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FAILURE DIAGNOSTICS AND RECYCLING OF LITHIUM-ION BATTERIES

by

NIKOLAOS KOILAKOS

Supervisor: Professor Panagiotis Tsiakaras

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Approved by the Members of Examination Committee:

First Examiner (Supervisor)	Dr. Panagiotis Tsiakaras Professor Department of Mechanical Engineering University of Thessaly
Second Examiner	Dr. Alexis Kermanidis Professor Department of Mechanical Engineering University of Thessaly
Third Examiner	Dr. **A**ngeliki Brouzgou Assistant Professor Department of Energy Systems, Faculty of Technology University of Thessaly

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Με την διεκπεραίωση της παρούσας διπλωματικής εργασίας, ολοκληρώνεται ο κύκλος σπουδών μου. Ένα ταξίδι γεμάτο προκλήσεις, αποτυχίες, επιτυχίες και πληθώρα γνώσεων. Θα ήθελα να ευχαριστήσω θερμά τον καθηγητή και επόπτη κύριο Παναγιώτη Τσιακάρα για τη στήριξη, γνώση και βοήθεια που μου προσέφερε κατά τη διάρκεια συγγραφής της εργασίας αλλά και για την ευκαιρία που μου έδωσε να εντρυφήσω σε ένα τόσο ενδιαφέρον αντικείμενο.

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ΠΕΡΙΛΗΨΗ

Η διπλωματική με τίτλο ‘Διάγνωση Αστοχιών και Ανακύκλωση Μπαταριών Ιόντων Λιθίου’ επικεντρώνεται στη διάγνωση των αστοχιών των μπαταριών ιόντων λιθίου και την ανακύκλωση αυτών των μπαταριών για την αντιμετώπιση της αυξανόμενης ζήτησης για βιώσιμα συστήματα αποθήκευσης ενέργειας. Η έρευνα περιλαμβάνει αρχικά μία ανασκόπηση στους νόμους της ηλεκτροχημείας και τις εφαρμογές της σε ηλεκτροχημικές συσκευές καθώς και τη μηχανική των μπαταριών ιόντων λιθίου. Έπειτα η διατριβή ερευνά τις τεχνικές διάγνωσης για τις μπαταρίες ιόντων λιθίου και τους περιορισμούς τους. Επιπλέον εξετάζει την ανάπτυξη αποδοτικών και βιώσιμων διαδικασιών ανακύκλωσης και την επίδραση διαφόρων παραγόντων στην απόδοση της ανακύκλωσης. Συνολικά η διπλωματική εστιάζει στη βιώσιμη χρήση των μπαταριών ιόντων λιθίου με τη βελτίωση της διάγνωσης των αποτυχιών τους και την πρόταση βιώσιμων διαδικασιών ανακύκλωσης.

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ABSTRACT

"Failure Diagnostics and Recycling of Lithium-Ion Batteries" is a thesis that focuses on the diagnosis of failures in lithium-ion batteries and their recycling to address the increasing demand for sustainable energy storage systems. The research includes an overview of the laws of electrochemistry and their applications in electrochemical devices as well as the engineering of lithium-ion batteries. Hence, it investigates diagnostic techniques for lithium-ion batteries and their limitations. Additionally, it examines the development of efficient and sustainable recycling processes and the impact of various factors on recycling performance. Overall, the thesis aims to contribute to the sustainable use of lithium-ion batteries by improving their failure diagnosis and suggesting sustainable recycling processes.

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CHAPTER 1

INTRODUCTION

With the impending threat of global warming, a rapidly increasing global population, and expanding energy demands, major concerns have been raised regarding the future of our energy system. Energy is crucial for our century. It provides lighting, heating, cooling as well as transportation, and is essential for all modern tools of communication, entertainment, and information. The list of its uses is endless. Since the Industrial Revolution, the energy demand has grown exponentially, fueled by the increasing wealth and population of countries. However, this growth in global energy consumption, particularly the dependence on fossil fuels, undermines many climate and environmental aspects. Thus, climate change has become the biggest challenge and priority of our era.

Artificial global warming and other environmental consequences from fossil fuel overuse are responsible for climate-related physical and socio-economic effects. In addition, a significant number of deaths are attributed each year to air pollution. Hence, renewable energy and sustainable development have been a challenge for scientists since the late 20th century to decarbonize much of our energy use. **Figure 1** graphs the global energy consumption and the fossil fuel and renewable energy dependence from 1800 onwards [1],[2].

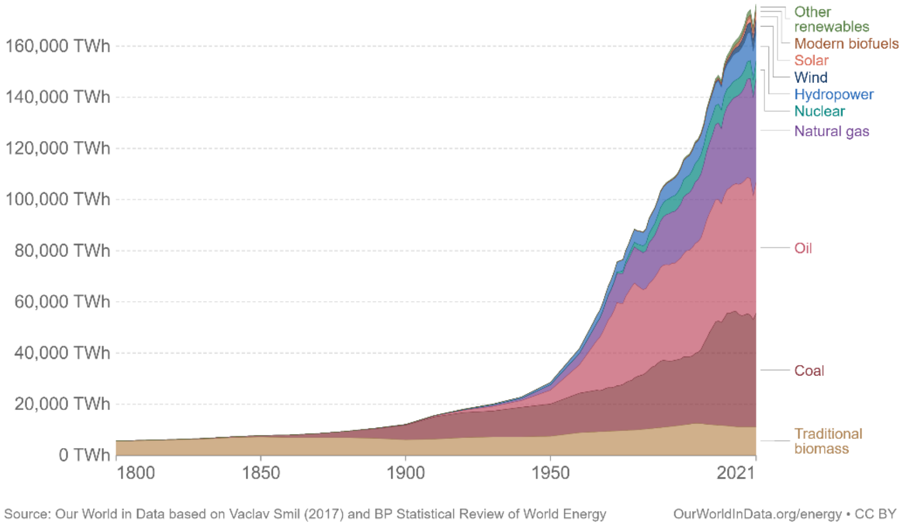

Figure 1: Global primary energy consumption chart from 1800 to 2021 [1].

Renewable energy technologies generate marketable energy by converting natural phenomena into useful clean energy. However, to amplify the electric grid flexibility, and balance the electricity production and consumption, efficient and effective energy storage technology is indispensable [3].

Energy storage development is a dominant factor in the energy field and its demand increases simultaneously with the need for conversion to electricity. Although with the privilege of gravity, we can store electricity through hydro and pumped hydropower, chemical bond forces have proved to be a powerful type of energy storage. These forces are involved in electrochemistry and can be used to store bulk electricity through batteries and hydrogen storage. The most famous electrochemical storage technology is Lithium-ion Batteries, which is the main topic of this thesis [2].

Lithium-ion batteries are taking over the battery market, being the core storage technology for small consumer electronics, renewable energy storage, power tools, medical devices, or even in the transportation sector for electric vehicles and aerospace applications. This is due to their remarkable properties such as high specific energy, small size, good capacity, low self-discharge rate, and lack of memory effect, etc. [4].

In this paper, the engineering behind lithium-ion batteries will be discussed in depth. Hence, diagnostic techniques and their limitations as well as the development of efficient and sustainable recycling processes and performance will be investigated.

Before examining the mechanics and challenges that lithium-ion batteries face, the following chapter (**Chapter 2**) will introduce us to energy use and environment interaction as well as the fundamentals of electrochemistry and electrocatalysis. Thereafter, some basic principles about electrochemical devices will be provided such as the features and classification of batteries leading us to **Chapter 3**, which focuses on the main part of this thesis, the lithium-ion batteries.

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CHAPTER II

ENERGY AND ELECTROCHEMISTRY FUNDAMENTALS AND APPLICATIONS

2.1 Climate Change and Renewable Energy

Climate change is not only a threat to nature but also to the ability of humankind to live in nature. Before analyzing the principles and applications of electrochemistry it is very important to make a reference to climate change, which is the biggest challenge of our era, as well as to renewable energy. Climate change refers to long-term shifts in climate patterns by rising temperatures in the atmosphere. Global warming is the driving force of climate change. In the impending section, the causes of global warming will be discussed.

2.1.1 Causes of Global Warming

Solar radiation is electromagnetic radiation emitted by the sun. Thirty percent of solar radiation is reflected in space. This reflective capacity is referred to as Earth's planetary *albedo*. Seventy percent may be absorbed by the atmosphere, clouds, or the surface. To maintain thermodynamic equilibrium this amount must be radiated back to space. This equilibrium is complicated by the presence of greenhouse gases, mainly carbon dioxide (CO_2), methane (CH_4), and nitrous oxide that absorb some of the escaping radiation and emit it equally in every direction. The amount of radiation emitted downward towards the earth's surface and lower atmosphere increases the surface temperature to maintain thermodynamic balance [5].

The most significant and abundant greenhouse gas is carbon dioxide with a high percentage of concentration in the atmosphere, accounting for approximately two-thirds of greenhouse gases. Natural sources of CO_2 are balanced by a set of physical, biological, and chemical processes, called *sinks*, that remove the emissions. These natural sinks include terrestrial vegetation (photosynthesis), oceanic processes, and others. Amplified carbon load from human activity exceeds the offsetting capacity of natural sinks, being equal to approximately 3 percent of the total emissions of CO_2 by natural sources. Carbon dioxide is accumulated in the atmosphere by burning fossil fuels, principally oil, coal, and secondarily natural gas. These fossil fuels provide heating, transportation, the production of electricity and cement, as well as many other industrial applications. Today the concentration of CO_2 has reached 420 ppm while scientists consider the safe level to be 350 ppm [5].

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Figure 2 illustrates the growth of concentration over the last 800,000 years articulating anthropogenic interference.

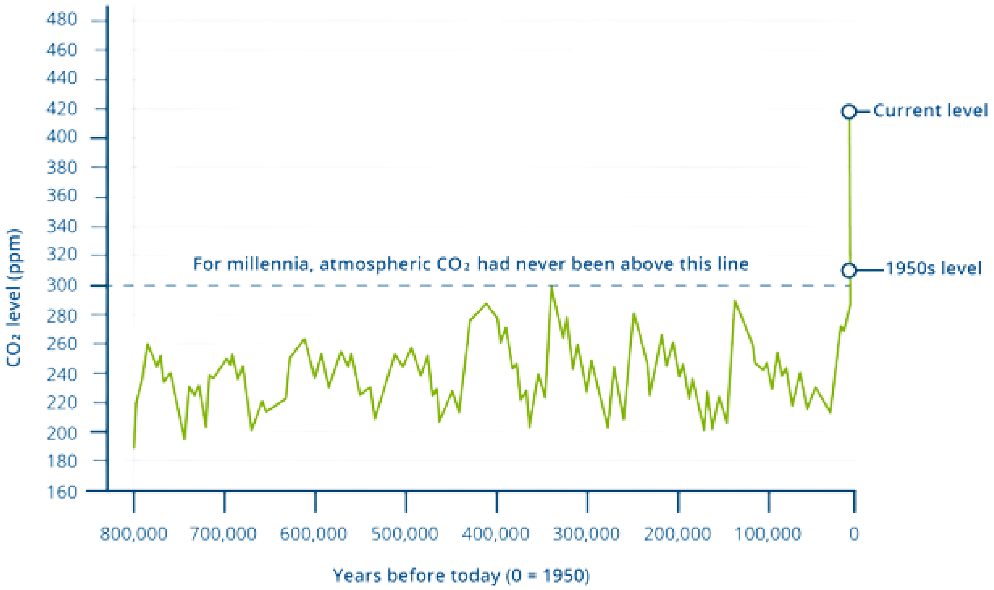

Figure 2: Fluctuations in the concentration of atmospheric CO_2 over the last 800,000 years [6].

Methane is more potent than CO_2 due to the greater radiative forcing produced per molecule. However, it exists in far lower concentrations than CO_2 and has a smaller residence time (10 years for methane, and hundreds of years for carbon dioxide). Again, human intervention is increasing the CH_4 concentration faster than it can be offset by natural sinks. Humanity is responsible for 70 percent of the total amount of emissions, leading to substantial increases in concentration over time. Some of the emission sources include agricultural and farming activity, biomass combustion, as well as the burning of coal and oil [6].

By the end of the century, scientific data indicate that the global temperatures will increase by around 4° to 5° C. In the next chapter features of climate change as well as the impacts will be analyzed.

2.1.2 Climate Change Indicators and Impacts

In addition to rising temperatures some other indispensable indicators of climate change include:

- **Ocean warming**: Oceans that have a great heating capacity are warming up at a rapid pace while absorbing huge amounts of heat.
- **Rising global sea levels**: In the last 100 years while oceans are getting warmer, they expand, increasing the global mean sea level by around 20cm.

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- **Melting of ice sheets and glaciers and shrinking sea ice**: Temperature increase has an important impact on ice levels reducing the mass of ice sheets, further contributing to bigger sea levels, and threatening the biodiversity of arctic regions.
- **Ocean acidification**: Oceans act as natural sinks since the amount of CO_2 they absorb is intensified, and surface water PH is depleted due to the ocean acidity increase, threatening marine life [6].

Even a small increase in average global temperatures can make significant changes in the climate. These changes have crucial impacts equally important on ecosystems and the socioeconomic interface.

All the indicators discussed previously are a big threat to ecosystems and biodiversity. One of the most endangered ecosystems is coral reefs, which suffer from temperature changes. Scientists predict that by the time global average temperatures rise 2° C, only 1 percent of the world's coral species will remain. Furthermore, extreme weather events such as wildfires and prolonged droughts destroy not only habitats for fauna and flora, reducing their biodiversity but also forests releasing large amounts of CO_2 into the atmosphere.

The consequences of climate change also affect societies. Deprived and vulnerable communities that lack essential infrastructure services, live in exposed environments, and depend on natural capital are most likely to get hit by considerable climate changes. Nevertheless, economic shifts and socio-political disruptions such as unstable financial markets and climate-related migration will affect societies on a global spectrum [6].

Fossil fuel dependence can be very devastating. Thus, renewable energy sources are very important to avoid the impacts of climate change and finally decarbonize our energy system. In the next sector, renewable energy sources and technology are classified and analyzed.

2.1.3 Renewable Energy

Renewable energy is the harnessing of energy produced by natural phenomena. Solar radiation is the cornerstone of every renewable energy source on the planet and solar energy can supply thousands of times what we require. The utilization of these energy sources provides electricity while depleting the fossil fuel dependence. Thus, renewable energy is a significant step in the mitigation of climate change. In **Figure 3** the levelized cost of energy in 2021 is graphed showing that some renewable energy technologies like selected solar PV and onshore wind energy are cost-competitive with conventional technologies. Then, the primary renewable energy sources are presented.

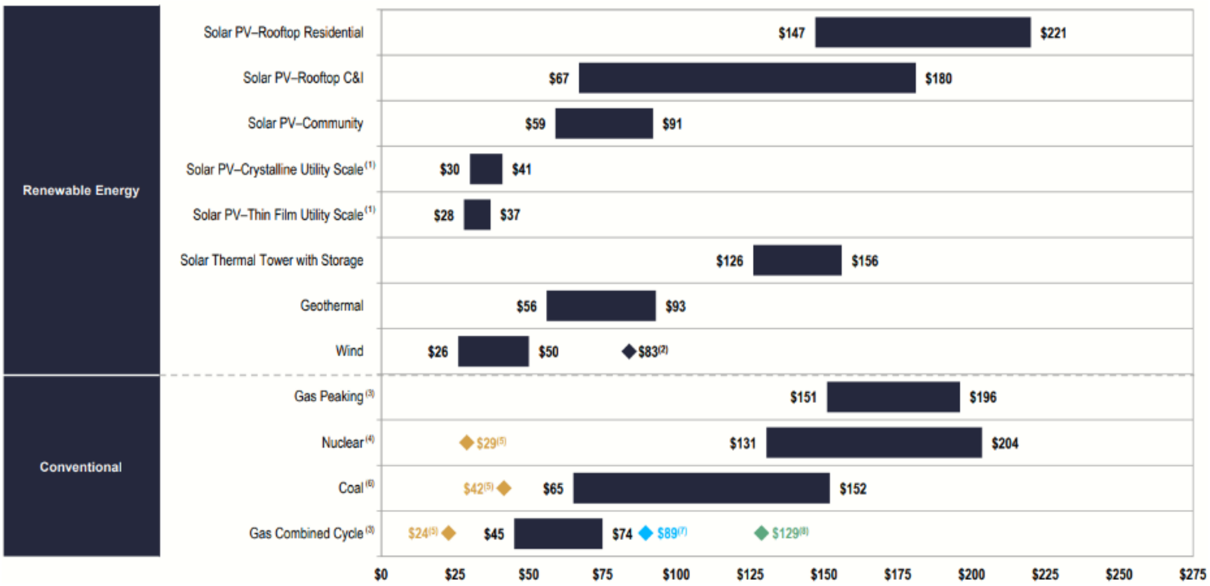

Figure 3: Levelized cost of energy comparison ($/MWh) [7].

Wind Energy

Wind energy alone can provide enough for human needs every year. The source of wind energy is heat from the sun. Differential heating on land and sea causes the wind. Some important features of wind like wind shear and surface roughness show that wind farms are more efficient away from cities as well as in offshore regions. The technology that harnesses wind energy is wind turbines. Wind turbines have a considerable lifespan of 20-25 years and range from 5-15 MW. Offshore wind technology is expected to increase its efficiency by 25% soon, reaching an amount of 20 MW power. Intermittency is the biggest challenge of wind turbines. However, strong operating regional grids and rapidly developing battery technology can assist. In the last 10 years onshore and offshore wind energy have contributed to an important percentage of energy consumption and the cost of wind energy is expected to decline further over the next decade by 20-40 %.

Solar Energy

Humanity needs less energy every year than the amount of solar energy the sun provides in an hour. Engineers harness the sunlight and convert it to clean energy for buildings, machinery, and more. The most common solar technology is the photovoltaic which converts solar radiation to electricity. Silicon-based solar photovoltaic panels are the only technology that can generate large-scale commercial electric power without a rotating generator. They produce clean energy without emissions, and they are fossil fuel and water-independent for power generation. Additionally, they make no noises, have no moving parts, and can be located where the power is needed or directly tied to the power grid. In recent years, solar energy technology has made remarkable progress, to the

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extent that it is now being used to power critical missions in outer space, such as the Mars Rover, the Hubble Telescope, and the International Space Station [8].

Hydropower

Hydropower is the largest source of renewable energy in the world. The ancient Greeks harnessed the energy from rivers and streams using wooden wheels to grind grain and make bread more than two thousand years ago. Presently, we still utilize this waterpower to produce inexpensive and carbon-free electricity to power a wide range of industries. It is a mature and widely used technology with very high efficiency. However, large initial costs and environmental issues are only two of the many challenges that make the future of hydroelectricity uncertain. It is remarkable to mention that hydroelectric storage technology is dominating in large-scale energy storage [8].

Other renewable energy sources include **Biomass**, where agricultural and forest waste, municipal solid waste, landfill gases, and more are used to produce biofuels and electricity. It's important to note that this assumes sustainable harvesting and management practices are used, such as replanting and managing the rate of harvesting to allow for regrowth. **Ocean energy** derives from waves, tides, currents, and thermal gradients. Finally, **Geothermal energy** is heat energy that is generated and stored within the Earth's crust and can be used to produce electricity and heat buildings [8].

Intermittency is one of the biggest challenges for renewable energy technologies. Thus, energy storage is critical for the energy system. Batteries, particularly lithium-ion batteries, are expected to dominate energy storage technologies while others have specialized roles. In the next sector electrochemistry and electrocatalysis principles as well as some electrochemical devices will be explored for a fundamental introduction to lithium-ion batteries.

2.2 Fundamentals of Electrochemistry

The science of electrochemistry is a branch of chemistry concerned with the relation between electrical currents and chemical reactions. Electrochemistry can be studied through a device called *Electrochemical Cell* where chemical reactions generate electrical energy and vice versa. In 1800, Alessandro Volta invented the first battery by assembling a voltaic pile with stacks of copper and zinc disks separated by paper soaked in acid solutions. By 1835, Michael Faraday had already defined the basic instruments of an electrochemical device: anode, cathode, electrolyte, ion, and electrode [9]. Nowadays, electrochemistry has many important applications for energy storage on electronic devices but is also essential for carrying out non-spontaneous chemical reactions for a variety of technological aspects, such as the production of hydrogen through the electrolysis of water.

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The chemical reactions taking place in an electrochemical cell are called oxidation-reduction reactions. These electrochemical changes involve electron transfer to or from a molecule or ion. The reaction can occur spontaneously by releasing chemical energy or non-spontaneously by the application of an external voltage. In detail, oxidation is the process of a molecule or ion losing electrons in contrast to reduction which is the process of gaining electrons. The skeleton reaction combines both processes whereas the half-reaction method gives a more detailed analysis of each separately. The general forms of these half-reactions are [10]:

$$\text{Reduced species} \rightarrow \text{oxidized species} + ne^{-}$$

$$\text{Oxidized species} + ne^{-} \rightarrow \text{reduced species}$$

2.2.1 Voltaic Cells

Voltaic cells, also known as galvanic cells, are electrochemical cells that convert chemical energy to electrical current through spontaneous oxidation-reduction reactions. A voltaic cell consists of two half-cells in which metal strips, called *electrodes*, are added to an *electrolyte*. The electrolyte bulk solution prevents the passage of electrons but allows the flow of ions. The half-reactions that occur in each half-cell are separated so that current can flow through an external wire. The oxidized electrode is called *anode* while the reduced *cathode.* A *salt bridge*, a tube of an electrolyte in a gel connecting the two half-cells, is responsible for preventing the mixing of the two solutions while keeping them electrically neutral [10]. An illustration of a voltaic cell, including copper and zinc electrodes, is presented in **Figure 4.**

Today the framework of many kinds of batteries depends on the voltaic cell principles. They include batteries for a variety of electronic devices, mobile phones, calculators, and watches, as well as larger batteries to power electric cars or communicator satellites [10].

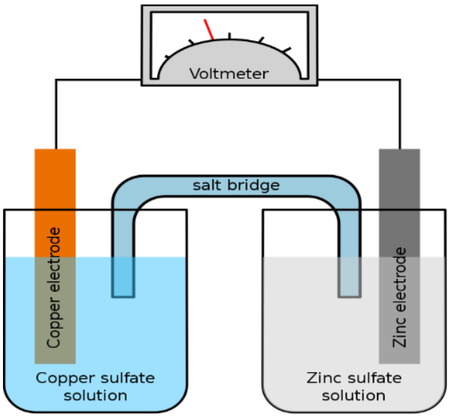

Figure 4: Zinc-copper voltaic cell illustration [11].

