected by the surrounding temperature. In practical Electric Vehicles (EVs), the most common condition for power batteries occurs during storage when the vehicle is parked and all electric systems are off. The battery temperature is primarily influenced by the climate in this state. Both temperature and State of Charge (SOC) are key variables impacting battery calendar life. Regions with high environmental temperatures experience significant capacity fade during storage. The battery's cycle life is also affected by temperature, which is influenced by climate, weather, and season. Generally, temperature increases as latitude decreases, but in high latitude areas with winter lows below 0°C, installing a heating system becomes necessary to prevent lithium deposition during low-temperature charging, addressing safety and durability concerns [153].

Ohmic heat is generated significantly during the battery's charging and discharging processes, and the resulting temperature change depends on the battery's thermal characteristics, resistance, and the current passing through it. Rational cell and system design can enhance the battery's thermal characteristics and resistance. Additionally, the vehicle's design can impact current intensity. The battery's operating state is directly influenced by driving style and road conditions, and under harsh working conditions, the current can intensify, leading to a substantial increase in battery temperature [153].

3.10.3 State of Charge (SOC)

A battery's lifespan is significantly influenced by its State of Charge (SOC), which establishes a relationship with voltage. Voltage can be determined using SOC and current through the battery model. In vehicle applications, SOC reflects the available battery capacity, predominantly determined by the vehicle itself. Higher SOC generally correlates with a lower anode potential, a higher cathode potential, and a higher terminal voltage. However, this condition may accelerate battery aging due to side reactions like Solid Electrolyte Interface (SEI) thickening, especially with a lower potential graphite anode [153]. Specific charging conditions, such as overcharging or charging at low temperatures, can drive the anode potential too low, reaching the lithium deposition potential and expediting internal reactions that contribute to battery aging. Similarly, a higher potential cathode can lead to electrolyte oxidation and cathode decomposition. A lower SOC contributes to a higher anode potential and a lower cathode potential, which can positively impact battery longevity. Nevertheless, an excessively low SOC may result in structural disintegration of the cathode active material and anode copper current collector corrosion, significantly reducing battery life [152].

Standard procedure involves charging the battery to maximum capacity and discharging it to a specific Depth of Discharge (DOD) while operating a Battery Electric Vehicle (BEV). For instance, an 80% DOD means the battery is cycled between 20% and 100% SOC. The relationship between DOD and battery life is complex, as shown in **Figure 35**. Increasing DOD has both positive and negative impacts on battery life. Higher DOD results in a lower average SOC, reducing anode potential and side reaction rates, thus enhancing battery life. However, increased DOD introduces multiple phase change regions in cathode and anode materials, causing significant structural and volume changes that degrade battery life. Consequently, an optimal DOD exists for improving battery life, balancing customer driving range requirements while preserving battery longevity. Hence, careful research into battery capacity in Electric Vehicles (EVs) and avoidance of large DODs are essential considerations [149].

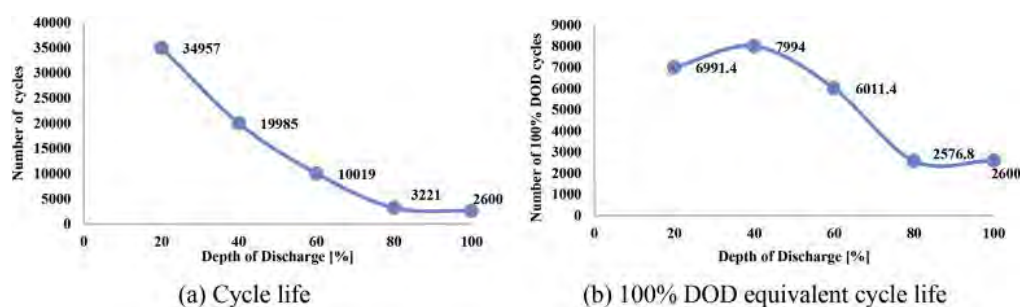


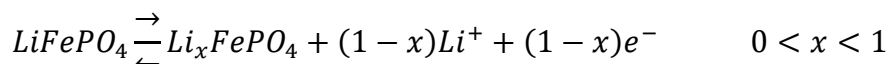
Figure 34 : Cycle life vs DOD [40].

CHAPTER 4

LiFePO₄ as a cathode material in lithium-ion batteries

4.1 Characteristics of LiFePO₄

Lithium iron phosphate (LiFePO₄) possesses an olivine-type structure known as triphylite, a phosphate mineral naturally occurring in the Earth. Despite its presence, its electrochemical properties were not explored until 1997 when Padhi et al. [62] conducted investigations. In their research, they successfully electrochemically extracted and inserted lithium into the lattice, resulting in a capacity of up to 110 mAh/g. This demonstration highlighted the electrode's promise, albeit with the acknowledgment that enhancements were needed to address issues such as rate capability and to approach its theoretical capacity. The capacity corresponds to one Li mole insertion and de-insertion. We can see the above through this equation where at room temperature Li_xFePO_4 is composed of two phases, a lithiated triphylite phase (LiFePO₄) and a delithiated heterosite phase (FePO₄):



Lithium iron phosphate undergoes cycling compared to lithium at a potential of 3.4V, which is slightly lower than that of metal oxide LiMO_2 cathode materials (M = cobalt (Co), nickel (Ni), manganese (Mn)). Despite this, it still represents a reasonably high potential. Alternative lithium transition metal phosphates, such as LiMPO_4 (where M = Co, Ni, Mn, Cu), present potential as cathode materials for lithium-ion batteries. LiMnPO_4 and LiCoPO_4 , specifically, exhibit higher potentials compared to lithium (4.1 V and 4.8 V, respectively), potentially leading to greater energy densities than LiFePO₄. However, neither LiMnPO_4 nor LiCoPO_4 has been electrochemically cycled with as high a specific capacity as LiFePO₄ electrodes due to inferior rate capabilities [63]. As a cathode material, LiFePO₄, offers several advantages, including its environmentally benign and non-toxic nature, as well as its cost-effectiveness. The substitution of Co or Ni with Fe is particularly beneficial due to the abundance and lower

cost of iron as a more common element. The escalating use of lithium batteries worldwide has contributed to increased demand and higher prices for Co. Additionally, LiFePO_4 stands out for its safety and thermal stability features. Differential scanning calorimetry (DSC) experiments involving charged Li_xFePO_4 electrodes, when compared to a Li_xCoO_2 electrode charged to a similar specific capacity of 170 mAh/g, demonstrated significantly smaller exothermic reactions [64][65]. In general, the reduced heat release observed in LiFePO_4 during heating, in contrast to the abrupt and more substantial heat generation seen in metal oxide cathodes like LiCoO_2 , LiNiO_2 , and LiMn_2O_4 suggest that LiFePO_4 stands out as a significantly safer cathode material. This safety aspect is particularly crucial for larger batteries or even smaller batteries designed for medical applications where safety is paramount. The stability of LiFePO_4 cells at elevated temperatures further underscores the desirability of LiFePO_4 cathodes for high-temperature applications, such as implantable medical devices and hybrid electric vehicles [66]. At temperatures that are above 60 °C, LiFePO_4 demonstrates superior capacity retention characteristics compared to LiMn_2O_4 in LiPF_6 -based electrolytes [67].

Nonetheless, different studies have validated the effectiveness of LiFePO_4 as a capable electrode material in electrochemical cells operating at 60 °C. The choice of electrolyte salt plays a crucial and big role in mitigating electrolyte acidity. In general, $\text{LiB}(\text{C}_2\text{O}_4)_2$ or LiClO_4 are more common options than LiPF_6 . The purity of the materials of the electrode and electrolyte in combination with the choice of electrolyte salt, is critical in elevated-temperature applications. Electric vehicle manufacturers see the LiFePO_4 as a potential candidate for use in hybrid-electric or electric vehicles. This is cause LiFePO_4 is being recognized as a very stable battery choice [68].

