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Review

Review on Aging Risk Assessment and Life Prediction Technology of Lithium Energy Storage Batteries

Zhiwei Liao *, Dongze Lv, Qiyun Hu and Xiang Zhang

School of Electric Power Engineering, South China University of Technology, Guangzhou 510640, China; 202221015523@mail.scut.edu.cn (D.L.); 202321014480@mail.scut.edu.cn (Q.H.); 202321014493@mail.scut.edu.cn (X.Z.)

* Correspondence: epliao@scut.edu.cn

Abstract: In response to the dual carbon policy, the proportion of clean energy power generation is increasing in the power system. Energy storage technology and related industries have also developed rapidly. However, the life-attenuation and safety problems faced by energy storage lithium batteries are becoming more and more serious. In order to clarify the aging evolution process of lithium batteries and solve the optimization problem of energy storage systems, we need to dig deeply into the mechanism of the accelerated aging rate inside and outside the lithium ion from the perspective of the safety and stability of a lithium battery in view of the complex and changeable actual working conditions during the operation of the battery. This paper takes a lithium-iron phosphate battery and a lithium-ion battery as examples to analyze. According to the specific scene of lithium battery operation, the actual operating conditions of lithium battery environmental impact factors and attenuation mechanisms are described in detail. The damage to the internal structure of lithium batteries was systematically analyzed. Furthermore, the correlation between the external influencing factors and the aging rate of lithium batteries under the coupling effect of internal failure mechanisms is analyzed. Finally, future energy storage failure analysis technology is anticipated, hoping to play a positive role in promoting the development of energy storage and lithium battery failure analysis technology.

Keywords: energy storage battery; battery aging; battery life; lithium battery; aging factors

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1. Introduction

The global environmental situation is becoming increasingly severe, with climate warming posing significant challenges to sustainable development. Against the backdrop of the dual-carbon initiative, the stable operation and feasible control of safety risks in new power systems are particularly important. As one of the main technologies that can break through the spatiotemporal application and allocation of power supply and demand and achieve the planning and construction of new energy power systems [1,2], lithium batteries, with their unique advantages of high energy density, high cycling rate, long cycle life, and high response speed, play a pivotal role in new energy storage systems [3]. However, the high chemical reactivity of lithium batteries also poses significant safety hazards. This has led to numerous safety incidents, resulting in property damage and personal casualties [4,5]. Such incidents have severely hindered the development process of lithium batteries.

The lithium battery is coupled with multiple physical fields, such as electricity and heat. It is structurally composed of positive and negative electrodes, electrolytes, separators, and current collectors. Lithium ions are mainly distributed in the positive and negative parts of the battery. During the normal charge and discharge process of the lithium battery, a reversible lithium extraction and insertion reaction will occur. The electrolyte acts as a transmission medium to transport lithium ions in the electrolyte to achieve normal charge and discharge of the battery. The pores on the separator can only pass through lithium ions [6,7], so they play a role in protecting the battery from short circuits and working

normally. The current collector part transports the electric energy and active substances inside the battery, collects the electrons generated by the electrochemical reaction, and transmits them to the external circuit to realize the normal charge and discharge process. The lithium battery life decay mechanism is shown in Figure 1.