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2.2.2 Cell Potential

In a voltaic cell, two metallic electrodes carry out oxidation and reduction reactions spontaneously, making the flow of electrical current possible. The driving force of the cell reaction is called *cell potential* or *electromotive force (emf)*, or $E_{cell,}$ which is the maximum potential difference between the electrodes. The unit of cell potential is volts (V). The maximum electrical work that we can obtain from the cell for molar amounts of reactants is:

$$W_{e,max} = -nFE_{cell}$$

Where n is the number of moles of electrons transferred in the cell equations and F is the Faraday constant, 9.6485×10^4 C/mol e^-. The anode oxidation potential and the cathode reduction potential contribute to the composition of cell potential. With a table of reduction potentials, a list of oxidizing agents can be obtained and thus, a way to calculate the cell potential. By convention, reduction potentials are used to measure cell potentials, as the anode oxidation potential of a half-reaction equals the negative value of the cathode reduction potential for the reverse half-reaction, which is a reduction. These reduction potentials are called electrode potentials, denoted by the symbol E. Then

E_{cell} = reduction potential + oxidation potential and $E_{cell} = E_{cathode} - E_{anode}$

To tabulate electrochemical data more efficiently, thermodynamic standard-state conditions (gas pressures at 1 atm, temperature usually at 25^o C, and solute concentrations at 1 Molarity) are chosen. A cell operating under standard state conditions is called the standard cell potential, E^o_{cell}. The standard electrode potential, E^o, is the electrode potential under standard-state conditions vs the hydrogen standard electrode potential (SHE).

The maximum useful work of a reaction is equal to the Gibbs free energy ΔG of the reaction, or the We, max = G. The subsequent association provides the standard change in free energy, ΔG°, and the free energy (G) for any given reaction:

$$\Delta G = \Delta G^o + RT \ln Q$$

where Q is the thermodynamic reaction quotient. Substituting $\Delta G = -nFE_{cell}$ and $\Delta G^o = -nFE_{cell}{}^o$ into the previous equation, the **Nernst equation** is obtained:

$$E_{cell} = E^o - \frac{RT}{nF} \ln Q$$

The Nernst equation demonstrates that as the cell reaction progresses, the cell potential (Ecell) decreases. This decline is a result of the increasing concentrations of products and decreasing concentrations of reactants as the reaction proceeds within the voltaic cell.

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2.2.3 Electrolytic Cells

An electrolytic cell is an electrochemical cell in which chemical reactions are driven by electric current. The process of producing electrical changes in the electrolytic cell is called electrolysis. Electrolytic cells consist of two electrodes, an anode, where oxidation occurs, and a cathode, where reduction occurs, that are immersed in an electrolyte solution. When a voltage is applied across the electrodes, electrons flow from the anode to the cathode, and ions in the electrolyte solution move toward their respective electrodes.

The electrolyte solution typically contains ions that will participate in the reaction. For example, in the electrolysis of water, the electrolyte solution is water, and the ions are H+ and OH-. When a voltage is applied across the electrodes, the H+ ions are attracted to the cathode, where they gain electrons and form hydrogen gas. At the same time, the OH- ions are attracted to the anode, where they lose electrons and form oxygen gas. Electrolytic cells are used in a variety of applications, such as electroplating, metal refining, and the production of chlorine, lithium, and other industrial chemicals [10].

2.3 Electrocatalysis

2.3.1 The Science of Catalysis

Catalysts provide an alternate reaction mechanism by decreasing the activation energy and achieving an increased reaction rate. A catalyst can change the kinetics but not the thermodynamics of a reaction. Hence, the free energy and enthalpy of the uncatalyzed reaction equals that of the catalytic reaction while both forward and reverse reactions accelerate [12]. *Katals* are a common unit to measure catalytic activity. One Katal refers to an enzyme catalyzing the reaction of one mole of substrate per second. [13].

Catalysts allow a reaction to occur at lower energy costs and affect the reaction without getting consumed. If the recycling and the reaction of the catalyst is immediate only small amounts often suffice [13]. The reaction rate can be expressed as the molar concentration increase of the product reacting per unit time or the molar concentration decrease of the reactant per unit time. The catalyst increases the rate of the reaction either by increasing the frequency of molecule collisions with proper orientation or by decreasing the Activation Energy, which has the most dramatic effect [10].

A lower activation energy that leads to a reaction rate increase can be observed by the Arrhenius equation. The equation expresses the dependence of the rate constant on temperature as well as the reaction activation energy [10],[12]:

$$K = A \cdot \exp\left(\frac{-Ea}{R\,T}\right)$$

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Ea: Activation Energy

R: Gas constant

T: Absolute Temperature

A: Frequency Factor (frequency of collisions with proper orientation)

K: Rate constant

2.3.2 Classification of Catalytic Processes

Catalytic processes can be classified into three categories: **Homogeneous Catalysis, Heterogeneous Catalysis, and Enzyme Catalysis** [10].

A **Homogeneous Catalyst** is present in the same phase as the reacting species. It interacts with the reactant producing an intermediate substance, which then decomposes. An important example is the destruction of the ozone because of catalysis. Chlorine atoms formed by chlorocarbons, or chlorofluorocarbons catalyze the breakdown of ozone, which is responsible for absorbing biologically destructive, short-wavelength ultraviolet radiation in the form of a stratosphere layer [12]. The ozone breakdown process as well as the activation energy barriers are illustrated in **Figure 5**.

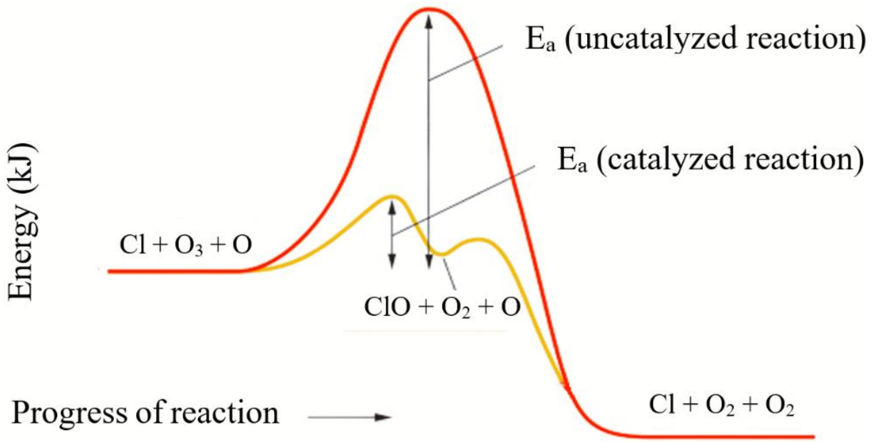

Figure 5: Depiction of the impact on the activation energy of the ozone breakdown reaction, due to catalytic activity [10], [104].

A **Heterogeneous Catalyst** is present in a different phase than the reactants, usually solid. This catalytic process has at least four steps [12]:

1. Adsorption: The reactant molecules adsorb or stick onto the surface of the catalyst.
2. Activation: The adsorbed reactant molecules form chemical bonds with the catalyst surface.
3. Reaction: The adsorbed reactant reacts to form the desired products.
4. Desorption: The products desorb or detach from the surface of the catalyst, leaving the surface available to adsorb new reactant molecules.

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Enzyme Catalysis is the catalysis process of biological systems. Enzymes are mostly composed of protein molecules and can catalyze the conversion of thousands of reactant molecules into products in just one second. Enzymes are highly specific and can only catalyze a particular reaction on a specific substrate or a specific type of substrate [10].

2.3.3 Introduction to Electrocatalysis

An Electrocatalyst is a catalyst that engages in electrochemical processes. It operates on electrode surfaces or is the electrode surface itself. Electrochemical reactions require a certain amount of energy to occur, known as the activation energy. This energy is directly related to the potential or voltage at which the reaction takes place. By modifying this voltage, electrocatalysts can lower the activation energy required for the reaction to occur, thus increasing the reaction rate. The transfer reaction that occurs at the electrode-electrolyte interface is dependent on the nature of the electrode material. In other words, the composition and properties of the electrode material can greatly influence the rate and mechanism of the electrochemical reaction taking place [14].

Electrocatalysis is a vital process in fuel cells and electrolysis devices, as it enables the conversion of chemical to electrical energy and its storage. In electrocatalysis, chemical bonds are broken and formed by the transport of electrons and ions at electrode surfaces. This process is crucial for the efficient functioning of these devices. Electrocatalytic reactions that facilitate chemical or electrical interconversions are necessary for the development of ecologically acceptable and renewable energy technologies that contribute to the long-term infrastructure for energy. Electrocatalytic activity occurs at both the cathode and anode of fuel cells and electrolysis devices, and the performance of these devices is significantly affected by the materials used for electrocatalysis, their composition, and interfacial structures. Therefore, developing effective electrocatalysts is essential for the advancement of a sustainable energy future [15], [105].

There are three core factors to evaluate electrocatalysts [15]:

Activity: The ability to catalyze an electrochemical reaction, which is typically measured by its current density or reaction rate under a given set of conditions.

Stability: The ability to maintain its catalytic activity and efficiency over time under the electrode reaction conditions.

Selectivity: The capability of an electrocatalyst to catalyze a specific reaction or produce a specific product with high efficiency and minimal side reactions. A selective electrocatalyst favors a particular electrochemical reaction or product formation.

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2.3.4 Sabatier Principle

Sabatier's principle is applied in both heterogeneous catalysis and electrocatalysis, suggesting that the ideal catalytic surface has an optimized adsorption strength for reaction intermediates that is neither too strong nor too weak. This principle is used as a key criterion in designing and screening electrocatalytic materials, represented by a "Volcano Plot" curve showing the qualitative dependence of electrocatalytic activity on the chemisorption strength of reaction intermediates.

Moderating the interaction between catalyst and reactants to an appropriate level of adsorption strength is essential for catalytic activity, as **Figure 6** indicates.

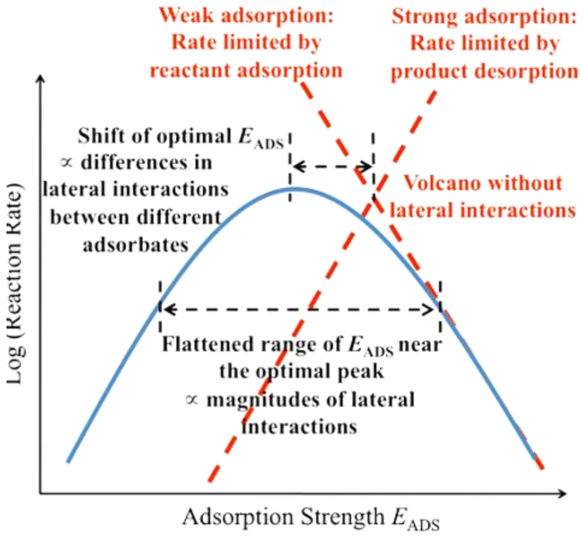

Figure 6: The relation between the reaction rate and the adsorption strength for ideal electrocatalytic material selection, illustrated by a Volcano Plot [16].

Weak interactions result in low reaction rates due to poor binding, whereas strong interactions can prevent the desorption of products formed on the catalyst [16].

2.3.5 Electrocatalytic Materials, Recent Advances and Applications

Throughout the years noble-metal-based compounds tended to be the most efficient electrocatalysts, especially in fuel cell technology. For instance, Pt is known for its excellent catalytic properties in reactions such as the oxygen reduction reaction (ORR) or Pd as an efficient catalyst for the oxidation of hydrogen. However, noble-metal-based catalysts have many limitations and drawbacks such as high cost and scarcity. Hence, fuel cells and transition metal-air batteries require low-cost, durable, and efficient catalytic materials to meet the energy demands [15], [28].

Electrocatalysts based on carbon nanomaterials are a recent advance in the industry. Research from 2009 indicates that earth-abundant Carbon-based Metal-free Electrocatalysts or CMFECs can replace traditional catalytic materials for electrochemical reactions, crucial for clean electricity generation

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and renewable energy technologies. Graphitic carbon materials, including conventional porous carbons, graphene, and carbon nanotubes doped or co-doped with heteroatoms, are several catalytic materials that reveal a solid performance in catalytic and energy processes. More precisely, these energy applications encompass water splitting, to generate hydrogen fuel and oxygen gas through Hydrogen Evolution Reactions (HER) and Oxygen Evolution Reactions (OER), Oxygen Reduction Reaction (ORR) for fuel cell technology, electrochemical reduction of CO_2 and N_2 as well as electrochemical reactions in dye-sensitized solar cells **(Figure 7)** [17].

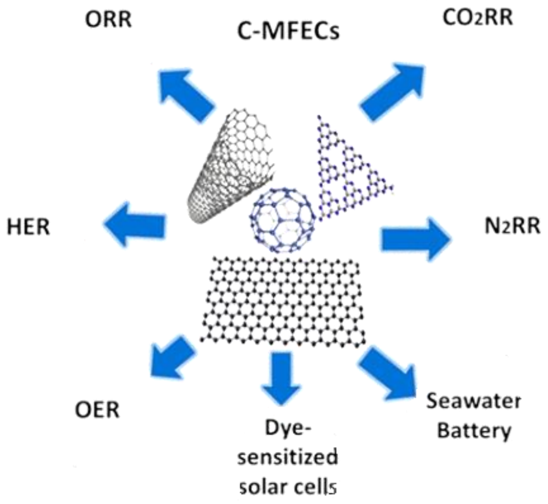

Figure 7: Catalytic Applications of Carbon-Based Metal-Free Electrocatalysts [17].

2.4 Hydrogen and Fuel Cell Engineering

Hydrogen, the most abundant element in the universe, has the highest gravimetric energy density, generating 119.97 kJ/kg. It is strongly believed that hydrogen technology will dominate the future of the energy sector due to its applications in renewable energy, energy storage and generation. Fuel cells are a significant and recent technology, which converts chemical energy directly into electricity. The pivotal difference with battery technology is that in fuel cells there is no fuel depletion, achieving a greater lifespan and efficiency duration. Most fuel cells operate directly by using hydrogen. However, other types are fueled by hydrogen-rich compounds such as ethanol, methanol, and hydrocarbon fuels. A fuel cell is fueled continuously to the anode and the cathode, usually with hydrogen and oxygen respectively. In the anode, the negative electrode, and the cathode, the positive one, oxidation-reduction reactions occur. An electrolyte (membrane) not only separates the two electrodes and reactions but also isolates the ion transfer. Hence, the electrons that break free due to electrochemical reactions in the catalyst's surface, cannot penetrate the membrane and get transferred from the anode to the cathode via an electric circuit, generating electricity [18],[20-25], [101].

Six core types of fuel cells are distinguished by the electrolyte they use:

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

2.4.1 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

PEMFCs are among the most well-known and widely used fuel cells. They have gained significant attention due to their wide range of applications. They are suitable for transportation, portable power applications, backup power systems, remote power generation, renewable energy storage, military, and several other applications. Their efficiency fluctuates between 40% and 70% with operating temperatures between 50° and 220°. PEMFCs commonly use a Nafion membrane as an electrolyte, which is a thin polymer membrane. The electrodes are constructed with noble metals, and coated with a catalyst material such as Platinum, Iridium, and Ruthenium. The electrochemical reactions that occur when hydrogen is the fuel are:

$$\text{Anode (-): } H_2 \rightarrow 2H^+ + 2e^-$$

$$\text{Cathode (+): } \tfrac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

In the anode, hydrogen splits by means of the catalyst and forms electrons and protons (H^+). Protons are transferred through the electrolyte and electrons through the external circuit to the cathode where they react with oxygen and form water. This process as well as the key components of a polymer electrolyte membrane fuel cell are depicted in **Figure 8**.

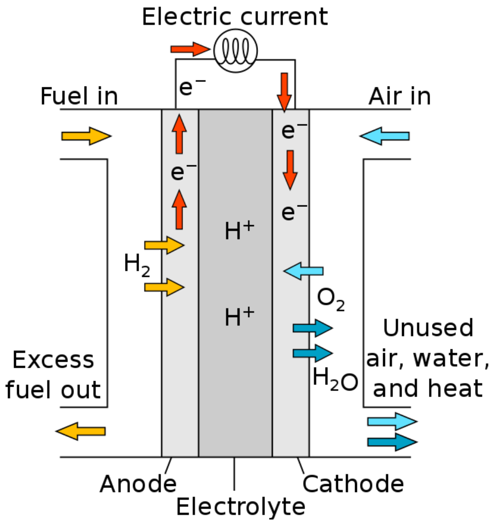

Figure 8: Polymer Electrolyte Membrane Fuel Cell illustration [19].

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Polymer electrolyte membrane fuel cells seem to be promising for the future especially if technological advancements occur in the electrode materials resulting in similar or even greater efficiencies [18], [102].

2.4.2 Fuel Cell Advantages and Disadvantages

Fuel cells are extremely advantageous since they combine positive elements of different energy conversion devices. They constantly produce electricity while being fueled, like internal combustion engines, and their operation depends on electrochemical reactions, like batteries. They have no mechanical losses as they do not have moving parts and thus, they have an efficient lifespan and economical maintenance. In addition, their size and capacity induce a wide range of power production from one Watt (portable power) to many MW (power plant). Finally, one of the most important advantages of fuel cells is that when the appropriate fuel is used, they do not produce greenhouse gases.

While the fuel supply is rapid and efficient for a fuel cell, hydrogen production, and storage are extremely demanding procedures. Hydrogen can be produced either by means of electrolyzers or fossil fuels. Water electrolysis is an expensive process whereas fossil fuels are threatening the environment. Moreover, hydrogen is flammable and has a low volumetric energy density, making transportation and storage challenging, expensive, and dangerous [26-33],[34].

2.4.3 Hydrogen Production and Environmental Activity

Hydrogen can be classified according to the production process that takes place:

Grey Hydrogen

This type of production, although it is the most inexpensive procedure, produces an immense amount of CO_2, resulting in dramatic environmental consequences. Natural gas is the core fuel for production due to its hydrogen-rich components.

Blue Hydrogen

This term refers to hydrogen that is also produced from natural gas but supported by carbon capture and underground storage.

Green Hydrogen

This is the most eco-friendly process since it involves zero greenhouse gas emissions. Electricity which is produced from renewable energy sources is utilized from a device called an *electrolyzer*. An

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electrolyzer is an exceptional device that produces hydrogen using electricity in comparison to fuel cells that do the reverse process. More information will be provided in the next unit [35].

2.4.4 Electrolyzers

Electrolyzers [36-48] separate water's components, hydrogen, and oxygen, using electricity from renewable energy sources, via a procedure called electrolysis. These devices are very promising for the future due to the large amounts of hydrogen that they produce with zero emissions. However, it is an expensive procedure and lower electricity consumption is indispensable.

An electrolyzer particularly encompasses two electrodes and an electrolyte. In the positive electrode, anode, the oxidation of oxygen takes place, and in the negative electrode, cathode, hydrogen is produced via reduction. This non-spontaneous process is facilitated through an external load. It is noteworthy to mention that electrodes operate in reverse in comparison with fuel cells [35].

Likewise, electrolyzers are classified by the type of electrolyte:

1. Alkaline water (AW) electrolyzers.
2. Solid oxide (SO) electrolyzers.
3. Proton exchange membrane ή polymeric membrane (PEM) electrolyzers.
4. High-temperature steam (HTS) electrolyzers.
5. Molten carbonate (MC) electrolyzers.

Alkaline water electrolyzers are currently the most reliable technology but PEM electrolyzers are under development and promising. The general equation of an electrolyzer can be described as:

$$H_2O_{(l)} + \text{HEAT} + \text{ELECTRICITY} \rightarrow H_{2(g)} + \frac{1}{2} O_{2(g)}$$

<u>Proton exchange membrane electrolyzers</u>

PEM electrolyzers face numerous drawbacks. For instance, high installation costs, low hydrogen production capacity, and short life expectancy are only a few problems. Nevertheless, they achieve efficiencies between 48% and 65% under low temperatures and produce clean hydrogen under variable power supply.

When water is pumped to the positive electrode, anode, oxygen, electrons, and protons are produced. Protons are transferred via a membrane, usually Nafion, to the negative electrode, the cathode, where they meet the electrons and produce hydrogen gas. The electrochemical reactions that occur are [49]:

$$\text{Anode (+): } H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e$$

$$\text{Cathode (-): } 2H^+ + 2e^- \rightarrow H_2$$

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Investing in new catalyst materials for inexpensive installations and high efficiencies is indispensable for both electrolyzers and fuel cells.

2.4.5 Hydrogen Storage

In a gaseous state storage system, hydrogen can be stored as a pressurized gas between 35 and 75 MPa. Hydrogen has a density of 0.089/m^3 and thus, leaking from containers is possible. It can be stored in vast underground storage or vessels made of steel and aluminum materials. However, a carbon fiber-reinforced plastic composite vessel although safe due to its strength and impact resistance is too expensive.

In a liquid-state storage system, the cryogenic liquid method is used. In the liquid form, hydrogen is denser than the gaseous form. Liquid hydrogen storage is extremely expensive due to its low boiling point of 20 K. It can be stored either in liquid organic hydrogen carriers (LOCHs) or as Ammonia.

In a solid-state storage system, hydrogen can be stored by either physisorption or chemisorption on solid surfaces or nanostructure materials that absorb it and release it in demand [50].

2.5 Supercapacitors

Supercapacitors, also known as ultracapacitors, are advanced energy storage devices that have gained important attention in recent years. They combine high power density, which means they can store and deliver energy rapidly, with long cycle life. Thus, they seem a prospective alternative to traditional batteries. In comparison to simple capacitors, they use an electrolyte instead of dielectrics and greater surface area electrodes, such as activated carbon, which is a highly porous form of carbon. According to the energy storage mechanism, supercapacitors can be classified into three different types, Electric Double Layer Capacitors (or EDLC), Pseudocapacitors, and hybrid supercapacitors, which are a combination of the previous two [51]. The structure of the three types of supercapacitors is illustrated in **Figure 9**.

Electric Double-Layer Capacitors encompass two electrodes, particularly carbon, an electrolyte, and a separator. They use a non-Faradaic process to store energy electrostatically. The two electrodes that are charged through an external voltage, attract the opposite charged ions of the electrolyte. Thus, an electric double-layer is created in each electrode that stores energy in the form of electrostatic potential.

Pseudocapacitors combine the principles of both capacitors and batteries. The storage mechanism involves redox reactions at the electrode-electrolyte interface. During the charging process, oxidation reactions occur in the electrode material with simultaneous reduction reactions in the electrolyte ions. In the discharge procedure, the reactions are reversed. Pseudocapacitors offer a greater energy storage capacity than EDLC due to the Faradaic reactions, but lower power density and lifespan due to the slow kinetics and the nature of the reactions.

<u>Hybrid Capacitors</u> involve a combination of electrostatic double-layer capacitance and electrochemical reactions. Two different electrodes, one from pseudocapacitive material and one from high-surfaced-area-carbon-based material, offer the potentialities of the two supercapacitor principles. Thus, they offer a balance between high energy density and high power density.

