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Bibliographic study of lithium-ion batteries and their limitations

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A la Universitat de Roma, vull expressar el meu sincer agraïment per haver-me concedit l'oportunitat de participar en el programa Erasmus i realitzar una estada de formació professional a l'estranger, una experiència que marca la conclusió d'una etapa, en el meu cas, llarga i important, una etapa que m'ha vist créixer, amb tot el que això implica de bo i de negatiu.

També vull agrair a la meva família, a la meva mare i a la Rita, per donar-me el suport i l'estima necessària durant aquest camí.

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SUMMARY

Lithium-ion batteries (LIBs) have become essential components in modern portable energy systems, powering devices ranging from smartphones to electric vehicles. This study identifies critical challenges facing LIB technology, focusing on their types, technical characteristics, and limitations. The research begins with a detailed analysis of various LIB types, particularly those using graphite carbon anodes combined with multiple cathodes. Emphasis is placed on temperature control in LIBs, examining the effects of both low and high temperatures, as well as abusive conditions, on battery performance. Additionally, the study identifies major real-world accident causes such as the Samsung Galaxy Note 7 recall and issues with the Boeing 787 Dreamliner, enhancing understanding of inherent safety challenges. These case studies underscore the critical need for rigorous design and manufacturing quality assurance in batteries. It also includes simulations of thermal runaway in battery packs, highlighting how different cathode materials (LCO, LMO, LFP, and NMC) influence thermal stability. Findings emphasize the critical role of advanced simulation tools like COMSOL Multiphysics in enhancing LIB safety and efficiency. This work documents ongoing development towards safer and more efficient lithium-ion batteries, supporting the transition to renewable energy sources and cleaner technologies.

Keywords: lithium-ion batteries, thermal runaway, safety, cathode materials, temperature control, COMSOL Multiphysics.

RESUM

Les bateries de ions de liti (LIBs) s'han convertit en components essencials dels sistemes moderns d'energia portàtil, alimentant dispositius des de telèfons intel·ligents fins a vehicles elèctrics. Aquest estudi identifica els reptes crítics que enfronta la tecnologia LIB, centrant-se en els seus tipus, característiques tècniques i limitacions. La recerca comença amb una anàlisi detallada dels diferents tipus de LIBs, especialment aquelles que utilitzen ànodes de carboni grafit combinats amb diversos càtodes. Es posa l'accent en el control de temperatura en les LIBs, examinant els efectes de temperatures baixes i altes, així com de condicions abusives, sobre el rendiment de la bateria. A més, l'estudi identifica causes importants d'accidents reals el retir del mercat del Samsung Galaxy Note 7 i problemes amb el Boeing 787 Dreamliner, millorant la comprensió dels reptes inherents a la seguretat. Aquest estudi resalta la necessitat d'un disseny rigorós i de qualitat en la fabricació de bateries. També inclou simulacions de descontrol tèrmic en paquets de bateries, destacant com diferents materials de càtode (LCO, LMO, LFP i NMC) influeixen en l'estabilitat tèrmica. Les troballes emfatitzen el paper crucial d'eines avançades de simulació com COMSOL Multiphysics en la millora de la seguretat i eficiència de les LIBs. Aquest treball documenta el desenvolupament continu per a unes bateries de ions de liti més segures i eficients, donant suport a la transició cap a fonts d'energia renovables i tecnologies més netes.

Paraules clau: bateries de ions de liti, descontrol tèrmic, seguretat, materials de càtode, control de temperatura, COMSOL Multiphysics.

SUSTAINABLE DEVELOPMENT GOALS

The Sustainable Development Goals (SDGs) are a set of global goals for sustainable health at all levels: from the planetary biosphere to the local community. The SDGs are dictating the official agenda at the international level for governments and institutions. The goals aim to continue the progress made by the Millennium Development Goals (MDGs) set in Agenda 21 after the Rio de Janeiro summit in 1992. In 2015, the UN critically evaluated the progress of established objectives and developed the 2030 Agenda for Humanity and the 17 Sustainable Development Goals. These goals address social, economic, and environmental challenges to promote sustainable development.

Regarding lithium-ion batteries and their failures, it is important to highlight that the SDGs are directly related to various aspects. Access to affordable and clean energy (SDG 7) is especially significant, as lithium-ion batteries are essential for the storage of renewable energy. Additionally, the use of lithium batteries in electric vehicles and energy storage systems contributes to the creation of cleaner and more sustainable cities (SDG 11).

Research and development of lithium-ion batteries contribute to technological advancement and innovation in the energy sector (SDG 9), while proper management of failures helps improve safety and efficiency, supporting the transition to cleaner and renewable energies (SDG 13). We can also relate this to access to safe technologies, as they protect the health and well-being of individuals (SDG 3).

The 17 Sustainable Development Goals can be classified into the 5 Ps: People, Planet, Prosperity, Peace and Partnership.

1. INTRODUCTION

Lithium-ion batteries have revolutionized the portable energy industry and have found applications in a wide range of electronic devices, from smartphones to electric vehicles. Their popularity stems from their high energy density, long lifespan, and low self-discharge rate. Operating on the principle of lithium-ion migration during charge and discharge cycles, these batteries effectively store and release energy. Over the years, significant advancements have been made in lithium-ion battery technology, improving their efficiency, safety, and capacity. In this introduction, we will explore the historical background, technical challenges, operating principles, and composition and structure of lithium-ion batteries.

1.1. HISTORICAL BACKGROUND

The oil crisis of the 1970s led to the development of the lithium-ion battery. Stanley Whittingham worked on techniques that could result in energy technologies that do not require fossil fuels. He began to study superconductors and found an incredibly energy-rich substance. He used this material to develop a new cathode for a lithium battery. This was created using titanium disulfide, which contains molecular gaps that allow lithium ions to intersect and reside there. A part of the battery's anode comprised metallic lithium, rendering it impractical due to its reactivity, which made the battery highly explosive. [1]

John Goodenough thought that if you used a metal oxide instead of a metal sulphide to make the cathode, it would have even more potential. He showed that cobalt oxide with intercalated lithium ions can produce up to four volts. In 1985, Akira Yoshino developed the first lithium-ion battery that could be produced on a commercial scale using the Goodenough cathode as a model. He used petroleum coke, a carbon substance that can interchange lithium ions, instead of the reactive lithium in the anode. [1]

In 1991, Sony Corporation released the lithium-ion battery for the first time on a commercial scale. This breakthrough signaled the start of the revolution in rechargeable batteries and had a big influence on the growth of energy storage technologies as well as the portable electronics market. [2]

The ensuing years saw an enormous increase in research interest because to the groundbreaking LIB technology in portable electronics. Energy storage systems are at the heart of these solutions as governments over the world have started several efforts in green energy technologies and electric vehicles because of growing awareness of the role greenhouse gases play in climate change. Between 2010 and 2017, there has been a significant surge in battery research worldwide, with at least 119,188 new publications published by researchers worldwide.[2]

1.2. TECHNICAL CHALLENGES

The advance of lithium-ion batteries has been crucial in the technological revolution of the last two decades, covering a wide range of applications ranging from mobile devices to electric vehicles and renewable energy storage. Despite their significant impact, these batteries still face several technical and development challenges that require attention. [3]

One of the key challenges is to increase the energy density, that is, the amount of energy a battery can store in relation to its size and weight. In addition, the safety of lithium-ion batteries needs to be improved, especially after incidents such as fires in electric vehicles and electronic devices.

Another important aspect is to reduce the production costs of lithium-ion batteries to make them more affordable and affordable for a variety of applications. This involves finding cheaper and more sustainable electrode materials and optimizing manufacturing processes.

Nanotechnology promises to improve the performance of lithium-ion batteries by enabling the handling of materials at nanoscale to improve efficiency and durability. However, it also presents challenges in terms of energy density, as nanostructured materials often have lower energy densities compared to volume materials.

In addition to technical challenges, there are also environmental and sustainability considerations. Life cycle assessment and techno-economic analysis are important tools for assessing the environmental and economic impact of lithium-ion batteries throughout their cycle, from the extraction of the raw material to final disposal.

Continuous research and development are essential to address these challenges and move towards a new generation of high-performance, environmentally friendly batteries.

1.3. OPERATING PRINCIPLES

The Li-ion battery, referred to as the lithium-ion battery in scientific circles, is a type of secondary rechargeable battery that is distinguished by its cell configuration. During discharge, lithium ions in these cells migrate from the anode through an electrolyte and finally arrive at the cathode. On the other hand, this process is reversed during the charging phase, with lithium ions traveling from the cathode to the anode. Is an electrochemical device that facilitates the electrochemical process of converting chemical energy stored in the battery into electrical energy. It functions as a direct current (DC) power source. Table 1 provides an overview of the main advantages and disadvantages of Li-ion batteries in comparison to other battery types.