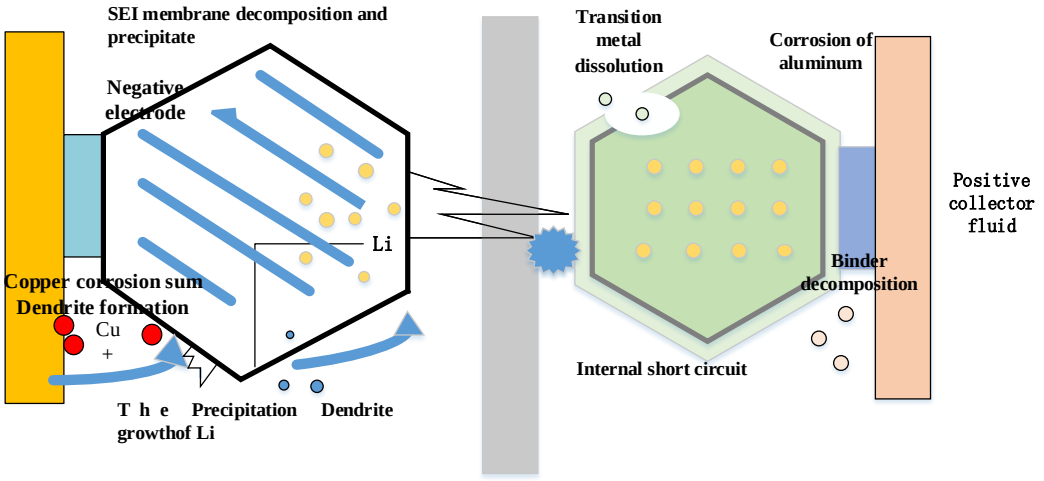


Figure 1. Internal mechanism of lithium-ion battery life decay.

Within the operational time scale of lithium batteries, various components of the lithium battery structure undergo performance degradation and structural changes to varying degrees over extended periods of operation [8,9]. Therefore, it is essential to explore the degradation mechanisms of lithium batteries from their working principles, including the chemical reactions and phase changes that occur throughout their life cycle [10]. A detailed analysis of different aging factors is required to establish a mathematical model for life monitoring. Additionally, the development stage of battery production technology, the shortening of the development cycle, the reduction of warranty and insurance costs, and the assurance of safe and reliable operation during energy storage power station operation all necessitate a comprehensive cycle of energy storage power station health status (SOH) and accurate life prediction for lithium-ion batteries. There has been considerable research on the failure modes of lithium-ion batteries, but most studies only discuss environmental factors or the internal structural material system. In fact, environmental factors, the coupling relationships between the internal materials of lithium-ion batteries, and the evolution of the battery's production and assembly process all have a certain impact on the aging rate of the battery [11–13]. A storage system formed by the series and parallel connection of multiple lithium batteries has more complex structures and more failure characteristics. The reasons for failure and the coupling relationships between environmental factors and the material structure of the battery are also closely and intricately related. Therefore, study of the aging mechanisms throughout the entire life cycle of energy storage power stations is an important step in the development of the energy storage industry.

In this paper, the effects of internal and external factors on the aging of lithium batteries are classified and sorted out. The structural damage mechanism of a lithium-iron phosphate battery and the accelerated aging factors of a lithium-ion battery were analyzed respectively. By analyzing external factors such as environmental temperature, charging rates, and charge–discharge intensities and their impact on internal structural damage and active material loss, this study aimed to provide a detailed explanation of how these factors contribute to the aging and lifespan reduction of lithium batteries. This analysis offers theoretical support for the risk prediction, design optimization, and modeling of lithium-ion batteries.

2. Mechanisms of Lithium-Ion Battery Degradation

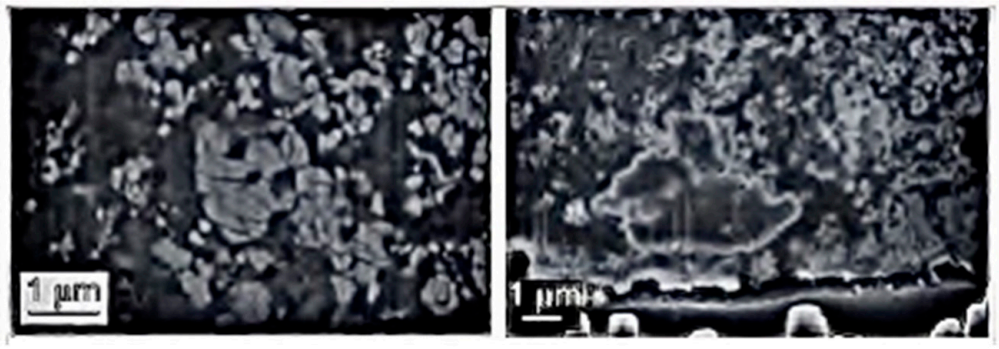
The attenuation of the available capacity of lithium-ion batteries and an increase in the internal impedance of lithium-ion batteries are the external manifestations of the aging of energy-storage lithium-ion batteries. The aging mechanism of lithium-ion batteries has attracted wide attention in the field of electrochemistry due to its certain complexity [14]. In the process of lithium ion charging and discharging, the chemical process produced by the normal operation of a lithium-ion battery will not cause structural damage or a decline in the life of the battery. In addition to the normal charge-discharge chemical reaction, many side reactions are the reasons for the aging of lithium-ion batteries. These side reactions have different effects on the aging of lithium-ion batteries. Because its attenuation mechanism and aging mechanism are related to many physical and chemical processes, its aging situation is very complex. The direct causes of the aging process of lithium-ion batteries can be summarized as the following three aspects: the loss of electrode active materials, the growth of solid electrolyte membranes, and the loss of lithium ions [15].

