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SCHOOL OF ENGINEERING

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**REUSE AND RECYCLING: ENVIRONMENTAL SUSTAINABILITY OF
LITHIUM-ION BATTERY ENERGY STORAGE SYSTEMS**

Diploma Thesis

ASIMINA ATHANASIADI

Supervisor: Panagiotis Tsiakaras

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Approved by the Examination Committee:

Supervisor: **Panagiotis Tsiakaras**

Professor, Department of Mechanical Engineering, University of Thessaly

Member: **Angeliki Brouzgou**

Assistant Professor, Department of Mechanical Engineering, University of Thessaly

Member: **Georgios Charalampous**

Assistant Professor, Department of Mechanical Engineering, University of Thessaly

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ASIMINA ATHANASIADI

Abstract

The success of modern civilization is fundamentally linked to our ability to harness energy, primarily in the form of fossil fuels. However, their extraction and use have created problems for our health and the environment. The quest for alternative energy sources has led to the development of electrochemical devices, with one of the most promising ones being lithium-ion batteries. Nevertheless, there are key uncertainties surrounding the emergence and management of these batteries. As their demand grows, so does the amount of waste produced, and, because some of their materials are harmful to the environment, they should not be disposed of directly to it. Furthermore, several batteries are driven to their retirement after a few years of use, despite the fact that they can still be used in other energy storage systems. Finally, due to their scaled-up productions, lithium resources will be in short supply in a few years. For all these reasons, a deeper understanding and better implementation of battery reuse and recycling patterns have become an imperative issue.

Περίληψη

Η επιτυχία του σύγχρονου πολιτισμού συνδέεται θεμελιωδώς με την ικανότητά μας να αξιοποιούμε ενέργεια, και έως τώρα κυρίως με τη μορφή ορυκτών καυσίμων. Ωστόσο, η εξόρυξη και η χρήση τους έχουν δημιουργήσει προβλήματα τόσο στην υγεία μας, όσο και στο περιβάλλον. Η αναζήτηση εναλλακτικών πηγών ενέργειας οδήγησε στην ανάπτυξη ηλεκτροχημικών συσκευών, με μία από τις πιο υποσχόμενες να αποτελούν οι μπαταρίες ιόντων λιθίου. Ωστόσο, υπάρχουν βασικές αβεβαιότητες σχετικά με την εμφάνιση και τη διαχείριση αυτών των μπαταριών. Καθώς αυξάνεται η ζήτησή τους, αυξάνεται και η ποσότητα των παραγόμενων απορριμμάτων και, επειδή ορισμένα από τα υλικά τους είναι επιβλαβή για το περιβάλλον, δεν πρέπει να απορρίπτονται απευθείας σε αυτό. Επιπλέον, αρκετές μπαταρίες οδηγούνται στην απόσυρσή τους μετά από λίγα χρόνια χρήσης, παρά το γεγονός ότι μπορούν ακόμη να χρησιμοποιηθούν σε άλλα συστήματα αποθήκευσης ενέργειας. Τέλος, λόγω της κλιμακούμενης παραγωγής τους, οι πόροι λιθίου πρόκειται να είναι σε έλλειψη σε λίγα χρόνια. Για όλους αυτούς τους λόγους, η βαθύτερη κατανόηση και η καλύτερη εφαρμογή των μοτίβων ανακύκλωσης και επαναχρησιμοποίησης των μπαταριών αυτών έχουν καταστεί επιτακτική ανάγκη.

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Abbreviations

EES	Electrochemical Energy Storage
LIB	Lithium-ion Battery
EOL	End Of Life
ECS	Energy Storage and Conversion System
FC	Fuel Cell
FCV	Fuel Cell Vehicle
GHG	Greenhouse Gas
UPS	Uninterrupted Power Supply
SC	Supercapacitor
MAB	Metal-air Battery
HER	Hydrogen Evolution Reaction
AM	Active Material
CM	Conductive Material
BS	Binder Solution
PVDF	Polyvinylidene Fluoride
PP	Polypropylene
PC	Polycarbonate
PE	Polyethylene
LCO	Lithium Cobalt Oxide
LMO	Lithium Manganese Oxide
NCM	Nickel Cobalt Manganese
LFP	Lithium Ferrophosphate
NCA	Nickel Cobalt Aluminium
EV	Electric Vehicle
SEI	Solid Electrolyte Interface
SPE	Solid Polymer Electrolyte
ICE	Internal Combustion Engine
PV	Photovoltaic
SOH	State of Health
EIS	Electrochemical Impedance Spectroscopy
IC-DV	Incremental Capacity-Differential Voltage
ML	Machine Learning

Chapter 1

Introduction

Energy harvesting is essential for life on Earth. However, the amount of energy we use has far-reaching repercussions. Human activities, producing massive levels of carbon emissions, have significantly increased the concentration of greenhouse gases in the atmosphere, resulting in global warming. Even simple tasks, like driving a car every day, consume fuel that is eventually leading to the intensification of the phenomenon of climate change [40].

For more than a hundred years, fossil fuels have supplied most of our energy needs for industrial and domestic purposes. They are an appealing energy source because they can be transported relatively easily and deliver highly concentrated energy. Nowadays, oil, gas, and coal still cover around 80% of our energy requirements and humans are paying the price. Using fossil fuels as the main energy source has had a major impact on individuals as well as the whole on the planet, leading to air and water contamination and also contributing to global warming [41]. To further understand the energy ‘footprint’ of the average person in a given country, the chart in **Fig. 1** shows per person CO₂ emissions.

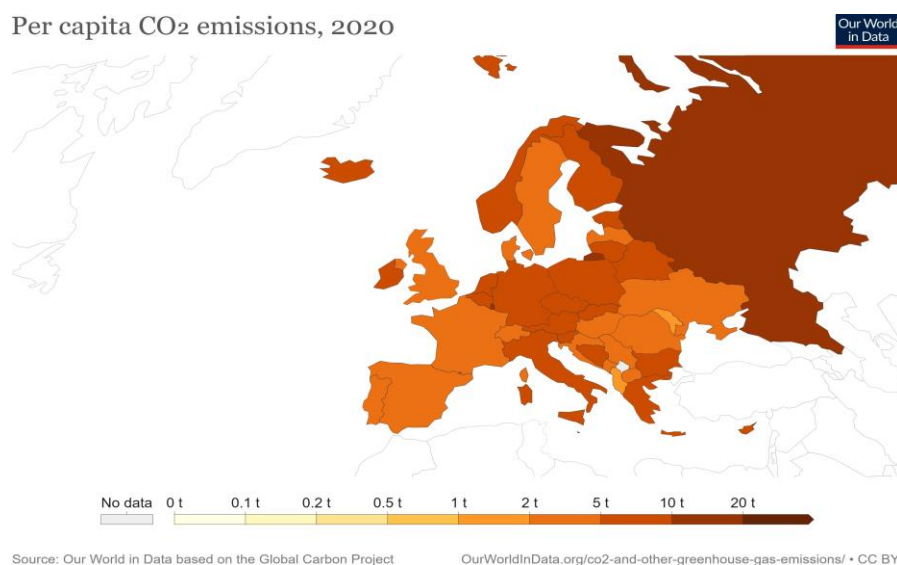


Figure 1: Carbon dioxide emissions from fossil fuel use for energy and cement production [1].

In the upcoming few decades, fossil fuels are still going to be an essential part of our energy demands. The question is how quickly sustainable energy solutions can be scaled up to replace fossil fuels, meet the global energy needs and eliminate the catastrophic repercussions of climate

change [42].

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 [43]. The limited resources and increasing demand for innovative energy technologies have further spurred great interest in green electrochemical energy storage (EES) devices. A series of rechargeable batteries, metal-air cells, and supercapacitors have been extensively explored, because of their high energy densities and high cycle retention. Structural and operational insights for these devices will be provided in **Chapter 2** of this paper.

One of the most widely used types of rechargeable batteries is the lithium-ion batteries (LIBs). For the last few decades, LIBs have proven to be an effective energy storage technology, owing to their inherent benefits, including high efficiency, quality operation, high energy density, superior rate capability, as well as long life cycles when compared to other types of batteries [44].

Since they were first commercialized in the early 90s, LIBs have been employed as energy sources for many small portable electronic devices, including mobile phones, laptops, digital cameras, medical devices, etc. Recent advances in LIB technology have enabled these batteries to be used in an even larger variety of applications, such as solar and wind stationary energy storage systems, power sources for electric vehicles, smart grids, and even space technologies [44]. Their structure, features, manufacturing cost, and market demand will be further analyzed in **Chapter 3**.

Due to this widespread and rapid uptake of lithium-ion battery applications, the world LIB market has shown explosive growth. The large production rate, combined with the fact that their replacement time is gradually being shortened, has led to a huge number of these batteries being discarded. These batteries entering the waste stream are usually considered to have reached their end of life (EOL), even though some of them still retain a big percentage (over 80%) of their original capacity, show high reuse potential, and could still be used in further applications. The output of spent power batteries is estimated to rise from 10,700 tons in 2012 to 464,000 tons in 2025, representing a 59% compound growth rate per year [45].

The vast generation of spent lithium-ion batteries has led to massive waste accumulation, posing environmental risks, and spreading great concern around the globe. Wasted LIBs still contain their original elements, but also new chemicals formed by reactions occurring during charging and discharging, like lithium, cobalt, nickel, manganese, organic electrolytes, and other additives. When wasted batteries end up in landfills, the chemical bonds are broken leading to their compounds entering the ecosystem, causing serious damage and contamination.

The ensuing pressure to create EOL strategies for these devices has offered great potential for reusing LIBs in second-life applications, compared to other battery types [44]. These second-life batteries could come from either recycling or reusing the lithium-ion batteries that were firstly used in various applications.

In **Chapter 4**, several technological methods for reusing and recycling LIBs will be introduced. Discharge, crushing, sorting, binder removal, physical separation, pyrometallurgy, and hydrometallurgy are some of the most critical recycling methods. Moreover, recent advances and key technologies will be mentioned.

The recycling infrastructure is still incipient, with numerous foundational and technological challenges to conquer, such as technical, logistical, economic, and regulatory constraints [46]. To make the best of a battery's life, a sustainable circular economy for LIBs should be established. Thus, recycling and reusing LIBs are required to maintain the physical resources and achieve environmental and economic sustainability.

Finally, **Chapter 5** includes conclusions and final remarks.

Before examining the potential and challenges that current LIB reuse and recycling infrastructures face, the following chapter (**Chapter 2**) will introduce us to the science of electrochemistry and its basic principles. In addition, an overview of some electrochemical devices and their electrochemical processes will be provided. The chapter concludes with a discussion of several battery technologies, leading to **Chapter 3**, which focuses on the main part of this paper, the lithium-ion batteries.

Chapter 2

Electrochemical Devices for Energy Conversion and Storage

2.1 Electrochemistry

Electrochemistry is the science that studies the relation between an electrical potential, which is a measurable phenomenon, and an identifiable chemical change, with either electrical potential being the outcome of a chemical change or vice versa [47]. In simpler terms, electrochemistry is the field of chemistry concerned with the electricity produced during spontaneous chemical reactions, as well as the use of electrical energy to cause non-spontaneous chemical transformations. This topic is important because electrochemical processes can generate various metals, chlorine, fluorine, sodium hydroxide, and other chemicals [48]. Electrochemical reactions have the advantage of being energy-efficient and friendly to the environment. Therefore, exploring this field is essential for the development of novel green technologies.

Electrochemical power sources are devices that convert chemical energy into electrical energy (**Fig. 2**). During their operation, at least two reaction partners go through a chemical reaction. At a specific time and voltage, this reaction's energy becomes available as an electric current [2].

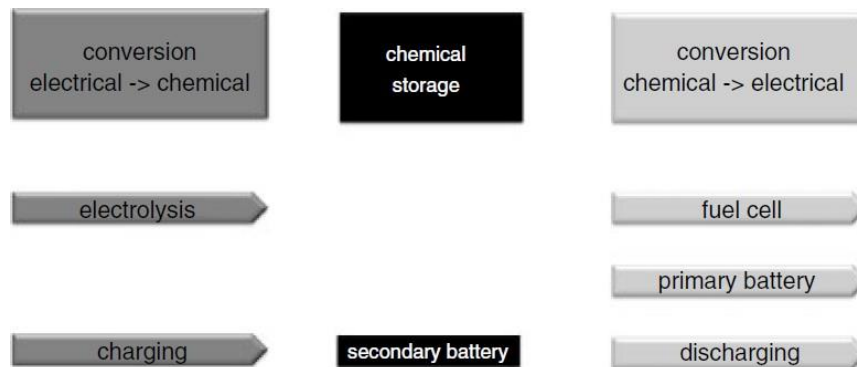


Figure 2: Chemical and electrical energy conversion and possibilities of storage [2].

Electrochemical power sources are different from other energy sources, like thermal power plants, as the conversion of energy happens in only one step; in thermal power plants, for example, the first step is converting the fuel into thermal energy, afterward into mechanical energy, and finally into electric power via generators. This process using multiple steps is replaced by a single step in electrochemical power sources [2]. As a result, they present several advantages, including high energy efficiency, low cost, and using non-toxic compounds.

An electrochemical device is composed of two electrodes, which are separated by an electrolyte. During its operation, electrons are driven to flow from the negative electrode, called the anode, to the positive electrode, the cathode. This process ends when the electrode material is consumed (e.g. first generation/non-rechargeable batteries) or continues to the opposite direction due to potential difference (e.g. reusable batteries). These are typically metals or chemical compounds of various types. The electrolyte might be either solid or liquid. Electrolytes in solid state serve two purposes. Firstly, they are able to conduct ions, and secondly, they separate the positive and negative electrodes. In liquid-state electrolytes like electrolyte solutions, an inert porous separator sheet is used, allowing ions to move through it, resulting in conducting current [49,47].

2.1.1 Reduction-Oxidation

Electrochemistry involves the production or consumption of free electrons during reactions. These are referred to as redox reactions, which is a term that stands for reduction-oxidation. Reduction and oxidation are electrochemical processes that change the oxidation state of a molecule or ion by transferring electrons to or from it [47]. This reaction of the transfer of electrons between chemical species can take place when an external voltage is applied or when chemical energy is released. It usually includes one species, called reducing agent, undergoing oxidation, while another species, called oxidizing agent, is undergoing reduction. The first species is being oxidized, whereas the second one is being reduced [50]. Simply put:

- Oxidation means losing electrons (or increasing an atom's oxidation state)
- Reduction means gaining electrons (or decreasing an atom's oxidation state)

2.1.2 Electrochemical Cell

The most basic system consists of one electrochemical cell. Electrochemical cells are devices that produce an electric current by releasing energy from a spontaneous redox reaction. Such cells are the Galvanic cell and the Voltaic cell, which were named after the scientists who developed them, Luigi Galvani and Alessandro Volta respectively, whose research concerned chemical reactions, as well as the electric current in the late 1800s [51]. The electrochemical cell - also called galvanic element - provides a 0.5–5 V cell voltage, which is relatively low. The cell can be joined in series with others to acquire a greater voltage, and for a higher capacity, it must be linked in parallel with others. Either way, the final ensemble is referred to as a battery [51].

Based on their operation principle, electrochemical cells are classed as follows [51]:

1. Electrolytic cell
2. Galvanic or Voltaic cell
3. Primary cell
4. Secondary cell
5. Fuel cell
6. Half cell

The chemical reactions, the design, as well as the structural components all influence the sorts of electrochemical storage systems that are currently available. This represents the enormous variety of applications that may be used [2].

2.2 Electrochemical Devices

Two of the most essential fields that have received great attention from research communities are energy harvesting and storage. The reliance on fossil fuels confines the energy-generating process to one single domain, thus immediate actions should be taken to enable the pursuit of various promising energy harvesting and generation choices. In this regard, renewable energy sources are being increasingly popular in the last few decades, and breakthrough technologies have been developed to improve the efficiency in energy carrier generation, transmission, and distribution among domestic and industrial consumers [52].

Electrochemical energy production has been considered as an alternative energy source, as long as it is used in a sustainable and environmentally friendly way. Fields like energy management, storage and conservation, the controlling of pollution, and the reduction of greenhouse gases all need eco-friendly types of technology, like electrochemical sources. Numerous electrochemical energy technologies have been studied during the past years. The research around these systems continues to optimize their cost, longevity, and performance, resulting in their growth into existing or new market sectors. Batteries, fuel cells, electrochemical sensors, and electrochemical capacitors are examples of electrochemical energy storage and conversion systems (ECSs) [52].

2.2.1 Fuel Cells

Fuel cells are devices that use fuel as an input and generate electricity as an output (as seen in **Fig. 3**) As long as a fuel cell receives fuel as raw material, it will produce electricity constantly, and this is what differentiates fuel cells from batteries. While both fuel cells and batteries rely on electrochemistry to function, a fuel cell is not being used up during electricity generation [3].

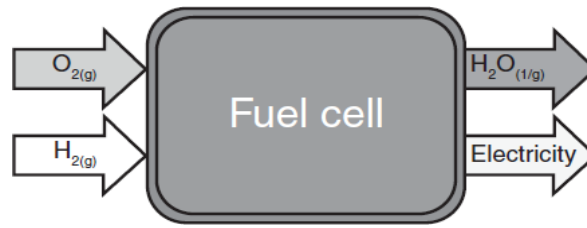


Figure 3: General concept of an (H₂ – O₂) fuel cell [3].

A Simple Fuel Cell

A fuel cell consists of two electrodes, the anode and the cathode, and between them, a polymer membrane is found, called the electrolyte. For the electrons to flow there is also an external circuit, i.e. a wire. The anode catalyst splits the fuel, which is usually hydrogen, into one positively charged ion (H⁺) and one negatively charged electron (e⁻). This splitting process is called oxidation [3].



The electrolyte is a material designed to allow ions to travel through it but not electrons. Therefore, the positively charged ions (H⁺) flow through the electrolyte to the other side, the cathode. The electrons (e⁻), on the other hand, flow via an external circuit, producing an electric current, and finally reach the cathode too. There, they reunite with the hydrogen ions and react with a third chemical element to form water. Usually, the catalyst is made from platinum powder, the fuel is hydrogen and the third chemical at the cathode is oxygen. This reaction is called reduction and is performed by the cathode catalyst (often nickel) [3]. **Fig. 4** shows a model of a direct-methanol fuel cell.

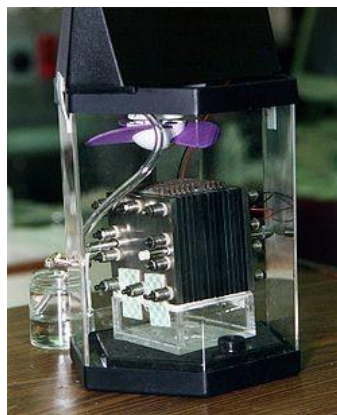


Figure 4: Demonstration model of a direct-methanol fuel cell (black layered cube) in its enclosure [4].

A simple H₂ – O₂ fuel cell is illustrated in **Fig. 5** [3]. Its main components are:

- 2 platinum electrodes

- Sulfuric acid (an aqueous acid electrolyte), which acts as a “sea” of H^+
- Hydrogen gas as the fuel at the anode
- Oxygen gas at the cathode
- A light bulb as an external circuit

Following the aforementioned process, the light bulb will start to glow, and this fuel cell will generate electricity. The original fuel cell, invented in 1839 by scientist William Grove, was most likely similar to the one described here.

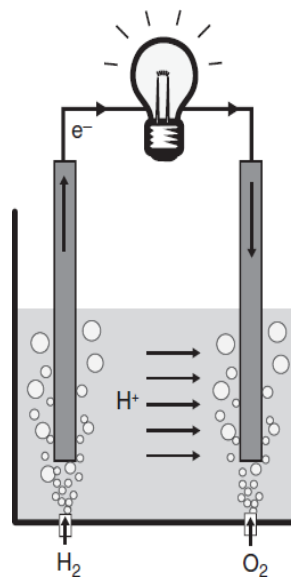


Figure 5: A simple fuel cell [3].

Seven major types of fuel cells are distinguished by their electrolyte [53]:

1. Phosphoric acid fuel cell (PAFC)
2. Polymer electrolyte membrane fuel cell (PEMFC)
3. Alkaline fuel cell (AFC)
4. Molten carbonate fuel cell (MCFC)
5. Solid-oxide fuel cell (SOFC)
6. Direct methanol fuel cell (DMFC)
7. Reversible fuel cell

The PEMFC and SOFC look to be the most well-positioned fuel cell types to deliver on the technology’s promise. The rest of the fuel cell types also have distinct benefits, features and historical importance [54]

Advantages of Fuel Cells

Fuel cells have some similarities to combustion engines and batteries. Both fuel cells and combustion engines generate electricity while being supplied with fuel, while both fuel cells and batteries are electrochemical energy conversion devices that work based on electrochemical principles. Fuel cells, in fact, combine many of the benefits that engines and batteries offer [3].

Fuel cells are frequently significantly more efficient compared to combustion engines, since they generate electricity that is directly coming from chemical energy with conversion efficiencies of up to 60%. Fuel cells can be entirely solid-state, meaning that they do not have moving parts and, therefore, they operate quietly. As a result, they are very reliable and long-lasting systems. In addition, fuel cells emit fewer emissions than combustion engines or no emissions at all. Unwanted products including NO_x , SO_x , and particle emissions are essentially non-existent. Since hydrogen fuel cells produce only water and zero carbon dioxide, they can serve in resolving critical environmental problems. During their operation, no smog- or health-causing pollutants are produced [3].

Fuel cells, unlike batteries, allow for independent scaling of power (which is defined by the size of the fuel cell) and capacity (which is determined by the size of the fuel reservoir). Fuel cells operate efficiently for a wide range of applications from 1-W (i.e., cellphones) to megawatt level (i.e., power plants), whereas batteries perform poorly at big sizes. Fuel cells have the potential to offer higher energy densities compared to batteries and can be recharged fast by refueling. On the contrary, batteries must be discarded or plugged in for a lengthy recharge [3].

Applications of Fuel Cells

Fuel cells are being used in a wide range of applications. They can serve as power sources in the transportation sector, in industrial or residential structures, and even in long-term grid energy storage applications [53,55].

1. Transportation

- Automobiles

Hydrogen fuel cell vehicles (FCVs) convert hydrogen into electricity. As a result, fuel cell vehicles that work with pure hydrogen do not emit dangerous air pollutants or greenhouse gases (GHGs), only heat and water. They may also minimize our reliance on foreign oil because hydrogen can be produced domestically [56]. For the time being, hydrogen automobiles offer a longer distance range than pure electric cars [57].

- Buses

As governments set more rigorous laws and restrictions on internal combustion engines, fuel cell buses are becoming the ideal option for transit operators wishing to shift their fleets to lower emissions. In comparison to natural gas or diesel buses, fuel cell buses offer a 39-141% higher fuel economy [55].

- Trucks

The trucking industry is a big contributor to greenhouse gas (GHG) emissions and air quality problems all around the world. Trucks account only for around 10% of all vehicles on the road, but they are responsible for almost half of carbon emissions, approximately 40%. It is advantageous to equip electric trucks with fuel cells since this green technology enables trucks to travel long distances with short refueling time [55].

- Trains

Fuel cell trains eliminate smokestack emissions without using overhead catenary infrastructure. Hydrogen FC trains have been used in Germany and in the next five years, further types of hydrogen FC trains are expected to be found in the UK, Italy, Japan, France, South Korea, and the US [55].

- Planes

Various experimental projects, including as the Pathfinder [58] and Helios [59] prototypes, have looked into the use of hydrogen FCs in the aerospace industry. These long-range unmanned vehicles use a hybrid system consisting of hydrogen FCs recharged by solar panels, allowing for endless flights, theoretically [60,4].

- Boats and Submarines

Hydrogen-powered fuel cells have been integrated into a range of naval applications. Using solar panels or wind turbines, certain boats, such as the Energy Observer [60], generate their own hydrogen for fuel cell systems. Hydrogen fuel cells provide an alternative to nuclear power for military stealth submarines such as the German Type 212 [4], offering longer range, silence, and lower exhaust heat.

Various applications of fuel cells in transportation are depicted in **Fig. 6**.

2. Backup Power Generation

Stationary fuel cells are used in uninterruptible power supply (UPS) systems at a local level, where continuous uptime is crucial [60,4,61]. In order to meet their uninterruptible power supply

requirements, data centers and hospitals are turning more and more to hydrogen. Microsoft recently announced a successful test of its new hydrogen backup generators, which involved powering the servers of a data center for two days using just hydrogen [62].



Figure 6: Fuel Cell Applications: (1) 2021 Toyota Mirai [5]; (2) Electric Hydrogen Fuel Cell Bus [6]; Helios prototype, an unmanned aerial vehicle [7]; (4) The Energy Observer, the first vessel autonomous in energy [8].