Advantages	Disadvantages
Sealed cells; no maintenance required	Moderate initial cost
Long cycle life	Degrades at high temperature
Broad temperature range of operation	Need for protective circuitry
Long shelf life	Capacity loss or thermal runaway when over-charged.
Low self-discharge rate	Venting and possible thermal runaway when crushed
Rapid charge capability	Cylindrical designs typically offer lower power density than NiCd or NiMH
High rate and high power discharge capability	
High coulombic and energy efficiency	
High specific energy and energy density	
No memory effect	

Table 1. Advantages and Disadvantages of Li-ion Batteries [4]

The **cathode** of a lithium-ion battery is typically composed of lithium metal oxide ($LiMO_2$), while the **anode** is usually made of porous lithiated graphite. The electrolyte, which serves as a medium for ion transport between the cathode and anode, can exist in liquid, gel, polymer, and ceramic. And the separator is porous to allow the transport of lithium ions and prevent overheating and short circuits. [4] During **discharge**, lithium undergoes oxidation from Li to Li+ (changing its oxidation state from 0 to +1) at the graphite-lithium anode, as described by the following reaction:

$$Li_xC \rightarrow C \text{ (graphite)} + x\, Li^+ + x\, e^-$$

Following this, the lithium ions migrate through the electrolyte to the cathode, where they are incorporated into lithium metal oxide through a reaction that reduces the metal:

$$Li_{1-x}MO_2 + x\,Li^+ + x\,e^- \rightarrow LiMO_2$$

The overall reaction can be expressed as:

$$Li_{1-x}MO_2 + Li_xC \rightarrow LiMO_2 + C\ \text{(graphite)}$$

Throughout the charging process, Li+ ions migrate from the Li anode, passing through the electrolyte-soaked separator before intercalating into the cathode's structure. As a result, electrons flow through the external circuit in the opposite direction. [5]

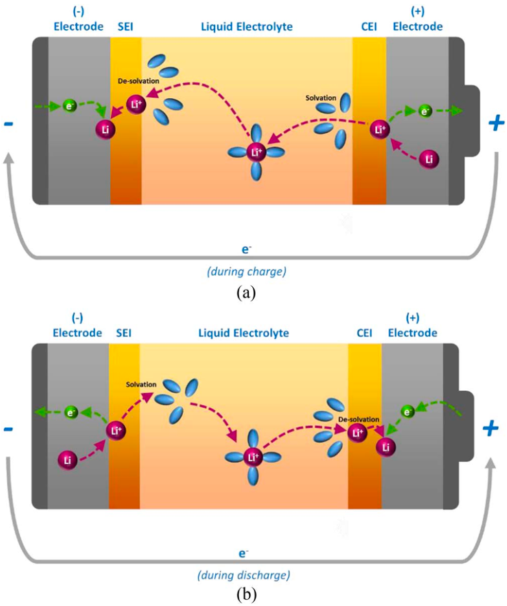

Figure 1. Schematic of the operating mechanism of LIBs**.**

(a) Charge process (b) Discharge process. [6]

1.4. COMPOSITION AND STRUCTURE OF BATTERIES

1.4.1. Characteristics depending on the cathode material

Various battery types can be differentiated by the metal oxide that serves as the active component of their positive electrode. [4]

Viable electrode materials must meet several requirements to be considered suitable.[3] These include the ability to incorporate a large amount of lithium to enable high capacity, exchange lithium reversibly to allow long cycle life, high coulombic efficiency, and high energy efficiency. It is also important that the lithium exchange reaction occurs at a high potential relative to lithium to achieve high cell voltage and high energy density. Additionally, they must have high electronic conductivity and Li+ mobility for fast charging and discharging, and of course, be compatible with the other cell materials. To select the material to be used as a cathode, it is essential to consider that both chemical composition and crystal structure are fundamental parameters in maximizing energy density and reducing resistance to lithium-ion intercalation. They must have an acceptable cost, preferably prepared from inexpensive materials in a low-cost process.

Among the materials used in lithium-ion batteries, $LiCoO_2$ stands out for its high potential, $LiFePO_4$ for its thermal stability and safety, $LiMn_2O_4$ for its high capacity and stability, and $LiNiMnCoO_2$ for its high energy density. The choice of cathode material depends on various factors, such as the specific application and cost. [4] [13]

1.4.2. Characteristics depending on the anode material

Development efforts for secondary lithium batteries focused on the use of metal lithium as a negative electrode, due to its high capacity to store electrical charge per unit of mass or volume. Metallic lithium presented safety concerns due to its changing morphology during the cycle, so the industry focused on using intercalation of carbon-lithium instead of metallic lithium, as this has a stable morphology throughout its lifetime. [4]

Industrially, there are many types of carbon materials. The structure of carbon is important because it influences the potential for lithium intercalation. Lithium intercalation is the fundamental process that allows storing and releasing energy in the form of electrical current within the lithium battery, meaning it directly affects the amount of energy the battery can store.

We can classify the different types of carbon based on the precursor material and how the material is processed [5], as shown in the figure 2, as temperature and treatment time are determinants of the final properties of the material.

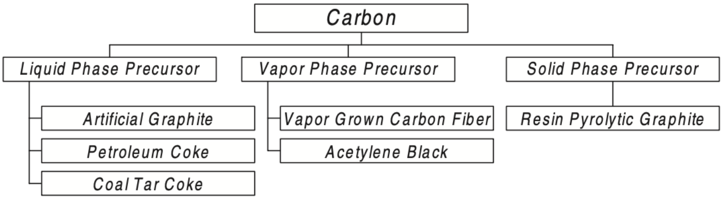

Figure 2. Carbons classified by the precursor phase [4]

Carbon materials produced from the liquid phase undergo partial carbonization under critical conditions (high pressure and temperature). This means that part of the organic material present in the liquid phase transforms into solid carbon, contributing to the formation of more stable materials.

On the other hand, carbon materials produced from the vapor phase exhibit diverse chemical and physical properties. This process results in dense and interconnected structures because their carbon molecules are small and highly excited, allowing for a regime controlled by kinetics. These materials can enhance battery performance and lifespan by providing greater mechanical strength, stability, electrical conductivity, and lithium-ion storage.

Finally, carbon materials produced from the solid phase do not become as good electrical or thermal conductors. This is because they retain highly disordered polymeric chains that can act as barriers to the flow of electrons through the material.

An ideal material would offer high specific capacity without irreversible capacity. [5] The performance and physical characteristics of various carbon materials depend on:

- Particle size: Smaller particles generally allow for faster charging and discharging and can facilitate the diffusion of lithium ions within the material, which can improve battery efficiency and reduce internal resistance. They may also experience less mechanical stress during charge and discharge cycles, thereby enhancing battery durability and lifespan.
- Specific surface area measured by BET (Brunauer-Emmett-Teller): This can be an important indicator of a material's ability to store and release lithium ions during charge and discharge cycles. A higher specific surface area generally allows for greater interaction between the electrode material and lithium ions, which can improve battery capacity and efficiency.
- Energy density: This indicates the amount of energy that can be stored relative to its mass or volume, higher energy in less volume is always desirable.
- Irreversible capacity: This is a measure of battery efficiency and can affect its long-term performance, as it represents a permanent loss of the battery's energy storage capacity. Therefore, low irreversible capacity is preferable in a lithium-ion battery. Generally, irreversible capacity may be related to the surface area of a material, hence spherical materials with low surface area are preferred.

1.4.3. The separator

The **separator**, a strategically positioned permeable membrane between the anode and cathode of the battery, plays a critical role in the functionality and safety of the electrochemical device. Its primary function is to ensure physical separation between the electrodes to prevent electrical short circuits, while allowing the selective passage of ions necessary for the electrochemical reaction. The choice of materials and the design of the separator are crucial factors in the performance and lifespan of the battery. [8]

Lithium-ion cells employ thin microporous films, typically ranging in thickness from 10 to 30 µm, for the electrical isolation of the positive and negative electrodes. Commercial separators utilized in liquid electrolyte cells are primarily manufactured from microporous polyolefin materials, such as polyethylene (PE) or polypropylene (PP). [4]

To utilize polyethylene (PE) as a thermal fuse, it is important to consider the low melting point of PE materials, as porosity is affected when the temperature approaches the polymer's melting point (135°C for PE and 165°C for PP). Presently, tri-layer materials (PP/PE/PP) have been engineered, with a polypropylene layer preserving the structural integrity of the film, while the polyethylene layers melt at elevated temperatures, effectively deactivating the cell in case of overheating. [4]

1.4.4. Types of electrolytes

The **electrolyte** in a lithium battery plays a crucial role as an ionic conducting medium facilitating the transport of lithium ions between the anode and cathode electrodes during charge and discharge processes. It is imperative for the electrolyte to exhibit high ionic conductivity to enable efficient diffusion of lithium ions throughout the solution. [9]

Furthermore, the chemical stability of the electrolyte is paramount in preventing undesired secondary reactions that could lead to battery capacity degradation or pose safety risks. Careful selection of electrolyte components and their appropriate proportions are pivotal in ensuring optimal performance and long-term reliability of the lithium battery.

One of the main obstacles to the widespread adoption of lithium-ion batteries in electrical equipment is their poor performance at low temperatures and their lengthy charging times. It has been shown that in order to achieve the proper balance between electrolyte solvation and desolvation and allow for quick charging at low temperatures in lithium-ion batteries, the solvation structure of the electrolyte is essential. [10]

As I've previously stated, choosing the right **solvents** for the electrolyte is essential to preserving the lithium battery's stability and conductivity while also guaranteeing its effectiveness and safety. Carbonate solvents are used in the formulation of the electrolytes that are now in use. Because carbonates are polar, aprotic, and have a high dielectric constant, they may solvate lithium salts at concentrations as high as around 1 M. They also offer a broad potential range of compatibility with cell electrode materials. Although propylene carbonate (PC) solutions were the industry's first focus, other carbonates, such as ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC), are now used in formulations because PC degrades graphite electrodes by co-intercalating with lithium, which causes exfoliation. Solutions with low freezing points and low viscosity are used in low-temperature electrolytes. [4]

To enhance the ionic conductivity within the lithium battery, **lithium salts** are employed. When dissolved in the solvent, these salts break down into lithium cations and anions, facilitating the movement of ions between electrodes during charging and discharging. Lithium hexafluorophosphate ($LiPF_6$) and lithium tetrafluoroborate ($LiBF_4$) are two of the most often utilized lithium salts. [9] For an electrochemical reaction to be both effective and stable throughout a range of operating circumstances, the combination of solvents to lithium salts must be balanced.