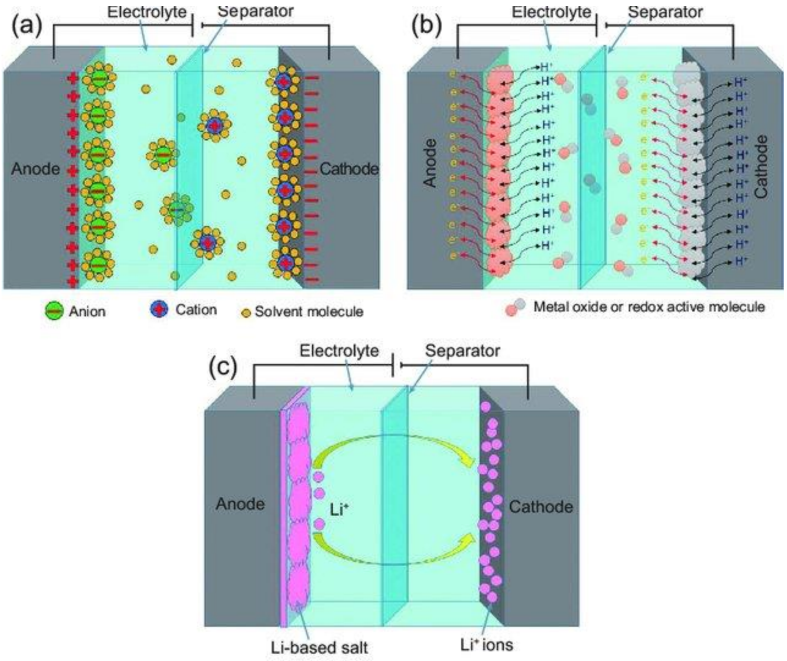

Figure 9: Schematic illustration of Supercapacitor categories: (a) EDLC, (b) Pseudocapacitors, (c) Hybrid Capacitors [53].

Supercapacitors will have a pivotal role in the future of energy. Their exceptional power density is suitable for applications requiring quick bursts of energy, such as regenerative braking systems in electric vehicles, portable electronics, and numerous industrial processes. In addition, they possess a prolonged cycle life compared to batteries due to their reversible electrostatic processes. Supercapacitors also exhibit excellent temperature performance in contrast to batteries.

However high-power outputs, their energy storage capacity is still lower compared to traditional batteries. A hybrid technology that involves both a supercapacitor and a battery seems to be an advanced integration. The combination aims to leverage the high energy density of batteries and the high power density of supercapacitors. In an electric vehicle, a supercapacitor is ideal for capturing or releasing energy from regenerative braking or acceleration, while a battery is responsible for energy storage for longer durations and regular driving conditions. Hence, by handling the power peaks, the supercapacitor reduces the stress on the battery and enhances the overall system efficiency [52].

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2.6 Electrochemical Sensors

Electrochemical sensors [54-64] are revolutionary in the way we detect and quantify analytes. These sensors harness the principles of electrochemistry to convert chemical information into measurable electrical signs, enabling accurate analysis.

An electrochemical sensor is mainly composed of three three-core part electrode, which is in contact with the analyte and undergoes electrochemical reaction, made of various materials, such as metals, metal oxides, or conductive polymers. A reference electrode provides a stable reference potential against which the potential of the working electrode is used. Finally, a counter electrode, which is made of an inert material like platinum or graphite, allows the flow of electrons during the electrochemical reaction at the working electrode. The basic structure is depicted in **Figure 10**.

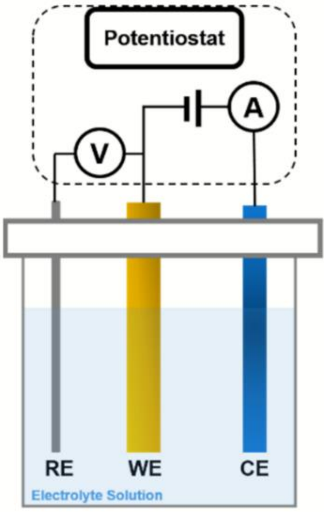

Figure 10: An electrochemical sensor with three electrodes: Reference (RE), Working (WE), and Counter (CE) connected to a potentiostat [66].

The operation is based on various electrochemical techniques, including amperometry, where amperometric sensors measure the current by an electrochemical reaction at a constant applied potential, and potentiometry and voltammetry, where potential difference and the resulting current response are measured respectively.

Electrochemical sensors have a wide range of applications in several sectors. Environmental monitoring is one of them where pollutants in air, water, and soil are detected. Healthcare and biomedical applications where cholesterol, glucose, and biomarkers for disease diagnosis are detected. Energy storage and conversion by monitoring electrode reactions and optimizing performance. Food safety and quality control where discovering contaminants in food products is essential to secure consumer safety [65], [103].

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2.7 Electrochemical Batteries

Battery is an electrochemical device [67-82] that converts chemical energy into electrical through reduction-oxidation reactions. A typical battery encompasses two electrodes, an anode, and a cathode, which are the negative and the positive electrodes respectively.

When an external circuit is connected to the battery, chemical reactions occur at the electrodes. The anode is the electrode where oxidation takes place whereas the cathode is the electrode where reduction takes place. The anode releases electrons into the external circuit and generates charged ions. The cathode accepts and combines the electrons and the charged ions resulting in reduction reactions. The electrons flowing into the electrical circuit are responsible for electric power generation. The process is represented in **Figure 11** by a lithium-ion battery.

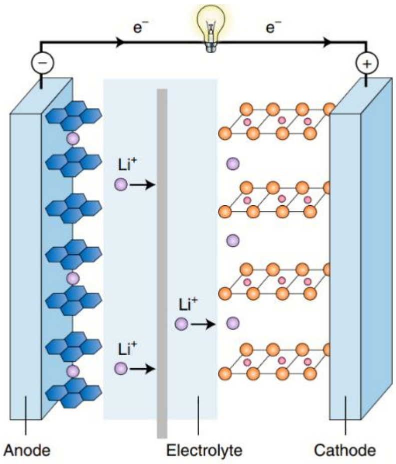

Figure 11: Lithium-ion battery illustration [84].

Types of Batteries

Primary Batteries

A primary battery is a non-rechargeable battery that is designed for one-time use. Once the chemical energy is depleted, the device is discarded. This battery is usually a lightweight and inexpensive storage device, ideal for portable electronics, lighting and photographic equipment, toys, and several other applications with utility power freedom. Some important advantages are their high energy density, good shelf life, and ease of use.

Primary types: Zinc-carbon, Magnesium and Aluminum, Lithium Batteries.

Secondary Batteries

This type of battery can be recharged electrically, after discharge, reversing the electron flow procedure. They can be categorized into two types of applications, those where energy is stored and

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then used when there is demand, and those in which the secondary battery is used or discharged as a primary battery but recharged and not discarded after use. Although they have generally lower energy densities than primary batteries, they are characterized by high power density, high discharge rate, and good temperature performance.

Secondary types: Lead-Acid, Iron Electrode, Nickel-Zinc, Silver-Oxide, Lithium-Ion batteries.

Reserve Batteries

A key component of these primary types is separated from the rest of the device resulting in limitation or even elimination of self-discharge and chemical deterioration. This type of battery is designed to meet long and environmentally severe storage conditions in comparison with the other types of batteries. They can be designed, for instance, to deliver high power for military applications for short periods.

Reserve types: Magnesium Water-Activated, Zinc/Silver oxide, Thermal Batteries [83].

Battery characteristics

- Energy Density: Indicates the amount of energy the battery can hold per unit mass or volume.
- Power Density: Indicates how quickly the battery can deliver energy.
- Voltage: The electrical potential difference between the positive and negative terminals.
- Capacity: It refers to the total amount of electric charge that a battery can store.
- Cycle life: The number of charge and discharge cycles a battery can undergo before its capacity declines.
- Charge and discharge efficiency: The ratio of the energy returned during discharge to the charging energy.

CHAPTER III

LITHIUM-ION BATTERIES

3.1 Introduction

Lithium-ion batteries are a revolutionary power storage solution of our modern age. These versatile rechargeable batteries have transformed the way we power our devices enhancing our productivity and efficiency in numerous applications. Li-ion batteries are at the forefront of our global shift toward a green and more sustainable future. In this chapter, the engineering and chemistry of li-ion batteries will be revealed. More specifically, the sophisticated operation and the material progress will be investigated in depth. As we delve deeper into lithium-ion technology a comprehensive understanding of the commercially available Li-ion batteries, their characteristics, and their applications will be gained. Finally, the manufacturing methods will be demonstrated [85]. Before delving into the lithium-ion battery technology it is significant to highlight the importance and success of these batteries. Lithium-ion batteries combine low weight, long cycle life, and low self-discharge rate.

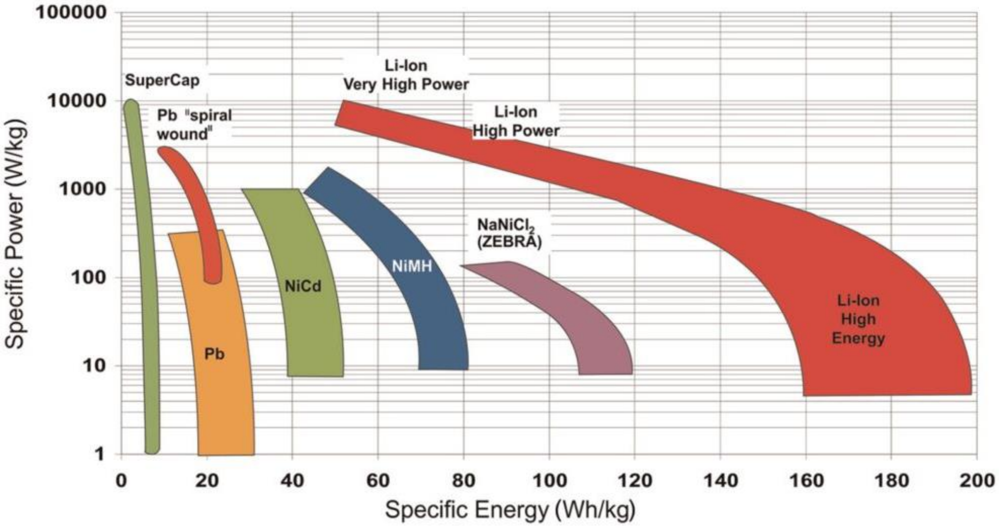

Figure 12: Specific energy density and power comparison [87].

The two most important features, however, are the high energy density and power. The ability to store vast amounts of energy and deliver them quickly, relative to the other rechargeable technologies, and being more eco-friendly than traditional fuels, is unique. Indeed, in Figure 12 the specific energy density and power properties are distinguished from other rechargeable battery technologies [86].

3.2 Brief History

Lithium-ion batteries have a transformative history marked by continuous innovation and collaboration. Emerging in the 1970s, their development gained momentum with key contributions from scientists like

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John B. Goodenough, who laid the groundwork by identifying the family of lithiated transition metal oxides, such as lithium cobalt oxide, as a cathode material to reversibly deintercalate and intercalate lithium ions at high energy potentials. Earlier, Stanley Whittingham explored intercalation processes for energy storage. The 1980s saw Akira Yoshino's pioneering work at Asahi Kasei Corporation, discovering the potential of lower-temperature carbons and introducing the main elements of a lithium-ion battery. Sony Corporation played a pivotal role by incorporating these battery patents into consumer electronics, reshaping the technology landscape. This journey culminated in the Nobel Prize in Chemistry being awarded to Goodenough, Whittingham, and Yoshino in 2019, cementing their contributions to a technology that powers modern portable devices and electric vehicles [88],[89],[90].

3.3 Lithium

In 1817 one of the students of John Berzelius, Johan August, discovered a new element. Berzelius called it Lithium, from the Greek word *Lithos* which means stone, due to its color and shape. Lithium belongs to the alkali metals, a highly reactive element family with their outermost electron in an s-orbital. It has an atomic number of 3. The two electrons are in the 1s orbital and do not participate in chemical bonds due to their lower energy. The third and lone electron is further away from the nuclei's attractive forces, and it's barely held in place (**Figure 13)**. Thus, lithium is eager to share its outer electron due to its relatively low ionization energy. However, reactivity is relative and depends on the energy behavior of one atom compared to another. Using hydrogen as a benchmark (standard hydrogen electrode) we can observe that lithium can release its electron with around three volts more force than hydrogen. This high reactivity is responsible for the fact that lithium is only found in the form of compounds in nature. Additionally, it can react with water or even air molecules, including nitrogen making it flammable, explosive, and dangerous. Lithium at room temperature is the least dense metal and the least dense solid element while providing high specific theoretical capacity as an anode material. It is undeniably a vigorous and efficient element for rechargeable batteries [90],[91].

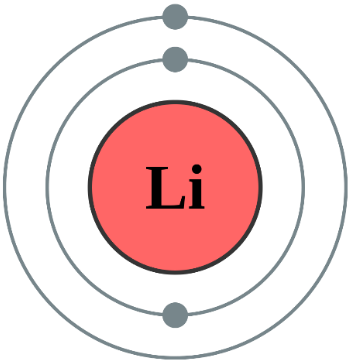

Figure 13: Bohr diagram for Lithium [92].

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3.4 Operation

Lithium-ion batteries are a revolutionary technology combining energy generation and storage with high efficiency. They have a unique operation called *Rocking-Chair* Chemistry.

To generate electricity, electron motion through a circuit is essential. The driving force of the electron motion is an electric potential difference that two electrodes can offer. When an electrode that tends to lose electrons (oxidation) is bridged with an electrode with a tendency to gain electrons (reduction) through an external circuit, electrons move from one electrode to the other generating electricity. The electrode with the lower tendency to be reduced is called anode and the electrode with the higher tendency to be reduced is called cathode. The names anode and cathode come from the Greek words *Anodos* and *Kathodos* which means upwards and downwards respectively. The names result from the tendency to move from higher points to lower points to come to balance. Like a ball on the edge of a hill. In this case, we refer to the electrons moving from the anode to the cathode spontaneously due to the potential difference of the electrodes, which is electric and not gravitational. Applying an external voltage higher than the potential difference of the electrodes the redox reactions in the two electrodes and the electron path are converted.

In the case of a lithium-ion battery (**Figure 14**) a cell with an anode active material as graphite and a cathode with an active material as lithium iron phosphorate ($LiFePO_4$) will be used to explain the rocking-chair mechanism.

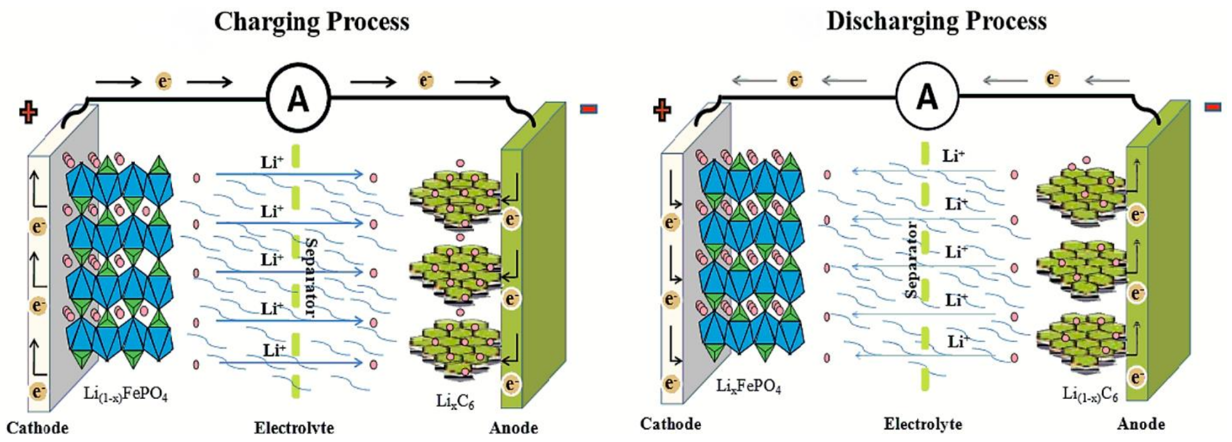

Figure 14: Lithium-Ion Battery *Rocking-Chair* Chemistry.

Active materials refer to electrode materials that undergo chemical reactions and structure reformations. The graphite is connected to a copper current collector and $LiFePO_4$ to an alumina collector. Both are excellent electrical conductors and are connected through an external circuit. They are the path for electron movement and the medium for electricity generation and pumping. An electrolyte, often $LiPF_6$, enables ion conductivity, maintains a charge balance, and prevents the movement of electrons. It is the vehicle of the lithium ions. A separator prevents the anode and cathode interaction [93],[94]. When the battery is fully charged the Li^+ ions are intercalated to the graphite structure. During the **discharging** process reduction reactions take place at the anode: $LiC_6 \rightarrow Li^+ + e^- + C_6$. Electrons then move from the negative collector to the positive collector providing electricity to an appliance and Li^+ are released to the electrolyte solution. Electrostatic interactions with the negative solvent molecules result in a salvation shell of the Li^+ which enables the movement of the ion through diffusion. Simultaneously, to maintain charge balance Li^+ ions from the electrolyte close to the cathode surface meet the electrons, lose the salvation shell, and react with the active material and thus, reduction occurs: $FePO_4 + Li^+ + e^- \rightarrow LiFePO_4$. While **charging** the process converts into the opposite direction [95].

3.5 Architecture and Material Advancements

3.5.1 Design

Depending on the application lithium-ion batteries have different setups. They can be categorized into four types, coin/button cells, pouch cells, cylindrical, and prismatic cells. Pouch cells offer flexibility and a good possibility of stacking, like electrical vehicle battery design. Button cells are ideal for small devices but have a limited capacity. Cylindrical and prismatic are the most popular cell designs. They are widely used in mobile phones, cameras, and even electric vehicles. Each sheet builds a repeat unit that is stacked and winded in a container. All sheets can be wetted with liquid electrolyte including a conducting salt making the stacking procedure and construction possible. **Figure 15** shows the architecture and the stacking capability of these cell designs. Higher capacity or voltage is achieved when the cells are connected in serial or parallel [95].

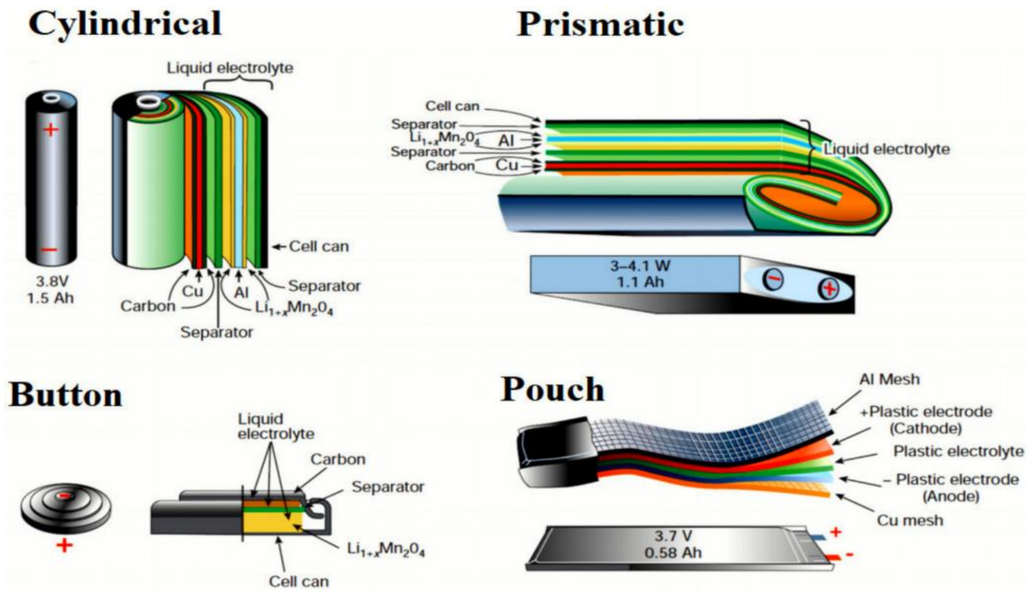

Figure 15: Commercially available cell configurations [96].

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3.5.2 Anode

There are several materials that the industry uses for the negative electrode, the anode.

Lithium is expected to be the ideal material for the anode due to its high theoretical capacity, low density, and very low electronegativity. However, lithium is very reactive and is very difficult to handle in the manufacturing processes.

Several efforts have been made with **Transition Metal Oxides** owing to some great electrode properties. They include iron, cobalt, nickel, copper, zinc and more. They have high power density and theoretical capacity, are abundant in nature, non-toxic, and have low fabrication costs. A good case is iron oxide with a theoretical capacity of 926 $mAhg^{-1}$. Nevertheless, poor cycling stability, rapid capacity decrease, and poor electron conductivity compared to graphite are some of their main drawbacks [97].

Alloy-based materials also seem to have an impact on the negative electrode selection. In this case, lithium will form an alloy with elements such as Al, Sn, Mg, Ge, Si, and Ag. They have greater specific capacity than carbon-based materials, but they experience low lithium-ion diffusion rates, poor electrical conductivity, and massive volumetric expansions during the intercalation and deintercalation of Li^+.

Silicon appeared to be a promising material in recent years. It is environmentally friendly, abundant in the earth’s crust, has an affordable cost, a high theoretical specific capacity close to that of lithium, and a low charge voltage against Li^+/Li. However, this ideal material has an indiscreet problem. During the intercalation and deintercalation of lithium ions, the volume can expand at 300% causing a lot of problems.

Carbon-based materials, and primarily **Graphite**, are the most famous anode materials. Graphite has exceptional electrical conductivity, low half-cell potential, and low production costs. Its main negative feature is the low specific capacity of 400 $mAhg^-$. Nevertheless, graphite seems to dominate the lithium-ion battery industry [98].

In the first cycle on a lithium-ion battery, a small amount of intercalated Li^+ is irreversible and contributes to the formation of a **Solid Electrolyte Interface (SEI).** During the intercalation of the Li^+, the distance between the graphite layers increases, and some solvent molecules and solvated Li^+ enter and react forming the SEI. This formation occurs in the first cycle and grows in every cycle consuming Li^+, decreasing the battery’s capacity, and increasing the resistance for Li^+ migration. This solid interface can exist also in solid inorganic and polymer electrolytes [94].

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Recent advances in **Nanotechnology** and material science have shown great potential in microstructure materials for the anode. These kinds of materials have numerous active sites for Li^+ accommodation resulting in an increased capacity. They can provide thin films of SEI and effective pathways for both Li^+ and electrons. Some nanomaterials can provide flexibility with strength achieving higher quality materials. **Carbon-based Nanomaterials** are extremely efficient with high specific capacity and electrical conductivity. They can classified in carbon nanostructures as [99],[100]:

- 1D: nanotubes, nanorods, nanofibers
- 2D: Graphene
- 3D: Porous Carbon sphere and core-shell structures

Mixing and utilizing the potential of these materials can result in significant progress. Hybrid anode materials seem very promising. For instance, silicon-nanolayer-embedded graphite (SGC) leverages the capabilities of both materials. Additionally, graphene-based nanostructure electrodes with other components, such as carbon, oxide, and metals are investigated [98].

3.5.3 Cathode

Efficient active cathode materials are characterized by a high reactivity with lithium as well as easy intercalation and deintercalation of Li^+, high voltage, lithium diffusion paths, low volume changes, good electric conductivity, and low cost. Goodenough's group began to investigate cathode materials in the 1980s at the University of Oxford and introduced the oxide material family that combines all these features [106].