4.2 The atomic structure of LiFePO_4

Triphylite LiFePO_4 is a member of the ordered olivine family within lithium-ortho phosphates, characterized by an orthorhombic lattice structure in the space group. This structure comprises corner-shared FeO_6 octahedra in the b-c plane, forming zigzag planes. Additionally, there are edge-shared LiO_6 octahedra aligned parallel to the b-axis and PO_4 groups that share one edge with a FeO_6 octahedron and two edges with LiO_6 octahedra, as it is presented in the **Figure 36**. Consequently, phosphorus atoms occupy tetrahedral sites, while iron and lithium atoms reside in octahedral 4a and 4c sites, respectively. The oxygen atoms are arranged in a slightly distorted hexagonal close-packed array.

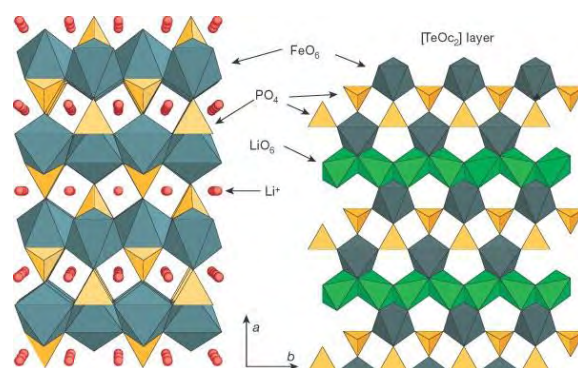


Figure 35 : Structural diagram of the LiFePO₄ and FePO₄ [17].

Upon the extraction of Li⁺ ions from LiFePO₄, the residual FePO₄ framework retains a similar structure with a slight deviation towards orthorhombic symmetry. This alteration results in a 2.6% rise in density. The noted structural resemblances between LiFePO₄ and FePO₄ play a crucial role in preventing capacity degradation caused by substantial volume fluctuations during the charging or discharging processes in cathodes. Additionally, these similarities may potentially contribute to efficiently mitigating volume changes in the carbon anode [112].

4.3 Electrochemical function of LiFePO₄

The Gibbs' phase rule is reflected in the flat voltage profile, indicating that the extraction/insertion reactions progress through the movement of a two-phase interface. Evaluating the material's rate capability, Padhi et al. observed that increasing current density doesn't diminish the open-circuit voltage, but it does reversibly reduce cell capacity. Cycling at lower rates again restores capacity, suggesting that the capacity loss is a diffusion-limited phenomenon associated with the two-phase nature of the insertion process or the material's low electrical conductivity [62][68][69]. In **Figure 37** we can see a comparison of discharge capacity retention diagram and how cycle number and capacity are linked together.

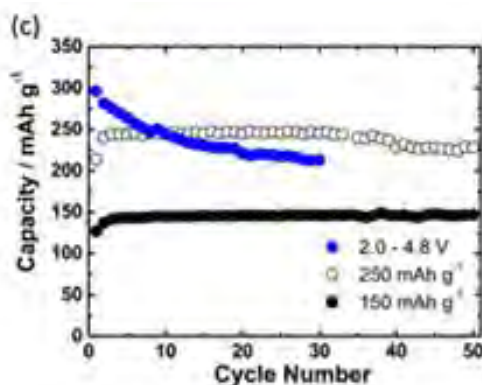


Figure 36 : Comparison of discharge capacity retention [19].

4.4 Problems of LiFePO₄

LiFePO₄ (Lithium Iron Phosphate) batteries, while popular for their safety and stability, have some drawbacks. One notable challenge is their lower energy density compared to other lithium-ion batteries, impacting their overall capacity and weight. Additionally, LiFePO₄ batteries can be sensitive to overcharging, which may affect their performance and longevity. Despite these limitations, their enhanced safety features make them preferred in applications where stability is a top priority, such as electric vehicles and renewable energy systems.

4.4.1 Low tap density

The theoretical density of LiFePO₄ is merely 3.6 g cm³. It is significantly less than that of LiCoO₂ (5.1 g cm³), LiNiO₂ (4.8 g cm³) and LiMn₂O₄ (4.2 g cm³). This concludes that the tap density of LiFePO₄ powder is modest. In general, most LiFePO₄ materials exhibit an actual density ranging from 1 to 1.4 g cm³, markedly lower than the commercially utilized LiCoO₂, which surpasses 2.2 g cm³ [75]. The diminished tap density significantly constrains the volumetric power density of a lithium-ion battery intended for handheld devices. In the case of powder materials, tap density is influenced not only by the theoretical density but also by particle characteristics such as size, shape, and distribution. As a general rule, smaller particle sizes and increased carbon content tend to result in lower tap density. In LiFePO₄, the particle size and carbon coating are both important for rate performance. Moreover, spherical particles usually have higher tap density than those with irregular shapes.

Table 4 : The comparison between LiFePO₄ and LiCoO₂ batteries [79].

Cathode	LiFePO ₄	LiCoO ₂
Density (g cm ⁻³)	3.60	5.10
Potential (V)	3.50	3.90
Specific capacity (mAh g ⁻¹)	169	274
Specific energy (Wh g ⁻¹)	0.59	0.98

4.4.2 Inadequate performance in low temperatures

LiFePO₄ batteries for electric vehicles exhibit suboptimal performance in low temperatures, as evidenced by discharge capacity data from the 45th Battery Symposium in Japan. The Sanyo 18650 battery, for instance, displays a discharge capacity of 888 mAh at 25 °C, which significantly drops to 375 mAh at 0 °C [76]. This is far below the requirements for use in electric vehicles. The problem lays in the LiFePO₄ itself and the electrolyte that it uses. Both

responsible for the poor low temperature performance. The electrolyte of LiFePO₄ cells is the conventional LiPF₆-EC/DMC/EMC system. The low diffusion coefficient of Li⁺ with LiPF₆ salt result in poor conductivity of the electrolyte at low temperature. To enhance the Li⁺ ion conductivity in the electrolyte, the development of new lithium salts is required. Meanwhile, for improving the rate of Li insertion into LiFePO₄, effective strategies involve reducing the particle size and managing the distribution of any andesite defects.

4.4.3 Formation of Dendrites

Dendrites in the context of LiFePO₄ batteries generally refer to lithium dendrites. Dendrites are thin, branching structures that can form on the surface of the lithium electrode in a lithium-ion battery, including those using LiFePO₄ as a cathode material. These dendrites are metallic lithium formations that can grow over time during certain battery conditions, such as overcharging or cycling [77].

Based on experimental observations, as the charging reaction progresses, lithium ions are released from the cathode, enter the electrolyte, and diffuse into the SEI film. Upon reaching the anode–SEI interface, they are reduced and deposited on the anode surface through an electron transfer process. The nucleation of lithium metal is depicted, and as the charging reaction continues, dendrites expand. The dendrites evolve into a dendritic form, with longer dendrites being more attractive to lithium ions due to the strong electric field distribution.

The formation of lithium dendrites is a concern in lithium-ion batteries as they can penetrate the separator between the anode and cathode, leading to short circuits, reduced battery performance, and safety hazards, including the risk of battery fires. According to the experiments conducted by R. Zhu and his associates they were able to observe dendritic evolution in a graphite – LiFePO₄ full cell in real time. Through the experiment they were able to confirm that when dendrites connect the anode to the cathode the voltage is significantly affected. Also, during the discharge process, the dendrites were disturbed by bubbles generated in the side reaction. This can be seen in the **Figure 35** where a bubble has formed and has penetrated the separator. This made the dendrites fragment releasing the fragments into the electrolytes. According to the experiments conducted by R. Zhu and his associates and according to the next figure we can spot [78]:

- a) Dendrite morphology near a newly released bubble
- b) Dendrite morphology after disappearance of the bubble
- c) Morphology of dendrite 1 pushed upward by bubbles

- d) Effect of a flow bubble on dendrite
- e) Fragmentation of the original dendrite

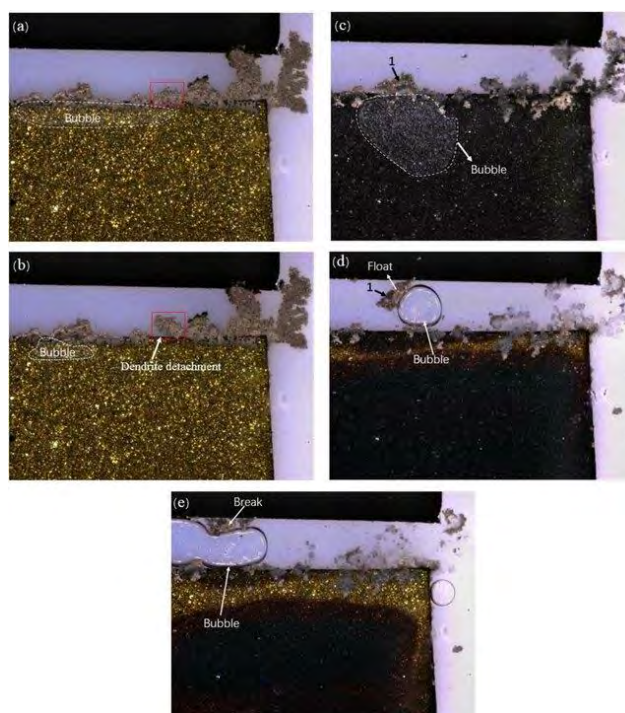


Figure 37 : This is the effect of bubbles on dendrites in a graphite-LiFePO₄ cell [22].