3. Mobile Power Generation

Hydrogen provides a variety of mobile power generation alternatives [60]. NASA, in fact, produced some of the first hydrogen fuel cells to power space rockets and shuttles [63].

4. Portable Power Applications

Portable fuel cell systems are lightweight devices (under 10 kg) that provide power of less than 5 kW, in order to prolong the time a gadget can be used without being recharged [61]. With a potential annual growth rate of up to 40 percent and a market size of more than \$10 billion, the potential market for smaller FCs is rather substantial, prompting a lot of research into their development. There are two distinct groups within this market: the microfuel cell market, which provides a 1-50 W range, and generators ranging from 1 to 5 kW, designed for large-scale power applications, such as military outposts. [4].

5. Stationary Power Applications

For almost twenty years, FCs have been utilized in stationary applications. Stationary fuel cells can be used as a primary power source. However, they are also commonly used to provide supplemental electricity to off-grid residences. In hybrid power systems, fuel cells can also be combined with batteries, photovoltaics, wind turbines, or capacitors to supply either primary or secondary power [61].

6. Other Applications [4]

- Telecommunication
- Base load power plants
- Distributed generation
- Food preservation
- Breathalyzers

Fuel Cells and the Environment

Fuel cells can be eco-friendly, but their influence on the environment is highly dependent on the context in which they are produced and used. Indeed, this may be their most significant benefit over other energy conversion methods. If not implemented appropriately, FCs may not be much better than the currently existing fossil energy conversion systems. Today, hydrogen is produced on an industrial scale, usually by reforming hydrocarbons like natural gas produced by the gas and oil sector. Carbon dioxide is one of the main by-products of this carbon-intensive manufacturing process, adding to the global atmospheric load. Thus, it is imperative to implement alternative hydrogen production methods. In fact, several green methods already exist or are in development, such as electrolysis, renewable liquid reforming, fermentation, and water splitting [64].

2.2.2 Supercapacitors

Supercapacitors (SCs), also called ultracapacitors (see **Fig. 7**), are high-capacity devices that store electrical energy in an electric field between conducting surfaces [10]. A supercapacitor is the evolution of a conventional electric capacitor [49]. An electric capacitor also plays a role in charge storage and delivery.



Figure 7: Supercapacitors [9].

In contrast with batteries, which are also storing energy devices that will be mentioned later, capacitors do not need chemical reactions in order to store and release energy; These reactions

lead to the degradation of batteries over time, giving them a finite lifespan. But capacitors are different, because they store potential energy electrostatically or, in other words, create a difference in charge. This means they are based on a structure that does not wear out as easily [65].

Capacitors contain two conducting plates (usually formed of metal), the electrodes, and between them an insulator known as the dielectric. Air, mica, oiled paper, porcelain, titanate, and glass, are some of the most common dielectrics. A charging process is started with the application of an external voltage difference across the two plates. Positive charges build on one plate (the positive electrode) while charging, whereas negative charges accumulate on the other plate (the negative electrode). Both charges (positive and negative) stay at their corresponding electrodes after the external voltage difference is removed. The capacitor helps to separate electrical charges in this way. This separation allows the device to store energy and quickly release it. It is essentially capturing static electricity. The capacitor's cell voltage is the voltage difference between the positive and negative electrode. If the original voltage source is removed, the capacitor will keep its charge. A discharging process occurs when these electrodes are linked to a conductive wire with or without a load - the positive and negative charges gradually mix through the wire. The capacitor serves as a charge storage and delivery device in this manner [49].

Unlike batteries, capacitors have a far higher power throughput, which means they can charge and discharge in a much shorter time. Their downside, however, is that they have a low specific energy, which means they are only effective for short bursts of power [49].

This is where supercapacitors enter the scene. Having a capacitance value substantially larger than ordinary capacitors, but at the same time lower voltage restriction, a supercapacitor spans the gap between rechargeable batteries and electrolytic capacitors (**Fig. 8**) [10].

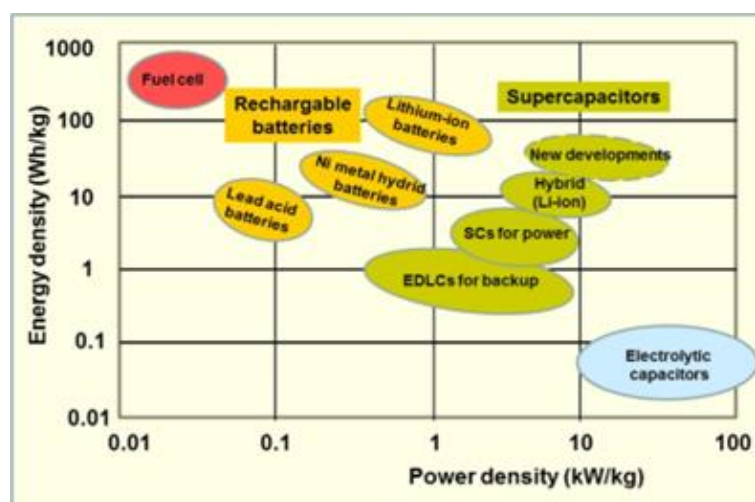


Figure 8: Ragone plot of power density vs. energy density of various capacitors and batteries [10].

The superiority of a supercapacitor over a standard capacitor or even a battery is owed to its high power density. This is regulated by the distance between the metal plates. This can be noticed by the capacitance equation: $C = (\epsilon \times A) / d$, where ϵ = permittivity of free space, A = electrode plate surface areas, d = distance between plates; C increases with increasing surface area and decreasing charge separation distance of the electrodes [11,66].

The distance in a common capacitor is approximately 10 to 100 microns. In a supercapacitor, however, this gap is reduced to one-thousandth of a micron, resulting in a greater electric field and increased energy storage. In addition, the carbon-coated plates of supercapacitors multiply the available surface area for storage by up to a factor of 100,000.

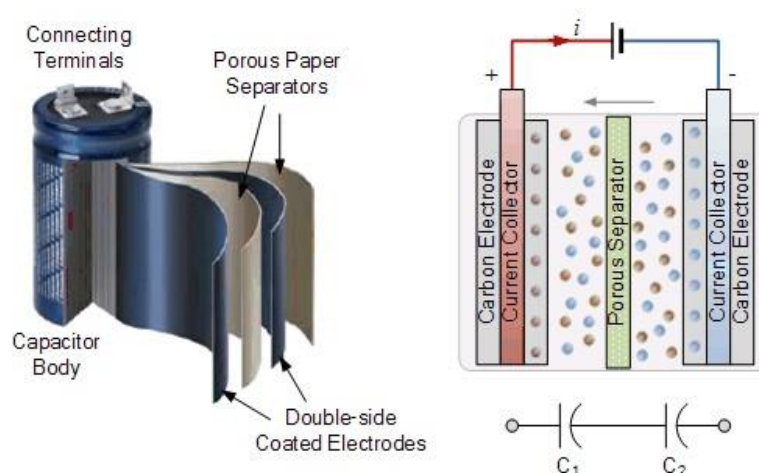


Figure 9: Structure of a supercapacitor [11].

Supercapacitors, unlike regular capacitors, do not use a solid dielectric. Instead, an electrolyte along with a thin insulator, such as cardboard or paper, are used. In addition, a supercapacitor accepts and delivers charge much faster than batteries. The charging and discharging times vary from milliseconds to several minutes. Under different application situations, their operating temperatures range from -20°C to 55°C . One final advantage that supercapacitors present is that they can withstand many more charge and discharge cycles than rechargeable batteries, exceeding 100,000 cycles [67]. **Fig. 9** shows the structure and schematic design of a supercapacitor.

Types of Supercapacitors

Supercapacitors are divided into different types, depending on the way they store energy (**Fig. 10**). There are 3 main categories [10]:

- Double layer electric capacitors (EDLC), with activated carbon electrodes or derivatives with much higher electrostatic double-layer capacitance than electrochemical pseudocapacitance

- Pseudocapacitors, which were designed to further increase energy density, with transition metal oxide or conducting polymer electrodes with a high electrochemical pseudocapacitance
- Hybrid supercapacitors, which are a combination of the two previous ones, with asymmetric electrodes, one of which exhibits mostly electrostatic and the other mostly electrochemical capacitance, such as lithium-ion capacitors

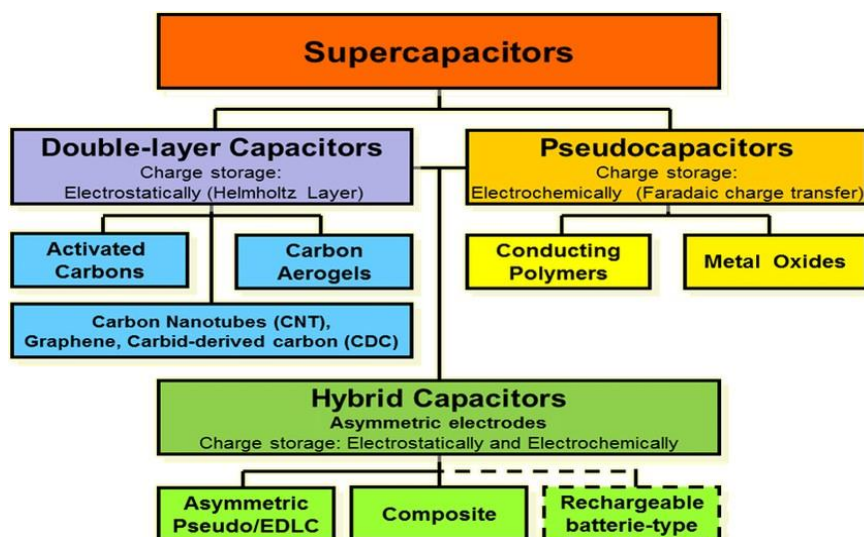


Figure 10: Types of supercapacitors [10].

Unfortunately, even the greatest supercapacitors available today can only store 10 watt-hours per kilogram (Wh/kg), or roughly 5 percent of the energy density of the same-weight lithium-ion battery. However, several experiments conducted using polymer have shown that it can store larger amounts of energy. A 2016 test of a polymer material revealed that it stored 100 times the amount of energy estimated by researchers. After more than one year of research, it was found that the material could eventually store 180Wh/kg, bringing it on par with battery energy density, at least in terms of weight. The polymer-based supercapacitors could be as much as 30% larger in volume than a comparable battery. Still, they would be quicker to charge, cheaper to build, and safer to use [68].

Applications of Supercapacitors

Due to their unique storage capability, supercapacitors have been widely used in a variety of applications. Some of them are shown in **Fig. 11**. Supercapacitors are primarily used in applications that demand quick charge and discharge cycles, like regenerative braking in automobiles, rather than applications that require long-term compact energy storage, such as smartphones and other consumer-grade products [13].



Figure 11: Various Applications using Supercapacitors; (1) Lamborghini built a supercapacitor into its Sián hybrid for a faster, smoother ride [12]; (2) Hybrid Bus in Mumbai, India [13]; (3) Laser gun fitted in a destroyer using supercapacitor [14].

In an electric vehicle, the back emf produced by the motors is used to charge the supercapacitor while braking. In just a few seconds, supercapacitors can be charged. This stored energy is utilized to start the engine, power the vehicle's electrical system, and charge a vehicle's battery [13]. For static random-access memory (SRAM), smaller supercapacitor units are employed as a backup power system. Because of their rapid recharging and a long life cycle, supercapacitors are also used in some consumer-grade applications. MP3 players and the flash for a professional-grade camera are two examples. Wind turbines are another prominent application for supercapacitors. For larger-scale applications, one example is large supercapacitors used to balance the wind's intermittent power supply [69].

Some other supercapacitor application areas also include memory protection, power quality improvement, battery enhancement, high power actuators, adjustable speed drives (ASDs), hybrid electric vehicles, renewable and off-peak energy storage, military and aerospace applications [10].

2.2.3 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 measureable 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 [35].

Chemical sensors are classed as optical, electrochemical, electrical, magnetic, mass-sensitive, and thermal sensors, or sensors based on other physical attributes like radioactivity, depending on the transducer's operating principle. Because of its quick, simple, and sensitive qualities, electrochemistry has superior properties over other measurement technologies. Electrochemical sensors, in particular, are a type of chemical sensor that transforms the effect of an electrochemical interaction that takes place between the analyte and the electrode into an exploitable electric signal (current or potential) [70]. Analytes are the purest compounds in analytical chemistry, the science that uses instruments and methods to separate, identify, and quantify matter.

Modern electrochemical sensors use a number of features to detect chemical, physical, and biological aspects of our daily lives. Environmental monitoring, health and instrumentation sensors, and sensors related to machinery like cars, airplanes, mobile phones, and technology media are some examples. Modern sensing systems have profited from improvements in microelectronics and micro-engineering in recent decades, primarily through the development of smaller sensors with higher sensitivity and selectivity, as well as cheaper production and maintenance costs [35].

Brief History

The usage of electrochemical sensors dates back to the 1950s, when they were first used to monitor industrial oxygen. Labor rules requiring the monitoring of harmful gases and fuels in confined places sparked a rush of research into electrochemical sensors with good selectivity for detecting different gases. The oxygen sensor concept was proposed by Leland C. Clark, who used two electrodes in a cell with an oxygen permeable membrane separating the electrodes and the electrolyte solution. The oxygen in the indicator electrode was lowered as it diffused over the membrane. As a result, the current was proportional to the oxygen concentration in the sample. Clark oxygen sensors were then widely used in medicine, as well as environmental and industrial monitoring. During the Cold War, a different oxygen sensor was created and used in the former Union of Soviet Socialist Republics to measure the quality of water. Despite its commercial success, the Clark oxygen sensors' electric current signal was unstable, and oxygen analyzers required periodic pre-calibration, which limited their use [35].

Structure

The structure of an electrochemical sensor includes the sample (or analyte), a receptor that binds the sample, and the transducer that converts the reaction into a quantifiable electrical signal. In electrochemical sensors, the electrode serves as the transducer [15]. **Fig. 12** depicts a schematic diagram of an electrochemical sensor.

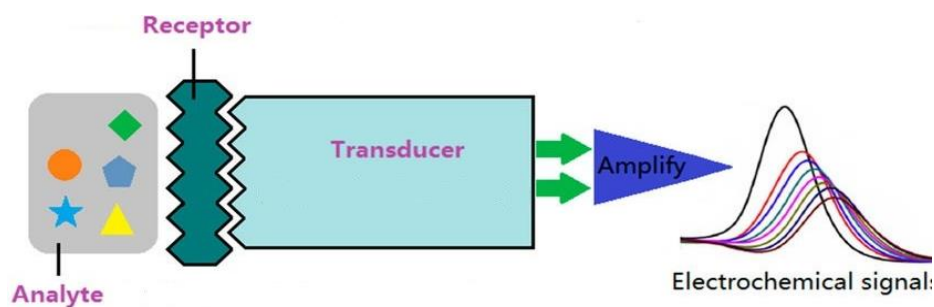


Figure 12: Schematic diagram of the electrochemical sensor [15].

In most electrochemical sensors, the reaction takes place on an electrode surface. The analyte will either be oxidized or reduced by this electrode. The current generated by the reaction is measured and then used to derive essential data such as sample concentrations. A popular electrochemical sensor is the nitric oxide (NO) sensor shown in **Fig. 13** below. Because NO is a potent vasodilator, it's necessary to keep track of its levels while diagnosing cardiovascular problems. Therefore, the nitric oxide sensor monitors the NO oxidation on the surface of the electrode. In several electrochemical sensors, the surface of the electrode can be adjusted with membranes, catalysts, or other metals to increase the electrode's sensitivity or selectivity towards the analyte [15].

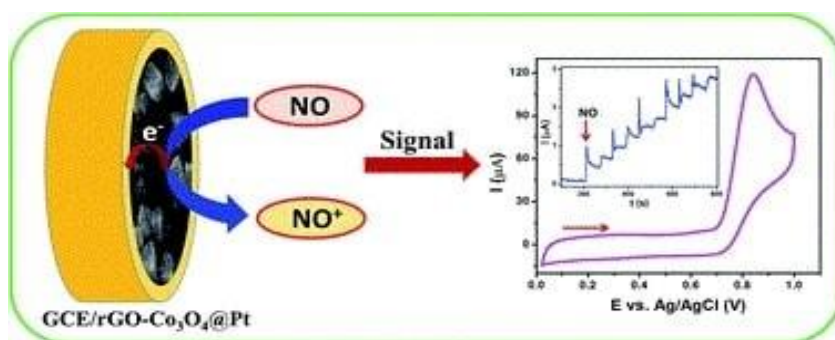
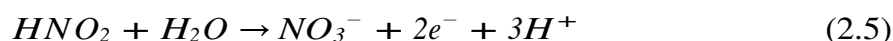


Figure 13: Nitric oxide sensor developed by the Masef research group [15].

The direct electrooxidation of NO in solutions follows a three-step process:



As previously stated, an electrochemical sensor's signal is typically derived from an electrical response in the presence of an analyte. **Table 1** shows some of the most prevalent electrochemical methods and the electrical signals that they monitor.

Table 1: Main Electrochemical Methods, Monitored Electrical Properties, and Respective Units [35].

Electrochemical Methods	Monitored Electrical Properties	Units
Potentiometry	Potential difference (volts)	V
Conductometry	Resistance (ohms)	Ω
Amperometry and voltammetry	Current (amps) as a function of applied potential	I
Coulometry (Q)	Current as function of time (coulombs)	$C = I \times s$
Capacitance (C)	Potential load (farads)	$F = CV^{-1}$

Applications

Electrochemical sensors have been developed and used for a wide range of applications. They can be used as gas sensors for CO detection in houses, heavy metal sensors for water quality studies, and hydrocarbon, alcohol, and ketone sensors for evaluating motor oil degradation. Electrochemical sensors have also been used in the following applications [71]:

- Chemical/Biological Warfare (Homeland Security)
- Food Inspection Medical Diagnostics
- Manufacturing
- Automotive
- Environmental/Home Monitoring

2.2.4 Metal-air Batteries

A metal-air electrochemical cell is an electrochemical cell with an anode constructed of pure metal and a cathode of ambient air, typically with an aqueous or an aprotic electrolyte. Metal-air batteries (MABs) have the unique feature of not storing the active cathode material (i.e., oxygen) in the battery, unlike most other batteries, which carry both the anode and the cathode inside the storage system. Instead, oxygen from the environment can be absorbed and subsequently reduced by catalytic surfaces within the air electrode. This way, the metal-air battery is essentially free of space for the positive electrode active material (just a thin catalyst layer is required) and may contain as much of the negative electrode active material as possible. This illustration is shown in **Fig. 14**.

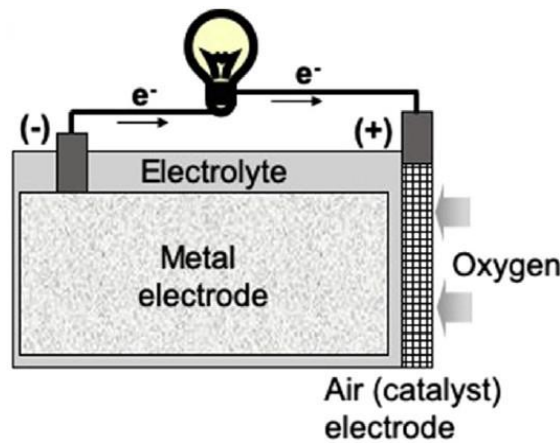


Figure 14: Configurations of metal-air batteries [16].

This is only one of the advantages of using oxygen from the air as the active material for the positive electrode. Furthermore, the active material, oxygen, is lightweight and has a high redox potential (1.23 V vs. RHE), allowing it to provide a large specific capacity (3.35 Ah/g). In addition, oxygen in the air is environmentally friendly, as well as freely available everywhere on the planet, thus reducing the cost of the cathode [16]. MABs are devices with high specific capacity and high energy density. Because of the endless nature of oxygen, the MAB can provide electricity until the negative metal is completely depleted. This advantageous trait has been recognized for a long time and has practical uses as long-lasting power sources, especially as primary batteries. Even while the air electrode in MABs is similar to that in fuel cells, the MAB is essentially a storage battery, whereas the fuel cell is a power producer without the ability for energy storage.

Components of a Metal-air Battery

- Metal Electrode

Because the type of metal used in the negative electrode affects the type of electrolyte, as well as the air electrode design, the MAB structure is heavily influenced by it. These metals should be light, compact, and have great reducing power. They also affect the cost of the battery, because the air electrode is cost-free. Therefore, the metals on the negative electrode should not be too expensive. Lithium, magnesium, aluminum, iron, and zinc are common base metal components utilized for this purpose. Metal hydride (hydrogen as an active material), alloys, organic compounds such as sugar, and other reducing agents can also be employed as negative electrode active materials. Metal oxides, which are basically a mixture of metal and oxygen, are the most common discharge products of typical MABs, as shown in Equation (2.7):



where M is a representation for the metal anode.

Fig. 15 depicts the typical reaction processes in aqueous-based metal-air batteries (see Equation (2.7)), where $M = \text{Zn, Mg, Al, Ca}$ and Fe . A significant attribute is that hydroxide (OH) is the ion carrier moved from the air electrode to the anode, resulting in the accumulation of the reaction products ($\text{M}(\text{OH})_n$) in the anode. The benefit of these batteries lies in the fact that the reaction products do not build up in the air electrode, and therefore prevent additional oxygen diffusion. As a result, a very thin layered carbon-based air electrode (0.2–0.3mm thick) can be used to make electrochemical processes easier in MABs [16].

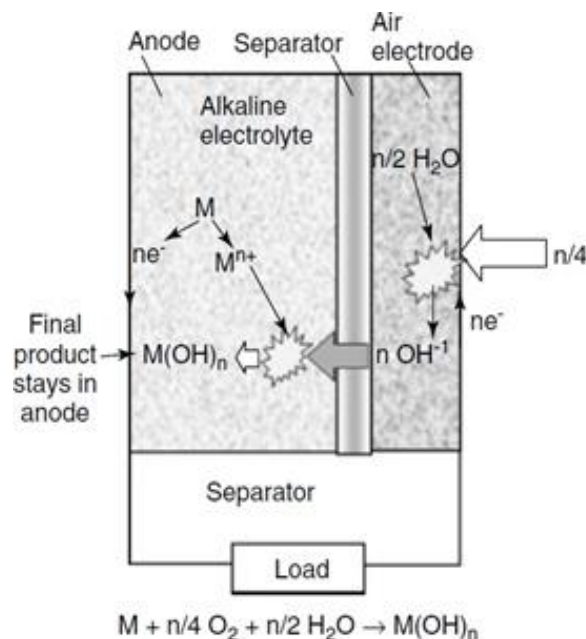
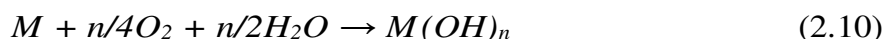


Figure 15: Schematic of reaction processes in metal-air batteries [16].

Metal peroxides/superoxides and metal hydroxides are sometimes generated as discharge products. When the hydroxides develop, water is consumed along with oxygen during discharge. Equation (2.10) describes the typical reaction in a MAB using aqueous-based electrolytes.



where M is used to represent the metal anode. Metals with strong reducing power such as Li, Na, Fe, Zn , etc. can be used as materials for the anode. According to Equation (2.10), the aqueous electrolyte's solvent (water) is also a reactant in these metal-air batteries, and the product from the reaction is metal hydroxide [16].

- Electrolyte

The electrolyte in MABs must have strong ionic conductivity, electrically insulating abilities, and be stable against the negative metal's reducing potential as well as the oxidizing potential of oxygen. Alkaline electrolytes are commonly used in aqueous systems because of their low proton activity, which prevents the hydrogen evolution reaction (HER). The HER can be severe in neutral and acidic aqueous electrolytes because it causes self-discharge, which consumes the negative metal.

Organic electrolytes, inorganic solid electrolytes, polymer electrolytes, and molten salts (ionic liquid) are mostly used and sometimes even a combination of these electrolytes is possible [16].

- Air Electrode

One of the most significant components of metal-air batteries is the air electrode (sometimes called the cathode, while the actual cathode active material in metal-air batteries is oxygen). The air electrode is a film that absorbs and reduces oxygen. Materials that are compact, light, and inexpensive are preferred, but a large electrochemically active area is necessary to provide adequate current density. Long operation life, electrode integrity, and catalytic activity are also critical for the air electrode [2]. To prevent electrolyte leakage, the air electrode must be water- or electrolyte-proof. Carbon is an air electrode substrate with a large surface area, strong electrical conductivity, and controllable wettability. A metal mesh is commonly used to support the carbon substrate while maintaining oxygen permeability and getting appropriate electrical conductivity, as well as mechanical stability [16].