Nowadays, some of the most common cathode-active materials are:

- lithium cobalt oxide ($LiCoO_2$, LCO)
- lithium manganese oxides ($LiMnO_2$ and $LiMnO_{4,}$ LMO)
- lithium nickel cobalt oxide (LiNi1-xCoxO2 (0.2 ≤ x ≤ 0.5, LNCO)
- lithium iron phosphate (LiFePO4, LFP)
- lithium nickel manganese cobalt oxide (LiNi1/3Co1/3Mn1/3O2, LNMC)
- lithium nickel manganese oxide (LiNi0.5Mn0.5O2, LNMO)
- lithium nickel cobalt aluminum ($LiNi_xCo_yAl_zO_2$), LNCA)

In **Table 1** the specific capacity, crystal system, space group, and typical voltage range of the most commonly active cathode materials used are listed.

Table 1: Most Commonly active cathode materials used for lithium-ion battery applications [107].

Cathode Active Material	**Crystal System/Space Group [Point Group]**	**Specific Capacity/mAh-g-1**	**Typical Voltage Range/V**
$LiCoO_2$	Orthorhombic/R3m	274	2.5-4.45
$LiFePO_4$	Orthorhombic	170	2.5-4.2
$LiMn_2O4$	Cubic/Fd3m	148	3.0-4.3
$LiNiO_2$	Trigonal/R3m	275	3.0-4.3
$LiNi_{1-}xCo_xO_2$ $(0.2<x<0.5)$	Rhombohedral/R3m	~275	3.5-4.3
$LiN_{1/3}Mn_{1/3}Co_{1/3}O2$	Rhombohedral/R3m	278	2.3-4.3
$LiNi_{0.5}Mn_{1.5}O_2$	Trigonal/R3m	147	3.5-4.9

Recent technological advancements focus on cathode active materials with optimized particle size, improvements in doping with different elements, and the development of composites with different particles and coating. All these strategies aim at the electronic and thermal properties advancement and particle stabilization concerning the electrolyte material. For instance:

$LiCoO_2$, although it has a great volumetric energy density, is unstable at high voltage. Thus, doping with different elements such as transition metals, surface coating with Li_3NbO_4 and Co_3O_4 layers, and electrolyte optimization are a few improvement choices.

$LiFePO_4$ which is a commonly used material in electric vehicles can improve its performance with a carbon coating implementation by means of phytic acid as a novel phosphorous source in comparison to the traditional phosphoric acid.

$LiMn_2O_4$ is also a widely used material, but it shows poor cycling behavior. This problem can be addressed by doping with Cu, Ni, and Co via sol-gel synthesis [107].

3.5.4 Electrolyte

The electrolyte is extremely important for battery operation. It is responsible for conducting the ions from one electrode to another, must be stable over several different potentials, and must solvate the ions allowing diffusion but also intercalation. Depending on the electrode materials different limits are set in the battery regarding its cycling efficiency, specific capacity, safety performance, and temperature range operation.

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An electrolyte in a lithium-ion battery, particularly, consists of organic solvents and lithium salts and can be categorized into two main types based on their chemical composition: liquid electrolytes and solid electrolytes.

For most commercial Li-ion batteries the traditional choice has been liquid electrolytes where lithium salts are dissolved in an organic solvent. Some common lithium salts include $LiPF_6$, $LiBF_4$, and LiTFSI which are dissolved in several organic solvents such as vinyl carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), propylene carbonate (PC).

Solid electrolytes are a modern development in Li-ion battery technology. They offer numerous advantages in comparison to liquid electrolytes such as safer operation, higher energy density, and wider temperature operating ranges. They can be categorized into polymer and ceramic electrolytes.

Polymer electrolytes are composed of polymer materials that have been merged with lithium salts. Some examples of polymer electrolytes include polyethylene oxide (PEO), polyvinylidene fluoride (PVDF), and Polyacrylonitrile (PAN). They are advantageous due to their flexible and lightweight structure.

Ceramic electrolytes are solid electrolytes made of inorganic materials such as lithium garnets or sulfides. They offer high ionic conductivity and can operate in higher temperatures.

Recent developments in hybrid solid electrolytes seem promising for lithium-ion battery applications. More specifically, a hybrid solid electrolyte leverages the potential of both polymer and inorganic compounds to achieve high ionic conductivity, good mechanical properties, and good contact with the electrodes. Ceramic-polymer hybrid electrolytes are particularly well-suited for use in solid-state lithium-ion batteries, which replace the liquid electrolyte with a solid or hybrid electrolyte, and innovations in materials science and engineering aim to reduce costs and make these electrolytes more practical for a wide range of applications.

The strategy behind the hybridization of two or more solid electrolyte components is to scatter high-surface-area fillers into a polymer matrix. For instance, a mixture of PEO polymer and ceramic $Li_7La_3Zr2O_{12}$ nanofibers is an efficient hybrid solid electrolyte offering relatively good ionic conductivity, mechanical, and electrochemical stability [94],[107],[109]. A summary of recent hybrid solid electrolyte performances including this one, as well as their ionic conductivity, and electrochemical stability vs Li^+/Li are demonstrated in **Table 2**.

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Table 2: Summary of recent hybrid solid electrolyte performances [108]**.**

Polymer	**Filler**	**Ionic conductivity (S/cm)**	**Electrochemical stability vs. Li$^+$/Li**
PEO	$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$	1 x 10^{-5} (R.T)	Up to 4.75 V
	$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$	1.11 x 10^{-3} (R.T)	1 V – 4.5 V
	$Li_{1.5}Al_{0.3}Ti_{1.7}(PO_4)_3$	1.9 x 10^{-4} (40 ° C)	1 V – 4.5 V
	$Li_{10}GeP_2S_{12}$	2.2 x 10^{-4} (R.T)	-0.5 V – 5 V
	Nanofiber $Li_{0.33}La_{0.557}TiO_3$	2.4 x 10^{-4} (R.T)	Up to 5 V
PAN	$Li_{0.33}La_{0.557}TiO_3$	2.4 x 10^{-4} (R.T)	Up to 4.7 V
PVDF-HPF	$Li_7La_3Zr_2O_{12}$	7.63 x 10^{-4} (30 ° C)	Up to 5.3 V
Poly(propylene carbonate)	$Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$	5.2 x 10^{-4} (20 ° C)	Up to 4.6 V
Poly(vinyl carbonate)	$Li_{10}SnP_2S_{12}$	2 x 10^{-4} (R.T)	Up to 4.5 V

3.5.5 Separator

The separator is significant for preventing the two electrodes from direct contact and allowing the Li$^+$ exchange. Nevertheless, solid electromechanical properties are indispensable. More precisely, a small thickness combining large porosity and high permeability is essential. Additionally, a robust separator should prioritize chemical stability against electrolyte and thermal stability to avoid melting. Excellent wettability is also pivotal for a separator membrane to absorb and retain the electrolyte.

Commercial separators are based on polyolefins, a family of thermoplastics that include polypropylene and polyethylene. These two materials are pivotal for separator technology due to their chemical stability, mechanical strength, and ease of manufacturing.

Recent material advancements involve ceramic-coated separators. These separators have a ceramic layer (alumina or other) on one or both sides of the polyolefin separator. This type of coating enhances thermal stability and reduces the thermal runaway risk. The conductivity and rate of transport of lithium ions in a separator can also be improved by adding ceramic crystallites, like soggy sand. In addition, biopolymers, recycled polymers, and materials such as silk and cellulose are being investigated as more environmentally friendly separators that do not need to use synthetic polymers (polymers that are artificially created through, for instance, petroleum oil chemical processes) [94].

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3.6 Commercially Available Lithium-ion Batteries and Characteristics

3.6.1 Battery Key Properties

Current commercial lithium-ion batteries are named after the cathode material. The most famous lithium metal oxides used in commerce are lithium manganese oxide (LMO), lithium cobalt oxide (LCO), lithium nickel cobalt aluminum oxide (NCA), lithium iron phosphate (LFP), and lithium nickel manganese cobalt oxide (NMC). Each commercially available lithium-ion battery meets the demands of a certain application. Several applications, such as electric vehicles, require high durability, performance, and specific energy density. Others demand higher power densities for immediate response, low costs, or even high safety features, especially in the case of customer consumption.

Thus, the lithium-ion battery needs to be evaluated using 8 variables: Specific Energy, Specific Power, Durability, Performance, Safety, Material Abundance, and Maturity. Each variable will be analyzed below.

Specific Energy depends on the anode and cathode material's nano and micro-structures. While the active material of a cell contributes only a fraction of its weight, the design of the cell affects this aspect. Current commercially available li-ion batteries cover a wide range of energy capacities, roughly from 85 to 250 Wh/kg. NCA batteries are the most efficient regarding the specific energy while LFP are the least. Specific energy remains one of the cornerstones of battery evaluation.

Specific Power is also an important feature of a battery. It depends on the voltage, the solid electrolyte interface, the diffusion coefficient, and the conductivity of electrodes, as well as the lithium-ion density.

Durability is a property that plays an immense role in the battery lifespan. It can be expanded as battery degradation and cycle aging. The battery's durability can be declined by external conditions, temperature, and usage conditions, such as overcharge. Cycle aging is a result of cyclable lithium and active electrode material loss, and it is noticed as power and capacity fade. Side reactions and structural degradation are responsible for cyclable lithium and active electrode material loss respectively. From a viewer's perspective, the durability indicator is the cycle life, which is the ability to operate in full cycles under standard conditions before the capacity and power of the battery drop to 80% of the initial conditions.

Performance can be described as the ability of a battery, for instance, to tolerate efficient operation in a wide SOC range. The state of Charge is an indicator of the energy available in a battery.

Safety is a challenge for the lithium-ion industry because the batteries contain oxygen, lithium, and flammable electrolytes. Thus, being able to be thermally stable in high temperatures is advantageous for a commercial battery.

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Maturity indicates the experimental and commercial usage of the technology throughout the years. An important example is the usage of cobalt which involves safety concerns and, nevertheless, is the most popular cathode active material for portable electronics and mobile phones due to the technology maturity.

Finally, **Material Abundance** and **Affordability** are strongly related to the material sources and manufacturing procedures [110].

3.6.2 Commercial Lithium-Ion Batteries

The most famous and commercially available LiBs are analyzed below [111]. In **Figure 16** the main characteristics of commercial lithium-ion batteries are graphically summarized.

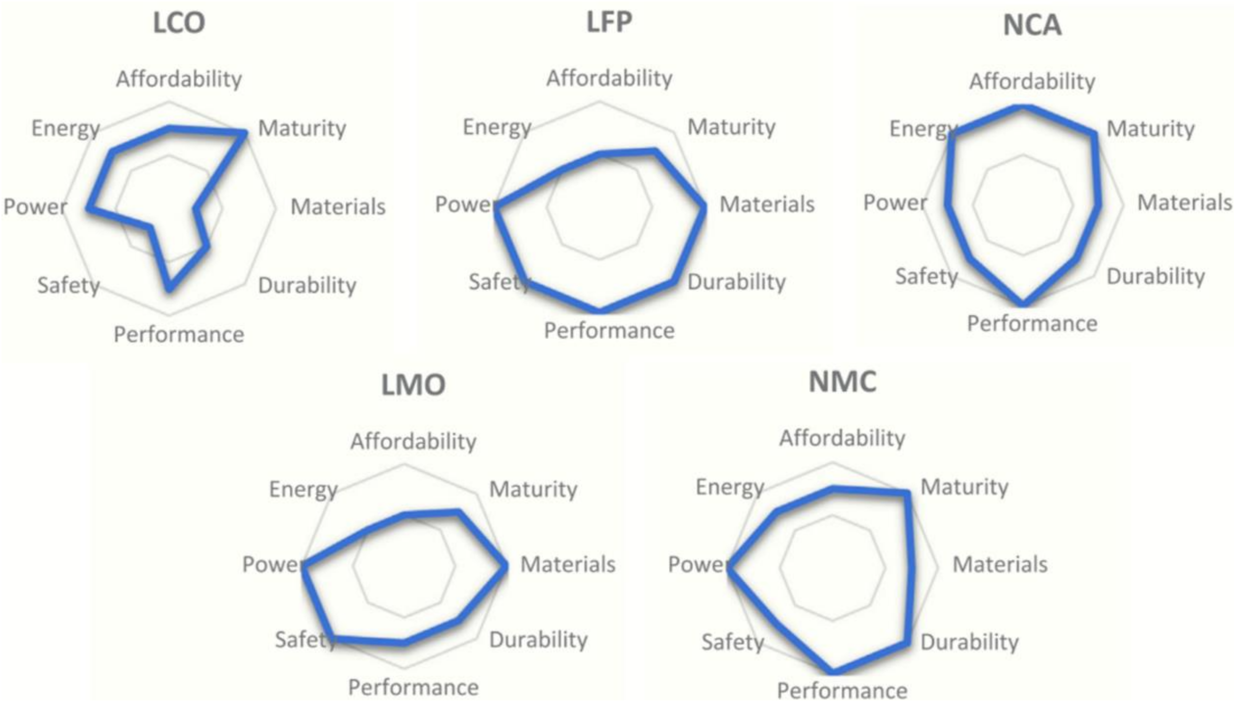

Figure 16: Summarization of Commercial Lithium-Ion Battery Characteristics [110].

- **LCO** (lithium cobalt oxide): In 1991, the LCO battery was the first lithium-ion chemistry to become commercial and it involves graphite (C_6) as the anode and $LiCoO_2$ as the cathode. It combines high specific energy (150-190 Wh/kg) and technological maturity, achieving applications in portable electronics and several other sectors. LCO has a relatively good durability of 500-1000 full cycles providing a robust device for a few years. The main disadvantage of this battery is the safety variable. The low thermal stability of cobalt-oxide results in thermal runaway even at 150° C.
- **LMO** (lithium manganese oxide): The $LiMn_2O_4$ forms a 3D spinel structure encouraging ion flow on the electrode and low internal resistance. This results in a relatively high specific

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power. The anode active material for LMO batteries is usually graphite and LTO. The durability is higher than LCO, 1000-1500 cycles, but the energy density is notably lower, in the range of 90-140 Wh/kg. Furthermore, this type is inherently safer as the thermal runaway occurs at roughly 250° C, and it is cobalt-free, utilizing abundant and eco-friendly materials. It was commercially available in 1996.

- **LFP** (lithium iron phosphorate): LFP batteries were introduced in commerce in 1999. While graphite is mostly used as the anode, LFP is distinguished from others due to its combination of durability, performance, and safety. These batteries can endure up to 2,000 full cycles and have a promising future regarding their duration. Efficient operation can be noticed in a wide state of charge range (15-100%) displaying constant voltage. Nevertheless, in relation to the other types, LFP has a low specific energy density ranging from 90 to 140 Wh/kg.
- **NCA** (lithium nickel cobalt aluminum oxide): Commercially available also in 1999, NCA combines $LiNiCoAlO_2$ as the active cathode and graphite as the active anode material. The composition of the cathode involves 80% nickel, 15% cobalt, and 5% aluminum. Thus, the cobalt reliance is relatively low compared to LCO batteries. They have an outstanding specific energy density range of 200-250 Wh/kg and simultaneously an efficient power density, and durability (1000-1500 full cycles) becoming ideal for EV applications.
- **NMC** (lithium nickel manganese cobalt oxide): Introduced later in 2004, they include graphite and $LiNiMnCoO_2$ as cathode and anode materials respectively. They have a lower energy density when compared to NCA (140-200 Wh/kg) but longer cycle life (1000-2000). The proportions of manganese, nickel, and cobalt can be varied to meet the demands. For instance, more nickel will provide higher energy density, while more manganese will offer higher power densities.

3.7 Applications

Portable Electronic Devices

Smartphones, laptops, tablets, and numerous other portable electronic devices have become pivotal parts of our daily lives. These devices rely heavily on lithium-ion batteries to meet the demands of modern consumerism. The global market for portable electronics is continuously expanding in proportion to the battery technology development making them more accessible than ever before. Lithium-ion batteries dominate this sector due to their superior capabilities compared to other chemistries like NiCd and NiMH. Currently, LCO batteries are the prime energy storage technology. This is due to their compactness and technological maturity. However, these batteries have several safety concerns, including thermal runaway incidents, as well as cycle-life challenges. Thus, scientists

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and manufacturers explore chemistries with higher energy density and safety and shift their interest toward NMC and NCA cells [110].

Road-Transport

The future of road transportation appears to be electric, harnessing the lithium-ion battery potential. High specific energy, power density, and durability are pivotal for transportation leading to a lithium-ion battery demand. Specifically, NCA and NMC batteries dominate this sector, marginalizing the LCO batteries due to their safety concerns, shorter lifespan, and critical cobalt reliance. Although LFP has been used as a battery for electric vehicles they proved to be inferior. In the NCA versus NMC debate, most car manufacturers favor the NMC's longer lifetime and specific power instead of the NCA's high specific energy. Overall, the development of both and new types is essential to electrify future transportation [110].

Military

Lithium-ion batteries have various applications in the military sector. High safety, high reliability, and high adaptability are features essential for military operations and technology. Small UAVs, marine technology, communication systems, submarines, torpedoes, rockets, and missiles are a few technology systems that require energy storage with high demands. Various lithium-ion batteries are used in the military sector. Standard lithium-ion batteries as well as polymer lithium-ion batteries with improved low-temperature performance are ideal [112].

Renewable Energy and Smart Grid

Lithium-ion batteries involved in this sector combine numerous advantages, including high reliability, low-temperature performance, long cycle life, high energy density, and convenience. They are crucial for storing energy from intermittent renewable energy sources like wind and solar offering high energy density, and charge-discharge performance while enhancing the balance of power supply and demand. Several types are utilized in this sector including LFP, NMC, and LCO harnessing the characteristics of high energy density, fast charge and discharge rates, lifespan, and safety.

Other lithium-ion battery applications involve medical devices, consumer devices, power tools, entertainment appliances, and more. The wide range of features li-ion batteries provide has an immense impact on every mechanism that depends on electrical energy.

3.8 Manufacturing

Lithium-ion battery manufacturing is a mature process in the energy industry but there is a lot of room for efficiency and cost improvement. A general workflow of lithium-ion battery production is presented in this module focusing on some manufacturing processes depicted in **Figure 17**. The state-of-the-art battery manufacturing includes three major parts: electrode preparation, assembly of the cell, and electrochemistry activation. These parts can be categorized into the processes of mixing, coating, drying, and solvent recovery, regarding the preparation of electrode material, calendaring, slitting, vacuum drying, and stacking, related to the cell assembly, and welding, enclosing formation, and aging of the battery, regarding the battery electrochemistry activation. Most of these processes will be analyzed below, presenting the workflow of battery manufacturing. Although we discussed different cell configurations their manufacturing processes are very similar [113].

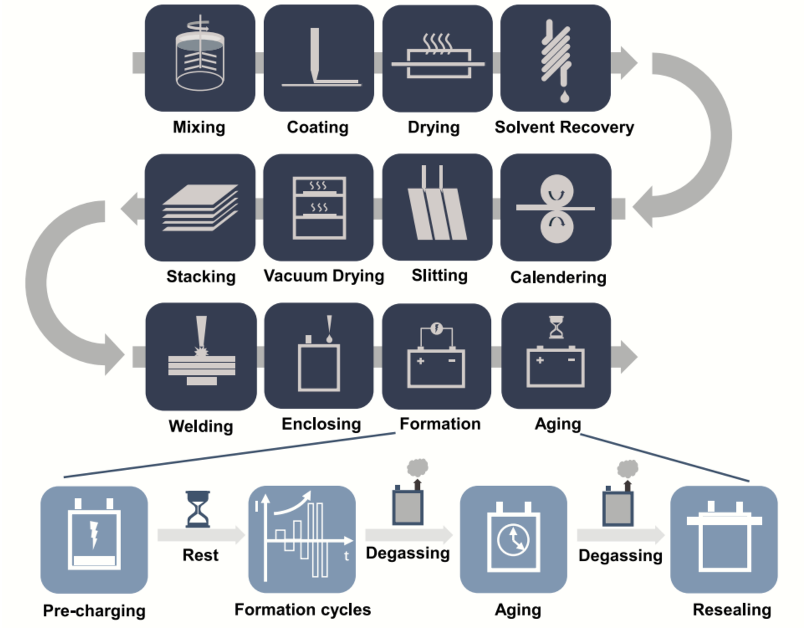

Figure 17: Schematic representation of the LiB manufacturing processes [113].

Slurry Mixing

Initially, the active material, binder, and conductive additive are mixed with the solvent to form a slurry. Normally, N-methyl pyrrolidone (NMP) is the solvent for the cathode, and the binder, polyvinylidene fluoride (PVDF), and water with carboxymethyl cellulose CMC) dissolves the anode, styrene-butadiene rubber (SBR) binder. Modified high shear mixing equipment and ball mining are commonly used to mix dry powder and slurry. Nevertheless, ultrasonic mixing seems to be a promising process that can offer higher quality uniformity while reducing the concentration of solvent usage which leads to material costs and drying time savings.

Coating, Drying, and Solvent Recovery

The slurry by means of slot die is pumped and coated on both sides of the Al foil collector for the cathode and Cu foil collector for the anode. The wet electrode is then delivered to the dryer for solvent

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evaporation. The solvent consumes the most amount of energy, so recovery is essential. It is therefore indispensable to replace or even avoid the usage of organic solvents to lower the time and energy consumption.

Calendaring and Slitting

Next, the electrodes are calendared to form thin, dense sheets through mechanical pressure between rollers. Thus, physical properties are adjusted, such as conductivity, bonding, density, and porosity. After calendaring, the electrodes are slit to achieve the required dimension to fit into the cell design. Laser cutting, instead of the traditional blades or chisels, can provide a clean edge with less deformation and prevent defects such as dross and burrs.

Vacuum Drying

Vacuum drying is an essential process with intense time and energy consumption, aiming to remove moisture from the materials. Current technology suggests a low-pressure environment with temperatures ranging from 60^o C to 150^o C heating for 12 hours with an inert gas supply option. Experiments have shown that reducing the moisture completely might negatively affect the electrochemistry performance while small portions of water can enhance SEI formation and stability.

Welding and Enclosing

Before welding the electrodes and separators are winded or stacked to form the internal structure of the cell. Copper and aluminum tabs are then welded to the anode and cathode current collector, respectively. Ultrasonic welding is the most common procedure and resistance welding may be a choice for some manufacturers. The cell is then delivered to the designed enclosure where the sealing with a protective casing occurs. Before the final sealing, the enclosure is filled with electrolytes.