At present, the battery system in the application field of energy storage power stations mainly includes two kinds, namely lithium-iron phosphate and ternary systems. Due to the long cycle life and high safety of the lithium-iron phosphate cathode, it has become the first choice for large-scale energy storage applications [16]. Therefore, this section mainly introduces the lithium-ion phosphate battery.

2.1. Aging Mechanism of Positive Electrode Structure

In the initial stage of lithium-ion battery decay, the main reasons for the decay revolve around the irreversible loss of lithium batteries and the loss of active materials. The deintercalation/intercalation mechanism of the positive side reaction of lithium iron phosphate batteries is manifested as a two-phase transition of orthorhombic lithium iron phosphate and hexagonal lithium iron phosphate. The unit cell volume of $FePO_4$ is 6.77% lower than that of $LiFPO_4$ after charging a lithium battery [14]. Due to the continuous insertion and migration of lithium ions, the repeated volume changes of the unit cell produce stress accumulation in the particles, which leads to defects in the cathode material. With an increase in the charge–discharge rate, this defect will lead to strong particle cracking, which is manifested by a sudden drop in the electronic conductivity of the electrode, the peeling of the electrode material coating, the loss of overall capacity, and a sharp increase in impedance [17,18]. Based on the structural failure mode, the following analysis methods are adopted, such as XRD, SEM, nano-CT, TEM, etc., to monitor the cell volume change, the degree of microcracks on the surface or cross section of the material, and the dislocation, stress, or strain inside the grain. On the basis of XRD technology, combined with in situ detection technology, the specific process of electrode phase transition and cell volume change can be further obtained.

For the SEM characterization method of directly observing the surface crack information of the material, ion cutting or focused ion beam etching (focused ion beam, or FAB) can be used to obtain an electrode level sheet and the internal crack distribution. The SEM observation results of the cross section of an aged lithium-iron phosphate cathode are shown in Figure 2. The aged lithium-iron phosphate granular interface often cracks. Combined with the multi-layer etching of FIB and the layer-by-layer SEM test, a comprehensive particle structure evolution process will be observed [19]. In addition, related non-destructive testing and analysis techniques use nano-CT as a characterization method to quantitatively analyze the crack of particles and the crack and proportion of three-dimensional structure information in the pole piece [20]. Wang et al. [18] observed by the TEM characterization method that the single crystal lithium-iron phosphate cathode obtained after a 70 °C cycle was transformed into polycrystalline nanoparticles, and the structural defects in the single crystal olivine structure were observed at high magnification TEM.



(**a**) (**b**)

Figure 2. SEM cross-section of lithium iron phosphate anode plate after aging. (**a**) The active material. (**b**) The interface between the fluid and the layer.

2.2. Aging Mechanism of Negative Electrode Structure

The negative copper foil is susceptible to corrosion and may even dissolve as the number of charge and discharge cycles increases. The destruction of the electrode structure after dissolution and the phase transition of the cathode material are also the main reasons for the decline in the life of lithium-ion batteries [21]. The copper ions accumulated on the surface of the active particles of the negative electrode will block the ion channel. During the initial charge and discharge cycle, due to the working potential of the anode active material being outside the voltage window of the conventional electrolyte, some active lithium ions and electrolyte are lost, and an SEI film is formed on the surface of the graphite anode. The generated SEI film can conduct lithium ions but cannot conduct electrons, which hinders the continuous decomposition reaction of the electrolyte on the surface of the graphite anode active material, and thus cannot guarantee the stability of the anode interface during the cycle [19]. The degree of dissolution of the electrode materials will also vary due to the different electrode materials.