- Catalyst

The catalyst has a substantial influence on the performance of metal-air batteries. The efficiency of the catalyst is also affected by the uniform distribution of the catalyst on the carbon-based air electrode. According to Korovin et al. [72], oxygen-electrode catalysts speed up the adsorption process, which involves either oxygen reduction or hydrogen peroxide decomposition. Platinum metals, silver, oxides (MnO_2 , $\text{NiO} + \text{Li}_2\text{O}$, and Co_2O_3), spinels (NiCo_2O_4 , MnCo_2O_4 , and CoAl_2O_4), and perovskites (LaCoO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) are common catalysts used in metal-air batteries. Platinum metal, unlike its function in fuel cells, is not a very effective catalyst for metal-air batteries, especially when it comes to charging. Silver, on the other hand, has shown high reduction efficiency and stability. Activated carbon, which has a large surface area, is the most cost-effective catalyst. For oxygen reduction in carbon-based air electrodes, manganese dioxide (MnO_2) is the catalyst most commonly used [2].

Types of Metal-air Batteries

- Below are mentioned types of metal-air batteries by anode element [73]:
- Lithium-air batteries
- Sodium-air batteries
- Potassium-air batteries
- Zinc-air batteries
- Calcium-air batteries
- Aluminum-air batteries
- Iron-air batteries

Some applications include electric vehicle and grid backup for lithium-air batteries, miniature hearing aids, grid storage and vehicle propulsion for zinc-air batteries, and marine applications for aluminum-air batteries.

Although a lot of research was carried out on the topic of MABs during the 1960s and early 1970s, efforts in this area decreased significantly in the 1980s due to issues associated with the air electrode, temperature management, and the system's reversibility.

After them, efforts were directed toward another type of battery with higher quality and overall better performance: the lithium-ion battery.

Chapter 3

Lithium-Ion Batteries

3.1 Introduction

The lithium-ion battery (LIB) has revolutionized the energy storage technologies and paved the way for the mobile revolution. It is the fastest-growing battery technology in recent years. This battery type has enhanced our lives due to its high performance and quality, and it is likely to keep doing so in the foreseeable future. Lithium-ion batteries, among other battery technologies, seem the most promising technology, offering a plethora of advantages useful for both small devices, as well as larger applications.

Significant effort has been invested in the construction and development of batteries since Alessandro Volta introduced his famous “voltaic pile” circa 1800 [74], and many scientists after him contributed to this development, as seen in **Fig. 16**.

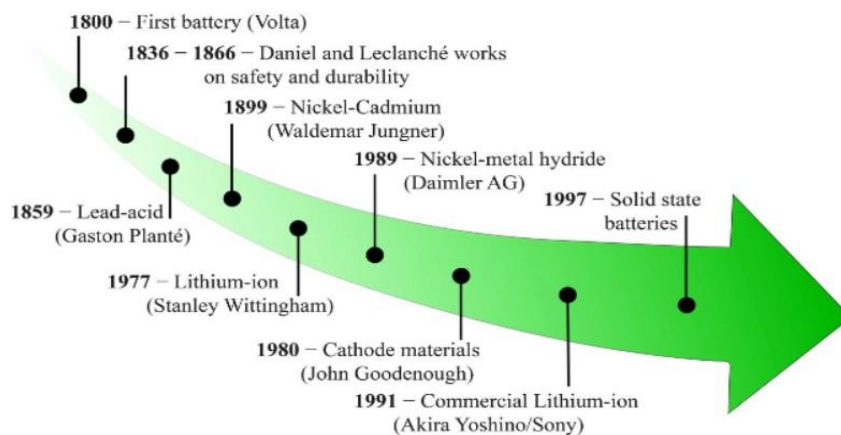


Figure 16: Advances in battery system development over the years [17].

However, battery development is a challenging and complicated task in general, and maybe much more so when dealing with lithium-based cells. As a result, progress has been slow, and only a few efficient battery types have been successfully designed over time [18]. For example, the lead-acid battery is still being used, even though it was invented in the mid-nineteenth century [75].

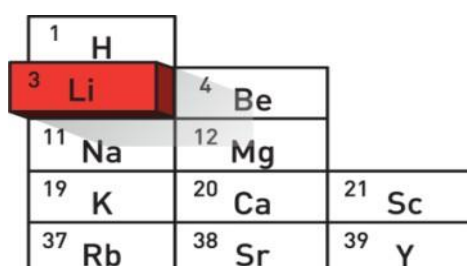
The scientific community in the sector of lithium-ion batteries is currently focusing on the development of new materials with high performance, as well as addressing environmental concerns by developing more sustainable and eco-friendly solutions [17].

3.2. Brief History

Lithium-ion technology is relatively new, having emerged in the late 1900s. Many scientists and engineers from academia, industry, or even independently have contributed to this development. M. S. Whittingham was the first to suggest lithium-ion batteries at Binghamton University in the 1970s. After him, several discoveries in the research of lithium-ion batteries took place by scientists like Rachid Yazami in 1980, Bell Labs in 1981 and Akira Yoshino in 1987 [76]. Goodenough solved the safety issues related to lithium dendrite formation also in the 1980s by developing novel cathode and anode materials, eliminating the usage of lithium metal anodes. Sony produced the first commercial battery in 1991, based on the work of Akira Yoshino. In 2019 Goodenough, Whittingham, and Yoshino were all awarded the Nobel Prize in Chemistry for developing lithium-ion batteries and contributing to the energy storage field [18].

3.3. Lithium

The restricted energy densities and capacities of established batteries stimulated the search for better designs during the mid-twentieth century, and lithium became a target. Lithium, a metal discovered and named by Johan August Arfwedson and Jöns Jakob Berzelius in 1817, was thought to have great qualities to be used as a battery element (see **Fig. 17**). Lithium is the most electropositive metal, with a potential of 3.045 V, a high energy density of 3860 mAh/g, and it is the least dense ($= 0.534 \text{ g} \times \text{cm}^3$) and lightest ($A_r = 6.94 \text{ g/mol}$) metal. This means that lithium carries a greater amount of energy per unit of weight than many other metals. It melts at 180.5 degrees Celsius its specific heat capacity is 3.56 J/g/K at 25 Celsius degrees [77].



1 H		
3 Li	4 Be	
11 Na	12 Mg	
19 K	20 Ca	21 Sc
37 Rb	38 Sr	39 Y

Figure 17: Lithium and the periodic table [18].

Another advantage of lithium for electrochemical energy storage is that it only has one valence electron. Valence electrons are the ones that are “mobile” and may be lost or gained easily, allowing for the creation of ionic bonds with other atoms to form molecules. This makes lithium a highly reactive metal – it even reacts with water and air. All of these qualities combine to make lithium the most distinctive and crucial element for energy storage currently, as seen by its widespread use in batteries.

3.4 Primary and Secondary Batteries

While batteries can be classed according to their sizes, compositions, forms, and purposes [23], they are commonly split into the following groups:

1. Primary Batteries

The most basic definition of primary batteries is that they are designed to be used once and then destroyed. Because they cannot be recharged and used again, these batteries are also known as non-rechargeable batteries. When the supply of reactants in this type of battery is exhausted, the battery stops producing current and is useless. Non-rechargeable batteries are inexpensive and have a run-time of up to 10 years. This feature makes these batteries extremely dependable and long-lasting. They come in a variety of sizes and forms, making them a good fit for a large number of applications. A few basic types of primary batteries are alkaline batteries, lithium batteries and mercury oxide batteries.

2. Secondary/Rechargeable Batteries

Lithium-ion batteries are included in this category. Secondary batteries, also known as rechargeable batteries, are reversible systems that convert their stored chemical energy into electricity. During their discharge phase, this electricity is used to power an external circuit. During charging, the chemical reactions can be easily reversed by applying electric current from an external energy source in the opposite direction. Secondary batteries, unlike primary batteries, can be recharged and reused. These cells are typically used in high-drain appliances or in situations where it would be too expensive or impracticable to utilize other types of cells. Some examples of secondary batteries except LIBs are lead batteries, nickel-cadmium batteries, and nickel-metal hydride batteries. These types of batteries can be found in mobile phones, MP3 players, computers, wristwatches, hearing aids, etc. [78].

3.5 LIBs Advantages

Lithium-ion batteries are finding an expanding variety of applications, resulting in a significant amount of research and development. Their popularity stems from its benefits over other rechargeable batteries, which include:

- High energy and power density

One of the most significant advantages of LIB technology is the high energy density compared to other battery technologies today (**Fig. 18**). This means it contains a great amount of energy compared to its weight, ranging from 100 to 265 Wh/kg. With electronic devices needing to operate

for longer time between charges while still consuming more power, batteries with a considerably higher energy density are always in demand. In addition, its high power density makes it able to deliver high amounts of energy in a short period of time [19].

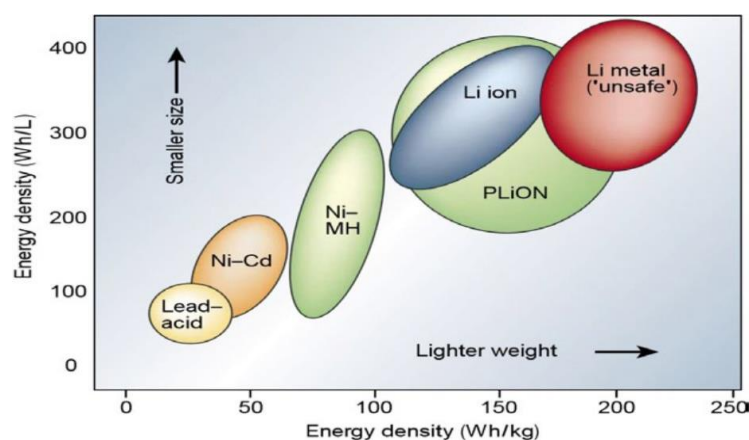


Figure 18: Comparison of energy densities and specific energy of different rechargeable batteries [19].

- Low weight

A direct consequence of the high energy density is that for certain energy requirements, a lithium ion battery is much lighter than similar batteries of another type. Li-ion batteries can be up to 40% lighter than nickel batteries.

- Low self-discharge

The discharge of batteries owing to inactivity is a major issue in battery technology. LIBs, in comparison to other battery types, have a fairly low discharge rate. Feature example is that LIBs lose roughly 5% of their charge every month, whereas NiMH batteries have a corresponding discharge rate of 20%.

- No memory effect

This translates as the ability to charge and discharge the battery many times without reducing its capacity. Also, it is not required to completely discharge and then charge them to avoid crystal formations in the battery, as in nickel type batteries. Therefore, they can be used for hundreds of charge/discharge cycles.

- Low maintenance

A major advantage of LIBs is that they do not need regular maintenance to ensure their quality operation. Other types of batteries need to be periodically discharged to prevent memory effects. Li-ion batteries do not have this problem, so they do not require scheduled active maintenance.

- High cell voltage

One lithium ion cell produces about 3.6 volts of power, a voltage higher than that of ordinary nickel cadmium, nickel metal hydride, or standard alkaline cells, which offer roughly 1.5 volts and lead acid approximately 2 volts per cell. Therefore, LIBs need a smaller number of cells in a lot of battery applications. For example, smartphones only require a single cell, which simplifies power management. Also, they can deliver great amounts of current for high-power applications.

- Long “shelf” life

Another significant benefit of lithium-based systems is their ability to be stored for lengthy periods of time. Hermetically closed components made of non-gaseous systems discharge, protect the element from outside impurities and prevent electrolyte leakage from the cell. This, in combination with the absence of self-discharge reactions or the slow rate at which they occur, enables lithium systems to be stored for 5 - 10 years without the need for a particular storage environment.

- Other advantages that make LIBs one of the most advanced types of battery include their easy production, persistence, and environmental benefits.

3.6. Composition and Operation Principle of LIBs

LIBs are a type of rechargeable (secondary) battery that consists of cells, where lithium ions flow to create electricity. Each cell includes two electrodes, a separator, and an electrolyte, all of which are contained within a shell. The positive electrode is called the cathode and the negative electrode is the anode. The electrolyte is a salt solution between the two electrodes and allows lithium ions to move between the anode and cathode. The electrons are not allowed to pass through the electrolyte, but rather via an external circuit. The separator is a porous membrane soaked in the electrolyte solution that prevents the contact of the two electrodes [79]. A schematic drawing of a cylindrical LIB cell is shown below in **Fig. 19**.

The function of the lithium-ion battery is based on a reduction-oxidation reaction, which occurs from the potential difference between the two electrodes. During discharge, there is an oxidation half-reaction taking place at the anode, which will create lithium ions (H^+) and electrons. The positively charged lithium ions will flow through the electrolyte and the electrons will flow via an external circuit. They will then recombine at the cathode, where a reduction half-reaction will recombine them. During charging, lithium-ion movement is reversed, and ions flow from the cathode towards the anode [79]. In detail:

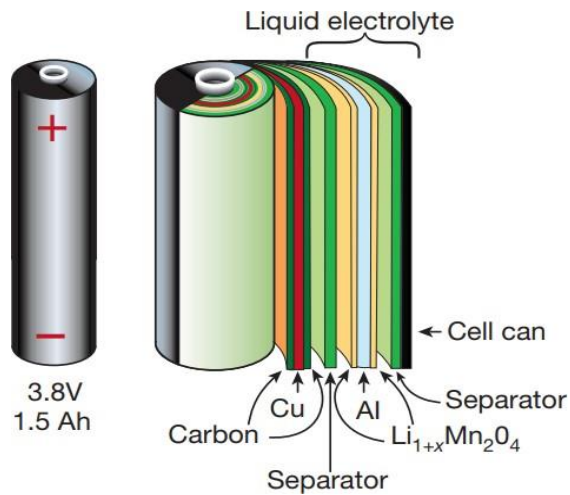


Figure 19: Schematic drawing of a cylindrical lithium-ion battery cell [20].

Charging: When a power source is connected to the two electrodes, it will attract the electrons from the lithium atoms in the cathode, which will flow via the external circuit and reach the anode electrode. In the meantime, the positively charged lithium ions will pass through the electrolyte and also end up in the anode. Once all the lithium atoms reach the anode, the cell is fully charged.

Discharging: During discharging an external circuit (load) is connected to the two electrodes. The lithium-ions will start to flow from the anode to the cathode through the electrolyte, while the electrons will flow to the cathode via the circuit, providing power to the load. This movement creates an electrical current through the load and thus discharges the cell. When all the ions reach the cathode, the battery is fully discharged. A lithium-ion battery cell's discharging process is shown in **Fig. 20**.

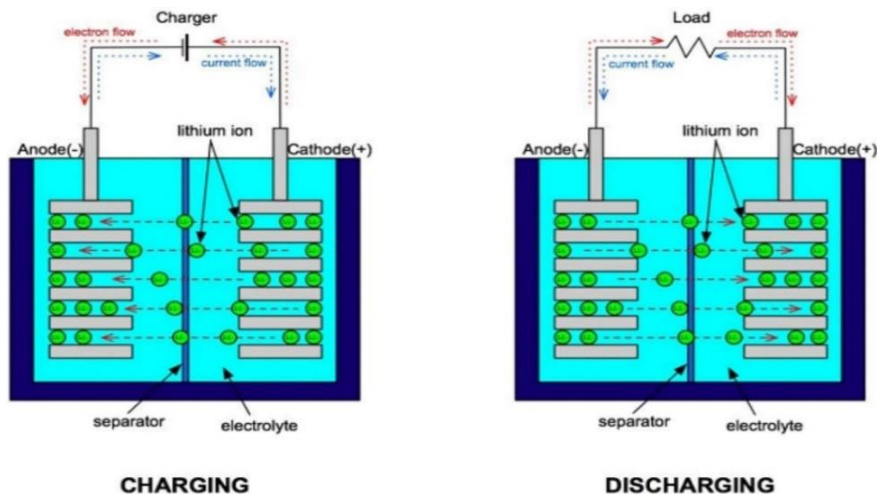
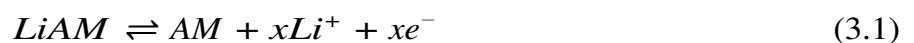


Figure 20: Schematic representation of charging and discharging of a Li-ion battery [21].

The general redox equation occurring inside a lithium-ion battery cell is:



Where AM represents the active material and e^- the electron.

Taking for example a LiCoO_2 battery, the oxidation reaction at the anode is:



While the reduction reaction at the cathode is:



The full reaction being:



3.7 Major Components Individually

1. Shell

The shell of a LIB is often made of stainless steel or nickel-plated steel with single component [80].

2. Current collectors

The electrode materials are supported by current collectors, which ensure that electrons will flow across the external circuit. The current collector should offer great electric conductivity, mechanical and chemical stability, as well as low weight and thickness. Such properties can be provided by copper and aluminum, which are two of the most popular materials for current collectors [77].

3. Electrodes

The active material (AM), the conductive material (CM), and the binder solution (BS) are the three basic elements of any type of electrode [77]. These three ingredients are combined to form a paste that covers one side of the electrode, where the current collector is found. While the active materials used in the anode and cathode, are different, the binder solution is usually common.

• Anode

The negative electrode, the anode, consists of a current collector (usually a thin copper foil) coated with active materials (mostly carbonaceous, such as graphite or silicon-based materials) coated by polyvinylidene fluoride (PVDF) binders [80].

The most common conductive material used in LIBs is carbon black [81]. It keeps the AM particles and the current collector in electrical contact. It also reduces the electrode polarization potential and

increases the cycle life of the battery due to its high electrical conductivity and large surface area.

Between the conductive agent surface and active material particles, a very thin PVDF layer (between 2 and 5%) has formed to provide enough bonds of AMs between particles and the conductive agent. Some of the most common carbon anode materials are graphite, carbon fiber, petroleum coke, pyrolysis carbon, carbon black, mesophase bituminous carbon microsphere (MCMB), and glass carbon. New anode AMs are being developed to increase the storage capacity of LIBs [80]; however, graphite remains the most common anode AM in commercial LIBs and therefore studies are putting great effort on improving the properties of graphite [82,83, 84].

- Cathode

The positive electrode, the cathode, has a similar structure to that of the anode. It mainly includes an aluminum foil coated with AMs containing Li, conducting agents, organic solvents, and binders, such as PVDF, uniformly coating both sides of the aluminum foil collector.

Some of the most popular cathode active materials are LiCoO_2 , LiMn_2O_4 , LiNiCoMnO_2 , LiFePO_4 , LiNiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiNiCoAlO_2 [80]. Increased AMs concentrations at the cathode, result in increased battery capacity [85]. As a result, typical cathode compositions comprise active material fractions ranging from 60 to 95%, CM between 2 and 25%, and BS between 3 and 30% [85].

Due to its high energy density, easy manufacturing, and persistence, the LiCoO_2 battery type has been widely employed in applications, such as mobile phones, laptops, digital cameras, watches, communications equipment, etc. [86, 87, 88]. Commercial LIBs usually include 90% LiCoO_2 , 8% conductive agent and 4% PVDF binder. The AMs of the cathode are coated on the sides of the aluminum foil by the PVDF binder [80].

4. Separator

The separator is a polymeric porous membrane between the electrodes that prevents them from shorting out. It is often soaked in an electrolyte solution that enhances the ionic conductivity of the structure. The separator's performance determines the battery's interface structure and internal resistance, and both these attributes have a direct impact on the capacity, cycle, and safety performance of the battery. The separator must meet the following specifications: a) high ionic conductivity, b) excellent wettability, c) uniform porous structure with porosity >50% and pore size <1micron, d) good chemical stability, e) low thickness (<25 μm), f) low electric conductivity, and g) limited shrinkage [89]. A high-performance separator serves a critical role in enhancing the battery's overall performance.

The separator is usually constructed from plastic, such as polypropylene (PP), polycarbonate (PC), and polyethylene (PE), with a membrane structure. These separators have a cost-effective pore structure, outstanding mechanical stability, and good overheat prevention features [90]. Biopolymers and materials like cellulose [91] and silk [92], as well as recycled polymers, are being studied as more environmentally friendly separators that do not need to use synthetic polymers.

5. Electrolyte

The electrolyte in a lithium-ion battery transfers charge between the two electrodes, the cathode and the anode, and is crucial for the battery's specific capacity, cycle efficiency, operating temperature range, and safety performance [80]. As a result, the optimal electrolyte must have low viscosity, great wettability for the separator and electrodes, a high flash point, and, most importantly, high ionic conductivity [93]. The choosing of electrolyte solution is determined by the final application [94], but it must also be compatible with the materials of the electrode and the fabrication process.

It is made up mostly of high-purity organic solvents and electrolyte lithium salts. Liquid electrolytes, colloidal electrolytes, polymer electrolytes, and ceramic electrolytes are the four types of electrolytes now used in lithium-ion batteries [80]. The most common liquid electrolyte is a liquid in which a lithium salt is dissolved in an organic solvent. Some lithium salts are LiPF_6 , LiBF_4 , LiCF_3SO_3 , $\text{Li}(\text{SO}_2\text{CF}_3)_2$ [95], LiAsF_6 , and N-methyl-2-pyrrolidone (NMP), whereas some solvents are dimethyl carbonate (DMC), diethyl carbonate (DEC), vinyl carbonate (EC), methyl ethyl carbonate (EMC), and γ -butyrolactone (BL). Propylene carbonate (PC), vinyl carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and methyl ethyl carbonate (EMC) are the most popular organic solvents used in commercial batteries [95, 96].

3.8 Most Common Types of LIBs and their Applications

Lithium-ion cells are named after the chemical composition of their cathode material. State-of-the-art cathode materials include lithium metal oxides, vanadium oxides, olivines and refillable lithium oxides. Lithium metal oxide structures include cobalt, manganese, and nickel metals. The presence and proportion of these metals vary according to the type of battery and where it is used. The most popular LIB types are LiCoO_2 , LiMn_2O_4 , LiNiCoMnO_2 , LiFePO_4 and LiNiCoAlO_2 .

- **LCO:** This is a term used to represent the lithium cobalt oxide battery. Lithium cobalt oxide is one of the most common lithium-ions and its chemical symbol is LiCoO_2 . Cobalt is the core active material (around 60%) of this battery, which is also referred to as Li-cobalt. This type of battery

includes a cobalt oxide cathode and a graphite carbon anode. This type is being used since 1991 and its characteristics include very high energy density and a long runtime, but limited specific power. It is mostly used in small scale electronics, such as mobile phones, tablets, laptops and cameras [97].

- **LMO:** The LMO battery with the chemical formula LiMn_2O_4 is a lithium-ion cell with a cathode made of manganese dioxide (MnO_2) and a graphite anode. Manganese-oxide-based cathodes are abundant on the planet, affordable, non-toxic, and offer high power and improved thermal stability. These batteries have emerged since 1996 and historically they have been used in electric vehicles (the LMO provides high current boost on acceleration) but nowadays they are mostly used in medical equipment, power tools, electric bicycles, etc. [98]. They are safe, provide high power, but have less capacity than LCO batteries.

- **NCM:** This abbreviation stands for LiNiCoMnO_2 , which means this battery consists of lithium, nickel, manganese, and cobalt oxides. The success of NMC can be attributed to the combining of nickel and manganese. Manganese has the advantage of developing a spinel structure to achieve low internal resistance but has a low specific energy. Nickel has a high specific energy but is unstable. Metals that are mixed together enhance the performance of each other. This type offers very high energy storage density, high power and higher cycle life in comparison with other cathode materials. It is used in electrical equipment, medical devices, electric bikes, etc.

- **LFP:** LFP is short for lithium iron phosphate battery (LiFePO_4). This type has been used since 1996; it has a very flat voltage discharge curve, but also low capacity capabilities. It is one of the safest lithium-ions. In addition, traits such as its low cost, low toxicity, long cycle life among other factors make them useful for EVs, backup power and portable and stationary applications needing high load currents and endurance [100].

- **NCA:** NCA stands for lithium nickel cobalt aluminum oxide (LiNiCoAlO_2) batteries, which were firstly used in 1999. The most important advantages of this battery are their high specific energy, high capacity and voltage, and long lifespan. Their application areas mainly involve EVs and e-bikes and are also found in batteries for electronic devices, mainly by Panasonic, Sony and Samsung [101].

In **Fig.21** several of the attributes of LIB different types are compared. Further of their properties are summarized in **Table 2**.

