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DEGRADATION OF LITHIUM-ION BATTERIES

by

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ABSTRACT

In the 21st century lithium-ion batteries are currently a powerful energy source for many applications, including electric vehicles, portable electronics, and renewable energy systems. However, due to several aging conditions like high temperatures, cycling, and manufacturing processes, their effectiveness degrades over time. It is additionally affected by a few chemical processes that take place when the battery is used for the first time, such as the development of Solid Electrolyte Interphase (SEI) and Cathode Electrolyte Interphase (CEI). It is also influenced by lithium plating and particle fracture. The electrodes, the current collector, and the separator are among the battery components that are prone to degradation. The widespread use of lithium-ion batteries in a variety of applications is significantly hindered by their degradation because it is a complex phenomenon and is yet to be fully understood. This thesis investigates how lithium-ion batteries degrade due to various conditions.

The introductory chapters of this thesis give a general overview of electrochemical devices, including several types of batteries. In the beginning, the essentials of catalysis and its operation are described. The following section includes several electrochemical devices that use catalysis as their primary mode of operation when converting and storing energy. The chapters that follow are only dedicated to lithium-ion batteries. There is a brief report about the history, chemistry, and working principles of lithium-ion batteries, as well as some of their applications. Lastly presented, are the reasons for battery degradation and an overall conclusion on the subject.

ΠΕΡΙΛΗΨΗ

Στον $21^{ο}$ αιώνα οι μπαταρίες ιόντων λιθίου αποτελούν μια ισχυρή πηγή ενέργειας για πολλές εφαρμογές, συμπεριλαμβανομένων των ηλεκτρικών οχημάτων, των φορητών ηλεκτρονικών ειδών και των συστημάτων ανανεώσιμων πηγών ενέργειας. Ωστόσο, λόγω μιας σειράς συνθηκών γήρανσης, όπως οι υψηλές θερμοκρασίες λειτουργίας, οι κύκλοι ζωής και οι διαδικασίες παραγωγής, θεωρούνται από τους κύριους λόγους που υποβαθμίζεται η ποιότητα τους. Επηρεάζεται επιπλέον και από μερικές χημικές διεργασίες που λαμβάνουν χώρα στο εσωτερικό της μπαταρίας όταν χρησιμοποιείται για πρώτη φορά όπως η ανάπτυξη του Solid Electrolyte Interphase (SEI) και του Cathode Electrolyte Interphase (CEI). Επηρεάζεται επίσης από την κατάθεση λιθίου σε μορφή μεταλλικού στρώματος και την δημιουργία ρωγμών σε διάφορα μέρη της μπαταρίας. Τα ηλεκτρόδια, ο συλλέκτης ρεύματος και ο διαχωριστής είναι μεταξύ άλλων μέρη της μπαταρίας που είναι επιρρεπής σε υποβάθμιση. Η υποβάθμιση της ποιότητας είναι ένα πολύπλοκο φαινόμενο το οποίο δεν έχει γίνει πλήρως κατανοητό, πράγμα το οποίο παρεμποδίζει την ευρεία χρήση των μπαταριών και σε άλλες εφαρμογές. Η παρούσα εργασία δίνει έμφαση στον τρόπο με τον οποίο υποβαθμίζονται οι μπαταρίες λιθίου ιόντων λόγω διαφόρων συνθηκών.

Τα εισαγωγικά κεφάλαια αυτής της διατριβής αποτελούν μια γενική επισκόπηση των ηλεκτροχημικών συσκευών, συμπεριλαμβανομένων και διαφόρων τύπων μπαταριών. Στην αρχή περιγράφονται τα βασικά στοιχεία της κατάλυσης και της λειτουργίας της. Στην ίδια ενότητα περιλαμβάνονται μερικές ηλεκτροχημικές συσκευές που έχουν την κατάλυση ως τον κύριο τρόπο λειτουργίας τους κατά την μετατροπή και αποθήκευση ενέργειας. Τα κεφάλαια που ακολουθούν είναι αφιερωμένο μόνο στις μπαταρίες ιόντων λιθίου. Υπάρχει μια σύντομη αναφορά σχετικά με την ιστορία, την χημεία και τις αρχές λειτουργίας των μπαταριών, καθώς και ορισμένες από τις εφαρμογές τους. Τέλος παρουσιάζονται οι λόγοι για τους οποίους υπάρχει υποβάθμιση της ποιότητας της μπαταρίας λιθίου-ιόντων, και μια συνολική περίληψη στο θέμα.

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CHAPTER 1

INTRODUCTION

Given the fast global transition to renewable energy systems, interest in energy storage technology has recently increased. The underlying forces behind these model shifts are concerns about energy security, the impending exhaustion of fossil fuel sources, global warming, and environmental pollution caused by their overuse. High gravimetric and volumetric energy densities are crucial for energy storage technologies to be developed for mobile applications due to weight and space limits on mobile platforms. To enable significant market penetration, a revolutionary energy storage technology should perform to the same requirements as systems based on fossil fuels in terms of cost, life span, and refuelling duration.

Batteries are one of the most significant technologies for energy storage in mobile applications. According to **Figure 1**, Lithium-ion (Li-ion) batteries offer the highest volumetric and gravimetric energy densities of all the commercially available rechargeable battery technologies, making them an attractive option for future energy storage systems.

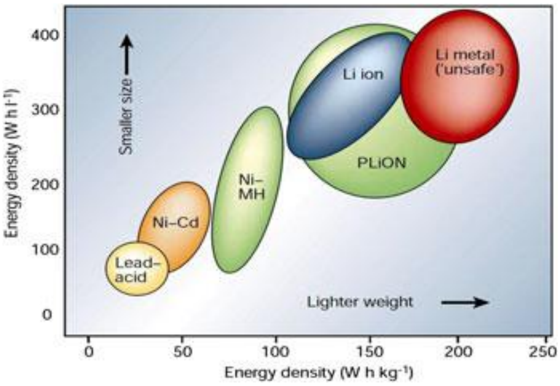


Figure 1 Gravimetric and volumetric energy density comparison for several battery chemistries [1].

In order to advance the use of Li-ion batteries in energy storage technologies, however, significant obstacles like cost, poor performance in increased or decreased temperatures, and limited cycle life should be overcome. A deeper comprehension of the Li-ion battery's degradation mechanisms is needed to make this development.

Lithium-ion battery (LIB) degradation frequently leads to capacity loss or power fade. It is considered a difficult task to analyse the several degradation pathways because of their interdependent nature. It should be obvious from the discussion above that to improve the performance and lifespan of LIBs, more attention and research must be paid to the mechanisms through which these batteries deteriorate. Determining and defining the degradation mechanisms that have been recognised thus far for each of the major battery components, as well as their influence factors will be the main objective of this thesis [1].

Understanding battery degradation is essential, not only to improve them in mobile applications, but also for decarbonizing energy grids and transportation systems at a reasonable cost. However, as a subject is frequently described as challenging to comprehend. Costs for Lithium-ion batteries are being driven down by the quick market growth, but extending the lifespan of LIBs is also crucial. Longer warranties, improvement of lifetime economics, and a decrease in environmental effects by raw material extraction and manufacture are some of the immediate benefits.

A range of degradation mechanisms, some of which coexist or trigger further mechanisms, LIBs lose storage capacity during usage or endure an internal resistance increase. These effects can be strengthened by certain important factors, either internal or external. The manufacturing line could be considered an internal factor since it will determine the structure and the quality of the final product that the consumer is going to use. Following this, the external factors take place with the operating conditions, such as working temperature, state of charge (SoC), and operating current. Temperature is typically the most important influence factor since divergence from the 25°C optimal temperature could expedite failure. Higher SoCs speed up degradation because of the connection between the electrode potentials and the frequency of parasitic side reactions, while a higher current operation is considered an important external degradation factor since it promotes lithium plating during charging and enhances the development of mechanical stresses in battery’s components.

1.1 Structure of this study

In this perspective, before the discussion of the main part which is degradation, some fundamentals and definitions of catalysis and electrochemistry have to be established. What is a catalyst, what is its purpose, and how does it accomplish that? Also, there are several ways to determine whether a catalyst is operating properly as well as various factors that affect it. As soon as these are comprehensible, a brief review of the most important electrochemical devices of energy conversion and storage will be conducted. Different types of capacitors shall be described always following their energy storage principle. Afterward, their primary applications will be discussed, along with those of fuel cells, which will be the next and last electrochemical device to be examined in this review apart from Lithium-ion batteries. The focus of chapter 3 will be exclusively on Lithium-ion batteries. A brief historical retrospective on the commercialization of LIBs and the necessity of the time is followed by an explanation of their structure and operation principles. Then the topic will be discussed is why and how LIBs penetrated the automotive market, which is currently by far the largest consumer industry of its production, and finally several other applications along with some future perspectives for LIB improvement. The most significant degradation mechanisms and their effects are covered in Chapter 4, which is the main part of the review. The actual mechanisms that will be analyzed include solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) formation, lithium plating, particle fracture, and electrode structure destruction. Factors that affect these mechanisms could be either internal (design and production) or external such as temperature, state of charge, and current will be the focus of the following section of the chapter 4.

CHAPTER 2

FUNDAMENTALS OF CATALYSIS & ELECTROCHEMISTRY

ELECTROCHEMICAL ENERGY CONVERSION AND STORAGE DEVICES

2.1 Fundamentals of Catalysis

2.1.1 Introduction to catalysis

A slow chemical reaction is sped up through catalysis when a foreign substance is present. Everyone working in chemistry nowadays is aware that a catalyst reduces the reaction's activation energy and accelerates the reaction, and does this by interacting with and binding to the reactant molecule. The catalyst participates in the process but is not consumed and has the ability to change a lot of molecules. Because of this, it just needs to be present in catalytic levels to change large amounts. Apart from that, there isn't much information on a catalyst's activities in primary textbooks [2].

At a solid's surface, heterogeneous catalysis takes place. Therefore, it stands to reason that materials with a large surface area make better use of the catalyst. However, whether the inside plane or just the exterior plane is responsible for the catalytic activity of porous materials is frequently questioned [3]. Of course, pore transport restriction is an issue here. Furthermore, there are other factors at stake in the decision to choose nanometer-sized catalytic particles over micrometer-sized catalytic particles in addition to the necessity to maximize the utilization of pricey materials like platinum metal. The percentage of atoms on the surface of small particles is higher. Nevertheless, an atom's electrical properties on the surface of a small metal particle differ greatly from those on the surface of a large one [2].

Kinetics makes it straightforward to comprehend the mechanical reaction in homogeneous (single phase) systems by measuring the initial rate R_0 of a reaction for a variety of reactants [4]. If the amount of a reactant determines R_0, the reactant is directly involved in the rate-determining step (RDS). According to the hypothesis, the reactant is regarded to be operating as a catalyst if it keeps its original form throughout the reaction and the R_0 continues to be dependent on it [5].

In heterogeneous catalysis, there is no similarity between the products and the reactants. The theory-process of turning methanol into gasoline using an acidic zeolite, is an illustration we may use to explain this (**Figure 2**) [6].

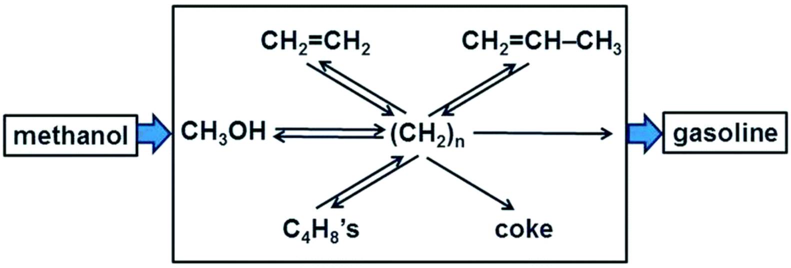


Figure 2 Graph illustrating the carbon pool method used to turn methanol into petrol [6].

The activity of catalysis for a solid compound comes down to two options if there is no present catalyst, it either occurs at a much slower rate or it doesn't occur at all [7]. However, it is much more challenging to demonstrate the mechanism because concentration can mean different things. The different types of reactants contribute appropriately to elucidate the mechanism [2,8].

2.1.2 Improving rate constants through a reduction in activation energy

Activation energy can be described by the equation found by Arrhenius:

$$k = A * \exp\left(-\frac{Ea}{RT}\right) \tag{1}$$

where k is the rate constant, E_a is the activation energy, A is the pre-exponential factor, R is the universal gas constant, and T the absolute temperature. Arrhenius equation is a mathematical expression that describes the effect of temperature on the velocity of a chemical reaction-rate constant [2].

Bond breaking is responsible for the high activation energies of chemical reactions. However, the activation energy of bond breaking reactions is getting increased and finishes on a high plateau. Such a reaction cannot be catalyzed. As the product is formed, the energy curve is lowered by the formation of new bonds. A catalyst can provide temporary weak bonds that lower the transition state energy by partially adjusting the energy needed to break the old bonds [2].

Much of the following discussion will be based on the decomposition of formic acid (FA). FA can spontaneously dissociate such as through dehydrogenation or dehydration. FA dehydrogenation is the method of producing hydrogen for fuel cell mobile applications. FA is non-toxic and is also considerably simpler to store and transport over large distances when used as a liquid fuel. Reducing the dehydrogenation that produces H_2O and CO is crucial since CO has the potential to be poisonous for Pt-based fuel cell catalysts [2].

2.1.3 Catalytic reactions: Reversibility and Compensation Effect

The issue is whether a catalyst that speeds up one reaction will be able to do the same with its opposite. Since the potential energy surface is independent of reaction direction, the answer is a conditional yes. If the catalyst is successful in catalysing both the forward and backward reactions, they will both travel along the same path of least energy and go through the same transition state. As a result, the forward reaction's activation energy decrease is equal to the reverse reactions. It is impossible to deduce anything about the transition state from the relationship between the equilibrium constant and the rate constants of the forward and backward reactions. Some catalysts can activate both the forward and backward reactions. The ability to catalyze both the forward and backward reactions hold true for processes like electrochemical hydrogen oxidation to water and water reduction in electrolysis. However, many catalysts function as one-way agents, meaning they can activate a reactant, but struggle to release the resulting product, which then becomes the reactant for the reverse reaction [9].

The concept of reversibility, as was previously mentioned, does not entail that the forward and backward reaction’s rate constant is equal. According to Eyring’s theory of absolute rate for homogenous kinetics, if the rate-determining step is unimolecular, the rate constant for the forward reaction is as follows [10]:

$$k = \frac{k\mathrm{bT}}{h} \exp\left(-\frac{\Delta G}{RT}\right) = \frac{k\mathrm{bT}}{h} \exp\left(-\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \quad (2)$$

The Boltzmann constant is denoted by k_B, the Planck's constant is denoted by h, the gas constant is denoted by R, and the activation of free enthalpy, activation enthalpy, and activation entropy are denoted by $\Delta G^{\circ\ddagger}$, $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$, respectively. The equation in question departs from the typical Arrhenius pattern as a result of the pre-exponential factor having a dependence on temperature, resulting in a minor curve on an Arrhenius graph [10].

Supposing that the rate-determining step is bimolecular, the rate constant is:

$$k = \frac{k\mathrm{bT}}{hc} \exp\left(-\frac{\Delta G}{RT}\right) = \frac{k\mathrm{bT}}{hc} \exp\left(-\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \quad (3)$$

where $c_0^{-1} = 24.45$ L/mol (molar volume at 298 K) is required to convert the thermodynamic parameters for gas phase reactants, which are specified at a standard pressure of 1 bar, into the concentration units of mol/L used for the rate constants. The activation energy is, $E_a = \Delta H^{\circ\ddagger} + 2RT$ and the pre-exponential factor = $\ln(e^2\, k_b\, T/h) + \Delta S^{\circ\ddagger}/R$ [10].

It can be beneficial to divide catalytic reactions into two parts: the initial step where the substrate is adsorbed onto the unoccupied sites on the catalyst, creating an adsorbed state and then the subsequent catalytic reaction that transforms the substrate into product.

$$\mathrm{S + Cat \rightleftharpoons SCat \rightarrow P + Cat} \tag{4}$$

The initial component of the above equation represents a pre-equilibrium of adsorption, which is defined by a constant known as K_A, as well as its associated thermodynamic parameters.

$$Ka = \frac{[SCat]}{[S][Cat]} = \exp\left(-\frac{\Delta Ga}{RT}\right) = \exp\left(\frac{\Delta Sa}{R}\right)\exp\left(-\frac{\Delta Ha}{RT}\right) \tag{5}$$

so that equation (5) becomes:

$$k = \frac{k\mathrm{bT}}{h} Ka \exp\left(-\frac{\Delta Gapp}{RT}\right) = \frac{k\mathrm{bT}}{h}\exp\left(\frac{\Delta Sa + \Delta S°‡}{R}\right)\exp\left(\frac{\Delta Ha - \Delta H°‡}{RT}\right) \tag{6}$$

It can be assumed, without explicitly stating so, that equations (2) and (3) represent the true values of activation free energy, enthalpy and entropy for the basic catalytic reaction. However, the initial apparent or effective values are depicted by the experimental Arrhenius parameters. According to equation (6), when an adsorption equilibrium is considered, the experimentally observed activation energy, represented by $E_a = \Delta H°_A + \Delta H^{°‡} + RT$, incorporates the actual activation enthalpy, as well as the enthalpy of the adsorption preliminary balance. Similarly, the pre-exponential factor, $\ln(ek_b\,T/h) + \Delta S^{°‡}/R + \Delta S°_A/R$, encompasses the entropy of the adsorption stage. As long as both the adsorption enthalpy and entropy are negative, they lower both the apparent activation energy and the pre-exponential factor in the Arrhenius equation as shown in equation (6) [2]. **Figure 3** depicts how the adsorption enthalpy, represented by ΔH_A, affects the calculated activation energy, referred to as $E_{app.}$

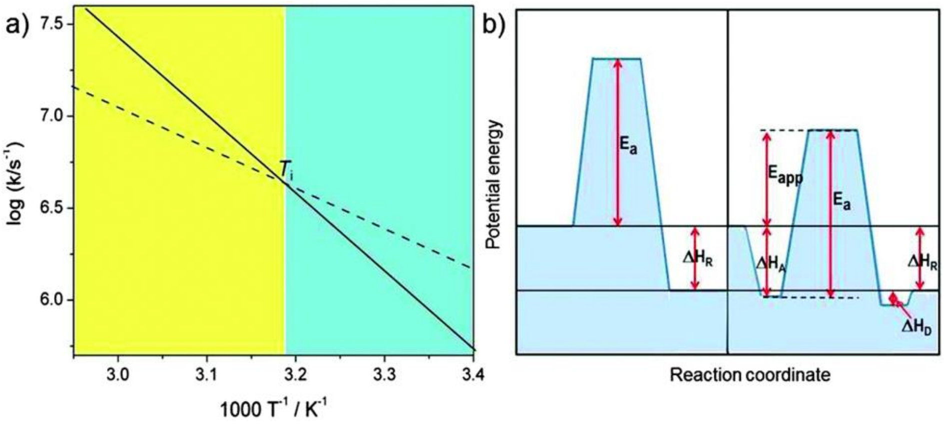


Figure 3 Adsorption pre-equilibrium effects with ΔH_A adsorption enthalpy [11].

2.1.4 The optimal adsorption concept of Sabatier

The initial adsorption of the reactant onto the catalyst, the actual catalytic transformation, and finally the release of the product are the three stages of catalytic processes that take place on the surface of a material rather than within it. Ideally, the catalyst remains unchanged after the final step and is ready to repeat the process multiple times, referred to as multiple catalytic cycles. A process where the catalyst is not able to be reused is not considered true catalysis [2].

Atoms that are less bonded to their surroundings, such as adatoms on surfaces or atoms situated at bends, corners, or edges, tend to form stronger bonds with substrates. In contrast to bulk material surfaces, metal nanoparticles, which have an electronic structure resembling both individual atoms and bulk metal, exhibit unique catalytic activity, which can be tuned by particle size [11]. This is due to the fact that metal nanoparticles have a unique electronic structure that resembles that of individual atoms and bulk metal, with similar ionization potential and electron affinity, resulting in catalytic activity that is different from bulk material surfaces and can be adjusted by changing the particle size [11].

2.1.5 Carbon based catalysts

Interest in carbon-based materials with heteroatom doping and various morphologies has recently increased due to research showing that they improve performance. These materials are composed of carbon structures doped with heteroatoms, such as carbides, oxides, sulfides, phosphides, and nitrides of both precious and non-precious metals. Engineering flaws, facets, stresses, interfaces, and electrical structure modulation can be used to change their morphology and surfaces in order to improve their catalytic performance. Recently, it has been discovered that single-atom catalysts (SACs), which feature isolated metal sites that are spread atomically on a carbon basis, are the best materials with an abundance of active sites as an alternative to Pt-based catalysts. The high cost and scarcity of Pt on Earth limit the widespread use of Pt-based catalysts for fuel cell applications, despite the fact that they are acknowledged as cutting-edge ORR catalysts. Since transition metal atoms are more frequently found in the Earth's crust than precious metal catalysts, they are classified as Non-Precious Metal Catalysts [11].

2.1.5.1 The perks and limitations of Single Atom Catalysts

Charge transfer can be facilitated, resulting in increased activity, by carefully regulating the coordination environment during the construction of single-atom catalysts (SACs). Catalytic mechanisms for certain reactions and sites can also be more easily identified thanks to SACs. Additionally, the size of the particles in SACs plays a crucial role in determining the effectiveness of the catalyst because smaller particles have a significant impact on the surface free energy of metals [12].

The advantages of single-atom materials are defeated when the atomic content of SACs rises because atoms have a propensity to recombine. This results in low metal-loading in SACs and makes it difficult to increase the metal-loading. Catalyst deactivation resulting from simple aggregation leading to cluster formation during synthesis also affects the stability and activity of SACs. Additionally, the reaction site might become inactive due to the powerful interaction between the one metal atom and the support. An additional factor to take into account is the production of diatomic dispersed metal electrocatalysts. Due to the strong synergistic interaction between the two metal atoms and between the metal atoms and the coordinating environment, this process has the potential to change the properties of each metal element. Activity rises as a result of this. SACs have consequently become quite in-demand because they enable a decrease in noble metal loading while retaining catalytic performance [13].

2.1.6 Conclusions

The subject of catalysis is more intricate than what has been briefly outlined here, including some fundamental concepts. To start with, the complexity arises from the intricacies of the chemical reaction, which may present multiple pathways leading to various outcomes and often involves multiple stages. Additionally, the surface of catalysts is often not uniform, leading to unclear observations and making it challenging to identify the primary active sites [2].

2.2 CAPACITORS:

2.2.1 Introduction

For quite a while now, electrochemical capacitors have been part of our everyday life. In 1957, Becker introduced a capacitor that utilized carbon with a vast surface area in his initial patent [14]. Subsequently, in 1969, SOHIO made the first efforts to commercialise this idea [15]The suggested uses mainly serve as auxiliary components that enhance batteries or serve as a substitute for batteries in electric vehicles. Additionally, there are other uses for electrochemical capacitors (EC) that do not compete with batteries but with standard capacitors, which are arising and demonstrate substantial commercial promise. **Figure 4** illustrates how electrochemical capacitors were able to attract a lot of attention.

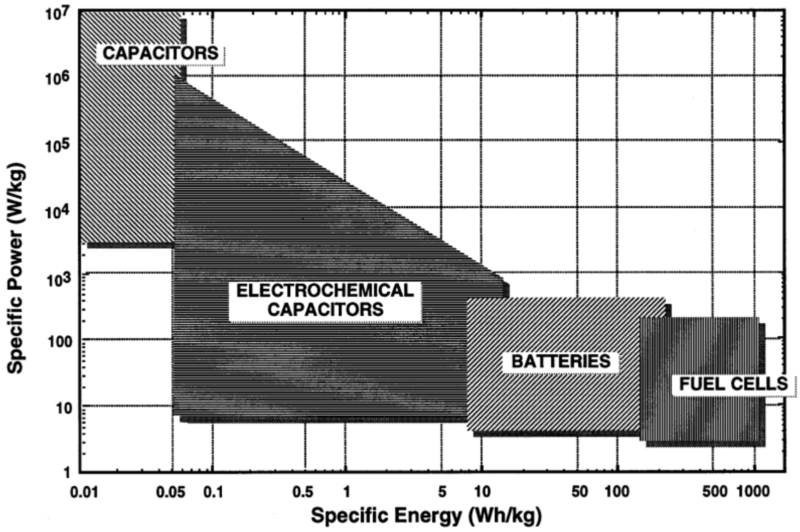


Figure 4 Sketch of Ragone plot for various energy storage and conversion devices [16].

In the ‘’Ragone plot’’ [16], Systems for energy storage and conversion are frequently described in terms of their specific power and energy. Batteries and electrolytic or metalized film capacitors, which span numerous orders of magnitude in specific energy and specific power, occupy the space between traditional capacitors.

2.2.2 Energy storage theory

In an electrochemical layer that forms at the interface between a solid material and an electrolyte, electrochemical capacitors store electrical energy. The solid electrodes surface attracts positively and negatively ions in the electrolyte, which counterbalance the electronic charge present. For a flat electrode in a concentrated electrolyte solution, the double layer capacitance typically ranges from 10 to 20 mF/cm^2. To increase the capacitance, porous electrodes with a significantly larger internal surface area are used. When two of these electrodes are combined, the resulting electrochemical capacitor possesses a substantially higher capacitance [17].

2.2.3 Classification of electrochemical capacitors

Electrochemical capacitors have various features that distinguish them, such as the type of electrode’s material, the electrolyte used and the cell’s structure. Among these, the electrode’s material can be broadly categorized into three types: carbon-based, metal oxide-based and polymeric materials [18].

2.2.3.1 Electrode material

2.2.3.1.1 Carbon

Carbon is the most frequently employed electrode material for electrochemical capacitors in various forms. This is due to several reasons, including its widespread availability, high surface area, affordability, and the fact that electrode production technologies for carbon are already established. Electrochemical capacitors that utilize carbon are akin to electrochemical double layer (solid material with electrolyte) capacitors (**Figure 5)** [18].

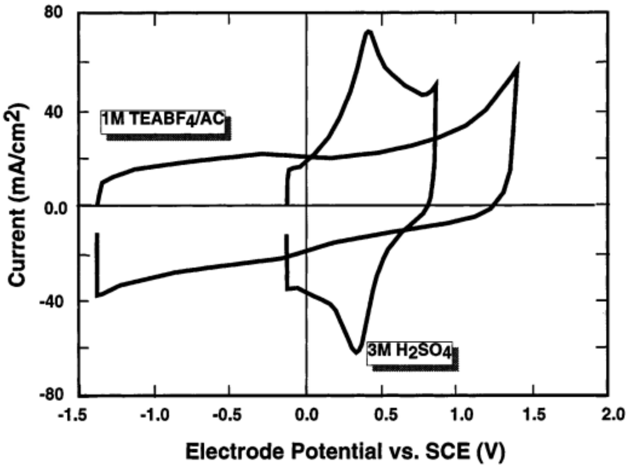


Figure 5 Activated glassy carbon electrode cyclic voltammograms at 100 mV/s [18].

2.2.3.1.2 Metal oxides

For space or military purposes [19], conducting metal oxides such as Iridium (IV) oxide (IrO_2) or Ruthenium(IV) oxide (RuO_2) were the preferred electrode materials in early electrochemical capacitors. They produced very high specific powers as a result of their high particular capacitance and low resistance. Unfortunately, the price of these capacitors has skyrocketed. An estimation of the cost of the capacitor indicated that the electrode material represents around 90% of the total cost. Moreover, because these capacitor materials are only compatible with aqueous solutions, the maximum cell voltage is restricted to 1 V [19].

Efforts were made to maintain the advantageous characteristics of these metal oxides while reducing costs. One approach that was explored involved the creation of perovskites, which involved diluting the expensive noble metal [20].