The common process determination methods for the dissolution, deposition, and re-dissolution of transition metals can be summarized as follows: ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) is used to determine the content of Fe in the electrolyte and graphite anode, and the detection results can reach the mg/kg level. Surface-sensitive analysis equipment such as XPS (X-ray photoelectron spectroscopy)/TOF-SIMS/s (time-of-flight secondary-ion mass spectrometry) XAS is used to qualitatively characterize the combined state of transition metals deposited on the surface of the negative electrode, in which XPS also has a semi-quantitative analysis function for the Fe content [22–24]. In addition, based on the combination of inert transfer device SEM (Scanning Electron Microscope)/TEM-EDS (Transmission Electron Microscopy Energy-dispersive X-ray spectroscopy), the deposition and spatial distribution of transition metals on the anode surface can be intuitively analyzed [25]. Yao et al. [2] characterized the content of Fe in the anode sheet of a fully charged lithium-iron phosphate battery after storage at a high temperature of 60 °C by ICP-OES. The results showed that the content of Fe in the anode sheet increased gradually with an increase in storage time.

2.3. Battery Aging Mechanism Caused by Other Structural Side Reactions of the Battery

The chemical side reactions on the positive and negative electrodes of the battery lead to an increase in the aging rate of the lithium-ion battery, some of which occur in the electrolyte, and the chemical side reactions on the separator will also catalyze the life of the battery. The long cycle stability and high efficiency of the energy storage battery are not only affected by the component stability, ionic conductivity, and viscosity characteristics of the electrolyte, but are also sensitive to factors such as high temperature and magazine residues. In the general analysis of the aging failure of energy storage batteries, this research focuses on the changes of electrolyte concentration components caused by the

aging of the electrolyte and the impurities of redox products produced by the secondary chemical reaction.

Aiming at the problem of the failure mechanism and aging monitoring of the electrolyte, a battery optimization method can be sought. Firstly, based on the principle of a single/double electron reaction and the decomposition reaction of solvent in electrolyte, combined with the characterization results of NMR (C spectrum/H spectrum), GC-MS (Gas chromatography-Mass Spectrometry) and LC-MS (Liquid Chromatograph Mass Spectrometer), and combined with IC and NMR (Li spectrum/P spectrum/F spectrum), the composition and content of lithium salt in the electrolyte can be tested and analyzed. Thompson [26] et al. qualitatively and quantitatively analyzed the aging of a battery in March, June, September, and December by means of GC and NMR, and found out that in the test cycle of December, more reactants and reaction products had a relatively stable growth rate. Therefore, in most cases, the test results from March to the end of June provide an evaluation reference for the battery status in December. Mönnighoff et al. [27] used supercritical carbon dioxide extraction and GC methods to analyze the composition of the electrolyte in the battery after aging at 20 and 45 °C (the capacity is less than or equal to 70% of the initial capacity) and analyzed 17 different volatile organic aging product reaction formation pathways. In addition, according to the product characteristics of gas and insoluble substances produced by the side reaction of the electrolyte characterized by GC detection and surface interface analysis technology, the adaptability of an electrolyte and electrode system can be judged, which provides a reference for the optimal design of a battery. Sun Xiaohui et al. [28] analyzed the changes of electrolyte components in several process stages of lithium-ion batteries (before liquid injection, after pre-charging, after formation, after high temperature aging) by IC and GC-MS. At the same time, the SEI film on the surface of the anode after formation was analyzed by XPS, and the relationship between solvent decomposition, lithium salt hydrolysis and the formation of gas and SEI formation was expounded.

In view of the high temperature on the battery separator and the oxidation failure under overcharge conditions, XRD, SEM-EDS, XPS, SIMS, FTIR and other analytical equipment are often used to characterize oxidation failure. The damage of oxidation failure generally causes the insoluble by-products of electrolyte and electrode side reactions to block the pore gap. Figure 3 clearly shows that the oxidation reaction of the separator and the by-product plugs the holes allowing them to interact with each other. When the blockage is too much, it will lead to a significant decrease in the kinetic performance. Lu Daban [29] et al. studied the aging of each component after 1444 cycles at 25 °C and 1258 cycles at 55 °C. The results showed that plugging-related side reactions occurred at both temperatures. Zhou [30] et al. analyzed the composition of the negative side diaphragm deposits at different overcharge rates. The results showed that the deposited metal contained the positive transition metal and the group elements in the electrolyte, such as oxyfluorine, which just indicated that the positive transition metal ions would deposit and block after overcharge.