In the **Figure 38**, a and b illustrate the morphology of dendrites near a newly released bubble and after the bubble disappears, respectively, in the full cell. Continuing, c highlights the upward impact of the bubble on dendrite, marked with number 1, causing it to detach from the anode. The flow of the bubble significantly influenced dendrite 1 resulting in its fragmentation into numerous pieces as can be seen in d and e. These floating dendrite fragments transform into inactive lithium, contributing to increased surface roughness of the electrode and promoting lithium growth.

4.4.4 Agglomeration of carbon coating

The typical coating applied to LFP (LiFePO₄) particles involves a carbon black derivative to enhance their conductivity. In the initial state of a battery, this coating is quasi-crystalline, but with cycling, it has been observed to agglomerate into an amorphous phase. The agglomeration is a consequence of mechanical stress caused by volume changes in the LFP particles, leading to detachment and reattachment of carbon black particles. This can result in a loss of contact with the coating, promoting agglomeration. The amorphous phase of the

carbon black coating exhibits lower electronic conductivity, thereby increasing the resistance of the cathode [83].

4.5 Methods of improving LiFePO₄

A significant concern regarding the performance of this cathode material is its inherently low electrical conductivity. Pure LiFePO₄ without any added carbon has an electrical conductivity that is lower compared to LiCoO₂. Though we have found solutions such as including particle-size minimization, the addition of carbon coating and doping that can enhance the electrical performance of LiFePO₄ [65][70].

4.5.1 Carbon coating in LiFePO₄

Carbon coating is a widely employed strategy to enhance the electrical conductivity of LiFePO₄, addressing one of the major drawbacks associated with this cathode material. The inherent low electrical conductivity of pristine LiFePO₄ is substantially improved by introducing a carbon coating. As presented by the **Figure 39**, we can see what a coated LiFePO₄ looks like. The carbon layer serves as a conductive matrix that facilitates electron transport during charge and discharge cycles, mitigating the limitations posed by LiFePO₄'s intrinsic conductivity. This coating not only enhances the overall electrochemical performance of LiFePO₄ but also contributes to better rate capabilities and cycling stability. The incorporation of carbon coatings has become a standard practice in the fabrication of LiFePO₄ electrodes, playing a pivotal role in optimizing the functionality of lithium-ion batteries employing LiFePO₄ cathodes. Researchers continue to explore and refine carbon coating techniques to further enhance the conductivity and overall performance of LiFePO₄-based battery systems.

Among the organic precursors that can be used for carbon coating, sucrose and glucose emerge as the most widely utilized. Numerous investigations have explored the synthesis of high-performance carbon-coated LiFePO₄ composites, employing these compounds as carbon sources [116].

An appropriate calcination condition is critical for the performance of the final product using sucrose as carbon sources. Insufficient calcination temperature or time could result in the residual CH_x remaining in the electrode and lead to a decrease of electrode performance. Compared with sucrose, glucose was found to be a better candidate. Chen et al. conducted a comparison of C/LiFePO₄ synthesized using sucrose and glucose as carbon sources. They

observed that the C/LiFePO₄ composite prepared with glucose demonstrated superior initial discharge capacities [117]. Furthermore, Lai and his associates also demonstrated commendable rate performance and favorable cycling stability for carbon coated LiFePO₄ when employing both glucose and carbon sol–gel as the carbon sources [118].

Organic carboxylic acids are frequently utilized as carbon sources, with citric acid standing out as one of the best choices because of its low pyrolysis temperature. This characteristic ensures a lower synthesis temperature for the coated LiFePO₄ composite, resulting in a material with a high surface area and small particle size [119].

Beyond these, other diverse polymeric precursors have been researched. The research indicates that the pyrolysis of functionalized aromatic or ring-forming compounds on LiFePO₄ yields highly graphitized carbons. Notably, polyaromatic compounds such as polystyrene, featuring multiple functionalized aromatic groups, exhibited enhanced performance. This improvement was attributed to the close match between its decomposition temperature and the temperature of the LiFePO₄ phase transformation. This alignment led to the formation of fine particle sizes and a uniform distribution of carbon on the composite surface [120].

One of the crucial functions of carbon coating is to enhance both intra- and inter-particle electronic conductivity while preventing the aggregation of nano-particles, and to create pathways for lithium ions. The homogeneous dispersion of conductive carbon throughout the cathode is essential for promoting electronic conductivity and particle connectivity. The presence of incorporated carbon has been shown to impact the lithium-ion diffusion coefficient in nano composites. Synthesizing LiFePO₄ in the presence of high surface area carbon black, added to the precursors before the crystalline phase formation, has been proven to enhance its electrochemical performance. However, it's important to note that carbon coating may lead to a reduction in the volumetric energy density of the electrode. Therefore, optimizing the carbon content in LiFePO₄ during the carbon coating process becomes crucial. To improve electronic conductivity, the key aspect of carbon coating methods lies in identifying the most suitable carbonaceous material or combination of materials and discovering simple, cost-effective, and efficient fabrication procedures. Notably, the particle size of LiFePO₄ decreases as the carbon content increases during carbon coating [73].

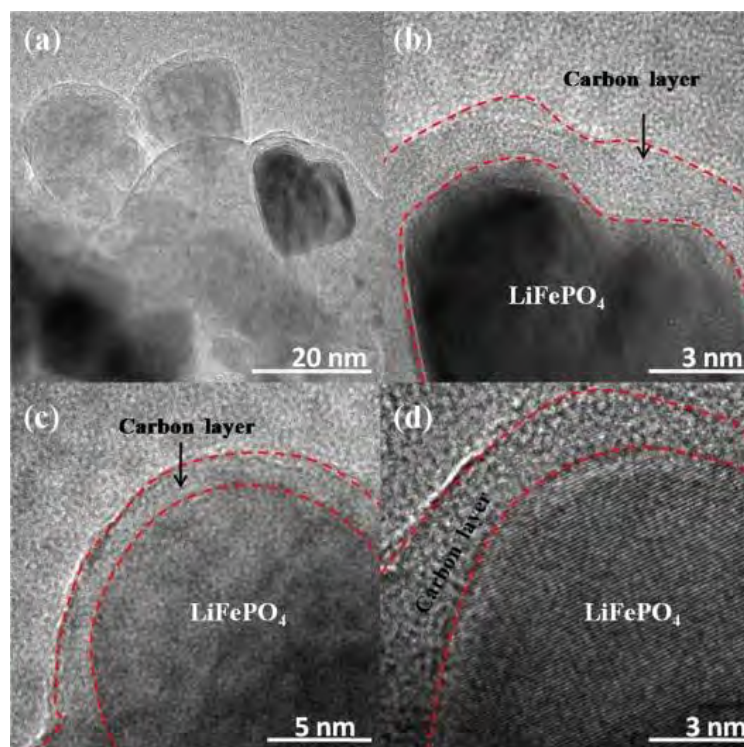


Figure 38 : Carbon coating over the nano particles of LiFePO₄ [21].