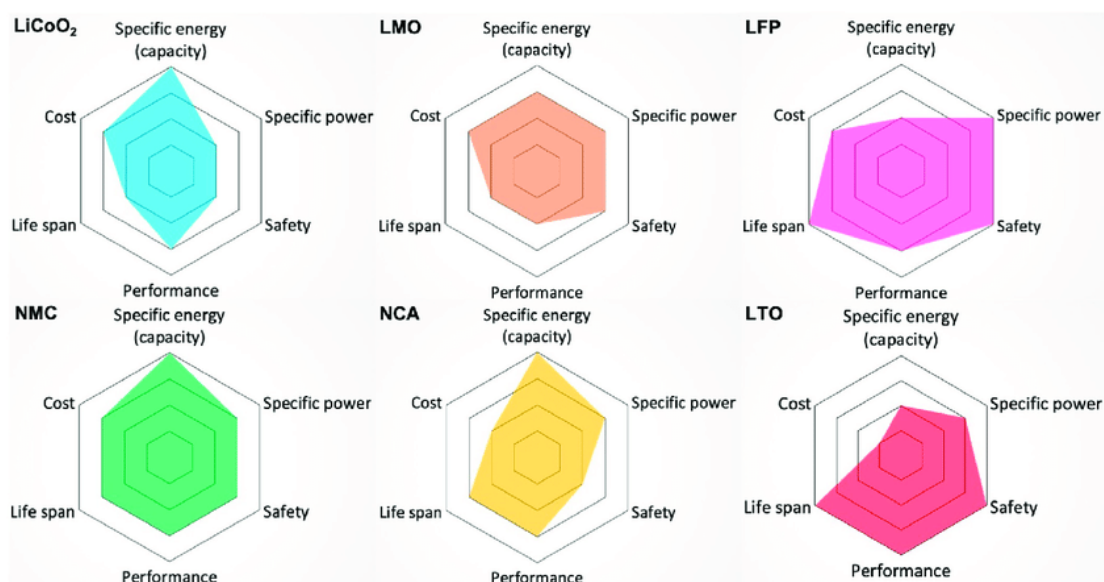


Figure 21: Comparisons of different types of Li-ion batteries used in EVs from the following perspectives: specific energy (capacity), specific power, safety, performance, life span, and cost (the outer hexagon is most desirable) [100].

Table 2: Development progress and estimated market share of popular cathode materials [36].

Chemical Formula	Cathode Types	Li / wt%	Voltage / V	Cycle	Developed year	Estimated marketshare 2018/%
LiCoO ₂	LCO	7.09	3.8	500-1000	1991	37.2
LiMn ₂ O ₄	LMO	3.84	3.3	300-700	1997	21.4
LiNiCoMnO ₂	NCM	7.20	3.7	1000-2000	2001	29.0
LiFePO ₄	LFP	4.40			2003	5.2
LiNiCoAlO ₂	NCA	7.20	3.6	500	2009	

Currently, 80% of LIBs are used in small electronics, with electric vehicles (EVs) and ESS applications accounting for less than 20%. Some other applications of lithium-ion batteries also include UPS, marine vehicles, solar energy storage, grid level energy storage systems [102], military applications, medical instrument power supplies, and even aerospace applications [76, 103].

3.9. Recent Advances on Materials for Lithium-ion Batteries

The constantly developing field of lithium-ion batteries requires the systematic comparative collection of the most recent advances in battery technology, in order to meet the ever-increasing number of components, methods, and battery performance data, and thus enabling progress in the area. As a result, in attempt to optimize LIB systems, this section focuses on several materials that have recently been created for the different batteryparts - the current collectors, the electrodes, the separator and the electrolyte.

3.9.1 Current Collectors

To optimize the current collector properties, for example the electric conductivity and the surface chemistry, surface treatments such as plasma treatment [104] and coatings such as carbon [105] and vanadium oxide [106] can be applied.

3.9.2. Electrodes

As previously mentioned, the component that differentiates the anode and the cathode is the active materials. As a result, below are presented some recent advancement regarding the active materials for each type of electrode.

These advancements are proposed as potential solutions to issues that emerge and reduce the electrode's overall performance and durability. Some of these issues include volume expansion during charging and discharging, mechanical failure caused by external mechanical or thermal loadings, thermal failure due to battery overheating, and limitations on tortuosity/percolation.

Active Anode Materials

The main anode's AMs are carbonaceous materials, alloys containing Si, Al, Sn, Ge, Ga, Sb, Pb and metal oxides, etc. Carbonaceous materials, such as graphite or carbon nanotubes, are the most popular active anode materials, because of their low cost, reversibility, low volume variation and high number of charge/discharge cycles. However, these materials alone face some difficulties. For example, one disadvantage of using graphite as an anode material is the formation of the solid electrolyte interface (SEI) layer. Newer technologies are studied every day, in order to solve such issues and improve the anode's performance [17].

1. Carbon-based anode materials

Although graphite is frequently used in anode electrodes, graphite intercalation compounds (GICs) have been used to enhance their energy density and thereby improve electrochemical performance. The molten-salt method was used to synthesize advanced anode materials based on cobalt chloride–ferric chloride–graphite bi-intercalation compounds ($\text{CoCl}_2\text{-FeCl}_3\text{-GICs}$), which showed a high capacity of $1033 \text{ mAh}\cdot\text{g}^{-1}$, a retention rate of 94.2 percent at $200 \text{ mA}\cdot\text{g}^{-1}$, and a charge capacity of $536 \text{ mAh}\cdot\text{g}^{-1}$ after 350 cycles under $1000 \text{ mA}\cdot\text{g}^{-1}$ [108]. Vertical graphene sheets (VGS)/graphite is another carbon material developed with high specific capacity to improve the graphite's intrinsic electrical conductivity [109]. Their electrochemical performances are shown in **Fig.22 (a), (b) and (c)** respectively.

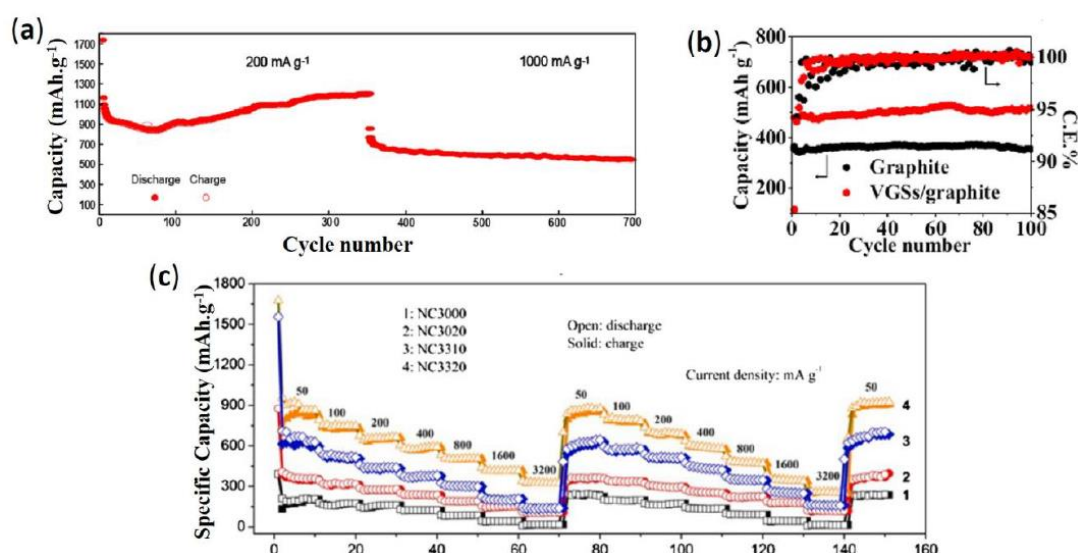


Figure 22: (a) Long-term cycling performance of $\text{CoCl}_2\text{-FeCl}_3\text{-GICs}$ at 200 and 1000 mA g^{-1} [108]. (b) Cycling curves of graphite and vertical graphene sheets (VGs)/graphite at 0.2 C [109].

2. Metal alloys-based anode materials

These perform well under volume changes during lithiation. For instance, the Li-Sb-Sn system using metal alloys anode active materials can contain 15% more Li without altering their crystal structure [108].

3. Silicon-based materials

These materials have more than 10 times higher specific capacity than graphite [109]. However, they present problems such as large changes in volume and unstable SEI formation. To solve these difficulties, advances on the silicon-based anode materials have been developed. Examples include combining silicon nanostructures with carbon structures, such as coral-like porous Si/C (CLP-Si/C), which has stable capacity of $990.6 \text{ mAh}\cdot\text{g}^{-1}$ and can be kept at a stable rate of $250 \text{ mA}\cdot\text{g}^{-1}$ after 100 cycles [110]. Another example is using amorphous carbon cascade-coated nano-silicon materials for anodes, which have high reversible capacity of $874.5 \text{ mAh}\cdot\text{g}^{-1}$ after 300 cycles and high initial coulombic efficiency (ICE), around 89% [1]. Other examples include Si/carbon nanotube microspheres (Si/CNTsS) from chemical vapor deposition [112], silicon/carbon composites by mixing hydrocarbon resin [113], Si powder, polyacrylic acid, etc.

4. Conversion-type Transition-Metals and their Compositd-Based Anode Active Materials

These materials are inexpensive and offer high theoretical capacities and easy availability. Research for these materials is focused on developing new compositions to improve their electrical conductivity. Iron oxide (Fe_2O_3) is a popular transition metal oxide due to its large reserves and low cost [114]. Several approaches have been applied to enhance its performance, such as in situ encapsulation of Fe_2O_3 nanoparticles into micro-sized ZnFe_2O_4 capsules [115], a new synthesis

method based on chemical precipitation with tin ore tailings sulfuric acid leaching liquor as a Fe source [116], and a new material based on Rosa roxburghii-like hierarchical hollow sandwich-structure C@Fe₂O₃@C microspheres. Furthermore, in situ Co₃O₄/Co nanocomposites were synthesized to enhance SEI performances [117]. Other examples also include mixed Co/Mn vanadate for improved performance and low cost [118], as well as TiO₂/carbon composite-fiber anodes, which improve stability and specific capacity [119].

Active Cathode Materials

The optimization of particle size, geometry, specialized functionalization, doping with different elements, and building composites with diverse particles and coatings are all recent breakthroughs in the development of cathode active materials.

All these optimization methods are aiming to improve electrical and thermal properties, as well as stabilizing the particle in relation to the electrolyte, optimizing synthesis processes (such as sol-gel synthesis and co-precipitation), and improving mechanochemical activation [17]. For instance:

- LiCoO₂ (LCO), used in batteries for laptops, smartphones, watches, etc., is one of the most popular active materials for cathode. However, during high voltage its structure is not stable and as a solution Li₃NbO₄ and Co₃O₄ layers are coated on the surface [116]. Also, doping with transition metal ions improves its electrochemical properties [117].
- LiFePO₄ (LFP) is an active material used in batteries for electric vehicles. To enhance its performance, a carbon coating with biomass of phytic acid has been used to replace the traditional phosphoric acid [118], among other doping materials.
- LiMn₂O₄ (LMO) is also a popular active metal, but shows poor cycling behavior. To solve this, doping with Cu, Ni and Co through sol-gel synthesis has been tested and showed satisfying results [119].

Other examples include: a new synthesis of LiFe_{0.25}Mn_{0.75}PO₄/C@reduced graphene oxide (rGO) [120], the ZnO surface coating of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) [121], materials based on single crystal LiNi_{0.83}Co_{0.10}Mn_{0.07}O₂ (SC-NCM) [122] and Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ doped with carbon [123].

Hybrid structures are also being researched, with materials like MXenes and MOFs being used to improve the electrode's efficiency, with a focus on enhancing cycle behavior. Future advancements in this area include research into cobalt-free active materials, which will allow for lower battery costs because cobalt is a scarce and expensive component. These improvements are aimed at improving the electrical and thermal characteristics, as well as improving mechanochemical activation [17].

3.9.3 Separator

Among the advances in the field of separators, focus is given on the creation of new porous membranes based on ecofriendly materials, enhancing thermal and safety qualities, increasing the wettability of polyolefin polymers, and suppressing dendrite growth. The latest developments in separator materials are summarized in **Table 3** and **Table 4**.

Table 3: Recent advances in Li-ion battery separators based on different materials with main properties, goals, and achievements for improving separator characteristics [17].

Materials	Electrolyte Solution	Porosity and Uptake (%)	Conductivity ($\text{mS}\cdot\text{cm}^{-1}$) and Capacity ($\text{mAh}\cdot\text{g}^{-1}$)	Main Goal/Achievement
Polyimide (PI) with poly(amic acid) (PAA)	1.0 M LiPF_6 (ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by weight)) with 5% of fluoroethylene carbonate (FEC)	89.1/-	1.79/1.930 mAh	Improved mechanical strength
Polyimide (PI)	1.0 M LiPF_6 (EC/dimethyl carbonate (DMC) (1:1 in vol.))	-/-	-/-	Improved thermal stability
PE with phenolic resin (AF)	1 mol L^{-1} LiPF_6 (DMC/EC (1:1 in vol.))	57/228	0.6/119	Improved thermal stability and electrochemical properties
Untreated $\text{Al}_2\text{O}_3/\text{PE}$	1.0 M LiPF_6 (EC/DEC (1:1 by weight)) with 5% of Fluoroethylene carbonate (FEC)	-/-	0.39/140@0.2C	Good wettability, high thermal stability, and good electrochemical performance
Polyethyleneimine (PEI)/dopamine coating layer in PP separator.	1.0 M LiPF_6 (EC/DMC (1:1 in vol.))	-/144	0.58/128	High electrolyte uptake
PVDF containing titanium dioxide (TiO_2) and graphene oxide (GO)	Commercial electrolyte based LiPF_6	86.50/494	4.87/-	High electrolyte uptake
Polyimide (PI) with ZSM-5 zeolite filler	1.0 M LiPF_6 (EC/DMC (1:1 in vol.))	61/260	1.04/133@2C	Enhanced wettability and electrolyte uptake
Poly(aryl ether sulfone) (PES) and poly(vinylidene fluoride) (PVDF)	1.0 M LiPF_6 (EC/ethylmethyl carbonate (EMC)/DMC (1:1:1 in vol.))	-/595	1.69/162.8	Enhanced wettability and high ionic conductivity
Poly(vinylidene fluoride)hexafluoropropyl-ene (PVDF-HFP)/poly(mphenyleneisophthalamide (PMIA)	1.0 M LiPF_6 (EC/DEC/EMC (1:1:1 in vol.))	94.28/~900	-/-	Good electrolyte affinity and enhanced interfacial compatibility

Table 4: Continued [17].

Materials	Electrolyte Solution	Porosity and Uptake (%)	Conductivity ($\text{mS}\cdot\text{cm}^{-1}$) and Capacity ($\text{mAh}\cdot\text{g}^{-1}$)	Main Goal/Achievement
PE with ammonium persulfate (APS) coating	1.0 M LiPF_6 (EC/EMC (3:7 in vol.)) with 2 wt % vinylene carbonate as an additive	-/-	0.36/~170	High lithium-ion migration and ionic conductivity
PVDF/13X zeolite particles	1.0 M LiPF_6 (EC/DEC/DMC (1:1:1 in vol.))	76/475	~1/144.14	Excellent ionic conductivity
PAN@PVdF-HFP	-	-/-	1.2/170@0.1C	Excellent cycling performance, good rate capability
PE with controllable polyamine (PAI) layer	1.0 M LiPF_6 carbonate solution	60/-	-/-	Enhanced safety
PVDF coated with ZnO	-	85.1/352	2.3/148@1C	High safety in high temperature.
Thin layer of low-density polyethylene microspheres onto a commercial porous PP	1.0 M LiPF_6 (EC/DMC/EMC (1:1:1 in vol.))	-/-	0.30/158	Rapid thermal shutdown at elevated temperature ($\approx 110^\circ\text{C}$)
Aramid nanofiber/bacterial cellulose	1.0 M LiPF_6 (EC/DMC/DEC (1:1:1 in vol.))	83.9/-	12.54/157	Excellent tensile strength and ionic conductivity.
Poly (L-lactic acid) (PLLA)	1.0 M LiPF_6 (EC/DMC (1:1 in vol.))	$\approx 72/350$	1.6/93@1C	Environmentally friendly separator
Cellulose/PVDF-HFP with TiO_2	1.0 M LiPF_6 (EC/DMC (1:1 in vol.))	86/403	1.68/103.8@8C	Excellent thermal stability and high ion conductivity
Silk fibroin	1.0 M LiPF_6 (EC/DMC (1:1 in vol.))	86/350	2.2/131.3 @8C	Environmentally friendly separator

Polyimide (PI) is a polymer commonly used in separators, because of its good thermal stability. Various separators based on polyimide are being developed, including PI nonwovens with diphenyl phosphate (DPhP) as a plasticizer [124], PI with organic montmorillonite (OMMT) [125], and coating of silicon nitride on both sides of polyimide separator [126].

Furthermore, in order to improve electrolyte wettability and thermal stability of the separator-electrolyte system, different substances were used. Some of them include the coating of Al_2O_3 [127] or melamine-based porous organic polymer (POP) [128] on the membrane, polyethylenimine (PEI)/dopamine coating layer [129], a thin layer of low density polyethylene microspheres [130], etc.

To enhance the ionic conduction of the separator, composite separators are extensively used, and different combinations of polymer matrix and specific fillers are being developed. Specifically, separators made of PVDF coated with ZnO have been designed with higher ionic conductivity (2.261 mS/cm) and porosity (85.1%), excellent electrolyte wettability (352%), and lower interfacial impedance (220 Ω) [131].

Future advancements in separator technologies include the creation of more sophisticated and multifunctional membranes, as well as the addition of shutdown capabilities to the separators to increase device safety [130].

3.9.4 Solid Polymer Electrolytes

Solid polymer electrolytes (SPEs) are a solvent-free salt solution in a polymer host that can be considered as solid in the macroscopic scale [132]. They play an important role in the function of solid-state batteries, because they replace the liquid electrolytes from the system, making it safer. However, its development is slow due to several issues, like their poor ionic conductivity and the problematic interfacial interaction of the electrolyte with the electrodes [133, 134]. A high performance SPE in LIBs must require basic properties, such as strong ionic conductivity ($>10^{-4}\text{S/cm}$), interfacial compatibility with the electrodes, high numbers of lithium-ion movement, and excellent mechanical and thermal stability.

A major drawback of the lithium use in batteries is the forming of lithium dendrites [17]. These are metallic microstructures that grow on the negative electrode while the battery is charging. Lithium dendrites are created when extra lithium ions build on the anode surface and cannot be absorbed into the anode in time. This can lead to short circuits, and therefore catastrophic failures or even fires. Many studies have been conducted to address this problem. Some of the solutions

that emerged are the production of a sandwiched PVDF/LLTO by tape casting [135], LLZO nanofibers [136], a 3D cross-linked network formed by a mixture of PEO, GO, and 1-butyl-3-methylimidazolium [Bmim][DCA] and ionic liquids such as Pyr13TFSI [137].

Another strategy to suppress lithium dendrites is the combination of different kinds of polymers. Examples include adding PAN electrospun nanofibers to a blend of PDMS and PEO [138], adding a PEO/LiTFSI solution in an electrospun PVDF nanofiber matrix [139], or developing of a hybrid polymer-in-ceramic composite electrolyte [140].

Frequently, the prevention of lithium dendrites is strongly linked with the improved interfacial contact between the electrodes and the electrolyte. Studies showed that this can be achieved by combining different functional units, as PEG and HDI in one SPE [141], using additive containing solid lithium-ion conductors where lithium salts are combined with polymers such as PS [142] and substituting the conventional lithium salts by LiPCSI [143].

A way to simultaneously solve both the lithium dendrite formation and the interfacial problems is the self-healing capacity in SPEs, which also improves the battery's life cycle. Tests included the addition of lithium nitride as an artificial SEI in the interface between the SPE and Li metal [144], the use of UV copolymerization of polymers [145] and the application of polymeric ionic liquids (PILs).

More traditional approaches include studies in order to increase the performance of the batteries, their cycling stability, and to minimize the operating temperature of an SPE. For example, the production of a PAES-g-PEG polymer blend, using room temperature ionic liquids as fillers leads up to 500 cycles [146]. In order to improve the ionic conductivity the addition of PVDF-HFP to the structure of an ETPTA UV cured polymer and the use of ionic liquids through the inhibition of the polymer crystallization showed satisfying results [147]. Particularly, polymeric ionic liquids (PILs) [148], BaTiO₃ nanoparticles [149], ultrasonic treatments in the PEO matrix [150] and polymer-in-ceramic composites [151] have all been used in studies and proved they can enhance the battery's ionic conductivity. Furthermore, in order to prevent the deterioration of the battery due to the SEI layer, fluoroethylene carbonate and other additions have been considered.

Finally, the need for more sustainable equipment in modern society has also reached the SPE field. Therefore, using environmentally friendly materials, such as natural polymers as a matrix, and avoiding chemical solvents are gaining traction. Some materials that improved ionic conductivity are iota-Carrageenan [152], chitosan combined with a PEG plasticizer [153], pectin, and guar gum [154].

3.10 Geometry of LIBs and Battery System

3.10.1 Geometry

Batteries come in a variety of shapes and sizes, as well as different types of housing [23]. Cylindrical, prismatic hard-case and prismatic pouch cells are the most common (**Fig. 23**).

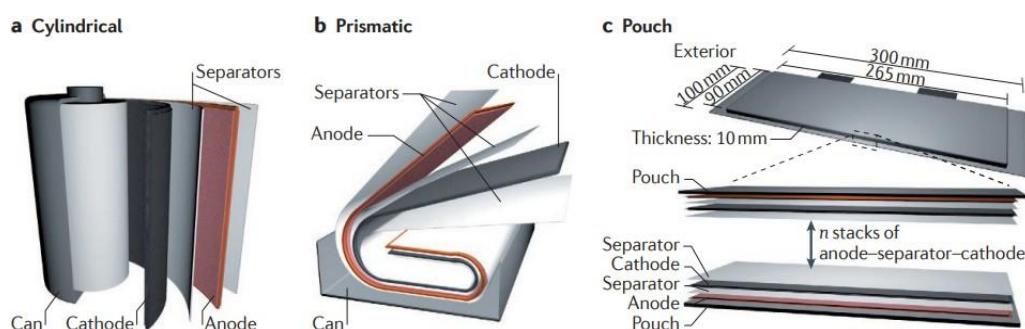


Figure 23: Three representative commercial cell structures. (a)Cylindrical-type cell. (b)Prismatic-type cell. (c)Pouch-type cell. The pouch dimensions are denoted, along with the internal configuration for n-anode-separator-cathode stacks [22].

Pouch cells are composed of prismatic stacks encased in laminated aluminum foil. Hard-case prismatic or cylindrical cells are more rigid than pouch cells. The prismatic cells have a prismatic winding and can be packed closer than pouches because they do not expand during use. The cylindrical ones fit straight into the casing and can be stored close together because of the tight casing and lack of expansion. Because the goal is to get a high energy density, the cells should be arranged near together. To achieve high voltage or capacity, the cells are connected in parallel or serial [36].

3.10.2 Battery System

In larger applications, the entire battery system is made up of cells and modules that are combined with electronics in a battery pack, as seen in **Fig. 24**.

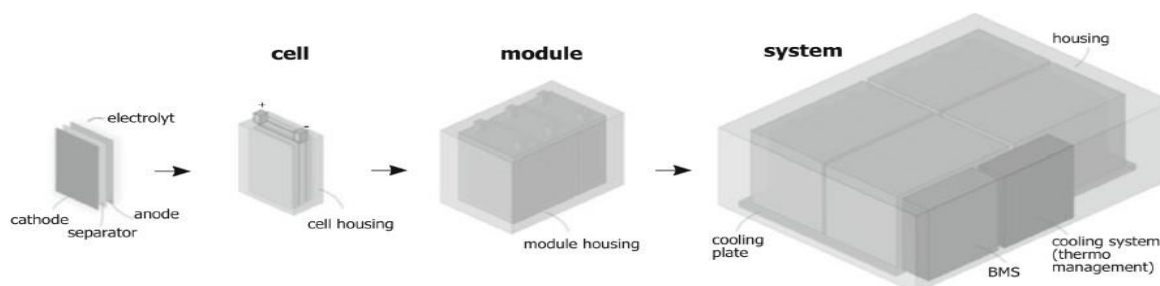





Figure 24: The complete battery system from cell components to pack [23].

The modules are designed using cell characteristics such as capacity, voltage, and current. The modules also include cell holders and current collectors, as well as thermal components, such as cooling tubes, cold plates, and connections. A module also has sensors, electrical connectors, and an enclosure.

The modules are then combined in a battery pack to create a system with power charging and temperature management capabilities. The modules are then combined in a battery pack to create a system with power charging and temperature management capabilities [36].

The next table (**Table 5**) lists the features of three different types of LIBs for electric vehicles. Each battery pack weighs 200-500 kg and has a voltage of around 350V. A pack consists of 10-50 modules, each of which includes several hundred to several thousand 3.6-3.8 V cells [39].

Table 5: Characteristics of three types of LIBs for electric vehicles [24].