In addition, the current collector, separator and other components will also have other side reactions of the battery. As an ion channel component, the change of porosity will affect the ion transmittance and thus affect the battery capacity [30]. The self-discharge phenomenon of the battery during standing will lead to the attenuation of the lithium-ion battery capacity [31].

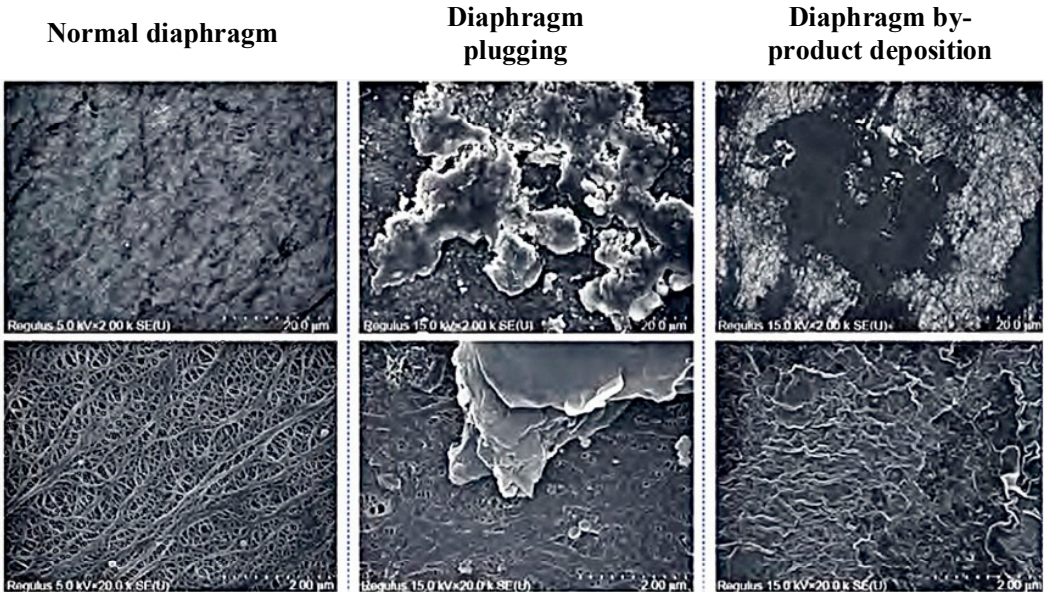


Figure 3. SEM images of the surface of a normal diaphragm and a failed diaphragm.

3. External Factors Affecting Lithium-Ion Battery Life

An energy storage station is a complex power system composed of a large number of battery modules in series and parallel. The external influencing factors of system life attenuation caused by this complexity are also multiple. It mainly includes time, temperature, charge–discharge rate, state of charge (SOC) and so on. These external factors will affect the membrane decomposition of the battery, causing lithium evolution to show different functions and different modes of decline. On the other hand, the difference in different battery module parameters is also the cause of life attenuation of an energy storage system, such as voltage, capacity, current, impedance, and so on. The inconsistency of these state parameters induces an uneven distribution of temperature and an increase of SOC difference during the cycle of the battery, which makes the battery charge and discharge rate and overcharge and over discharge effects lead to the occurrence of safety accidents in energy storage power stations. Therefore, it is of great significance to analyze these factors and study the primary and secondary relations of these influencing factors for the safety of energy storage power stations.

3.1. The Effect of Temperature on the Life of Lithium Batteries

Temperature is a critical determinant in the performance and aging of lithium-ion batteries, exerting a profound influence on their lifespan and operational characteristics. Lithium-ion batteries will exhibit good performance at appropriate temperatures. Generally speaking, an appropriate increase in temperature is helpful to strengthen the discharge capacity of lithium-ion batteries because the viscosity of the electrolyte will generally decrease with an increase in temperature, and the conductivity will also increase. Therefore, the utilization rate of lithium will be fully strengthened [32,33]. However, in addition to increasing the chemical reaction rate of lithium-ion batteries, the increase in temperature will also increase the rate of secondary chemical reactions inside the battery. The duality of temperature effects makes the aging mechanism of lithium-ion batteries more complicated at different temperatures.