1.4.5. The function of the solid-electrolyte interface

The **SEI** (Solid Electrolyte Interphase), is a complex, organic, heterogeneous and structurally disordered passivation layer that develops on the surface of the negative electrode in lithium-ion batteries. The mobility of Li^+ ions, which permits reversible charging and discharging of lithium-ion batteries and thus a prolonged cycle life, is made possible by the creation of the SEI. Notably, this interfacial layer facilitates the passage of lithium ions from the layer to the negative electrode while simultaneously preventing further electrolyte deterioration. [11]

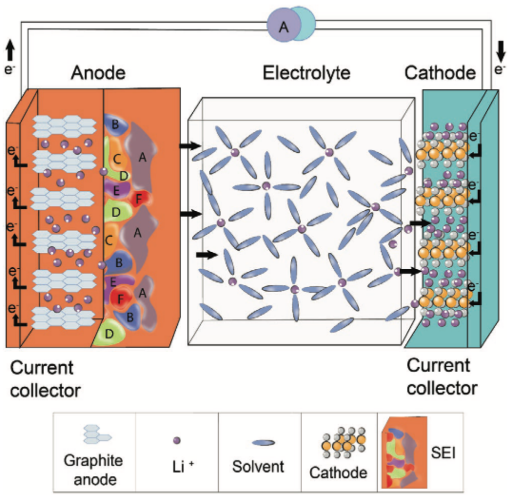

Figure 3. Schematic of a conventional LIB detailing the SEI layer. [11]

The anode and cathode materials, as well as the electrolyte's composition, have an impact on the SEI's formation. The development of the SEI is strongly influenced by the electrolyte reactivity of the electrodes. It is crucial for the SEI to be stable, as it can limit electronic transfer and prevent electrolyte reduction to maintain the chemical stability of the battery. [11]

The formation of the SEI proceeds through two steps: the polarization of the graphite electrode and the decomposition of species in the electrolyte, followed by the precipitation of new compounds that form a protective layer on the anode. [12]

In the first step, the polarization process, a voltage is applied to the graphite electrode, causing it to become negatively charged. When the electrode is polarized, the chemical species present on the electrode undergo a reduction reaction, gaining electrons and decomposing into new compounds. These new compounds, in the second step, are deposited onto the surface of the graphite electrode, gradually forming a solid layer over the graphite surface, known as the SEI layer. This formation process continues until all graphite surfaces are covered, thus acting as a protective barrier against the continuous reaction of the electrolyte.

1.4.6. Cell design type

The type of battery cell design varies depending on the internal arrangement of components, the shape and size of the cell, as well as the specific construction techniques that determine its capacity, efficiency, and applicability. The choice of the right design is important as it directly influences the energy density, power, durability, and safety of the battery. The most commonly employed cell design types in the use of lithium-ion batteries are [4]:

Cylindrical cells have a high specific energy, good mechanical stability, and are suitable for automated manufacture. Cell design enables for additional safety features that are not achievable in other forms. It cycles well, has a long calendar life, and is inexpensive, but the package density is less than optimal. The cylindrical cell is often utilized in portable applications.

To provide stability, **prismatic** cells are enclosed in aluminum or steel. The jelly-rolled or stacked cell preserves space but is more expensive for manufacturing than the cylindrical cell. Modern prismatic cells are employed in electric vehicle powertrains and energy storage systems.

The **pouch** cell employs layered design in a bag. It is lightweight and cost-effective, but humidity and extreme temperatures might limit its life. Adding some stack pressure improves durability by preventing delamination. Swelling of 8-10% over 500 cycles must be reconsidered in some cell designs. Moderate charge periods and modest loading are ideal for large cells. The pouch cell is growing in popularity and has comparable uses to the prismatic cell.

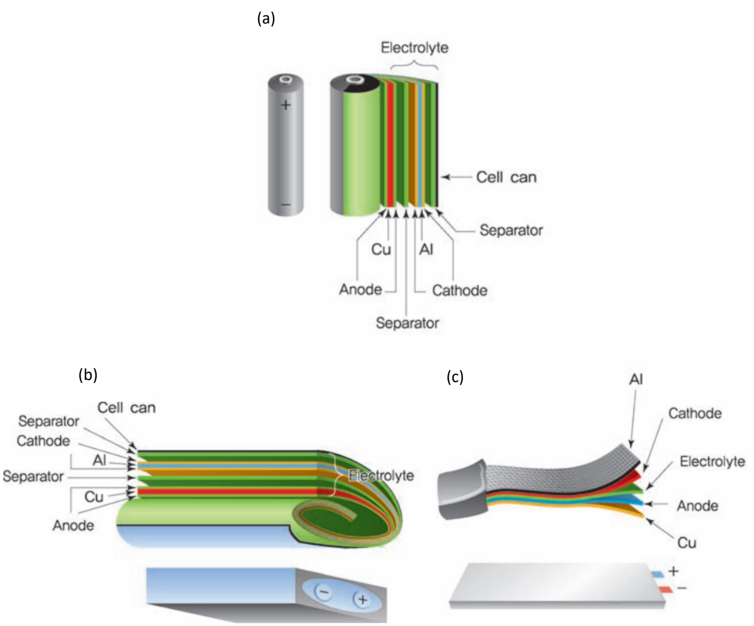

Figure 4. Different shapes of lithium secondary batteries: (a) cylindrical (b) prismatic (c) pouch. [14]

1.5. COMSOL MULTIPHYSICS OVERVIEW

COMSOL Multiphysics 5.5 is an advanced simulation software that allows modeling complex physical systems by integrating multiple phenomena simultaneously. [13] It is widely used for simulating lithium-ion batteries due to its capability to incorporate different relevant physics such as heat transfer, fluid flow, chemical reactions, and electromagnetism.

For lithium-ion battery simulation, COMSOL offers specific interfaces that facilitate the inclusion of components like electrodes, separators, and electrolytes. This enables modeling of complex interactions such as ion diffusion, heat generation, and couplings between electrochemistry and material mechanics. Furthermore, the software allows for defining specific material properties such as diffusion coefficients and thermal conductivities, crucial for simulating material behavior under various operating conditions. It also supports modeling of custom materials for specific research needs.

COMSOL Multiphysics provides advanced postprocessing tools to analyze and visualize detailed results such as electric potential distributions, ion concentrations, temperature profiles, and material deformations at critical points within the battery.

In summary, COMSOL Multiphysics 5.5, is an interactive modeling and simulation software highly suitable for solving engineering problems. COMSOL's graphical interface is intuitive and designed to simplify model creation and management. This interface is divided into several key sections: the Model Builder, where the model is defined and organized; the Settings window, which allows for configuring properties and parameters of the model components; and the Graphics window, which provides 2D and 3D visualizations of the model. Each of these sections is designed to give the user full control over the simulation process, from conceptualization to final visualization. [38]

2. OBJECTIVES

The present project aims to conduct a comprehensive literature review on lithium-ion batteries to understand the various characteristics that different types of cathodes can impart to these devices. The initial phase of the research aims to conduct a detailed analysis of the diverse types of lithium-ion batteries employing a graphite carbon anode combined with a wide range of cathodes.

Furthermore, the project aims to identify the primary causes of real accidents associated with lithium-ion batteries to enhance the understanding of the inherent safety challenges in this technology. This will enable the analysis of different factors contributing to these accidents, addressing both technical and operational aspects to broaden the comprehension of the risks involved in the use of these batteries.

Additionally, the thermal behavior of a battery pack under specific conditions will be graphically illustrated. The cells exhibit variation in terms of cathode type (LCO, LMO, LFP, and NMC), enabling an assessment of how the different characteristics of these materials influence the thermal stability of the cells and the onset of the thermal runaway phenomenon.

3. LITERATURE-BASED ANALYSIS OF LITHIUM-ION BATTERIES

3.1. DIFFERENT TYPES OF BATTERIES ACCORDING TO THEIR CATHODE

This analysis is based on a literature review of lithium-ion batteries. As explained in section 1.4.1, batteries can have different types of cathodes that will provide the device with specific characteristics. The initial phase of this investigation aims to conduct a comprehensive analysis of the various types of lithium-ion batteries that employ a graphite carbon anode and a variety of cathodes. In the following section, data detailing the operating conditions and the limitations of the different types of cathodes have been compiled, with the purpose of facilitating a comparison among the different commercially available cathode options for lithium-ion battery applications. Additionally, real-life battery accidents are included and will be examined later to draw conclusions about the inherent issues that these technologies may present.

To address which are the main materials used in the cathodes and their properties, as well as to understand how the composition of the cathode influences the battery, in Table 2, a compilation of operating conditions has been made, both under normal operation and under limit conditions. It is these latter conditions that lead to various failures in the batteries, and in some cases, accidents. The table provides a detailed comparison of the characteristics and applications of different types of cathodes used in lithium-ion batteries.

The data provided in Table 2 allow for an understanding of the performance of cathodes under standard operating conditions and limit conditions are essential for comprehending the characteristics of the resulting battery.

Table 2: Comparison of operating conditions of different types of cathodes in lithium-ion batteries.