Various carbon coating methods have proven effective in enhancing the rate capability of LiFePO₄, enabling electrochemical cycling with a performance close to its theoretical capacity at room temperature. One of the initial instances of successful carbon coating was demonstrated by N. Ravet and his associates, achieving nearly the full theoretical capacity at 80 °C in a polymer electrolyte cell [71]. Another approach by Huang et al. involved creating LiFePO₄/C composites through the incorporation of carbon gel during material synthesis. This method led to particle size reduction and intimate carbon contact, resulting in a capacity of 162 mAh/g at a C/10 rate (95% of lithium accessible) and 153 mAh/g at a C/2 rate (90% of lithium accessible), with a carbon content of 15% in the composite. Huang et al. adopted an alternative strategy to produce coated LiFePO₄ composites by introducing carbon gel during the material synthesis process. This technique facilitated a decrease in particle size and fostered close interaction between LiFePO₄ particles and carbon. According to the results it showcased the efficacy of this approach in enhancing the electrochemical performance of LiFePO₄ [72]. Chen and Dahn incorporated table sugar into the raw materials, yielding a coated LiFePO₄ composite with 3.5 weight % carbon [70]. Ercan Avci successfully produced a lithium iron phosphate cathode material coated with carbon using a straightforward and effective solid-state synthesis method, involving the pyrolysis of polytetrafluoroethylene [74].

Typically, the reported optimal carbon content varies across the literature due to the influence of synthesis processes, including precursors, experimental conditions, and methods. These factors

strongly shape the physical characteristics of the resulting carbon material, consequently leading to distinct electrochemical behaviors in coated LiFePO₄ materials. Therefore, the suggested optimal carbon content should be regarded as a reference value in these studies, considering that the total carbon in the electrode needs to be taken into account. This total carbon encompasses the carbon coating, other particulate carbon introduced during LiFePO₄ synthesis, and any additional carbon incorporated into the binder during the formulation of the composite electrode. Recognizing the impact of carbon on tap density and volumetric capacity, maintaining a lower carbon content is crucial for practical applications [115].

During the process of carbon coating, the carbon typically originates from organic precursors introduced into the reaction mixture before undergoing firing. During the manufacturing phase of the coating, the organic material undergoes decomposition and carbonization within an inert or reducing atmosphere. Consequently, the thickness of the carbon coating can be regulated by adjusting the quantity of carbon precursors added. In the **Figure 40** we can see different carbon thicknesses ranging from 1 nm thick to 10 nm. It is evident that the carbon coating thickness corresponds to the amount of carbon precursor; an increase in the precursor amount results in a proportional increase in the carbon coating thickness. For instance, Dominko et al. achieved a carbon coating thickness of approximately 1–2 nm using 3.2 wt% citrate anion as a carbon source, whereas it escalated to about 10 nm with the utilization of 12.3 wt% citrate anion [115].

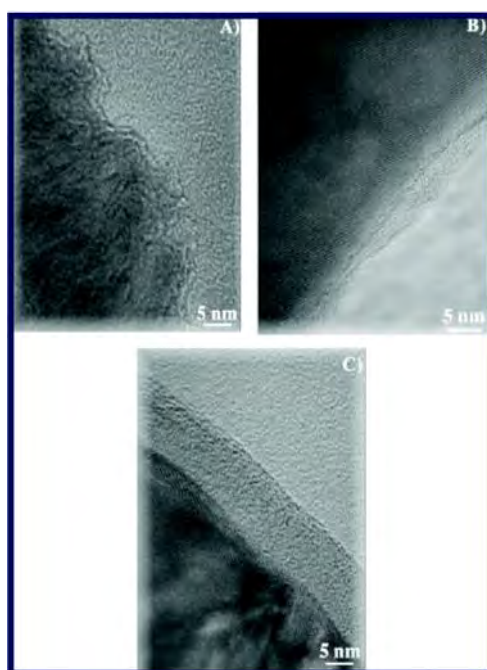


Figure 39 : HRTEM images of tiny edges of coated LiFePO₄/C with different carbon thicknesses. (A) 1 nm thick carbon layer (B) about 2–3 nm thick carbon layer (C) 10 nm thick carbon layer [30].

Furthermore, there are reports providing direct proof that the thickness of the carbon layer is intertwined with the particle size and surface area of LiFePO₄. In instances where the carbon quantity and physical properties remain constant, smaller-sized LiFePO₄ particles characterized by higher surface areas typically exhibit thinner carbon layers. This phenomenon occurs because the expanded surface area of smaller-sized LiFePO₄ particles leads to more extensive coating.

4.5.2 Particle size minimization

Various processing methods have been explored to enhance the performance of LiFePO₄, given its relatively low-rate capability. One approach is the minimization of particle size, aiming to reduce the length of lithium ionic diffusion pathways. The optimization of the synthesis method is a critical factor in this pursuit. Moreover, and through experiments, Yamada et al. conducted experiments on sintering temperature, revealing that while the pure olivine phase could be achieved at lower temperatures (around 300 °C), cathode performance exhibited a strong dependence on sintering temperatures [84]. In their research, the material achieved a specific capacity of 160 mAh/g at 550 °C, with particles having radii less than 30 microns. It's worth noting that the material included 20% conductive carbon and was likely cycled at low rates [113].

Through the experiments that were conducted Tiefeng Liu et al [114], it has been affirmed that reducing the particle size of the LiFePO₄ has positive effects on diminishing the size of active particles to the nanoscale, increasing the specific surface area, and forming a single-crystal structure. Consequently, minimizing the size gave the advantageous physical features of carbon-coating and a high specific surface area contribute to excellent electrochemical performance. Also, the narrow grain size distribution at the nanoscale enhances the uniformity of the as-prepared materials for electrochemical performance. Consequently, these physical properties collectively account for the outstanding electrochemical performances of carbon-coated single-crystalline LiFePO₄ nanocomposites. Lastly, this straightforward methodology is deemed cost-effective, obviating the need for expensive facilities and streamlining the manufacturing process. Furthermore, optimizing the grain size in the precursor emerges as an effective means to regulate the morphology and particle size distribution for LiFePO₄-based composites, thereby favoring the economical commercial production of LiFePO₄ materials [114].

4.5.3 Doping

One significant drawback in employing LiFePO_4 as a cathode material lies in its remarkably low conductivity. Strategies such as carbon coating and minimizing particle size have been explored to address this challenge. Nevertheless, both methods come with trade-offs: carbon coating involves the introduction of electrochemically inert additives, impacting total energy density, while reducing particle size can lead to decreased tap density and volumetric capacity. Chung et al. proposed a technique to enhance the lattice electronic conductivity of the material by selectively introducing super valent cations. This resulted in a significant conductivity increase at room temperature. Several dopants were examined, such as zirconium (Zr^{4+}), titanium (Ti^{4+}), niobium (Nb^{5+}), and magnesium (Mg^{2+}). The electrochemical testing of the resulting material demonstrated exceptional high-rate performance, achieving over 110 mAh/g for 20C discharge rates at room temperature. This LiFePO_4 material is thus well-suited for high-rate applications like power tools or hybrid electric vehicles [80].

The enhancement in conductivity is theorized to occur by expanding the solid solution region for the pure LiFePO_4 phase, creating a lithium-deficient solid solution, $\text{Li}_{1-a}\text{FePO}_4$. This potential extension may facilitate charge compensation through Fe^{3+} , leading to p-type conductivity. Similarly, for the FePO_4 phase, where Fe is trivalent, cation doping could result in the formation of Fe^{2+} , inducing n-type conductivity. Following the significant conductivity improvement demonstrated in this study through doping with supervalent cations, despite LiFePO_4 typically being an insulating material, several other research teams have attempted to replicate the doping process. However, their efforts have not yielded similar conclusions or success. It is believed that what caused the positive results was the combination of carbon coating and doping the nanoparticles. This forced Delacourt et al. to conduct a study on similar doping methods and contended that aliovalent doping of LiFePO_4 is unattainable [81]. Also the Cl doping lowered the migration energy thus obtaining the high diffusion rate of lithium ions is possible in lithium-ion batteries. The effects of Cl doping on LiFePO_4 have been investigated and it was discovered that anion doping plays an essential role in improving electrochemical performance. The impact of chlorine (Cl) doping on LiFePO_4 has been investigated, revealing that anion doping plays a crucial role in enhancing electrochemical performance. The substitution of oxygen (O) atoms with chlorine (Cl) is found to enlarge the LiFePO_4 lattice, resulting in an increased diffusion rate of lithium ions and improved internal conductivity. Additionally, the bandgap is reduced from 3.71 to 1.64 eV, indicating enhanced electrical conductivity in the

modified LiFePO₄. The doping with Cl is also associated with a lower migration energy, facilitating faster Li-ion diffusion within the electrode, as can be seen also from the **Figure 41**. Collectively, these findings suggest that anion doping with Cl in LiFePO₄ can induce significant changes with a positive impact on electrochemical performance.