Formation and Aging

Finally, during the formation and aging of the battery, an SEI layer will be formed in the anode due to electrolyte decomposition. This is referred to as an electrochemistry activation to enable operation stability. A stable SEI layer can protect the anode from overpotential during fast charging, avoid Li dendrites forming, and prevent the irreversible consumption of the electrolyte. The process of formation and aging starts with charging with a relatively low voltage (e.g., 1.5V) aiming to prevent copper from corrosion. Then, after a rest session for electrolyte wetting, gradually increased charging/discharging rates are applied for a stable SEI formation on the surface of the anode. The gas generated from the formation procedure needs to be removed for safety issues. The cells are stored, after or during the formation cycles, in aging shelves for complete electrode wetting and SEI

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stabilization, followed by a degassing step. Normally, after a few weeks, the cells are ready for future applications. In **Table 3** the breakdown of manufacturing costs, calculated by the BatPac model from Argonne National Laboratory is presented, based on a 67-Ah $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)/graphite cell, with 100,000 EV battery packs/year plant. The cost, throughput, and energy consumption of the manufacturing processes are analyzed for this model.

Table 3: Cost, throughput, and energy consumption of lithium-ion battery most important manufacturing processes [113].

Manufacturing processes	**Cost per year/$**	**Percentage %**	**Throughput**	**Manufacturing processes**	**Energy consumption per cell/kWh**	**Percentage %**
Slurry mixing	7,396,000	7.91%	30 min-5 h	Slurry mixing	0.11	0.83%
Coating/drying	13,984,000	14.96%	35-80 m/min	Coating	0.18	1.36%
Solvent recovery	4,296,000	4.60%	NA	Drying/solvent recovery	6.22	46.84%
Calendering	4,849,000	5.19%	60-100 m/min	Calendering	0.38	2.86%
Slitting	2,891,000	3.09%	80-150 m/min	Slitting	0.71	5.35%
Vacuum drying	2,990,000	3.20%	12-30 h	Stacking	0.77	5.80%
Stacking	8,086,000	8.65%	NA	Welding	0.25	1.88%
Welding	6,864,000	7.34%	NA	Enclosing	0.69	5.20%
Enclosing	11,636,000	12.45%	Depending on the cell design	Formation/aging	0.07	0.53%
Formation/aging	30,482,750	32.61%	Up to 1.5-3 weeks	Dry room	3.9	29.37%

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CHAPTER IV

LITHIUM-ION BATTERY FAILURE DIAGNOSTICS

4.1 Introduction

The widespread usage of Lithium-ion batteries has raised considerable alarm due to safety incidents such as explosions and fires, as illustrated in **Table 4** [114]. Given lithium's highly reactive nature, strict temperature, and pressure controls are essential to prevent accidents in LIBs. Faults in LIBs typically manifest in three scenarios: mechanical, electrical, or thermal abuse. It's worth emphasizing that many safety incidents with LIBs result from thermal runaway. Consequently, many researchers have undertaken extensive investigations into the realm of diagnosing faults in LIBs. Accident prevention is not essential only for the integrity of the battery's company, but particularly for human safety. In this chapter, the types of faults, failure diagnostic methods, and safety strategies for lithium-ion batteries will be analyzed.

Table 4: Lithium-ion battery accidents and their causes [114].

Date	Location	Accident description	Cause
7-Jan-13	America	Circuit fire smoke from the cabin in a Japan Airlines Boeing 787 aircraft	Battery pack fire
14-May-16	China	An electric vehicle bus caught fire	Short-circuit of the battery pack
24-Aug-16	Korea	A Samsung Note 7 exploded while charging	Manufacture and design of the battery
9-Jan-18	Switzerland	An iPhone battery exploded in the hands of a person, causing injury and poisoning	The reason has not yet been announced
15-Aug-18	Switzerland	Tesla crashed into a barrier and flipped, resulting in the death of the driver	Battery caught fire due to car accident
Jan-18	Spain	The battery of an iPhone exploded, creating massive smoke in the store	The reason has not yet been announced
31-Mar-21	China	A factory caught fire	Spontaneous combustion of lithium-ion batteries

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4.2 Types of Faults

4.2.1 Internal Battery Faults

Internal battery faults can emerge due to the battery operation, voltage supply, material properties, or even external elevated temperatures. These faults are extremely dangerous since they can affect the battery’s efficiency, or even harm the users. Some fundamental types of internal faults regarding the lithium-ion battery are discussed below [116].

4.2.1.1 Overcharging and Lithium Plating

Overcharge is a type of fault that can lead to more serious consequences such as thermal runaway and ultimately to an explosion of the battery. It can emerge due to incorrect voltage or current measurement, inaccurate SOC estimation from the battery management system, or even due to the capacity variation existing in the cell. It is very important, thus, to understand the mechanism of overcharging.

Every battery design has an upper threshold within the voltage range, beyond that unintentional side reactions occur. In the case of $LiCoO_2/LiPF_6$-EC-DEC/C (graphite), the charge and discharge rate ranges between 2.8 - 4.2 V. During charging, electrons migrate and lithium ions de-intercalate from the cathode active material, increasing its electronegativity, and therefore, the voltage difference between the two electrodes. Nevertheless, to maintain the reversibility of intercalation and deintercalation of Li^+, the cathode active material is designed to stabilize its crystal structure and phase transition within the voltage normal range of the battery (2.8-4.2 V). Li_xCoO2 achieves this stabilization and reversibility when deintercalated Li^+ from the cathode’s layers do not exceed 50% ($x=0.5$), establishing the voltage upper threshold of 4.2 V. Overcharging will result in excessive deintercalation of lithium ions ($x < 0.5$) until lithium is completely removed $x \approx 0$. Irreversible phase transitions and Li_xCoO2 crystal structure collapse will occur. The active material will experience a series of phase transitions resulting in CoO_2 conversion, decomposed to Co_3O_4, and O_2 generation. As the voltage increases to higher values, when roughly all the Li^+ are removed from Li_xCoO2, some new redox reactions will occur on the cathode side to maintain the excess current. These include the decomposition of flammable organic electrolytes and the O_2 release. The decomposition of the electrolytes, being exothermic, will produce gases, such as CO, CO_2, H_2, C_2H_6, CH_4, and C_2H_4, resulting in high pressure and internal high temperature due to heat generation. Thermal runaway, therefore, is triggered and unavoidable [115],[116].

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Overall, overcharging, from a scientific view, is a consequence of the intrinsic stability of materials (electrodes and electrolytes), interface reactions, thermodynamic, and kinetic properties, arising high currents, pressure, and temperature, leading to failure.

There is a strong correlation between lithium side reactions and higher energy densities. During overcharging lithium plating on the anode surface and thus dendritic growth are primary outcomes. The larger the current density the more aggressive the dendritic formation. Lithium plating is a side reaction on the anode occurring at lower temperatures. From the electrochemical perspective, with excessive currents li-ions cannot be intercalated to the anode active material quickly enough resulting in surface accumulation, deposited as metallic lithium. More specifically, the electron transfer reaction and electron demand are more evident than the intercalation, and thus, the li-ions are reduced immediately instead of intercalating into the host layers. Consequently, the available lithium ions are reduced, and hence capacity loss is irreversible. When the plating becomes non-homogeneous, for instance, in a dendritic form, a short circuit between the electrodes occurs. What is a short circuit will be explained in the next unit. In **Figure 18** the lithium plating procedure is illustrated [94],[117].

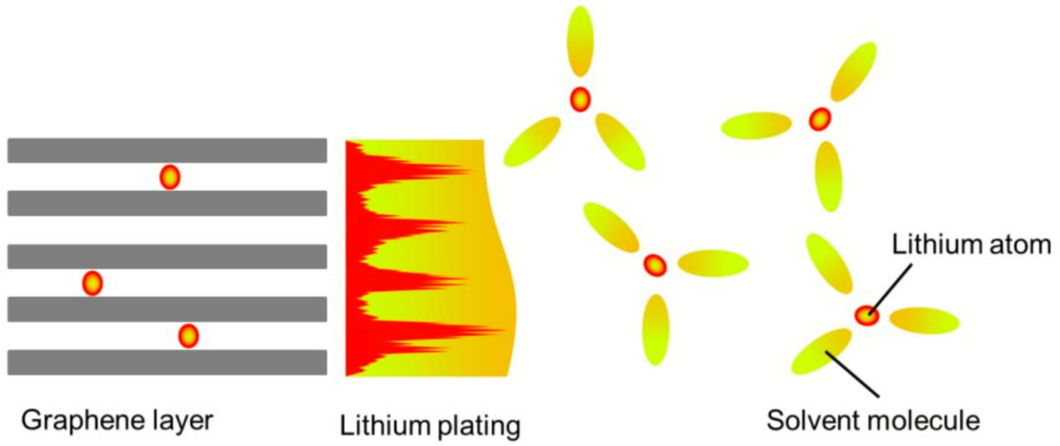

Figure 18: Overcharging leads to lithium plating [94].

To deal with this problem, the batteries should be charged under nominal conditions in lower temperatures. Nevertheless, polymer electrolytes provide a solution, due to their diffusion pathways delaying the dendrites to grow along these channels, punctuate the separator, and reach the cathode.

4.2.1.2 Internal and External Short Circuit

An internal short circuit is a dangerous fault that can occur in a battery, arising from several factors. It happens when an unintended electrical pathway between the two electrodes is created while disrupting the separator’s integrity. Thus, an uncontrolled electron flow travels through a low-resistance conductor producing extreme heat and pressure inside the cell. Lithium dendrites, physical damage leading to separator decomposition, or current-collector dissolution can result in internal short circuits.

Similarly, an external short circuit is a connection between the two electrodes, but in this case, outside the battery, through the collector tabs. A possible cause is when the two electrodes are bridged through conductive materials, such as metal materials, liquids, or wires that come simultaneously, in direct contact with the two electrodes, supplying more electric current which is not governed by the battery's designed normal circuitry.

Both internal and external short circuits generate uncontrolled and often high-current flow directly between the battery's terminals resulting in excessive heat. Therefore, overheating can arise. Overheating can lead to capacity loss, SEI growth, accelerated degradation, or even material breakdown. In more severe conditions, thermal runaway can be triggered [115],[116].

4.2.1.3 Accelerated Degradation

Accelerated degradation is crucial for the operation and efficiency of the battery but also for the safety of the user. Small traces of battery degradation can lead to decreased efficiency, which is observed as capacity loss and shortened cycle life from a user perspective. An increased rate of degradation can be an indicator of severe conditions inside the cell and raise safety concerns. Heat generation, thermal runaway, and explosion are unfavorable consequences, which are possible.

Accelerated degradation can occur from numerous factors. The quality of charging and discharging can play an important role. More specifically, high-frequency charging and discharging, as well as deep discharges and overcharging can generate additional stress on the components and lead to irreversible damage. Age and natural degradation, even under ideal conditions, can lead to capacity diminishing. Finally, chemical and side reactions can occur in normal or abusive conditions, affecting the SEI or other byproducts, leading to performance migration, short circuits, or even thermal runaway [115],[116].

What exactly is a thermal runaway, being a consequence mostly of every type of fault?

4.2.1.4 Thermal Runaway

All the above faults can lead to thermal runaway. It is usually related to temperature rise resulting from external or internal heat generation during unpropitious conditions. A definition for thermal runaway could be: It is an uncontrolled chained heat expansion, initially, generated from a localized heat accumulation that triggers exothermic reactions, which in turn accelerate the temperature increase enabling more exothermic reactions, resulting in battery failure. An example can be more descriptive.

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In the case of a lithium-ion battery with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ as the cathode and MAG-10 graphite as the anode in a 1.2 M EC: EMC electrolyte, thermal runaway can be divided into three stages [115]:

1. At 90 ^{o} C low-rate anodic reactions occur and can increase the temperature. The solid electrolyte interface breakdown will occur at 120 ^{o} C, resulting in electrolyte and anode reactions, such as the SEI initial formation process, but at an uncontrolled, higher temperature. This exothermal reaction will further increase the temperature.
2. At 140^{o} C exothermic reactions at the cathode material, electrolyte decomposition, and gas release will increase the temperature, in combination with the separator meltdown which enables short circuits.
3. Above 180 ^{o} C the cathode materials generate O_2 which enables interfacial oxidation of the electrolytes, leading to a thermal runaway with a 100^{o} C/min rate. The combination of the gases released from the inflammable electrolyte (ethane, methane, and others), the oxygen released from the cathode decomposition, the high temperature, and high pressure could result in an explosion. Hence, the thermal stability of the individual components is crucial for preventing heat generation. $LiFePO_4$ seems to have the most appealing thermal safety. Internal heat generation, and therefore, thermal runaway is highly related to overcharge due to joule heat [118].

4.2.2 External Battery Faults

External battery faults have an important impact on the battery management system’s functions and can lead to internal battery faults. Some of the most common and serious faults, such as the cooling system fault will be investigated, before analyzing the failure mitigation strategies [116].

4.2.2.1 Sensor Fault

Sensors are critical for performance inspection and thus, faults can affect battery safety and trigger internal faults. Sensor faults include failures of current, voltage, and temperature faults. They are caused by electrolyte leakage, vibration, or other physical factors such as corrosion around the battery sensor. Sensor faults can undermine the functionality of the battery management system and lead to overcharge, inaccurate estimation of state of charge, and overheating due to voltage, current, and temperature sensor failure, respectively.

4.2.2.2 Cooling System Fault

The cooling system is responsible for the thermal management of the battery. Operating in an optimal temperature range is critical and highly dependent on the cooling system. Additionally, it cannot be separated from the temperature sensor since they both depend on a temperature range. Either the temperature fault, or the cooling system fault can affect the battery system management and result in overheating, thermal runaway, and ultimately direct failure. Cooling system faults arise when the cooling motor or fan fails to properly operate, when the fuse is broken, or as we said, when the temperature sensor's information is inaccurate.

4.2.2.3 Cell Connection Fault

Battery connection fault is caused by inefficient electrical connection of the electrodes, as they become loose due to vibrations or impurities over time. Consequently, the cell resistance can increase, resulting in uneven current, overheating of the faulty cell, and thus cell imbalance. Although this fault can be easily diagnosed through voltage, and temperature sensors, it must be solved to avoid, for instance, an external short circuit.

4.3 Failure Diagnosis Methods

4.3.1 Battery Management System

Battery Management Systems are vital for mitigating and controlling the battery's health. State of Charge, State of Health, Depth of Discharge, and State of Function are all parameters and stats monitored by a battery management system. Software and hardware systems are combined for data collection, diagnostics, and cell balancing, through multiple sensors. Prediction, identification, and response are the key characteristics of a battery management system to set up a safe operating area. Furthermore, diagnostic checks should be run regularly, along with working cycles, and thermal management. Once a fault is detected, actions including isolating the faulty cell or even the entire module are indispensable and depend on the severity of the failure. As the software and hardware implementation of lithium-ion batteries becomes more complex fault diagnostic algorithms are required to improve battery safety. These algorithms are responsible for detecting the failure early and providing immediate control actions. The main methods for failure diagnosis will be investigated in this unit [116].

4.3.2 Analytic Model-Based Methods

Model-based methods rely on the accuracy of a battery model. The model is used to detect parameters with fault information and determine residuals. The models that can be utilized are several with the electrochemical model and the equivalent circuit model, being among the most popular. Electrochemical models reflect the chemistry and the changes of parameters inside the battery, like the dynamics of Li-ion concentration, and kinetics. However, this model is too complicated to be ideal for practical uses. The equivalent circuit model transforms the battery complexity of electrochemistry into a simple circuit involving a few elements. Thus, in terms of complexity and computational accuracy, the equivalent circuit model is more widely used [119]. In this unit, the most popular model-based methods, the state estimation method, the parameter estimation method, and the parity space method will be discussed [116].

4.3.2.1 State Estimation Method

State estimation methods are mathematical models utilizing algorithms, such as the extended Kalman filter, the Unscented Kalman filter, and the Luenberger observer, to reconstruct a measured signal, estimate a new variable, and then, compare it to the true value. The comparison between the estimated value and the sensor measurement is called a residual. The residual signal, compared to a given threshold value, will reveal a case of fault. The key technique of this method is to reconstruct and estimate a state, such as the battery's, state of charge, using observers and filters.

To detect the heat generated during operation, observers, and filters, can monitor the internal resistance of the battery. Specifically, a Lyapunov-based observer can monitor the internal resistance and battery open circuit, and by means of an electro-thermal coupling model, describe the dynamic behavior of the charge heat. Also, a Kalman filter-based observer can estimate the dynamic behavior of the surface temperature and establish a failure diagnosis scheme with adapting thresholds to effectively detect failures in cylindrical cells [116],[121].

The state estimation method has a good real-time performance and is independent of a large amount of data input. It does not need a continuous excitation signal and can monitor efficiently the functional and behavioral properties of the battery. However, the method, due to its focus on battery states, is deficient in determining the location and magnitude of the failure. A simplified representation of the state estimation diagnosis method is shown in **Figure 19**.

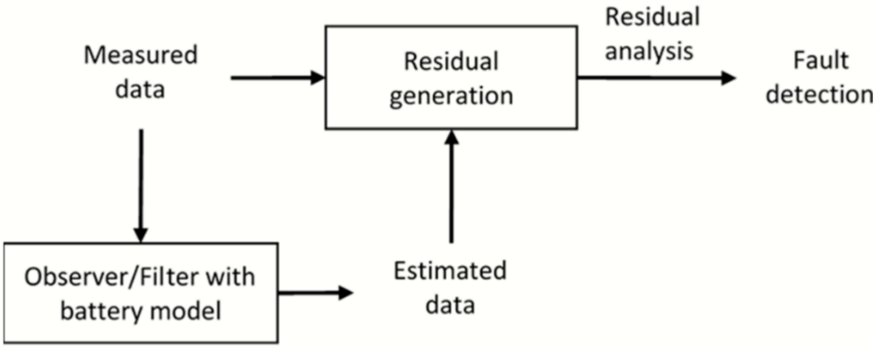

Figure 19: A State Estimation Method Simplified Representation [116].

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4.3.2.2 Parameter Estimation Method

Faults and battery malfunctions will affect the physical properties leading to model parameter alterations. The idea of this method is to identify the relevant parameters, monitor their variation behavior, and compare them to the normal operation values. This examination between the two values will feature a possible fault. The most common methods are genetic algorithms, the recursive least squares, and particle filtering.

Internal short circuits can affect the temperature, or voltage of the system indicating a fault. The recursive least squares algorithm used in an equivalent circuit model can efficiently estimate these parameters, observe changes, and detect faults. The recursive least square algorithm and the Kalman filter can be combined for state and parameter estimation, such as the state of charge, voltage, internal resistance, and temperature. Thus, extra capacity depletion, internal short circuits, and heat generation can be detected.

The parameter estimation method is conducive to fault isolation, but highly dependent on high-precision modeling and decent input excitations [121],[122].

4.3.2.3 Parity Space Method

The parity space method analyzes the relationship of the input and output variables. The most fundamental measurements for lithium-ion battery systems are temperature, voltage, and current. Dynamic equations and residual vectors can describe the internal consistency between these measurements and their analytic relationship. In case of a fault, this relationship will be affected and reflected in the residuals, revealing its presence. Due to the structure of the method, solving linear equations or linear optimization is deficient in nonlinear systems, and sometimes, inaccurate in complex and unstable battery conditions [121],[122].

4.3.3 Knowledge-Based Methods

These methods do not require a mathematical model, are suitable for complex, nonlinear systems, like lithium-ion batteries, and depend on subjective analysis, logical judgment, and inferential analysis. Nevertheless, they require an in-depth knowledge background of the lithium-ion battery mechanism. These methods include the expert system method, the fuzzy logic method, and the graph theory method.

The **expert system** is a computer program that uses expert experience and historical data, to construct and simulate the reasoning behavior of human experts. Thus, it is limited in learning and adapting to new conditions. The **graph theory** method includes a signed directed graph, fault tree, and failure mode and effects analysis. It easily interprets fault diagnosis results, but it is inefficient in complex systems. Widely used, the fault tree analysis is a simple, deductive method, with clear cause-effect relationships. Events and records branch down, connected by logical symbols, to result in a single point, the fault. Although it is effective, it is deficient in more complex systems, where more steps are required for a fault to occur. Fuzzy **logic** is ideal for qualitative knowledge and reasoning handling, but it is deficient in self-learning. Using fuzzy relationship equations and membership functions, the fuzzy logic method can identify the relationship between fault phenomena and fault causes to solve the problem of state identification and fault cause [121].

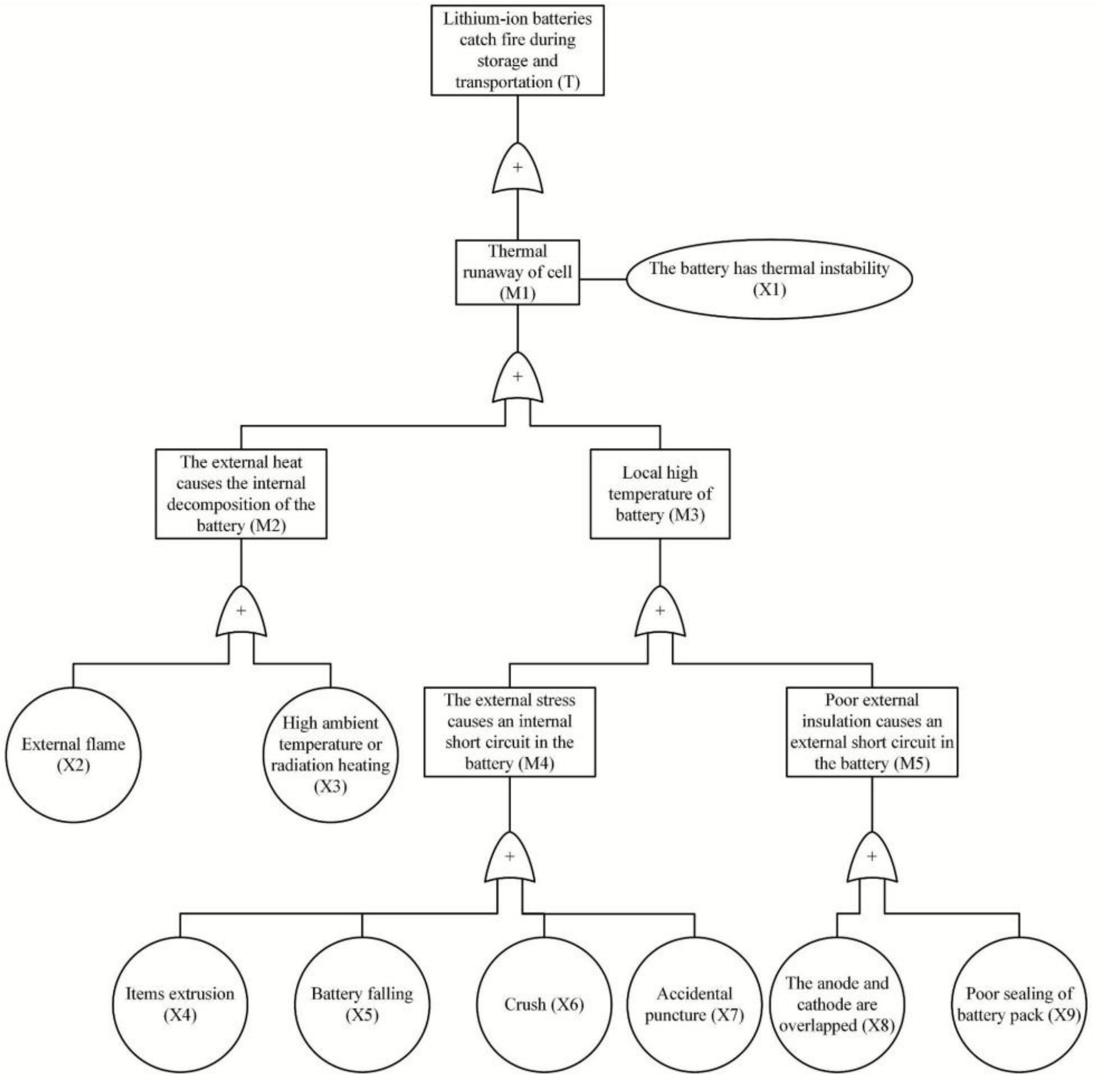

Figure 20: Battery fire during transportation and storage analyzed by fault Tree method analysis [123].