Component	LIBs shape					
	Cylindrical		Prismatic			
			Hard case		Pouch	
Pack	375 V, 530 kg		355 V, 235 kg		360 V, 294 kg	
Module	25 kg, 16 modules per pack		25 kg, 8 modules per pack		3.8 kg, 48 modules per pack	
Cell	444 cells per module		12 cells per module		4 cells per module	
Composition of case	Steel (Fe-Ni alloy etc.)		Aluminum		Aluminum	
Example	Height / mm	 70	 120	 260		
	Width (diameter) / mm	20	170	230		
	Thickness / mm		50	10		

3.11 Lifetime

Over time, the characteristics of a battery system will alter. The battery cells are made up of various components that are in contact with one another and may react. These reactions are accelerated at high temperatures. Temperatures ranging between -20 and 60 °C are usually acceptable for LIBs. Lower or higher temperatures outside of this range will cause capacity loss and permanent damage, such as lithium plating and thermal runaway. As a result, the performance of the battery degrades with time. Additionally, the internal resistance of the battery cell increases, resulting in a reduction in the cell's output. The capacity and/or internal resistance of battery cells are dimensioned in such a way that they are guaranteed till the end of their lifetime [155].

Another process that leads to the battery's degradation is the forming of the solid electrolyte interphase (SEI) layer. During the first charge and discharge of a lithium-ion battery, the electrode material reacts with the electrolyte at the solid-liquid phase interface. Following the reaction, a thin film forms on the surface of the anode material, where Li⁺ can be embedded and removed freely while electrons cannot. This thin film is a passivation layer called the solid electrolyte interphase and its role is to prevent electrolyte decomposition and ensure continued electrochemical reactions. However, in the long run this film is getting thicker, due to chemical activities building additional layers on top of the SEI. Because some of the dissolved lithium ions in the electrolyte are converted into compounds that are no longer available for electrochemical reactions, this will eventually reduce the battery's capacity [156].

3.12 Market demand, natural resources, and LIB production costs

At the moment lithium is more than simply a metal used in multiple applications. Lithium is recognized as a critical element for replacing fossil fuels and therefore it is a part of the answer to the pressing problem of climate change [157]. Introducing LIBs in EVs and other renewable ESSs, has already reduced the consumption of fossil fuels.

Over the last few years, end-use lithium usage has risen dramatically. Batteries (35%) and ceramics and glass (32%) were the two primary end-use markets for lithium in 2015 [27]. As one can see in **Fig. 25**, in 2019 the global lithium battery market grew to 65%, whereas the ceramics and glass industry shrank to 18%.

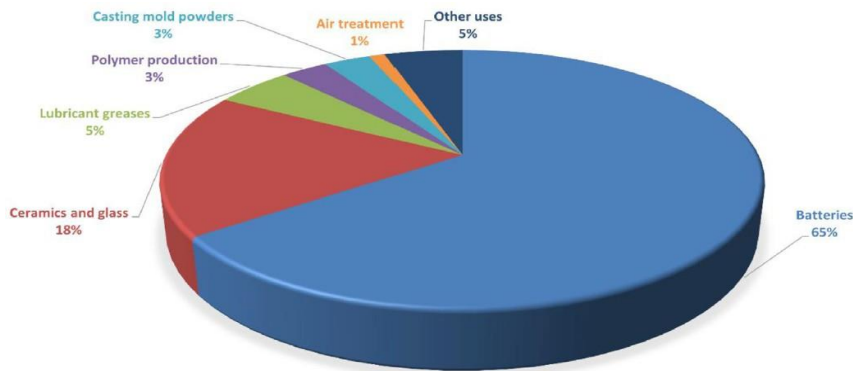


Figure 25: Global lithium end-use market shares [25].

To put this rise of the lithium use in various applications in context, it should be noted that the global energy industry is expected to reach 250 billion euros net worth by 2025. The growth in consumer electronics is exponentially increasing the demand for lithium found in LIBs. Both supply and demand are expected to grow in the near future, according to **Fig. 26**.

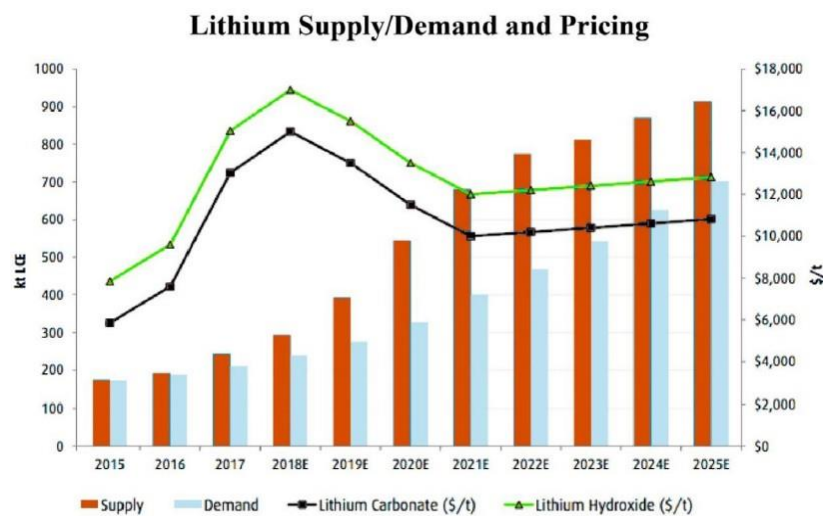


Figure 26: Estimated world lithium consumption and production (excluding U.S. production) [26].

Only in 2016–2017, this surge in demand resulted in a 61% price increase for battery-grade carbonate [26].

3.12.1 The cost of LIB manufacturing

Lithium prices are influenced by supply and demand, but three major factors have a significant impact: (i) the Chinese market monopoly, (ii) the global control of natural lithium reserves, and (iii) political and social turbulence in South America. China is the world’s largest producer of consumer electronics and LIBs, yet its market is significantly reliant on imports from Australia.

Although Chile has the biggest reserves, the current leader in production is Australia. Second, three companies (SQM, American FMC Lithium, and Albemarle Corporation) dominate 90% of the global lithium market. Lastly, the large production volumes, which are extensively damaging groundwater and will approach the legal lithium extraction limitations for 2030 near 2023, are causing political and environmental turbulence in South America, and especially in Chile [27].

In addition to lithium, the cost of LIBs is also dependent on other materials such as cobalt, graphite, nickel, and manganese. For example, 6-12% cobalt and 36-45% nickel are found in lithium battery cathode types such as LCO and LiNiO₂. Therefore, the price of these metals will also rise as battery demand grows [158]. Between 2012 and 2018, the cost of cobalt climbed from 22 to 81 US \$/kg. Cobalt is pricey due to its relative scarcity and high demand. Nickel is also scarce, with only 10⁸ tons of the total 10¹⁵ tons available being economically viable to mine.

The leading country reserves and costs for lithium, nickel, cobalt, and graphite are presented in **Fig. 27**. Like lithium, cobalt and nickel prices vary depending on accessibility in different places with different socio-economic situations.

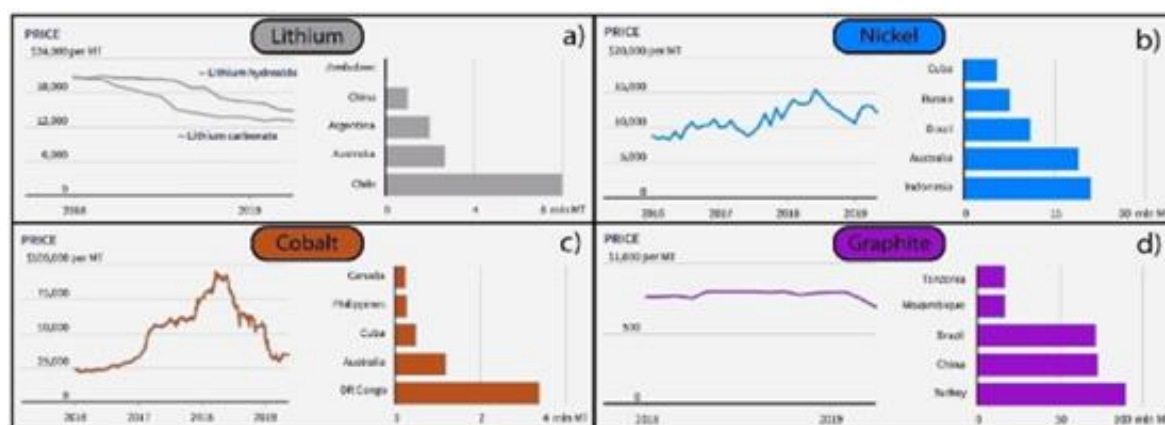


Figure 27: Main country reserves and price trends for a) lithium, b) nickel, c) cobalt and d) graphite [27].

Graphite, on the other hand, has a relatively constant cost because of its widespread availability.

Regardless of the fact that some materials like cobalt and nickel, are used in small quantities, it is noted that their contribution to the LIB’s final price is substantially greater due to their high pricing [77].

3.12.2 Lithium sources

The global lithium reserves (brines and ores) by nation are summarized in **Table 6** below. Since 2017, all of these countries have grown their lithium mine production, although Australia remains the leader overall, producing 42.000 tons of lithium in 2019, which is about 55% of the total world output. Chile, on the other hand, has the largest lithium deposits, with 8.6 million tons. Other nations, including Bolivia, Canada, and Namibia, have significant lithium resources, but they aren’t currently being exploited, despite the possibility of developing mining operations in these areas [37].

Table 6: Lithium reserves and production. Australia is the leading producer, but Chile has the largest reserves [37].

Country	Mine production (tons) 2018	Mine production (tons) 2019	Reserves (tons)
Chile	17.000	18.000	8.600.000
Australia	58.800	42.000	2.800.000
Argentina	6.400	6.400	1.700.000
China	7.100	7.500	1.000.000
United States	-	-	630.000
Zimbabwe	1.600	1.600	230.000
Brazil	300	300	95.000
Portugal	800	1.200	60.000
World total (rounded)	92.000	77.000	15.115.000

In terms of total global reserves, current production, and predicted demand growth, there appears to be enough lithium for the next 100 years. However, it has been predicted that the demand for lithium will soon outstrip supply if recycling technologies are unable to reverse this trend [159]. According to some projections, the cumulative need for lithium will vary between 74 and 248% of reserves by 2050, while cobalt cumulative demand in the same year will be 50% of the reserves [159]. The variability noticed in these forecasts originates in the uncertainties of the assumptions that were used to generate them.

Lithium, cobalt and natural graphite are today classed as important raw materials due to their economic importance and supply risk. Nickel and cobalt are the two metals that are expected to present supply issues far before lithium. It is also fair to expect that new, cleaner, and more efficient energy sources will have been created by then [160]. However, if reliance on LIBs continues for an extended period of time, the environmental damage caused by the mining and processing of lithium and other (even rarer) metals can be extremely severe. These environmental concerns should be adequate to stimulate recycling regulations and initiatives around the world.

Chapter 4

Reuse and Recycling of Li-ion Batteries

4.1. Introduction

There are numerous environmental advantages of storing energy in lithium-ion batteries, with the overriding benefit being the replacement of expensive, inefficient, and environmentally destructive fossil fuel operations [46]. However, the ever-expanding battery production will not only exhaust several metal resources, but cause environmental problems associated with extraction and mineral processing, too. Furthermore, lithium-ion batteries are electronic consumables that have a lifetime of up to 3 years in small electronic devices, and 5-10 years in a larger device (8-10 years for an EV [161]), on average.

A vast quantity of used LIBs will also be produced as the rate of the replacement increases. Finally, LIB disposal, which is frequently done alongside with their electronic devices, is economically wasteful, because most of these expensive materials could be recovered and repurposed. As a result, having a proactive approach to dealing with future waste streams of end-of-life batteries is critical.

As the market for LIBs develops, recycling and reusing batteries becomes extremely important in order to acquire scarce and valuable raw materials [162], as well as assisting countries in making a quick and long-term transition in delivering green energy. However, the recycling of batteries is still in its early stages, and has many fundamental hurdles to overcome, such as high costs and a lack of efficient technology [163]. Additionally, due to the complexity of their component composition, LIBs are harder to recycle than traditional batteries. But if recycling and reuse activities are correctly implemented, then greenhouse gas (GHG) emissions, primary metal extraction and expenses will all be reduced. This chapter focuses on current recycling and reusing methods and the benefits that they offer. The latest developments and proposed processes are also mentioned, along with their advantages and disadvantages.

4.2 Environmental Impacts of LIBs

Despite their advantages, lithium-ion batteries present several environmental issues. These problems emerge from the mining and processing of the lithium reserves, but mainly from the toxic waste that occurs due to the improper disposal of LIBs, that contain toxic metals, such as cobalt and nickel (heavy metals) [164]. According to a survey conducted in 2012, LiCoO_2 and

$\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, are two battery types that contain dangerous heavy metals such as cobalt and nickel, accounted for more than half 50% of the cathode material market. Furthermore, organic electrolytes may include dangerous chemicals like flammable organic solvents or lithium salts that contain fluorine. Therefore, throwing LIBs in the trash will pollute the environment significantly.

Focusing back on lithium, this metal comes from the extraction of two natural sources: salt lakes/brines and ores. In order to make one ton of lithium, it is required to mine about 250 tons of a mineral ore named spodumene and 750 tons of mineral-rich brine. Lithium composition in ores ranges in low percentages, some of which are shown in **Table 7**. The processing of huge volumes of these raw materials has significant environmental consequences. Two examples of brine production are the digging of a salt flat or the pumping of mineral-rich solutions up to the surface. This mining activity, however, exhausts water tables. An example is the largest salt lake in Chile called Salar de Atacama, which is a significant center of producing lithium. There, mining activities absorb 65% of the water in the area. Such activities influence negatively the local farmers, who must then import the water they need from other places. The processing of the lithium that is extracted in this way needs huge volumes of water, especially when considering that 1 ton of lithium needs around 1,900 tons of water in order to be extracted, which is lost to evaporation [24].

Table 7: Various lithium ores and their lithium content [38].

Ore	Chemical formula	Li contained (wt%)
Spodumene	$\text{LiAlSi}_2\text{O}_6$	3.73
Petalite	$\text{LiAlSi}_4\text{O}_{10}$	2.09
Amblygonite	$(\text{Li, Na})\text{AlPO}_4(\text{F, OH})$	3.44
Lepidolite	$\text{K}(\text{Li, Al})_3(\text{Si, Al})_4\text{O}_{10}(\text{F, OH})_2$	3.58
Eucryptite	LiAlSiO_4	5.51

Secondary manufacture, on the other hand, would only require 28 tons of used spent LIBs (about 256 used EV LIBs) [165, 166, 167]. If some of the materials can be recovered or refurbished from EOL lithium-ion batteries, then the negative influence of LIB manufacturing could be significantly reduced [168]. However, recycling alone will not be sufficient to replace mining, but rather complement the supply chain of LIBs. Other than that, not all materials are recyclable [169]. Therefore, both recycling and extraction of natural resources will be needed, at least for the near future.

In addition, lithium has limited resources but is in huge demand. **Fig. 28** depicts the projected worldwide battery demand by application for the years 2020 until 2030. At current paces of

demand, lithium reserves will soon be significantly reduced which will result in higher lithium prices and will arise many economic and environmental difficulties. In the long run, higher lithium costs could result in making the extraction of several low-concentration sources much more appealing. This tactic may currently be more convenient and profitable compared to recycling, but mining, extraction, and purification activities may cause extensive environmental damage. Although it is urgent to use lithium as well as other LIB metals in a greener and more sustainable way, only about 1/10 of their components are recycled today worldwide. The remaining percentage, which is a large number of around 90% eventually, ends up in landfills, leaving precious materials unrecoverable [170].

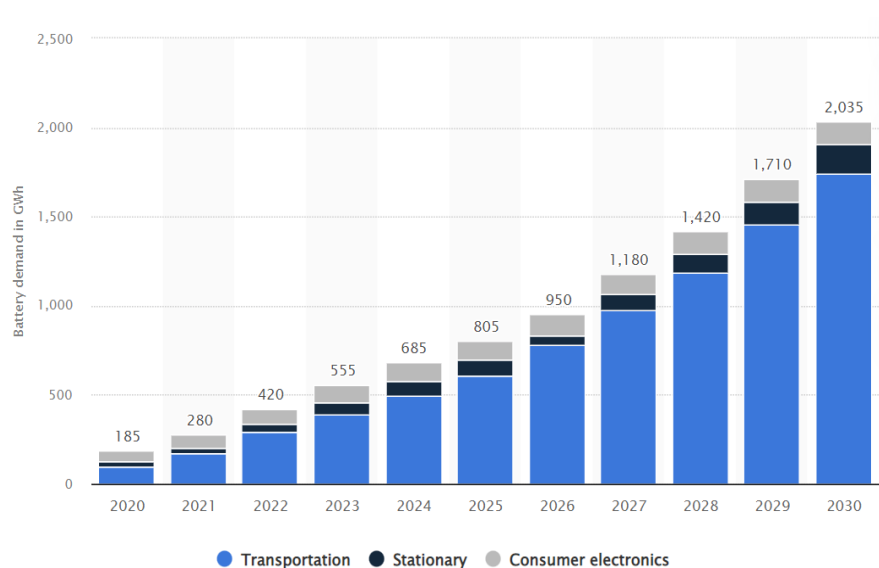


Figure 28: Projected global battery demand from 2020 to 2030, by application (in gigawatt hours) [28].

The reserves of cobalt are primarily found in the Democratic Republic of the Congo, a nation with great political instability. The cobalt reserves there have experienced huge price fluctuations in the short term and have raised many social and ecological worries regarding their extraction, with the concerning example of artisanal miners that use child labour. Except for the environmental benefits that recycling offers, the supply chain of LIB materials has indeed major ethical implications. These social burdens are posing challenges to some of the world’s most vulnerable populations. Given the industry’s global nature, all nations need to coordinate and find a way to support the effort towards LIB recycling using circular economy strategies.

This situation must change since natural supplies alone will be insufficient to meet LIB future demand. The major driver for the huge growth of LIBs is the demand for automotive batteries, which aim to replace conventional internal combustion engines (ICE). According to a study by the European Commission, the emissions produced by an EV are much lower than those of an ICEV, especially when the EV is charged using renewable sources of energy. By 2026, it is expected for the EV battery

market to be worth \$90 billion at minimum. By 2030, around 140 million EVs are anticipated to be used all over the world [171]. This shift towards vehicle electrification is leading to vast LIB production and is creating a big flow of EOL or wasted batteries. In a decade, it is predicted that 11 million tons of EOL LIBs will be produced, with yearly waste flows of EV batteries reaching up to 340,000 metric tons by 2040 [161]. From 2025 to 2030 the EV battery sector, is expected to be the leader in the market of LIB recycling in terms of value and quantities. Because of the predicted rise of the EV market for the reasons described above, there will be a great need for LIB in the automotive industry, highlighting the importance of recycling used batteries to meet the needs of production chains while also reducing spent battery disposal.

LIBs also raise concerns about human health. Short-circuits, overcharging, and overheating in malfunctioning or incorrectly operated LIBs can result in fires and explosions. To avoid such accidents, safety checks have been established. However, because there are so many different devices with varying compositions and properties, the outcomes of these studies vary. Consequently, despite these precautions, accidents do occur on occasion [172]. Furthermore, several battery types include larger quantities of copper, nickel, and cobalt than is recommended [173]. Several also include lead or thallium, raising the toxicity of batteries dramatically [173].

For all these reasons stated above, a battery recycling and reusing system should be seen as a financial and an environmental obligation.

4.3 LIB recycling and reusing for a circular economy

LIB recycling and reuse can help countries' economy flourish in an environmentally and socially responsible way. A 'circular economy' strategy for EOL batteries can be used to establish such an approach. Circular economies are developed around a simple concept: it is able to recognize that focusing solely on economic expansion has limitations, particularly in terms of ecological issues. As a result, it aims to reduce pollution by developing green products and sustainable materials whose production does not exceed environmental or natural system boundaries [46].

End-of-life management is becoming increasingly important in the design of LIBs, with the goal of prolonging the lifespan of materials and products to the best feasible extent for either first or secondary uses. To the degree possible, disposal should be avoided, keeping dangerous materials and components in a reuse/recycle state. Illegal and unsustainable disposal procedures affect poor and vulnerable countries. LIBs must take a full life cycle approach to ensure that they will not contribute to the toxic waste pollution. The idea of a circular economy is shown in **Fig. 29**.

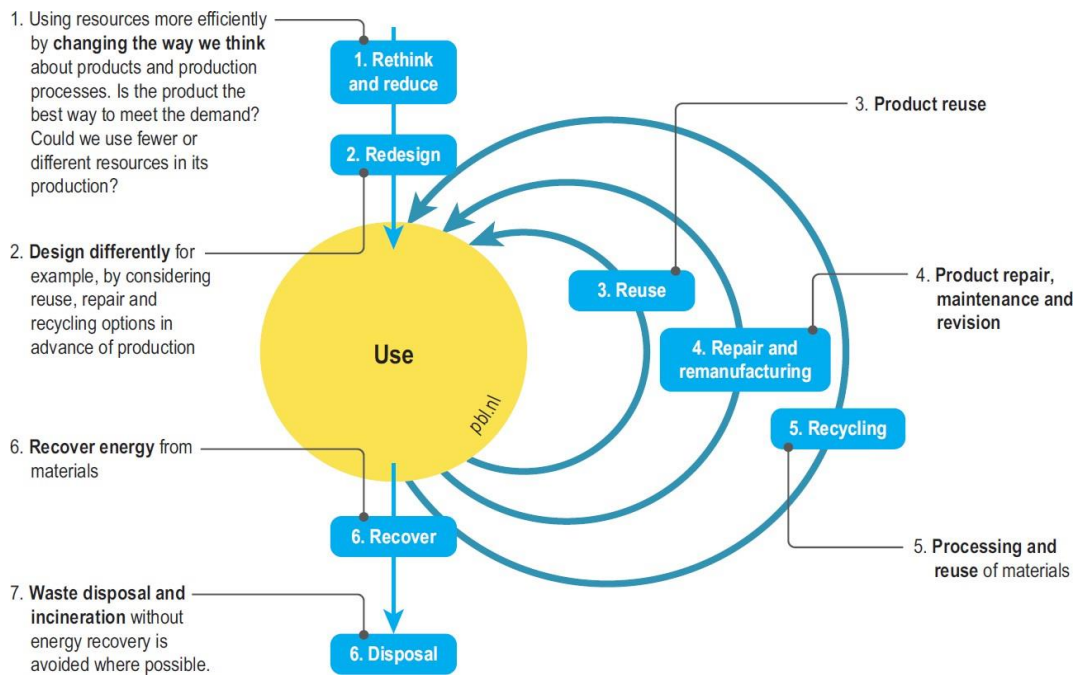


Figure 29: The Circular Economy: A Pictorial Depiction [29].

Circular economies decide the fate of batteries after they have fulfilled their original purpose and shouldn't be considered as compromising to meet environmental and economic goals. In this regard, recent findings from the World Economic Forum Global Battery Alliance (GBA) in 2020 predict that shifting to circular economy strategies might lead to a decrease of 34 metric tons of greenhouse gas (GHG) emissions as well as an additional economic value of \$35 billion US dollars. This would be accomplished by decreasing reliance on primary material extraction and processing and increasing emphasis on recycling and repurposing activities. To give an example, merely repurposing or reusing spent batteries from EVs as power generators could reduce the cost of EV charging infrastructure by 90% by 2030 while also providing 65% of stationary power grids [174].

Repurposing LIBs would mean shifting its primary purpose to delivering a variety of stationary power services, such as direct energy applications at the micro grid level or even supplying backup power for wind/solar energy. A LIB used in an EV typically operates at up to 80% capacity in a car for about ten years without having its performance affected. After this, it be utilized as a permanent energy source and provide a variety of extra services. According to Casals et al. [175], it could support electric vehicles, which would expand its lifetime by 30 years, or mini grids, expanding its lifetime by 6 years, given that the products have been properly reconditioned and tested.

As previously mentioned, it is worth noting that even though circular economies are critical for establishing a sustainable future, they don't rule out the necessity of mining and processing metals and minerals from the natural resources in the future for clean energy technology. Lithium and other critical metals are just not recycled in sufficient quantities to fulfill global climate goals.

Furthermore, expanding LIBs applications beyond portable electronics and EVs to include stationary sources (by reusing rather than recycling), could lead to an increase in primary extraction to meet battery demand for their initial applications. Therefore, extraction and recycling/reuse cannot be regarded as mutually exclusive; on the contrary, both are required.

The majority of battery research and development, particularly in terms of recycling and reuse alternatives, comes from some nations, primarily China and also South Korea. Furthermore, the EU, the USA, and the UK have recently announced ambitious projects aimed at integrating battery technologies into the framework of circular economies, with a focus on recycling and reuse modalities [46].