Cathode		LiFePO4	$LiCoO_2$	$LiMn_2O_4$	$LiNiCoAlO_2$	$LiNiMnCoO_2$
Normal operating conditions	Voltage (V)	3.30	3.60	3.70	3.60	3.70
	Specific capacity (Wh/kg)	100	155	120	220	200
	Charge-rate (C)	1	0.7 - 1	0.7 - 1	0.7	0.7 - 1
	Discharge-rate (C)	1	1	1	1	1
	Midpoint V vs. Li (at 0.05C)	3.40	3.88	4.00	3.60	3.70
	Cicle life	2000	500 - 1000	300 - 700	500	1000 - 2000
Safe operating limits	Voltage (V)	2.5 – 3.65	3.0 - 4.2	3.0 – 4.2	3.0 – 4.2	3.0 – 4.2
	Specific capacity (Wh/kg)	90 - 120	150 - 200	100 - 150	200 - 260	150 - 220
	Charge-rate (C)	1	1	3	1	1
	Discharge-rate (C)	2.50	2.50	2.50	3.00	2.50
	Temperature (°C)	270	150	250	150	210
Real failure scenarios		Battery Room Fire at Kahuku Wind Energy Storage Farm (2012)	Boeing 787 Dreamliner Grounding (2013) Samsung Galaxy Note 7 Recall (2016)	Incidents with Hoverboard Batteries (2015-2016)	Tesla Model S fire incidents	Delayed Explosion Incident in Arizona
Applications		Portable and stationary needing high load currents and endurance.	Mobile phones, tablets, laptops, cameras	Power tools, medical devices, electric powertrains	Medical devices, industrial, electric powertrain	Electric and hybrid vehicles, energy storage systems

A higher voltage suggests a greater capacity to supply energy to electrical devices or store it in energy storage systems. A higher specific capacity means the battery can retain more energy, which translates to longer charge duration for electronic devices or greater range in electric vehicles. The charge and discharge rate determines how quickly the battery can be recharged or discharged, which is crucial in applications that demand a rapid response in this process. The lifecycle, in turn, indicates the number of full charge and discharge cycles the battery can withstand before its performance is significantly affected, with a longer lifecycle being preferable for greater durability. Finally, the midpoint voltage against lithium provides information about the battery's electrochemical stability, where a higher midpoint voltage suggests more stable and safer operation.

Each type of lithium-ion battery chemistry has its own benefits and drawbacks. By considering all these characteristics and with the assistance of bibliographic reports [4][14][15][16] , we obtain an overview associated with each type of chemistry used in the cathode of the lithium-ion battery:

- $LiFePO_4$: These batteries offer better safety and durability compared to other types. They stand out for their high thermal stability, significantly reducing the risk of overheating and the possibility of the battery entering a combustion state. Also significant is their long cycle life, as they can withstand a higher number of charge and discharge cycles before showing significant signs of degradation. However, they have a lower energy density, resulting in larger and heavier batteries for equivalent energy capacity. This characteristic can be a significant limitation in applications such as electric vehicles or portable devices where space and weight are crucial.

- $LiCoO_2$: It's the most commonly used option in the market due to its high energy density, as it can store a large amount of energy in a relatively small space, allowing for lightweight and compact batteries. However, they also come with limitations. Cycle life is one of the main concerns, as it has been observed that the cathode degrades at high temperatures or with high charging currents, reducing its lifespan. Additionally, they are susceptible to thermal runaway, which means they can experience overheating and, in extreme cases, may lead to dangerous conditions such as fires or explosions.

- $LiMn_2O_4$: One of its main advantages is its safety and thermal stability, as well as its low cost. However, it has a low energy density and therefore can store less energy compared to other cell types. Another important point is the capacity loss they experience over time; they have a low cycle life and performance, factors that can be very limiting for some applications such as electric vehicles or portable electronics.

- $LiNiCoAlO_2$: It presents various advantages, one of which is its high energy density, meaning it can store a large amount of energy relative to its weight and volume. It remains stable throughout charge and discharge cycles, ensuring the product a long lifespan with stable performance as well. It's also important to note that this type of cathode is used because its high power doesn't affect its capacity and allows for maintaining useful charge for extended periods. However, what limits the use of this type of battery is its cost in the market and the fact that it can become unstable under certain conditions, which could lead to overheating and, in extreme cases, explosions.

- $LiNiMnCoO_2$: Stands out for its energy density and capacity compared to other cathodes, as well as for its long-life cycles. However, like the $LiNiCoAlO_2$ cathode, it has expensive production costs and can become unstable under certain operating conditions, overheating, and posing risks.

3.2. IMPORTANCE OF TEMPERATURE CONTROL IN LI-ION BATTERY

Most of the effects of temperature on lithium-ion batteries are directly related to chemical reactions and the materials used.[17] Temperature is the most important factor in the control of LIBs, as it directly impacts their performance and also limits their applications. Therefore, understanding its effects is crucial for proper battery management.

In this section, these effects have been summarized, both at low and high temperatures, and abusive battery conditions have also been considered to prevent damage.

3.2.1. Low temperature effects

There are several studies that assert that, for various reasons, battery performance will degrade at temperatures below 0°C. [17] One of them is that low temperature will affect the properties of the electrolyte; the viscosity of the electrolyte will increase with decreasing temperature, reducing ionic conduction. Charge transfer resistance will also increase with decreasing temperature, a factor that affects kinetics in batteries. Additionally, the charge transfer resistance of a charged battery is typically lower than that of a discharged one, so at low temperatures, it will be even more difficult to charge than to discharge.

- Another effect that occurs is lithium plating.[18] Cooling down, the anodes may polarize, slowing down the intercalation of ions during the charging process.

3.2.2. High temperature effects

It is essential to consider that during the operation of lithium-ion batteries, internal heat generation occurs. This heat generation produces effects that are much more complex than those at low temperatures, and it is necessary to minimize these effects as they can lead to failures in the batteries.[17]

The heat generation within lithium-ion batteries during normal operation can occur in both the reversible and irreversible processes. Generally, it is associated with charge transfer and the chemical reactions that take place during the charging and discharging process.

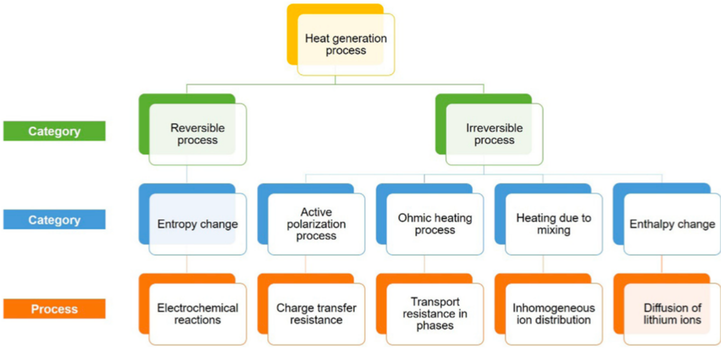

Figure 5: Diagram that categorizes the heating processes that can occur in a LIB. [17]

The heat generated in the reversible process is due to the change in entropy during electrochemical reactions. In contrast, there are many irreversible processes that can generate heat within a battery. Among them is the active polarization process, that results from the overvoltage between the operating potential and the open circuit potential. This process increases the resistance to charge transfer in the SEI, leading to heat generation. Another example is the ohmic heating process, that impedes charge transport, presenting resistance from electrodes and electrolytes during the charging or discharging process. During overcharging, the generation of gas and heat are typical phenomena. The amount of heat generated originates from the heat due to the Ohmic effect and parasitic reactions that occur during the process. Ohmic heat represents the main source of temperature increase, as evidenced by a proportional correlation between the heat generated and the charging current.

Aging is another effect that occurs during the use of lithium-ion batteries. Increasing the operating temperature above the optimal range will result in battery degradation and accelerate aging. Studies focus on explaining thermal aging primarily in electrodes and electrolytes.

Thermal runaway often occurs when high temperatures initiate exothermic reactions in operating batteries. There are five different kinds of reasons why this happens [19]:

1. Uncontrollable internal heat generation lead to the cathode material's oxygen getting out, which sets off a series of side reactions.
2. Separator defects lead to short circuits in the battery, which quickly consume its stored energy and cause unwanted chemical reactions as well as a significant release of heat.
3. At the cathode interface, electrolyte decomposition and electrical abuse take place, particularly when the SOC is high. This causes heat accumulation, causing the cathode to release oxygen and damaging the separator.
4. The separator in that location will contract or collapse if the heat produced by regular LIB operations is not rapidly enough dissipated.
5. During mechanical battery damage, which causes short circuits and/or air to penetrate the battery

This heat generation must be controlled to prevent fires and explosions.