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In **Figure 20** the fault tree analysis is used to categorize the causes and events that lead to thermal runaway, and ultimately to fire, during the transportation and storage of batteries. The fuzzy logic method can be combined to quantitively assess the hazard risk, by evaluating the likelihood, severity, and control parameters for the events. Then, actions like cell isolation will be enabled if high severity is triggered through fuzzy calculations [123].

4.3.4 Signal Processing-Based Methods

Signal processing can be effective in fault diagnosis, by setting threshold values, and comparing the target with the threshold. The amplitude, frequency, and phase can be related to the target values of the output signal and detect a fault. This method does not require a specific battery model. Two commonly used methods are wavelet transform and impedance spectroscopy analysis.

Wavelet transform is very effective in noise suppression and thus, very efficient in determining whether a fault occurs. During the operation of batteries in electric vehicles, multiple factors such as driving habits, electromagnetic interference, and road conditions can increase the complexity of fault diagnosis. Wavelet transform can eliminate the noise of voltage signals that may result in misjudgment of faults and precisely monitor the behavior of the battery.

Electrochemical impedance spectroscopy can provide ageing mechanisms with electrochemical information and predict the remaining useful life, by collecting indicators about the battery's state of health [121],[116].

4.3.5 Data-Driven Methods

Machine learning and artificial intelligence are constantly developed and gradually applied to battery failure diagnosis. Operational data can be directly analyzed and processed for fault detection and separation. These methods are dependent on historical data to compose the fault rules for diagnosis. Thus, efficiency is proportional to the amount and accuracy of historical data. The training process for the establishment of the rules is time-consuming but neglects the requirement of accurate models with large computational volumes. The data-driven methods are based on artificial intelligence and hence, they can manage complex systems. Neural Networks and support vector machines are common methods for fault identification.

Methods utilizing neural networks collect data and fault cases as inputs and outputs, respectively. Sensor fault, overcharge fault, SOC fault, and several other types of failure data can be used to train a neural network model and predict in real time a battery fault.

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Support Vector Machine is a supervised classification technique used to distinguish between faulty and normal data. It excels in scenarios with limited data and exhibits superior generalization when compared to neural networks. In the context of battery diagnosis and state of charge estimation, SVMs have been employed by researchers. They have developed predictive models and utilized grid search optimization to enhance accuracy and robustness in identifying battery faults [122].

4.3.6 Statistical Analysis-Based Methods

In the field of battery system analysis, statistical analysis methods are indispensable tools for comprehensively assessing and diagnosing various aspects of battery performance. These methods encompass a range of statistical techniques, including Information Entropy, Gaussian distribution, Correlation Coefficient, and Maximum Likelihood Estimation. Information Entropy is applied to quantify data uncertainty and identify unusual patterns indicative of potential faults, while Gaussian distribution is used to assess data adherence to a bell-shaped curve, with deviations signaling anomalies. The Correlation Coefficient quantifies linear associations between variables, aiding in understanding relationships within the battery system. Lastly, Maximum Likelihood Estimation contributes to parameter estimation and system modeling. By scrutinizing these methods, this research aims to advance our understanding of battery system monitoring, fault detection, and modeling for improved system reliability and efficiency [121].

4.4 Safety Strategies

4.4.1 Overcharge Protection Additives

Overcharge is one of the most common battery faults. A higher voltage than the end-of-charge voltage, or the designed upper voltage, can lead to other, more catastrophic issues for the battery’s integrity. The voltage of lithium-ion batteries is currently controlled by the battery management system, which coordinates sensors touching each cell of the battery individually. This electronic circuit system can be accurate and efficient in voltage control. However, the weight, volume, and cost of the system, as well as the concern of hardware failures due to abnormal conditions have demanded scientific research for more protective solutions.

The **redox shuttle** is an economical and efficient mechanism that acts internally, in the chemistry of the battery, to overcharge protection. It is an electrolyte additive that can produce reversible redox reactions at a defined voltage slightly higher than the voltage-designed upper threshold. During the overcharge of lithium-ion batteries, the oxidation of the additive will occur before the oxidation of the electrolyte, on the surface of the cathode. More specifically, the shuttle molecule has a defined redox potential, where it is inactive during normal charging, and it is activated when the voltage of charging is slightly higher than the end-to-end voltage. During activation, redox reactions occur, and the shuttle molecule is oxidized on the cathode and reduced on the anode. The redox cycle aims to shuttle the charge-forced externally, through the cell without forcing intercalation and deintercalation of lithium in the electrodes [124],[125]. The performance of a redox shuttle for efficient overcharge protection can be evaluated with four characteristics:

1. The shuttle should have a higher and a lower oxidation potential, from the end-to-end charge potential, and the electrolyte decomposition potential, respectively.
2. High kinetic reversibility of the redox reactions is required on the positive and negative electrons.
3. The shuttle needs to have a very high solubility and diffusion coefficient.
4. Chemical and electrochemical stability is required for the redox shuttle to provide long protection from overcharge.

Some examples of redox shuttles, that can endure high voltages are phenothiazines, organometallic metallocene, triphenylamine, dimethoxybenzene, and more. A few redox shuttle additives, as well as some of their derivatives, are demonstrated in **Table 5.**

Table 5: Some redox shuttle additives and their oxidation potentials [114].

Abbreviation	Full names of redox shuttle additives	Onset oxidation potential for overcharge protection (V)	Deployed battery chemistry
TEMPO	2,2,6,6-tetramethylpiperidinyloxide	3.52	LFP
MPT	10- methylphenothiazine	3.74	LFP
BODTB	1,4-bis(2- methoxyethoxy)-2,5-ditert-butylbenz	3.80	LFP
DBBB	2,5-di-tert-butyl-1,4-bis (2-methoxyethoxy) benzene	3.90	LFP
DBDB	2,5-di-terbutyl-1.4- dimethoxybenzene	3.96	LFP
TDTN	1,2,3,4-tetrahydro-6,7- dimethoxy-1,1,4,4-tetramethylnaphthalene	4.05	4V cathodes
PFPTFBB	2-(pentafluorophenyl)- tetrafluoro-1,3,2-benzodioxaborole	4.30	4V cathodes
PFPTFBB, 1	Tetraethyl-2,5-di-tertbutyl-1,4-phenylene diphosphate	4.43	4V cathodes
TEDBPDP	diphosphate lithium	4.80	LCO, LMO
Li2B12FxH12− x	fluorododecaborates	4.90	LMO

Another way to mitigate overcharge failures is the **Shutdown overcharge additives** which are irreversible and suspend the battery operation permanently once a higher voltage is triggered. The overoxidation of conductive polymers can lead to the loss of electroactivity and electric conduction, and thus, they can be efficiently applicable for the overcharge protection of lithium-ion batteries. These additives, during overcharge, at a specific potential, are oxidized on the positive electrode surface leading to shut down and terminating the cell's function. Additionally, these kinds of additives, such as biphenyl, hexylbenzene, and more, at higher potentials can also release gases that trigger the current interrupting device and shield the cell, isolating the external circuit. The huge drawbacks of these are the calendar life shortening, due to the irreversible oxidation, and the complete shutdown of the cell [114].

4.4.2 Overheating Protection

4.4.2.1 Improved Cathode Materials

Three strategies will be suggested regarding the improvement of cathode materials to prevent overheating, element substitution, coating, and electrode partition.

The thermal performance of a lithium-ion battery can be improved with the element substitution of the layered oxide metals. For instance, in a coin $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ Co was partially substituted by Ni and Al for enhanced thermal stability. In addition, experiments have shown that doping and alloying elements like Ni and Mn can improve the decomposition onset temperature of $LiCoO_2$.

Protective coating on the outer surface of the cathode can also be efficient. More precisely, the coating can be either chemical or inert thermal materials. Chemical inert materials can be inorganic films [MgO, ZnO, ZrO, AlF_3], organic films, and protective films. Thermal inert materials can be poly(3-decylthiohene) and poly(3- octylthiopene). These coating materials can prevent side reactions, stop electrochemical reactions, or even shut down the battery. Finally, electrode partition is a promising technology. In a vehicle car accident, abnormal conditions and stress can lead to the contact of the two electrodes. Nevertheless, with this technology the electrodes are designed to separate into parts and break, neglecting the electricity movement. Thus, the battery terminates before punctuating the separator and triggering an internal short circuit [114],[124].

4.4.2.2 Improved Anode Materials

In the case of anode materials coating can be effective regarding thermal stability and cycle performance. This enhancement mitigates the electrochemical reactivity with the electrolyte and improves the SEI layer stability. $Li_4Ti_5O_{12}$ (or LTO) is a promising material for producing artificial SEI layers in various materials and thus prevents the thermal decomposition of the layer [1124].

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4.4.2.3 Thermally Protective Separators

The separator is crucial for cell safety. A solution to achieve thermal stability is a separator with a considerable difference between the shutdown and melting temperature. The separator shutdown is the process of the separator pores shutting down, at a temperature close to the melting point. This is an unwanted procedure that occurs in high temperatures. However, it can prevent ion transport through the separator during thermal runaway by closing the pores. Tri-layer separators, for instance, triple-layer polymer separators where two PP layers encase a PE layer, have been researched and have already been commercialized achieving the polyethylene’s shutdown and melting lag. Nevertheless, this combination has a narrow temperature margin. Ceramic coating can enhance wettability and the melting temperature of polyolefin, as well as the reduction of material melting in high temperatures.

4.4.2.4 Flame-Retardant Additives

The safety concerns linked to lithium-ion batteries relate to their use of flammable materials as electrolytes. To make them safer, researchers are exploring flame-retardant (FR) additives that reduce the risk of fires. These additives, like trimethyl phosphate TMP(a) and trimethyl phosphite TMP(i), are showing promise by improving thermal stability and reducing heat production. An interesting discovery is dimethyl methyl phosphonate DMMP, which significantly decreases flammability and can make electrolytes non-flammable with just a small amount added. However, some FR additives, like alkyl phosphates, have stability issues, and scientists are trying new ideas, such as lengthening carbon chains or using different chemical groups, to improve them. Other additives, like IPPP and fluorinated propylene carbonates, aim to balance fire safety and battery performance. Finding the right FR additive that doesn't harm battery performance is an ongoing challenge, driving further research in this area.

4.4.3 Protective Devices

Protective devices are essential for the integrity and safety of the battery. These features can prevent potential hazards and minimize the risk of accidents. Some key protective devices are investigated below:

- Safety Vents: These devices are small thin membranes, made of a pressure-sensitive material, and designed to release excess pressure, produced inside the battery, to prevent failure. While the pressure builds up, two grooves in the membrane provide localized stress to break an opening, when the pressure is sufficient [126].

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- Positive Temperature Coefficient Devices (PTC): These thin conductive polymer layers have a resistance sensitivity to the temperature. When the temperature reaches a critical point, they are activated by overheating and increase their resistance to mitigate the current flow across the cells. Once the device cools down, it can remain conductive again. This reversibility can restrict thermal runaway through uncontrolled current flow. Carbon black polyethylene and epoxy carbon composites have been proposed as PTC devices.
- Current interrupting device (CID): This device is responsible for monitoring and controlling the excessive current flow of the battery. They are set to a specific current threshold, slightly above the maximum charge or discharge for the battery. When it detects an overcurrent condition, a mechanical or electronic switch is triggered within the battery, disconnecting the battery, and cutting off the electrical flow. If the abnormal conditions are temporary, the CID can reset itself and allow the battery to be used safely again. These devices are still under investigation and research. In **Figure 21** the arrangement of the PTC, CID, and safety vent, connected to the positive tab, in a cylindrical cell is illustrated.

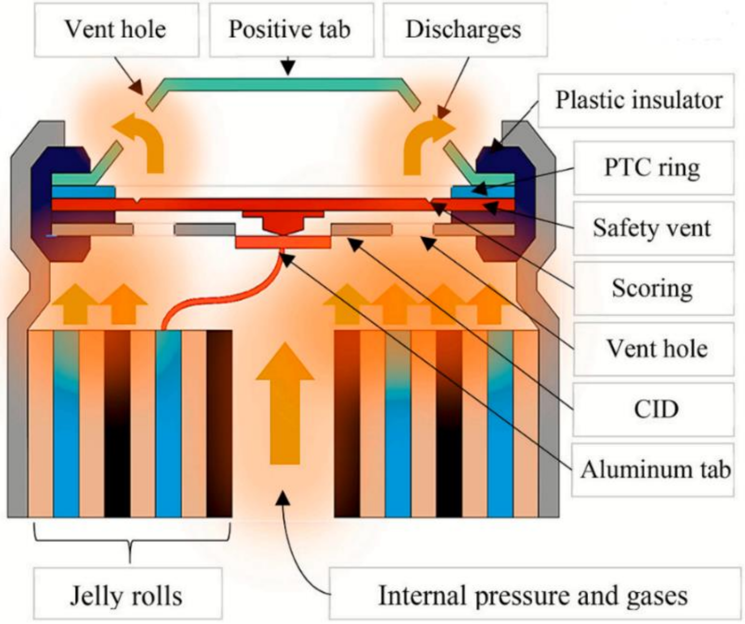

Figure 21: Safety device's location in a cylindrical cell [124].

4.4.4 Thermal Management

Battery Thermal Management Systems (BTMS) play a critical role in maintaining the ideal temperature for batteries and improving their electrochemical performance, particularly in extreme weather conditions. These BTMS can serve various functions such as cooling to prevent overheating in hot weather, providing heat for fast charging in cold conditions, reducing temperature differences through insulation, or expelling hazardous gases via ventilation. Traditional BTMSs employ either

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air or liquid cooling methods, with liquid cooling being more efficient but requiring careful tuning of factors like channel design. Commercial electric vehicles often employ a combination of both air and liquid cooling systems. Emerging technologies include thermoelectric coolers, thermo-acoustic refrigeration, and phase change materials. As an example, some cell phones now use heat pipes with paraffin wax to effectively manage temperature in various situations, aiming to enhance battery performance and safety in diverse environments [124].

4.4.5 Lithium-Ion Fire Suppression in Electric Vehicles.

During electrochemical abuse the above techniques can be efficient in preventing fire in the cell, but now always. After the failure of a cell heat isolation and enhanced cooling between cells can mitigate the fire propagation. The same design can be effective in the case of module thermal runaway propagation. A module is a collection of cells. When the whole pack catches on fire, a fire extinguishing system, using water or water mist, will enhance fire mitigation. Water mist combined with fire-fighting powders and foams can be more efficient. Dodecafluoro-2-methylpentan-3-one (C6F12O) is a gaseous suppression agent, commercially used, enhancing fire suppression. Regarding passenger protection, when the vehicle is set on fire, a fireproof layer between the battery pack and the passenger seats can be integral for the safety and escape of the passengers. [127]

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Chapter V

LITHIUM-ION BATTERY RECYCLING

5.1 Introduction

The lithium-ion battery usage, particularly in electrical transportation, as well as the number of batteries reaching their end-of-life are exponentially increasing making the recycling process indispensable for an efficient and sustainable energy system. From 1996 to 2022 lithium-ion battery sales increased more than 16% every year, especially in the last 3-4 years. This indicates the immense amount of spent lithium-ion batteries in the next decades.

Valuable metals, including Co, Ni, Li, and Mn, and organic electrolytes are critical components, and harmful components of retired lithium-ion batteries, respectively. Hence, recycling is not only essential to conserve resources but also to protect the environment.

A lithium-ion battery cannot be recycled directly due to its component complexity and perhaps its residual high voltage. Thus, pre-treatment procedures are essential before the recycling of the batteries to reduce risk and improve production efficiency. A screening process can determine the battery’s recycling route. Batteries with better performances can be regrouped for a second usage, and thus, repurposed, and the others for individual component separation and recovery. Pre-treatment is crucial for recycling because the variety of lithium-ion battery packs, modules, and cells is immense, making the procedure complex. Thus, improvement for initial separation, safety consideration, and efficiency is important. Sorting is also significant.

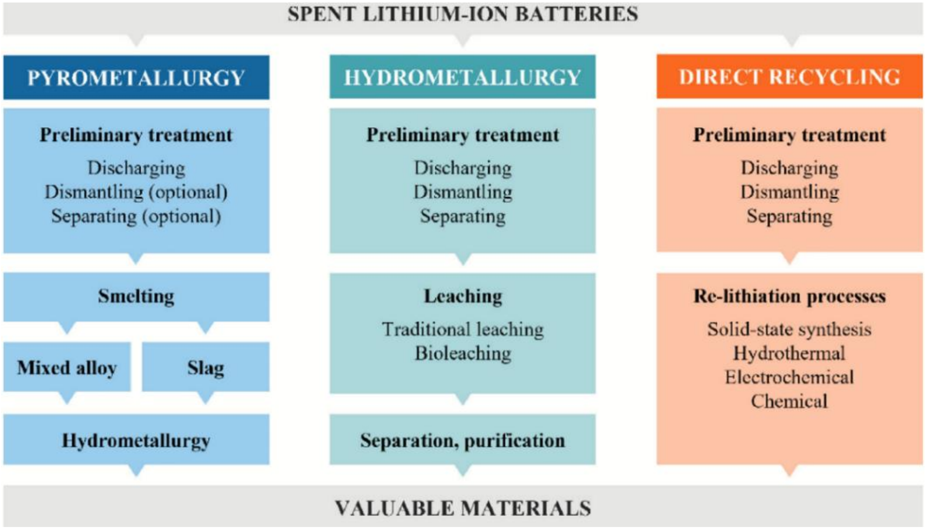

Figure 22: Typical processes for lithium-ion batteries representation [128].

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Based on battery chemistries, sizes, or shapes, batteries are sorted to facilitate the recycling process. The element recovery and component recycling methods, pyrometallurgy, hydrometallurgy, and direct recycling are depicted in **Figure 22** [128]. Initially, the lithium resources and usage will be investigated to emphasize the importance of recycling. Next, the recycling methods will be analyzed, including some experimental results from the bibliography.

5.2 Lithium Resources and Usage

Progress in material technology shows that several elements in lithium-ion batteries, harmful to the environment and difficult to extract, such as cobalt, will be partially or completely substituted. However, lithium is the pivotal element of lithium-ion batteries, and thus, efficient extraction strategies and recycling are indispensable to meet the market demands. Lithium, although it is used widely, is stored mainly in South American Nations, such as Argentina, Chile, and Bolivia. These countries contain more than 55% of the world's lithium. China is a crucial country in lithium-ion battery production, as well as lithium production, and has significant amounts of lithium resources. In **Figure 24 (b)** global lithium resources are represented.

Lithium is extracted mainly from ores and salt lakes. Petalite, amblygonite, eucryptite, spodumene, and lepidolite are some of the mineral sources of lithium, with the latter two being the most typical. The composition of lithium in these ores fluctuates between 2 - 5.5 %. Typically, through a series of processes, separation, water leaching, acid treatment, and pressure leaking, Li is extracted in the form of Li_2CO_3. Brines accommodate more than 60% of the world's lithium. Several methods exist to extract lithium, but the precipitation method is the first and simplest. In this process, the Mg/Li ratio is critical since the separation of these two elements is extremely difficult. The process begins with the solar evaporation of the water and is followed by the precipitation of NaCl and KCl. After adding $Ca(OH)_2$ to the concentrated lithium brine, Mg and sulfate are removed through precipitation. Similarly, Ca and Na_2CO_3 are removed via precipitation by adding $CaCO_3$. Finally, filtration, washing, and heat will result in the reaction of lithium and $CaCO_3$. While this is a popular method, it can last from 18 to 24 months. Although ores store higher concentrations of lithium, the production costs are higher. Thus, brines remain the main source of lithium production. In **Figure 23** the precipitation method is illustrated [129],[131].

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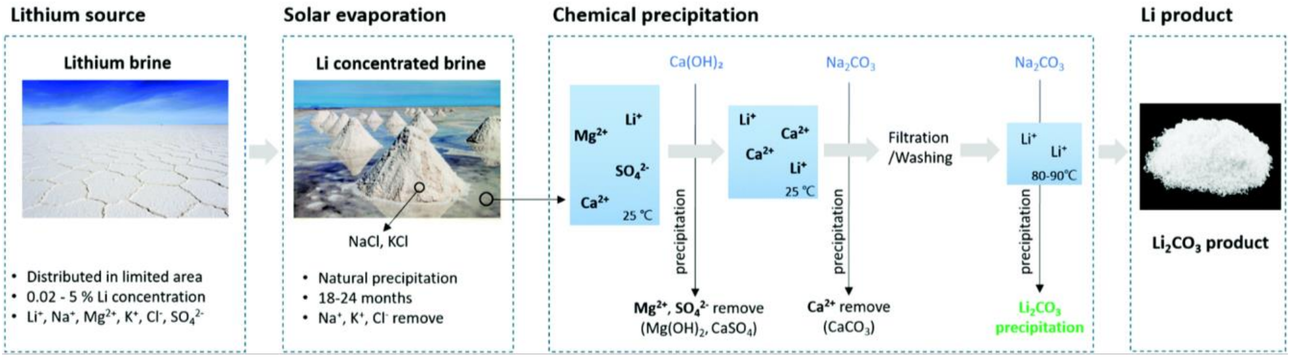


Figure 23: Lithium extraction *via* chemical precipitation [129].

According to the Mineral Commodity Summaries 2023 of the U.S. Geological Survey, the global lithium consumption in 2022 was approximately 134,000 tons. This is 41% more from 2021, and 570% more from 2010. In addition, in this period the proportion of lithium in battery consumption skyrocketed from 23% to 80%. In **Figure 24 (a)** lithium usage distribution is illustrated [132].

