DEGRADATION MECHANISMS IN LITHIUM-ION BATTERIES: A CRITICAL ANALYSIS OF PERFORMANCE DECLINE IN ELECTRIC VEHICLES

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ABSTRACT: The present paper provides a critical analysis of the performance degradation associated with electric vehicle batteries, specifically focusing on lithium-ion (Li-ion) technology. Within this framework, it elucidates the four predominant mechanisms that contribute to the gradual decline in battery performance over time: (1) the deposition of solid lithium; (2) the formation of passive films; (3) the development and propagation of cracks; and (4) the dissolution of active material within the electrolyte. Each of these mechanisms is examined comprehensively within the broader context of the entire battery system, highlighting the intricate interactions between the various processes at play. The discussion underscores that the degradation of battery performance is not merely a linear phenomenon but a complex interplay of multiple factors, both statistical and random in nature. This inherent complexity presents significant challenges for accurate modelling and prediction of battery behaviour over its operational lifespan. By providing a thorough exploration of these degradation mechanisms, this paper aims to enhance the understanding of the underlying processes that lead to reduced battery performance, thereby informing future research and development efforts in the field of electric vehicle battery technology. The findings also emphasize the need for sophisticated modelling approaches that can adequately capture the multifaceted nature of battery degradation. Such models will be discussed in the second part of the paper.

Key-Words: electric, vehicle, batteries.

1.INTRODUCTION

The increasing adoption of electric vehicles (EVs) as a means to combat climate change and reduce dependence on fossil fuels has significantly accelerated research in the field of energy storage systems. Among various energy storage technologies, lithium-ion batteries (LIBs) have emerged as the most prominent due to their high energy density, long cycle life, and relatively light weight. However, a major concern surrounding the widespread implementation of electric vehicles is the degradation of their battery systems over time, which directly impacts vehicle performance, range, and overall economic viability. Understanding the mechanisms and factors contributing to battery degradation is essential to extending the lifespan of these batteries, optimizing EV performance, and ensuring the sustainability of this technology.

Battery degradation is a multifaceted problem, influenced by a combination of chemical, thermal, and mechanical factors that occur during normal battery operation. These factors lead to a gradual decline in the battery's capacity to store and deliver energy, reducing the driving range of electric vehicles and necessitating expensive battery replacements over time. The degradation of lithium-ion batteries can be attributed to both calendar aging, which refers to the loss of performance over time regardless of use, and cycle aging, which is directly related to the number of charge-discharge cycles the battery undergoes.

Both forms of degradation are driven by complex electrochemical reactions within the battery that, over time, lead to phenomena such as loss of active material, growth of the solid electrolyte interphase (SEI), lithium plating, and electrolyte decomposition.

A key challenge in mitigating battery degradation lies in the dynamic and non-linear nature of the aging process. The rate of degradation is highly sensitive to various operational conditions, such as temperature, depth of discharge, charging speed, and overall battery management practices. For instance, exposure to extreme temperatures—either too high or too low—can significantly accelerate aging by intensifying unwanted side reactions. High temperatures, in particular, promote the decomposition of the electrolyte and the growth of the SEI layer, which consumes lithium ions and reduces the battery’s available capacity. Conversely, low temperatures can lead to lithium plating, a process where metallic lithium is deposited on the anode surface, further contributing to capacity fade and increasing the risk of internal short circuits. Moreover, aggressive charging protocols, such as fast charging, have been shown to exacerbate degradation by inducing mechanical stress on the electrodes and enhancing thermal effects.

Research into understanding and preventing battery degradation has focused on several key areas, including the development of advanced battery materials, improved thermal management systems, and optimized charging strategies. The use of novel electrode and electrolyte materials that are more resistant to degradation could help mitigate the loss of active material and extend the cycle life of lithium-ion batteries. In addition, enhancing battery management systems (BMS) to monitor and control battery temperature and state of charge more precisely could significantly slow the aging process. Machine learning algorithms and predictive modelling techniques have also been proposed as tools to anticipate and manage battery degradation by analysing large datasets on battery performance.