The operational temperature range of lithium-ion batteries can be categorized into low temperatures (<0 °C), ambient temperatures (0–40 °C), high temperatures (80–300 °C), and extremely high temperatures (>300 °C). Most lithium-ion batteries operate effectively within an ambient temperature range of −30 °C to 50 °C, with the optimal performance typically observed between 15 °C and 35 °C [34]. To extend battery lifespan, thermal management systems are often employed in energy storage devices to maintain the battery's

operating temperature within this ideal range. Accelerated aging studies are generally conducted at temperatures below 80 °C. Extensive research indicates a V-shaped relationship between aging rate and temperature, as illustrated in Figure 4a. Beyond a certain threshold, the aging rate increases with temperature, whereas below this threshold, the aging rate decreases as temperature rises, highlighting distinct aging mechanisms at high and low temperatures [35,36].

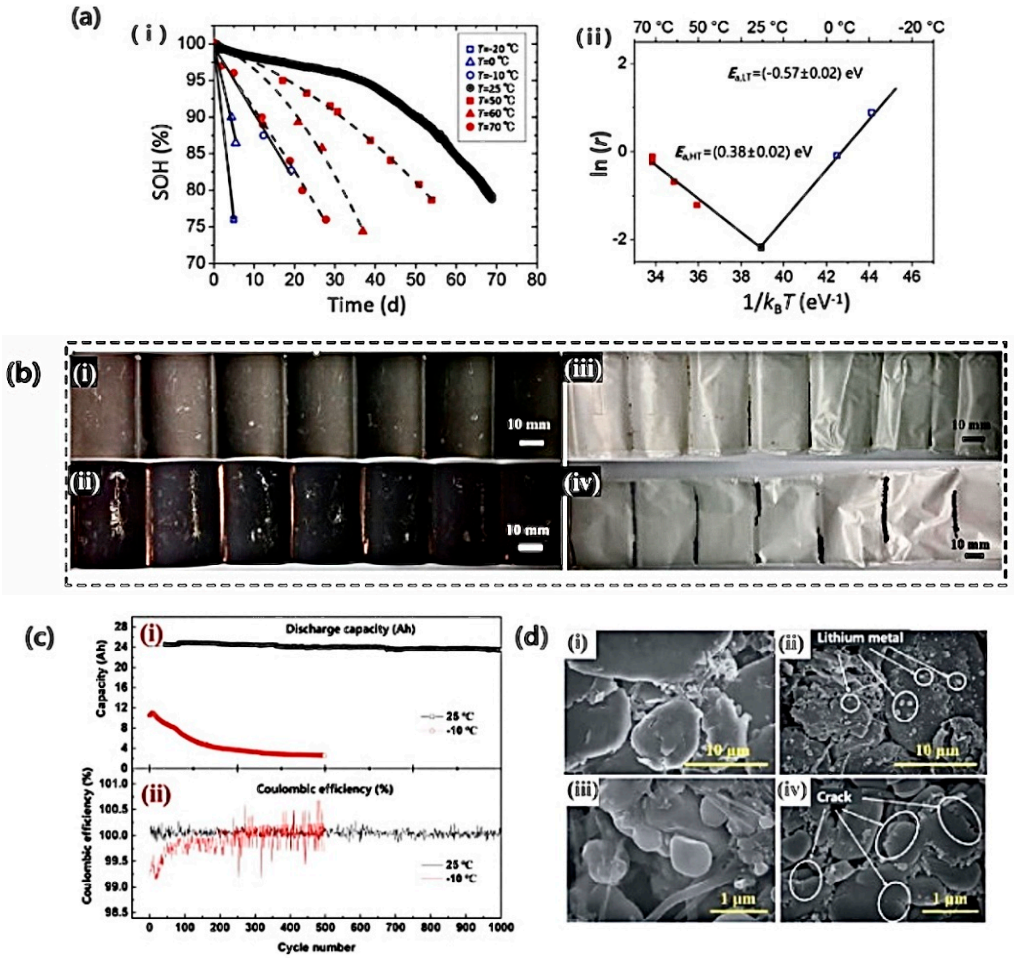


Figure 4. (**a**) (**i**) The SOH curve is measured as a time function of 1 °C and different temperature cycles. (**ii**) Arrhenius diagram of aging behavior of 18,650 batteries cycling at 1 °C in the temperature range −20 to 70 °C [26]. (**b**) Digital photographs of the anode and diaphragm of the full battery aged to 80% at different temperatures. ((**i**),(**iii**)) 25 °C and ((**ii**),(**iv**)) 55 °C. [35] (**c**) (**i**) Discharge capacity and (**ii**) coulomb efficiency of commercial NCM batteries vary with the number of cycles at 25 °C and −10 °C (voltage range 2.7–4.15 V). (**d**) (**i**) SEM images of the new battery and (**ii**) the negative electrode after 500 cycles at −10 °C; SEM images of (**iii**) the new battery and (**iv**) the positive electrode after 500 cycles.

Additionally, temperature will increase the aging rate of lithium-ion batteries by inducing the occurrence of internal side reactions in the lithium-ion batteries. The influence path can be distinguished according to the temperature. The main principle of aging in a continuous high-temperature environment is based on reaction kinetics. High temperature leads to irreversible capacity loss and impedance increase by inducing the growth of SEI films, transition metal dissolution, and electrolyte decomposition [34].

In the electrolyte, LiPF6 will decompose under the conditions of trace water and high temperature to generate hydrogen fluoride, which will corrode the positive surface of lithium-iron phosphate and lead to iron overflow. The iron ions in the electrolyte will promote the growth of a solid electrolyte interface (SEI) film and the deposition of lithium

caused by the lithium evolution effect at high rates of charge and discharge [37]. The chemical composition of the SEI film includes salt degradation products (inorganic components), electrolyte solvents, and active materials for reduction products. The excessive growth of SEI will lead to a large loss of active lithium and an increase in impedance [38].