3.2.3. Abuse conditions

It is important to consider battery abuse conditions to prevent damage. Failures can occur due to mechanical, electrical, and thermal abuse conditions. [20]

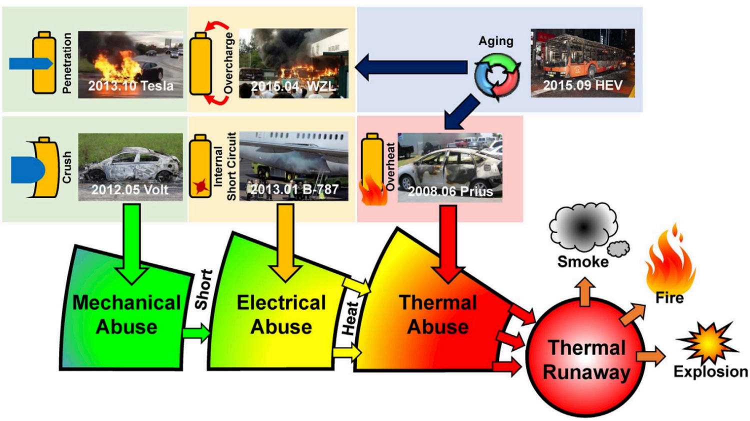

Figure 6: Abuse conditions leading to a thermal runaway. [21]

Mechanical abuse occurs when the battery undergoes destructive deformation or displacement due to forces applied to the system, such as collisions between vehicles. Therefore, battery pack design plays a crucial role and is currently one of the major challenges. Battery deformation can lead to serious consequences, including separator rupture resulting in internal short circuit, electrolyte leakage, and potential subsequent fires. Penetration during collisions can also immediately cause internal short circuit. The temperature rises as heat generated by the short circuit is absorbed, and it continues to increase until fully discharged; if the temperature rises too high, it can trigger thermal runaway. [22] [23]

When a battery undergoes overcharging, over-discharging, or experiences an external short circuit, it is undergoing **electrical abuse**, which can initiate a series of electrochemical reactions that have a negative impact on the battery's thermal characteristics and safety. During electrical abuse, the adiabatic conditions of the cell increase, trapping generated heat, which can lead to serious overheating issues. [24] One of the phenomena associated with electrical abuse is external short circuit [25], this occurs when the cell is misused. The separator of the battery cell, located between the anode and the cathode, undergoes physical deformation due to high temperatures, which can also lead to an internal short circuit and a severe thermal reaction.

The overcharging process is a state where there is an excess of stored energy. It initiates when the cell operates outside the optimal voltage conditions, and although it does not always lead to thermal leakage, it causes a reduction in cell capacity. Overcharging can cause lithium ions in the cathode to de-intercalate, collapsing the cathode and generating heat while releasing oxygen. The released oxygen increases electrolyte decomposition and produces gases (CO_2, CO, H_2, CH_4, C_2H_6 y C_2H_4), which increase cell pressure and temperature. [26]

The mechanism of over-discharge is similar to that of overcharging. This abuse condition can cause damages that are often underestimated. During forced over-discharge, Li+ continuously releases from the anode, altering the graphite structure and damaging the integrity of the SEI with the formation of gases such as CO and CO_2, consequently swelling the cell. In cases of deep over-discharges, the copper current collector oxidizes, releasing copper ions that can deposit on the cathode surface forming dendrites. This, along with the capacity loss, can lead to an internal short circuit or even thermal leakage. [19]

Thermal abuse is the direct cause of thermal runaway and is characterized by an increase in temperature. As mentioned earlier, mechanical and electrical abuse can generate heat, but the temperature rise in a cell can also occur because the rate of heat release from the electrode is often greater than its rate of cooling. If heat accumulates instead of dissipating, secondary exothermic reactions begin to occur, leading to undesired thermal stress. [19] One of the main causes of thermal runaway is internal short circuiting, which occurs when the anode and cathode come into contact due to separator failure. The energy stored in the cell is released, leading to an increase in temperature within the cell, potentially resulting in thermal runaway and posing health and safety risks. [27]

3.3. LIMITATIONS AND ASSOCIATED REAL ACCIDENTS

After conducting a study on the characteristics and properties of lithium batteries, it is crucial to consider safety aspects and understand real accidents that have occurred with these batteries in recent years. This allows us to comprehend the risks associated with their use and know how to address them.

Although lithium batteries provide an efficient energy source, when exploring the advantages and disadvantages of different types of cathodes, we can recognize that they may be susceptible to conditions that can lead to accidents. Therefore, it is fundamental to consider real incidents from the past to guide our decisions regarding the design, use, and management of these technologies.

In this context, the second part of the literature review examines six real accidents that have occurred with lithium-ion batteries in the last decade, with the purpose of offering a broader insight into the real risks associated with their use and the potential consequences associated with the use of these batteries in various applications, as well as with the aim of identifying the main causes of accidents and the contributing factors. Data collection has been based on real facts, which have been organized and classified into tables with the objective of providing a clear and structured view of the information to facilitate its analysis and understanding. The tables (3, 4, 5, 6, 7, 8,) detail aspects related to the cause, the involved mechanism, the failures, and the resulting consequences.

- Samsung Galaxy Note 7 Recall (2016) [28] [29]

The recall of the Samsung Galaxy Note 7 in 2016 was one of the most notorious incidents involving lithium-ion batteries in the smartphone industry. Shortly after its release in August 2016, numerous cases of devices catching fire or exploding spontaneously began to be reported. In Table 3, detailed information has been gathered about a specific incident that serves as a real example of the risks associated with $LiCoO_2$ cathode batteries.

Table 3: Analysis of the Samsung Galaxy Note 7 Recall (2016)

	Cause	Mechanism	Failure	Consequences
Samsung Galaxy Note 7 Recall (2016)	Battery design flaws	Internal short circuits and overly long electrodes	Overheating, fires and explosions	Initial series of reported explosions, global recall of Note 7
	Replacement battery issues	Corner deformation and irregular coating areas	Continued incidents of overheating and explosions	Second market recall, loss of consumer confidence
	Thermal runaway	Inadequate internal space and corner deformities	Internal short circuits and thermal failures	Fires, explosions, loss of consumer trust
	Separator issues	Irregularities in separator coating and structure	Damage to separator and internal short circuits	Increased risk of fires and explosions, degradation of battery structural integrity
	Electrochemical characterization	Defects in ceramic coating cohesion	Potential dendrite growth and short circuits	Increased risk of battery failures and user safety hazards
	Quality control failures	Inadequate testing and manufacturing procedures	Failure to detect battery defects during production	Significant damage to Samsung's reputation

The main cause of the problem was a design flaw in the battery, where insufficient internal space led to cell deformation and internal short circuits, resulting in battery overheating and consequently thermal runaway. From the information collected and presented in Table 3, several important conclusions can be drawn: it is crucial to prioritize a proper and meticulous design that considers thermal expansion. Manufacturing issues, such as defective cell coating, can increase the probability of inherent battery risks materializing, which is why quality control measures must be implemented during the manufacturing process.

Additionally, $LiCoO_2$ cathode batteries are commonly used due to their high energy density, but it is important to note that they present significant risks of overheating and thermal runaway if not designed and manufactured correctly.

All of this underscores the need for stringent regulations in the manufacturing of lithium-ion batteries. In summary, Table 3 highlights the importance of a rigorous approach to the design, manufacturing, and quality control of lithium-ion batteries to prevent serious incidents.

- Boeing 787 Dreamliner Grounding (2013) [30] [31]

Another example involving $LiCoO_2$ cathode batteries occurred in 2013 when the Federal Aviation Administration (FAA) ordered the temporary suspension of all Boeing 787 Dreamliner flights due to issues with lithium-ion batteries, which caused overheating and fires. This incident emphasized the importance of safety in aviation and the need for effective regulatory oversight in the introduction of new technologies in the aerospace industry. Detailed information about the incident has been compiled in Table 4.

Table 4: Analysis of the Boeing 787 Dreamliner Grounding (2013)

	Cause	Mechanism	Failure	Consequences
Boeing 787 Dreamliner Grounding (2013)	Defective lithium-ion batteries	Internal short circuits and overheating	Aircraft fires	Grounding of entire Boeing 787 Dreamliner fleet, significant financial losses
	Inadequate battery management systems	Failure to prevent battery abuse	Overcharging and overheating of batteries	Risk of battery fires and failures, compromised safety of aircraft and passengers
	Faulty integration into aircraft systems	Inadequate safety measures	Inadequate detection and response to battery failures and overheating incidents	Potential safety hazards for passengers and crew, operational disruptions, regulatory scrutiny
	Lack of root cause identification	Inability to determine the root cause of battery failures	Uncertainty about the root cause of battery fires and failures	Challenges in implementing effective safety modifications, continued risk of battery-related incidents
	Temporary solutions	Implementation of temporary solutions without understanding root cause	Adoption of temporary modifications to address potential causes of battery failures	Uncertainty about effectiveness of temporary solutions and questions about long-term safety.

In this case, what led to a critical incident were the failures in the management and design of the lithium-ion batteries of the Boeing 787 Dreamliner. The consequences were severe, as it resulted in fires and grounded the entire fleet. One of the major mistakes was the inability to specifically analyze the causes of the accident, leading to the implementation of temporary solutions that only created more uncertainty.

From this, it is concluded that the Boeing 787 Dreamliner case should have placed greater importance on comprehensive quality and safety management in the engineering of complex systems. Identifying the root cause of problems is essential for implementing permanent and effective solutions to critical issues.

- Delayed Explosion Incident in Arizona (2019) [32]

In Arizona, an Energy Storage System (ESS) equipped with $LiNiMnCoO_2$ batteries experienced a deflagration. Firefighters responded to a report of smoke and discovered a buildup of gas/vapor that caused the battery cells to overheat. The ESS was owned by the local utility company and consisted of an array of lithium-ion batteries, comprised of 27 racks, each housing 14 battery modules. Each of the modules contained 28 lithium-ion battery cells. Detailed information about the incident has been compiled in Table 5.