2.2.3.1.3 Polymers

Several authors have proposed polymeric materials, such as p- and n-dopable, as electrodes for electrochemical capacitors [20].

The utilization of polymeric materials in the construction of electrodes for electrochemical capacitors raises a concern about whether these devices should still be classified as capacitors or if they are more appropriately considered as batteries. With regards to the voltage fluctuation while charging and discharging, they are more alike to batteries. Nevertheless, when compared to metal oxides, it’s appropriate to refer to them as capacitors [18].

2.2.3.2 Electrolyte

The kind of electrolyte that each type of electrochemical capacitor uses is another characteristic that is used to classify them. Recent available capacitors utilize an organic electrolyte [21].

Organic electrolytes provide a unit cell voltage greater than 2 Volts (V). Typically, the cell float voltage is 2.3 V, with the option of temporarily increasing the voltage to 2.7 V. The water content of the electrolyte is most likely limiting the cell voltage. Certain companies suggest reaching a higher voltage by increasing the float voltage to 3.2 V. This necessitates extensive purification procedures for certain electrolytes and specialized protective coatings to mitigate the corrosion of the carbon electrodes [21].

In contrast, organic electrolyte possesses a significantly greater specific resistance. As the electrolyte resistance increases, the distributed resistance of the porous layer decreases, resulting in lower maximum usable power. Nonetheless, the increased cell voltage attained with organic electrolytes offsets some of the power loss [16].

2.2.4 Cell design

In electric vehicles (EV) applications, achieving high efficiency is a major concern for electrochemical capacitors (EC). The effective series resistance (ESR), which represents the internal resistance, causes some energy to be dissipated. This loss can become the predominant factor at high power, such as with high current. It was discovered in studies comparing electrochemical capacitors (ECs) and batteries for EV applications that a high-performing capacitor has a slight edge over a a powerful battery in terms of round-trip effectiveness. Reducing the ESR of electrochemical capacitors is crucial to match the performance of other energy storage devices. ‘’ESR is composed of at least four factors: (i) electrolyte including separator, (ii) current collector, (iii) porous layer including contact to current collector, and (iv) other contact resistances’’ [16].

Using a porous separator is necessary in electrochemical capacitors to prevent short circuits between adjacent electrodes. To minimise resistance, the separator must be thin and highly porous, irrespective of the type of electrolyte used. This makes selecting the appropriate electrolyte, separator thickness and porosity a challenging task, as it must be balanced against mechanical stability, volume, and resistance [16].

2.2.5 Applications

Electrochemical Capacitors (ECs) are best suited for applications that require energy for a small period. In such scenarios, both batteries and traditional capacitors have an unfavourable stored energy to accessible power ratio, which necessitates over-sizing of technology to meet the power or energy requirements. The need for a prolonged life span, frequent charge and discharge cycles, or fast charging the duration could be extended to weeks or days. Because of their energy density, ECs are also appropriate for pulse power applications that fall inside the millisecond window [16].

Although ECs with carbon electrodes do not require polarity for their fundamental operation, applications involving significant ripple current in alternating current (AC) are not now feasible. This is because their internal resistance is greater than that of regular capacitors, which can result in heat degradation. The device has polarity because some manufacturers use asymmetric electrode systems or special treatments for one of the electrodes.

Most ECs have undergone testing for short-circuit conditions. While the higher internal resistance of ECs limits their peak power in comparison to standard capacitors, their lower energy storage capacity than batteries allow for a restricted heating of the ECs, thus avoiding the risk of self-ignition. ECs have a notable advantage in that they typically do not contain hazardous or harmful components, making them easy to dispose of. They also require minimal maintenance and can endure numerous charge-discharge cycles with cycling efficiency of 95% or higher in well-designed systems. Furthermore, they can operate in a broad range of temperatures and exhibit superior performance in comparison to standard batteries, particularly in low temperature environments [16].

Consumer electronics are where most ECs are found, typically as backup power sources for clocks, system boards, clocks, memory, and microcomputers. Typically, in these applications, the load is powered by a primary power source, as shown in the system setup in **Figure 6**.

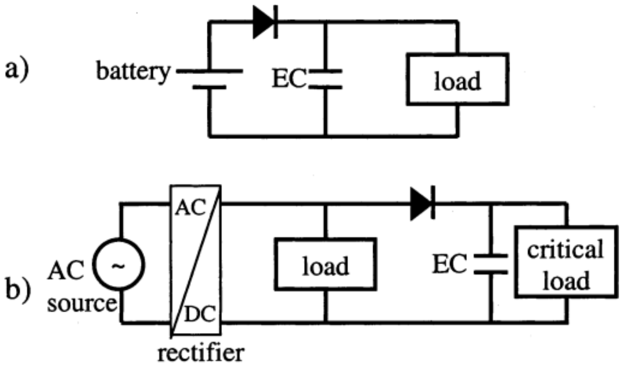


Figure 6 (a) battery-powered gadget experiences a disconnect, the EC supplies backup power for the load, (b) a device that uses high switching currents and AC voltage [16].

The EC can act as a vital backup power source in the case of a power loss brought on by the disconnecting or shutting down of the primary power source, contact issues brought on by vibration or shock, or a system voltage drop brought on by the activation of additional heavy loads. For optimum performance, placing the EC close to the critical load is advisable. [16] ‘’Some typical applications are:

- Backup of TV-channel setup, recording times, and clock time is available on video recorders and TV satellite receivers. The backup is offered for a time frame ranging from h to weeks.
- Car audio system, taxi metre: backup of radio station memory, taxi fare programmes and accumulated fare data while removing the car-radio or taxi metre from the vehicle or disconnecting the battery. Several hours to a few days of backup.
- Alarm clock radios, process controllers, home bakeries, and coffee makers guard against lost time and programmed actions in the event of a brief power interruption. Backup for up to a day.
- Mobile phones, programmable pocket calculators, electronic agendas and organisers, and photo and video cameras. For s to min, a backup is offered while the batteries are being replaced.

In many of those applications, the price of an EC is equivalent to or less expensive than the price of a rechargeable battery. The most significant advantages of ECs are their longer lifetime, higher cycle capability, fast charging capabilities, and environmental compatibility.

2.2.6 Electrochemical capacitors face a challenge

There are traditional replacements for many of the previously described applications, such as capacitors or batteries. Despite ECs having a superior energy to power ratio, capacitors or batteries are more frequently used due to commercial considerations. Consequently, for ECs to be viable, they must be competitively priced. Studies have shown that it is feasible to produce ECs in large quantities with good reliability and at a low cost for electronic applications. However, a challenge arises in the high voltage requirement for several applications. Due to the restricted voltage of a single cell, dozens or even hundreds of cells must be connected in series. It is essential that the capacitance and leakage resistance of each cell are consistent throughout the life of the EC [16].

2.3 FUEL CELLS:

A fuel cell in an energy converter that utilizes electrochemical reactions to generate electricity and heat. It combines a gaseous fuel, typically hydrogen, with an oxidant gas such as oxygen from air, across an ion-conducting electrolyte through electrodes. In the process, water is produced at the exhaust. Unlike a battery, the fuel cell does not discharge or necessitate recharging, and it will continuously generate energy as long as fuel is supplied. The primary attribute of a fuel cell is its capacity to transform chemical energy directly into electrical energy, resulting in greater conversion efficiencies than conventional thermomechanical systems. This allows the extraction of more electricity from the same quantity of fuel. Their technology provides a number of advantages over traditional power generating techniques, the most significant of which is its high efficiency. This indicates that a larger part of the fuel’s energy is converted into useful power. Additionally, fuel cells produce negligible emissions, making them a much greener alternative to conventional combustion-based power generation [22]. Fuel cells also operate without combustion, which makes them virtually pollution free and they operate quietly due to the absence of moving parts [23].

2.3.1 Design and operation of the fuel cell

In a fuel cell, there are two electrodes positioned on either side of an electrolyte. The anode of the fuel cell is supplied with hydrogen fuel, while the cathode receives oxygen from the air. With the aid of a catalyst, the hydrogen fuel undergoes a process of splitting into protons, or hydrogen ions and electrons, which move in opposite directions towards the cathode. **Figure 7** shows that the proton and electron produce a separate flow of electricity that can be utilized prior to reaching the cathode, where they combine with hydrogen and oxygen to produce pure water and heat [24].

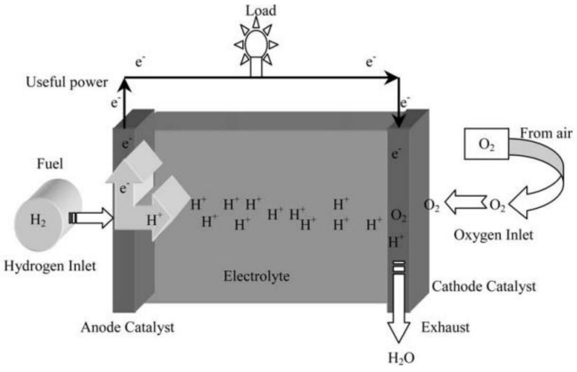


Figure 7 Fuel cell design [24].

2.3.2 Parameters of the fuel cell

The fuel cell comprises the anode, cathode, catalyst, electrolyte, and fuel, with the latter usually being converted into hydrogen. While fuel is a critical parameter, it is independent of the other components. The electrode's primary role is to initiate a reaction between the reactant, between fuel or oxygen, and the electrolyte, without undergoing consumption or corrosion. It is also responsible for bringing together the three phases: the gaseous fuel, the solid or liquid electrolyte and the electrode itself. The fuel cell's negative electrode is the anode, which evenly distributes hydrogen gas over the entire surface of the catalyst and conducts the resulting electrons for use as power in an external circuit. The cathode, which is the positive electrode of the cell, distributes the oxygen it absorbs across the catalyst's surface and returns electrons from the external circuit to the electrolyte, where they combine with hydrogen ions and oxygen to produce water. The catalyst is a special material used to facilitate the reaction between oxygen and hydrogen. The fuel cell's operating temperature is influenced by the type of electrolyte used, which can be either a liquid or a solid. The primary role of the electrolyte is to prevent the two electrodes from making direct electrical contact by impeding the flow of electrons, while permitting the movement of charged ions from one electrode to the other. Depending on whether it is an oxygen ion or hydrogen ion conductor, the electrolyte determines which side of the fuel cell produces water. Proton conducting fuel cells produce water on the oxidant side, while oxygen ion conductor fuel cells produce water on the fuel side [24].

2.3.3 Types of fuel cells

Fuel cells are typically classified based on the type of electrolyte used and their operating temperature. There are several types of fuel cell technologies being developed for different applications, each using a different chemistry.

2.3.3.1 Proton Exchange Membrane Fuel Cell (PEMFC)

Proton-conducting polymer electrolyte membranes, lower temperature (40-80°) and pressure ranges, make PEMFCs distinctive. Due to their exceptional power density, high energy conversion efficiency, and emission-free operation, these fuel cells are seen as a possible solution for future energy conversion devices [25].

2.3.3.2 Solid Oxide Fuel Cell (SOFC)

Their efficiency, autonomy, and their ability to use a variety of fuel sources like methane, methanol, and ethanol since they operate at high temperatures (600-1000°C), gives them a clear advantage over conventional energy generation techniques. This characteristic offers a considerable ecological benefit for effective energy conversion. The most common electrochemically combustible species found in SOFCs are hydrogen (H_2), carbon monoxide (CO), and methane (CH_4), which are produced when raw fuels are externally steam-formed. However, it is standard practice to just consider H_2 as the source of energy since the others are transformed on the spot by steam reforming to produce more H_2 [22,26].

2.3.3.3 Other types of Fuel Cells

1. An alkaline electrolyte is used in an alkaline fuel cell (AFC), which is powered by pure oxygen and hydrogen [23].
2. The phosphoric acid fuel cell (PAFC) is constructed up of a silicon carbide structure that houses the phosphoric acid electrolyte and an anode and cathode made of a platinum catalyst that has been scattered finely on carbon. It is functional up to 200^{o}C.
3. Molten carbonate fuel cells (MCFC) operate at temperatures of about 650^{o}C and use molten carbonate salt suspended in a porous ceramic matrix as the electrolyte with fuel gases produced from coal, methane, or natural gas.

Table 1 lists their characteristics, while **Table 2** lists various fuel cell reactions [25,27-28]:

Table 1 Fuel cells classification

Characteristics	Polymer electrolyte	Alkaline	Phosphoric acid	Molten carbonate	Solid oxide
Fuel cells Operating Temperature [^{o}C]	40-80	65-220	205	650	600-1000
Electrolyte	Hydrated polymeric ion exchange membrane	Mobilized or immobilized potassium hydroxide	Immobilized liquid phosphoric acid in SiC	Immobilized liquid molten carbonate in $LiAlO_2$	Perovskites
Electrodes	Carbon	Platinum	Carbon	Nickel and nickel oxide	Perovskite
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carmon or metal	Metal	Graphite	Stainless steel	Nickel or ceramic
Change carrier	H^+	OH^-	H^+	CO_3^+	O^-

Table 2 Fuel cells reactions

Fuel cell kind	Reaction at the anode	Reaction at the cathode
Polymer electrolyte and Phosphoric acid	$H_2 \rightarrow 2H+ + 2e^-$	$O_2 +4H^+ +4e- \rightarrow 2H_2O$
Alkaline	$H_2+2OH- \rightarrow 2H_2O+2e^-$	$O_2+2H_2O+4e^- \rightarrow 4OH^-$
Molten carbonate	$H_2+ CO_3^2 \rightarrow 2CO_2+2e^-$	$O_2+CO_2 +4e^- \rightarrow 4OH^-$
	$CO+CO_3^2 \rightarrow 2CO_2+2e^-$	
Solid oxide	$H_2+O_2- \rightarrow H_2O+2e^-$	$O_2+4e^- \rightarrow 2O^{2-}$
	$CO+O_2 \rightarrow CO_2+2e^-$	
	$CH_4+4O_2 \rightarrow 2H_2O+CO_2+8e^-$	

2.3.4 Fuel cell benefits and limitations

The fuel cell operating system offers numerous advantages, but it also has some limitations. Increase energy independence by reducing the reliance on oil and increasing the domestic electricity supply. The fuel cell system offers high reliability, with operating times exceeding 90% and power availability reaching 99.99% of the time. Additionally, its efficiency results in lower operating costs and significant reductions in energy bills. Fuel cell systems provide continuous power generation, unlike backup generators and diesel engines, which may suffer from downtime. Moreover, they offer a wide range of fuel options including natural gas, propane, butane, methanol and diesel among others. The fuel cell's quiet operation makes it suitable for indoor installation and people can converse normally neat it without requiring hearing protection. This contrasts with combustion engines which produce a lot of noise. Additionally, the fuel cell is highly efficient, converting up to 50-70% of available fuel into electricity, leading to reduced fuel costs and conservation of natural resources [24].

Electricity is produced by fuel cells through a process that combines oxygen and hydrogen. While oxygen is easily obtainable from the air, hydrogen is challenging to store and distribute and that is why readily available hydrocarbon or alcohol fuels are used instead. These fuels must be reformed into hydrogen through a reformer before being delivered to the fuel cell. However, some fuel cells encounter problems related to electrolyte management and some require expensive materials like platinum, as seen in the PEMFC. Other types need their electrolyte material to be hydrated, while some have a high operating temperature, such as the MCFC and SOFC [24].

2.3.5 A fresh outlook on the application of fuel cells

Batteries and internal combustion engines could be replaced with fuel cells in a variety of applications, including house heating, mobile phone charging, and automobiles. In addition, a number of fuels, including bio-methane and waste hydrogen, can be used to generate hydrogen in fuel cells, opening up a wide range of potential applications for the technology. The portable sector, which currently accounts for only 2.6% of global electricity supplied, is the fastest growing market for micro-portable fuel cells [29].

A fuel cell could be developed into an (APU) auxiliary power unit, providing power to hotels with up to 100W loads or integrated into vehicles. The APU industry is rapidly growing because fuel cells offer a technology that is low in emissions and noise. When methane is utilised as a fuel, fuel cells may produce up to 8 Nm^3 of hydrogen per hour, providing electricity and heat during the day and hydrogen to fuel buses and other vehicles at night. Additionally, the exhaust gas of fuel cells contains only 15% oxygen, making them suitable for fire suppression systems that require low-oxygen air [24].

2.3.6 Applications of fuel cells

There are numerous potential applications for fuel cells and each one presents unique challenges and considerations. Fuel cells have a variety of important applications, including [24]:

1. Ensuring reliable high-power supply for critical operations such as computer facilities, call centres, communication facilities, data processing centres and high-tech manufacturing facilities.

2. Reducing or eliminating emissions in transportation, urban areas, industrial facilities, airports, and other areas with strict emission standards.

3. Providing power in locations with limited access to the utility grid, such as rural or remote areas and areas with maximum grid capacity.

4. Utilizing biological waste gases from sources such as waste treatment plants, which can be converted into electricity and heat with minimal impact on the environment.

2.3.7 Conclusions

Fuel cells are an eco-friendly option for producing electricity, but to utilize them, it is essential to assess their efficiency in terms of the second law of thermodynamics and specifically the losses that occur. To accomplish this, a thermodynamic analysis of fuel cells and a comprehension of the associated losses have been developed. The outcome is a set of thermodynamic and thermochemical equations that facilitate the assessment of the following losses: the potential at the electrodes is a mix of different forces resulting from the chemical reactions occurring at the electrodes. Losses in activation are caused by kinetic restriction at the electrodes. Losses occur due to resistance in the electrodes and electrolyte, referred to as Ohmic losses. Diffusion and transport of mass in the electrolyte cause losses related to mass transport [24].

Despite the presence of losses and dissipation, fuel cells have remarkable efficiency and have the potential to become a significant technology for power generation with minimal environmental impact in the near future [30].

2.4 Hydrogen production

The most common element in the universe is hydrogen, which is also the lightest and simplest element in the periodic table. It is primarily present in water and organic compounds on earth. It consists of one electron and one proton, and it is a colourless, odourless, flammable gas [31]. The widespread use of fossil fuels has raised numerous environmental issues as well as the energy problem, both of which can be addressed by using hydrogen (H_2) energy. A promising method for producing H_2 and establishing a sustainable energy cycle is water electrolysis. An applied voltage causes the cathode and anode of the water electrolysis process to produce H_2 and O_2, respectively. Electrocatalysts are used in both electrodes to quicken the kinetics of gas production. By reducing the overpotential necessary to produce an identical number of gases, catalyst efficiency can reduce the amount of electricity needed to produce the same amount of H_2 energy [32]. This sort of energy can be produced by electrochemically splitting water, where the cathode and anode work together to enhance the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively [33].

2.4.1 History of hydrogen

Hydrogen is not a new discovery, in fact, there is information about this material since over 200 years ago. As early as the sixteenth century, scientists observed that a gas was produced when sulfuric acid and iron reacted. This gas turned out to be hydrogen. The use of hydrogen has a long history. The first-time water was electrolyzed to create hydrogen was in 1800. A British scientist developed the first hydrogen-powered fuel cell almost 40 years later. The development of hydrogen technology was significantly aided by NASA, which was founded in 1958 for the purpose of space exploration. The Soviet Union made history in 1988 when it successfully piloted the first jet engine aircraft to use liquid hydrogen fuel [31].

Compared to other fuels, hydrogen has a number of safety benefits. Since it is non-toxic and lighter than air, once discharged, it disperses quickly. In the case of a leak, this makes it safer. But, if a leak goes undetected and hydrogen builds up in a small area, it could ignite and trigger an explosion. Consequently, for safe hydrogen use, early leak detection and appropriate ventilation are required. All fuels, including hydrogen, have some risk, thus taking measures to prevent all three aspects of combustion-ignition, oxidant, and fuel is necessary for their safe usage. To ensure safe use, additional technical controls are necessary due to hydrogen's special properties. For instance, the concentration range of hydrogen in the air that is flammable ranges from 4% to 75%. Furthermore, compared to other fuels, it has lower ignition energy, requiring additional safety measures to prevent accidental fire [31].

2.4.2 Hydrogen specifications

It's important to take into account the possibility of material damage at leakage points and metal hydrogen embrittlement when choosing materials for hydrogen systems. Safe hydrogen use requires careful material selection and design, as well as a complete grasp of the characteristics and safety features of hydrogen. To further assure the safe use of hydrogen and to prevent accidents, training in safe handling and storage procedures is essential. With a higher heating value of 141.8 MJ/kg and a lower heating value of 120 MJ/kg at 298 K, hydrogen contains an amazing amount of energy. This is a lot higher than the majority of conventional fuels. However, compared to hydrocarbon fuels like gasoline, liquid hydrogen has an energy density by volume that is roughly one-fourth lower. Yet, although having a higher energy density by weight than hydrocarbons, hydrogen gas has a lower energy density by volume, necessitating the need of larger storage tanks. In order to use hydrogen gas safely, it must be taken into consideration that it is flammable and has a low ignition temperature. In addition, hydrogen can penetrate materials due to its small molecule size, which can cause mechanical failure and degradation when leaks occur. Due to hydrogen's destructive nature, it is crucial to use the right materials and put the right safety measures in place to prevent tragedies [31].

2.4.3 Hydrogen economy

There is a lot of excitement about the promise of hydrogen-based energy and transportation as new advancements are often reported. As hydrogen emits zero carbon at the point of use, it may easily be integrated into current energy and transportation networks. This could drastically reduce air pollution. Hydrogen is a possible option because it is widely used and has been linked to a number of environmental problems, such as oil spills and global warming. Policymakers should place a high priority on preserving price stability and securing the energy supply. As a result, the world is moving away from an economy based on fossil fuels and towards a cleaner hydrogen-based one, commonly known as the hydrogen economy. Since this idea was first put forth in the 1970s, it has undergone extensive study. To keep track of developments and highlight the potential of hydrogen in the energy sector, a number of reviews, case studies, and roadmap reports have been produced. In order to gain a complete grasp of the topic, there is growing interest, according to recent literature research, in examining the techno-economic, environmental, policy, and social consequences of a hydrogen-based economy. As a result, numerous national and international organisations have been set up to inform the public, professionals in the sector, and decision-makers, as well as to create a framework for getting ready for the era of the hydrogen economy. A possible approach to achieving a 100% renewable electric grid and eventually transitioning to a 100% renewable energy supply, leading to the hydrogen economy, looks to be developing various parts of hydrogen systems and producing renewable hydrogen using renewable energy sources [31].

2.4.4 Pathways for Hydrogen Production

The many methods for producing hydrogen have received a lot of attention recently as a means of simplifying the transition from fossil fuels to a sustainable energy economy and to improve the integration of future energy systems. Any hydrogen production pathway's efficiency, cost-effectiveness, and safety depend on the method employed to produce the hydrogen. The material that contains hydrogen (which can be either a hydrocarbon or a non-hydrocarbon), the energy source, and the catalyst material are the three key aspects of a hydrogen production pathway. These elements determine whether the hydrogen manufacturing process is feasible. The type of material used as a feedstock to extract hydrogen, the size of production, and the availability of energy resources are therefore some of the factors that influence the choice of the hydrogen production pathway. As depicted in **Figure 8**, hydrogen production is possible with the use of one or more different forms of energy, the right technology, and the right catalyst. A variety of energy sources, including electricity, photons, bioenergy, chemicals, heat, or a combination of these, can be used to extract hydrogen from materials that contain hydrogen [31].

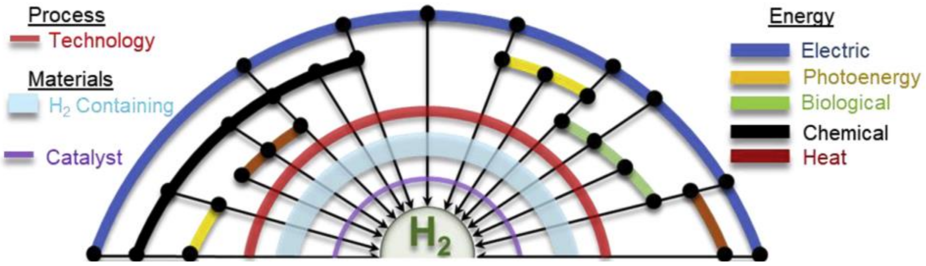


Figure 8 Recommended hydrogen production methods [31].

For the procedure to be possible and increase the production's efficiency, a catalyst is necessary. Consequently, the most quickly developing field of research at the moment is the creation of a cheap and effective catalytic material. Direct energy or catalytic energy can be used to remove hydrogen from stored hydrocarbons or non-hydrocarbons. By dividing the energy value of the hydrogen generated by the energy used in the manufacturing process, the efficiency of a hydrogen production pathway is determined. According to the literature, several energy sources are used in various hydrogen production processes, either directly or after conversion. In these processes, the presence of catalyst materials is also crucial. For instance, electrolysis might not be the best technique if the goal is to recover hydrogen from organic waste or hydrocarbon fuel. Similar to this, purification may be required if bio-hydrogen is to be used in a fuel cell application, adding to the cost [31].

The development of permeable membranes that can separate and purify hydrogen from gaseous mixtures has advanced quickly, opening up new uses for membrane reactors. This cutting-edge technology creates a new route for producing clean hydrogen from regular fuels when combined with carbon capture techniques. Moreover, integrating a catalytic chemical reaction with a membrane-based separation process can improve the efficiency and purity of blue hydrogen production while also raising the cost of the process overall.

Ammonia (NH_3) is considered a potential source material for producing hydrogen through decomposition, and hence, it has been incorporated into various hydrogen production technologies. However, it is important to note that industrial ammonia is initially synthesized from hydrogen, which means that it serves as a hydrogen storage medium instead of being a primary Hydrogen Production Pathway [31].

To have more efficient and less cost-effective hydrogen production we can use bifunctional electrocatalysts. The complexity of using different catalysts is reduced, and contamination between the reaction electrodes is prevented by developing a bifunctional electrocatalyst with outstanding capabilities. However, because the reaction pathways for HER and OER are so different, it can be challenging to build a bifunctional electrocatalyst. Few bifunctional electrocatalysts for water electrolysis have been developed to date. However, most of their structures are in a powder-like form and are not interconnected. In order to apply them to the conductive current collectors, they must first be made into a paste. Metallic glass has attracted the most attention among self-standing electrocatalysts in recent years because of its ability to withstand acidic and basic solutions, unsaturated atomic coordination of catalytic sites with favorable activity, and the variety of component and electronic structure options that exhibit various catalytic behaviors [32].

2.4.5 Conclusion

Hydrogen is an energy source that is growing in popularity, which aims to speed up the decarbonization of the world's industrial and energy sectors. As a result, it is now of utmost importance to produce hydrogen using renewable energy sources. The first corner of the proposed Hydrogen Square model is represented by hydrogen production, which is connected to and depends on the model's other three corners. When selecting a hydrogen production pathway, it is crucial to consider the other three key stages of the entire hydrogen energy system represented by these other three corners. As the other three corners of the Hydrogen Square may have an impact on prices and pollution, it is crucial to consider hydrogen purification when choosing the production pathway. Finding the ideal balance between purity and recovery inclusion is crucial. Although hydrogen has zero carbon emissions when used in applications, its cleanliness also depends on the cleanliness of the production process. Assuring the source of hydrogen should therefore be the most important consideration when assessing the cleanliness of any hydrogen energy.

2.5 Metal-Air Batteries (MABs)

Energy storage can aid in the shift to renewable energy sources by enabling the storage of energy generated from wind or solar power, ensuring its availability when needed rather than only when produced. The effectiveness of such a system is determined by its ability to adapt to diverse demands, its overall energy storage capacity, and its recharging time. A technology that can meet these criteria is a battery. It is a tool that creates electricity by using electrochemical reactions in a single cell or several connected cells. Battery’s three main components that make up the cell are: the anode (a negative electrode that causes oxidation), the cathode (a positive electrode that causes reduction), and the electrolyte (a substance that helps ions move between the two electrodes). There are two types of batteries: primary batteries, which can't be recharged once they run out of energy, and secondary batteries, which can be recharged because they use reversible chemical reactions to store and release electricity [34].