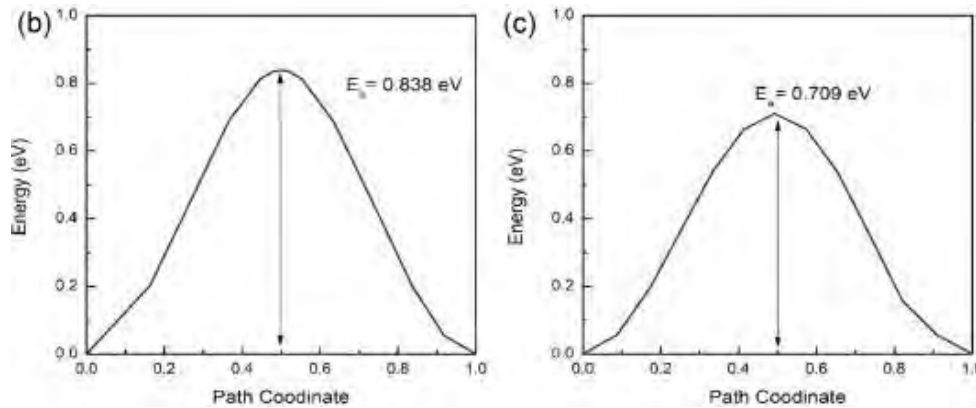


Figure 40 : Energy profiles of the ion migration and its migration energy for (b) LiFePO₄ and (c) Cl-doped LiFePO₄ [23].

In new experiments conducted by N.H.M._Zaki and his associates about Cl doping LiFePO₄, was found that expands the lattice volume of it and allows easy migration of lithium-ion along the pathway. In addition, the bandgap has reduced from 3.71 to 1.64 eV. That means that the modified LiFePO₄ will also exhibit higher electrical conductivity. Finally, migration energy is obtained as the doping with Cl correlates to faster Li-ion diffusion throughout the electrode. All of the above points imply that the anion doping method for Cl in LiFePO₄ can lead to changes that will significantly impact electrochemical performance [82].

4.5.4 Using different electrolytes

The electrolyte used in LiFePO₄ (LFP) batteries typically consists of lithium salts dissolved in a solvent. The most common lithium salt used is lithium hexafluorophosphate (LiPF₆), and the solvent is often a mixture of organic carbonates. The electrolyte plays a crucial role in facilitating the movement of lithium ions between the cathode (LiFePO₄) and anode during the charge and discharge cycles of the battery. The composition of the electrolyte can affect various aspects of battery performance, including its safety, thermal stability, and electrochemical properties. In recent research and development efforts, there has been exploration into alternative electrolyte formulations to address safety concerns, improve performance at extreme temperatures, and reduce the environmental impact of battery technologies.

According to experiments completed by Shengshui Zhang and his associates they were able to develop an electrolyte was developed for the operation of a LiFePO_4 cathode across a broad temperature range (-50 to 80 °C) by formulating a mixture of LiBF_4 – LiBOB (lithium bis(oxalato)borate) salts in a solvent blend of 1:1:3 propylene carbonate (PC)/ethylene carbonate (EC)/ethylmethyl carbonate (EMC). The LiBF_4 electrolyte exhibits superior conductivity below -10 °C, while the LiBOB electrolyte demonstrates higher conductivity above -10 °C. In terms of cell performance, the LiBF_4 cell demonstrates enhanced low-temperature performance and higher power capability but has limitations above 60 °C. Conversely, the LiBOB cell performs well at high temperatures, even up to 90 °C, but experiences challenges below -40 °C. Through the use of a LiBF_4 – LiBOB salt mixture, the temperature performance of LiFePO_4 cells can be optimized. Additionally, an interesting observation was made regarding an inverse correlation between the ionic conductivity of the electrolyte and the power capability of the cell [85].

Another experiment made by Xianglong Chen and his associates examines the use of composite polymer electrolytes in LiFePO_4 . Results show an increase in ionic conductivity by 10 times compared with CPE and GCPE. It is capable also to achieve more uniform lithium precipitation and significantly inhibits the growth of lithium dendrites. Also, this form of electrolyte shows good performance in lower temperatures [86][105].

CHAPTER 5

Reuse and Recycling of Li-Ion and LiFePO₄ batteries

5.1 Importance of Recycling

The expansion of battery production presents challenges, depleting metal resources and contributing to environmental issues associated with extraction and mineral processing. Moreover, lithium-ion batteries, commonly utilized in diverse electronic devices, generally exhibit a lifespan of up to 3 years in smaller gadgets and 5-10 years in larger devices. The disposal of batteries, often coinciding with electronic devices, is economically wasteful, overlooking the potential recovery and repurposing of valuable materials. Hence, proactive management of future waste streams from end-of-life batteries becomes imperative. Recycling batteries has become crucial for acquiring scarce raw materials and assisting countries in a swift and sustainable transition to green energy. Nevertheless, battery recycling is still in its new idea and has not been fully developed to its maximum potential yet. With the help of the **Figure 42** we can see what it takes to make a new battery through recycling old ones.

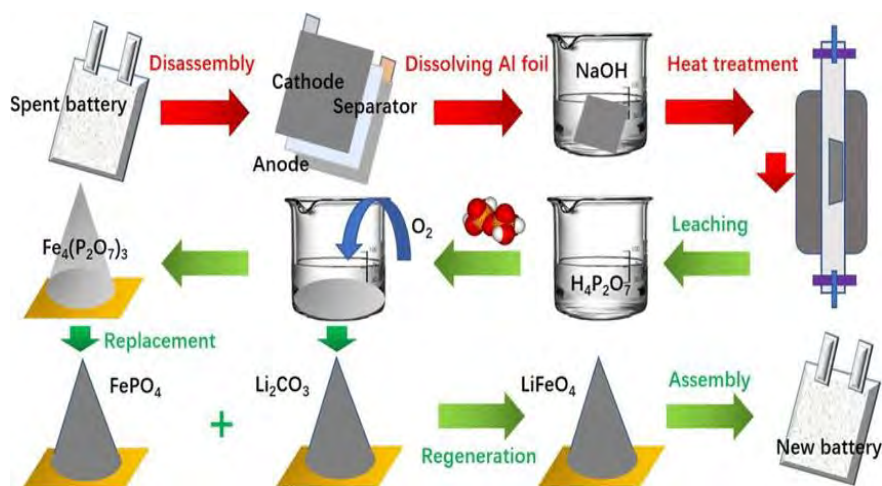


Figure 41 : LiFePO₄ batteries complete recycle circle [28].

5.2 Policies and Regulations

Dedicated recycling firms have emerged to address the rising volume of lithium-ion battery waste. However, many of these companies still rely on conventional, energy-intensive techniques like pyrometallurgy.

Countries like New Zealand are increasingly acknowledging the importance of its indigenous Māori population and their cultural values. The idea of *hanga āmiomio*, or the circular economy, is evident in regulatory frameworks such as the Resource Management Act and the Waste Minimisation Act. These legislations define sustainable management and promote efforts to minimize the generation and disposal of waste. Despite these measures, there is currently no specific inclusion of end-of-life lithium-ion batteries in New Zealand's legal framework [143].

In August 2018, China implemented regulatory measures concerning the recycling and reutilization of batteries, particularly focusing on lithium-ion batteries used in electric vehicles. These guidelines enforce strict protocols for maintenance, collection, transportation, and the development of reuse and recycling technologies [145]. Electric vehicle manufacturers are now obligated to manage the entire process, including collection, sorting, storage, and transportation of lithium-ion batteries, emphasizing the need for tracking mechanisms for future recycling purposes. Additionally, the regulation encourages thoughtful initial design considerations for disassembly and recycling, promoting the availability of open-source information throughout the supply chain [144].