4.4 Recycling of LIBs

4.4.1 Introduction

Once the battery has been used, it can follow different paths. The first decision to make is whether to get rid of the expended batteries and throw it in landfills, a strategy that must not be the first option, or whether to reuse or recycle it. It was previously indicated, that reusing batteries is possible, but firstly their state of health should be taken into account. Different recycling routes can be taken when the components are too deteriorated to use, considering whether the battery was used in a first- or second-life application. The question regarding recycling isn't whether to recycle or not, but rather how to recycle as efficiently as possible [77]. Market pressures and regulations will affect whether and when spent batteries are remanufactured, refurbished, or recycled, as well as which techniques are most effective in achieving those goals.

Because of the complex design of LIBs and their packs, and also the variety of LIB materials, a single technique cannot be sufficient to deliver a cost-effective and environmentally beneficial solution. As a result, an effective recycling process usually includes two types of processes: physical and chemical.

Spent LIBs still retain some amount of energy, and this could result in a fire or explosion during the recycling steps [176]. This is why discharging wasted LIBs is essential before they are recycled. Examples of physical processes are pretreatments like disassembling, crushing, thermal pretreatment, etc. [177], as well as some procedures that allow direct recovery of materials without needing chemical treatment [31]. Pyrometallurgical and hydrometallurgical methods are two types of chemical processes, which are major branches of metal recovery from wasted LIBs. Both of them include leaching, separation, extraction, and chemical/electrochemical precipitation [178].

4.4.2 Difficulties of LIB recycling

Several variables make LIB recycling more difficult than that of other batteries, such as lead–acid (Pb–acid) batteries or nickel–metal–hydride (Ni–MH) batteries. To begin with, compared to these batteries, LIBs use a broader range of materials in the components of each cell, as **Table 8** shows.

Table 8: Comparison of cell materials [30].

Cell component/ battery type	Pb-acid	Ni-MH	Li-ion
Cathode	PbO ₂	Ni(OH) ₂	LiMO ₂
Cathode plate/foil	Pb	Ni foam	Al
Anode	Pb	MH(AB ₅)	Graphite
Anode plate/foil	Pb	Ni-plated steel	Cu
Electrolyte	H ₂ SO ₄	KOH	Organic solvent + LiPF ₆
Separator	PE or PVC w/silica	Polyolefin	PE/PP
Cell case	PP	Stainless steel	Varies (metal or laminate)

The active materials of the electrodes are often in a powder form that is applied on a metal foil, and during recycling the separation of these materials is demanded. Lead-acid batteries don't have many big lead plates stacked together inside one plastic case, whereas a lithium-ion pack is likely to comprise at least 100 single cells (for a Tesla EV this number reaches 5000). These are joined into modules and then into a pack (see **Fig. 30**). These components inside the pack may be entirely recoverable or may contain worthy materials, providing an economic incentive to recycle the battery pack.

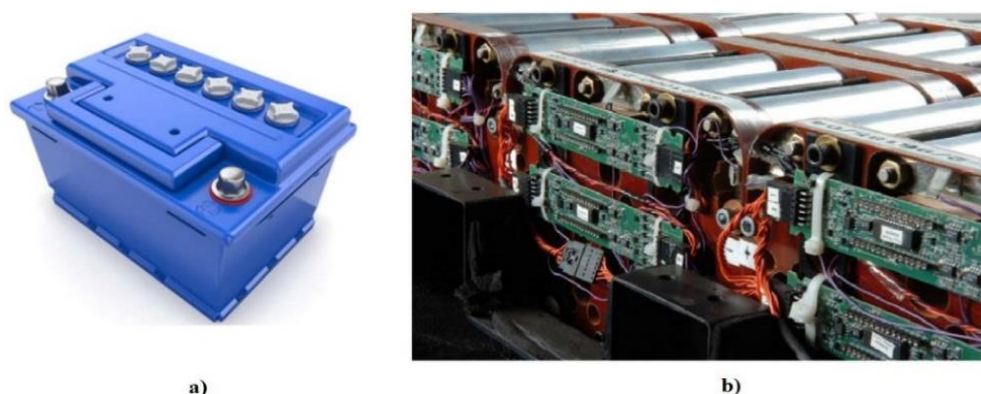


Figure 30: a) Lead-acid battery and b) Li-ion pack [30].

Inside the lithium-ion battery the chemistry of the active materials (AMs) - and particularly the cathode - within the cells vary, because they are produced by different manufacturers and each type is used for a different application. In addition, batteries are constantly evolving, and might never standardize. The most popular cathode material for consumer electronics batteries is LiCoO₂ (LCO), nickel, manganese

and aluminum can also be employed to substitute part of the cobalt or even all of it, to improve performance and at the same time cut raw material costs, which is critical for EV batteries. Another cathode material with low costs of production is LiFePO₄ (LFP). For the anode, most producers use graphite, but silicon and other promising materials and mixes are also being explored.

Lead–acid batteries are small, compact and easy to remove from the battery hood, whereas lithium-ion packs are larger and more complex, with varying shapes and locations inside the car. As a result, their removal is harder to achieve. However, the presence of a professional performing the removal processes would lead to fewer persons being instructed on correct handling and separation. If LIBs have almost the same lifetime with a vehicle, they will end up together in scrap yards or car dealers. Such companies are big enough to make collection sufficient. After collection, batteries can be employed for reuse as stationary energy storage devices and then be collected from utilities; but, collecting from households or smaller installations would not be an easy task.

There are currently no existing laws for the recycling of large-format LIBs. This situation could be considered as beneficial for recyclers, because they would have no constraints in terms of process design. They would, however, run the major risk of severe restrictions being introduced in the coming years. As a result, processes need to be built in compliance with the upcoming rules. Furthermore, battery technologies are constantly evolving. Therefore, recycling procedures tailored to a certain design or chemistry could quickly become obsolete.

Automobile LIBs have only been commercially available for about a decade, and only in recent years they have started being used in big quantities. The biggest percentage of spent lithium-ion batteries comes from consumer electronics together with processing scrap and provides enough waste as feedstock for the developing LIB recycling industry. The next chapter provides information about several recycling methods, which are currently used in the LIB recycling industry [30].

4.4.3 LIB Recycling Methods

Pre-treatment

For LIBs recycling to acquire distinct components, the pretreatment process is needed, which includes discharging, disassembling, and separating spent LIBs and their components [179]. Pretreatment needs to be conducted based on LIBs' different physical parameters such as geometry, density, conductivity, magnetic property [177], etc. Pretreatments can separate and enrich components, materials, and metal scraps with similar physical qualities, resulting in higher recovery rates and lower energy consumption in the processes that follow [31]. **Fig. 31** shows a

flowchart of typical recycling LIB processes.

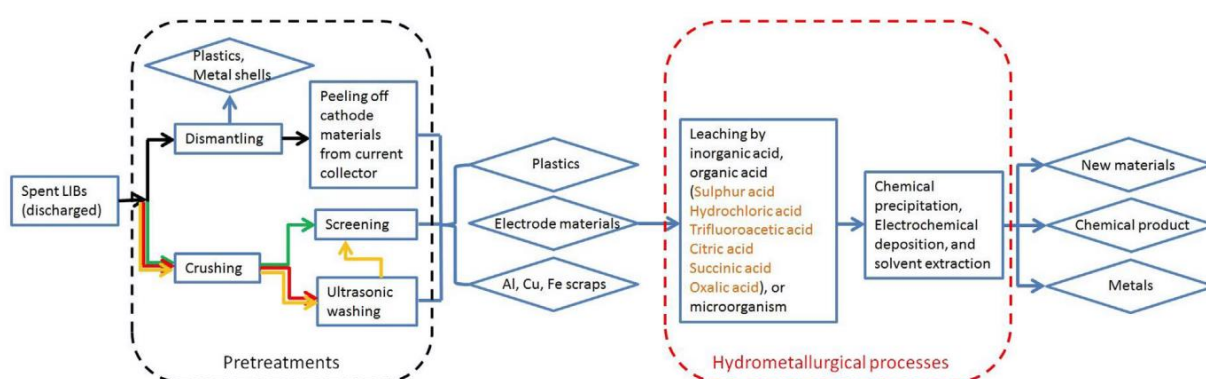
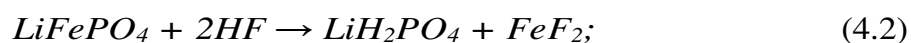
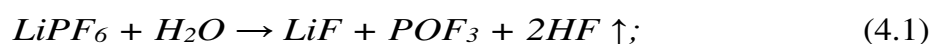


Figure 31: Flowchart of typical processes for recycling spent LIBs [31].

- Discharge of used LIBs for recycling treatment

In pyro-metallurgy, an incineration with very high temperatures takes place, which can automatically discharge LIBs. However, hydrogen fluoride (HF) and other dangerous gases are produced via heating or thermal runaway. LIBs are also discharged when they are immersed in a salt solution, for example a 5wt% sodium chloride (NaCl) aqueous solution [180].

In hydrometallurgy, discharging is used to keep the battery safe and avoid short-circuiting or self-ignition. To lower their voltage, LIBs are discharged inside salt aqueous solutions, for example 0.8 mol/L NaCl, 0.8 mol/L FeSO₄, or 0.4 mol/L MnSO₄. Two models were tested while discharging: a quick model decreased the residual voltage from roughly 3.6 V to 1.0 V in 2 hours, while a full model lowered this voltage to 0.5 V in around 3 hours [181]. To achieve discharge, LIBs are also often immersed in Na₂SO₄ or other saturated salt solutions. For instance, wasted LIB electrodes are immersed in brine water and discharged via the following reactions:



Gas generation is also produced, which can be reduced using supercritical and subcritical conditions, according to Y.R. Smith and H. Pinegar in 2019 [182]. The discharging of LIBs makes the following processes and reuse much easier.

- Crushing

For achieving LIB material separation, a variety of crushing processes can be used. A hammer-

mill is commonly used for this method in a variety of crushing environments; However, it can produce poisonous gases like hydrogen fluoride (HF), phosphorus pentafluoride (PF₅), among others. Crushing can take place in a sealed environment, i.e., glove box, in water, or in an inert atmosphere, like CO₂ or argon (Ar) [181]. Zenger, et al. (2010) reported the Batrex process, in which mechanical processing is carried out in a CO₂ environment within a securely closed chamber [183]. To avoid HF gas formation, cryogenic crushing has been tested using liquid nitrogen at around 200°C [184] or liquid CO₂ at 56 to 20°C [182]. Abrasion mills are also able to successfully remove tiny particles from the metal foils, while cutter mills can efficiently separate plastics. For grinding, ball mills are often used. For example, the planetary ball mill is widely used for mechanochemical grinding with polyvinyl chloride (PVC). Furthermore, the crushing underwater explosion avoided the production of hazardous HF gas with calcium salts [185]. During the crushing operation, fire and harmful gas emissions should be avoided.

- Binder removal

The cathode binders are made of PVDF and the anode binders consist of carboxymethyl-cellulose, according to infrared spectrometry reported by He, et al. (2019) [186]. Powders at the anode, like graphite, are applied as a coat on Cu foil, while powders at the cathode containing lithium transition-metal oxides are coated on Al foil. The binder must be removed in order to recycle the foil particles. **Table 9** lists a variety of binder removal techniques. The removal of binders from foils has been proposed using different methods, including thermal treatment at the optimal temperature, microwave roasting, solvent use, mechanochemical process, the supercritical CO₂ approach, and the pulse method with high voltage [39]. Controlling the atmosphere when LIBs are thermally processed is critical because, according to thermogravimetry [186], thermal treatment including 20% oxygen creates toxic gas. To avoid harmful gas emissions, thermal treatment takes place in a vacuum atmosphere, for example in N₂ gas at 550°C for 2 hours [180]. Aqueous exfoliating and extracting solution (AEES) procedures have been documented in the use of solvent to separate the binder from powders as well [186]. Chemical reagents including N-Methyl-2-pyrrolidone (NMP), and dimethylformamide (DMF) are used as well, despite the fact that they are toxic solvents [187]. An extremely green method is using the juice of citrus to dissolve the binder and also leach the metal, making the removal very effective, with 94-100% success. To remove the binder from electrode materials inexpensively, a combination of solvent and thermal procedures may be required.

Table 9: Various binder removal methods [39].

Method	Condition
	·Air atmosphere at 150–500°C for 1 h to burn binder with emission of harmful gas
Thermal treatment	·Nitrogen atmosphere at 550°C for 3 h to evaporate or decompose binder
	·Vacuum atmosphere at 600°C for 0.5 h to evaporate or decompose binder
Microwave roasting	Cathode particles with carbon mixing by ball milling and then microwave treatment
	·N-methyl-2-pyrrolidone (NMP) at 100°C to dissolve PVDF
	·N,N-dimethylformamide (DMF), dimethylacetamide (DMAC), and
Solvent utilization	dimethyl sulfoxide (DMSO) to dissolve binder (PVDF and PTFE)
	·NMP + NaOH aqueous solution and thermal treatment combination
	·Citrus fruit juice to dissolve PVDF
Mechanochemical method	Mechanical abrasion and Fenton reaction assistance
High voltage pulse	Separation of PVDF from cathode particle (LiCoO ₂) in aqueous phase

Pyrometallurgy

Pyrometallurgy is the area of science that uses high temperatures to extract and purify metals [31]. It is a method used for reducing metal oxides inside the battery to their metallic form and then recovers them as alloys. The purpose of these techniques is to recover valuable elements from spent LIBs, which can then be used as raw materials in the production of new lithium-ion batteries. [77]. **Fig. 32** shows a schematic representation of a typical LIB pyrometallurgy process.

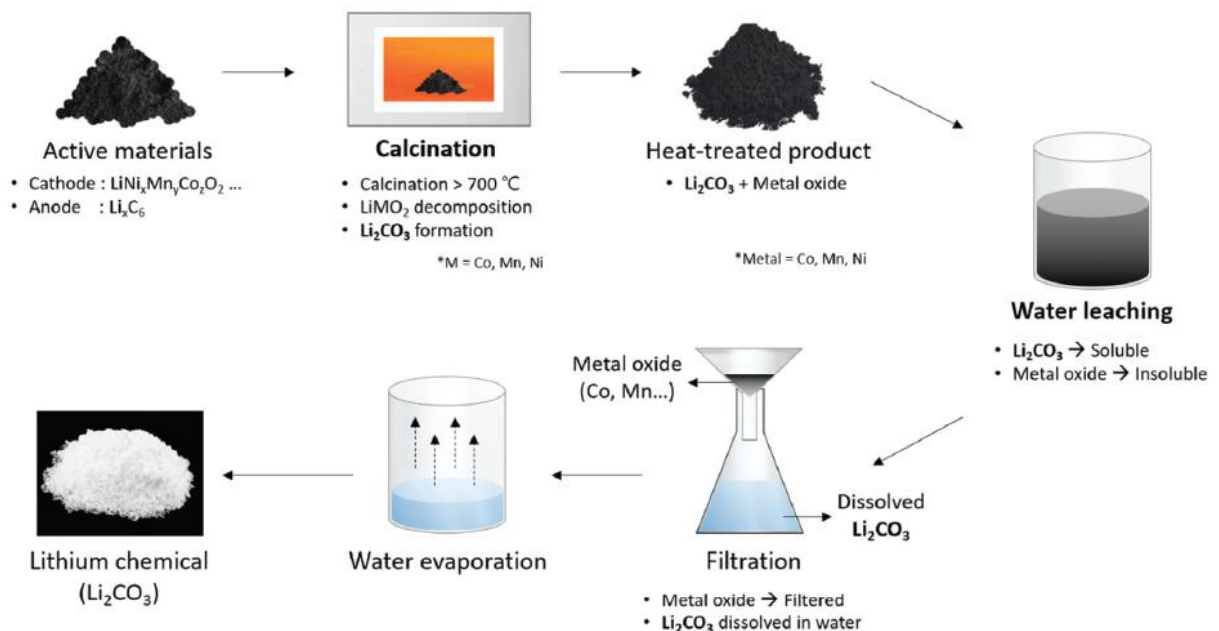


Figure 32: A schematic representation of a typical LIB pyrometallurgy process [37].

The only pretreatment step during this method is to simply dismantle the large battery packs and convert them into single cells. The latter are then placed inside shaft furnaces that operate at 3

temperature zones: firstly preheating, then pyrolyzing and lastly smelting and reducing. During preheating, used LIBs are exposed to less than 300 degrees Celsius. In this way, the electrolyte vapor is discharged without facing the risk of explosion.

The plastic pyrolyzing zone operates at around 700°C, incinerating the plastic parts of discarded LIBs, and maintains the temperature. By using this tactic, the energy demands of the smelting process are lowered. The ingredients are smelted in the final zone, and the product is an alloy that contains nickel, cobalt, copper and iron, as well as a slag with silicon, aluminum, lithium and a small iron amount. This alloy is then separated and can be split into the individual components. This method can only recover the aforementioned materials, i.e., nickel, cobalt, copper and a small iron amount, but in an extremely clean state, and providing a high yield too [31].

The cost-effectiveness of this technique is heavily influenced by cobalt prices and battery cobalt concentration. It is commonly acknowledged that cobalt is increasingly being phased out of vehicle LIBs, and LIB cathode materials are constantly changing [188, 189]. The cathode material that GM-Volt batteries use, for instance, is LiMn_2O_4 , while A123 batteries use LiFePO_4 . The industrialized pyro-metallurgical method is not able to achieve lithium recovery, which is projected to become scarcer with the increasing production of electric vehicles [190]. As a result, such conventional pyro-metallurgical processes may become unprofitable in the future.

An example of recovering both lithium and cobalt from wasted LIBs is that of Georgi-Maschler et al. [191], who devised a pyro-metallurgical method employing an electric arc furnace. This furnace can turn the materials of wasted LIBs into an alloy that contains cobalt, as well as concentrates that contain lithium. A hydrometallurgical step might be used to recover lithium from those concentrates in the form of Li_2CO_3 . The rest of the materials, i.e., aluminum, copper, and iron-nickel can also be recovered and further processed.

However, the pyro-metallurgical method has some downsides, like the massive amounts of energy consumption, materials loss, different processing steps, and toxic gas emissions (such as dioxins, furans, etc.) [192], potentially resulting in health and safety issues. Therefore, different recycling techniques with a greater recovery rate, reduced energy consumption, and fewer environmental dangers will be required.

Recycling of slag and dust after pyro-metallurgical treatment: After the pyro-metallurgical treatment of wasted LIBs, chlorination roasting was tested to recover the lithium contained in the slag. CaSiO_3 and $\text{LiAl}(\text{SiO}_3)_2$ make up the majority of the prepared slag. The best chlorination reagent is CaCl_2 . CaCl_2 , is mixed together with the slag at a Cl:Li molar ratio of 1.8:1. The mixture

is then calcined for 90 minutes at 1000 degrees Celsius, with 97%wt% of the lithium being evaporated as LiCl [193].

Hydrometallurgy

The hydrometallurgical process aims to convert the cathode materials that are already pre-treated into ion forms inside solutions, as well as separating metal ions to produce new cathode materials, mono-metal salts, etc. It takes place at moderate temperatures and recovers high rates of cobalt, nickel, and copper. Because of its high recovery efficiency its low impurity concentration in the resulting product, and the low energy demands, hydrometallurgy is considered a suitable method for recycling wasted LIBs. More than 50% of the documented recycling methods are hydrometallurgical, and thus hydrometallurgy is the most popular method for LIB recycling. It includes leaching (for example bioleaching, organic and inorganic acid leaching, etc.), as well as recovery stages (for example, solvent extraction, electrochemical deposition, chemical precipitation, etc.) [31]. **Fig. 33** shows several steps of the lithium-ion battery hydrometallurgy method.

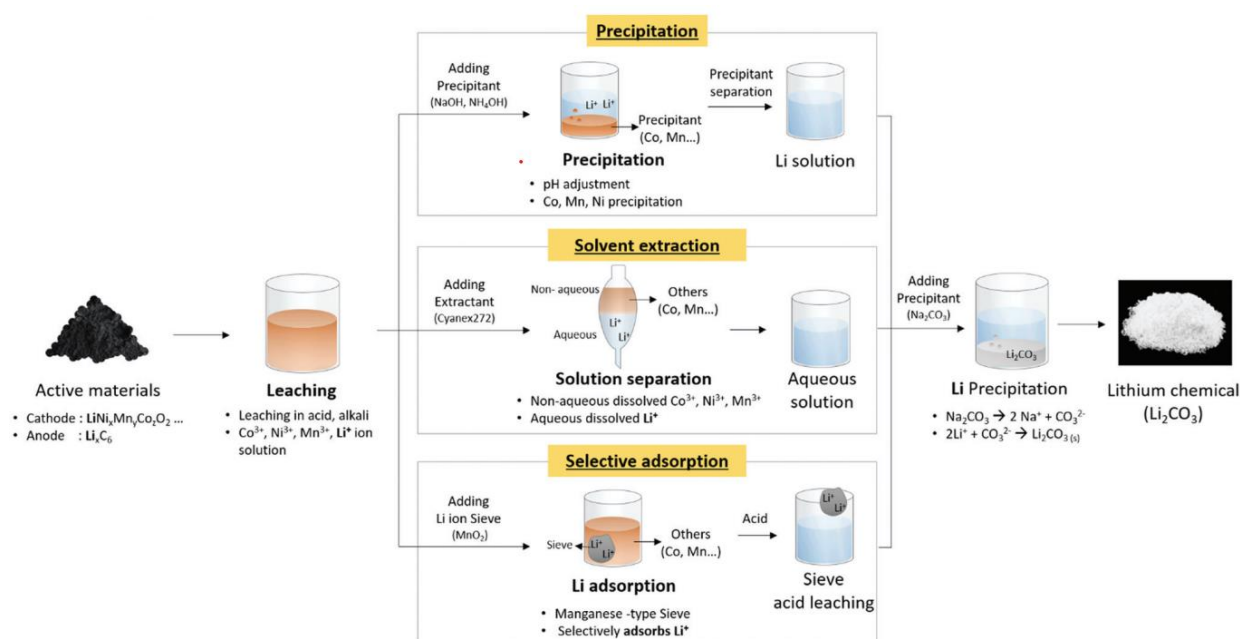


Figure 33: Overall schematic of lithium recycling from pre-treated waste LIB components by hydrometallurgy process [37].

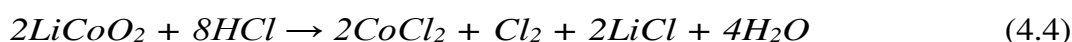
Hydrometallurgy is a really useful technique for metal recovery of LIBs. For instance, a method described by Zhang et al. gave excellent results, with more than 99% of lithium and cobalt being recovered by leaching [194]. Nan's hydrometallurgical process retrieved approximately 98% copper and 97% cobalt. Mousavi et al. designed a green bioleaching process, where organic acids that come from a type of mold called *Aspergillus Niger* are leaching the metals from wasted LIBs. Using this process, they were able to recover 100% of the copper and lithium, as well as 77%

manganese, 75% aluminum, 64% cobalt, and 54% nickel [195].

Leaching: The leaching of cathode metals plays a really important role during the hydrometallurgical step, because it leads them into a solution state. Only in this state can later separation and recycling be done easily. Leaching is classified into several categories, including organic/inorganic acid leaching, bioleaching and ammoniacal leaching, based on the various leaching agents used [179].

Acid Leaching: Acid leaching recovers cathode materials with higher efficiency than pyrometallurgy, because of the high solubility of the materials in acidic solutions [179].

Inorganic acid leaching: Inorganic acid leaching agents include hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), and phosphoric acid (H₃PO₄). The next equation describes an example of the reactivity of LiCoO₂ cathode material in HCl acid:



During this process using HCl, the Co (III) contained into the LiCoO₂ powder is converted to Co(II), and is consequently readily soluble in aqueous phase. As a result, HCl solution as a leaching agent is able to extract cobalt very efficiently. However, the HCl method produces toxic Cl₂, and thus additional treatment is required. Researchers recommended H₂SO₄ leaching as a solution to this problem. Meanwhile, reduction agent hydrogen peroxide (H₂O₂) is required in this process to reduce Co (III) to Co (II), as seen in the next equation:



Organic acid leaching: Aside from powerful inorganic acids, using mild organic acids for leaching has gotten a lot of attention in latest years. For example, oxalic acid can speed the lithium and cobalt recovery from the LiCoO₂ cathode, owing to the simultaneous precipitation and leaching during the leaching stage (formation of CoC₂O₄).

Cobalt and lithium are then directly separated from each other, without needing extra treatment or reduction agents, because of the reducing nature of the oxalic acid. Another mild inorganic acid is H₃PO₄, which has also been shown to simultaneously achieve leaching and separation of both cobalt and lithium. Cobalt is then directly recovered as Co₃(PO₄)₂ via precipitation during the H₃PO₄ leaching process, leaving lithium in the leach fluid [179].