Metal-air batteries are a secondary type of electrochemical battery that utilize a reactive metal anode, such as aluminium or lithium, and oxygen from the atmosphere as the cathode to generate electrical energy. Metal-air batteries are seen as a potential replacement for conventional lithium-ion batteries in the field of electric vehicles and energy storage due to their better energy density

[30]. Nevertheless, metal-air batteries are still in the experimental phase, and several obstacles must be overcome before they can become a practical and economically viable energy storage solution.

2.5.1 Structure and Mechanism

Figure 9 displays the three fundamental constituents of a MAB cell. The anode may be consisted of different metals such as Lithium, Iron, Aluminium, or others, while the electrolyte could be aqueous, non-aqueous (aprotic), solid-state, or a combination of them. Different metals are compatible with different electrolytes based on their susceptibility to water.

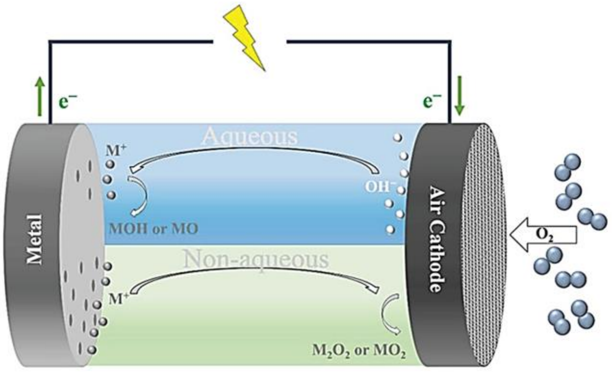


Figure 9 Diagram of a MAB cell [34].

In contrast to Lithium-ion batteries, in MABs, the anodic electrode induces a transformation of metals into ions, while at the cathodic electrode, oxygen changes into hydroxide ions, via the gas diffusion layer depicted in **Figure 10**.

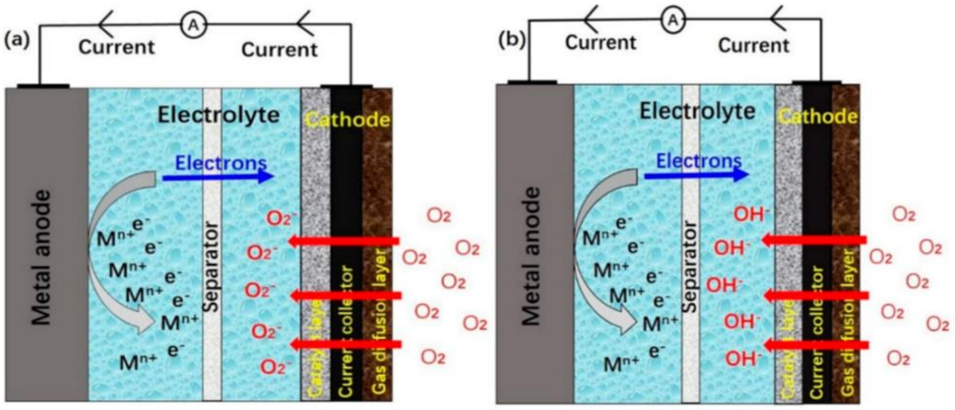


Figure 10 MAB's operation in (a) non-aqueous and (b) aqueous electrolyte [34].

The behaviour of oxygen in an aqueous electrolyte is different from that in an aprotic one. The conversion of metal to metallic ions produces electrons, and the metallic ions eventually disintegrate into the electrolyte. While charging, every reaction is the opposite. The **Table 3** is portraying a typical MAB cell operation during charge or discharge, of any metal in an aqueous electrolyte, and particularly for a Lithium anode with a non-aqueous one.

Table 3 MAB operation

Metal Anode	Anode Reaction	Cathode Reaction	Overall Reaction
General	$M \rightleftharpoons M^{n+} + ne^{-}$	$O_2 + H_2O + 4e^{-} \rightleftharpoons 4OH^{-}$	
Lithium Li	$Li \rightleftharpoons Li^{+} + e^{-}$	$O_2 + e^{-} \rightleftharpoons O^{-}_{2}$ $O^{-}_{2+} Li^{+} \rightleftharpoons LiO_2$ $LiO_2 + Li^{+} + e^{-} \rightleftharpoons Li_2O_2$	$O_2 + Li \rightleftharpoons Li_2O_2$

2.5.2 Electrochemical Performance

To evaluate their electrochemical capabilities, it is necessary to contrast them with established and proven batteries such as Lithium-ion and metal-sulphur ones. MABs have a specific energy capacity that falls within the range of 500 to 1500 Wh/kg, which exceeds the maximum capacity of 200 to 500 Wh/kg for the respective metals used in the other two types of battery.

2.5.2.1 Lithium-Oxygen (Li-O_2) Battery

The Li-O_2 battery is a unique choice since it uses oxygen and lithium metal as the cathode and anode reactants, respectively. Since oxygen can be continuously extracted from the air and lithium has the highest energy density of any metal (3860 mAh/g), the Li-O_2 battery has a very high energy density. Due to its outstanding potential energy density of 11,400 Wh/kg, which is higher than that of commercial Li-ion batteries (500 Wh/kg) and almost on par with gasoline, the Li-O_2 battery has recently attracted a lot of interest [35]. The electrochemical reaction involving Li^{+}, O^{2-}, and electrons, as well as the depositing of the discharge product, occur at the cathode, which is a fundamental part of Li-O_2 batteries. The insulating and insoluble lithium peroxide (Li_2O_2) builds up on the catalytic sites and finally covers the electrode surface as the discharge depth rises, blocking the mass transfer channels. To obtain higher performance in Li-O_2 batteries, it is essential to design a novel cathode with an efficient electron transfer rate, Li^{+} transfer, oxygen transmission, and high discharge product carrying capacity. Cathodes are the subject of most of the scientific inquiry because of their still-high cost and difficult manufacturing procedure [36].

2.5.2.2 Zinc-Air Battery (ZAB)

Zinc-air batteries (ZABs) are an excellent option for energy storage because of their high energy density, low price, safety, and scalability. However, the ZABs thar are now available are primary batteries (not rechargeable), and because their anode is prone to dendrite growth, they cannot be recharged. In addition, the cathode’s oxygen reduction reaction (ORR) kinetics require catalysts to be sped up. Commercially available noble metal catalysts, such as Pt/ C and IrO_2, can only be used to induce either ORR or OER, they are expensive, and unstable at high current densities [37]. MABs in general, do not fare as well in terms of specific power as their theoretically possible range of 0.1 – 1 kW/kg is not as competitive as the commercially available Lithium-ion batteries that can reach up to 10 kW/kg.

2.5.3 Applications

MABs possess extraordinary energy density, making them suitable for powering electronic devices and electric cars. The integration of reliable MABs in electric cars can considerably extend their lifespan. Additionally, MABs are well-suited for grid applications that require energy storage, particularly in scenarios where renewable energy sources produce excess energy that exceeds the current demand. With their exceptional storage capacity, MABs can help to equalize the demand and supply during peak production periods.

In addition to serving as energy storage devices, MABs have the potential to function as water treatment units in electricity production. Specifically, MABs can be used as: water compound collectors, water heavy metals removers, and household sewage and wastewater treatment units. One instance where this is employed on a small scale is in a pre-treatment device for residential wastewater. In such a scenario, the utilization of a MAB can effectively lower the levels of chemical oxygen demand (COD), phosphorous, and ammonia nitrogen in domestic water.

Water desalination is a high energy-consuming process that requires advanced technology for optimal results. **Figure 11** shows a Metal-Air Desalination Battery (MADB), a self-sustaining device that produces power and desalinates water at the same time. MADB is an Aluminium-Air battery that uses seawater as an electrolyte. However, like all MABs, its efficacy is limited by the cathode’s ability to dissolve oxygen.

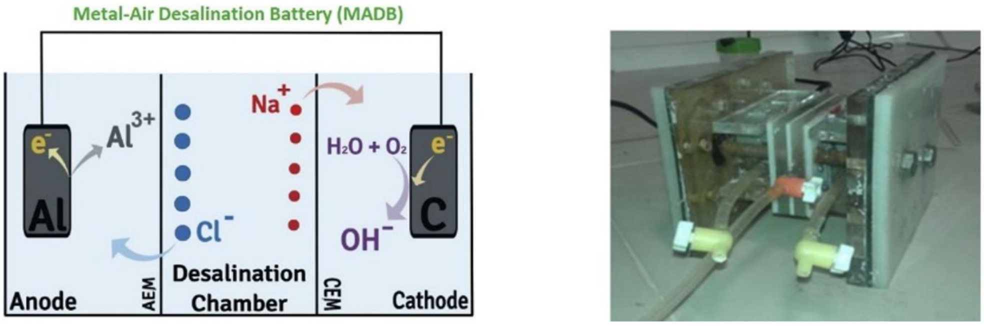


Figure 11 Schematic diagram of a MADB and a photograph [34].

2.5.4 Challenges

Despite the impressive theoretical properties of MABs, there are still significant technical challenges that impede their commercialization. These difficulties can be categorized based on the components they affect. Beginning with the anode, the major challenges involved are corrosion, passivation, and dendritic formation. The metallic anodes corrode in the presence of an aqueous electrolyte as per equations (7) and (8) [34]:

$$M + (2 + x)H_2O \rightarrow 2M(OH) + H_2 \tag{7}$$

$$M + H_2O \rightarrow MO_x + H_2 \tag{8}$$

As the voltage of MABs is typically above the level of M/MO, they are generally susceptible to hydrogen evolution reactions. Corrosion in MABs can be detrimental to the battery’s performance, leading to a decrease in its columbic efficiency and even causing battery explosions. Another issue is passivation, which develops when a coating forms on the electrode's surface and ultimately hinders the passage of discharge products. Lastly, dendritic formation gradually alters the shape of the metal electrode and causes uneven roughness on its surface. The development of dendrites can lead to an unstable battery system or even a short circuit. The primary issue with an aqueous electrolyte is the dissolution of CO_2 from the air, which reacts with OH^- to generate CO_3^2. To mitigate this, MABs can utilize a CO_2 filter to prevent the formation of CO_3^2 and the subsequent reduction in cell conductivity. However, this approach would inevitably raise the cost. Additionally, the evolution of hydrogen and its insoluble by-products, as well as the absorption of moisture from the air, pose significant challenges for the electrolyte. To address these issues, a more effective design and calculation of the humidity balance within the cell could be the key to MAB’s success. The primary challenge faced by the cathode is the increased precipitation of solid Li_2O_2, which creates a thick insulating layer that eventually impedes the flow of electrons and air [34].

The practical application of $Li\text{-}O_2$ batteries is severely hampered by the sluggish electrocatalytic kinetics of oxygen reduction (ORR) and oxygen evolution (OER) reactions happening on the air-cathode electrode during the discharge and charge operations. Due to this, $Li\text{-}O_2$ batteries exhibit poor electrochemical performance, which adversely affects their ability to be used in real-world situations. These issues include poor cycling stability, insufficient reversibility of Li_2O_2 formation and decomposition, capacity degradation, and a significant voltage difference between the charge and discharge cycles [34].

Noble metals like Pt, Ir, and RuO_2 have extraordinary catalytic activity in ORR/OER, but their broad application is constrained by their high price and scarce supply of resources. In Zn-air and Li-O_2 batteries, transition metal oxides and sulfides (TMOs and TMSs) have been developed as catalysts for ORR and OER because of their high activity, but at the same time their low cost and their simplicity. But many TMOs are considered as current insulators, which reduces their overall performance. Therefore, the current research is concentrated on the creation of effective and affordable bifunctional catalysts for ORR/OER [35]. Recently, transition metal phosphides (TMPs) have emerged as potential substitutes for the ORR, OER, or even supercapacitor processes. Their exceptional redox activity and electronic conductivity are the cause of this. The NiFeP catalysts, through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and capacitance-voltage (CV) measurements, were found to be the main causes of the enhanced performance of the cells. The catalytic activity of both ORR and OER was significantly improved by the addition of NiFeP. The resulting Li-O2 battery with a NiFeP/BC cathode displayed outstanding performance by utilizing biochar's strong electronic conductivity and effective material transfer capabilities [34].

An alternative cathode upgrade involves the usage of a three-dimensional biochar doped with CO and N, made from wood in a molten salt medium. This procedure creates a co-doped, self-supporting electrode that is suitable for use as a cathode in a lithium-air battery. With a discharge capacity of 9.44 mAh/cm^2 at a current density of 0.05 mAh/cm^2, the resulting battery has a high specific capacity and outstanding cycle stability. In conclusion, synthesis of wood-derived systematically porous and heteroatom-doped carbon materials in a molten salt medium can result in an effective air cathode for metal-air batteries [38].

2.5.5 Conclusion

Metal-Air Batteries are a promising alternative to conventional batteries due to their high energy densities, low weight, and their potential for low cost. Nevertheless, MABs are confronted with substantial challenges in terms of their commercialization. Addressing these challenges on every component is crucial for achieving a battery that is commercially viable. Overcoming these issues, means a significant potential for transforming the energy storage sector and creating a sustainable power source for different applications.

2.6 Electrochemical Sensors

2.6.1 Introduction

Hydrogen (H_2) is considered by the scientific sectors but also by the industrial ones as one of the most significant reducing gases, due to its involvement in several chemical processes and its wide range of applications in the industry. The generation of power, petrochemicals, transportation, and organic synthesis are among these applications. The use of hydrogen as a sustainable energy carrier in fuel cells for power generation in automotive applications has recently attracted more interest. Environmental pollution can be decreased by using fuel cells because they produce fewer emissions than internal combustion engines. In consideration of this, hydrogen fuel has the ability to meet energy needs while also advancing both environmental and human safety [39].

Hydrogen differs from other explosive gases like propane, methane, and gasoline in a number of ways. In particular, it is the lightest element, has the lowest boiling point (20.39 K), and has a high fluidity. Hydrogen ignites with a heat of combustion that is much greater (142 kJ/g H_2) and an air ignition temperature between 520 and 580 °C. Furthermore, hydrogen has a wide range of flammability in the air (4-75 vol%) and a minimum ignition energy of about 0.02 mJ. Hydrogen sensors are an essential part of the future of hydrogen energy because if a hydrogen leak were to occur, it might easily start a fire. The usage of hydrogen sensors is specifically required for the detection of hydrogen leaks and measurement of hydrogen concentration during storage, manufacture, and transportation. As a result, hydrogen sensors have many uses, such as in hydrogen production facilities, storage facilities, and automobiles, and they are essential to the safe operation of these systems [40].

Given that hydrogen is a gas with no odor, colour, or taste, it can only be detected and measured for its concentration by specifically designed sensors. These sensors must be able to measure hydrogen accurately, quickly, and precisely in the conditions required by the relevant applications. Hydrogen sensors that can function in extreme conditions and at high temperatures are also required in a number of industrial fields, such as metallurgy, petrochemicals, nuclear, and manufacturing. For example, monitoring hydrogen during the casting process of molten aluminum or in nuclear power plants to ensure the reactors are safe. Different hydrogen detecting systems have been developed as a result of ongoing scientific research. A well-established technology that has a considerable impact on the market is the electrochemical hydrogen sensor. They use solid electrolytes that conduct oxygen ions and protons to detect hydrogen at high temperatures [40].

Based on its working principle and response signal, electrochemical hydrogen sensors can be divided into three categories: potentiometric, amperometric, and mixed amperometric-potentiometric sensors. Potentiometric hydrogen sensors are available in two different forms: equilibrium (Nernst type) and non-equilibrium (mixed potential). The response signal in potentiometric sensors is the voltage between the electrodes, which has an inverse correlation with the hydrogen concentration. Amperometric hydrogen sensors use the output current generated by an externally applied voltage to provide information about the amount of hydrogen present in the gas being analyzed. Combined amperometric-potentiometric hydrogen sensors have two electrochemical cells, with one functioning as an amperometric and the other as a potentiometric sensor. Although the operating principle is more complex than that of single amperometric or potentiometric sensors, the detection reliability is improved. Mixed amperometric-potentiometric sensors have two electrochemical cells, one of which serves as an amperometric sensor and the other as a potentiometric one. The detection reliability is increased even though the working concept is more complicated than that of a single amperometric or potentiometric sensor [40].

It has been extensively studied how to detect hydrogen using solid electrolytes that conduct oxygen and potentiometric sensors. For gas analysis, Ytria Stabilizer Zirconia (YSZ) solid electrolyte-based chemical sensors are typically used. Combustible gases like CO and H_2 as well as oxygen are included in an electrochemical system of a gas mixture sensor, which is frequently employed for analysis [41]. These technologies still have trouble detecting hydrogen despite much investigation. Due to the high working temperatures of more than 600°C, the main challenge is finding a reference electrode that can maintain a constant potential during sensor operation [40].

2.6.2 Types of electrochemical devices

2.6.2.1 Potentiometric Gas Sensors

A potentiometric sensor consists of an electrolyte, which is commonly shaped like a closed tube at one end, and two electrodes, one of which is on the inside and the other of the electrolyte. At the sensing electrode, a balanced potential is produced while the potentiometric sensor is in use. The concentration of the gas being detected will affect this potential. The reference electrode establishes a reference potential, which is used to estimate the potential of the sensing electrode. Usually, a noble metal like platinum coats the electrodes as a catalyst, to speed up the reaction and upgrade its performance. Potentiometric sensors work by measuring the voltage in an open circuit, which prevents any electrical current from passing through the sensor. On opposite side of the sensor, which serves as a concentration cell, are various chemical potentials of ionic species. A well-known illustration of a potentiometric oxygen sensor that makes use of a solid oxide electrolyte is the lambda sensor, which is frequently used for detecting oxygen in exhaust gases. It is demonstrated in **Figure 12** [40].

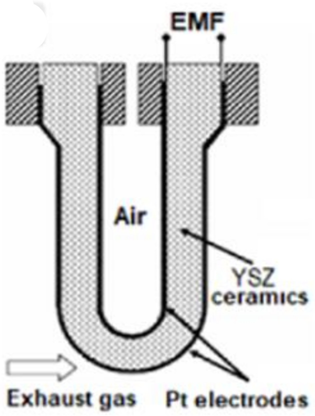


Figure 12 The potentiometric sensor's panel showing oxygen content in exhaust gases (lambda sensor) [40].

Potentiometric sensors measure the open circuit voltage (OCV, E) in order to operate. In this technique, the electrolyte mimics a concentration cell by having reversible electrodes and exposing it to a gradient of ionic species' chemical potentials. By taking into account specific factors, understanding the experimental OCV value, and being aware of the gas composition in the reference environment, it is possible to determine the composition of the second gas atmosphere. Most potentiometric sensors work on the basis of this simple idea [42].

2.6.2.2 Amperometric Gas Sensors

Amperometric sensors operate on the principle of measuring the electrical current, which is linked to the diffusion flow of the analysed gas onto the working electrode. This diffusion takes place either in an inner chamber or as a component of the electrode itself, across a capillary or porous barrier. The ambient gas fills the chamber or porous electrode when it is exposed to the atmosphere being evaluated [43]. The cathode catalyzes the reaction of the desired gas once the electrodes have been charged with an external voltage. The diffusion barrier, typically a porous layer or a laser-drilled hole, is crucial since it makes it easier for gas to diffuse into the sensor's inner chamber from the surrounding atmosphere [44]. The reaction rate rises as the applied voltage rises until it reaches a particular point where the concentration of the target gas inside the sensor becomes negligible. The target gas's diffusion flow through the capillary barrier has now reached its maximum value. When this occurs, an additional boost in the applied voltage has no effect on how the current responds. Amperometric sensors' ability to operate without a reference atmosphere gives them a great benefit over potentiometric ones. Particularly hydrogen potentiometric sensors need a reference environment for good operation, which can be challenging given that the working temperature of the sensors is normally above 600 °C to generate a stable reference potential. Potentiometric sensors, on the other hand, are less sensitive at these concentrations due to the detecting signal's logarithmic relationship with the gas concentration. A number of gases can be detected via amperometric sensors, including O_2, H_2, CO, NO_x, CH_s, and NH_3, using a variation of materials and geometries [40].

2.6.2.3 Combined Gas Sensors Amperometric-Potentiometric

A combination of sensors comprises two electrochemical cells - one functioning as an amperometric sensor and the other as a potentiometric sensor. The capillary barrier and the connectors between the cells are both sealed with high-temperature glass sealant. Compared to a single amperometric or potentiometric sensor, the working mechanism of these devices is more complicated [36]. The sensor is made up of two electrochemical cells, one of which serves as an oxygen pump and measures the amount of oxygen in the gas being studied using the value of the limiting current. Utilizing the calibration curve of the oxygen potential versus the limiting current, which was recorded concurrently with the calibration curve of the oxygen concentration versus the limiting current, the second cell, which functions in a potentiometric regime, verifies the sensor's operating capacity [45]. As a result, the reliability of the sensor is increased by the ability of the combined sensor to measure both the limiting current in the target gas pump and the electromotive force in the potentiometric cell simultaneously.

2.6.2.4 Electrical Biosensors

A biosensor typically consists of two parts: i) a bioreceptor, which is typically a biomolecule like an enzyme or antibody and captures the target analyte (such as a virus), and ii) a transducer, which transforms the signal generated by the bioreceptor into an electrical current or potential or some other form of signal depending on the transducer type used. A signal processing circuit will typically amplify the generated signal, and a computer or smartphone will display the results when they have been evaluated [46].

Electrochemical biosensors are portable, inexpensive, simple to construct, highly selective, and somewhat sensitive. Regardless of whether the target analyte is labelled or not, these biosensors function by detecting the electrical signal produced when the bioreceptor reacts with it in a specific manner. The electrical signal's strength reflects the analyte's concentration. Based on how they identify the target-analyte, electrochemical biosensors can be divided into biocatalytic and affinity sensors. Enzymes are often utilized in biocatalytic electrochemical biosensors to identify the target analyte by creating electroactive species. On the other hand, affinity electrochemical biosensors work by preferentially engaging with a bioreceptor such as an antibody, enzyme, nucleic acid, or other receptor, which results in the production of an electrical signal [46].

2.7 Electrocatalytic Reduction of Carbon Dioxide

2.7.1 Introduction

Since the beginning of the industrial revolution, the amount of carbon dioxide (CO_2) in the atmosphere has considerably increased due to the excessive use of fossil fuels, causing considerable concerns. As a result, the amount of CO_2 in the earth's atmosphere has increased, rising from 280 parts per million (ppm) in 1750 to 415 ppm in 2021. According to scientific predictions, this concentration may reach almost 600 ppm by the end of the century. As a result, there are now a number of serious environmental problems, such as desertification, extreme weather events, and global warming. Therefore, one of humanity's most urgent concerns is how to effectively convert and use CO_2 in order to lessen the aforementioned environmental problems and, to some part, reduce our dependence on fossil fuels [47].

The CO_2 molecule is composed of two identical C=O double bonds arranged linearly. These double bonds are delocalized, or triple-bond-like bonds with three centres and four electrons that are thermodynamically stable. However, the tremendous energy required to activate CO_2 makes the reaction energetically impossible. Furthermore, the CO_2 reduction cycle frequently yields undesirable by-products. The conversion of CO_2 into alternative carbon compounds, such as electrochemical, photochemical, thermochemical, and biological chemicals, has thus been the topic of extensive research. Being able to function at both room temperature and atmospheric pressure makes the electrochemical reduction of carbon dioxide incredibly appealing. It also exhibits superb compatibility and synergy with renewable energy sources due to its ability to use extra electrical energy at precise times and store it in chemical bonds. Therefore, the electrochemical reduction of CO_2 (CO_2RR)-based idea of carbon recycling shows enormous potential [47].

The CO_2 reduction reaction (CO_2RR) has been electrocatalyzed by metal oxides since 1990, and it has been theorised that transition metal oxides possess very efficient active sites for the CO_2RR. Metal oxides can further improve the CO_2RR performance in comparison to metal catalysts, drawing interest in current research. While other studies have focused on the metal-oxygen sites as active, this topic is still up for debate. Some studies have suggested that the active sites for CO_2RR in metal oxides arise due to surface reconstruction resulting from the reduced metal oxide surface at high negative operating potentials. Even for widely studied Cu-based catalysts, identifying the active areas of a catalyst is typically a difficult task and a current subject of research. This difficulty results from the CO_2 reduction reaction's (CO_2RR) complexity, which includes a number of potential proton-electron routes leading to various products. However, for creating electrocatalysts that are incredibly effective and selective for different products, locating the active regions of CO_2RR is crucial.

The development of intelligent and durable morphologies that boost the density of active sites and increase the resistance to NPs dissolving can improve the activity, selectivity, and stability of CO_2RR electrocatalysts. Recent years have seen the emergence of interface and defect engineering of metal oxides as a viable method for increasing the inherent activity of electrocatalytic active sites and thereby improving CO_2RR performance. Metal-metal oxide and metal oxide-metal oxide interactions have been shown to boost CO_2RR in a synergistic manner. The efficiency of metal oxide catalysts can be improved via interface engineering by altering the electronic structure of the catalysts, which encourages the adsorption and activation of the CO_2 molecule. Additionally, it is anticipated that the presence of oxygen vacancies and metal oxide defects will enhance the adsorption of CO_2 on the catalyst surface, which could further enhance the efficiency of CO_2RR [47].

2.7.2 The process of reducing CO_2 through electrochemistry

Anode, cathode, electrolyte solution enriched with CO_2, and membrane compose an electrochemical CO_2RR system, as shown in **Figure 13**. The oxygen evolution reaction happens at the anode, and the CO_2RR happens at the cathode.

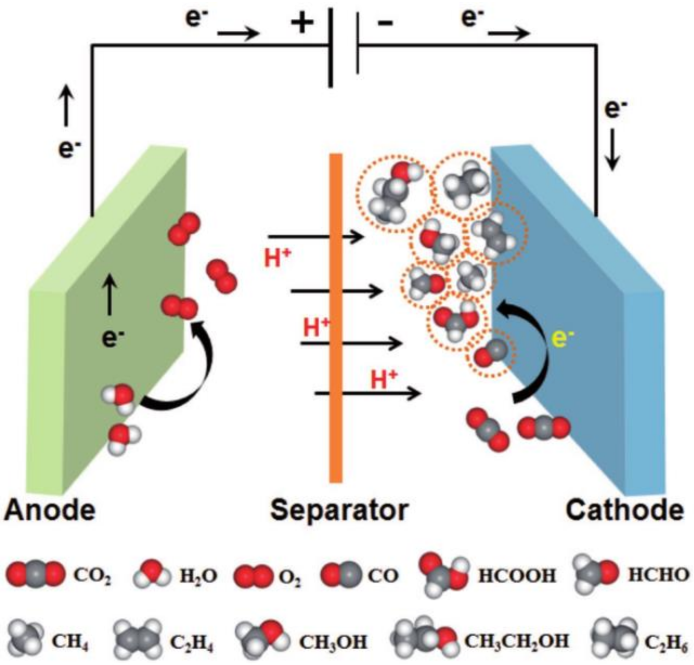


Figure 13 Schematic diagram of the electrochemical CO2 reduction reaction system [47].

Depending on the pH level, the electrolyte can change the energy barrier of the CO_2RR process and enhance the transportation of CO_2 to the surface of electrocatalysts. This can be done in two ways: by controlling the system's overall pH with various salts or salt mixes, and by adjusting the local pH with the help of the OH^- produced during CO_2RR. In order to transmit protons to the cathode, the membrane must separate the oxidation and reduction products, maintain charge balance, and create a closed loop [48].