Table 5: Analysis of the Delayed Explosion Incident in Arizona

	Cause	Mechanism	Failure	Consequences
Delayed Explosion Incident in Arizona	Overheating of lithium-ion battery module	Thermal runaway initiated in one cell and propagated to adjacent cells and modules in Rack 15	The fire suppression system was unable to stop the thermal runaway from spreading	Release of flammable gases and vapors, leading to accumulation in the ESS
	Lack of flammable gas detection	Inadequate fire and smoke detection system did not monitor flammable gas presence	No sensors to detect flammable gases or monitor toxic gas concentrations	HAZMAT team unaware of explosive gas levels, increasing risk of explosion
	ESS communication system failure	Communication system failed before HAZMAT arrival	Inability to monitor internal ESS conditions	Firefighters and maintenance personnel could not assess situation accurately
	Unpredictable gas/vapor composition	Variability in battery chemistry and failure modes affected gas/vapor emissions	Uncertainty in gas/vapor state and timeline of thermal runaway	Difficulty in predicting and managing the hazardous atmosphere inside ESS
	Suppression system limitations	Total flooding suppression system not designed for explosion protection	System prevented initial flaming but not gas accumulation or explosion	Gas buildup led to a delayed explosion when HAZMAT team opened the ESS door
	Design flaws in ESS	ESS lacked deflagration venting and adequate mechanical ventilation	Flammable gases accumulated without ventilation	Increased risk of explosion due to gas buildup

As observed in Table 5, the delayed explosion incident in Arizona involved various failures that led to the overheating of the lithium-ion battery module and the inability to effectively control this process. It is concluded that the lack of an adequate flammable gas detection system was a crucial failure that could have been avoided with the implementation of appropriate sensors.

This highlights the importance of having robust and redundant communication systems in ESS, ensuring that essential information is always available, especially during emergencies. Facilitating a quick and effective response can significantly minimize the impact on the affected environment.

- Incidents with Hoverboard Batteries (2015-2016) [33] [34]

Between 2015 and 2016, numerous incidents related to lithium-ion batteries carried by hoverboards, whose cathode was generally composed of $LiMn_2O_4$, were recorded. These incidents were due to defects in the design or manufacture of the batteries, leading to overheating and, in some cases, ignition. They were recalled from the market, and regulatory authorities warned of their lack of safety worldwide, leading to increased awareness of the risks associated with the use of hoverboards and the importance of choosing products with high-quality and safe batteries. Detailed information about the various hoverboard battery-related accidents has been compiled in Table 6.

Table 6: Analysis of the Incidents with Hoverboard Batteries (2015-2016)

	Cause	Mechanism	Failure	Consequences
Incidents with Hoverboard Batteries (2015-2016)	Defective, low-quality, or poorly designed lithium batteries	Overheating during use, charging, or storage due to poor quality materials	Batteries did not meet safety standards and had manufacturing defects	Fires and explosions, property damage, burn injuries
	Presence of metallic impurities in batteries	Impurities cause short circuits when current flows through them	Manufacturing flaws allowed impurities in the batteries	Internal short circuits, overheating, and battery explosions
	Highly flammable electrolytes within batteries	Electrolytes ignite quickly when exposed to air if the battery is damaged	Fragile batteries prone to physical damage	Fast-burning fires that are hard to put out
	Battery design not suitable	Bumps and abrupt movements during normal hoverboard use	Inadequate design to withstand physical strain.	Increased risk of explosion during hoverboard use
	Lack of proper safety certifications for batteries	Batteries were not tested or certified under stringent safety standards	Component certifications that did not guarantee overall product safety	Defective products on the market
	Massive and cost-effective production	Use of cheap materials to reduce costs and increase sales	Production and sale of low-quality batteries	Difficult to trace specific manufacturers, many defective products on the market

One of the main causes of the problems with hoverboards was the use of low-quality, defective, or poorly designed batteries, which experienced overheating during use, charging, or storage. As documented in Table 6, these failures resulted in fires and explosions, causing significant property damage and personal injuries. This underscores, once again, the importance of adhering to strict safety standards in the manufacturing of these devices.

From Table 6, we conclude that there is an urgent need to improve quality, safety, and design standards in the manufacturing of consumer technologies. It is essential to implement stricter quality controls and ensure compliance with safety regulations.

- Battery Room Fire at Kahuku Wind Energy Storage Farm (2012) [35] [36]

In 2012, there was a fire at the Kahuku Wind Energy Storage Farm, originating in the lithium-ion battery room, which was part of an energy storage system connected to a wind farm. The fire is believed to have been caused by a failure in one of the lithium-ion batteries, leading to overheating and subsequent ignition of other nearby batteries. The fire was contained by emergency response teams but caused significant damage to the battery room and associated equipment. This incident was one of the challenges associated with the safety control of large lithium-ion battery-based ESS. Detailed information about the incident has been compiled in Table 7.

Table 7: Analysis of the Battery room fire at Kahuku Wind Energy Storage Farm (2012)

	Cause	Mechanism	Failure	Consequences
Battery room fire at Kahuku Wind Energy Storage Farm (2012)	Electrical fault	Ignition of flammable material or battery	Ineffective fire suppression system	Destruction of building, shutdown of wind turbines, potential injury to responders, loss of entire battery system
	Overheating due to electrical fault	Thermal runaway	Inadequate cooling measures	Long-lasting fire, smoke emission, financial losses, environmental impact, shutdown of wind farm operations
	Insufficient safety protocols	Lack of adequate firefighting procedures	Delayed response time	Limited ability to contain fire, increased risk to responders, inability to prevent extensive damage
	Inadequate battery management system	Failure to detect and mitigate faults	Lack of early warning system	Inability to prevent fire propagation, to shut down systems in time
	Material fault	Ignition from external source	Inability to isolate ignition source	Difficulty in determining root cause, challenges in preventing future incidents, uncertainty in safety measures

The incident described in Table 7 also exposes a series of critical failures that triggered a severe fire in a battery room. The root of the problem was an electrical failure that ignited flammable material. The lack of proper safety protocols and a slow response time limited the ability to contain the fire, increasing the risk to emergency teams and preventing timely deactivation of the systems to avoid greater damage.

This incident highlighted the importance of conducting thorough risk assessments to protect infrastructure and ensure the safety of workers.

- Various Tesla Model S fire incidents [37] [38]

Between 2013 and 2019, several incidents involved Tesla Model S vehicles in different locations around the world, raising concerns about the safety of electric vehicles. One of the incidents occurred in 2013 when a Model S collided with a metallic object on the road, leading to a fire in the vehicle's battery. Following this incident, Tesla implemented changes in the vehicle's design to enhance battery protection in case of collision. Other incidents included fires occurring during vehicle charging, as well as fires related to traffic accidents. These incidents underscored the importance of potential risks associated with the lithium-ion batteries used in these Tesla vehicles. Detailed information about various accidents and failures related to Tesla vehicle lithium-ion batteries has been compiled in Table 8.

Table 8: Analysis of the Various Tesla Model S fire incidents.

	Cause	Mechanism	Failure	Consequences
Various Tesla Model S fire incidents	Metal fragment impact	Direct contact between a metal fragment and one of the lithium-ion battery modules	Mechanical damage to battery	Fire on 2 October 2013 in Washington State, significant damage to the vehicle, stock price drop for Tesla.
	Collision with barrier	High-speed impact with road barrier causing battery damage	Mechanical damage to battery	Fire on the A2 motorway, driver fatality, vehicle destroyed.
	Faulty charging plug	Faulty plug causing high resistance and heat buildup during charging	Electrical resistance overload	Fire in a garage at University of California, significant damage to the vehicle; no injuries or fatalities.
	Charging system short-circuit	Short-circuit in the vehicle connection during charging with a Tesla Supercharger	Electrical short-circuit	Fire in Norway in January 2016; owner had time to disconnect and move away; significant damage to the vehicle
	Reignition after crash	Multiple reignitions due to residual heat and damage to lithium-ion battery	Thermal runaway and damage	After crashing into a wall the vehicle reignited multiple times, ignificant challenge in managing fire

From the review of the final table, Table 8, various conclusions can be drawn about the safety and design of electric vehicles in relation to lithium-ion bateries. The analysis of incidents caused by impacts, such as metal fragments or collisions with barriers, highlights the need to design protection systems that are less vulnerable to mechanical damage. The failure of a defective charging plug that led to a fire underscores the importance of component quality and certification. The incident of multiple re-ignitions after a crash demonstrates the complexity of managing thermal runaway in batteries and underscores the importance of developing technologies for the early detection of overheating.

3.4. THE SIMULATION OF THERMAL RUNAWAY IN A BATTERY PACK

As previously mentioned, safety is a crucial factor that must be considered in the development and optimization of lithium-ion batteries due to the risks associated with the phenomenon of thermal runaway. To address this issue, simulations are employed to predict and analyze the thermal behavior of the batteries under specific operational conditions.

In this part of the work, and to complete the final section of the literature analysis, The Department of Chemical Engineering, Materials and Environment at Sapienza, University of Rome, has provided me with graphs aimed at representing, in temperature-time diagrams, the initiation of thermal runaway in a battery pack. Understanding the results of thermal runaway simulations and analyzing and interpreting the data will help extract conclusions about the behavior of lithium-ion batteries and complete the analysis of the study. Additionally, the simulations also compare different cathode materials, allowing me to comment on and contrast the results obtained in the simulations with previous literature.

Simulations conducted using COMSOL Multiphysics 5.5 will be described, and the thermal behavior of a battery pack after a thermal runaway event in one of them will be graphically depicted. These simulations include different types of cathodes to provide a more comprehensive view of the best materials.

This software features a very useful physical and materials interface [13], as it contains a database with all the necessary chemical and physical properties. To perform the simulation, the software requires the geometric description of the system, as well as its dimensions and shape. In other words, a component in COMSOL is defined once its geometry, material, and physical properties are known. Furthermore, physical phenomena to simulate, such as heat transfer, fluid flow, or structural mechanics, are configured, with the possibility of coupling multiple physics to simulate complex interactions between different phenomena. Boundary conditions must also be defined, specifying parameters such as temperatures, pressures, and forces at the model's boundaries. Finally, what allows the software to solve equations numerically is dividing the model into smaller elements and solving using methods such as the finite element method.