Certain operational parameters can have a substantial impact on acid leaching efficiency, including the temperature, the concentration of acid or H⁺, the duration of the leaching step, the solid: liquid ratio, and additives. Leaching conditions must be optimized in order to have a good balance

between efficiency and cost. Li et al. observed that after 2 hours of leaching in a 4M HCl solution at 80 °C, the lithium and cobalt from spent cathode materials in LiCoO₂ batteries was maximized, as the method dissolved 99% of the cobalt and 97% of the lithium under those conditions. [196].

Table 10 summarizes and lists some suitable operating parameters for the leaching of the materials fraction of wasted LIBs by various acidic leaching agents.

Table 10: Summary of optimal operating conditions for the leaching of materials fraction of spent LIBs by different acidic leaching agents [31].

Materials	Leaching agent	Leaching condition	Reduction agent	Solid/liquid ratio	Leaching rate
LiCoO ₂	4M HCl	80 °C + 2 h	N/A	N/A	Li 97%, Co 99%
LiCoO ₂	4M HCl	80 °C + 1 h	N/A	10% (w/v)	Li >99%, Co >99%
LiCoO ₂ + LiMn ₂ O ₄ + LiCo _{1/3} Ni _{1/3} Mn _{1/3} O ₂	4M HCl	80 °C + 1 h	N/A	5% (w/v)	Ni, Co, Mn, Li >99%
LiCoO ₂	3M HCl	80°C + 1 h	3.5% H ₂ O ₂ (v/v)	5% (w/v)	Li, Co 89%
LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	4M HCl	90°C + 18 h	N/A	5% (w/v)	Li, Ni, Co, Al 100%
LiCoO ₂	2M H ₂ SO ₄	75°C + 1 h	5% H ₂ O ₂ (v/v)	10% (w/v)	Li 99.1%, Co 70.0%
Mixed cathode materials containing Li, Co, Ni, Mn	1M H ₂ SO ₄	95°C + 4 h	N/A	5% (w/v)	Li 93.1%, Co 66.2%, Ni 96.3%, Mn 50.2%
LiCoO ₂	2M H ₂ SO ₄	75°C + 0.5 h	5% H ₂ O ₂ (v/v)	10% (w/v)	Li 94%, Co 93%
LiCoO ₂	2M H ₂ SO ₄	60°C + 1 h	6% H ₂ O ₂ (v/v)	10% (w/v)	Co 99%
LiCoO ₂	2M H ₂ SO ₄	60°C + 2 h	2% H ₂ O ₂ (v/v)	3.3% (w/v)	Li 87.5%, Co 96.3%
LiCoO ₂	1M HNO ₃	75°C + 0.5 h	1.7% H ₂ O ₂ (v/v)	1–2% (w/v)	Li, Co >95%
Mixed cathode materials containing Li, Mn	2M HNO ₃	80°C + 2 h	N/A	N/A	Li, 100%
LiCoO ₂	0.7M H ₃ PO ₄	40°C + 1 h	4% H ₂ O ₂ (v/v)	5% (w/v)	Li, Co >99%
LiCoO ₂	2% (v/v) H ₃ PO ₄	90°C + 1 h	2% H ₂ O ₂ (v/v)	0.8% (w/v)	Li, Co 99%
LiCoO ₂	Citric acid (100 mM) + ascorbic acid (20 mM)	80°C + 6 h	ascorbic acid in the acidic solution	0.2% (w/v)	Li, Co 100%
LiCoO ₂	1M oxalic acid	80°C + 2 h	N/A	5% (w/v)	Li, Co 98%
LiCoO ₂	1M oxalic acid	95°C + 2.5 h	N/A	1.5% (w/v)	Li 98%, Co 97%
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	1.5M Citric acid	80°C + 2 h	D-glucose	2% (w/v)	Li 99%, Co 92%, Ni 91%, Mn 94%

Ammoniacal leaching: Aside from acid leaching, employing ammonia-based agents to leach and separate metal ions from spent LIBs, particularly LNCM, has gained a lot of attraction in recent years. The chelating properties of NH₃ can be used to selectively leach metal ions to separate Mn²⁺ from Ni²⁺ and Co²⁺ ions, giving this approach a distinct advantage. In a typical example, Ku et al. applied ammonia-based leaching agents to leach the LNMC cathode materials. The results gave leaching efficiencies of 37% for Ni and 94% for Co [197]. In a similar two-step process, Zheng et al. [198] used NH₃H₂O as the leachate, ammonium sulfate ((NH₄)₂SO₄) as the reductant, and sodium sulfite (Na₂SO₃) as the oxidant. The residue from the first leachate was continually leached in the second phase in this approach, resulting in a greater leaching efficiency for Ni²⁺ ions. The ammonia from used leaching agents can also be reclaimed for reuse by ammonia distillation, offering this procedure unique environmental friendliness [179].

Bioleaching: This is a sort of hydrometallurgical method used to dissolve electrode materials from

spent LIBs and to extract precious elements using metabolites from microorganisms. Metals can be bioleached from wasted LIBs by certain bacteria and fungi. For example, to handle waste LiCoO_2 cathode material, Mishra et al. [199] used the chemolithotrophic and acidophilic bacteria *Acidithiobacillus ferrooxidans*. The bacteria used ferrous ion and elemental sulfur in the leaching medium to form ferric ion and sulfuric acids, which could dissolve the waste LiCoO_2 cathode material. The bioleaching process, however, is harder to manage due to living biomass being part of it and pulp density affecting the leaching efficiency.

Solvent extraction: The last step of the hydrometallurgical process involves separation and recovery of metals using solvent extraction, chemical precipitation, and electrochemical deposition. Solvent extraction is a liquid-liquid extraction procedure that uses extractants to separate metals from leach liquids. Several extractants have been employed to recover Li, Co, Mn, Cu, and other elements from wasted LIBs, like bis-(2,4,4-trimethyl-pentyl) phosphinic acid (Cyanex 272), di-(2-ethylhexyl) phosphoric acid (D2EHPA), Acorga M5640, trioctylamine (TOA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88 A), etc. In their experiment, Chen et al. [200] extracted Mn from Mn, Co, and Li-containing leach liquid using Co-D2EHPA (Co-D2EHPA). The following conditions were used to extract over 99 percent Mn: 5-minute extraction time, 3.5pH equilibrium, 15 vol % Co-D2EHPA concentration, and the O:A ratio of 1:1. The benefits from this method include low energy consumption, good separation effect, and simple operational conditions. However, because the extractants are not cheap, the cost of treatment in the recycling industry may rise.

Chemical precipitation: In the chemical precipitation process, precipitation agents are used to precipitate precious metals in the leach liquid. Contestabile et al. [201], for instance, employed bubbling CO_2 gas to precipitate lithium carbonate from dissolved lithium. Another example is the method of Zhang et al. [202], who used a saturated sodium carbonate solution to achieve lithium carbonate precipitation. Because the solubility of lithium carbonate in an aqueous solution is inversely proportional to temperature, Zhang's precipitation method was carried out at temperatures close to 100 °C. After the precipitation method, around 80% of the lithium could be recovered. Chemical precipitation has several benefits, such as low cost and reduced energy consumption, but the difficulties in separating and reusing metals from complex solutions may deter its use.

Electrochemical precipitation: Metals can also be recovered from leach liquor in the form of pure metal or metal hydroxide via electrochemical deposition. Freitas et al. [203] used electrochemical deposition to recover cobalt from used LIBs. In this process, pure cobalt was generated on the electrode's surface, and the highest charge efficiency of 96.9% was attained at pH 5.4. Lupi et al. [204] used galvanostatic and potentiostatic electrowinning to recover nickel from a waste

$\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ cathode. Nickel could be deposited with a current efficiency of about 87% and a specific energy consumption of 2.96 (kWh)/kg, at a current density of 250 A/m², 50 °C, pH value of 3–3.2, and an electrolyte containing about 50 g/l Ni and 20 g/l H₃BO₃, leaving less than 100 ppm nickel in the mother liquor. To recover cobalt from discarded LiCoO₂ cathodes, Myoung et al. [205] also used electrochemical deposition, and cobalt was retrieved in the form of Co(OH)₂. High-purity metals and a good recovery rate can be accomplished by electrochemical deposition; however, this method consumes a large amount of energy.

Direct Physical Recycling Process

The goal of direct physical recycling is to recover materials from wasted LIBs without the use of expensive chemical treatments [31]. These methods are used for recovering and refurbishing cathode materials (mostly the active cathode materials) in a physical and non-destructive way, without changing the chemical structure of the recovered material. Direct recycling procedures have a high level of specificity, as they appear to handle only one active material at a time [77].

Fig. 34 shows the flow chart of a typical direct recycling process of wasted LIBs with a LiMn₂O₄ cathode material [206]. During this process, wasted LIBs are first discharged and destroyed at the cell level. The cells are then exposed to supercritical CO₂, which extracts the electrolyte. After lowering the temperature and pressure, CO₂ may be removed from the electrolyte, and the electrolyte can be reused in battery manufacturing. The cells, which are electrolyte-free, are deconstructed and crushed. After that, physical procedures are utilized to separate the cell components, and the cathode components are gathered and reused in new batteries, commonly via relithiation.

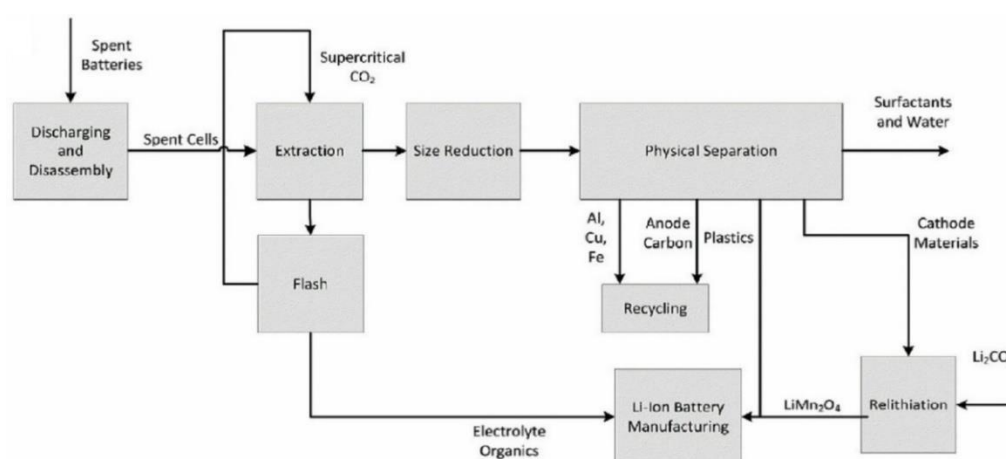


Figure 34: Flowchart of direct physical recycling of spent LIBs with LiMn₂O₄ as cathode material [31].

To recover LiFePO₄ from used soft package LIBs, Chen et al. [207] first devised a direct recycling technique and a small-scale model line. Discharged used LIBs in this process were

dismantled, disassembled, crushed, and cleaned in a seal box without electrolyte recovery. The recovered LiFePO_4 without any treatment had reduced tap density and low electrochemical performance, due to the residual of PVDF binder and the material's decomposition after several charge-discharge cycles. After heat treatment, though, the recovered LiFePO_4 had better tap density and electrochemical characteristics. Specifically at $650\text{ }^\circ\text{C}$ the cathode material showed about the same discharge capacity and energy density as the new one at high discharge current densities.

To recover graphite anode material from wasted LIBs, Rothermel et al. [208] compared 3 direct physical recycling methods. The first approach used a thermal treatment of the graphite without recovering the electrolyte. The second method involves extracting electrolyte using subcritical CO_2 and then heating it. In addition to using supercritical CO_2 as an extract, the third one featured electrolyte extraction and heat treatment. The second method was found to be the best recycling method in the experiments. The recovered graphite exceeded the performance of commercial synthetic graphite TIMREX SLP50, and the electrolyte was recovered by 90%.

Song et al. [209] also regenerated LiFePO_4 material from wasted LIBs. After physical direct recycling, the recovered material was sintered with fresh powder. Firstly, the spent LIBs were first disassembled to remove the cathode and anode plates. The cathode was then immersed in dimethylacetamide (DMAC) at $30\text{ }^\circ\text{C}$ for 30 minutes to separate LiFePO_4 material and Al foil, with a solid/liquid ratio of 1:20 g/ml. The used material was then recovered by sintering it with new LiFePO_4 . The electrochemical performances of recovered LiFePO_4 batteries can meet the basic criteria for reuse.

The benefits of direct physical recycling include a quick recycling route, environmental friendliness, low energy consumption, and a high recovery rate. However, it is unclear whether the recovered materials would perform as well as new ones in the long run. Finally, it is worth noting that while pyro-metallurgical and hydrometallurgical processes are measured in terms of recovery rates, direct recycling methods are measured in terms of battery performance. The latter does not offer information on the recovery rate. Instead, the battery's electrochemical performance is compared to that of the original one. Thus, it is more difficult to assess the method's efficiency [77].

In conclusion, all of the recycling procedures outlined above are focused on recovering resources from wasted LIBs. However, due to varying technological hurdles and economic benefits, recycling technologies are at various stages of development. The pyro-metallurgical technique, for example, has been commercialized because of its ease of use and high efficiency in recovering

cobalt, which is the most valuable metal in wasted LIBs. The amount of cobalt in the electrodes is decreasing as battery technology advances, whilst nickel and manganese use is growing. Furthermore, lithium reserves have emerged as a critical concern, as lithium usage for batteries has expanded rapidly in recent years due to the rapid growth of the electric vehicle market. As a result, recycling methods should shift away from cobalt recovery and toward a more complete use of wasted LIBs. Furthermore, when constructing a recycling process for wasted LIBs, proper disposal or recovery of some components that may affect the ecosystem should be considered.

Products from recycling spent LIBs

At the final step of the battery recycling processes, the metal values from wasted LIBs are transformed into various substances, like alloys, slags, solutions, and precipitates. Lithium, aluminum, and some iron, for example, will be transferred into the slag, which can then be used as a great component in concrete, whereas an alloy with copper, nickel, cobalt, and iron will be further separated and converted into pure metals for reuse. Furthermore, after the leaching stage, a solution containing various ions is formed, which can be processed into a variety of useful products, including metals, chemicals, novel electrode materials, as well as other functional materials [31].

- **Metals and chemicals:**

Pure metals are typically obtained via electrochemical deposition from leach solutions. Freitas et al. [203] used the electrochemical approach to extract pure cobalt from wasted cell phone batteries. Electrowinning was used by Lupi et al. to recover pure nickel from wasted $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ material. Prabakaran et al. [210] developed an electrochemical leaching technique followed by electrowinning to obtain 99.2% pure cobalt, 99.5% pure copper, and 96% pure electrolytic manganese dioxide (EMD). Bertuol et al. [211] used electrowinning to extract cobalt with a purity of 99.5% from waste LiCoO_2 leach liquor. The metals obtained can be further processed to make alloys or chemical raw materials.

Direct production of high-purity and high-value-added chemicals utilizing leach liquor is a smart shortcut for acquiring chemical raw materials from used LIBs. To date, instead of synthesizing pure metals, the focus of researches is directed at creating compounds. A few of them are reported, such as $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{OH})_2$, $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, CoCO_3 , $\text{Co}_2(\text{PO}_4)_2$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Ni}(\text{OH})_2$, NiCl_2 , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, Li_2CO_3 , Li_3PO_4 , CuSO_4 , MnO_2 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, FeCl_3 , Ni-Co-Mn hydroxide, etc. [31].

The majority of the compounds produced are of high purity, allowing them to be used as raw materials for the production of new materials without further purification. **Table 11** lists some of

the metals and compounds that have been reported as being obtained through the recycling of wasted LIBs, along with their purities.

Table 11: Summary of metals and chemicals obtained from recycling of spent LIBs [32].

Spent LIBs or materials	Obtained products	Purity	Recycling process
LiCoO ₂	Co	approx. 100%	Electrodeposition after leaching
LiCo _x Ni _{1-x} O ₂	Ni	approx. 100%	Electrodeposition after leaching and solvent extraction
Mixed spent LIBs	Co Cu MnO ₂	99.2% 99.5% 96%	Electrodeposition after electrochemical leaching
LiCoO ₂	Co	99.5%	Electrodeposition after leaching and supercritical fluid extraction
Mixture of LiCoO ₂ , LiMn ₂ O ₄ and LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	Li ₂ CO ₃ Co(OH) ₂ Ni(OH) ₂	96.97% 96.94% 97.43%	Chemical precipitation after leaching and separation (solvent extraction)
Spent LIBs from mobile phones	CoC ₂ O ₄ ·2H ₂ O	>99%	Chemical precipitation after leaching and solvent extraction
LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	Co ₂ O ₃ ·2H ₂ O Ni(OH) ₂	90.25% 96.36%	Chemical precipitation after leaching
LIBs wastes from an industrial pre-treatment plant	CoCO ₃ Li ₂ CO ₃	Commercial standard >98%	Chemical precipitation after leaching and solvent extraction
Mixture of LiCoO ₂ , LiMn ₂ O ₄ and LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	NiCl ₂ CoC ₂ O ₄ ·2H ₂ O Li ₂ CO ₃	97.81% 97.47% 99.18%	Chemical precipitation after leaching and solvent extraction
Mixture of LiFePO ₄ and LiMn ₂ O ₄	FeCl ₃ / MnO ₂ /Mn ₂ O ₃ Li ₃ PO ₄	97.91% 98.73% 99.32%	Ion flotation and chemical precipitation after leaching
LiCoO ₂	Co ₃ (PO ₄) ₂	97.1%	Chemical precipitation during leaching process
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	Li ₂ CO ₃	99.9%	Chemical precipitation after leaching
Spent LIBs from local recycling center	Li ₂ CO ₃ CoSO ₄ ·7H ₂ O NiSO ₄ ·6H ₂ O MnSO ₄ ·H ₂ O	Almost pure	Reduction roasting, leaching, solvent extraction and evaporation
Mixture of LiCoO ₂ , LiMn ₂ O ₄ and LiNi _x Co _y Mn _z O ₂	Li ₂ CO ₃	99.7%	Vacuum pyrolysis

- Electrode materials

Metals in the cathode materials of wasted LIBs, including lithium, cobalt, nickel, manganese, iron, and others, can be recovered with high purity by recycling procedures, as detailed above. Lately, many transition metal oxides have also been studied as suitable materials for the anode of LIBs. As a result, the metal values recovered from wasted LIBs can be a significant source of raw materials for the development of new electrode materials.

Lee et al. [212] used wasted LiCoO₂ leach liquor to make LiCoO₂ cathode material. By adding new LiNO₃ solution, the molar ratio of Li and Co in the leach liquor was initially adjusted to 1.1:1. The altered leach liquor was then converted into LiCoO₂ via a sol-gel technique. The regenerated

LiCoO₂ exhibited charge and discharge capabilities of 165 and 154 mAh/g, respectively. The capacity retention was more than 90% after 30 cycles.

Yang et al. [213] used spent commercial LIBs to regenerate LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. In this study, both the precursors Li₂CO₃ and Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)₂ were recovered with great purity from the leach solution. The regenerated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ had a spherical morphology and good electrochemical performance due to the lack of impurities. The regenerated material's discharge capacities at 0.5C, 1C, 2C, and 5C current densities were 150, 145, 130, and 100 mAh/g, respectively. Furthermore, after 100 cycles, capacity retention at 0.5C, 1C, and 2C current densities were 94%, 92.8%, and 88% after 100 cycles, respectively. These capabilities are equivalent to those of materials made from pure precursors.

Senanski et al. [214] used wasted LIBs to create a cathode material with LiCo_{0.415}Mn_{0.435}Ni_{0.15}O₂. After an acid leaching stage, the regenerated material was obtained by a combination of a precipitation and a thermal treatment. The results indicated that a high sodium storage capacity of 93 mAh/g could be achieved at a current density of 100 mA/g.

Hu et al. [215] used cobalt oxalate, which was recovered from wasted LIBs through chemical precipitation, to make nano-Co₃O₄ anode material. The nano-Co₃O₄ had a discharged specific capacity of 760.9 mAh/g at a current density of 125 mA/g, and a specific capacity of 442.3 mAh/g after 20 cycles at a current density of 250 mA/g.

- Other functional materials

The leach liquor and its derivatives acquired from the hydrometallurgical recycling processes, can be made into magnetic materials (e.g., NiCo ferrite, CuCo ferrite), electrocatalytic materials (e.g. spinel MnCo₂O₄), photocatalytic materials (e.g. Co₃O₄/LiCoO₂), as well as other functional materials (e.g. MnO₂/graphene adsorbent). Some of the materials are mentioned in the following paragraphs.

Using a sol-gel hydrothermal method, Yao et al. [216] created nano-crystalline cobalt ferrite powders with a spinel structure from the leach liquor of wasted LIBs. The morphology of the produced material was that of a hedgehog-like microsphere with a particle size of 5 μm. When the material was formed at 240 °C for 12 h under hydrothermal treatment, the highest magnetostriction coefficient was 158.5 ppm and the maximum train derivative coefficient was -1.69 A⁻¹m.

Santana et al. [217] used the leach liquor of discarded LiCoO₂ cathode material to make a Co₃O₄/LiCoO₂ mix. Agglomerated particles with a porous geometry made up this Co₃O₄/LiCoO₂ mixture. The discoloration of methylene blue dye was used to test its photocatalytic properties. The

material's discoloration efficiency was 90% after 10 hours and 100% after 24 hours.

For wastewater treatment, Zhao et al. [218] produced MnO₂-modified artificial graphite (MnO₂-AG) sorbents from wasted LIBs. The graphite coated copper foils were used as the raw material in their research. The obtained graphite powder was processed via a thermal treatment, and then it was immersed in KMnO₄ solution for MnO₂ particle loading. The MnO₂-AG had a high removal capability for Pb (II), Cd (II), and Ag (I), with removal rates of 99.9%, 79.7%, and 99.8%, respectively.

In conclusion, several advancements in recycling technology have been developed. As a result, metals, chemicals, and recovered functional materials can all be obtained. However, the majority of recycling procedures need expensive reagents and time-consuming treatment stages in order to recover such high-value-added products. Furthermore, mixing the LIBs that contain various materials may cause difficulties in recycling processes, as well as include impurities into the regenerated products, because the separation processes will be more complex. Some contaminants in regenerated products (for example, electrode materials) from the recycling process may cause poor performance. Fe, for example, could cause rapid self-discharge because the free Fe ions or metal in the electrolyte will be oxidized on the cathode surface and deposit on the anode during charging. That is why, despite greatly outperforming spent materials, regenerated materials may not be equal to fresh ones. As a result, wasted LIBs should be detected and sorted before recycling to ensure that different types of waste materials are not mixed together, allowing the recovery of high value-added products.

4.5 Reusing

4.5.1 Introduction

Reuse, as opposed to restoration, recycling, incineration, and disposal, provides retired batteries a second life [32]. Reuse, often referred to as repurposing, is putting the battery technology as a whole to a second use that is quite distinct from its primary production purpose; for example, transitioning a Li-ion battery from an EV to providing power, or backup power, as a stationary energy provider. LIBs that are commercially available must be reused several times. The term “reuse” refers to a long lifespan for energy and material conservation [39].

Reuse is a great, environmentally friendly option to traditional waste management methods. Typically reuse practices are classified as more sustainable than recycling, because the processes related to disassembly, transportation, and redeployment should be much easier, and hence more environmentally benign. The benefits of reusing LIBs are important in a number of ways, including the fact that they can replace diesel or gas-powered plants as a backup to renewable sources like

wind or solar, and they have significantly lower carbon footprint (when it comes to GHG emissions, energy consumption, and local environmental pollutants) than alternative recycling options. In the advantages, the lower GHG emissions involved with the manufacture of new batteries can also be included. According to one report, a used LIB has 25% lower GHG emissions during its life cycle, compared to a unit powered by a new battery [46]. Moreover, as the cell manufacturing sector seeks to cut costs by using cheaper raw materials or using fewer of them, the price of materials available after recycling decreases, favoring reuse over recycling. This is why, according to **Fig. 35**, reuse comes first, followed by reduction.

To be exact, reuse has various meanings and different pathways, in terms of whether wasted batteries are restored or directly reused and whether they are reused on the next application [32]. The majority of reuse research (as opposed to recycling) has been conducted at the academic level, usually as part of larger industrial operations. Reuse research has primarily been conducted by European and American organizations, while China has also helped. Reuse, in comparison to recycling, is still mainly uncharted ground in terms of practical study.



Figure 35: The waste management hierarchy and range of recycling options [24].