Electrochemical CO_2 reduction is a quite complicated process. Numerous carbon-based chemicals, such as carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4), hydrogen (H_2), formic acid (HCOOH), methanol (CH_3OH), and ethanol (CH_3CH_2OH), can be created through the transfer of two, four, six, or eight electrons. Even though the thermodynamic cost of CO_2 reduction is equal to that of the hydrogen evolution reaction, studies have shown that a larger energy input, such as a high overpotential, is necessary to achieve a significant CO_2 reduction reaction rate. Furthermore, the competing reaction may become problematic if enough negative potentials are applied. The CO_2 reduction process also comprises a number of elementary reactions, which heightens the reaction's chemical inertness and makes it more challenging to control selectivity. Various types of electrocatalysts can undergo CO_2RR through a variety of distinct reaction pathways, depending on the experimental conditions. **Figure 14** demonstrates that, even though some reaction pathways have common intermediates, they produce different products [47].

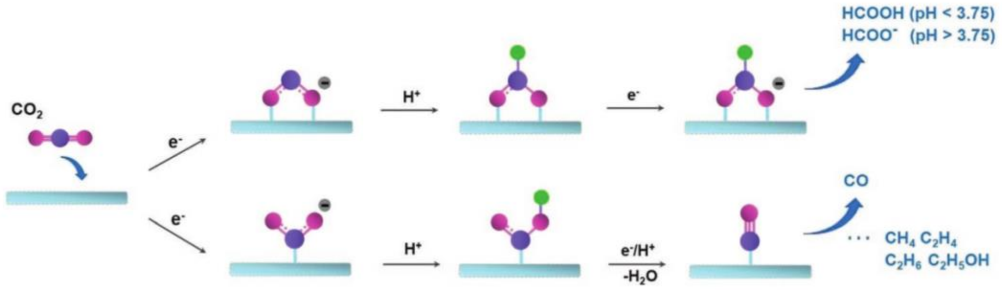


Figure 14 Different reaction pathways for electrocatalytic CO_2 reduction [47].

The end products are greatly influenced by how strongly the intermediates stick to the electrocatalyst surface. The relationship between the binding affinities of the metal surface and the final products was investigated both theoretically and empirically in order to manufacture desired metals from CO_2 reduction and produce certain products. The stable intermediates for the selected reaction pathway are identified using linear scaling relationships between the binding energies of reaction intermediates, such as OCHO, COOH, CO, and H, on the metal electrocatalyst surface. The principal product, which may be CO, format, a hydrocarbon, or a gas such as H_2, is predicted using an assessment measure called the CO binding strength on the catalyst surface [48].

2.8 Photoelectrochemical Splitting

Fossil fuel consumption causes harmful environmental problems including air pollution and the greenhouse effect, which endanger human existence. Right now, finding green energy alternatives to fossil fuels is crucial for attaining sustainable development in society. Due to its solitary byproduct of water upon burning, hydrogen is viewed as a possible energy source capable of tackling the current environmental concerns. The timely development of photocatalytic technology as a new strategy to balance economic and ecological development is encouraging [49]. Photocatalytic hydrogen production (PHP) is a cutting-edge method for capturing solar energy and turning it into a clean, renewable source of energy. This technology provides a workable response to the problems of environmental deterioration and energy scarcity brought on by the heavy reliance on fossil fuels. Researchers are working to create photocatalysts that are extremely efficient, environmentally benign, economical, exceptionally stable, and widely available in order to maximise the use of solar energy [50].

The three crucial stages of the photocatalytic process—light absorption, transport of photo-induced charge carriers, and catalytic surface reactions—are largely impacted by the chemical composition and physical structure of photocatalysts. Significant efforts have been made to continuously investigate and improve photocatalytic materials since the seminal work by some companies in 1972, in which they detected the formation of H_2 on a rutile titanium dioxide (TiO2) electrode [49].

Inorganic semiconductor catalysts have been the subject of intensive study in the field of photocatalysis during the past few decades, yielding major breakthroughs. However, because of their poor sensitivity to ultraviolet (UV) light and relatively quick rate of electron and hole recombination, the efficiency of PHP utilising these inorganic photocatalysts remains poor. On the other hand, organic photocatalysts have several benefits, including low cost, simple synthesis, the absence of hazardous metals, adjustable band gaps, customizable architectures, and functions. As a result, research teams around the world have concentrated heavily on the development and application of organic photocatalysts, resulting in rapid improvement in the field of photocatalysis [49].

The investigation of several kinds of conjugated organic polymer photocatalysts has significantly increased in recent years. Leading examples include linear conjugated polymers (CPs), conjugated microporous polymers (CMPs), covalent organic frameworks (COFs), and covalent triazine frameworks (CTFs). Graphitic carbon nitride (g-C_3N_4) is another. These materials have been the subject of extensive research. However, when exposed to visible light, the bulk of reported organic polymer photocatalysts only partially use it, leading to low PHP activity. As a result, it is still difficult to find organic polymer photocatalysts that are effective at utilising visible light [49]. Pure organic photocatalysts have drawn considerable interset due to its many unique qualities, such as adaptable architectures and compositions, effective visible light absorption, excellent stability, and the absence of metals. Porous organic polymers (POPs) stand out as a significant class of pure organic photocatalysts among them. POPs have good porosity, a wide range of structural variety, adaptable chemical compositions, and strong physicochemical stability. The creation of photocatalytic hydrogen, gas adsorption, light-responsive CO_2 insertion, and visible-light-driven CO_2 reduction to CH_4 are a few examples of the many uses for them [51].

Photocatalysts typically need an appropriate wide gap, broad responsiveness to visible light, and efficient transport and separation of photogenerated electrons and holes in order to attain remarkable photocatalytic performance. By carefully choosing the suitable building components to create polymer-based photocatalysts, these properties can be accurately altered. Certain conjugated polymers exhibit outstanding efficacy in photocatalytic water splitting by carefully choosing their building blocks [49].

CHAPTER 3

LITHIUM-ION BATTERIES

3.1 Introduction

Maximum growth potential exists for the usage of lithium-ion batteries outside of portable electronics. A high-density storage unit would significantly aid this effort to transition to sustainability as photovoltaic and wind energy parks may be easier investments. Since such a high-density LIB would significantly reduce carbon emissions while also becoming appealing to customers, there is also room for growth in the automotive industry. Transportation's transition to electric seems very promising, especially since LIBs have become commercially available. This is supported not only by the strategy of car manufacturers, who almost all have at least one EV for each vehicle category but also by the LIB production usage where more than half of them are used in the automotive sector [52].

3.2 History

The initial lithium-ion battery (LIB) to be commercialized was by Sony Co in 1991. As a result of LIB's revolutionizing of portable electronics, scientific interest exploded during the ensuing years. Since then, the concept of batteries was one of the most, if not the most frequently searched topics in scientific research. Governments all over the world began a number of initiatives on renewable energy sources (solar, wind, etc.) and electric cars as a result, with energy storage technologies at the basis of these solutions as they become increasingly conscious of the relevance of greenhouse gas emissions in global warming. Even while battery research has expanded significantly over the years, its objectives have remained constant: increase cycle durability and safety and decrease weight, size, and cost [52].

The need for batteries had started to increase with the development of portable electrical gadgets like portable electronic calculators or even flashlights. The 1970s oil crisis, the development of the transistor and the shortcomings of its predecessors' performance were among of the primary factors that prompted businesses, as well as consumers, to seek for alternative energy storage technologies. Predecessors of LIBs such as lead-acid and Ni metal hydride systems, for example, had low energy densities and little possibilities in the future. Lithium's highly reducing nature, low atomic mass and radius, and organic electrolytes' wide voltage window are some characteristics that attracted researchers looking for a solution with a higher energy density and power [52].

The invention of the LIB revolutionized portable electronics' design and made it possible for the numerous hand-held electronics that have come to characterize many facets of contemporary life. Research though did not end with the commercialization, while after that, LIBs had significant performance improvements in all of their components [52].

3.3 Battery chemistry

Lithium is until now the most important chemical element of all metals for battery chemistry. Its high electrochemical potential and its low weight are making it a highly promising element for a high-energy storage device. High potential together with the graphite's opposite one (most common LIB anode) provide an extremely potent electrochemical device for energy conversion and storage. Lithium's reactivity, which makes the safety aspect more challenging, is considered a disadvantage. However, lithium ions that penetrate the electrolyte instead of metallic lithium can diminish the issue [52].

3.4 Operating Principles

The fundamental operating principles of a Lithium-ion battery cell are shown in **figure 15**. The cathode, anode, electrolyte, and separator are the four main components of a Li-ion battery cell. Lithium ions travel from the cathode to the anode through the electrolyte during charge, and vice versa during discharge. The two electrodes are externally connected to an external electrical supply while charging in order to apply a significant force to the electrons and move from the cathode to the anode through an external cable. At the same time, lithium ions travel through the electrolyte from the cathode to the negatively charged anode. The external energy is thus electrochemically stored as chemical energy in the anode but also in the cathode with different chemical potentials. During discharge, with the electrodes now connected to an external load, solid phase Li diffuses to the surface of the anode where it experiences an electrochemical process that releases Li^+ ions into the electrolyte. By diffusing and ionizing their way across the electrolyte to the cathode, Li^+ ions undergo another reaction before returning to the solid phase. In the case of a graphite anode, the reaction that takes place on the negative electrode is [52]:

$$Li_xC_6 \leftrightharpoons Li_0C_6 + xLi^+ + xe^- \tag{9}$$

on either charging or discharging, while on the positive electrode the reaction is:

$$Li_0MO_2 + yLi^+ + ye^- \leftrightharpoons Li_yMO_2 \tag{10}$$

Graphite is the current dominant anode material, while other battery manufacturers have chosen different elements for anodes such as lithium titanate. The sole difference in the anode's production process from the cathode is the type of foil used to affix the electrodes. Cathode's foil material is aluminium while the anode is attached to a copper foil. Both coatings are connected to the LIB cell's terminals.

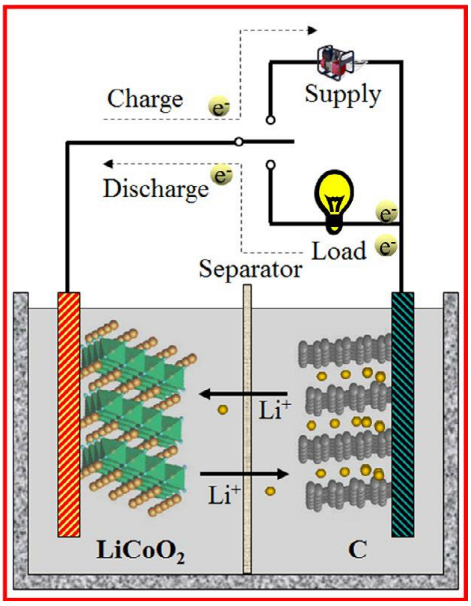


Figure 15 The basic components and operation principle of a Li-ion cell [29].

The electrolyte of a Lithium-ion battery is a mixture of lithium salts usually including lithium-hexafluorophosphate ($LiPF_6$), lithium-perchlorate ($LiClO_4$), and lithium-hexafluoroarsenate ($LiAsF_6$) and organic solvents. The most frequently used of them are ethyl-methyl-carbonate, dimethyl-carbonate, diethyl carbonate, propylene carbonate, and ethylene-carbonate, which are essential for improving Lithium-ions' mobility, and hence they are a crucial part of LIB's battery performance. A gel-formed electrolyte is used to avoid electrolyte leakage, since its casting is not particularly resistant, as in polymer Li-ion batteries. The separator functions as both a conductor for lithium ions and a safety barrier between the cathode and anode, preventing direct contact and consequent short-circuiting. The most popular separator materials are polyethylene and polypropylene. If the cell overheats, these materials melt, reducing ion flow and deteriorating their micro-porous properties, which is a sign of thermal runaway.. A battery's performance in general depends on a number of different components in addition to those thar are chemically necessary, such as insulators to prevent short circuits at the edges of the electrode and pressure relief vents [29].

LIB cells are either manufactured as cylinders or stacks, which are both illustrated in **Figure 16**. The layered components of a cylinder cell (cathode, anode, and separator) are rolled and enclosed by a metal can, whereas those of a stacked cell are sealed between two sheets of laminate film [52].

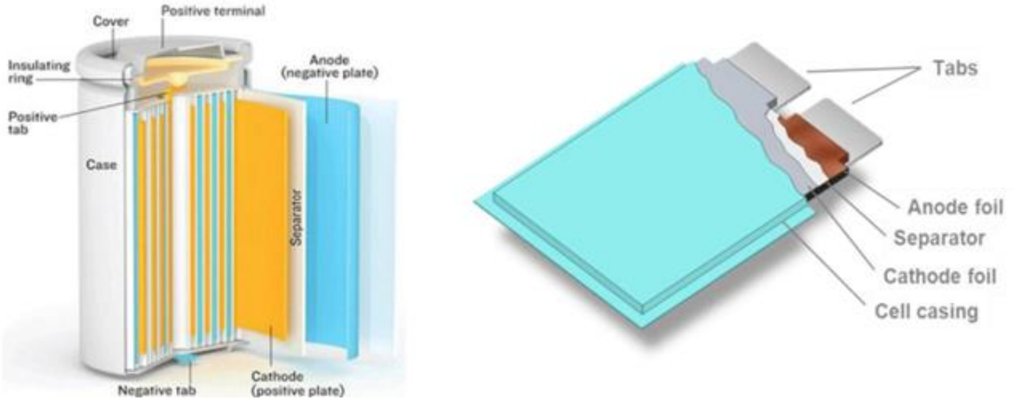


Figure 16 Li-ion battery cell configurations [52].

In order to monitor some important aspects of a LIB’s operation, a battery management system (BMS) is required. Temperature, state of charge (SOC), and current are a few of these factors that could be crucial for battery life. The complexity of a BMS depends on the demands of the system it is used in [52].

3.5 Battery important characteristics

Specific energy and power, durability, and safety are considered key characteristics of a battery, and cell design could have a decisive impact on each of these. The specific energy of Li-ion batteries ranges from 90 to 250 Wh/kg. This performance is critical, particularly in the mobile market where users become more demanding and need devices that last longer without the need of charging. However, specific power is typically expressed as a P/E ratio, where P denotes the maximum power in kW that a battery is capable to provide, and E stands for its maximum capacity in kWh. By adjusting the voltage, the density of lithium-ions, the SEI’s volume, the diffusion coefficient, and the conductivity, this ratio could be adapted to the requirements of each application. For instance, hybrid electric vehicles require a higher specific power ration than plug-in ones (higher output power and lower capacity), therefore cell manufacturers use wider and thinner electrodes to increase SEI’s volume [52].

An essential quality of a battery is its longevity. Battery deterioration happens under all circumstances, although to varying degrees depending on usage. The number of complete cycles of charge and discharge a battery can withstand while maintaining proven amounts of power and capacity that are at least 80% of their initial values is known as cycle life. This is the optimal indicator of a battery’s durability [52].

Engineering challenges arise from the coexistence of lithium, oxygen, and flammable electrolyte in Li-ion batteries. However, Li-ion batteries are frequently used in sensitive applications involving aircraft and road transportation and passengers carry their own LIBs inside their portable devices when using these means of transport. The engineering challenge is not just to produce safer LIBs, but at the same time to increase their specific power and energy. Li-ion battery safety issues are the subject of intensive research. Thermal runaway is a severe issue with Li-ion batteries. The breakdown of a battery cell's metal oxide and the subsequent reaction between the released oxygen and lithium, which occurs when a battery cell is overheated, such as through prolonged overcharging or short-circuiting, may result in fire inside the cell [52].

There are three stages where the safety of a LIB could be addressed. The first one is inherently which results from selecting the best materials for each application. As an illustration, lithium-ion phosphate (LFP) is inherently more thermally stable than lithium-cobalt (LCO). Cell design is the second stage of protection, whereby safety features and components could be included to the cell preventing short-circuiting accidents caused by cathode-anode contact. The battery management system (BMS), which should be able to regulate temperature, voltage, and current in order to prevent thermal runaways, overloads, and short circuits, is the third and final level of safety addressing [39].

3.6 Electric Vehicles and LIBs

It has been determined that one of the most important factors in lowering humankind’s greenhouse emissions is the electrification of transport vehicles. EVs have taken centre stage in many discussions in humanity’s future energy economy as they serve as both a green alternative to internal combustion engines and a possible equalizer for the energy grid’s production-demand. The majority of the world’s largest manufacturers now offer at least one hybrid model or a fully electric vehicle. Ev’s most distinguishing characteristic is its battery, and eventually all of its drawbacks such as those related to its driving range, its cost, or its charging duration could be attributed to a LIB problem [53].

The 1990s saw the commercial introduction of electric vehicles, however the products did not live up to expectations. All vehicles, which back then they were using lead-acid, Na-S or Ni-CD hydride batteries, either had an excessively short range (150 miles) or a high retail price and a lengthy recharging time. A fully electric vehicle’s potential was constrained by their expensive production and short range per charge and the interest was then turned to hybrids.

Hybrid electric cars (HEVs) of that time did not necessitate using a lot of energy battery so the Ni-Cd hydride battery was more than enough. In 1997 the Nissan Altra became the first electric vehicle to utilize a lithium-ion battery (LIB). Its battery pack consisted of 12 modules, each containing eight 100 Ah cells, and was based on a (LCO) cathode (Presented schematic on **Figure 17**). When compared to other EVs available then, the Altra's cell had the most efficient weight to range ratio. The Nissan Altra, however, had a high price for its meagre 192 km of range. Only 110 cars of the Altra model were ultimately leased or sold by Nissan [53].

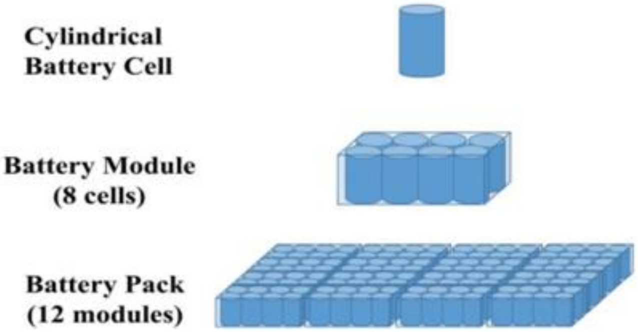


Figure 17 Nissan Altra's cell-module-pack design [53].

3.7 Electric Vehicles and LIB's state of the art

In general, the progress made in developing cathode materials based on Ni- based layered oxides has been remarkably effective. As of 2016, these materials had a 35% share in the worldwide battery market **Figure 18** [53].

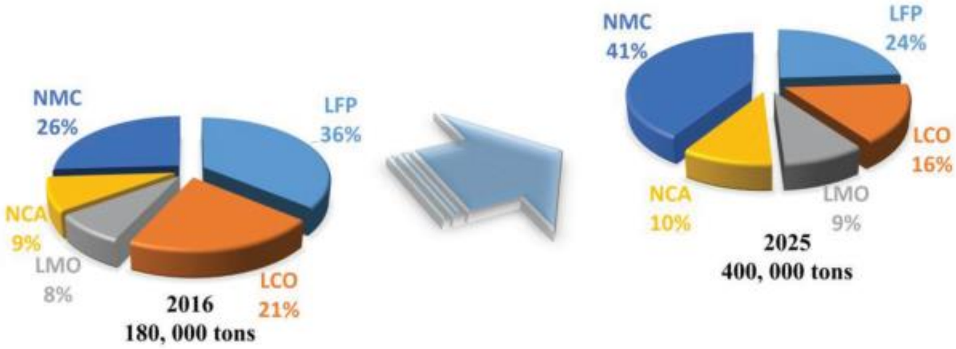


Figure 18 Market shares of the top materials for all LIBs in mass percent in 2016 and through 2025 [53].

Over the past few years, EVs have become much more extensively used. Over 320000 EVs were purchased in total in 2014, with more than half of those being plug-in EVs (182400 vehicles). However, just 0.3% of all the passenger automobiles sold at that time are represented by this number. The standards for EV energy density have always been an issue of intense discussion and it now seems that even pure EVs' present driving ranges are getting close to what consumers find to be satisfactory. The energy density targets (on a volume and mass basis) are practically reached by the current LIBs. In a study on the effects of longer-range EVs, the expected daily vehicle adsorption (DAP), as depicted in **Figure 19**, was proposed as a metric [53].

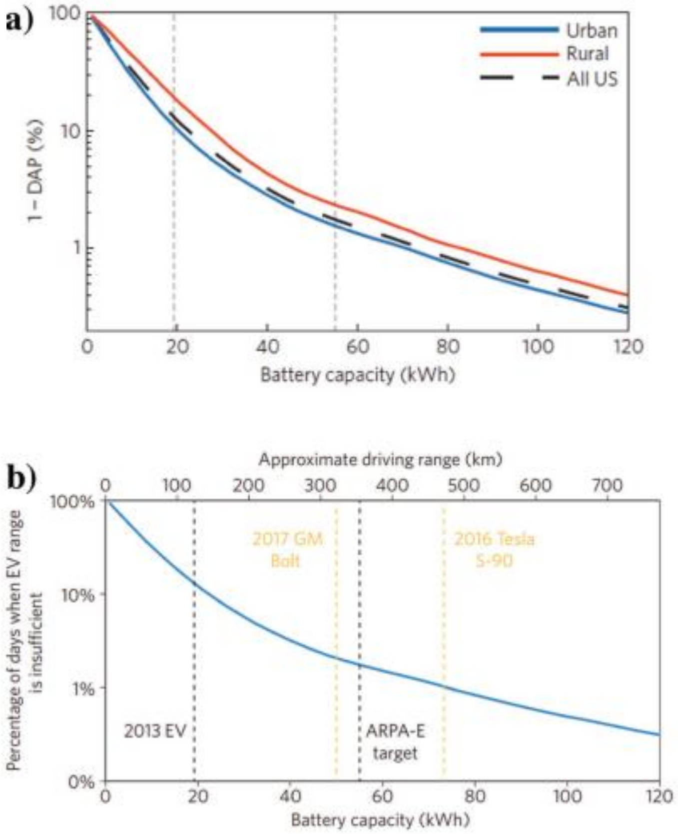


Figure 19 a) Impact of the driving type on the 1-DAP value. b) DAP value versus the battery capacity [53].

The DAP refers to the percentage of days in which a plug-in electric vehicle would be unable to complete the driver’s necessary trips on a single charge, while 1-DAP indicates the percentage of days in which EV drivers will need to recharge their cars during the day. The depicted 1-DAP percentages are already making EVs appealing for widespread adoption, and it is definite that as energy density research and development improves, 1-DAP will continue to decrease. This shows that the cost of LIBs, rather than the energy density, is the main obstacle to the electrification of transport. Cost and energy density are inextricably linked though since higher energy-density electrodes require less active material, which lowers production costs [53].

3.8 Other Applications

LIBs are found in a wide range of applications, not only on EVs. The largest market used to be portable electronic devices. The battery has also been used in satellites and other aerospace applications. Potential applications for the technology include grid-connected and off-grid power supply systems. Utilizing developments in lithium battery technology, medical devices, such as hearing aids, have seen significant improvements. Additionally, this innovation has ensured the availability of highly integrated, size-limited, dependable, hermetically sealed, high-density rechargeable power supplies for implanted devices used in applications like medication administration, glucose detection, and neurostimulation. Numerous self-powered microelectronics incorporate tiny Li-ion batteries, including tiny transistors, sensors, and actuators. Additionally, Li-ion batteries are the preferred option due to their exceptional specific energy and power as well as their low self-discharge rates, which are in line with the continued demand from experts for more powerful, effective, and comfortable equipment to use. Finally, Li-ion batteries are also used in a variety of different items, including wireless vacuum cleaners, radio-controlled toys, solar light emitting diode (LED) systems, wearable technology, and flashlights [53].

Portable electronic gadgets include, but are not limited to, mobile phones, tablets, computers, cordless home phones, cameras, MP3 players, portable game consoles, and toys. In terms of battery market share, cell phones, tablets, and laptops are by far the most popular applications, and the global market for portable devices is still growing quickly.

3.9 Reuse and Recycling

Every aspect of lithium-ion batteries' lifecycle should be considered accountable if they are to be seen as a green energy storage option and a low-emission mode of transportation. Not only do the mining and manufacturing phases that contribute to environmental pollution, but also the disposal stage. Inappropriate disposal of LIBs containing cobalt, nickel, and fluorine can have a significant impact on the environment, leading to pollution. The recycling or reuse of LIBs could result not only in eco-friendly products but also financially. The production of one ton of lithium currently requires approximately 250 tons of spodumene (a type of ore) and 750 tons of brine, whereas a recycling plant would only need 28 tons of used LIBs. Although this recycling process would not completely replace the production of new LIBs, it could significantly assist in meeting the rising demand of the market and eventually could contribute to reducing the average price. Despite these potential benefits, only 10% of LIB components are currently recycled [54].

Before the actual recycling methods take place, LIBs need to go through a pre-treatment process. Beginning with discharging completely, following with disassembling, and then separating each of their components. This stage is very important for LIB recycling, while by categorizing the components differently, the next processes become more efficient with less energy consumption. The first method for recycling LIBs involves pyrometallurgy, a process that utilizes high temperatures to extract pure metals. This method involves reducing metal oxides to form alloys, which can serve as the raw materials for creating new lithium-ion batteries. Following the disassembly of battery packs into individual cells, pyrometallurgy furnaces operate at different temperature levels **Figure 20**. Initially, preheating is carried out at temperatures below 300°C to eliminate the electrolyte vapor and reduce the likelihood of explosions. Next, the plastic pyrolyzing zone is reached, where the temperature climbs up to 700°C, and all plastic components are incinerated. Keeping the temperature stable, the final process is to smelt all the rest ingredients into an alloy containing nickel, cobalt, copper, and iron. That alloy is accompanied with a slag of silicon, aluminium, lithium, and iron too [54].

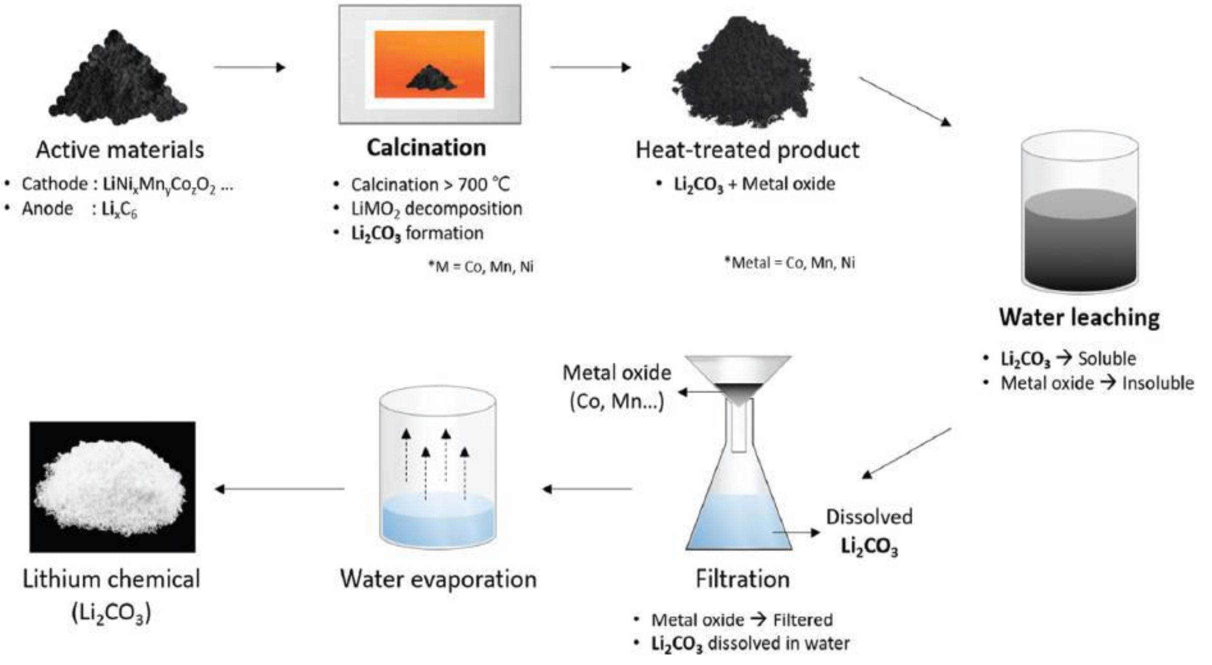


Figure 20 A representation of a usual LIB pyrometallurgy process [54].