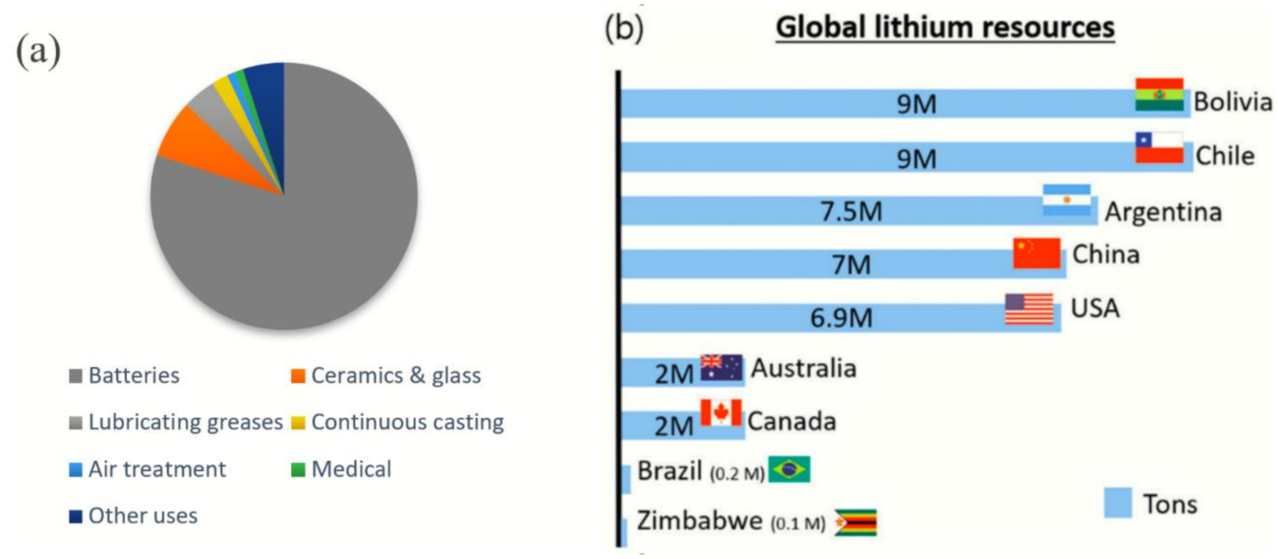


Figure 24: (a) Lithium usage distribution in 2022, (b) Global Lithium Resources [129].

The unexpected exponential increase in lithium consumption has led to an increase in the element’s prices. This is due to the demanding and time-consuming procedure of lithium extraction. Thus, more investments in the extraction and value chain of lithium, more gigafactories, and cooperation of the world’s countries are essential for a balanced lithium economy.

Finally, nuclear fusion is considered the key technology to solve energy problems, and an ‘artificial sun’ is not a science-fiction scenario anymore. Lithium is one of the most important metals of the 21st century, if not the most important, not only for its usage in lithium-ion batteries but also for its contribution to controlled nuclear fusion. The sun generates energy through the fusion of hydrogen isotopes, deuterium and tritium. Deuterium is abundant and easily extracted but tritium is nearly absent. However, the fission of lithium can release helium and tritium.

In **Figure 25** the global production of the key elements of lithium-ion batteries are represented.

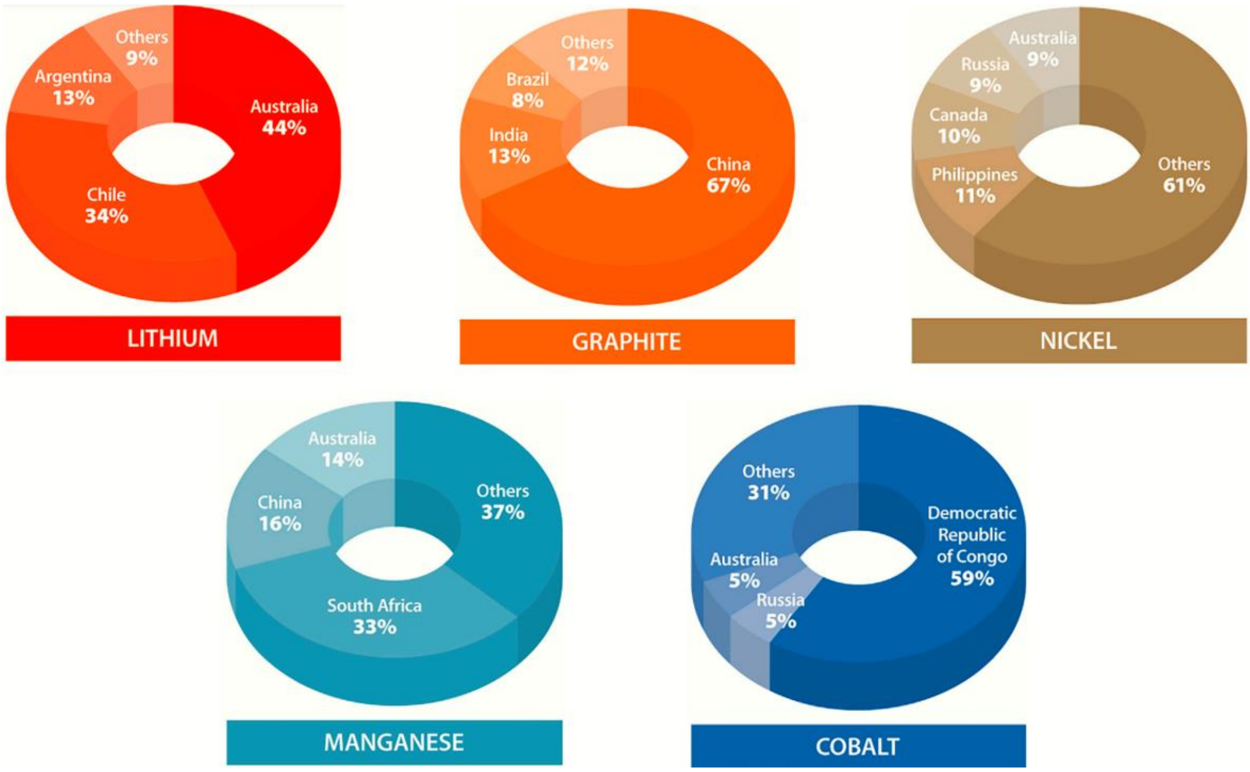


Figure 25: Representation of lithium-ion battery key elements global production [131].

5.3 Remanufacturing and Repurposing

When electrical vehicle lithium-ion batteries reach their end-of-life state, means that they have reached 80-85 % of their original capacity. These modules can be collected for remanufacturing or repurposing. This demands damaged cell replacement as well as reconfiguring of cells, such as the establishment of a new battery management system.

Particularly, in the case of remanufacturing refurbishing lithium-ion batteries is demanded to bring them back to their original, like-new condition. This process typically includes the replacement of subpar or worn-out components, such as individual cells or modules, and restoring the battery to meet or closely match its original specifications. The goal of remanufacturing is to ensure that the battery can be reused in its original intended application or a similar one that requires high performance and reliability. Remanufactured batteries are often expected to meet specific standards and may be used in applications where precision and consistency are critical, such as electric vehicles (EVs). Repurposing, on the other hand, involves taking lithium-ion batteries that may no longer meet the stringent requirements for their original application and finding new, alternative uses for them. These alternative uses might not require the battery to operate at its original, peak performance. Repurposed batteries may find applications in less demanding roles, such as stationary energy storage, renewables integration, EV charging, peak shaving, back-up, and frequency regulation, which are some of the second-use systems. The goal of repurposing is to extend the useful life of batteries by giving them a new purpose, even if they can no longer deliver the high performance needed for their initial application. Stationary storage, for instance, can offer an extended useful lifetime after automotive usage. However, several challenges in repurposing of lithium-ion batteries are faced. Collecting several electrical vehicle battery packs adds variation in designs, performance metrics, cost of configuration, and liability, which makes it difficult to compete with new, cheaper batteries [130],[138].

5.4 Pre-treatment Methods

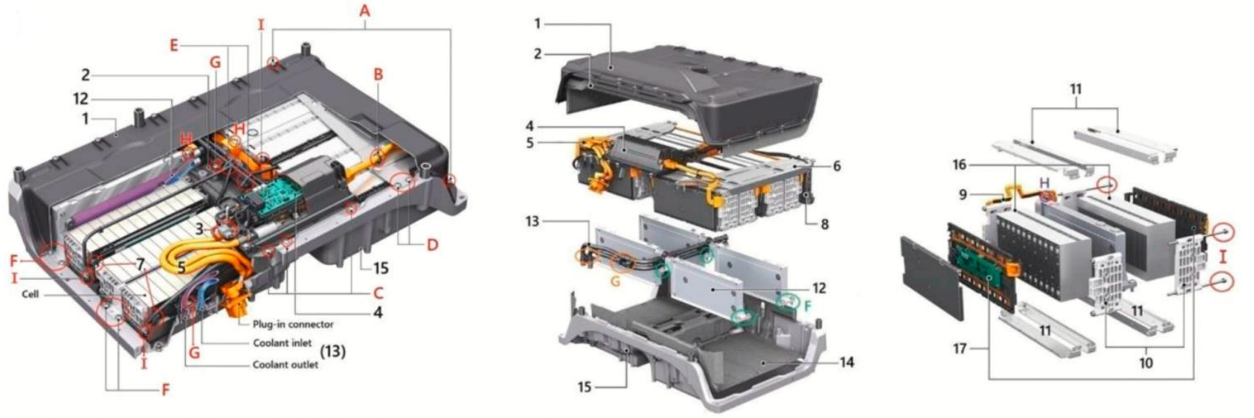
Deactivation

Retired batteries reaching the recycling facilities have residual power which, without deactivation, during physical separation can lead to electrical energy release, overheating, fire, or even explosion. Hence, the discharge of the batteries to a certain safe level is indispensable.

The most common and widely adopted method is the discharge by means of conductive liquids. Lithium-ion batteries are soaked in conductive media for residual power removement. Aqueous salt acts as a controlled short-circuit to discharge the batteries. Chloride salt (KCl or NaCl) is the most used solution for discharge due to its low price, availability, and discharge efficiency. Case corrosion resulting in electrolyte leakage is a challenge. Some sulfates, such as $MnSO_4$, are utilized to solve this issue. Mn ions can isolate oxygen and prevent battery case corrosion [133],[134].

Dismantling

Dismantling is essential for component separation. It is usually a manual procedure. The physical teardown of the battery can be dangerous for workers due to possible short circuits, electrolyte decomposition, and toxic gas release resulting in accidents. However, in some cases such as the dismantling of an electrical vehicle's battery pack, physical interaction is inescapable. In **Figure 26** the dismantling plan of an Audi A3 Sportback e-tron Hybrid Lithium-ion battery pack is illustrated. It involved numerous fasteners to be separated into the cells, housing board, and housing shell. This dismantling plan was conducted by the Umicore plant in Hanau. It is essential, hence, that automatic dismantling should be developed more in the future to achieve the dismantling of complex battery packs and increase the working environment safety. After dismantling the battery pack is separated into battery cells and modules. Then, for material separation, a variety of crushing processes can be utilized [134],[135].



Li-ion battery of the Audi A3 Sportback e-tron Hybrid

Exploded view of battery pack

Exploded view of battery module

Figure 26: Audi A3 Sportback e-tron Hybrid Lithium-ion Battery dismantling plan and exploded view representation [134].

Crushing

Crushing is a size reduction stage, essential to reduce the volume of the cells and release valuable components. Air presence is crucial for the safety of the procedure, due to the high reactivity of many components and elements, such as lithium. Thus, the crushing methods are mainly categorized into wet and dry crushing, regarding strict safety measures.

The wet crushing method has benefits but also important drawbacks. The water or a salt solution, being at room temperature can act both as a temperature controller to prevent overheating and as a scrubbing agent, suppressing dust and dislodging impurities. However, water consumption, wastewater generation, and Cu and Al foil over-crushing are issues limiting the potential of wet crushing. Hence, contamination of impurities and wastewater emissions indicate the incapability for large-scale commercial use.

Dry crushing demands strict discharge procedures to prevent exothermal chemical reactions. In addition, progress in crushing in an inert atmosphere is required for a safer and more efficient method.

The crusher type can point out the particle size distribution. Rotating crushing devices and methods, such as shredding, granulating, and hammer milling are commonly used (**Figure 27).** Regarding the sheet shape of the battery components, shredding is advantageous in producing smaller particle size matter.

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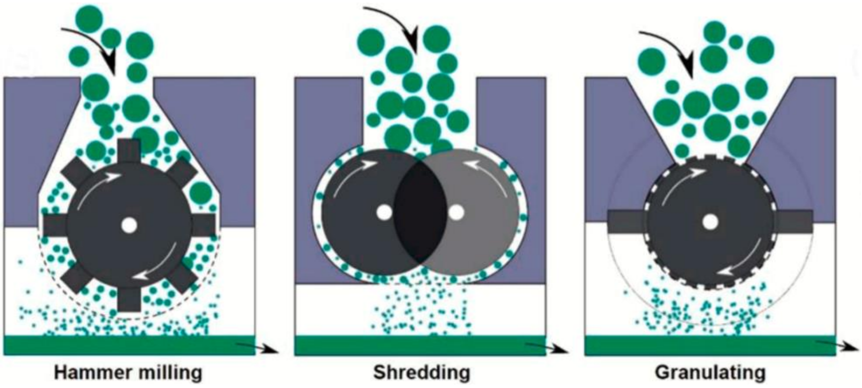

Figure 27: Commonly used rotating types of crushers [134].

Physical hazards, such as equipment overheating, and gas emissions due to electrolyte decomposition are concerning issues suggesting operation improvement [134],[136].

Electrolyte separation

Electrolytes, containing conductive lithium salts and organic solvents, account for more than 10% of the battery cost. Additionally, environmental concerns as well as the high costs of lithium salts necessitate electrolyte separation and treatment after their service. Thermal treatment and extraction are the two most common methods to recover electrolytes. Thermal treatment involves the heat of the electrolyte to achieve distillation or decomposition. Temperature and oxidizing atmosphere are the two variables for electrolyte distillation and decomposition. Nevertheless, an electrolyte exposed to air containing oxygen can result in uncontrollable conditions. Thus, thermal treatment at higher temperatures and oxygen-free atmospheres is preferred.

To achieve the distillation and recovery of electrolytes low temperatures can be utilized. For instance, the thermal treatment of retired $LiFePO_4$ at a temperature of 20-170^o C promotes the distillation of electrolytes. Additionally, Zhong et al. [130] showed that at 120^{o}C, electrolyte distillation is optimal regarding the temperature and recovery rate, and a pretreatment production line was applied by means of N_2 inert air recovering in 150 minutes 99.93% LiPF6 and 99.32% organic solvent. In higher temperatures electrolyte disposal occurs. This process concerns the effects on the environment, due to the toxic gas release through the electrolyte decomposition. Finally, organic solvents are utilized as extractants for electrolyte extraction. Acetonitrile, ethanol, and DMC can enhance the extraction of electrolytes [134], [137].

Separation of solid components

Before the metal extraction process, it is essential to separate several components to facilitate the procedure. Physical and chemical separations are significant methods in recycling pretreatment [134],[13].

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- **Physical separation** methods harness the size, density, electrical and magnetic, and other properties of the crushed material. Sieving is commonly used first to separate components such as steel cases, separators, plastics, and active materials leveraging the particle size distribution from the crushing procedure. Flotation separation is also significant for anode and cathode separation. It relies on the wettability difference between the two. Particles with hydrophilic properties will be separated from hydrophobic ones. More precisely, graphite particles tend to attach to the bubbles, since they are more hydrophobic. Transition metal oxides, in contrast, are settled in the bottom. A big challenge is the binder which eliminates the wettability difference between the two making the contact common. Fenton oxidation, pyrolysis, and grinding are examined for binder removal to enhance the wettability difference. Ultrasonic treatment is also efficient in facilitating the dissolution of binders, generating high-frequency sound waves, and creating cavitation effects that promote high pressures, and thus binder dissolution.
- **Chemical Separation** is indispensable for organic binder removal and active material separation for electrolytes. Organic solvents such as N-methyl-2-pyrrolidine (NMP) at 100^{o}C can remove the binder and separate the Cu and Al foils. A typical procedure involves the discharging of the lithium-ion battery by immersing it in a NaCl solution. Then, the manual separation of the battery components using sharp nose pliers, which included the plastic casing, metal case, electrode plate, and separator. Subsequently, the fragmentation of the cathode into smaller pieces. Immersion of these fragments in NMP at 80°C for 2 hours, led to the dissolution of the binder and the separation of the aluminum foil from the cathode material. It's worth noting that while most batteries utilize a PVDF binder to adhere to the active materials, some use PTFE binders, necessitating the selection of an appropriate organic solvent. However, this method involves the use of organic solvents at around 100°C, which increases costs and generates potentially harmful waste by-products.

  Calcination pre-treatment takes place within a temperature range of 150–500°C, serving to eliminate carbon and organic substances from the decommissioned lithium-ion battery. Furthermore, when calcinated at temperatures ranging from 250°C to 350°C, it becomes possible to remove the PVDF binder. This binder, responsible for binding the active materials to the metal foil, can then be separated, ultimately reducing the attachment of active materials to the aluminum (Al) and copper (Cu) foils.

5.5 Pyrometallurgy

Pyrometallurgy is a method where high temperatures are used to reduce metal oxides to their metallic form and recover them as alloys. Pyrometallurgy can be utilized without strict pretreatment, as dismantling the battery packs to single cells is enough. When the components are placed in a furnace, three temperature operation zones exist: preheating, pyrolyzing, and smelting and reducing.

In preheating temperatures, such as 300^o C, the electrolyte is discharged. During pyrolyzing, at around 700^o C, organic binders, solvents, and plastics are incinerated, while providing additional excess fuel heat, enhancing the smelting of the metals. In the final zone, the components are smelted, and the product is an alloy including cobalt, nickel, iron, and copper, as well as a slag with aluminum, lithium, and silicon. Thus, the nickel, cobalt, and copper are recovered, especially when they are further purified by leaching to obtain cobalt oxides, and other components [111],[139].

An immense drawback of pyrometallurgy is the huge loss of lithium in the slag phase. However, pyrometallurgy and hydrometallurgy can be combined to recover both lithium and metal alloys. Li et al. [140] roasted graphite and $LiCoO_2$ for 30 minutes at 1000^o C under an inert gas N_2 environment. The products were carbon, Co, and Li_2CO_3 which were later water leached and separated *via* magnetic separation. The lithium carbonate when undergoes water leaching dissolves in the water while the other components do not. Then, through filtration the solution which contains the lithium carbonate, is separated and proceeds to water evaporation. Finally, pure lithium carbonate can be obtained. In **Figure 28** a workflow of lithium extraction, involving pyrometallurgy is illustrated.

Significantly, pyrometallurgy is not eco-friendly due to the high energy consumption and gas release, resulting in pollution. Additionally, the loss of lithium in the slag signifies the necessity of extra steps to extract lithium [129],[140].

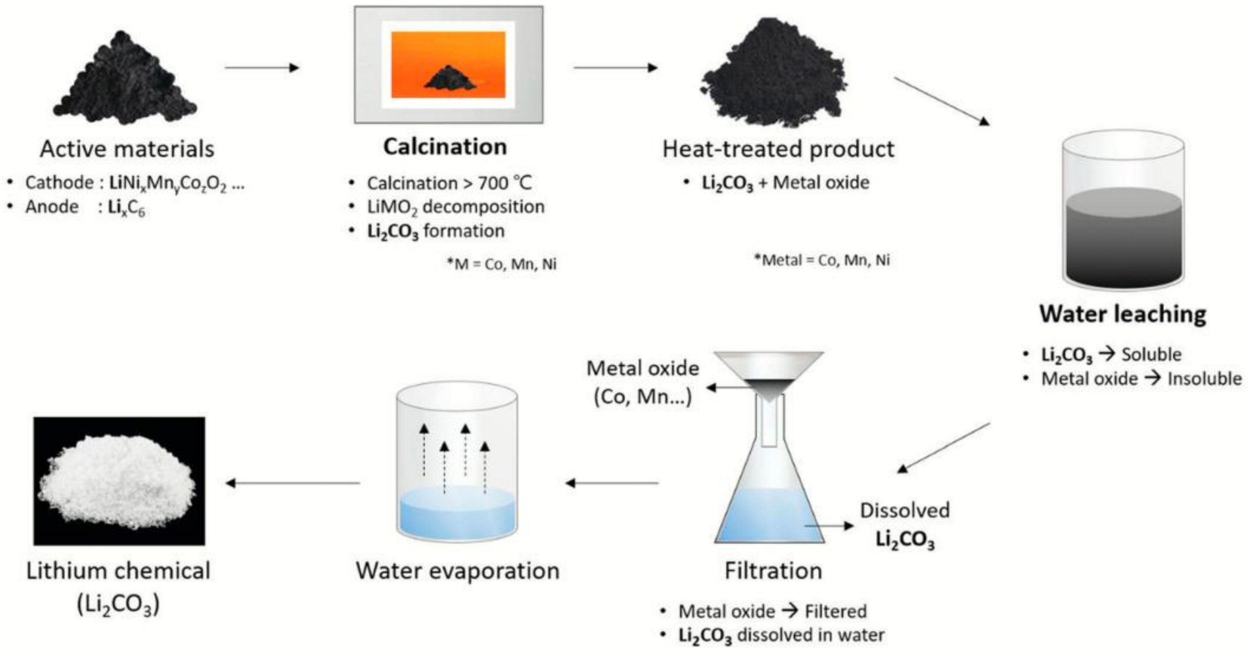

Figure 28: Representation of Lithium Recycling by pyrometallurgy process [129].

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5.6 Hydrometallurgy

Hydrometallurgy metal extraction in the case of lithium-ion battery recycling is feasible and efficient. More specifically, this process is ideal for pretreated cathode materials to be extracted. Although the moderate and low temperatures, high rates of cobalt, copper, and nickel can be recovered. Hydrometallurgy combines low energy demands, high impurity products, and high recovery efficiency, and thus, it is a suitable and popular method for lithium-ion battery recycling. It involves leaching, with several efficient leaching agents, followed by a recovery process to isolate the elements.

Leaching

Leaching is indispensable in hydrometallurgy because it dissolves the cathode materials into a solution state, in which separation and recovery can occur. There is a wide variety of leaching agents, such as acid leaching, ammoniacal leaching, and bioleaching agents.

Acid-leaching agents are commonly used and can be inorganic or organic. Inorganics include hydrochloric acid (HCl), sulfuric acid (H2SO4), nitric acid (HNO3), and phosphoric acid (H3PO4) and can be efficient in dissolving the cobalt element from the cathode active material $LiCoO_2$. Organic acid-leaching agents, such as oxalic acid, can enhance cobalt recovery [144].

The temperature, the concentration of acid, the duration of leaching, and the state of the solid can have an important impact on the leaching efficiency. HCl is an extremely efficient leaching agent that can dissolve even 97% of the lithium and 99% of the cobalt. However, Cl_2 can be produced, which is toxic. The next equation describes the dissolvement of lithium cobalt oxide in HCl acid:

$$2LiCoO_2 + 8HCl \rightarrow 2CoCl_2 + Cl_2 + 2LiCl + 4H_2O$$

In this equation, the cobalt is reduced to become more soluble. To solve the toxic component products, H_2SO_4 is used as the leaching agent but hydrogen peroxide (H_2O_2) is utilized as the reductant agent [129],[121],[142].