One of the most frequently investigated areas in research is the degree to which batteries could be profitably employed to support power generation and backup operations (off-grid and backup for power in rural contexts and underdeveloped countries) where new energy storage batteries would be economically unviable. Other research appears to support the claim that reuse is a viable and economical business for less affluent users (rural and developing countries). However, this situation changes quickly —as the cost of producing new Li-ion batteries decreases, the economic incentive to reuse becomes less compelling [219].

A comprehensive study of industrial projects that have been publicized on social media was performed and historically listed in the timeline in **Fig. 36** to show how they have progressed through time. These

projects' capacity is also supplied. There are four distinct trends that can be noticed.

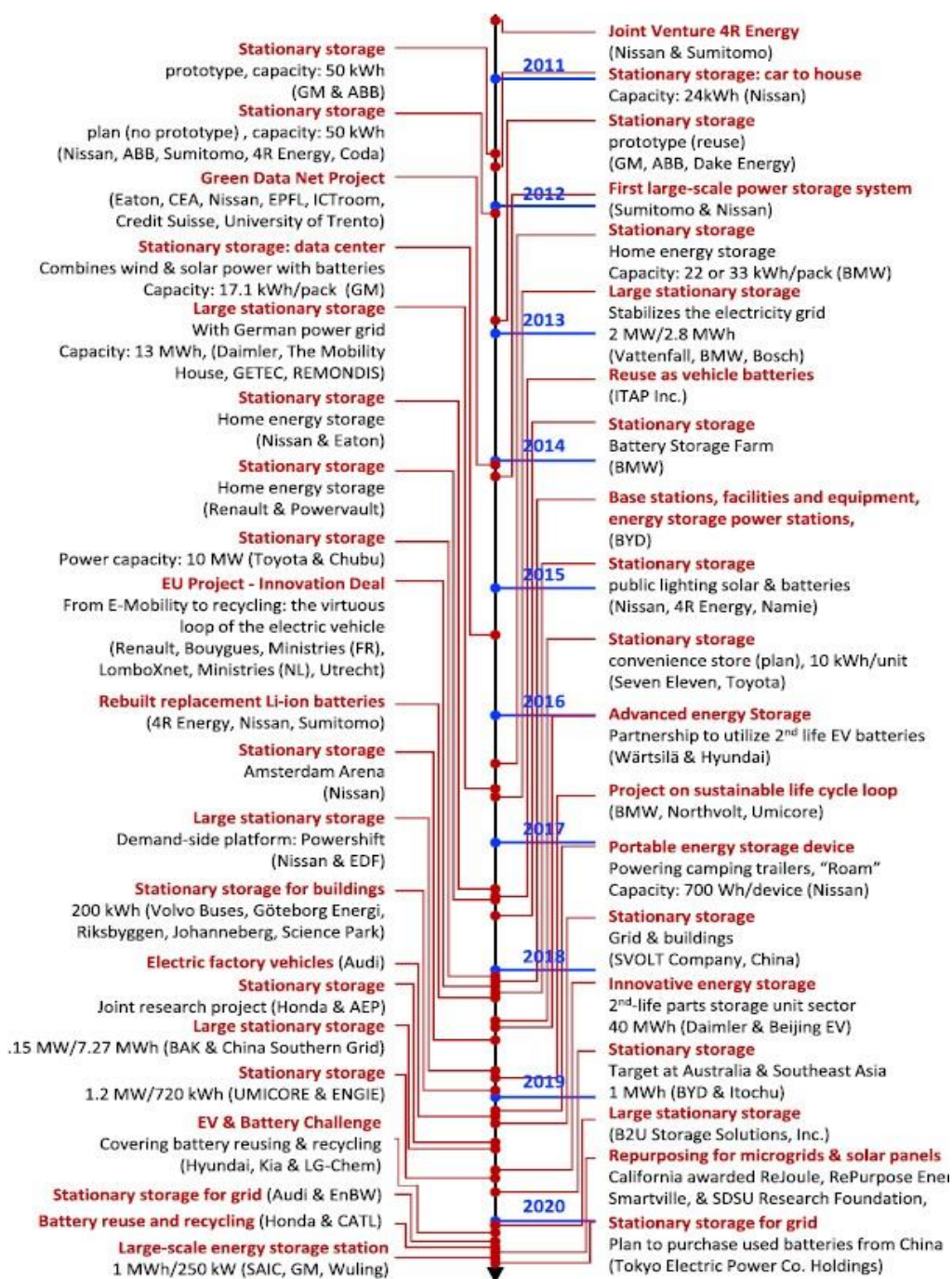


Figure 36: An historical overview of industrial projects of second-life battery applications [32].

To begin with, the number of initiatives has risen considerably in the last three years. Second, practically every major automaker has started or plans to start a second-life application project, either in collaboration with their battery provider or with the help of a third-party company. Third, large-scale stationary energy storage supply (ESS) applications are becoming increasingly prevalent, particularly for grids. Fourth, the kinds of second-life battery applications available are expanding [32].

What that historical overview fails to illustrate is that, despite the tremendous increase in volume,

the larger-scale industrialization of second-life battery applications is still hampered by a number of barriers. Tracing this perspective demands a thorough examination of the technical and economic issues. Real-world problems are more complicated because they include societal and environmental factors.

4.5.2 Technical challenges for second-life batteries

However, there are concerns regarding the overall effectiveness and appeal of basic reuse approaches. In real-world applications, there are several challenges that the Li-ion repurposing field faces. These include [46]:

- Great variety of form factors, designs, and chemistries of the existing modules and cells, which makes the development of a unified technical procedure for facilities impossible;
- Broad range of LIBs being produced, with only a few standardized regulations in place governing reuse and recycling methods and technologies, making disassembly and reassembly operations expensive and potentially dangerous;
- Continuous drop in the prices of new battery technologies;
- Lack of industry standards for battery performance; and
- Lack of legislative framework in place regarding the repurposing and disposal of LIBs, except for Europe and China.

Furthermore, there are usually no available data in the open literature regarding the detailed technical procedures, with just a few exceptions. Schneider et al. [220] reported a technique to restore small, cylindrical NiMH batteries for cellphones; additionally, Zhao [155] shared the successful results of some grid applications of EV LIBs in China in a very detailed technical process; and finally, Chung [221] carried out the procedure described in a safety standard called UL 1974 on a LiFePO₄ (LFP) reuse battery. Based on the knowledge from these researches, an exemplary approach for second-life battery applications is summarized in five major steps: (1) assessment of the wasted battery system according to historical information, (2) dismantling of the retired battery packs and modules, (3) evaluation of battery performance (mechanical, electrochemical, and safety), (4) sorting and regrouping, and (5) development of control and management approaches for second-life applications. In practice, numerous cycles of assessments and inspections are routinely conducted, some for modules and others for cells [222]. Overall, whether these stages can be accomplished effectively and efficiently determines the technical

feasibility of second-life applications of retired batteries.

4.5.3 Variables that affect the potential market for 2nd life batteries

The scale of the prospective market for second-life LIBs is expected to be based on four factors: electric vehicle sales, battery type, consumer behavior regarding battery updates, and the percentage of reused LIBs that actually make it to the market [46]. Reid et al. [223] predict that reused batteries might generate up to 1,000 GWh globally based on these parameters. Several variables could jeopardize this expansion, including:

- The market for energy storage systems: whether future legislation and public policies aid or prevent the development and use of energy storage batteries as new batteries and relevant materials become cheaper to produce - and the danger that reuse solutions become less compelling [175].
- More affordable options: the lower the production costs of first-life LIBs, the lower the profits guaranteed by second-life batteries [175].
- Cost of reusing: The cost of reusing is competitive
- Knowledge and data: there is not much detailed data and basic research on Li-ion battery lifetime and second-life capabilities.

4.5.4 Second life battery projects around the globe

The functional requirements for a retired battery's second life are typically less strict than for their first one, with lower demands on cycle and rate performances. These batteries can be reused in a variety of applications. Typical reuse applications of wasted LIBs include small-scale distributed energy storage systems (ESS) for homes, street lighting [33], low-speed electric bicycles and motor cars [155], large-scale stationary ESS for buildings as backup power supplies [34] and for renewable energy generation and grids [224], in order to stabilize the output power and to shift the peak load to ease the supply and demand imbalances of electrical loads [155], as well as portable charging devices in places where the chargers or even power outlets are unavailable. Prolonging the battery lifetime using reuse approaches, as well as lowering the total life cycle cost of batteries, are critical for the LIB industry's sustained expansion.

Examples of second-use applications for EV batteries

Electric vehicles are a key contribution to the vast numbers of spent LIBs (EV). The rapid expansion of EV demand and production (by 2040, more than 225 million EVs are expected to be sold),

particularly in the Chinese and US market, is creating millions of LIBs that will be considered unable to meet the demanding transportation duties in the future. EV owners are expected to replace their battery systems once they lose 20% of their capacity. These wasted batteries offer a huge possibility for repurposing in new applications with lower power demands than EV driving, as they can be used for another seven to ten years after their first life. According to a detailed review by Melin in 2017, by 2025 around 75% of wasted EV batteries will be used in second-life applications for several years following retirement from EVs, after which they will be recycled to recover all valuable components [225]. **Fig. 37** shows different EV LIB reuse projects around the world.

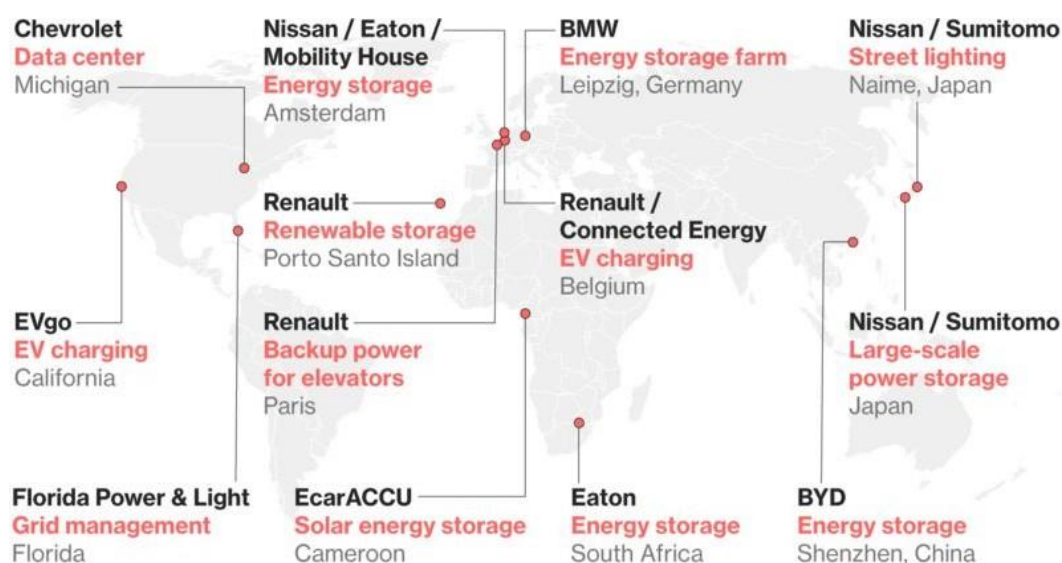


Figure 37: Second life projects for spent EV batteries around the world [33].

An important public display of reused battery applications for grid services is the 3 MW (nominal power)/ 2.8 MWh (nominal capacity) energy storage system used in 2018 at Amsterdam’s “Joahn Cruyff Arena”, (see **Fig. 38 a**). During events at the stadium, the need for different utilities (such as lighting, powering broadcasting, catering, information technology equipment, and security services) rises from a baseload of about 200 kW to more than 3000 kW, over the entire duration of the event [34].

The ESS installed at Amsterdam’s Arena is made up of 590 battery packs (from which 340 are new and 250 are second-life batteries originating from EV 24 kWh battery packs with an original capacity now slightly under 20 kWh). There are 61 battery racks that hold the batteries (**Fig. 38 b**). There is energy flowing from 4,200 rooftop photovoltaic (PV) modules, from and to the grid, and from the batteries to the stadium loads and to the grid, which is managed by four bidirectional inverters (the grid accepts and supplies only alternating current, whereas the PV modules and the batteries supply direct current only). During the night hours, the new ESS allows for effective exploitation of both solar PV and grid electricity collected at a cheap cost from the grid, which is managed by four bidirectional

inverters (the grid accepts and supplies only alternating current, whereas the PV modules and the batteries supply direct current only). During the night hours, the new ESS allows for effective exploitation of both solar PV and grid electricity collected at a cheap cost from the grid [34].

Similarly, the world's largest telecommunications tower operator in China has stopped buying lead-acid batteries since 2018. Second-life LIBs will replace all existing and quickly degrading lead-acid batteries which are installed for backup power at 98% of its 2 million telecom tower base stations (54 GWh battery storage demand). Second-life LIBs were estimated to have a cost of less than \$100/kWh in 2018, which is the same price as new lead-acid batteries, thus leading to partnership agreements with more than 16 EV and battery manufacturers. For comparison, China's telecommunication base station backup will require approximately 2 million retired EV batteries in the near future, as each tower requires roughly 30 kWh of backup battery [34].



Figure 38: a) Amsterdam's "Johan Cruyff Arena" multipurpose stadium, b) Racks with part of the 2.8 MWh energy storage system at the "Johan Cruyff Arena" [34].

Another possible application for used EV batteries would be the combination of these with grid-scale solar energy systems, as they have lower demands for power generation. The project sales will almost certainly lead to a large demand for batteries with lower costs. For example, the Sunbatt project included modelled applications, where the lifetime of the batteries was estimated to range between 6-30 years. Also, for a 40% end-of-life health state of a spent battery used for PV self-consumption, a second lifespan of 11.6 years was predicted [34].

Other examples include retired EV LIBs being reused for cooling beverages at 77-Eleven stores in Japan, powering car-charging stations in California, and storing energy for homes and grids in Europe [33].

4.5.5 Key technologies for LIB reusing

Automatic battery disassembly and inspection: The industry has agreed to use automated disassembly and inspection procedures for both the recycling and reusing processes for retired EV

batteries. However, reusing to some extent necessitates a more advanced technique because the process must be non-destructive. In the last five years, some designs for robotic disassembly of EV battery systems have been developed [226], but the majority of them have not been integrated with mechanical and electrochemical inspections, which require a high degree of robot cognition and a fully regulated inspection procedure, both of which are currently not available.

Progress in robotic intelligence and image-based object detection algorithms could provide insight into this technology. Recently a publication reported a “mobile robotic chemist” that autonomously operated for more than 8 days and performed 688 experiments considering 10 variables to effectively choose components of value and deselect the rest. However, in the real world the difficulties entail a substantially bigger number of variables and different objectives, therefore such a method still needs a lot of development to be used in battery inspections, screening, or sorting. Another problem is keeping the price of this automatic battery disassembly line relatively low. Kampker et al. [227] projected the cost to be V19.44/kWh (_\$23) in a 2016 report.

Fast screening and sorting: There is an obvious trade-off between the effectiveness and precision of the screening and sorting processes. Existing algorithms are often focused on a limited number of indications that can be immediately measured or inspected, and hence the accuracy is influenced by the indicators used. Current trends include the application of powerful statistical methods to examine large amounts of battery performance data, including model fitting of electrochemical impedance spectroscopy (EIS) data, IC data, and historical service-life data. Lai et al. [228] used a neural network to screen 5,000 cells for voltage and capacity performances, and the findings revealed a five-fold increase in efficiency over a standard full charge discharge strategy.

In addition, Zhou et al. [229] screened 240 battery cells with an accuracy of 96.8% using a support vector machine algorithm. Nissan, Sumitomo, and 4R examined all 48 modules inside each Leaf battery pack in 4 hours, processing about 2,250 packs every year. It should be noted, however, that machine learning (ML) algorithms are not always more efficient than classical techniques when it comes to data preparation and time of model training.

Nondestructive testing of batteries with acoustic waves: In order to evaluate the state of health (SOH) of batteries, a technique called acoustic emissions (AEs) has been developed. AEs are a method of passive measurement using a piezoelectric sensor to detect minor energy releases from the batteries [230]. Electrochemical activities such as corrosion, gassing, and SEI formation, as well as cracks in the active material all contribute to generating these emissions, which are measured in attojoules (10^{-18} Joules). The acoustic waveforms gathered with this method are

defined by properties like amplitude, rise time, duration, and frequency, and can compare the acoustic traces of various active materials, electrolytes, and cell designs, as well as identify deterioration mechanisms. Acoustic emissions (AEs) have recently made headway in predicting remaining useful life during accelerated-aging experiments.

Another approach for determining the SOH of batteries is a technique called acoustic time-of-flight (TOF). This is an active measurement approach in which a transducer generates an acoustic wave that interacts with the battery, and the transmitted and reflected signals are detected by a receiver. The speed of sound in the battery is measured by the change in amplitude and the time it takes to get at the receiver, which is primarily determined by the density, elastic moduli, density, and temperature of the battery components [32].

Recent advances in EIS-based and IC-DV techniques: Second-life batteries are currently sorted based on the states of various indicators, but scientific techniques such as electrochemical impedance spectroscopy (EIS) and incremental capacity-differential voltage (IC-DV) should be studied further in order to sort the batteries based on their degrading mechanism. Both strategies are currently time-consuming laboratory-based methods that will be difficult to deploy in industrial settings unless breakthroughs occur. EIS has proved a useful tool for assessing battery performance. Because of its non-destructive inspection, low cost, ease of programming, and rapid, online quality-control diagnostics, this technology is particularly beneficial for checking the functionality of retired EV batteries.

The EIS method includes modeling the battery's degradation by tracking impedance change as cycle numbers increase under various operational settings. In the open literature, there are two distinct trends toward enhancing EIS approaches. One is that data-driven techniques, such as various optimization and ML algorithms, are becoming more widely adopted. Another trend in EIS-based approaches is the development of an increasing variety of automated ECM fitting and analyzing software, which is a method used by Buteau and Dahn [231].

Data driven prognostics: Except the standard signal processing and statistical analysis approaches, machine learning (ML) approaches have also shown to be a potent data-driven tool for predicting the remaining useful life (RUL) of batteries. The battery lifespan or lifespan indications might be the output of the ML models, for example the capacity, impedance, or SOH. Finding the right input features is a more difficult task. To ensure high accuracy, traditional machine learning approaches require a significant amount of data for model training. Zhang et al. [232] recently introduced deep convolutional neural networks using ensemble learning and transfer learning to predict battery

capacity as a way to address this. Another promising approach to overcoming the challenge of large data sizes is physics-informed machine learning algorithms. Multiple techniques of merging ML algorithms with physics-based (PB) theories were summarized from various aspects in two recent articles from Finegan et al. [233] and Aykol et al [234].

4.5.6 Future areas of research and recommendations

Despite its substantial contribution to local economies, the reusing of LIBs (and other components), particularly from EV LIBs to stationary energy storage systems, is still in its early stages, as is the research on the topic [46]. The following are some of the areas where more research is needed:

- **Repackaged LIBs have the potential to supply and support large-scale energy storage systems:** The majority of studies have been focused on small grid electricity, which is typically used in private homes and buildings. There are four possibilities for systems with reused LIBs that are commercially competitive at a bigger scale: (1) Distributed energy storage (for both residential and small business use) (2) Utility-scale energy programs (an increasingly popular market field for LIBs), (3) EV charging (e-mobility will eventually reach remote places like some countries of Africa), and (4) modular-based energy systems (i.e. replacing lead batteries).
- **Piloting:** Reuse prototype case studies for community-based and microgrids in a variety of developing-country settings with varying geology and climates (Ambrose et al. 2014).
- **Capacity:** Studying the extent to which host countries are prepared to integrate reused batteries into their grids, buildings, and household power systems.
- **Research:** Research is required to determine whether vehicle battery packs and their chemistry are suitable for diverse ambient situations. A battery pack designed to perform in temperatures as low as 35 degrees Celsius may not be suitable for usage in other countries, where equipment temperatures might quickly surpass 80 degrees Celsius.
- **Social impacts:** There is a need for development of a comprehensive assessment of the environmental and social implications of spent batteries over their entire life cycle, including production, usage, and decommissioning.
- **Benchmarking:** It is required that locally robust benchmark statistics are developed to represent the current best practices in the sector.
- **Testing batteries after their first use for reuse:** Creating an ISO-style standards system for

recharging batteries could be considered.

- **Improvements in manufacturing:** The assembly process should be improved for reducing safety and environmental concerns in reuse projects.
- **Options in second life:** Reused battery systems are used for a wide range of stationary applications. The suitability and viability of different types of wasted LIBs should be evaluated.
- **Holistic approaches to improving recycling:** the extent to which LIBs can be designed to facilitate easier disassembly and collection processes.
- **Sorting, classification, and labelling procedures:** combining these phases with collection could significantly expand the market.

Chapter 5

Synopsis

Climate change mitigation and adaptation are two of the century's most pressing issues. Overpopulation and technological advancements have resulted in overconsumption of energy, in order to improve life quality. But the vast amounts of energy used by humanity have extensive consequences. Human activities, and mainly the burning of fossil fuels, have released large amounts of greenhouse gases and have progressively influenced the global climate, causing problems to the economy, human health, and whole ecosystems.

Clean energy innovations, including energy storage and conversion technologies, will be critical in addressing problems such as the exhaustion of fossil fuel and global pollution in order to ensure human society's sustainable development. Electrochemical energy storage and conversion are the most viable, environmentally friendly, and long-term clean energy solutions. Technologies like fuel cells, supercapacitors, electrochemical sensors and metal- air batteries have been or will be used in a variety of applications, including transportation and stationary and portable power supply.

Batteries are possibly the most significant and common electrochemical device on the planet. From the first battery ever made by Alessandro Volta, until current battery technological breakthroughs, a lot of work has been done from the scientific community. Specifically, lithium-ion batteries, which were introduced in the late 1900s, are the fastest-growing battery technology in recent years. Due to their numerous advantages, such as their high energy and power density, high voltage capabilities, low weight and long shelf life, they have revolutionized the energy storage field and have improved our lives. Lithium-ion batteries are currently used in a plethora of applications strongly connected to interconnectivity, mobility, energy storage and conversion. They can be found in mobile phones, laptops, electric vehicles, grid-level energy storage systems, uninterrupted power supply systems, among many other applications. This is why scientists are putting a lot of effort and focusing on the development of novel high-performance materials for these batteries.

However, the increasing relevance of lithium-ion batteries entails challenges for waste management and natural resources. With the current growth of electric mobility, the demand for more efficient and sustainable LIBs is expected to increase in the next years, exceeding the production. The price of scarce elements like cobalt, nickel, and lithium, rises as a result of this

increase in demand. The mining, extraction, and purifying of these metals to battery-grade quality are all extremely harmful to the environment and the natural resources will be depleted. Despite the considerable work necessary to manufacture lithium-ion batteries, the precious materials involved are ending up to landfills and become irrecoverable after only a few years. To make matters worse, electronic waste, which includes LIBs, is one of the most polluting on the planet, further harming the ecosystem.

As a result, battery recycling and reusing is both a financial and an environmental necessity, contributing to societies' adaptation to a circular economy. At the time of disposal, most cells still hold more than 80% of their original capacity. Therefore, they can be used in lower energy-demanding second-life applications, including low-speed vehicles or residential and industrial energy storage.

At the end of their useful lives they can be dismantled and recycled. It is at this point, that the battery's state is re-evaluated in order to determine the best recycling method. Pyrometallurgy, hydrometallurgy, as well as direct recycling, are the three main recycling methods. The goal of pyro- and hydrometallurgical processes is to recover the raw materials used in batteries, particularly metals, so that they can be reused in the manufacture of new cells or in other applications that require the same metals. These techniques provide for high metal recovery rates (over 90%), but they do so at the expense of large energy and hazardous materials consumption, and include multiple steps in the process. Direct recycling method, on the other hand, focuses on refurbishing battery materials, such as the cathode, in order to reassemble them in new batteries. This way, there is no need to manufacture a new battery component in this instance, lowering overall energy and hazardous material usage. This method, however, leads to reduced battery performance. As a result, a combination of this method is needed, in order to acquire an efficient and sustainable recycling path. Furthermore, newer technologies are being developed on a daily basis to improve recycling and reusing technologies, resulting in LIBs' long lifespan for energy and material conservation.

The great variety of cell designs in terms of materials and structure is one of the challenges facing LIB recycling. Because of this variability, developing a genuine "universal" recycling and reusing process is extremely difficult. This is one of the domains where government policies can possibly help to encourage and support proper LIB disposal and recycling. Furthermore, customers ought to be aware of the economic and environmental benefits of recycling, and businesses need to design a closed loop supply chain. In this way, the still-developing recycling and reusing infrastructure will be able to grow and sustainably meet a big part of lithium-ion battery demand in the future.

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