Despite the benefits, pyrometallurgy has some drawbacks and limitations. Its primary objective is to recover cobalt, not lithium, and thus the cost of cobalt heavily influences the effectiveness of this method. Moreover, pyrometallurgy requires significant amounts of energy and materials and generates toxic gas emissions. Given the increasing use of electric vehicles, and decreasing one of cobalt anodes, there is a growing need for a more efficient and environmentally friendly lithium recovery method. Therefore, alternative recycling methods should be used.

Hydrometallurgy is a viable alternative to pyrometallurgy in recycling lithium-ion batteries. In hydrometallurgy, cathode materials are pre-treated and then converted into ion forms using solutions, with the resulting metal ions separated to produce new cathodes. Compared to the previous method, hydrometallurgy does not operate at high temperatures, consumes less energy, and is highly efficient in recovering cobalt, nickel, and copper with minimal impurities. This makes it the most popular recycling method for LIBs. The process of hydrometallurgy is outlined in figure, with the first step being leaching, which involves converting the cathode metals into solutions using organic or inorganic acids, ammonia, or even metabolites from microorganisms. The final step is separation, which can be achieved through chemical precipitation, solvent extraction, or electrochemical precipitation, as shown in **Figure 21** [54].

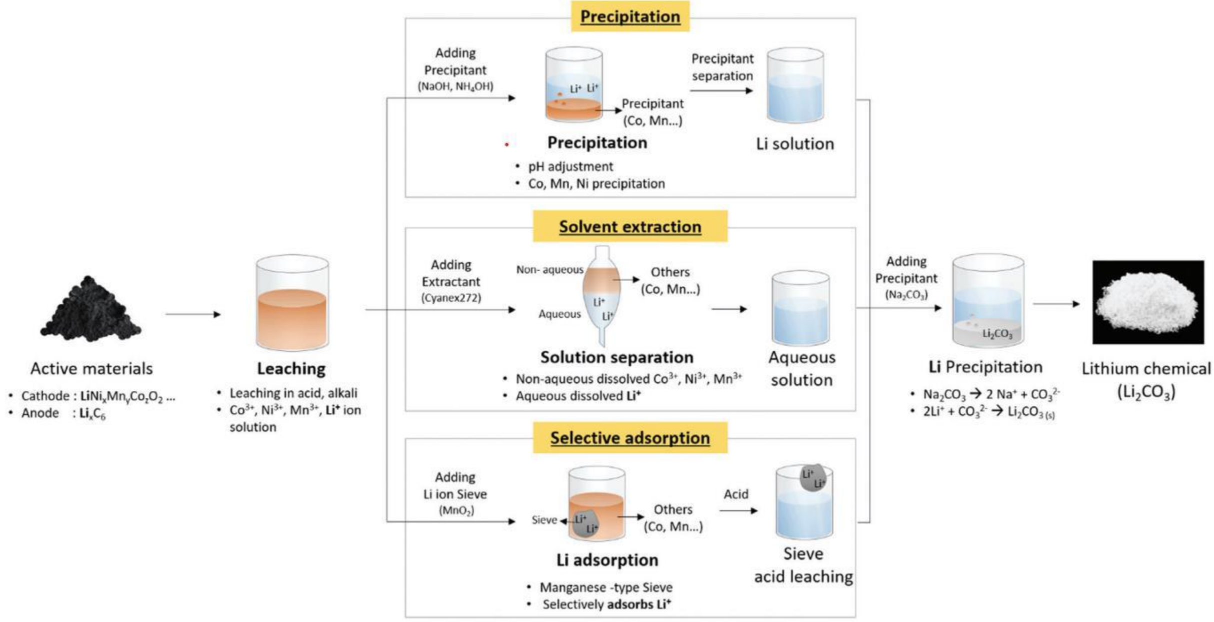


Figure 21 Overall schematic of lithium recycling from pre-treated waste LIB components by hydrometallurgy process [54].

Besides recycling, a second option for lithium-ion batteries is to reuse them, which means repurposing a second-hand battery for a different application. This method does not require expensive technologies such as pyrolyzing or leaching. For example, a used electric vehicle battery may no longer provide sufficient energy for the car, but it could still be useful as a stationary backup power source. Reusing is also more sustainable than recycling because the latter involves not only costly, but also environmentally harmful procedures. However, there are always downsides to any solution. The decreasing costs of materials used in new LIBs discourage producers and users from considering reuse. Additionally, the various designs, shapes, and chemistries of LIBs make automated disassembly and reassembly expensive and a unified procedure for facilities impossible. Nevertheless, whenever possible, reusing a lithium-ion battery, even with reduced efficiency, can be a cheaper and definitely a greener solution [54].

To conclude, reusing and recycling lithium-ion batteries could have significant economic and environmental benefits for the energy storage market. Discarding an electronic device that still has 80% of its initial capacity is unacceptable in a time when climate change and greenhouse gases are major concerns. Instead of being thrown away, a LIB could be reused in applications that require less energy before being discharged and recycled to recover useful metals [54].

3.10 Future Perspectives

3.10.1 Increasing the Cell Voltage

There is a significant amount of interest in increasing the operating voltage, storage capacity, or both lithium-ion batteries' energy densities. Since the currently used voltage in the anode is nearly identical to that of Li/Li^+, the sole approach to enhancing the cell voltage is to elevate the operating voltage of the cathode. Layered, spinel, and olivine are cathode structures that provide compositions with higher operating voltages than Li/Li^+. However, the cathode surface becomes unstable when in touch with the organic solvents of the electrolyte (EC, DEC, DMC). Even though the cathode-electrolyte interface is now unstable beyond 4.3 V because the cathode redox energy is lower than the electrolyte's highest occupied molecular orbital (HOMO), it might be possible to avoid this instability by generating an optimal SEI on the cathode surface and raising it above the electrolyte's HOMO (**Figure 22**), similar to what is currently accomplished with the graphite anode in commercial cells. The graphite anode has been improved through years of persistent effort, but there haven't been many attempts to stabilize the cathode SEI. In fact, the electrolyte compositions and additives now used in commercial cells are primarily designed to enable the operation of the graphite anode. The difficulty is that any attempts to make the cathode-electrolyte interface operational at higher voltages by altering the composition of the electrolyte or adding additives should be compatible with the graphite anode. In other words, the methods shouldn't damage the stability of the graphite-electrolyte interface or make it much more unstable than it already is [55].

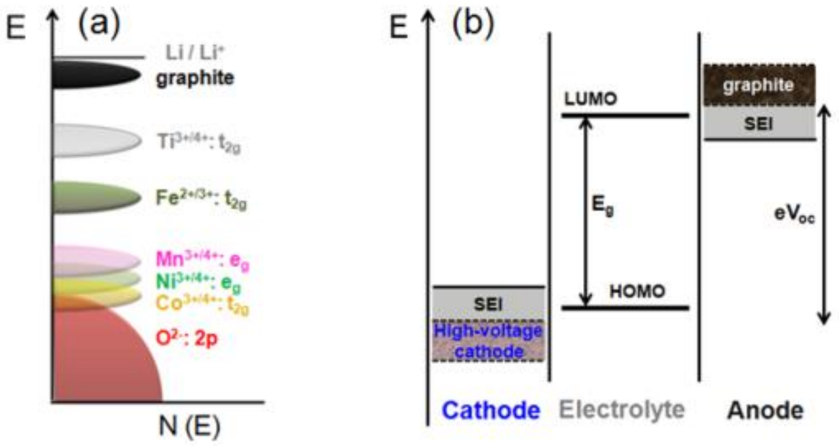


Figure 22 (a) Positions of the various redox couples relative to the top of the oxygen:2p band and (b) schematic energy levels of an anode, cathode, and electrolyte in an open circuit [55].

In order to raise LIB’s voltage, a thorough research must be conducted for new electrolytes that can operate well with both the anode and cathode interfaces. Developing organic solvents that contain appropriate lithium salts is crucial in achieving a wider electrochemical stability range and sustaining a higher operating voltage. However, obstacles such as mechanical stability, cost-effectiveness, large-scale production, and significant charge-transfer resistance at the solid-solid interface between the electrolyte and electrode still need to be addressed [55].

3.10.2 Increasing the Charge-Storage Capacity

Many efforts are being made to boost the charge-storage capabilities of both the anode and cathode because there is currently no viable way to raise the cathode working voltage. In recent years, a lot of interest has been focused on anodes and cathodes that use lithium in a conversion process rather than an insertion reaction, since the capacity of those would not be limited by the amount of crystallographic site available either for insertion or extraction [56].

Si, Sn, Sb, Ge, P, and other materials are examples of conversion-reaction anodes that have substantially higher capacities than graphite. The significant volume changes that occur during the charge-discharge process, particle pulverization, continuous SEI development, and the consequent trapping of the cathode’s active lithium in the SEI are the main difficulties with conversion-reaction anodes. Several methods have been attempted, including the decrease of the particle dimensions to the nanoscale or intentionally incorporating gaps in the active material’s design, but none of these have yet proven to be commercially feasible [57]. The methods mentioned above significantly boost SEI production while lowering volumetric energy density. Particle milling brought on by volume fluctuations causes the charge-discharge process to continuously produce new surfaces, which aggravates the growth of SEI [56].

Sulphur and oxygen are examples of conversion-reaction cathodes, which have substantially higher capacities than layered, spinel, and olivine ones. The oxygen-based cathodes are vulnerable to blockage by insoluble compounds, catalytic decomposition of electrolytes, moisture from the air, and poor cycle life, which makes it highly challenging, for them to be used in practical applications. The difficulties associated with sulphur-based cathodes are significantly less than those associated with oxygen-based cathodes, and significant advancements have been made recently. Enhancing the active material quantity and loading, preventing the migration of polysulfides between the anode and cathode, and reducing the amount of electrolyte were among the breakthroughs made [56].

3.11 Conclusions

Although the crystallographic sites of current insertion-reaction cathodes restrict their capacity, they appear to be the most promising technology of the near future, as conversion-reaction cathodes, despite their higher capacities, continue to face challenges in achieving practical viability [58]. Recently, there has been renewed interest in using solid electrolytes instead of liquid ones and using lithium metal as an anode because of their safety and higher operating voltages and storage capacities. However, those are still research results and not convincingly possible yet. Since the use of substitute electrodes encounters multiple challenges, a potential short-term remedy is to concentrate on utilizing stable SEI-forming liquid electrolytes and high-nickel layered oxide cathodes. Lastly, cell design with thicker electrodes and less inactive material, and advanced approaches to the BMS could produce safe, long-lasting, and cost-effective Lithium-ion batteries [57].

CHAPTER 4

DEGRADATION OF LITHIUM-ION BATTERIES

4.1 Introduction

The main scientific issue in battery research is battery degradation. The battery's degradation reduces the system's capacity for energy storage and power production as well as its performance, whether the system is an EV or a power grid. Despite all the positive features of lithium-ion batteries, such as high energy density, high power density, and low self-discharge rate, LIB's battery life still cannot meet the consumer's expectations. Therefore, to improve battery design and management, scientists need to take into consideration the battery's ageing mechanism as well as the effect of its degradation.

From the battery design viewpoint, to ensure high energy and power density, manufacturers should take into consideration almost every battery component. Starting from the cell level including the anode, cathode, electrolyte components, particle size, etc, and reaching to the mechanical, electrical, and thermal factors' influence which constitute the battery's operating system. Understanding how batteries age and degrade is essential for an effective battery management system, as it enables estimation of battery health based on its history, optimization of current working conditions, and prediction of future performance [59].

In general, battery degradation could be separated into different levels, including degradation mechanisms or side reactions, influence factors, degradation modes and external effects. Within the battery, many different chemical side reactions take place which can also be called degradation mechanisms. These reactions could either act separately or combined leading to different degradation modes. The two most important degradation modes are loss of active material (LAM) and loss of lithium inventory (LLI), which was explained simply by a tank of water. LAM describes any modification of the tank's body and LLI the loss of water. All mechanisms which will eventually lead to these modes are caused by some influence factors, either intrinsic or extrinsic. Intrinsic factors are related to the battery's design and manufacturing, while extrinsic ones are those related to working conditions and these are of interest to the consumers [60].

Within this chapter, different mechanisms will be explained and analysed in detail in order to primarily understand them and then avoid them as much as possible. Mechanisms that will be analysed are the formation of SEI and CEI, lithium plating, particle fracture and electrode structure destruction. Furthermore, there will be coverage of the most important influence factors such as temperature increase or decrease, state of charge (SOC) and charge-discharge rate. To conclude this chapter, there will be a discussion about the final effects which are mainly capacity fade or power fade and hopefully some helpful solutions to prevent them.

4.2 Introduction to Solid Electrolyte interphase (SEI)

An essential electrochemical junction where reactions involving both electrons and lithium ions take place is the electrolyte/anode interface. Electrolytes must work outside of their thermodynamic stability since the electrodes' design requires high potentials in order to produce high energy densities. A solid electrolyte interphase (SEI) is a film developed mainly on the negative electrode, initially a product of decomposition of small amounts of electrolyte trying to reach its kinetic stability. Its initial formation happens when the lithiated graphite anode encounters the organic compounds of the liquid electrolyte. This electrochemical reaction between the anode and the electrolyte takes place on the first few cycles of the battery, leading to a thin film development on the anode's surface which is a lithium-ion conductor and electrons insulator. SEI consists of several components, for instance: lithium fluoride (LiF), lithium carbonate (Li_2CO_3), lithium ethylene dicarbonate (LEDC), and lithium oxide (Li_2O) [61].

The formation of the SEI consumes lithium irreversibly, diminishing the lithium inventory available for cycling. Despite the initial volume decrease of lithium in the graphite anode and the fast degradation of the battery's capacity approximately by 10%, this formation is essential for the prevention of any further reactions between electrolyte and a graphite anode. However, further growth of SEI's thickness could be bothersome as it is evolving into a harmful degradation mechanism than just a protective layer [61].

First, it is crucial to ascertain both the anode and the electrolyte composition. Electrolytes on commercial batteries are composed of lithium hexafluorophosphate ($LiPF_6$) in a mixture of organic carbonate solvents including ethylene carbonate (EC), while the anode is composed of lithiated graphite. The initial SEI is a product of the reduction reaction of the electrolyte during the first 4-6 cycles where electrolyte decomposition products are deposited on the graphite surface during the potential decrease. While SEI's exact composition is characterized as complicated, several spectroscopies such as (internally reflected beam- attenuated total reflection) IR-ATR and XPS conclude with similar results that the primary organic compound is lithium ethylene di-carbonate (LEDC) and the main fluorine-containing species is lithium fluoride (LiF) as it is shown in **Figure 23**. These results are also consistent with Auerbach's and Xu’s mechanisms concluding in a 50 nm thick film composed predominantly of LEDC and LiF, which can serve as a passivating layer, preventing additional electrolyte decomposition and graphite exfoliation [40]. Even though SEI is formed on the anode composed of reduction products of the electrolyte, more components can be detected due to solvent oxidation reactions on the cathode. This oxidation generates CO_2, which passes through the electrolyte and is reduced on the anode to form lithium carbonate (Li_2CO_3) [61].

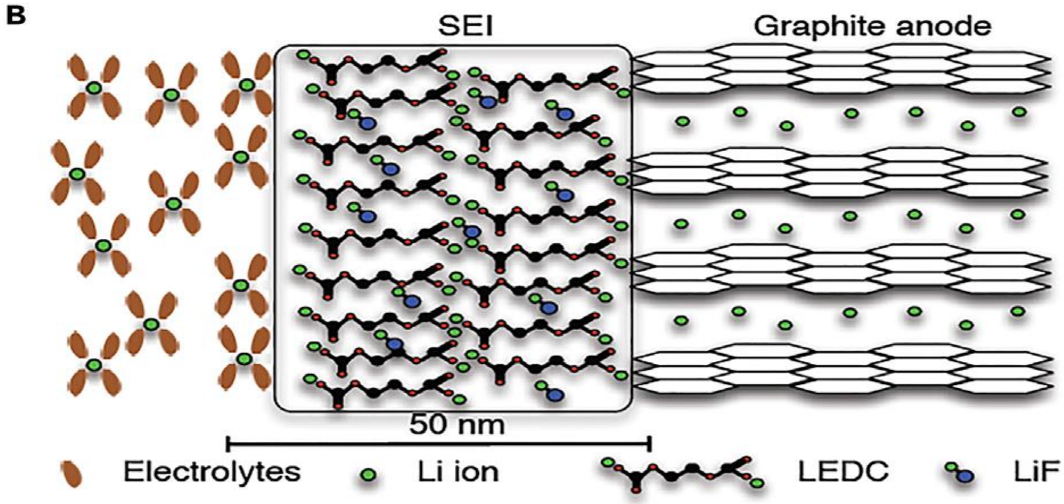


Figure 23 Initial SEI composition [61].

This previously referred to as passivating layer is though unstable and evolves over the calendar life of battery cycling. Due to this evolution, which is mainly a composition change, the SEI becomes a hazardous layer and slowly an unrelenting consumer of the anode material. Composition changes are the growth of inorganic species such as LiF and Li_2CO_3 and a decrease of organic species such as lithium alkyl carbonates such as LEDC. In-depth investigations of the thermal, hydrolytic, and acid-mediated gases have been conducted on each of the components, to have a better image of the SEI’s evolution. Equations of those reactions can be observed in **Figure 24**. Hydrolytic examinations (**Figure 24A**) showed that Li_2CO_3 has better hydrolytic stability and is characterized as a more stable component than LEDC. Acid-mediated examinations in the presence of $LiPF_6$ (**Figure 24B,24C**) have been conducted since commercial lithium-ion batteries are produced under carefully anhydrous conditions. The products of these reactions indicate that the quantity of insoluble SEI components is decreasing, transforming the SEI into a more porous film. LEDC has also been examined for its thermal decomposition (**Figure 24D**), which during the rising temperature evolves and produces different components. The most important of these are lithium carboxylates, which have been observed previously in SEI, but their presence could not be explained.

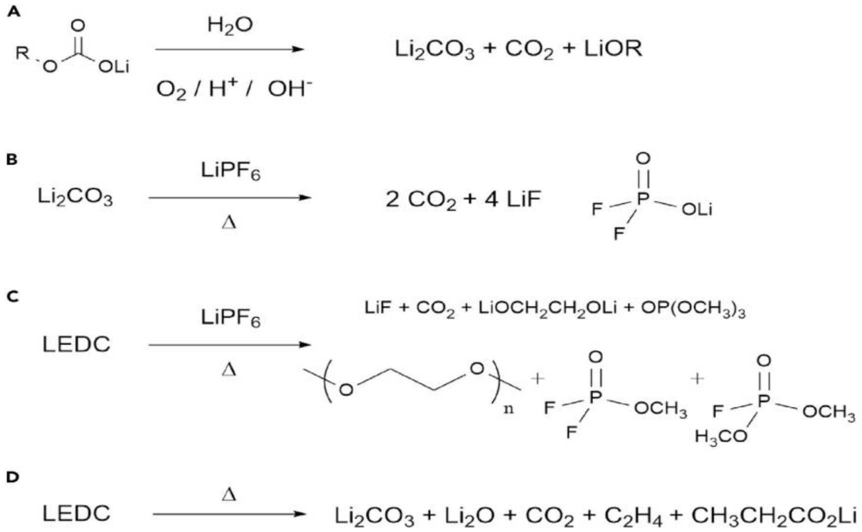


Figure 24 Primary Decomposition Reactions of the SEI initial components [61].

4.2.1 Solid Electrolyte interphase (SEI) in a nutshell

Capacity, cycling stability, and safety of electrochemical are some characteristics which are impacted by the passivated interface between the electrodes and electrolyte. Nevertheless, morphology, phase, and chemical composition are still not well defined, especially at the nanoscale. So, because SEI is a very thin layer with scarcely discernible boundaries with the electrolyte, defining it is tough. Since it is hard to determine its thickness directly on the carbon surface, precise peeling off creates a barrier for experimental analysis. Also, because the chemical species of the solvent and SEI are identical, it is challenging to distinguish and separate each component. And since sample preparation made this more difficult, it is almost impossible for the SEI to maintain its original composition and that some of its core elements won't suffer degradation and modification. Additionally, the SEI's components are extremely sensitive to humidity and air contaminants. It is also worth noting that additional factors, such as additives, concentration, current rate, state of charge, temperature, and voltage, have an influence on SEI formation [62].

4.2.2 Structural Challenges

The creation of battery electrolytes has up to this point been mostly guided by empirical observations, which led to the identification of ethylene carbonate (EC) as a potential electrolyte that may actively passivate graphite. The development of next-generation battery chemistry and the optimization of LIBs are being hampered by the lack of a correlation between the properties of electrode and electrolyte materials. The constantly changing interphase microstructure results in the SEI evolving across multiple length and time scales, making it challenging for current modelling efforts to rely solely on proposed SEI structures and mechanisms. Current computational technique is restricted to orderly and frequently periodic systems, thus falling short of accounting for the diverse phenomena and impacts of multi-component polydisperse nature of the SEI. As a result, a comprehensive model that incorporates heterogeneities and functional disorder has not yet been developed [62].

The study of the SEI is constrained by the absence of experimental techniques capable of providing sufficient image quality or magnification to understand its structure. To safeguard the layer's durability, it is necessary to utilize non-destructive and in situ techniques that prevent its exposure to environmental conditions capable of causing damage. Two frequently employed in situ microscopies, atomic force microscopy (AFM) and transmission electron microscopy (TEM), offer limited molecular information, while X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques are incapable of achieving the spatial resolution required to establish a correlation between chemical observations and the electrochemical interface. XRD, which analyses the whole electrode, is unable to distinguish specific interactions taking place on the electrode surface between electrolytes and particles. Despite the most analytical methods available, such as cryogenic TEM, they can only determine structural and chemical data connected to the SEI, and they are therefore incapable of providing insights into the growth dynamics of the layer in actual operational conditions. The results and conclusions obtained are likely to be merely qualitative, as the utilization of microscopic and spectroscopic methods is limited due to the normal working temperatures and pressures that exceed the battery's atmospheric range [63].

Batteries function in a closed environment, making it impossible for researchers to examine the electrolyte and electrode materials before opening the device. This makes analysis retrospective and vulnerable to the possibility of system modification due to changing operating conditions. These constraints in the research of battery interphases can be solved by interdisciplinary collaborations with combined advancements in theoretical methodologies, experimental capability, and enhanced characterisation techniques [63].

Last but not least, the creation of high energy density batteries using contemporary electrolytes necessitates the inclusion of a variety of additives, frequently up to 5% per volume or weight. The use of additives further increases the intricate nature of the reactions take place between the electrode and the electrolyte. According to considerable research, additives like vinylene carbonate (VC) or fluoroethylene carbonate (FEC) preferentially degrade on the anode to form an improved SEI, boosting LIBs' cycle life. Electrolyte additives generate SEI components with increased stability that prohibit the SEI layer from degrading, growing, and thickening. However, it is unknown how these additives function, how they influence the SEI, or how they function properly. Therefore, in order to comprehend the future lithium and post-lithium batteries, substantial study is needed to understand how electrolyte additives impact the SEI composition, shape, and final characteristics [63].

4.2.3 Key factors

The critical features that the SEI must possess have been identified. The layer must initially be chemically inert, meaning it can't react with or dissolve into the electrolyte. Additionally, the SEI has to be mechanically robust, preventing cracking or volume expansion during charge-discharge cycles. Secondly, the SEI must not interfere with the transport of Li-ions from the electrolyte to the electrode. Despite advancements made in incorporating carbon additives or coatings, such as in silicon composite anodes, the significant volume change still remains a primary concern for the design and development of alloy anodes. Since the SEI is a polydisperse material, a single component of the layer cannot meet the criteria outlined in this paper. It is critical to establish a structure-property connection for SEI kinds that takes into account dynamics, form and the chaos that results in the changing SEI structure [63].

A feasible approach for optimizing and customizing the desired chemistry and properties of the layered interphase is the rational creation of an artificial SEI. The artificial SEI can be improved using predictive computational methods, especially when paired with accurate data and evaluation of important electrode surface-coating technology. Utilizing techniques, such as atomic layer deposition and molecular layer deposition, thin isolating films with consistent atomic-scale thickness can be applied to electrode surfaces to cover them and adhere to their shape. However, a transition towards employing complementary approaches in three crucial domains computational modelling, machine learning models and advanced operando experiments will be indispensable to achieve a rational development of a stable SEI [63].

4.2.4 Conclusion

To conclude, the initial formulation of Solid Electrolyte interphase (SEI) consists of LiF and lithium ethylene dicarbonate (LEDC) which are reduction products of $LiPF_6$ and EC respectively. Nevertheless, the continuous decomposition reactions have as a result a more complicated formulation of soluble, insoluble, and gaseous compounds. Soluble electrolyte compounds force the insoluble ones to create an inner porous SEI layer which is also penetrable for the electrolyte to reach the surface of the anode and create further LEDC and LiF. These products will form the outer less porous SEI layer, which will later form further reduction and decomposition reactions leading to the continuous thickening of SEI composed always of an inorganic, porous inner layer and an organic, less porous outer one. Battery research will advance to new breakthroughs by artificial intelligence, and large-scale facility trials within a regulatory capture (**Figure 25**).

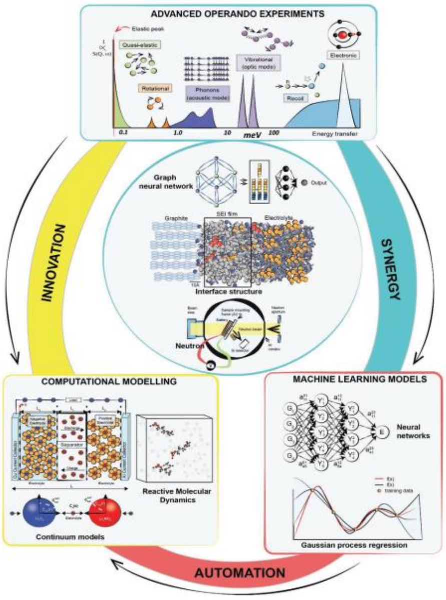


Figure 25 Overview of the cutting-edge cross-discipline characterisation methods that can produce complexity [63]

4.3 Cathode Electrolyte Interphase (CEI)

Cathode electrolyte interphase (CEI) is a coating just like SEI, but it is formed on the positive electrode. CEI, on the other hand, has been less thoroughly studied and its species are thought to be related to those of SEI. However, there are still disagreements among reports from various study organisations about its form, usefulness, and even its existence as a protective coating. These misunderstandings are most likely caused by a lack of both structural and chemical knowledge. The CEI's nanoscale morphology, complicated chemical composition, reactivity to air and moisture, and susceptibility to X-ray and electron beam radiation have made it challenging to characterize [64].

To guarantee perfect electrochemical performance, CEI should be an electronic insulator and a Li-ion conductor. Electrolyte decomposition, through redox reactions, on the cathode surface leads to the development of CEI. Different electrolytes tend to oxidize if the cathode's Fermi energy is lower than the electrolyte's HOMO, or highest occupied molecular orbital. On the contrary, when the anode's Fermi energy exceeds that of the lowest unoccupied molecular orbital (LUMO), electrolyte reduction takes place. When the applied voltage exceeds the electrochemical stability of the electrolyte, the CEI as well as the SEI will develop. Engineering the CEI's stability and thickness can reduce the cathode's consumption of Lithium-ions and stop further corrosion from occurring because of electrolyte reaction. The CEI is portrayed as a thick film consisting of a complicated mixture of many components in **Figure 26**, which shows the different interfaces in a Lithium-ion battery.