The European Union mandates that manufacturers of batteries bear the responsibility for collecting and recycling spent lithium-ion batteries [144]. This directive promotes the incorporation of plans for lithium-ion battery disposal during the design phase, fostering a proactive approach. The mandate aimed for the recovery of 45% of battery production, including lithium-ion batteries, by 2016, a target that most member states have successfully met [146]. At the national level in the United States, there is currently no policy addressing the recycling of lithium-ion batteries. Despite being classified as hazardous substances by the Department of Transportation due to their fire risk, lithium-ion batteries are not considered dangerous under the United States Environmental Protection Agency Universal Waste Rules, and thus, are not covered by the Battery Act [144]. While eight U.S. states have waste management regulations and mechanisms for battery disposal, only three explicitly include provisions for lithium-ion batteries [144]. Overall, recycling contributes positively to society by establishing a cyclic and sustainable approach.

5.3 Recycling Factories

Consumer electronics, stationary energy storage, and the electric vehicle (EV) sector are predominantly reliant on lithium-ion batteries. However, the sustainability of Li-ion batteries hinges on their complete lifecycle, encompassing end-of-life management. Growing apprehensions about the availability of raw materials, such as cobalt, underscore the importance of recycling. Recycling can recover the intrinsic value of battery metals, fostering

additional revenue and establishing a circular supply chain that is resilient to fluctuations in the prices of battery components. The Li-ion battery recycling sector is poised for substantial growth in the next two decades. This is driven by increasing recognition of the recycling potential across the supply chain for batteries. According to estimations by 2042, approximately 12 million tons of Li-ion batteries will undergo recycling, resulting in valuable metals valued at \$49 billion USD [87]. Even now a lot of batteries are being recycled but a key part that will need to be solved is the recycling of electric vehicles batteries.

While the significant size and ease of collection of electric vehicles batteries present a considerable opportunity, they also bring forth various technological and financial challenges. Due to the diverse designs and high voltage of EV battery packs, safe disassembly remains a complex and time-intensive process. Moreover, the \$/kWh value of EV batteries is expected to be lower than that of consumer electronics batteries, necessitating recyclers to extract more material at higher purity and efficiency levels to achieve a break-even point in their recycling operations. Another critical question surrounding end-of-life EV batteries is whether they should be recycled to recover raw materials or repurposed for secondary applications such as stationary energy storage. Opting for recycling should be considered as a last resort when batteries reach the end of their usable life, as it is the least sustainable action within a circular economy. However, several factors need to be taken into account. Technically, providing old EV batteries with a second life should not impede their eventual recyclability. Nevertheless, this approach may extend the recycling process, influencing the logistics and economic aspects of recycling. In this context, we delve into the economic considerations of recycling Li-ion batteries and the key factors that can impact their overall value. For now, there are some start-ups and companies that are recycling lithium-ion batteries [88]. The most recognized recycling companies are:

- Inc. Lith ion Recycling (Canada)

The Canadian company Lith ion Recycling facilitates the efficient and profitable management of lithium-ion batteries. The company has an annual processing capacity of 7,500 metric tons, one of the biggest in the world. Impressively, the company achieves a 95 percent recovery rate.

- Li-Cycle Inc (Canada)

For recycling lithium-ion batteries, the Canadian start-up Li-Cycle combines mechanical size reduction and hydrometallurgical resource recovery methods. Their recycling method's main advantage is the creation of a nonhazardous product, which reduces transportation liability and sharply reduces expenses [89].

- Firma Duesenfeld (Germany)

German Duesenfeld develops an electrolyte recovery technique. This method combines mechanical and thermodynamic procedures to recover more raw materials while reducing the energy needed for recycling. In 2020, the company reported a processing capacity of more than 3000 tons of recycled Li-ion batteries per year [90].

- Fortum (Finland)

In order to recycle the battery materials this company combines mechanical and hydrometallurgical processes. The company's capacity for recycling has already reached 3000 tons annually. Lithium, cobalt, manganese, and nickel from the battery can be recovered using low-CO₂ techniques and used to make new batteries. The methods used to treat batteries are reliable, efficient, and sustainable. They assert that the combination of mechanical and hydrometallurgical recycling techniques can recycle 80% of a battery [91].

- Envirostream (Australia)

Envirostream has multiple collecting units, drop-off locations and fully battery processing facility. In general Australia produces up to 3,000 tons of lithium-ion battery trash annually [92].

- Maxim (China)

Maxim machinery equipment co.,ltd is specialized in design, research, producing and marketing of waste recycling equipment and providing waste processing and recycling solutions. Provides tailor-made total solutions and services covering the entire product life cycle [93].

- Sunny Recycling (China)

This factory is equipped with a lithium battery recycling plant. The plant can be used for dismantling and recycling the soft package battery, cellphone battery, shell battery, cylindrical battery etc [94].

5.4 Methods of recycling Li-ion

There are two primary methods for recovering lithium from a lithium-ion battery. The first step involves subjecting the discarded battery to a pre-treatment process to separate the lithium-containing active materials (cathode, anode) from the peripheral components, as extracting lithium from the assembled battery (plastic, polymer) is challenging. Subsequently, lithium is chemically extracted from the active components using pyrometallurgy, hydrometallurgy, and

electrochemical methods. In the **Figure 43** we can see the different steps of recycling batteries, from the pretreatment to Li-extraction.

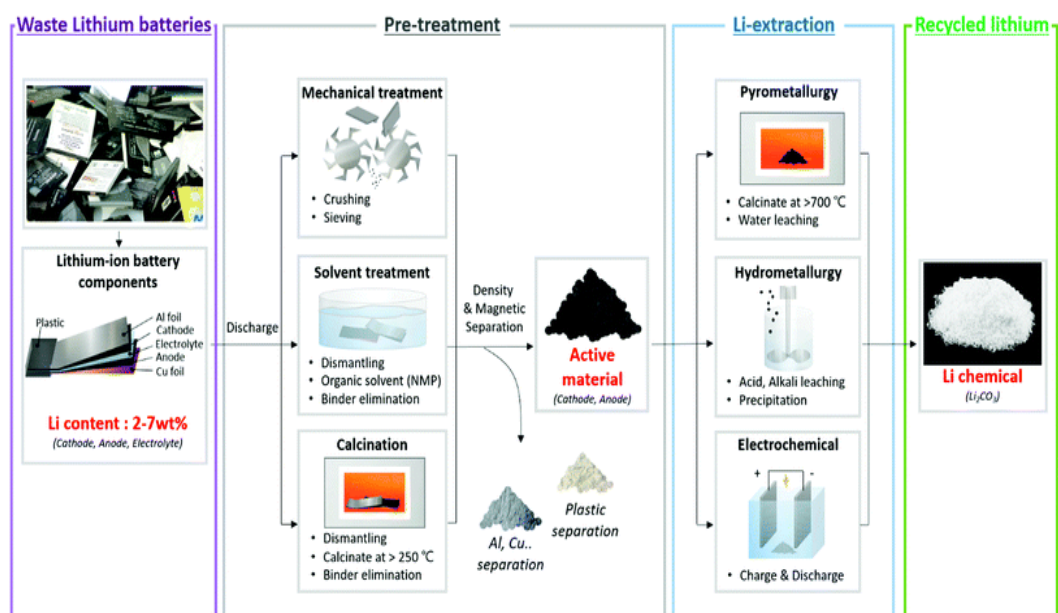


Figure 42 : Complete recycling phases and techniques for extracting lithium from used lithium-ion batteries [25].

5.4.1 Mechanical pretreatment

Mechanical pretreatment plays a pivotal role in the comprehensive recycling process of lithium-ion batteries, employing a range of physical methods to ensure the efficient recovery and responsible disposal of battery components [96]. The initial stages involve meticulous collection, sorting, and segregation of used batteries, taking into account their diverse types and sizes. The subsequent shredding phase involves breaking down batteries into smaller fragments, facilitating the subsequent separation of various components such as casings, electrodes, and electrolytes. Sieving further refines this process, categorizing fragments based on size, while magnetic separation efficiently removes ferrous materials like steel casings. Air classification, utilizing air currents based on density, enhances the separation of materials, particularly plastic casings. Vacuum filtration is employed to extract liquid electrolytes, and a subsequent drying step ensures that the recovered components are prepared for subsequent processing. This meticulous mechanical pretreatment sets the stage for subsequent hydrometallurgical or pyrometallurgical processes, contributing collectively to the sustainable recycling of lithium-ion batteries and promoting responsible resource management in the realm of energy storage technologies.