2.PROBLEM FORMULATION

In contemporary practices for designing and dimensioning battery packs for electric vehicles (EVs), original equipment manufacturers (OEMs) typically oversize the onboard battery systems. This approach is intended to accommodate the inevitable degradation of the battery over time, thereby ensuring that the vehicle meets performance and range expectations throughout its lifespan and fulfills the warranty requirements. The oversizing strategy serves as a safeguard, compensating for the reduction in battery efficiency as the system ages. The United States Advanced Battery Consortium (USABC) provides specific criteria for determining the End-of-Life (EOL) of EV battery packs, establishing two primary degradation metrics. Firstly, EOL is considered to be reached when the battery experiences a 20% reduction in its power output capability, a phenomenon known as power fade [1-2]. Secondly, the battery is also deemed to have reached EOL if its capacity to store charge diminishes by 20% relative to its original rated capacity, a condition referred to as capacity fade. Both of these parameters play critical roles in assessing the long-term viability of EV batteries, as they directly impact the vehicle’s operational performance, range, and overall efficiency.

These thresholds are central to the design and management of battery systems, influencing the durability, lifecycle, and reliability of EVs in real-world conditions. Manufacturers generally anticipate that a battery will experience a 20% decline in performance throughout the vehicle's operational lifespan and plan accordingly. To accommodate this expected degradation, battery packs are designed with larger-than-necessary capacities. This oversizing strategy is intended to compensate for the gradual loss in efficiency over time. In essence, the battery pack is engineered with additional capacity from the outset to ensure that it can maintain acceptable performance levels despite the anticipated deterioration in its power output and storage capacity. The most widely used EV batteries in market, are lead acid, NiMH, ZEBRA and Li-ion. The characteristics of these batteries are presented in Table 1.

Caracterstics	Lead Acid	NiMH	ZEBRA	Li-ion
Nominal cell voltage (V)	2	1.2	2.58	2.5/3.3/3.6-3.7
Specific energy (Wh/kg)	30-45	30-80	90-100	90-220
Energy density (Wh/L)	60-75	140-300	160	280-400
Specific power (Wh/kg)	180	250-1000	150	600-3400
Cycle life	500-800	500-1000	1000	1000-8000
Self-discharge (%/month)	2-4	20-30	0	2-5
Temperature range(°C)	-20-60	-20-60	270-350	-20-60
Relative costs ($/kWh)	150	500	270	700
Efficiency	85	80	75-85	93

Table 1. The most prevalent EV battery types available on the market and their main parameters [3].

2.1.Li-Ion batteries degradation mechanism

The main Li-Ion batteries components, their functions and the materials are presented in Figure 1.