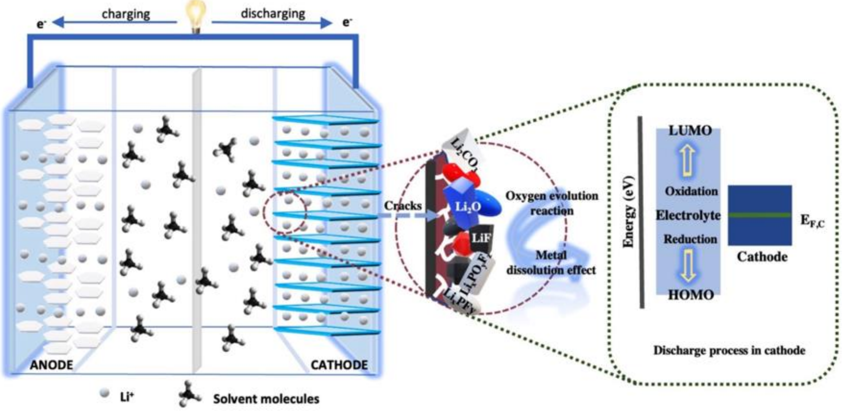


Figure 26 Schematic representation of the formation of the CEI in a typical LIB. The formation of the CEI is subjected to the chemical potential of the cathode materials and the nature of the electrolyte solvent, salt, and other additive species [64].

There have been numerous attempts to build an appropriate electrode-electrolyte interface system. However, stability of CEI needs significant work because the electrolyte and cathode are in close contact, which causes oxidative electrolyte degradation.

The active region on the cathode surface could be shielded from oxidation and subsequent corrosion of electrolyte by-products, and the transition metal could also be kept from dissolving, thanks to a uniform and thin CEI. During the hydrolysis of $LiPF_6$, hydrogen fluoride (HF) is produced. A stable CEI made of organic polymers could prevent $LiCO_3$ from reacting with HF and generating LiF, which with its high ionic impedance prevents Li^+ ions from diffusing through the electrolyte. Finally, the CEI layer is capable of reducing the voltage polarization by avoiding local overload on the surface and inhibiting electrolyte side reactions by limiting excessive electrolyte consumption. The performance of a LIB is heavily dependent on the chemical structure, composition, and stability of the CEI layer. Unfortunately, sometimes the CEI's membrane made mainly of Li_2CO_3, LiF, R-O-Li, and R-O-CO_2-Li, is frequently fragile, inconsistent, and thick. This unavoidably raises the overall impedance of LIBs and decreases cycle life [64].

One of the most value-for-money methods to generate a stable and accessible CEI passivation layer is to use a small number of additives in the electrolyte. The deterioration of the interface has been altered and reduced using additives in the electrolyte such as salt or solvents. Typical electrolyte additives usually serve as sacrifices since they have a greater HOMO energy than the electrolyte itself. For that reason, their decomposition happens before this of the electrolyte and most importantly their by-products are able to control the composition of the CEI without affecting cathodes and electrolyte's materials. Thus, a consistent and stable CEI with a more durable interface structure on the cathode can be produced by adding a relatively small proportion of electrolyte additive, which would significantly improve the LIB's electrochemical performance [65].

There are different functions of electrolyte additives depending on the system they are used for. Here are some of the most important ones.

- Encouragement of the formation of the electrode-electrolyte layer (EEI), acting as a passivation membrane between the cathode and the electrolyte.
- Protection of LIB's cathode material from overcharging
- Prevention of electrolyte's decomposition and eventually decrease of electrolyte's harmful by-products.
- Increase the LIB's safety by improving the electrolyte's thermal stability and thus reducing its flammability.
- Decrease of transition metal dissolution in the cathode.
- Improvement of electrolyte's physical properties (conductivity and viscosity).

Concluding, each electrolyte additive with distinct characteristic components frequently has diverse functions. Carbonate-based additives improve the CEI's stability since they add metal fluoride. Borate additives, due to their electron deficiency, can stop PF6 from decomposing in the electrolyte and produce PF_5, LiF, and HF. Finally, a CEI film consisting of sulphur due to the respective additives, could result in a decreased cathode/electrolyte interface impedance [65].

4.4 Lithium Plating

Battery ageing, such as the formation of an SEI film on the anode side of LIBs, is frequently attributed to lithium plating. Lithium plating is typically identified as dendrites or mosses. In typical conditions, Li-ions move between the cathode and anode and rapidly insert themselves into the anode's active material, which impedes anode lithium plating. Due to the chemical properties of graphite, the process of lithium plating is thermodynamically favored, as its operational potential is very close to that of metallic lithium deposition. The rate at which lithium plating occurs is determined by a variety of factors, including the battery's charging conditions, such as high charging rates, overcharging and low temperatures, as well as design characteristics for example a low anode/cathode ratio and manufacturing flaws. These environments lead to increased polarization in the anode, which promotes the occurrence of lithium plating [66].

The deposited lithium metal not only absorbs electrolyte's active lithium, but also results in a loss of electrical contact between the deposited lithium and the anode, accelerating this way capacity fading. Furthermore, this reaction creates a redundant interfacial coating that enhances anode polarization and as a result, promotes further anode Lithium plating.

This section will describe the electrochemical reactions related to anode lithium plating and how it adversely affects the electrochemical performance of LIBs. During charging, the total current splits through two separate processes: intercalation current, which involves the insertion of lithium into the active materials and anode lithium plating current. These processes occur simultaneously and can be represented as follows:

$$xLi^+ + Li_\delta C_6 + xe^- \rightarrow Li_{\delta+x}C^6 \tag{11}$$

$$yLi^+ + ye^- \rightarrow yLi \tag{12}$$

As charging continues, the current for Lithium intercalation decreases rapidly because there are fewer vacant sites available for Lithium intercalation and the solid-state diffusion in graphite is restricted. At the same time, the current for lithium plating rises and the transport rate of Li-ions from the electrolyte surpasses that of lithium intercalation, resulting in a greater buildup of surface Li-ions and reducing the anode's potential (**Figure 27**).

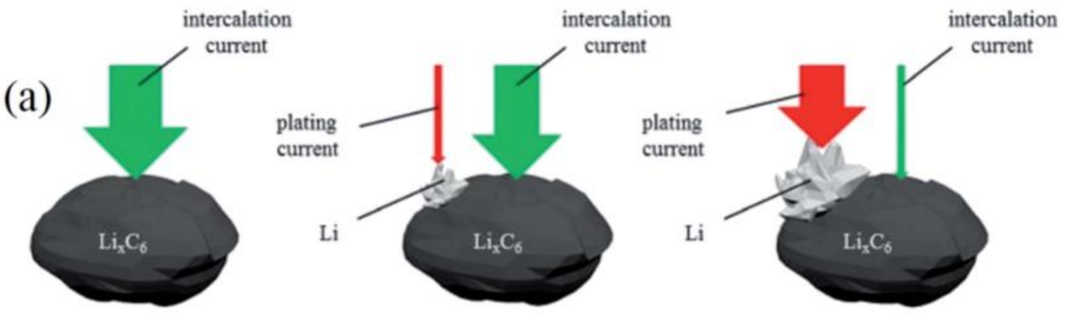


Figure 27 Currents for intercalation and plating while charging to higher SOCs [66].

4.4.1 How lithium plating occurs

Numerous investigations have been carried out to identify the reason and the manner of lithium plating, during typical charging but in fast charging too. However, due to its complexity, the processes of lithium plating have not been fully explained. Numerous prior studies have found that lithium plating occurs because of two key factors: (1) hazardous operating conditions and (2) cell defects (**Table 4**).

Table 4 Factors Causing Lithium Plating

Factors	Causes and conditions
Hazardous Operating Conditions	(a) Low temperatures (b) High Charging C-rates (c) High SOCs
Cell Defects	(a) Cell properties and poor design
Aging of the Cell	(a) Leading to cell unbalance (b) Kinetic degradation (Capacity fade, energy fade, CE decrease, energy efficiency fade and resistance increase

The following are the different types of hazardous conditions that may arise during fast charging: the primary challenge to quick charging is the adverse impact of low temperatures. A notable reduction in capacity of about 3.6% is observed when charging a 7.5 Ah cell with a 1 C-rate at 0 °C. The performance and power density of LIBs are typically impaired under low temperature conditions, particularly during charging, because of the next three key factors: 1) diminished ionic conductivity in the electrolyte, 2) limited solid-state diffusion of lithium ions through the electrode and 3) inferior charge-transfer rates [65]. The internal resistance of the cell rises at low temperatures as per the Arrhenius equation due to diminished ionic conductivity in the electrolyte. Nonetheless, the main problem with charging at low temperatures is not the reduced ionic conductivity. Poor diffusivity of Li-ions within the electrodes has been identified as a leading cause of lithium plating at low temperatures, resulting in the accumulation of lithium ions at the interface between carbon particles and electrolyte. Lithium plating happens when the maximal surface concentration of lithium ions in graphite particles is reached. The other main issue in low-temperature charging is the slow charge transfer kinetics. After the application of the current, a significant overpotential is generated, as a result, the polarization of the anode increases its potential fall below 0 V, resulting in lithium plating, rather than intercalating, the Li^+ accumulate ate anode interface (**Figure 28**). The anode's compound possible decrease is greater near the separator than it is elsewhere, indicating that the anode's lithium plating occurs there as well [66].

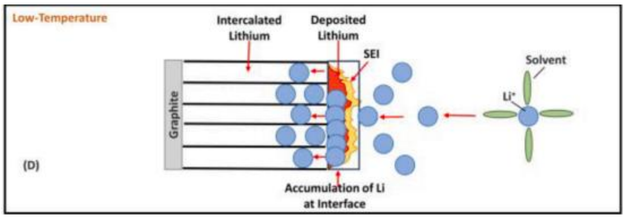


Figure 28 Due to the low diffusivities of lithium ions and the slow charge transfer kinetics in graphite at low temperatures, lithium plating occurs [66].

The deposition of lithium at low temperatures can be regulated by employing a pre-heating technique before the cell’s charge, or by charging at lower rates [66]. In a recent development, a team of scientists have created a cell design incorporating the nickel foils that have embedded within the cell. In less than 10 seconds, the interior heating element in these foils produces heat. Thanks to the absence of lithium plating, the structured cell can be charged to 80 percent state of charge (SOC) in just 15 minutes, even with high charging currents and in extremely low temperatures. It is worth noting that, the majority of current EVs include an efficient thermal management system that avoids excessive running temperatures. Furthermore, at low temperatures, grid energy is frequently utilized to warm the cells.

The following condition to be evaluated is the impact of high charging rates, as fast charging is growing more crucial in the realm of electric vehicles and other applications. High charging currents that are part of fast charging led to accelerated aging and exert a significant influence on battery performance and cycle life. When charging at high speed, the polarization of the battery increases due to diffusion and kinetic overpotentials, creating favourable conditions for lithium plating. During high charging-rate, Li-ions begin to accumulate on the anode surface, resulting in high Li-ions concentrations on the graphite surface. Lithium plating occurs when the concentration on the anode surface reaches its maximum (**Figure 29**).

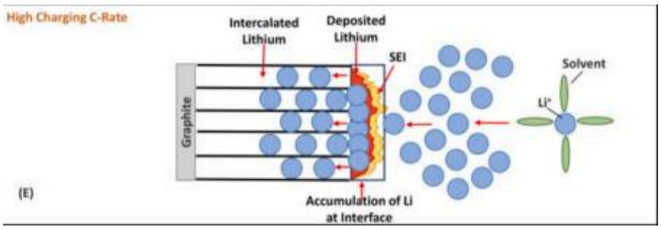


Figure 29 Due to the slow diffusion of the lithium solid at high charging rates, a significant amount of Li+ ions gather at the electrode interface and cause lithium plating [66].

One more hazardous condition to be discussed is the high SOC, which occurs when the LIB is already fully charged, but the current continues to flow into the battery. The risk that the amount of Li-ions on the anode surface will surpass the allowed highest threshold and become saturated increases as the SOC increases during the charging process. When the anode reaches its saturation point, it initiates precipitation of lithium on its surface. Scientists studied the consequences of high SOC on graphite/LCO 5 Ah pouch cells at different cut-off voltages between 4.2 V and 4.8 V [67]. Cells that have been charged above 4.5 V have exhibited capacity fading, electrolyte breakdown, volume expansion and lithium plating. Additionally, dendrite formations have been noticed in cells charged higher than 4.5 V. A micro-internal short circuit was caused by the dendrite penetrating the porous separator. In addition, at high SOCs, the degradation of the electrolyte also occurs on the cathode electrode site, indicating that side reactions are not limited to the anode electrode. Additionally, at high SOCs, the anode is not the only electrode that has side effects, since electrolyte degradation occurs on the anode too [65].

4.4.2 Manufacturing process

This section will be emphasized on the effects of the cell manufacturing process and cell characteristics on lithium plating. The local cell flaws may affect the lithium plating. As a result of internal mechanical stress building up while charging or aging, lithium plating may develop through separator deformation after insufficient closure, that could happen during production or usage of the cell [68]. Additionally, the activation energy barrier may be used to describe the kinetics at the material level. It was discovered that the charge-transfer process's most energy-intensive stage, desolation, uses 50 $kJmol^{-1}$ of energy, but the graphite/total electrolyte's activation energy barrier is between 60 and 70 $kJmol^{-1}$ [69]. Different research discovered that lithium intercalation occurs primarily at the edge plane rather than the basal plane of graphite, due to the different energy barriers for lithium dissolution. It is noteworthy that, during lithium plating, Li-ions have a tendency to accumulate in areas where lithium has already been deposited [66].

The final aspect of lithium plating that will be addressed is how to prevent it from occurring on the anode side. It is generally known that Li dendrite formation remains a significant barrier to the widespread use of Li-ion batteries. Based on the aforementioned anode lithium plating affecting variables and processes, extensive research has been conducted to avoid anode lithium plating, including altering the anode's interfacial characteristics and improving cell design and charge procedures.

4.4.3 Key factors

It is imperative to prioritize the evaluation of anode material properties. These materials indisputably impact both the electrochemical effectiveness and lithium plating of the anode, charge-transfer kinetics activation energy and the potential to modify the surface of anode materials to change solid electrolyte interphase resistance formation. As carbonaceous materials possess a high reversible capacity, low working potential, and low cost, they are frequently utilized as anode materials for LIBs. Hence, modifications to carbonaceous materials are being actively researched. These adjustments usually improve graphite's overall performance, for example, by increasing reversible capacity and rate capacity. The main modifications that could be done on the anode surface materials are (1) coating non-graphite carbon layer, (2) doping or coating with metals or metal oxides such as gold, copper, or tin (II) oxide, (3) surface decoration, and (4) nanostructured carbon [66].

Research has revealed that applying non-graphite carbon coatings can enhance the electrochemical performance of graphite. This improvement is reflected in its higher reversible capacity, cyclability, and its performance on low temperatures. Emphasizing the significance of strict control over the thickness and consistency of the carbon coating is crucial. A thinner carbon coating may not offer complete protection, while an excessively thick coating may hinder Li-ions diffusion and impede intercalation capacity by acting as a barrier. The ideal range of carbon coating levels is determined by the carbon sources and substrate materials utilized and usually falls between 5 to 15 mass percentage.

At lower temperatures, adding metal coatings and dopants, particularly Cu and Sn, can increase the kinetics and intercalation capability of graphite electrodes. A Sn-coated oxidized graphite showed superior rate performance, likely due to Sn's involvement in creating a solid electrolyte interphase layer that enhances electronic conductivity and improve the charge transfer process. Unfortunately, once the metal coating was applied, it was discovered that the graphite's coulombic efficiency decreased significantly during the first cycle. Furthermore, to minimize the negative consequences, the amount of metal should be optimized, because of metal agglomeration and loss in a specific capacity [66].

Rapid lithiation - delithiation of graphite at low-temperature of high-rate cycling is limited by lithium solid state diffusion in the bulk graphite. Two technologies can help to achieve lithium solid diffusion: (1) increase of graphite interlayer spacing and (2) decrease of the diffusion distance. Various methods have been suggested to achieve the first technique, including mild expansion and edge-exfoliation modification of graphite. Although, because of the lower graphitization degree and increased number of flaws, the reversible capacity of expanded graphite is generally lower than that of pure one. Moreover, deteriorating imbalances cause a reduction in electrical conductivity, which hinders intercalation and deintercalation. The usage of nanostructured carbonaceous materials significantly decreases the distance of lithium diffusion. Furthermore, the lithium solid-state diffusion can be significantly improved by a nanostructured graphene design with increased interlayers. However, a large surface has the consequence of a substantial interface between electrode and electrolyte and subsequently in more pronounced parasitic reactions and reduced coulombic efficiency, making these nanostructured materials better suited as conductive additives rather than the primary active material. Using them in this manner could aid in reducing anode lithium plating to some degree [66].

The kind of carbon material that will be used also influences anode lithium plating behaviour. Both soft and hard carbons outperform graphite in terms of rate capacity and performance at low temperatures. As a result, they are less susceptible to lithium plating on the anode. Carbonaceous materials have differences in their electrochemical behaviours due to the varying structures. Due to its excellent crystallinity organized layered structure, graphite is suitable for Li insertion through its interlayers. The structures of soft and hard carbons, on the other hand, are disordered and feature a variety of Li insertion sites, which leads to a shorter diffusion distance of Lithium ions. Unfortunately, because of their high irreversible capacities, soft and hard carbons are not often used in industrial LIBs.

4.4.4 Operating principles

As has been mentioned before another method to avoid lithium plating is by optimizing the design of the cell. By lowering polarisation, cell design parameters may be optimized to increase anode performance. According to studies, anode porosity can be increased while anode thickness is decreased to efficiently prevent anode lithium plating, while enhancing residual capacity and anode thickness can help delay or even prevent the occurrence of anode lithium plating. Conversely, excessively increasing anode capacity would cause capacity degradation and higher costs, which must be considered when designing functional LIBs. Additionally, the current distribution, particularly for large format cells, is influenced by the amount and positioning of the existing collecting tabs. In order to enhance the evenness of current density distribution and minimize the danger of localized anode lithium plating in large format LIBs, it is recommended to steer clear of having positive tabs situated at the same ends with negative ones, as this results in the rapid generation of non-uniform current distribution. Consequently, increasing the number of tabs has been suggested as a solution [66].

To achieve optimal performance and prevent anode lithium plating at low temperatures, it is important to follow recommended charging protocols. One such protocol involves avoiding high charging rate at a high SOC or overcharging, both of which can contribute to anode lithium plating. In addition, the constant current voltage charging method is more susceptible to anode lithium plating at high rates and low temperatures, which results in rapid capacity degradation. To address this issue alternative charging methods have been proposed, such as high charging rate up to the anode potential of 0 V, an then low charging rate until the charge voltage reaches its endpoint. According to a theory that proposes lithium solid diffusion as the major limiting factor for charging rate, selecting the appropriate parameters for the current waveform can expand the capacity range available for lithium ions at the interface, resulting in better performance at low temperatures. Low temperature charging can cause intense interactions between electrochemical and thermal reactions, leading to damage from anode lithium plating. Therefore, it is necessary to develop a thermal strategy to minimize or mitigate the damage. One proposed approach is pulse charging at lower SOCs, which will rise the cells' temperature. Additionally, to mitigate the risk of anode lithium plating during low temperature cell operation, preheating measure have been suggested. Preheating methods include the usage of electric resistance heaters as external jacket heating or heat pumps for airflow heating. These methods aim to raise the cell's temperature to a level where the risk of anode lithium plating is reduced before starting its operation [66].

The propagation of anode lithium plating is highly dependent on the operating conditions and cell design, including temperature and charge rate. During high charging rate at ambient temperature, insufficient solid phase diffusion of Li-ions is the primary cause of anode lithium plating. Moreover, the interfacial reaction is also impeded by a decrease in temperature. The underlying cause of anode lithium plating at low temperatures is yet a subject of debate, with some suggesting slow charge transfer kinetics, while others propose limited diffusion of lithium ions in graphite as the primary factor. Currently, to prevent anode lithium plating, coating and doping procedures are being utilized to improve the electrolyte composition and modify the graphite surface structure. Limiting the occurrence of anode lithium plating can be achieved through appropriate operating conditions and charging methods. Nevertheless, the inhibition of anode lithium plating has not been totally realized because of the intricate nature of the process [66].

4.5 Electrode

The battery’s performance may be negatively impacted or result in cell failure due to alterations in the electrode configuration, which can happen on both the anode and cathode aspects of the battery. When electrical or mechanical contact is lost within the anode, the internal resistance of the cell rises, which is a source of degradation. The anode’s active materials experience a change in volume that inevitably leads to contact loss and consequently, mechanical failure of the anode structure. Contact loss may happen in four ways: 1) between carbon particles, 2) between carbon and current collector, 3) between carbon and binder and 4) between current collector and binder [70]. The porosity of the electrode plays a crucial role in the effectiveness of the anode as it permits electrolytes to penetrate the anode’s bulk. However, the alternation in volume of the active material has an adverse effect on the electrode’s porosity [2].

As previously stated, degradation mechanisms can have both chemical and mechanical causes. Regarding mechanical disruption, the process of lithium intercalation can result in either an expansion or contraction in volume, generating mechanical stresses and strains on the active material particles. Consequently, the electrode structure and the mechanical properties of the other battery components are in danger. Additionally, during the lithiation process, certain cathode oxides may undergo phase alterations, causing crystal lattice distortion and additional mechanical strains [2].

4.6 Separator

A thin membrane positioned between the positive and negative electrode, serving as a barrier which isolates the cathode and anode. However, the separator also permits the diffusion of lithium ions for charging and discharging. When choosing a separator, these are several crucial factors to consider, including: 1) providing good electronic isolation, 2) minimizing resistance during ion transport and having a high capacity for electrolyte absorption and retention, 3) reducing air permeability to maintain low electrical resistance and high porosity, 4) possessing sufficient physical strength and dimensional and mechanical stability, 5) ensuring its thickness and tortuosity consistency, 6) being chemically stable and resistant to deterioration brought on by electrode reactants, electrolytes, and impurities, 7) demonstrating thermal stability and 8) having a high capability of preventing soluble species or particles from migrating between the two electrodes. In non-aqueous Li-ion batteries, microporous polyolefins are the most employed separators. These separators can be formed as a single layer of polypropylene (PP), polyethylene (PE), or as laminates consisting of both [2].

Degradation of the separator can cause power fading and eventual cell failure. Lithium dendrite formation due to separator pores, electrolyte corrosion and blockages in the separator from frequent cycling or high temperatures are among the primary reasons for separator deterioration. Additionally, the structural integrity of the separator may deteriorate due to an increased number of cycles or elevated temperatures. Exposure to high temperatures ranging from 130 ℃ to 150 ℃ can cause separator films to soften and their pores to close, leading to a cessation of the charge/discharge process by obstructing ion movement between the electrodes. Although separator materials are electrically neutral and do not affect energy storage or electrical output, their physical properties can significantly impact the safety and performance of the cell. To achieve optimum performance in Li-ion batteries, separators should have a homogeneous pore structure, minimal shrinking, and a low amount of resistance. Those with high resistance not only function poorly at high discharge rates but also prolong the charging time of the battery. Separators also exhibit minimal shrinking, which is especially important for higher capacity batteries. High temperatures should be avoided because they can induce separator shrinkage, excessive cell resistance and finally poor cycling [2].

Oxidizing cathode and reducing anode present harsh conditions on each side of the Li-ion cell’s separator. Therefore, their design should maintain their durability during prolonged periods of high temperature cycling. Reduced storage capacity at elevated temperatures and unstable long-term cycle performance can arise from poor oxidation resistance [2].

A method to increase the cell’s capacity is by changing the structure of the separator, or in simple words reducing the separator thickness. As thin the separator is the lower the resistance they have. Unfortunately, this approach often has a disadvantage in that thinner separators might contain less electrolyte, resulting in poor mechanical strength and cell failures. Cell performance at low temperatures can also be enhanced by separators with lower resistance. Given that the electrolyte has a high resistance at decreased temperatures, a tiny impact from the separator may help the cell maintain a low overall resistance.

4.7 Current collector

The role of the current collector is to distribute current evenly to the active materials in the battery, provide the electrode's active materials with structural assistance, and make mechanical contact with the internal leads that transmit current into the battery. Typically, thin foils made of aluminium or copper are used as current collectors for the positive and negative electrodes in Lithium-Ion batteries. However, these materials are susceptible to environmental degradation and have been shown to be vulnerable.

Copper's relatively stable behaviour in the anodic potential of LIBs, made it a suitable current collector for the anode. The degradation of current collectors is influenced by three primary factors: over-discharging, interactions with the battery electrolyte, and the microstructure of the metal [71].

The copper foil current collector of the anode is susceptible to damage from over-discharging. Over-discharging should not occur under typical Lithium-Ion battery operation. However, in applications such as electric vehicles, battery cells are often linked in series to produce the required high levels of power and energy. This arrangement can create a significant variation in cell capacity, leading to a wider capacity range. Due to this configuration, the battery's overall capacity is only as large as the cell with the lowest one. Furthermore, it indicates that during battery operation, the electrodes of each cell will encounter different voltage levels, which may lead to some undergoing overcharging or discharging. Overcharging or discharging can also occur when a Lithium-Ion battery is not functioning under normal circumstances. The anode and cathode materials used determine the normal operation range of a Lithium-Ion battery, which is typically between 2.5 to 4.2 V. Consequently, the copper anode's potential ranges from 0 and 1.5 V. Copper has to be cathodically secured and undissolved at these potentials. **Figure 30** displays the anode's, cathode's, and cell's potential during (a) standard operation and (b) 20% over-discharge of a lithium-ion phosphate ($LiFePO_4$) versus a graphite cell. During standard operation, the anode potential ranges from 0.2-0.9 V. However, if the anode is over-discharged, the potential sharply rises to over 4 V, which significantly increases the likelihood of copper oxidation/dissolution. According to thermodynamic theory, copper dissolves only at potentials higher than 3.5 V. Once such potentials are achieved and copper dissolves, it initiates a sequence of electrical, chemical, and electrochemical reactions throughout the cell [71].

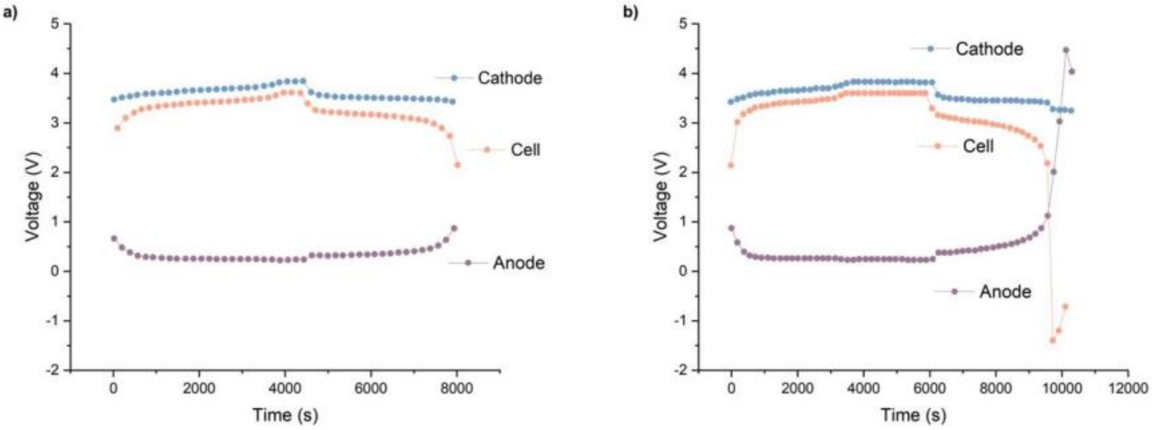


Figure 30 Voltage versus time graph (a) a standard charge/discharge cycle and (b) a charge/ over-discharge cycle of a three-electrode cell [71].