Mechanical pretreatment is typically followed by hydrometallurgical or pyrometallurgical processes to extract valuable metals and materials from the battery components. This combination

of mechanical and chemical treatments forms a comprehensive approach to lithium-ion battery recycling, contributing to the sustainable management of electronic waste and the responsible reuse of valuable resources [96].

5.4.2 Solvent pretreatment

This method involves separating the active components by eliminating the additional binder material that reinforces the contact between the foil and the cathode or anode. The cathode and anode are typically bonded to Al and Cu foil using a binder. Removing the binder facilitates the separation of the active substance and metal foil. One established technique involves immersing the electrode plate in N-methyl-2-pyrrolidone (NMP) at 100 °C to dissolve the binder and separate the Al and Cu foils. In a study, researchers discharged the lithium-ion battery by soaking it in a NaCl solution and manually disassembled it using needle-nose pliers [95]. Following the removal of the electrode plate, separator, metal case, and plastic, the cathode was fragmented into small pieces. These cathode pieces were then immersed in NMP for two hours at 80 °C, causing the binder to dissolve and separating the Al foil from the cathode material. Many batteries use a PVDF binder to attach the active components, while some use PTFE binders, requiring an appropriate organic solvent. Additionally, this process involves using organic solvents heated to around 100 °C, which increases costs and generates hazardous waste products [136].

5.4.3 Lithium extraction with Pyrometallurgy

The pyrometallurgical approach, commonly employed by the iron and steel industries to extract metals from various ores, minerals, and raw materials, can also be adapted for recycling lithium batteries. This method utilizes high temperatures to induce reactions in the cathode and anode, making lithium soluble in H₂O by evaporating organic materials. One primary mechanism within this process is calcination, a thermal process occurring in a low oxygen or oxygen-free atmosphere at 700 °C. This process is applied to solid materials to eliminate volatile components, leading to changes in the material's phase or decomposition reactions. Subsequent water leaching and filtration are performed, followed by the evaporation of the water, thereby making the lithium chemical available. Conversely, roasting, another pyrometallurgical method, occurs in an oxygen-rich atmosphere and is typically used for sulfide materials to achieve more efficient lithium extraction. However, a drawback of the pyrometallurgy process in lithium battery recycling is the need for additional procedures after

calcination, as mentioned earlier. Moreover, specialized equipment is required for calcination, and the process may emit harmful gases [96].

5.4.4 Lithium extraction with Hydrometallurgy

The primary recycling method for lithium extraction from lithium batteries involves a hydrometallurgical process encompassing leaching, crystallization (selective absorption), extraction, and precipitation. The objective of this hydrometallurgical process is to reconstitute battery materials, establishing a closed-loop recycling system. The initial stage is the leaching of the black matter, a fundamental step in standard hydrometallurgical treatment. During leaching, metal components undergo dissolution in inorganic or organic acids, laying the groundwork for subsequent processes such as precipitation, solvent extraction, and solvent absorption. This step is crucial for minimizing impurities present in organic residues and ensuring the production of the purest possible product metals [97][100]. In the **Figure 44**, we can see a typical recycling plan using Hydrometallurgy.

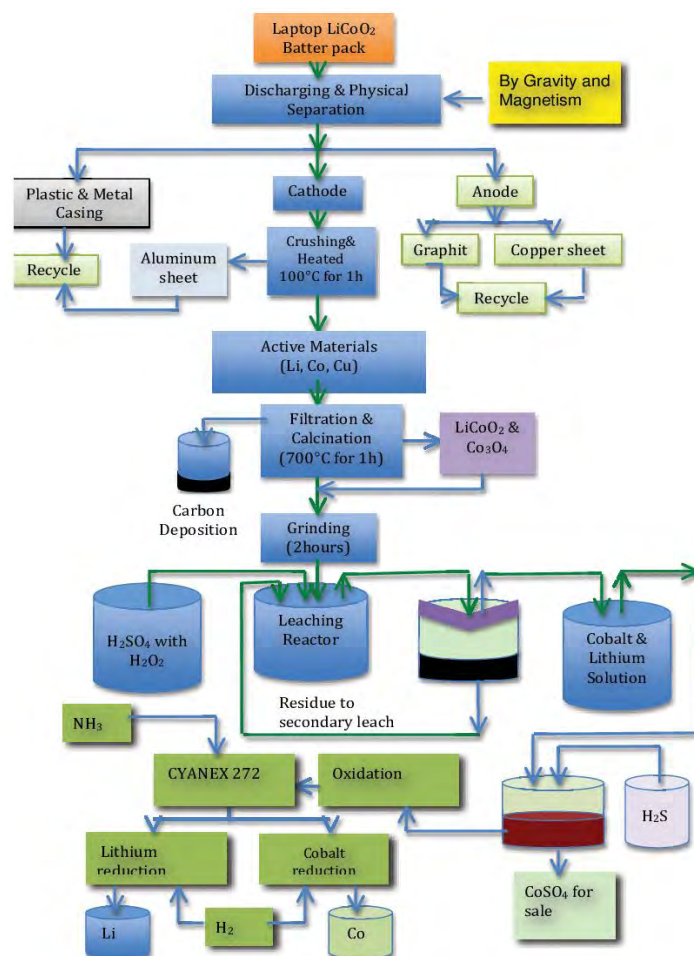


Figure 43 : Typical hydrometallurgical model for recycling lithium batteries [24].

5.4.5 Leaching

The initial step in a conventional hydrometallurgical treatment is the leaching of the black matter, where metal components undergo dissolution in either inorganic or organic acids. This step is crucial for subsequent processes like precipitation, solvent extraction, and selective absorption. Its primary objectives are to minimize impurities in organic residues and produce the purest possible product metals. The leaching process is highly influenced by kinetic data, as it depends on the heterogeneous phase transition among solid, liquid, and gas. Factors such as the solid-liquid ratio, reaction temperature and concentration of leaching agents play significant roles. Recent studies demonstrate the advantageous chemical properties of metals in aqueous solutions, highlighting the potential for separating and recovering valuable products like lithium. The effectiveness of this initial step relies on the cathode's nature, the reducing agent and its concentration, the acid used, and the duration of the leaching process [98][100]. In the **Figure 45** we can see that the leaching is the first step for recycling the lithium.

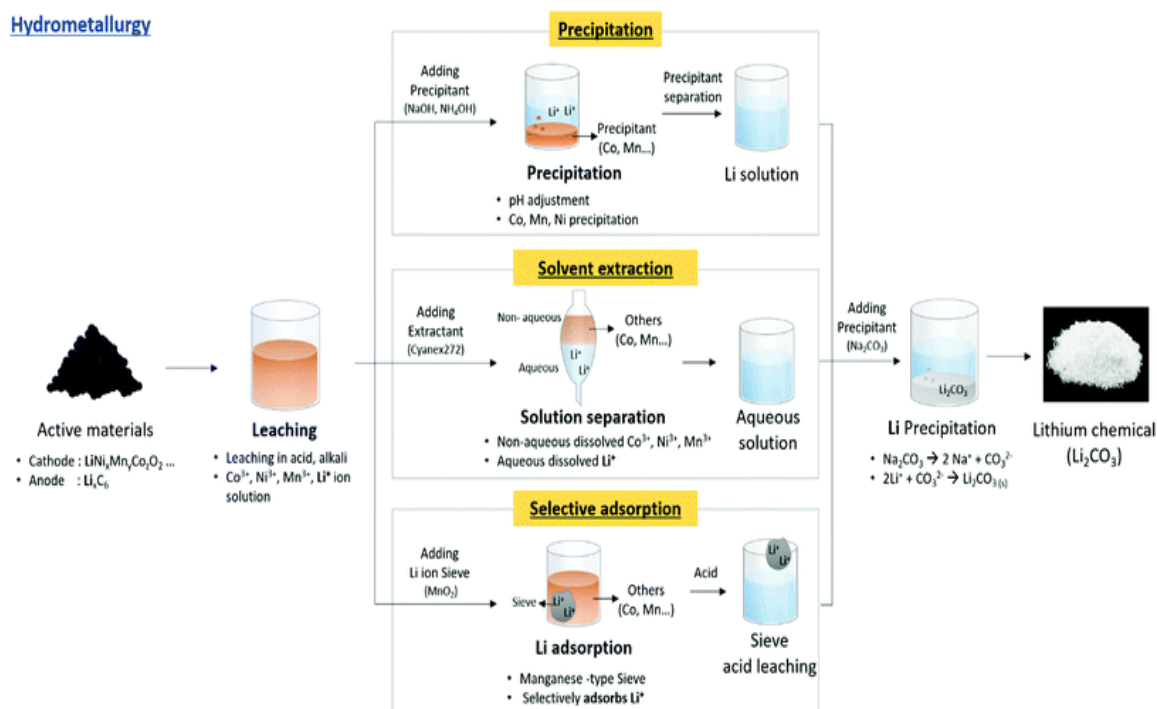


Figure 44: Diagram illustrating the electrochemical extraction process for recycling lithium from pre-treated waste components of lithium-ion batteries [25].