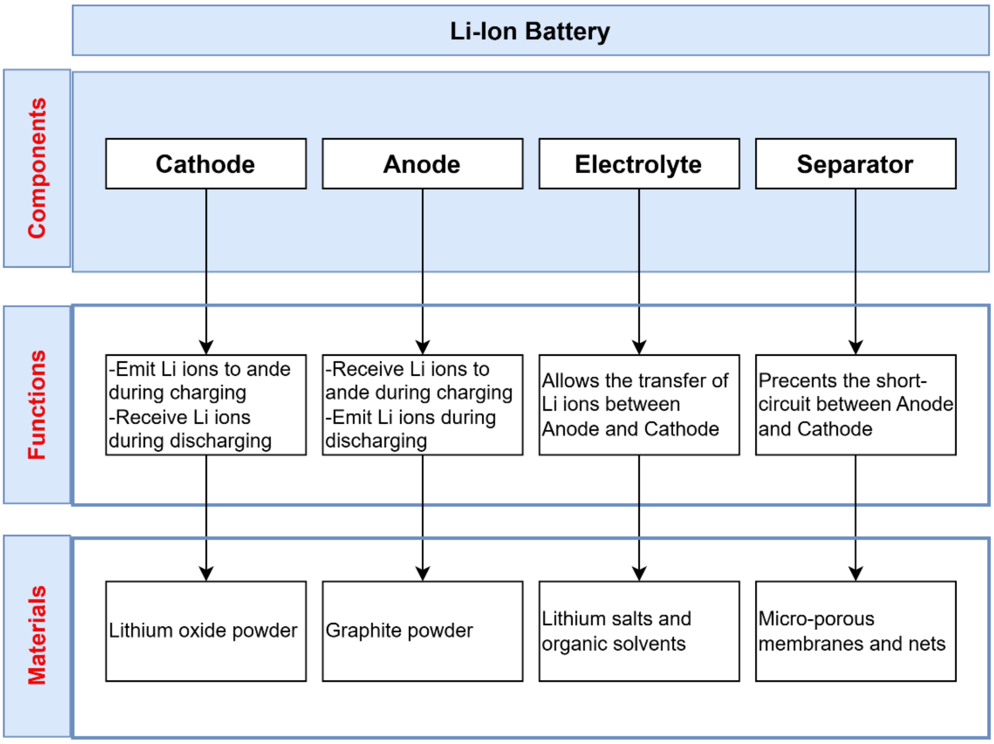

Figure 1. The main EV batteries components, functions and materials

Like all electrochemical cells, a basic Li-ion battery consists of four key components: an anode, a cathode, an electrolyte, and a separator. During discharge, lithium ions from the anode (typically made of carbon) move through the electrolyte and a porous plastic separator into the cathode, while electrons flow from the anode to an external circuit, generating electrical current. During charging, lithium ions move back from the cathode to the anode, enabling the process to repeat. This occurs as part of a REDOX reaction, with electrons leaving the anode to power the external circuit.

Li-ion batteries experience degradation and capacity loss due to various factors. Based on current research, the key contributors to the deterioration of Li-ion batteries include the following, as detailed in [4], [5] and [6]:

1) Deposition of solid Lithium
2) Passive film formation,
3) Crack development and propagation
4) The dissolution of the active material in the electrolyte

2.1.1. Degradation due to deposition of solid lithium

The reduction in battery capacity over time, attributed to calendar aging, is primarily driven by the deposition of lithium ions. This phenomenon occurs as a result of lithium accumulating on the anode, and it is exacerbated by specific environmental conditions. The rate at which calendar aging progresses is significantly influenced by both the temperature and the state of charge (SOC) under which the battery is stored. Elevated temperatures, in particular, have been shown to accelerate the degradation process, leading to more rapid capacity loss. Another crucial factor contributing to the degradation of lithium-ion batteries is lithium plating, which plays a significant role in cycle aging. Lithium plating occurs when lithium metal is deposited onto the surface of the anode rather than being intercalated into its structure. The occurrence of this phenomenon is strongly dependent on two key variables: the intensity of the current flow during charging and discharging cycles, and the operational temperature of the battery [7]. High current rates, as well as lower temperatures, have been shown to accelerate the rate of lithium plating. Paradoxically, although one would expect that lower temperatures might reduce reaction rates according to Arrhenius’ law, the decreased rate of charge transfer away from the electrode at lower temperatures accounts for this acceleration of lithium plating [8], [9], [10].

Additionally, experimental studies have indicated a relatively linear relationship between the cycling behavior of the battery and its overall lifespan within the range extending from the Beginning of Life (BOL) to the End of Life (EOL) [11]. This linear degradation pattern has been primarily associated with two key degradation mechanisms: the loss of lithium inventory and the deterioration of active material in both the anode and cathode. The depletion of available lithium and the degradation of the electrode materials progressively limit the battery’s ability to hold and deliver charge, thereby reducing its overall capacity. This observation highlights the cumulative nature of cycling-induced aging, reinforcing the importance of operational conditions such as current flow and temperature in managing the long-term health of lithium-ion batteries.

2.1.2. Passive film formation

Throughout the process of calendar aging, the impact of passive film formation on battery degradation remains relatively minimal. However, during cycling aging, its influence becomes more pronounced, particularly when combined with the effects of lithium plating. At elevated cell voltages, the oxidation of the graphite anode is primarily driven by the high potentials within the cell, increasing the likelihood of reactions between the electrolyte and lithium ions. These reactions lead to the formation of various species, most notably lithium carbonate, which plays a pivotal role in the development of the Solid Electrolyte Interphase (SEI) layer. This SEI layer is a known contributor to the loss of battery capacity and the increase in internal impedance, both of which degrade the battery's performance over time. [7]. Furthermore, the presence of fluoride ions within the electrolyte, often introduced as impurities, facilitates the formation of lithium fluoride, which also deposits on the anode surface. Simultaneously, similar degradation reactions occurring at the cathode lead to the production of metal fluorides, further contributing to the accumulation of these by-products on the electrode surfaces. These deposits, in conjunction with the SEI layer, collectively contribute to capacity fade and increased resistance within the cell. Interestingly, the formation of the passive film during cycling aging has been demonstrated to occur independently of the specific charging profiles or protocols employed. Rather than being influenced by how the battery is charged, the thickness of this passive layer is closely linked to the number of charge-discharge cycles the battery undergoes. This direct correlation between cycle count and passive film thickness underscores the progressive nature of cycling-induced degradation, reinforcing the importance of operational management to prolong battery life.