Copper degradation has been detected immediately following conteact with the $LiPF_6$-based electrolyte. The extent of this dissolution was discovered to be affected by the electrolyte's condition and composition. The existence of hydrofluoric oxide (it is being formed because of the LIB cells’ dry-environment assembly) in the electrolyte can result to copper corrosion. After immersion in a $LiPF_6$-based electrolyte, copper current collectors can develop pitting and even microcracks. This pitting is related to water impurities, copper oxide is produced in the presence of small quantities of water. Furthermore, in the presence of water, the $LiPF_6$ salt decomposes to generate HF. A substantial pH drop, and a significant copper oxide dissolution are the outcome of this HF separation [71].

Current collectors’ behaviour to corrosion is also affected by the microstructure of copper foil. When heated over 200 ^oC, the current collectors’ quantities of Cu_3O_4 and CuO rose significantly, as did the surface roughness. On the surface, these copper oxides created microscopic needle-like structures. When the heat-treated Cu films were cycled against lithium, non-negligible capacities were discovered. This increased capacity is a result of the electrochemical interactions between heat-generated copper oxides and lithium ions.

Aluminum is the main material of the cathode’s current collector in LIBs because of its low cost and high electrical conductivity. Moreover, it forms passive layers that offer excellent resistance to corrosion under cathodic conditions. Despite its favourable characteristics in Lithium-Ion batteries, aluminum is not immune to corrosion. Corrosion of aluminum may lead to significant cell degradation, loss of capacity, and complicated cell recycling and reuse. Redeposition of dissolved aluminum onto the active cathode material can occur, which restricts lithium intercalation and elevates electrical resistance. The electrochemical features of aluminum current collectors are influenced by various factors such as the potential application, electrolyte composition, foil coating, and microstructure [71].

Alloying may occur when the potential is approximately 0 Volts (V), making aluminium unsuitable for use as a current collector. Nevertheless, at higher voltages, aluminium is considerably more stable because a passive fluoride layer has formed, which aids in the preservation of the current collector's stability during Lithium-Ion battery cycling and prevents significant corrosion. When the battery is operating above 4 V, an oxide layer generated from the air can effectively prevent the corrosion of the aluminium metal. When potentials larger than 4 V are applied, the salt within the electrolyte decomposes and creates an AlF_3 layer, which contributes to the corrosion resistance of aluminum. At voltages over a threshold potential value, which was determined as 4.1 V, the AlF_3 component of the film forms and its thickness increases with applied potential [71].

As previously mentioned, $LiPF_6$ based electrolytes in Lithium-Ion batteries can lead to the formation of a protective layer on aluminium current collectors. The presence and composition of the electrolyte’s impurities can influence the passive layer's creation. The utilization of $LiPF_6$ rather than other electrolyte salts has been shown to increase the protection of aluminium by corrosion while operating. $LiPF_6$-based electrolytes produce fluoride-rich passivating layers on aluminium, improving its durability over time. However, despite the benefits, fluorinated electrolyte salts dissolve to create hydrofluoric acid (HF), which eventually contributes on LIB’s degradation, as previously noted for copper current collectors [71].

The content of electrolyte salts has also been reported to affect how resistant the aluminium current collector is to corrosion. After an experiment, it was proven that the salt concentration needed to generate a protective layer on the current collector was greater than 0.005 M. In certain circumstances, the presence of HF contaminants was proved to limit aluminum dissolution. The presence of HF is anticipated to increase the protection of the AlF_3 passive layer. Successful passivation is observed to offer enough corrosion protection in $LiPF_6$-based electrolytes.

The microstructure and surface characteristics of aluminum, including cracks, affect corrosion behavior in LIB systems, as experimentally proven. The aluminum foil production and cell assembly processes can both result in defects like mechanical cracks and native grooves, which can initiate pitting corrosion. The cathode coating's porosity promotes penetration through the electrolyte while staying attached to the electrode's active material.

Conversely, it creates isolated blocked sites and can lead to crevice corrosion, as depicted in **Figure 31**. As crevice corrosion increases, power fade and capacity fade seem to follow [71].

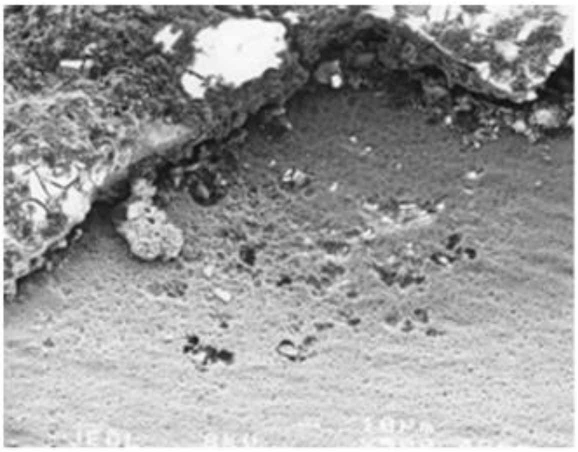


Figure 31 Crevice corrosion through a SEM image of an aluminum foil's surface, coated with a $LiFePO_4$ cathode and anodically polarized at 100 μA cm-2 for 36 h in 1 M $LiPF_6$ in a mixture of EC and DMC electrolyte [71].

4.8 Particle fracture

Particle fracture is considered as one of the most important degradation mechanisms of lithium-ion batteries, which takes place on both electrodes. During charging or discharging lithium ions travel through the electrolyte and enter either in the anode or the cathode. This penetration causes volume change and subsequently a significant stress on the electrode's particles. Mechanical stress due to volume change will eventually lead to particle fracture where the crack propagates through the particle until the separation of it into different pieces. One of the main reasons for battery capacity to fade is battery material fracture since the above-mentioned fracture has the ability to isolate active components of the battery, leaving them without contact with either electronic or ionic pathways with the result of losing their electrochemical activity.

Due to higher local current densities close to the electrolyte and separator there are larger stresses [59]. Fractures, especially near the electrolyte, create fresh surfaces of active materials vulnerable to continuous reactions resulting in SEI formation and growth. The battery's calendar life may be significantly reduced due to electrolyte consumption or decreased cycling efficiency caused by this process [72].

4.8.1 Mechanisms of particle fracture

The mechanism of particle fracture can occur through two different paths, intragranular and intergranular cracking. Most of the commercial batteries use as a cathode, polycrystalline materials composed of many randomly located monocrystalline grains, where between those there are grain boundaries. This formation can be seen in **Figure 32**, where monocrystalline grains are named as primary particles which form the micron-size secondary ones. Intragranular cracks spread into primary particle, while intergranular cracks propagate through the boundaries between them. Examples of both cracks are illustrated on **Figure 33**, where intergranular cracks are indicated by the yellow arrows to the left and to the right on a closer shot. On the anode side, crack's propagation depends on the morphology of each of the anode's material. When considering graphite anodes, an intergranular crack spreads along the boundaries of the particles. Intergranular cracks in alloying anodes, however, only appear in single-crystalline or amorphous materials, whereas polycrystalline alloying anodes can display both types.

There are differences between origins of each type of crack and each electrode affected. Stress brought on by concentration gradients and the coherency stress between two phases acting on particles results in cracks in intercalation cathodes. These cathodes undergo considerable strain during charging as a result of oxygen release and the phase change from a layered structure to a spinel phase. As vacancies of Li or O initially build up near the dislocation core during the formation of cracks, intergranular cracks in particular are linked to material effects. The edge of this core eventually transforms into an intergranular fracture due to stress caused by the change in the material's volume and composition. Intergranular cracks' origin though, is due to close particles facing different strain sizes and shear stresses. Both the single-phase solid solution stage and the phase-transformation process exhibit the observed phenomena. It involves an anisotropic change in the lattice dimensions, which causes strain mismatch in the fundamental particles of different orientations [72].

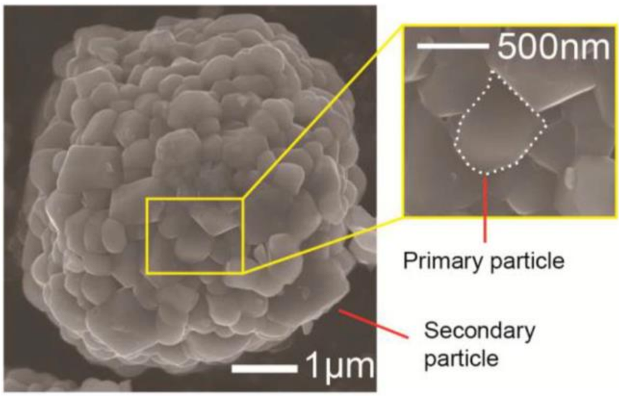


Figure 32 Micrograph of $LiNi_{0.8}$ $CO_{0.15}Al_{0.05}O_2$ primary and secondary particles [72].

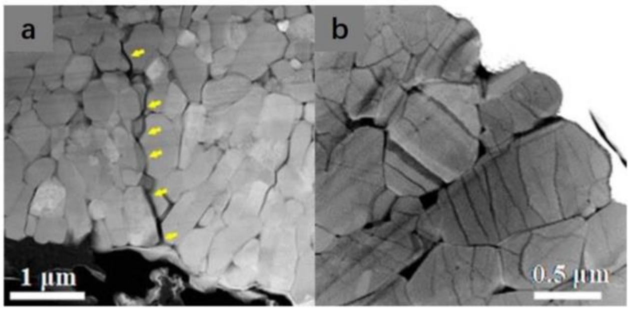


Figure 33 (a) SEM image of intergranular fractures in $Li\ [Ni_{0.9}\ CO_{0.05}Mn_{0.05}]\ O_2$. (b) TEM image of intragranular fractures in the primary particles of a $Li\ [Ni_{0.9}\ CO_{0.05}Mn_{0.05}]\ O_2$ [72].

During the intercalation or extraction of Li ions from the anode, changes in volume appear to cause tension that leads to the fracture of graphite anodes. Due to those movements, there is a significant production of gas by surface side reactions. Illustration of this mechanism could be seen on **Figure 34**. SEI formation could protect the anode from these surface reactions since it is considered as a cohesive and dense film preventing intercalation of solvent and ions. This protection can last up to a point, where Li ions intercalation into the anode causes a volume expansion to almost 13% due to LiC_6 formation. The existing compressive stress inside the SEI caused by gas evolution during formation reactions, can be accommodated by the significant tensile pressure created due to this mechanism of expansion and eventually solvent penetrate the film. The reaction of this solvent with graphite leads to gas generation between layers and finally an interlayer fracture.

The similarity on crack origin in intercalation cathodes and graphite anodes is that intergranular crack creation is primarily caused by anisotropic changes in the lattice parameters, due to numerous phase transformations. Although the difference between them is the process explained above, where solvent intercalates with ions on the anode side causing layer exfoliation and gas generation between graphitic layers, while this lethal mechanism fortunately does not occur on the cathode side. On the basis of similarities and differences, it may be concluded that the primary cause of particle fracture in lithium-ion batteries is the volume change of active electrode materials [72].

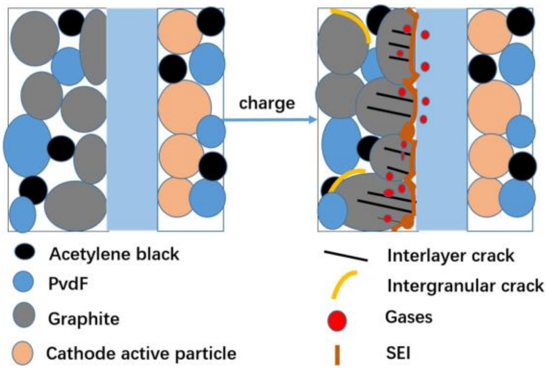


Figure 34 Crack formation on graphite anode [72].

4.8.2 Fracture Modelling

Referring to fracture modelling, linear elastic fracture mechanics (LEFM) and elastic-plastic fracture mechanics (EPFM), may be used to classify fracture propagation based on the mechanical characteristics of battery materials. According to LEFM, elastic calculations can be used to determine the stress field up to the fracture tip under the assumption that the material has linear elasticity. This modelling strategy is only applicable if the material's plastic zone is noticeably less than the solid's characteristic lengths, such as the ligament width and fracture length. The LEFM method can be used as fracture analysis for materials such as oxide electrolytes and cathode materials that have large Young's moduli. EPFM is required though if a significant plastic deformation zone forms close to the fracture tip. The last observed point or value on the stress-strain curve signifies the material's fracture strength. The idea that an initial crack begins as soon as the tensile stress surpasses this critical value, is one of the criteria used to model crack initiation. Once a crack initiates, the main concern is whether the crack propagates or not. The assessment of crack propagation possibility commonly relies on two widely recognized and fundamentally equivalent criteria: the stress intensity factor (SIF) and the energy release rate criterion. SIF simply explains that if $K_I>K_{IC}$ the crack will propagate, where K_{IC} is the material’s critical intrinsic parameter proportional to its properties, which cannot be surpassed. Several variables, including charging time, pre-existing crack length, and current density, have an impact on the value of K_I. The fracture will propagate if the strain rate is greater than the surface energy of the recently formed interface as a result of the cracking, according to the energy release rate criterion. The criterion is explained by the equation $G = \partial\pi/\partial A$, where π is the elastic strain energy and A is the crack area [73].

4.8.3 Influence Factors

Figure 35 presents a visual representation of the factors, both intrinsic and extrinsic, that impact fracture behavior. The inherent battery material qualities are connected to intrinsic variables like particle size, morphology, structure, and mechanical properties, while extrinsic factors are linked to battery operating conditions, for example, c-rate, cut-off voltage, and thermal treatment. In order to be more precise, the effect of these factors will be discussed separately for the two electrodes.

For the anode, an important intrinsic factor is the material’s particle size. A threshold particle size below which no fracture occurs has been discovered by scientists. This demonstrates that smaller particles exhibit greater resistance to the development of cracks. The morphology of the active particles also influences fracture behaviour, in addition to size dependency. The crack locations seem to vary depending on the particle morphology. The third intrinsic factor that affects the fracture behaviour is the crystallinity of the anode material. During lithiation of the anode, there is a two-phase transition and a creation of a two-phase interface. Depending on the interface's components there is a different fracture behaviour. The crystallinity will affect the critical size of the particles, whether the expansion will be isotropic or anisotropic leading to the corresponding fracture, and the gradient in the Li-ion concentration, that influences the stress distribution and ultimately the fracture behavior. As extrinsic factors, although after scientific experiments C-rate showed a small effect on crack propagation in Si nanoparticles, most of the modelling results showed that a significant C-rate leads to greater stress and eventually to easier crack formation [74].

Similar material intrinsic characteristics that can influence anode and cathode crack propagation. Particle size is still one of the most important ones since it has been calculated and confirmed experimentally that below a critical size fracture will not propagate. Synchrotron X-ray tomography, illustrated in **Figure 36**, proves that the size of the fracture is proportional to the size of secondary particles, given that the bigger the diameter the wider and longer the crack. Another crucial factor affecting the particle fracture is the electrode's chemical composition. For example, higher Ni content in a nickel cobalt manganese (NCM) cathode causes more and worse cracks and in time could evolve as the main reason for capacity to fade. The explanation for that is: with higher Ni concentration comes a higher volume change in the NCM cathode, since the initial particles generate an intergranular fracture network during oxidation, there is a larger de-lithiation and greater change in nickel-ion radius. The last observed intrinsic factor affecting the cathode fracture is any pre-existing defect. Defects in the centre of the particle probably will create a crack during discharging, while cracks will most likely propagate during charging if defects are located at the particle's surface. As extrinsic factors, a cathode's state-of-charge heterogeneity speeds up fracture development. This phrase describes the unequal distribution of an element's oxidation state at various length scales on a cathode. The remaining chemical outliers in the bulk of the particles during discharging, have as a result a concentration gradient stress. At the electrode scale, the uneven distances and rates of electron and ion transport are what cause reaction heterogeneity to exist. The presence of depth-dependent particle fracture indicates a more severe crack near the separator than near the collector. Cut-off voltage has been shown to have a large impact on crack formation and density. For layered cathode materials, while lower voltage generally causes intergranular cracking, higher voltage causes both intergranular and intragranular cracks to develop. It has been proven experimentally too that layered cathode particles grow intragranular cracks only under high cut-off voltages. To conclude, the last extrinsic factor affecting the cathode is thermal runaway. A thermal abuse at around 400°C can cause similar results as those of long-term electrochemical cycling, such as micro-cracks in primary particles. After thermal runaway, the temperature of the cell can reach up to 800°C which will only worsen the cracks and make the cell less thermal stable [73].

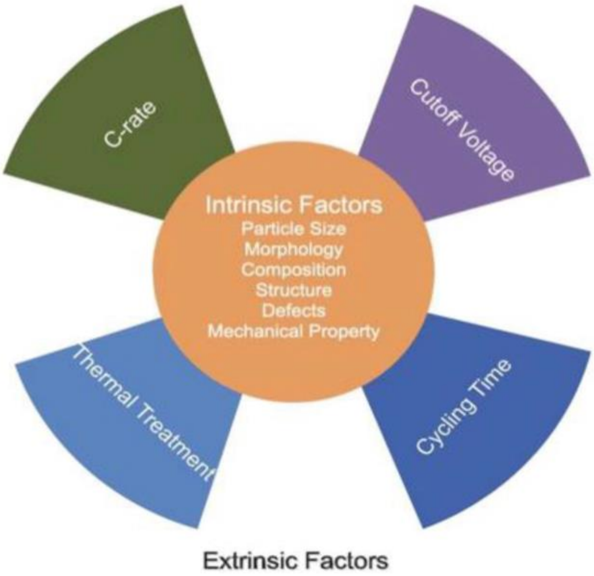


Figure 35 A combination of internal and external factors affects how battery materials fracture [73].

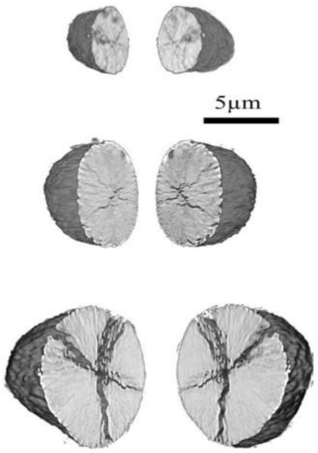


Figure 36 Synchrotron X-ray tomography was utilized to obtain two-dimensional virtual slices of LiNi0.6Mn0.2Co0.2O2 particles of different sizes [73].

4.9 Battery’s ageing Influence Factors

Battery aging can result in the occurrence of capacity or power fading, or both phenomena. Those phenomena can be intensified by some influence factors which will be analysed in this section. Several factors can contribute to the ageing of a battery, including its production process and working conditions. These conditions may include high cycling rates, exposure to high or low temperatures, being at high or low states of charge (SOC), overcharging or over-discharging, high depth of discharge (DOD), and exposure to moisture [75].

4.9.1 Production

The first thing should be reviewed is battery production. In order to create a high-performance and long-lasting battery, it is necessary to develop production technologies and optimize the manufacturing processes in a systematic way. The manufacturing processes for Li-ion batteries are presented in **Figure 37**, including mixing, coating, drying, calendaring, cutting, stacking, welding, and sealing, as well as filling them with electrolyte and performing other processes like testing and sorting. Although the fundamental procedures are generally comparable, different batteries may require unique manufacturing processes due to variations in their chemistry, structure, and shape.

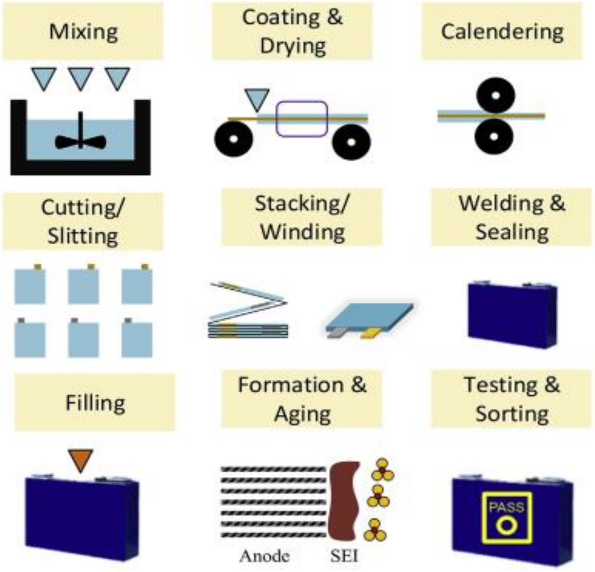


Figure 37 Manufacturing processes of Li-ion batteries [75].

First, it should be mentioned that water can significantly affect the lifespan of batteries. Hydrofluoric acid may be produced as a result of the electrolyte's water and the lithiated graphite anode interacting, which may damage the cathode material and cause transition metal dissolution. As a result, strict control of the manufacturing environment's humidity is crucial before the formation process. Typically, the air dew point should be below -50°C to prevent significant reduction in battery life caused by water present in the electrolyte [75].

4.9.1.1 Mixing

In particular, the dispersion equipment is used for mixing the powders of active materials, conductive additives, binder, and solvent during the slurry preparation process. The mixing process is essential for determining both the active material's particle size distribution and the uniform distribution of materials that transmit electricity throughout the battery [75].

4.9.1.2 Coating

During the coating and drying process, the slurry is applied onto the current collector and subsequently dried to remove the organic solvent contained within the slurry. During the production process, the flow of conductive additives and binders within the electrode might be impacted by solvent evaporation and sedimentation of active material particles. Therefore, important parameters like air flow speed and drying temperature must be meticulously optimized [75].

4.9.1.3 Calendering

The process of calendering or pressing is used to compact the battery electrodes and affects important electrode parameters such as thickness, porosity, and compaction density. Key operational parameters such as roller speed and rolling force must be carefully selected. Anode or cathode active materials may be distributed unevenly due to poor homogeneity of active material distribution. This can result in too much or too little of these materials in certain areas. Uneven electrode thickness can produce deformation and wrinkles, which are bad for battery performance and result in local lithium deposition in the wrinkled area. Insufficient local anode materials may also result in localised lithium deposition, which can reduce battery life. Therefore, to ensure the longevity of the battery, the thickness and uniformity of the electrode must be carefully monitored during manufacturing using tools such as a microscope or laser-based equipment [75].

4.9.1.4 Size Control

Size control is critical during the cutting and slitting processes. It is recommended that the active components of anode be significantly bigger than the cathode active materials to avoid lithium deposition at the anode's edge and burrs during the cutting process. Cracks can cause an internal short circuit or a higher self-discharge rate, which shortens the battery's life and compromises its safety. The longevity and safety of the battery could be jeopardised if there is metal debris on the electrode surface after cutting. This could lead to localised metal deposition, dendrite growth, and separator penetration.

The efficiency of the stacking production process is generally low for batteries with stacked structures, but this method typically has little impact on battery life. On the other hand, the winding technique used in batteries with wound-type structures offers excellent manufacturing efficiency but can have a negative effect on battery life. When wound too tightly, it can result in an enhanced battery performance and decreased internal resistance. However, tightly winding can make it difficult to completely saturate the electrodes and separator pores with electrolyte and may result in mechanical structure degradation of the anode and cathode particles, which will shorten battery life. Conversely, loose winding can result in insufficient restriction of the active materials, and volume fluctuations experienced while charging and discharging may increase internal resistance and cause the active materials to lose contact [71].

4.9.1.5 Filling and Forming

The major steps in the battery production processes are filling and forming. Establishing a trustworthy SEI film is the major goal of these techniques. The amount of electrolyte in the battery is determined by the filling process, which is also known as electrolyte injection. If too much electrolyte is used, it can lead to wastage, a reduction in battery energy density, and a compromised battery seal. On the other hand, a battery's separator and internal active elements can become improperly moist due to insufficient electrolyte, which can increase internal resistance, cause an unstable SEI film, as well as raise the danger of lithium plating. If the electrolyte amount is inadequate, the battery's capacity can decrease rapidly due to continuous electrolyte usage. After the injection of the electrolyte, the electrode and separator absorb it. If the electrolyte does not completely wet the entire electrode, battery performance may be affected, and areas of the active materials may not participate in the charging and discharging process, leading to lithium deposition, and reducing battery life. The wetting process can be viewed and tracked using methods like ultrasonic or neutron imaging to assure battery life [71].

The formation process plays a critical role in ensuring the longevity and effectiveness of the battery. The electrolyte and lithium ions combine on the surface of the anode particles to produce the SEI layer during the first charging and discharging cycles following the injection of the electrolyte. Similarly, the CEI layer may also form on the surface of the cathode particles, as depicted in **Figure 38**. However, film development during this process can cause the loss of usable lithium ions, electrolyte consumption, and increased battery resistance, which can lead to a rapid decrease in battery capacity.

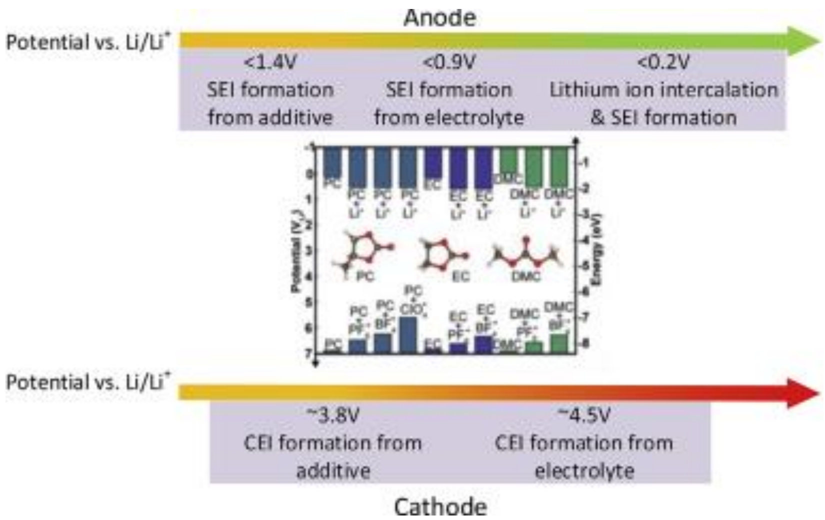


Figure 38 Formation process of SEI and CEI [75].

Currently, throughout the creation process, cells are subjected to charging and discharging processes at a significantly slow rate. Furthermore, during the creation process, the cells may be subjected to a few ageing processes at high temperatures and pressures. One of the most expensive procedures in the production of lithium-ion batteries is the electrolyte wetting process. Temperature, current, voltage, and pressure have an impact on SEI film quality and battery performance. High current or voltage may cause rapid gas formation that is hard to exhaust, leading to poor contact between the electrode and the separator, resulting in low efficiency and lithium deposition. Conversely, insufficient current levels can lead to high production costs.

It is crucial to get rid of the created gas during the creation process and make sure the cells are completely sealed. If it is not correctly sealed, the battery life will suffer as well. If the battery is not adequately sealed, its life will be shortened. Continuous electrolyte leakage is directly related to electrolyte loss, resulting in lithium breakdown and active material loss [71].

4.9.1.6 Testing and Sorting

Testing and sorting are the last steps in the manufacture of batteries. In this stage, specific indicators and threshold values need to be defined, allowing unqualified cells to be filtered out and qualified cells to be classified. Implementing an effective sorting system can help identify cells with inferior quality, which is crucial to ensure the longevity of the battery. The main determinants of battery durability are impedance, capacity, and self-discharge rate. Setting appropriate thresholds for these parameters can effectively ensure cell longevity. Battery manufacturers typically conduct 1 kHz AC impedance testing at the end of the production line since impedance has the most significant impact on battery power performance. Under the same operating conditions, a battery with a higher impedance produces more heat, which reduces battery life. A large impedance may also indicate manufacturing defects within the cells, such as inadequate electrolyte wetting or non-uniform distribution of conductive additives, which can lead to high polarization inside the battery and impact battery life [75].