5.4.6 Precipitation

Following the leaching process in lithium recovery, precipitation emerges as the predominant technique, leveraging the differential solubility of metal compounds. Renowned for its cost-effectiveness and security, precipitation stands out among the methods in

hydrometallurgical treatment, surpassing solvent extraction and selective absorption. The process capitalizes on temperature elevation, reducing solubility and facilitating efficient precipitation. Moreover, adjusting the pH upwards leads to the separation of hydroxides after precipitation, encompassing elements like cobalt, manganese, and nickel. For instance, the introduction of a saturated sodium carbonate (Na_2CO_3) solution to the mixture results in the formation of lithium carbonate (Li_2CO_3), achieving an impressive lithium extraction efficiency of nearly 98% [98]. This method not only ensures efficacy in lithium separation but also underscores its applicability in sustainable and efficient recycling processes.

5.4.7 Solvent extraction

To extract lithium from the leached cathode material, solvent extraction necessitates a two-phase system, leveraging relative solubility to segregate ions between nonpolar and polar liquids. Within this stratified solution, lithium is selectively separated, while metals like manganese, nickel, and cobalt are extracted from nonpolar agents. Notably, a recent advancement introduces a compound named Cyanex 936P,[99] demonstrating promising capabilities in lithium battery recycling for lithium extraction. The effectiveness of the solvent extraction process is contingent on pH conditions and solvent concentration [96].

5.4.8 Lithium electrochemical extraction

This method involves the extraction of lithium from pre-treated active material by immersing the active material in water and utilizing a ceramic solid electrolyte to separate lithium. Furthermore, the success of the process hinges on the purity of lithium, with high purity lithium being the optimal outcome; however, most brines lack this level of purity as they are typically of relatively low purity. A significant advantage of electrochemical extraction, also referred to as electrochemical ion pumping, lies in its inherent flexibility. This flexibility allows for the treatment of brines containing diverse components and concentrations by adjusting input parameters. Additionally, by applying current to execute the process, there is no need for additional chemicals to regenerate the active material. This process has four main steps [100]:

- Lithium cations from an artificial brine and an electrolyte are selected to be placed between a lithium captured electrode through current.
- The solution is then exchanged with a recovery one for the release of lithium.

- Lithium cations are released into the recovery solution, simply by changing the direction of the current.
- The lithium brine is flushed in the cell so the cycle can start again from the first step.

5.4.9 Innovative technics for LiFePO₄ recycling

The increasing attention on recycling spent lithium iron phosphate (LFP) batteries has prompted researchers to explore various methods for continual improvement in recycling techniques, with the goal of achieving greater economic and practical applicability. The need for new and advanced recovery approaches becomes imperative in response to rising environmental standards, promoting energy conservation, emission reduction, and accelerating industrial advancement. Many documented recycling processes for spent lithium iron phosphate (LFP) cathodes are based on studies involving degraded powder. However, in practical applications, the initial crucial step involves the efficient separation of active materials from aluminum foils [101][102].

The majority of recycling technologies focus on the individual recycling of spent batteries, but practical recycling processes often involve the mixing of various types of lithium-ion batteries (LIBs). Consequently, if the cathode components can be processed collectively or if collaborative recycling of degraded LIBs based on their similar physicochemical properties can be achieved, there is a potential for significant improvement in recycling efficiency [103]. In their study, Jiang and his colleagues introduced a collaborative recovery method utilizing a dilute sulfuric acid medium and capitalizing on the redox properties between spent lithium iron phosphate (LFP) and lithium cobalt oxide (LCO) [104]. Through systematic optimization of the system, they achieved efficient leaching, obtaining extraction rates of 99.9% for Li, 92.4% for Co, 99.8% for Fe, and 99.9% for P, all achieved without the use of any additives. The kinetics of the leaching process revealed that LFP primarily underwent decomposition, releasing Li⁺ and Fe²⁺ into the acidic solution. Subsequently, Fe²⁺ underwent transformation into Fe³⁺ concurrently with the leaching of LCO. The collaborative leaching system of LFP and LCO demonstrated a noticeable reduction in reagent dependence. In another example, Wang et al explored a recycling approach involving thermal treatment, acid leaching, and alkali leaching with the primary goal of efficiently recovering lithium. Initially, the cathode material underwent calcination at 600 °C for 4 hours, followed by leaching with H₂SO₄ to separate aluminum (Al), iron (Fe), and copper (Cu). Subsequent to acid leaching, an alkali solution with a solid-liquid ratio of 1:4 was employed to eliminate Fe. In the second step, the acid leaching

filtrate was used to adjust the pH of the alkaline leaching filtrate to a suitable value of 6. In the third step, the addition of LiNO_3 solution induced a precipitation reaction at $60\text{ }^\circ\text{C}$ for 4 hours. Finally, after filtration, 94% of the lithium in the filtrate was successfully recovered. This method effectively eliminates interferences from iron and aluminum impurities in lithium metal recovery, maximizing the recovery of precious metals. Although the process is straightforward and easy to execute, it does entail a significant energy consumption, either from fuel or electric sources. Moreover, since spent LiFePO_4 batteries typically lack cobalt and other precious metals besides lithium, this simple recovery method may not yield high economic benefits [104].

CHAPTER 6

Conclusions

It is clear that LiFePO₄ holds a prominent position among the materials anticipated to shape the future. Its diverse applications underscore its pivotal role in numerous fields. The prevalent reasons for its utilization typically include its cost-effectiveness, eco-friendliness, favorable performance in charge-discharge cycles, and the safety it affords. Another noteworthy factor is the versatility in LiFePO₄ manufacturing methods, with each approach occasionally imparting additional characteristics. Certainly, some researchers posit that a combination of these methods could yield a material with superior attributes. Notably, LiFePO₄'s widespread use is attributed to its capability to augment capacity, electrical conductivity, and charge-discharge cycles. This enhancement can be achieved either by introducing additives within its structure or by coating the material's surface with carbon. By coating the material's surface with carbon, we enhance the LiFePO₄ batteries. This external modification serves multiple purposes. Firstly, the carbon coating acts as a protective layer, shielding the material from undesired reactions and improving its stability. Additionally, it enhances electrical conductivity, facilitating more efficient electron transport during charge and discharge cycles. This dual role of protection and improved conductivity contributes significantly to optimizing the overall performance of LiFePO₄ batteries. In essence, the choice between internal modification through additives and external modification via carbon coating provides researchers and engineers with versatile strategies. These strategies can be selectively employed based on specific performance goals, allowing for a tailored approach to meet the evolving demands of energy storage technologies. The versatility in enhancing LiFePO₄ characteristics underscores its adaptability and potential for continued advancements in the field of battery materials. One of the biggest problems is the recycling of lithium batteries and more specifically the LiFePO₄ batteries. In general, there are some factories that recycle the spend batteries but it's not cost effective yet and there is a big debate for which method of recycling is the best and what it should be used to recycle the LiFePO₄ batteries. LiFePO₄, being a versatile material and subject to ongoing research, stands out for its significance in diverse applications. The combination of cost-effectiveness, environmental compatibility, favorable electrochemical behavior, and adaptability to various manufacturing methods positions LiFePO₄ as a material with multifaceted importance for the future. A potential avenue for future exploration could involve examining better ways to enhance the LiFePO₄ batteries, like carbon coating does, but with a most cost-effective way. Also, it is deemed necessity that we find solutions for the recycling of the batteries and their materials because lithium is not a renewable source.

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