Once the simulation is completed, COMSOL Multiphysics 5.5 also offers analysis tools. The results can be visualized and analyzed using 2D and 3D graphics, animations, and data export for further analysis. It allows for detailed investigation of temperature distributions, deformations, flow fields, and other crucial physical parameters. That's why it is a very useful tool in simulating lithium battery packs, as it allows simulations that closely resemble reality and enables us to anticipate and correct faults.

Here are the descriptions of the geometries and materials used:

The cells used for the study are of the 18650 cylindrical type (diameter = 18 mm, height = 65 mm). As depicted in Figure 4(a), each cell consists of multiple consecutive laminate windings of electrodes, two collectors, and a separator, all wrapped around a mandrel serving solely as a support structure. Graphite was used for the anode, the most commonly employed material in this component due to its conductive properties and chemical stability. Additionally, the electrolyte was analyzed, using $LiPF_6$ as the lithium salt and a solvent mixture in a 1:1 ratio of EC, which is commonly used in the lithium-ion battery industry due to its good conductivity and thermal stability. As for the cathode, a material change was made to observe how the behavior of thermal runaway varies depending on the type of cathodic material used. Cells with cathodes of type LCO, LMO, LFP, and NMC were simulated, allowing an evaluation of how the different characteristics of these materials influence the thermal stability of the cells and the initiation of the thermal runaway phenomenon. It is also noteworthy that the battery pack was exposed to a hot environment, using a fixed value of the constant heat transfer coefficient equal to 7.5 $W/(m^2 \cdot K)$ and in the presence of an external flow at a temperature of 420 K.

Figure 7 provides a critical technical evaluation of the thermal behavior of different battery chemistries. It illustrates the variation of temperature over time for various battery packs, where the curves represent different chemistries: LCO, LMO, NMC and LFP. The horizontal axis indicates time in seconds, while the vertical axis shows temperature in Kelvin.

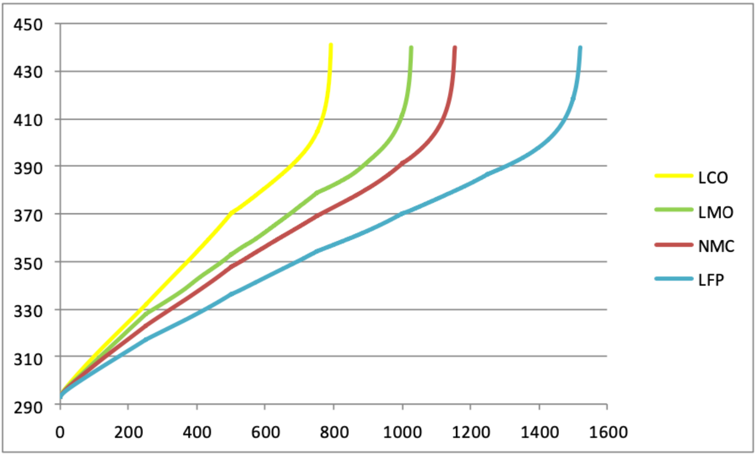

Figure 7: Temperature behavior over time for a battery pack.

[Dip. Ingegneria Chimica Materiali Ambiente, Sapienza, Università di Roma]

The curves demonstrate that LCO exhibits a rapid temperature increase, reaching approximately 450 K at around 800 seconds; LMO shows a more moderate rate of increase, reaching 420 K at around 1000 seconds; NMC has a gradual increase, reaching 410 K at 1200 seconds; and LFP exhibits the slowest and most stable increase, reaching about 370 K at 1600 seconds. In terms of safety and thermal efficiency, LFP stands out as the safest chemistry due to its slow and less pronounced thermal increase, while LCO, despite its high energy density, poses a higher risk of overheating due to its rapid thermal rise. Therefore, LFP is more suitable for applications requiring high safety and thermal stability, such as electric vehicles and stationary energy storage, while LCO may be more appropriate for applications where high energy density is prioritized. LMO and NMC offer a balance between safety and energy density, making them applicable in a variety of contexts depending on the specific requirements of each application.

Finally, based on the interpretation of the simulations and their comparison with the previous literature, conclusions and recommendations are drawn.

The choice of cathode material is crucial for balancing energy density and safety in a lithium-ion battery. LFP cathodes have demonstrated greater thermal stability and a lower propensity for thermal runaway compared to other materials like LCO, which, although offering high energy density, presents higher risks of overheating.

From the simulations, it is observed that LFP shows the slowest and most stable temperature increase, making it ideal for applications where safety is a priority, such as in electric vehicles and stationary energy storage. Effective temperature control is fundamental to prevent thermal runaway. Both simulations and literature agree that the implementation of advanced thermal management systems is essential to cut off ion flow in the event of overheating, thus preventing dangerous reactions. The necessity of efficient cooling systems is reaffirmed, especially for batteries with LCO cathodes and, to a lesser extent, LMO and NMC.

Additionally, the importance of conducting further simulations and tests under real operational conditions is highlighted to validate results and ensure the performance and safety of batteries in their final application. Furthermore, the potential for research using computational and thermal modeling to simulate thermal runaway and other failures is evident, contributing to the development of safer and more efficient batteries.

4. CONCLUSIONS

The bibliographic study first thoroughly analyzed various types of lithium-ion batteries classified by the cathode material used, including: $LiFePO_4$, $LiCoO_2$, $LiMn_2O_4$, $LiNiCoAlO_2$, and $LiNiMnCoO_2$, as they are the most commercialized. Each of these materials possesses specific properties that affect energy density, thermal stability, cycle life, and battery safety. $LiFePO_4$ batteries, noted for their thermal stability, are highlighted for their high safety due to this characteristic. In contrast, $LiCoO_2$ offers high energy density, enabling significant energy storage in a compact space but suffers from safety issues, limiting its lifespan due to dendrite formation and electrolyte decomposition. $LiMn_2O_4$ also exhibits good thermal stability and longer cycle life but with intermediate energy density. Cathodes like $LiNiCoAlO_2$ and $LiNiMnCoO_2$ provide a balance between high energy density, thermal stability, and safety, making them suitable for demanding applications, albeit at a higher cost due to expensive materials and complex manufacturing processes.

The study also addressed the critical importance of temperature control in lithium-ion batteries for safe and efficient operation. It concluded that controlling overheating is vital to prevent thermal runaway, a phenomenon where internally generated heat (due to various factors analyzed) can lead to uncontrolled chemical reactions, resulting in severe accidents such as fires or explosions. Literature indicates that one of the most effective ways to enhance thermal stability is through specialized separators and electrolytes designed for this purpose. Examples include polyethylene and polypropylene separators, acting as thermal fuses that shut down in case of overheating, thereby halting ion flow and preventing dangerous reactions.

The study examined the limitations of these batteries and documented real incidents resulting from failures. Limitations include cathode degradation, dendrite formation, electrolyte decomposition, and inadequate temperature management, all of which can lead to thermal runaway. These limitations were correlated with actual incidents through tables based on previous studies and article analyses, aiming to provide a comprehensive view of associated risks and potential consequences. The analysis underscored the importance of continuing to develop and optimize thermal management technologies and selecting materials that not only offer high energy density but also ensure long-term stability and safety of lithium-ion batteries.

Lastly, understanding the results of thermal runaway simulations in battery packs, alongside data analysis and interpretation, proved instrumental in validating information and drawing conclusions for the study. The graphical representation of these simulations clearly illustrates how different cathode materials affect battery thermal stability under abusive conditions. Specifically, it demonstrates that $LiFePO_4$ cathodes maintain lower and more stable temperatures compared to $LiCoO_2$ cathodes, which reach critical temperatures more rapidly. This visual representation reinforces the conclusion that cathode material choice is crucial for battery safety and efficiency, highlighting $LiFePO_4$'s superiority in thermal management and its ability to prevent thermal runaway.

In summary, the study emphasizes the importance of material selection, temperature control, and thermal modeling in developing safe and efficient lithium-ion batteries. Choosing the right cathode material is essential for balancing energy density and safety, while effective thermal control prevents catastrophic failures. Studying and understanding limitations and historical accidents provide a foundation for improving current technologies, and thermal runaway simulations offer tools for designing safer batteries, thus mitigating potential risks.

Continuing research and development in these areas are essential for advancing energy storage technology to meet the growing demands of modern applications such as electric vehicles and portable electronics. Adopting these perspectives will not only drive technological and economic development but also promote a more sustainable and secure future for society.

REFERENCES AND NOTES

[1] The Nobel Prize in Chemistry 2019. (2019). [March 2024] Available at: NobelPrize.org. https://www.nobelprize.org/prizes/chemistry/2019/press-release/?cid=2019-XBU-Nobel-Batteries&utm_source=Comms-Blog&utm_medium=EM%20Blog&utm_campaign=2019-XBU-Nobel-Batteries

[2] Li, M., Lu, J., Chen, Z., & Amine, K. (2018). 30 years of lithium-ion batteries. *Advanced Materials*, *30*(33), 1800561.

[3] Deng, D. (2015). Li-ion batteries: basics, progress, and challenges. *Energy Science & Engineering*, *3*(5), 385-418.

[4] Linden, D., & Reddy, T. B. (Eds.). (2002). *Handbook of batteries* (3rd ed.). McGraw-Hill.

[5] Khavryuchenko, O. V., & Khavryuchenko, V. D. (2014). Classification of carbon materials for developing structure-properties relationships based on the aggregate state of the precursors. *Chinese Journal of Catalysis*, *35*(5), 793-798.