Battery consistency is clearly affected by both capacity and self-discharge rate. There is a general belief that greater cell capacity leads to better battery performance. The pack consistency hypothesis states that the smallest cell capacity limits the total capacity of a battery pack, prohibiting the full utilisation of bigger cell capacities. Additionally, a high self-discharge rate is a sign of internal side reactions within the cell, which could negatively impact the battery's ability to store energy.

4.9.2 Working Conditions

In this section, the influence of the battery working conditions will be stated. Under different working conditions, batteries may have different lifetimes. Factors that can affect battery life include high temperature, which can accelerate internal reactions, and low temperature, which can affect the reduction of metal ions, lithium plating, and the crystal structure of the material, making it more prone to damage. High SOC or overcharge have a considerable negative influence on lithium plating, electrolyte breakdown, and interactions between the electrolyte and the cathode. On the other hand, low SOC or over-discharge can cause corrosion of the anode copper current collector and collapse of the crystal structure of the active material. High charge and discharge rates can cause fatigue of the crystal structure of the active material, while high rates can lead to temperature rise and acceleration of the internal negative effects [76].

The battery typically operates within a reasonable range, as depicted in **Figure 39**. The major objective is to maintain the battery's performance within the boundaries of high efficiency and long life, and to avoid operating it in the danger zone, which should prompt a warning and immediate action.

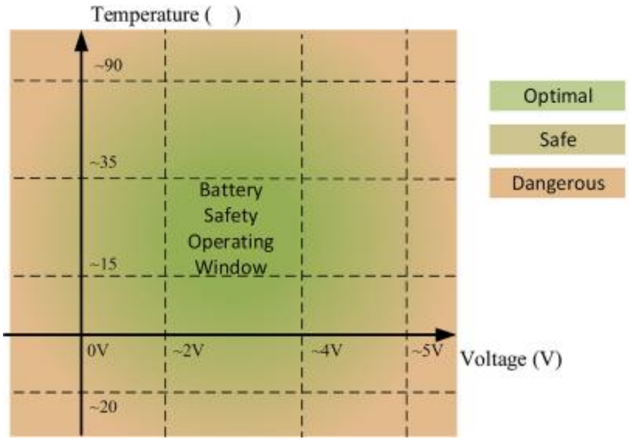


Figure 39 Battery operating window [75].

4.9.2.1 Temperature

One of the most crucial factors affecting a battery's longevity is temperature, and it should be understood that both high and low temperatures may accelerate the battery's degradation. Hence, acknowledging the impact of temperature is of utmost importance. The ideal operational temperature range for the majority of commercial lithium-ion batteries is typically between 15 and 35 degrees Celsius. Temperature is a critical parameter that affects multiple processes within the battery, including both primary and secondary reactions. An increase in temperature leads to an increase in the rate of side reactions. Additionally, if the battery's temperature rises above a particular point, it may start to self-heat even more, leading to battery thermal runaway. Under low temperatures the rise in internal resistance will cause the polarisation to increase, which could result in more negative effects. Particularly, charging at low temperatures can result in lithium deposition, which can speed up battery deterioration and potentially pose safety risks. Additionally, the battery life may be impacted by the material embrittlement caused by low temperatures. Therefore, the key to extending battery life is to make sure the battery operates within a proper temperature range [76].

Several factors determine the temperature of a battery, such as the ambient temperature, the battery's heat capacity, its thermal conductivity, how much heat the battery produces, and the presence of heating and cooling systems, are shown in **Figure 40**. The battery temperature may be more affected by each of the variables.

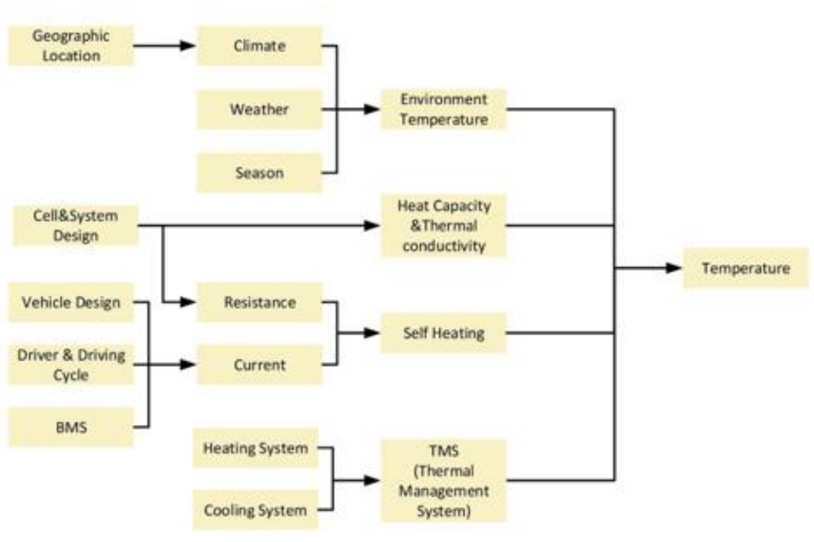


Figure 40 Battery temperature-related parameters [75].

Battery life is significantly impacted by the ambient temperature. The most frequent condition for power batteries in the majority of practical EVs is actually the storage state, which is the same as when a car is parked. All of the vehicle's electric systems are currently off, and the temperature of the battery is mostly influenced by the climate. The temperature and SOC are the main variables impacting the battery calendar life. The capacity fade is significant during the state of storage in these regions with high environmental temperatures. The battery's cycle life is additionally influenced by temperature. The environmental temperature is mainly influenced by the climate, weather, and season. It is commonly recognised that temperature rises as latitude decreases. However, in high latitude regions, where winter lows can drop below 0°C, installing a heating system becomes necessary to stop the deposition of lithium during low-temperature charging, which could raise safety and durability issues [77].

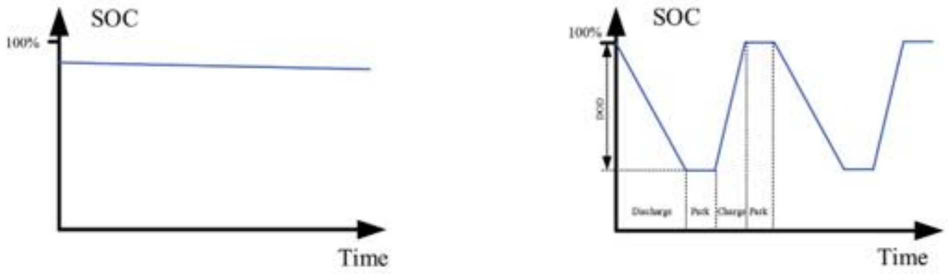
Ohmic heat is produced in significant amounts throughout the battery's charging and discharging processes. The magnitude of temperature change in the battery resulting from this phenomenon is influenced by the battery's thermal characteristics and resistance, together with the amount of current passing through the battery. Using a logical cell and system design will improve the battery's thermal characteristics and resistance. Moreover, the vehicle's design can also impact the current intensity. The battery's operating state can be directly affected by the driving style and road conditions, and under harsh working conditions, the current can become more intense, leading to a substantial increase in battery temperature [77].

Additionally, a trustworthy battery management system (BMS) can accurately predict the battery state of power (SOP) while considering safety and life concerns, restricting the battery's current flow. Besides, the battery temperature will be significantly impacted by the charging system. As an illustration, the speed of charging for the planned 350 kW ultra-fast charger would be far higher than the rate of discharging when driving. The battery temperature will then rise significantly because of the charging procedure, potentially affecting battery life.

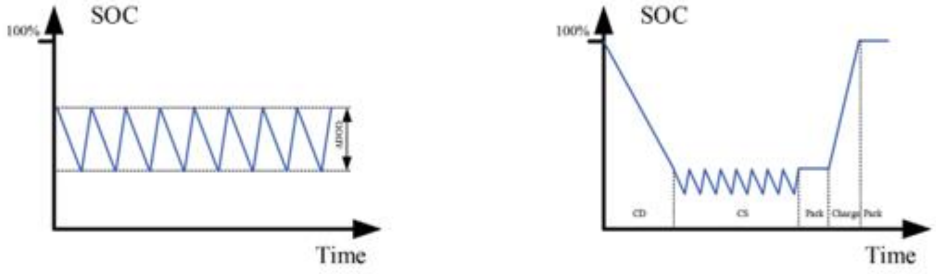
In addition to having the ability to heat or cool at low or high temperatures and using thermal insulation measures, a battery can be guaranteed to function within the proper temperature range. Cooling systems can be broadly categorized into air cooling, liquid cooling, and phase change cooling, depending on the type of cooling medium used. Heating systems, on the other hand, can be classified as either internal or external heating methods. The external heating methods consist of several techniques such as heating plates, heating films, Peltier heating, and more [68]. Although the external heating approach is simple to use, there is a higher energy waste and poorer battery temperature consistency. Then using an indirect heating technique to warm the thermal medium could aid in evenly heating the battery. It is possible to extend battery life and maintain battery temperature in an EV with a trustworthy thermal management system (TMS). High-performance air conditioning systems are used to properly control the temperature of used batteries working in an energy storage station [77].

4.9.2.2 State of Charge (SOC)

A battery's longevity is strongly impacted by its level of charge. It's critical to understand the relationship between a battery's SOC and voltage. It's important to keep in mind that voltage and battery SOC are related. Voltage can be calculated by considering the battery SOC and current, which can be represented as the battery model. For applications involving motor vehicles, the battery's available capacity is indicated by the SOC. **Figure 41** demonstrates that the vehicle primarily determines the battery SOC.



(a) Storage Mode (b) BEV Mode



(c) HEV Mode (d) PHEV Mode

Figure 41 Different types of vehicles SOC [71].

Typically, A higher state of charge (SOC) in a battery is associated with a lower anode potential and a higher cathode potential, which are both reflected in the higher terminal voltage. The side reactions, such as SEI thickening, may happen more quickly with a lower potential graphite anode, hastening the ageing of the battery [78]. Under certain charging conditions, such as overcharging or charging at low temperatures, it is possible for the anode potential to drop too low and reach the lithium deposition potential, causing internal reactions like lithium deposition that could speed up battery ageing. Additionally, a cathode with a higher potential can cause electrolyte oxidation and cathode decomposition to occur. When the state of charge (SOC) of a battery is lower, it can contribute to a higher anode potential and a lower cathode potential, which can have a positive impact on battery longevity. However, if the battery's SOC drops too low, it could result in structural disintegration of the cathode active material and corrosion of the anode copper current collector, resulting in a considerable reduction in battery life [79]. The battery's calendar life at various SOC levels is shown in **Figure 42.** Therefore, during battery storage, a low SOC level, such as approximately 20% SOC, can improve battery life. Additionally, the safety performance is better at a lower SOC than at a higher SOC level [75].

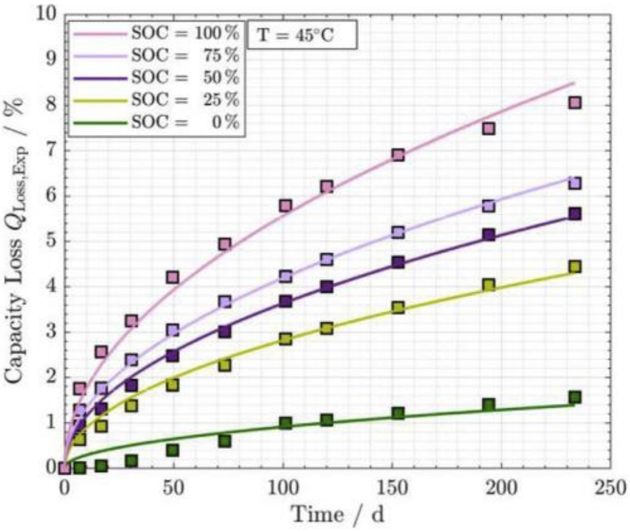
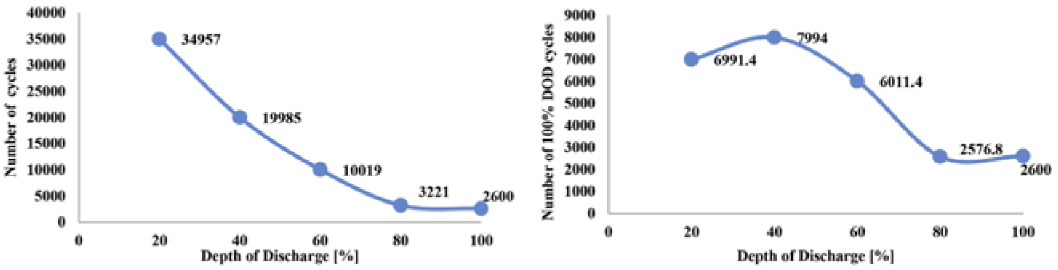


Figure 42 Capacity loss vs SOC [75].

It is standard procedure to charge the battery to its maximum capacity and then discharge it to a particular depth of discharge (DOD) while the battery electric vehicle (BEV) is operating. A DOD of 80% implies that the battery has been cycled between 20% and 100% SOC. In this context, the DOD significantly influences battery life, and the relationship between the two is complex. Fig. 39 illustrates the findings of an experiment on this topic [80]. Increasing DOD has both positive and negative effects on battery life. A higher DOD results in a lower average SOC, which in turn reduces the anode potential and side reaction rate, thereby improving battery life. However, the increased DOD also leads to multiple phase change regions in the cathode and anode materials, causing severe structural and volume changes that deteriorate battery life. Therefore, while an optimal DOD exists to improve battery life, this DOD may not meet driving range requirements. To suit customer needs while preserving battery life, the battery capacity in EVs should be carefully researched, and large DODs should be avoided (**Figure 43**) [75].



(a) Cycle life (b) 100% DOD equivalent cycle life

Figure 43 Cycle life vs DOD [75]

In HEV mode, the battery undergoes frequent cycling within a particular SOC range. **Figure 44** shows that cycling at lower SOC levels can extend battery life. Moreover, it is preferable for the battery to cycle outside of the active material's phase change zone. The operating SOC range must, however, guarantee adequate discharging and regeneration capacity to fulfil the needs of the vehicle. HEV batteries are typically cycled between 30% and 80% SOC.

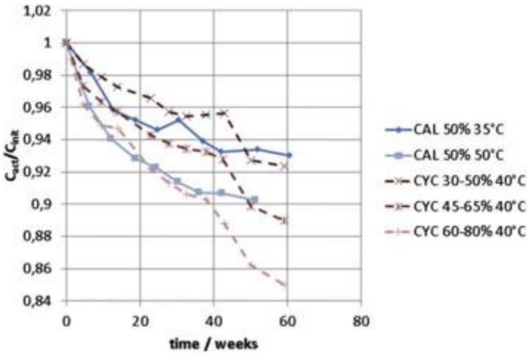


Figure 44 Battery ageing under different SOC [73].

The battery of a PHEV usually operates in CDCS mode, wherein the battery undergoes two stages: charge depleting (CD) and charge sustaining (CS). During the CD stage, the battery SOC decreases gradually, like the EV mode. Conversely, during CS stage, the SOC of battery, remains stable with some fluctuations, similar to the HEV mode. As previously said, it is vital to create an acceptable operating scope for the battery, taking in consideration both life and driving range needs. Similar to the HEV mode, the battery cycling profile for the second-used battery in an energy storage station must also be correctly constructed.

4.9.2.3 Battery Current

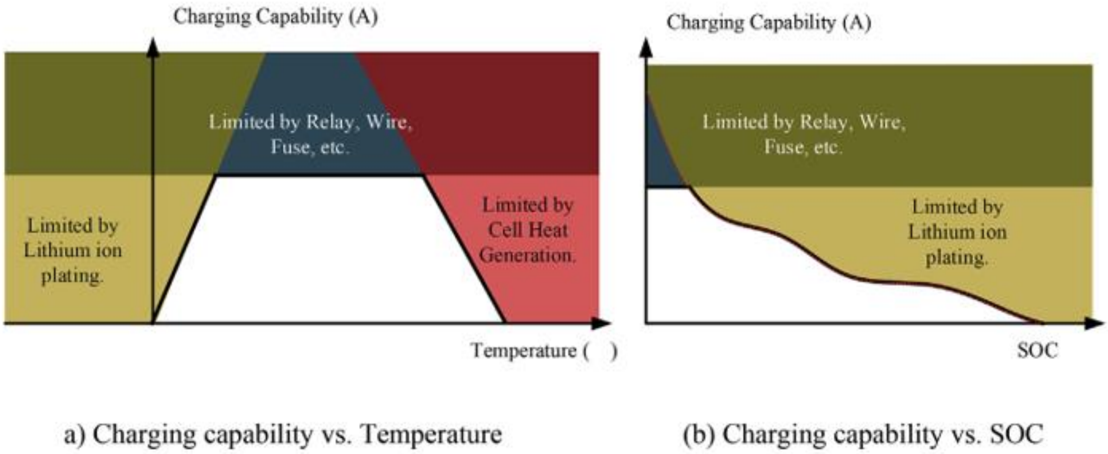
Battery life is directly affected by the battery current. Firstly, the battery's temperature is altered by the Joule heat produced by the current flowing through it. The temperature increase can be significant during high charge and discharge rates, leading to a decrease in battery life. Secondly, current affects the battery terminal voltage and internal potential, causing side reactions that deteriorate battery life. Specifically, during the charging phase, there exists a critical current that can cause lithium deposition. High current can also result in quick processes of lithium-ion intercalation and deintercalation on the surface of particles, which can harm and degrade the structure of the active material. Furthermore, an excessive current might result in an unequal distribution of current within the battery, which can lead to uneven structure deformation or localised lithium plating. Moreover, the limited pace of lithium-ion migration during fast charging can result in lithium deposition and affect battery life. Overall, lower current through the battery generally results in longer battery life, but in real-world EVs, it is challenging to reduce current due to power requirements and charging time constraints [75].

The energy storage facility or vehicle's construction, which comprises the battery system, motor system, and other components, has a major impact on the battery current rate. In comparison to BEV and PHEV, HEV charge, and discharge rates are typically higher. While a more powerful battery system in BEV or PHEV would result in a longer electric range and lower discharge rate, the cost of the vehicle would be prohibitively expensive. owever, the battery system may be effectively maintained, and the current flowing through the battery can be regulated, helping to prolong battery life. This is made possible by a dependable battery management system (BMS) and an effective algorithm.

4.9.2.4 State of power and State of energy

When discharging a battery, the BMS plays a crucial role in estimating both the state of power (SOP) and state of energy (SOE). SOP estimation helps predict the battery's short-term behaviour, such as the available current in the next 10-30 seconds, while SOE estimation anticipates the battery's long-term behaviour by estimating the battery's overall capacity at a given power level. If reliable SOP and SOE estimation results are available, the vehicle can optimise its driving behaviour, notably the battery system output. This enables management of the battery system output under low SOC, low or high temperature circumstances to prevent abuse such overdischarge. However, driving requirements normally directly affect the output current, and the BMS typically cannot directly adjust the output current [75].

Batteries are often charged on a charger, and a BMS can regulate the charging current. Therefore, charging may be easily optimised. Temperature increase and lithium deposition are the two main charging problems, as seen in **Figure 45**. By utilising a closed-loop observer of lithium deposition state, researchers created a battery rapid charging technique that takes into account lithium deposition, which was created using a stable reference electrode technology and a control-oriented electrochemical model [81]. The charging ability of a battery is limited when charging at low temperatures due to the slow lithium-ion transit rate. To address this issue a self-heating battery was developed that could rapidly warm up the cell [82]. After that, a technique was suggested that made use of optimal charging and alternating current heating while also taking the lithium deposition boundary into account [83].



a) Charging capability vs. Temperature (b) Charging capability vs. SOC

Figure 45 Analysis of the charging capability [75]

4.9.3 Conclusion

To improve the battery's lifespan, it's essential to consider its manufacturing and operating conditions. This involves investigating the various factors that impact the battery's ageing mechanism. Additionally, constructing a Degradation Model that considers the ageing mechanism is crucial. Using this model, streamlined production and management processes can be implemented to enhance the battery's life [75].

CHAPTER 5

CONCLUSIONS

There are several degradation mechanisms involved in Lithium-ion batteries, which make LIBs extremely complex, but at the same time interesting systems to study. The final effects on LIBs are the capacity and power fade, which are caused mainly by four different degradation modes: Loss of Lithium-ion inventory (LLI), loss of active material (LAM), loss of electrolyte (LE), and resistance increase (RI). A degradation mode is typically the result of a degradation mechanism or a combination of them. It is the actual process through which the battery will deteriorate. Through chapter 4, it has been explained thoroughly what a degradation mechanism and an influence factor is. The objective of the review’s final chapter is to link each of the previously discussed influence factors to each of the degradation mechanisms that have been analysed, in order to be clear for the reader and potentially a LIB user what is proper way to use a portable electronic device or an electric vehicle.

This connection is made clearer and more visible through **Figure 46,** where all the influence factors, degradation mechanisms and modes, and final effects are displayed along with their links. Beginning with the SEI, it is evident that its formation and propagation can happen either by the usage of the battery in high temperatures or through the manufacturing process, more precisely during the electrolyte’s filling in LIB. CEI can also develop during production, but only during the formation process, which is the last step in building a LIB cell, as well as if the user keeps the battery in a high state of charge for excessive periods. The most vulnerable mechanism seems to be lithium plating since it can occur under various working conditions. Particularly, during relatively high or low SOCs, when the temperature drops in the winter, but also through high current while fast charging. In addition to all of this, sometimes even the most meticulous and faultless user’s LIB may experience lithium plating while filling through the production. Finally high current or a low SOC can both cause a breakdown of electrode structure but also particle fracture. An electrode may potentially be destroyed during manufacture if the calendaring or stacking process is flawed. Particle fracture though is vulnerable to different stages of production like mixing and formation.

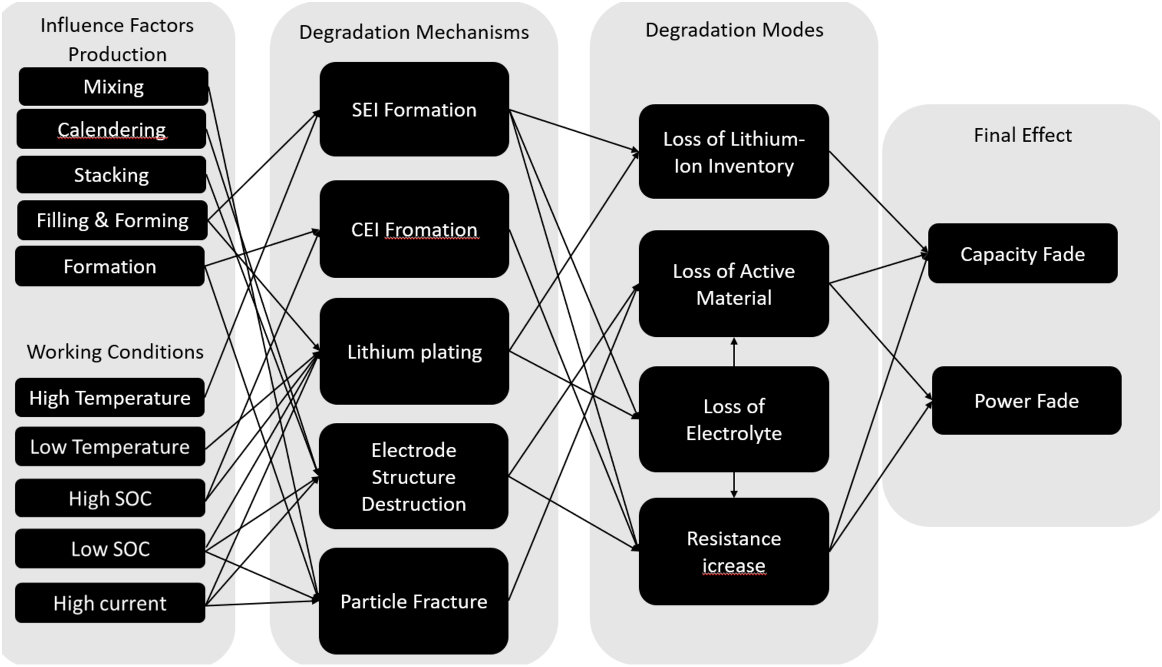


Figure 46 Lithium-ion battery's path to failure

Advancing to the degradation mode stage, their instigating mechanisms are more evident. Loss of Lithium-Ion inventory (LLI) is caused either by SEI formation and propagation or lithium plating. Particle fracture and electrode structure destruction give as a result significant loss of active material. Loss of electrolyte, which appears as an intermediate step, is considered as the SEI's or lithium plating's consequence, and resistance increase can be caused from SEI and CEI propagation or from electrode structure destruction. LLI, LAM and RI are the degradation modes causing capacity fade to a Lithium-ion battery and power fade is the final consequence of LAM and RI. The loss of electrolyte is an intermediate mode since it can not cause any of the final effects directly but instigates the other two modes.

Some significant conclusions extracted from this chart analysis and the entire review include the fact that lithium-ion batteries always degrade either with cycling or time. All of its components are vulnerable to deterioration from several influence factors. Assuming that all LIB cell manufacturing lines are flawless and that all production influence factors are eliminated, there is still potential for user-driven innovation. Batteries can last longer if exposure to factors that hasten degradation is decreased. Influence factors such as medium levels of temperature and state of charge could give LIB a significant amount of extra life.

These conclusions are also supported by manufacturers, the majority of whom provide users with detailed instructions on how to use the battery in their products properly. Many companies from different sectors, including those that manufacture cell phones, laptops, power tools, and electric vehicles will modify their recommendations in accordance with the demands of their customers and their battery management systems. In the smartphone and power tools industries, for instance, the key recommendations are temperature-related, with customers being cautioned not to use or charge their phones beyond 35 °C and below 15 °C, as well as not to store them at extreme temperatures like below -20 °C and above 45 °C. These temperature limitations are also added by the laptop manufacturers, along with some state of charge ones. Users are advised against keeping the battery at a high SOC for an extended amount of time. High and low temperatures or SOCs could have an impact on electric vehicles only if they are parked without charging. If they are parked and charging or driving their battery management system (BMS) is capable of protecting the LIB cells either from extreme temperatures through its cooling or heating systems or from low SOCs. However, overcharging seems to be an essential consequence for the car's BMS to function. Manufacturers are not so worried about the scientific results about high current, since the time a user is likely to fast charge his or her car is considered negligible [60].

Improvement of Lithium-ion batteries' lifetime means not only economic benefits but also environmental. Doing so requires better manufacturing lines with more precise techniques of assembly, technologically advanced BMSs, and educated users on Lithium-ion batteries in order to avoid storage and use scenarios that hasten degradation. The decreased demand and production of new LIBs are the reason why extended lifetime and decreased degradation are crucial for the environment since the majority of CO_2 emissions from portable devices comes from manufacturing. The economic benefits are mostly for the consumer since the cost of replacing a portable device's battery ranges from 5% to 30% and could reach as high as 40% for EVs.

An advanced battery management system is crucial for all the devices but especially for EVs, since they are a purchase that a consumer expects to last at least a decade. BMSs through their inputs (current, voltage, and temperature sensors) and outputs (fans, electric heaters, and capacitors) should be able to maintain an optimal operation of a LIB cell, module or pack. Large data sets, artificial intelligence-based machine learning, and reducing computing load are being investigated as potential techniques to enhance management systems.

Finally, an educated and cautious user may purchase the same item that contained the same LIB and use it for a significantly longer period of time compared to a careless and illiterate one. This review's objective is to gather and compile as much data as possible on LIB degradation in order to enable users to maintain their own devices longer without the need for manufacturing development, which will undoubtedly occur.

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