Chemical precipitation

After leaching, several methods are utilized to recover the metals. One of them is chemical precipitation where precipitation agents are used to precipitate a metal and separate it from the solution. The solubility difference between the metal compounds is the key behind precipitation. In [146] a 2M formic acid at 70 ^{o}C and H_2S_2 were used as a leaching agent and as a reductant, respectively, for the cathode $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$. NaOH and NH_4OH were then added for a pH increase. Hence, the pH increase enhances the precipitation of Co, Mn, and Ni as hydroxides, which are then separated from the lithium solution. In addition, Natarajan et al. [147] precipitated CoS by adding $(NH_4)_2S$, $MnCO_3$ by adding

Na_2CO_3 in a leached cathode containing Mn and Co. After removing Co and Mn, they added Na_2CO_3 to precipitate Li_2CO_3. Selective precipitation occurs by controlling the pH of the solution.

Solvent extraction

In this method, a two-phase system is used to separate the metals. A solvent is added to the leached solution to target a metal that has a different solubility in the solvent than the leached solution. Thus, a liquid-liquid extraction is achieved. The solvent is carefully selected to preferentially extract specific metals, and due to the immiscibility of the solvent and the leaching solution, the two phases are separated. These solvents include bis-(2,4,4-trimethyl-pentyl) phosphinic acid (Cyanex 272), Acorga M5640, trioctylamine (TOA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88 A), di-(2-ethylhexyl) phosphoric acid (D2EHPA), and more. For instance, $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ can be separated by being leached using 2 M H_2SO_4at 70°C for 90 minutes, followed by the addition of 0.1 M Na-Cyanex272 (PH=6), to separate lithium and nickel (as an aqueous solution), and cobalt and manganese (as an organic solvent). Then manganese and cobalt are separated by adding Na-D2EHPA (PH=2.95), while lithium and nickel are separated by adding DMG, which has high reactivity with nickel in contrast to lithium (PH=9). As the nickel is extracted as a solid, lithium can be extracted by adding Na_2CO_3 to obtain Li_2CO_3.

Selective adsorption

Selective adsorption, a crucial separation technique, significantly influences the lithium recovery process in Li-ion battery recycling. Inorganic adsorbents with exceptional selectivity for lithium in lithium-containing solutions are used. These sieves specifically permit only lithium ions to pass through by creating vacancies, utilizing the small size of lithium ions. Among the inorganic solvents, lithium manganese oxide stands out due to its superior qualities, including exceptional selectivity, high capacity, and stability. Additionally, it boasts low toxicity, making it a preferred material for this purpose. In a study conducted by Wang et al., the process involved leaching lithium from lithium-ion batteries using a solution composed of NH3, H2O, and NH4HCO3 with the addition of H2O2. A manganese-based lithium-ion sieve was employed to selectively adsorb lithium from the resulting solutions containing lithium, cobalt, and nickel. The lithium-loaded lithium-ion sieve was subsequently separated and dissolved in hydrochloric acid (HCl). Sodium hydroxide (NaOH) and sodium carbonate (Na2CO3) were then introduced to isolate lithium carbonate (Li2CO3). This method is straightforward and minimizes contamination, primarily due to the use of lithium-ion selective sieves. However, it's worth noting that spinel-structured manganese-type lithium-ion sieves can be expensive and necessitate an additional leaching process to separate the lithium bound with manganese dioxide (MnO2). In **Figure 29** these three types of recovery processes, chemical precipitation, solvent extraction, and selective adsorption, in hydrometallurgical recycling for lithium from lithium-ion batteries are illustrated.

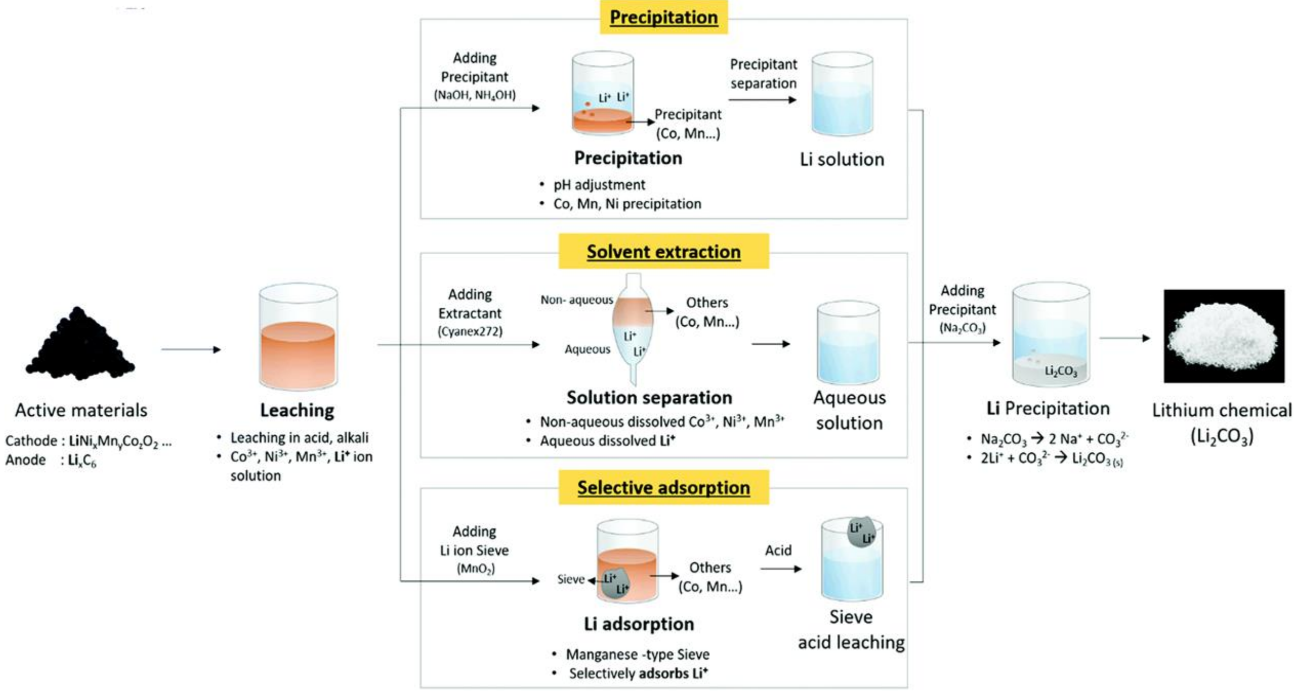

Figure 29: Lithium recycling from pretreated Li-ion battery components, using hydrometallurgy [129].

5.7 Direct Recycling

The principle of direct recycling is the recovery and harvesting of active materials of lithium-ion batteries while maintaining the original compound structure. This process involves pretreatment methods, such as discharging, dismantling, and battery constituent separation. The separation can be done with physical, magnetic, or other methods, preventing the chemical breakdown of the target substances. Next, the regeneration of active materials can be done through solid-phase, chemical, and hydrothermal re-lithiation. Direct recycling has advantages, as well as numerous disadvantages. This process is relatively simple, it provides direct reuse of the materials after regeneration, and compared to hydrometallurgy and pyrometallurgy the emissions and pollution are significantly mitigated. Although this process seems promising, it still has several deficiencies. Initially, the pre-processing process is extremely rigorous since it is based on exact active materials. The stream variety of cathodic active materials demands specific treatment, making the process inflexible and sensitive to input variations. In addition, not only achieving high purity is challenging, but this process exists, so far, only at a lab scale [128],[129].

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Solid-phase sintering

Capacity degradation of spent lithium-ion batteries is proportional to lithium loss, for instance, due to the solid electrolyte interface thickening. Thus, with solid phase sintering the active material is re-lithiated and recovered for reuse. More specifically, in elevated temperatures lower than the melting point of the active materials, but high enough to promote atomic diffusion, Li agents, such as lithium hydroxide (LiOH), Lithium Nitrate ($LiNO_3$), or lithium carbonate (Li_2CO_3) are integrated *via* diffusion for supplementing the loss of lithium and restore deficiencies. The amount of lithium required depends on the level of lithium loss of the active material. Song et al. [148] recycled cathode materials of LFP batteries using solid-state sintering. After the dismantling and separation processes, the spent materials were directly generated at 700° C achieving a capacity of 144 mAh g^{-1}. In addition, Li et al. [149] calcinated LFP cathodes at 650° for 1h achieving a capacity of 147.3 mAh g^{-1} during the first discharge. After 100 cycles the retention rate was 95.32 % meeting the requirement of the commercial LFP which is over 92.43 %.

Hydrothermal re-lithiation

Re-lithiation can also be achieved *via* hydrothermal processes. The active materials are exposed to an excess Li source solution, at higher temperatures, for lithium integration and material restoration. Unlike solid phase sintering, which demands stoichiometric lithium supplements, in hydrothermal the lithium restoration can be self-limited. A short annealing process can enhance the re-lithiation and improve efficiency. In a $LiCoO_2$ regeneration, Zhang et al, [145] used hydrothermal re-lithiation (2 M LiOH, 80 ° C, 6 h) and ultrasonic waves (600 W) simultaneously achieving 133.5 mAh g^{-1} in the first cycle, and 98.4 % retention rate after 40 cycles. (2 M: 2 moles/1 liter). Ultrasonic waves accelerate re-lithiation by producing cavitation effects, and thus by turbulence and microflows the kinetic barriers are reduced.

The technical advancements and significance of direct recycling processes are represented in **Table 6.**

Other regeneration processes

Other regeneration processes involve chemical and electrochemical processes. Electrochemical processes employ electrochemical techniques to recover degraded cathodes. Chemical processes are like hydrothermal but without thermal treatment. Ganter et al. [146] achieved discharge capacities from 150 to 155 mAh g^{-1} applying both chemical and electrochemical regeneration processes.

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Table 6: Technical advancements and significance of direct recycling processes representation [130]

Direct Recycling Process	Performance	Significance
Hydrothermal: 220°C 4 h: Short annealing: 800°C 4 h	LiCoO2; 91.2% capacity retention after 100 cycles at 1C (3-4.3V); 141.9 mAh/g at 2C and 130.3 mAh/g at 5C	A non-destructive and simple renovation process; mixed cathode can be processed together
Hydrothermal: 220°C 4 h; Short annealing: 850°C 4 h in O2	NMC 111: First-discharge capacity of 158.4 mAh/g at 1C and 122.6 mAh/g after 100 cycles; NMC 532: 128.3 mAh/g after 100 cycles	Cathode with higher nickel content is more sensitive to oxygen partial pressure during solid-state regeneration
Solid phase sintering: 700°C h; Doping ratio between spent LFP with new LFP: 3:7	LiFePO4; 144 mAh/g at 0.1C (2.5-4.1V); 135 mAh/g after 100 cycles	Simple regeneration process; satisfactory electrochemical performance
Solid phase heat treatment: 650°C 1 h under Ar/H2 flow; Li2CO3 as lithium source	$LiFePO_4$ First-discharge capacity of 147.3 mAh/g (2.5-4.2V); 140.4 mAh/g after 100 cycles at 0.2C and capacity retention is 95.32%	A green recycling process offering high yields; impurity phases are fully converted
Solid phase sintering: 850°C; Li2CO3 as lithium source	LiCoO2> First-discharge capacity of 150.3 mAh/g (3.0-4.3V) at 0.1C; 140.1 mAh/g after 100 cycles	A high total recovery rate of 95.78%; undesired phases are converted back to layer structure; Al and Cu impurities favor electrochemical performances
Electrochemical: cycle spent cathode coating with pure lithium metal; Chemical: immerse spent cathode power in lithium-containing solution	LiFePO4; 150-155 mAh/g	An innovative electrochemical method to regenerate the cathode; a decrease of 50% embodied energy, compared with virgin material production
Hydrothermal: 80°C 6 h; Ultrasonic power: 600W	LiCoO2> First-discharge capacity of 133.5 mAh/g; 99.5% capacity retention after 40 cycles	Ultrasonic radiation is used to facilitate the renovation process

5.8 Summary, Challenges, and Future of Recycling Processes

Lithium-ion battery recycling research and application needs to keep up pace with the rapidly evolving lithium-ion battery material research, where new materials and designs are brought to the market. In this unit some research needs and challenges for a variety of recycling processes are investigated [128],[130].

Sorting and separation

When the spent lithium-ion batteries reach the recycling facilities, vary in size, shape, and chemistry. Regarding the chemistry variations, proper labeling by lithium-ion battery manufacturers could solve this issue and enhance the separation. In addition, if the cell shape and size are standardized to a small range of designs, auto-procedures in dismantling and separation could be enhanced.

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Pyrometallurgy

Pyrometallurgical processes are the most mature technologies in Europe and North America. However, they have several challenges throughout the recycling procedure, including slag recycling, adaptation to the exponentially developing lithium-ion battery industry, and waste management.

Regarding slag recycling, most of the materials during the smelting process, such as lithium, graphite, separator, plastics, and organic electrolyte are burned, and thus, not recovered. One important research direction in pyrometallurgical processes is to recover lithium from the slag. Moreover, the future of the lithium-ion battery industry seems to focus on high nickel and low, or non-cobalt concentrations for cathode materials. Pyrometallurgy in recycling relies reasonably on high cobalt concentrations. Thus, the technologies must be more flexible to adapt to new material extraction with the same efficiency. Finally, slag and gas emissions, particularly CO_2, are environmental challenges that need to be investigated.

Hydrometallurgical processes

Hydrometallurgy is particularly deployed in China, regarding lithium-ion battery recycling. While this process focuses on cathode material recovery, development in electrolyte and graphite recovery is essential. In addition, water consumption is an immense challenge for hydrometallurgy. Hence, waste-water purifying, or water usage mitigation are indispensable.

Direct recycling processes

This method is on a laboratory scale and not commercialized yet. Advancements in pre-processing steps are essential for better cathode material purity, isolation, and recovery. Additionally, focusing on other materials except from the cathode active ones can enhance the process application in the industry. Cathode material mix from a wide variation of types is also a challenge and thus, separating methods or even direct utilization of the mixture is essential.

Finally, a combination of all these processes could be the solution for the recycling development, choosing the ideal procedure for the recovery of each material.

Within lithium-ion battery recycling, these processes offer a critical solution to the important issues of resource scarcity and environmental degradation. They provide an effective means of conserving valuable materials, reducing energy consumption, and lowering greenhouse gas emissions. Moreover, these processes align with the principles of a circular economy, encouraging sustainable materials management, job creation, and economic growth. Continuous advancements in recycling technologies promise a brighter future, with the potential to extract even greater value from discarded

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materials. Nevertheless, recycling is not without its challenges, including the complexity of modern products, issues of contamination, energy intensity, economic fluctuations, and regulatory inconsistencies. Addressing these challenges will be pivotal in realizing the full potential of recycling as a cornerstone of sustainable resource management.

As the demand for electric vehicles and energy storage systems continues to surge, recycling lithium-ion batteries becomes increasingly crucial. These processes contribute to a sustainable future by conserving critical materials, such as lithium, cobalt, and nickel, while also minimizing the environmental impact of battery disposal.

The future of lithium-ion battery recycling is ready for significant growth, driven by technological innovations in the treatment of battery waste and the development of efficient extraction methods for valuable battery materials. A circular economy model, where batteries are designed with recycling in mind, will gain traction. However, this future also comes with challenges, such as the complex nature of battery components, potential contamination issues, and energy-intensive recycling methods. Overcoming these challenges will be imperative to unlock the full potential of lithium-ion battery recycling and to ensure a sustainable, resource-efficient energy storage ecosystem.

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CHAPTER VI

CONCLUSIONS

Lithium-ion batteries are one of the most promising options for sustainable energy transition by enhancing the electrification system and assisting the renewable energy industry. Electrochemical energy storage and conversion are ideal for prolonged clean energy solutions. Fuel cells, supercapacitors, and electrochemical sensors are expected to expand rapidly in a wide range of applications including portable and stationary power supply, industrial, and transportation.

Batteries, often seen as everyday items, have come a long way in their development. Lithium-ion batteries have gained a lot of attention due to their remarkable features like high energy capacity, long-lasting power, and lightweight design. They've dominated various uses, from our phones and laptops to electric cars and backup power systems. Scientists are dedicating much effort to finding even better materials for these batteries to make them perform even more effectively. This focus on improvement is because lithium-ion batteries are such a big part of our modern lives, especially in areas like technology, transportation, and energy storage.

In the world of lithium-ion batteries, comprehending failure is just as vital as their outstanding performance. Investigating different failure types, diagnostic methods, and safety approaches has played a key role in guaranteeing the reliability and safety of these energy storage systems. Through diligent research and innovation, we are not only improving performance but also making these batteries better prepared against potential risks. As we continue to adopt these batteries in our daily lives, the insights gained from failure diagnostics help create a safer and more robust energy future.

Artificial intelligence-powered diagnostic tools can improve the early detection of battery issues, predict failures, and offer insights into performance optimization. Machine learning algorithms can continuously learn from data, improving diagnostic accuracy over time. This can be particularly beneficial for industries like electric vehicles, where early detection and prevention of battery failures are critical for safety and performance. This is extremely important, as the development of Artificial Intelligence is rapidly expanding in every technological sector. Hence, artificial intelligence can revolutionize and advance the field of failure diagnostics not only in lithium-ion batteries but also in various sectors.

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Battery recycling as well as repurposing and remanufacturing are not only environmentally responsible but also financially good solutions. At the point of disposal, a significant portion of batteries still retains over 80% of their original capacity. Consequently, they can be repurposed for lower-energy-demanding applications such as low-speed vehicles or energy storage in residential and industrial settings. As batteries near the end of their operational life, they can be disassembled and subjected to recycling. At this stage, the choice of the most suitable recycling method becomes essential. The primary recycling methods include pyrometallurgy, hydrometallurgy, and direct recycling. Pyrometallurgy and hydrometallurgy aim to recover the raw materials, particularly metals, used in batteries for reuse in new cells or applications requiring these metals. While these techniques achieve high metal recovery rates (exceeding 90%), they are associated with substantial energy consumption, and the use of hazardous materials, and involve multiple process steps. In contrast, direct recycling concentrates on refurbishing battery materials, like cathodes, and integrating them into new batteries, eliminating the need for manufacturing new battery components. However, this approach may lead to reduced battery performance. Thus, a combination of these methods is often employed to establish an efficient and sustainable recycling process. Moreover, ongoing advancements in recycling and reusing technologies continue to extend the lifespan of lithium-ion batteries, contributing to energy and material conservation.

Commonly commercial Li-ion batteries, each known for their specific cathode materials, have become indispensable in our daily lives. They've transformed the world of portable electronics, electric vehicles, and renewable energy storage. Nevertheless, the quest for improved energy density, longer lifespan, and eco-friendliness propels ongoing research and innovation within the battery industry. To advance Li-ion batteries further, it's advisable to diversify cathode materials, reducing dependence on scarce resources like cobalt. Sustainable alternatives should be developed to ensure the long-term viability of these power sources.

The future of Li-ion batteries is promising, with innovations on the horizon. New materials, including solid-state electrolytes and silicon anodes, have the potential to enhance energy density and safety. This could lead to more potent, compact, and durable batteries. The industry's focus on recycling and sustainable manufacturing processes will only strengthen, creating closed-loop battery systems to reduce waste and preserve resources. Automation and efficiency in manufacturing processes will also continue to evolve, making Li-ion batteries more cost-effective and competitive. As the world shifts toward cleaner energy sources, these batteries will play a pivotal role in energy storage and electric mobility, demanding ongoing technological advancements to meet these evolving needs.

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Humanity will exponentially increase its energy consumption in the future. To mitigate climate change and global warming a more ecological and environmentally friendly energy industry is indispensable. The rapid development and application of renewable energy and other modern technologies signifies an electricity-based future, neglecting traditional fuels. This electrical energy usage expansion requires storage technology. Lithium-ion batteries seem very promising, providing high efficiency and continuous development. However, are lithium-ion batteries environmentally friendly?

Critical material mining, regarding lithium-ion batteries, has expanded in the last few years to meet the market demands. Lithium can be found in ores and brines. Approximately 1.9 million liters of water are used to produce one ton of lithium. Mining activities consume large amounts of scarce water resources that local communities and ecosystem species depend on. In addition, toxic chemical leaks from lithium mines are reported in several incidents threatening the local ecosystem. As occurred in Tibet, toxic chemicals, such as hydrochloric acid, which are utilized in the processing of lithium, were leaked from the evaporation pools into the brine’s water supply. In North America and Australia, where lithium is typically mined from ores, chemical leakage has resulted in atmosphere and ecosystem contamination. In the case of cobalt, which is critical in today’s lithium-ion batteries, 70 % is located and 90 % is produced in the Democratic Republic of the Congo. A country where the average annual income is extremely low and child labor and artisanal miners are exploited for cobalt extraction.

Although producing a battery is less environmentally harmful than a barrel of gas, it is still threatening the environment. Except for the mining procedures for all the materials of the battery, which are harmful to the environment, the materials themselves are toxic and dangerous especially when they are exposed to the environment. With the rapid expansion of usage, lithium-ion batteries are ending up in landfills, where toxic and hazardous compounds can leak into oceans and underground reservoirs and contaminate water supplies and ecosystems. Electrolyte compounds, lithium salts, and cathode materials are self-igniting, highly volatile, and thus, can cause fire and explosion hazards. Moreover, when exposed to the environment, they have toxic effects for humans, including carcinogenic effects, or ultimately deadly decomposition compounds, [152], [153].

The immense amounts of lithium-ion batteries, new or spent, demand a lot of transportation which enhances the greenhouse gas concentration. For instance, China, along with South Korea, has become a significant global center for battery recycling, and hence, Europe, to satisfy new recycling rules, must import recycled material, contributing to a considerable carbon footprint.

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Despite the environmental consequences of lithium-ion battery improper disposal, the rate and efficiency of recycling are relatively low, as the process remains immature and costly. To lower the transportation costs recycling and pretreating facilities should be installed locally to accommodate the close-distance spent lithium-ion batteries [139],[130].

Instead of directly recycling spent lithium-ion batteries, they should be examined. Abandoned used batteries, on several occasions, include cells that still have efficient properties, despite the representation of the entire pack as degraded. Thus, remanufacturing of the batteries, where inferior modules or cells are replaced can be environmentally and cost-friendly, especially in the EV business. A potential solution is also the reuse of the battery in less intensive applications in case of relatively good performance after the first use.

To meet the market demands and reduce harmful environmental activities, numerous actions should be taken. Initially, proper mining, concerning the environment, species, and the locals is essential. Manufacturing and recycling processes should mitigate the harmful gases and waste release and achieve high performance simultaneously. The high amount of energy that these processes demand should be obtained from eco-friendly sources like renewable energy. Remanufacturing and repurposing of lithium-ion batteries should be considered more to manage the huge amounts of battery waste and establish a circular economy. Hence, a shift in eco-friendly and ethical thinking is required from the consumers as well as the manufacturers and suppliers. Finally, scientists should consider how materials can be repurposed or recycled as they design them [154].

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