[6] Matan. (2024). *Batería de iones de litio: cómo funciona | Reacción, ánodo y cátodo.* Electricity - Magnetism. [March 2024] Available at: https://www.electricity-magnetism.org/es/bateria-de-iones-de-litio-como-funciona-reaccion-anodo-y-catodo/

[7] Jow, T. R., Delp, S. A., Allen, J. L., Jones, J.-P., & Smart, M. C. (2018). Factors limiting Li+ charge transfer kinetics in Li-ion batteries. *Journal of The Electrochemical Society, 165*(2), A361.

[8] Matan. (2024). *Separador | parte de la bateria*. Electricity - Magnetism. [March 2024] Available at: https://www.electricity-magnetism.org/es/separador-parte-de-la-bateria/

[9] Ct. (2024). *Perspectivas electrizantes: navegando por el complejo mundo de los electrolitos de baterías de litio*. Professional Lithium Battery Manufacturer Vendor. [March 2024] Available at: https://www.lithiumbatterytech.com/es/electrifying-insights-navigating-the-complex-world-of-lithium-battery-electrolytes/

[10] Lei, S., Zeng, Z., Liu, M., Zhang, H., Cheng, S., & Xie, J. (2022). Balanced solvation/de-solvation of electrolyte facilitates Li-ion intercalation for fast charging and low-temperature Li-ion batteries. *Nano Energy*, *107*, 107265.

[11] Adenusi, H., Chass, G. A., Passerini, S., Tian, K. V., & Chen, G. (2023). Lithium Batteries and the Solid Electrolyte Interphase (SEI)—Progress and Outlook. *Advanced Energy Materials*.

[12] Yang, S., Yao, N., Xu, X., Jiang, F., Chen, X., Liu, H., Yuan, H., Huang, J., & Cheng, X. (2021). Formation mechanism of the solid electrolyte interphase in different ester electrolytes. *Journal Of Materials Chemistry. A*, *9*(35), 19664-19668.

[13] *COMSOL. (2019). Introduction to COMSOL Multiphysics (Version 5.5).* [May 2024] Available at: *https://cdn.comsol.com/doc/5.5/IntroductionToCOMSOLMultiphysics.pdf*

[14] Yuan, X., Liu, H., & Zhang, J. (2011). *LITHIUM-ION BATTERIES Advanced Materials and Technologies*. CRC Press, Taylor & Francis Group.

[15] Park, J.-K. (2012). *Principles and Applications of Lithium Secondary Batteries* (1st ed.). Wiley-VCH Verlag GmbH & Co. KGaA.

[16] Golubkov, A. W., Fuchs, D., Wagner, J., Wiltsche, H., Stangl, C., Fauler, G., Voitic, G., Thaler, A., & Hacker, V. (2014). Thermal-runaway experiments on consumer Li-ion batteries with metal-oxide and olivin-type cathodes. *RSC Advances*, *4*(7), 3633-3642.

[17] Ma, S., Jiang, M., Tao, P., Song, C., Wu, J., Wang, J., Deng, T., & Shang, W. (2018). Temperature effect and thermal impact in lithium-ion batteries: A review. *Procedia Manufacturing*.

[18] Petzl, M., & Danzer, M. A. (2014). Nondestructive detection, characterization, and quantification of lithium plating in commercial lithium-ion batteries. *Journal Of Power Sources*, *254*, 80-87.

[19] Chen, Y., Kang, Y., Zhao, Y., Wang, L., Liu, J., Li, Y., Liang, Z., He, X., Li, X., Tavajohi, N., & Li, B. (2021). A review of lithium-ion battery safety concerns: The issues, strategies, and testing standards. *Journal of Energy Chemistry, 59*, 83-99.

[20] Srinivasan, R., Demirev, P. A., Carkhuff, B. G., Santhanagopalan, S., Jeevarajan, J. A., & Barrera, T. P. (2020). Review—Thermal Safety Management in Li-Ion Batteries: Current Issues and Perspectives. *Journal Of The Electrochemical Society*, *167*(14), 140516.

[21] Feng, X., Ouyang, M., Liu, X., Lu, L., Xia, Y., & He, X. (2018). Thermal runaway mechanism of lithium ion battery for electric vehicles: A review. *Energy Storage Materials, 10*, 246-267.

[22] Liu, B., Jia, Y., Yuan, C., Wang, L., Gao, X., Yin, S., & Xu, J. (2021). Safety issues and mechanisms of lithium-ion battery cell upon mechanical abusive loading: A review. *Energy Storage Materials, 24*, 85-112.

[23] Wang, G., Guo, X., Chen, J., Han, P., Su, Q., Guo, M., Wang, B., & Song, H. (2020). Safety performance and failure criteria of lithium-ion batteries under mechanical abuse. *Energies, 13*(15), 3896.

[24] Zhang, G., Wei, X., Chen, S., Zhu, J., Han, G., & Dai, H. (2021). Revealing the impact of slight electrical abuse on the thermal safety characteristics for lithium-ion batteries. *Journal of Power Sources, 485*, 229320.

[25] Jung, J., Lim, M., Kim, J., Han, B., Kim, B., & Rho, D. (2022). Safety Assessment for External Short Circuit of Li-Ion Battery in ESS Application Based on Operation and Environment Factors. *Energies*, *15*(14), 5052.

[26] Wen, J., Yu, Y., & Chen, C. (2012). A Review on Lithium-Ion Batteries Safety Issues: Existing Problems and Possible Solutions. *Materials Express*, 2(3).

[27] COMSOL. (n.d.). Internal Short Circuit in a Lithium-Ion Battery. [May 2024] Available at: https://www.comsol.com/model/internal-short-circuit-in-a-lithium-ion-battery-34891

[28] Lan, T. (2023). A Critical Case Report of Samsung Note 7 Recall. *Francis Academic Research*, 5(11), 1-8.

[29] Loveridge, M., Remy, G., Kourra, N., Genieser, R., Barai, A., Lain, M., Guo, Y., Amor-Segan, M., Williams, M., Amietszajew, T., Ellis, M., Bhagat, R., & Greenwood, D. (2018). Looking Deeper into the Galaxy (Note 7). *Batteries*, *4*(1), 3.

[30] Pandian, G., Pecht, M., Zio, E., & Hodkiewicz, M. (2020). Data-driven reliability analysis of Boeing 787 Dreamliner. *Chinese Journal Of Aeronautics/Chinese Journal Of Aeronautics*, *33*(7), 1969-1979.

[31] Williard, N., He, W., Hendricks, C., & Pecht, M. (2013). Lessons Learned from the 787 Dreamliner Issue on Lithium-Ion Battery Reliability. *Energies*, *6*(9), 4682-4695.

[32] McKinnon, M., DeCrane, S., & Kerber, S. (2020). *Four Firefighters Injured in Lithium-Ion Battery Energy Storage System Explosion -- Arizona*.

[33] *Yoshida, J. (2019). Case study: How hoverboard makers neglected safety. Retrieved June 14, 2024.* [April 2024] Available at: *https://www.eetimes.eu/case-study-how-hoverboard-makers-neglected-safety/*

[34] Alex. (2024). The Hoverboard Craze: Lessons in Product Safety and Liability. *Assureful - Intelligent Commercial General Liability Insurance*. [April 2024] Available at: https://www.assureful.com/hoverboard-fires/

[35] Wesoff, E. (2012). Battery Room Fire at Kahuku Wind-Energy Storage Farm. *Wood Mackenzie*. [April 2024] Available at: https://www.greentechmedia.com/articles/read/battery-room-fire-at-kahuku-wind-energy-storage-farm

[36] Irfan, U., & ClimateWire. (2024, 20 febrero). *Battery Fires Pose New Risks to Firefighters*. Scientific American. [April 2024] Available at: https://www.scientificamerican.com/article/battery-fires-pose-new-risks-to-firefighters/

[37] Dorsz, A., & Lewandowski, M. (2021). Analysis of Fire Hazards Associated with the Operation of Electric Vehicles in Enclosed Structures. *Energies*, *15*(1), 11.

[38] Sun, P., Bisschop, R., Niu, H., & Huang, X. (2020). A Review of Battery Fires in Electric Vehicles. *Fire Technology*.

ACRONYMS

SDGs: Sustainable Development Goals

MDGs: Millennium Development Goals

LIB: Lithium-ion battery

DC: Direct current

$LiMO_2$: lithium metal oxide

$LiCoO_2$: Lithium Cobalt Oxide

$LiFePO_4$: Lithium Iron Phosphate

$LiMn_2O_4$: Lithium Manganese Oxide

$LiNiMnCoO_2$: Lithium Nickel Manganese Cobalt Oxide

BET: Brunauer-Emmett-Teller

PE: Polyethylene

PP: Polypropylene

PC: Propylene carbonate

EC: Ethylene carbonate

DMC: Dimethyl carbonate

EMC: Ethyl methyl carbonate

DEC: diethyl carbonate

$LiPF_6$: Lithium hexafluorophosphate

$LiBF_4$: Lithium tetrafluoroborate

SEI: Solid Electrolyte Interphase

LCO: Lithium Cobalt Oxide

LMO: Lithium Manganese Oxide

LFP: Lithium Iron Phosphate

NMC: Lithium Nickel Manganese Cobalt Oxide

SOC: State of charge

CO_2: Carbon dioxide

CO: Carbon monoxide

H_2: Hydrogen gas

CH_4: Methane

C_2H_6: Ethane

C_2H_4: Ethylene

FAA: Federal Aviation Administration

ESS: Energy Storage System