2.1.3. Crack formation

During the cycling of lithium-ion batteries, the anode experiences repeated expansion and contraction, a dynamic process that, when combined with gas-generating side reactions, can lead to the propagation of cracks within the passive film layer. This phenomenon is especially prevalent at higher states of charge (SOC) [12]. In addition to SOC, factors such as depth of discharge (DOD), operational temperature, and the number of charge-discharge cycles play significant roles in influencing the extent of crack formation and propagation.

The crack propagation mechanism, driven by the mechanical stress exerted on the anode during these expansion and contraction cycles, provides new pathways for unwanted side reactions to occur. These reactions further degrade the anode and contribute to overall battery capacity loss and performance decline. As cracks develop and grow, they expose fresh surfaces of the graphite anode to the electrolyte, increasing the likelihood of reactions that contribute to the growth of the Solid Electrolyte Interphase (SEI) layer and the deposition of degradation by-products.

A theoretical model, grounded in fundamental crack propagation laws, has been proposed to explain this degradation process. This model has been particularly effective in simulating the aging behaviour of lithium iron phosphate (LFP) cells under real-world driving conditions [12]. By focusing on the mechanical aspects of crack formation and propagation, the model successfully captures the degradation patterns observed during battery cycling, offering valuable insights into how such mechanical stresses accelerate the decline of battery performance.

Ultimately, the development of cracks across the graphite anode not only increases the surface area available for parasitic reactions but also enhances the degradation of the anode structure itself [7]. This synergistic effect accelerates the loss of active material, reduces battery efficiency, and shortens the overall lifespan of the battery, especially under conditions of high stress such as elevated SOC or extreme DOD.

2.1.4. The dissolution of the active material

The active material within the anode undergoes dissolution when ions or solvent molecules penetrate the Solid Electrolyte Interphase (SEI) and engage with the graphite electrode. This interaction contributes to the degradation of both the anode and the SEI, with the effect becoming more pronounced at elevated states of charge (SOCs). Additionally, while the radial architecture of the graphite anode is subject to changes during cycling, these alterations do not significantly impact the aging process of the battery [7].

CONCLUSIONS

This interplay between lithium plating, passive film formation, and the development of the SEI layer illustrates the complex degradation mechanisms at work during the lifecycle of a lithium-ion battery, with each contributing in varying degrees to the overall deterioration of performance.

Improper usage of batteries accelerates the aforementioned degradation processes; however, some of these phenomena also occur during standard operational conditions. The degradation of batteries is a complex phenomenon that poses significant challenges for modeling. It is influenced by the conditions under which charging and discharging occur. For instance, increased depth of discharge (DOD), elevated C-rates, or exposure to extreme temperatures can expedite the degradation process. Furthermore, the overall degradation of a battery pack is contingent upon the condition of each individual cell. Therefore, if a single cell within a battery pack experiences degradation, it can lead to the failure of the entire battery system [9]. When batteries operate under suboptimal conditions, the degradation process is further accelerated, highlighting the necessity of considering degradation factors during optimal operation.

As previously mentioned, two primary contributors to capacity fade include the loss of active lithium at the negative electrode and, more critically, the increase in impedance at the electrodes, primarily due to the growth of the Solid Electrolyte Interphase (SEI). From a macroscopic perspective, battery degradation can be categorized into calendar aging and cycle aging. In the case of cycling degradation, the growth of the SEI leads to an increase in the cell's internal resistance, which subsequently reduces battery capacity.

Calendar degradation is particularly significant in plug-in electric vehicles (PEVs) since these vehicles spend approximately 90–95% of their operational lifespan in a parked state, functioning as storage units [13]. Consequently, both degradation categories—calendar and cycle—must be considered in degradation modeling for smart grid studies.

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