Furthermore, during the operation of lithium-ion batteries, the gradual reduction of the thermal conductivity of the internal components will cause an uneven temperature inside the battery, that is, a temperature gradient distribution. This temperature gradient will become more obvious with a decrease in temperature. This will also make the current density distribution unevenly distributed and accelerate the aging speed of the battery. In a low temperature working environment, the chemical reaction rate of lithium ions will also slow down. The relationship between the chemical reaction rate and temperature can be expressed by the Arrhenius formula [39]:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

In the above formula, k represents the chemical reaction rate constant inside the battery; A represents the preexponential factor determined by the nature of the reaction; E_a is the activation energy of the chemical reaction; R is the ideal gas; and T is the chemical reaction temperature inside the battery.

Current research on the impact of temperature on battery aging often relies on electro-thermal coupling models to calculate the simulated temperature distribution within the battery. The thermal model of a lithium-ion battery has been widely studied, so the research methods have also been continuously developed from the initial lumped model to the Newman model. The dimensions develop from one-dimensional to three-dimensional models. From a single electrochemical model, electrical model, and thermal model, with the support of COMSOL5.3 and other multi-dimensional software, we advanced to an electrochemical–thermal coupling model and an electrical–thermal coupling model. In different fields, considering the cost of time and money, according to the purpose of this study, the most suitable model was selected. The battery model includes not only the thermal model of the battery, but also the estimation of the SOC of the battery, the heat abuse of the battery, and so on. These are an indispensable part of the battery thermal management model, escorting the performance and safety of the battery.

3.2. Effect of Charging Mode and Charge–Discharge Cut-Off Voltage on Battery Life

The charging process of lithium-ion batteries also has a significant impact on lithium-ion batteries. According to the relevant research results, the charging and discharging cut-off voltages of lithium-ion batteries play an important role in the life attenuation of lithium-ion battery. For instance, if the charging cut-off voltage of a lithium iron phosphate system battery is 4 V, then the aging speed can be greatly reduced by simply reducing the charging cut-off voltage by 0.05 V to 3.95 V. However, this strategy will reduce the available capacity of the battery. This conclusion provides an important reference condition for the fast-charging design of lithium-ion batteries [40].

Zheng [41] et al. set the discharge cut-off voltage of a lithium-iron phosphate battery to 2 V, 1.5 V, 1 V, 0.5 V and 0 V. With 0.5 V as the voltage drop gradient, the effect of the reduction of the discharge cut-off voltage on the attenuation of the energy storage capacity was found after the cycle test. When the discharge cut-off voltage is less than 1 V, the SEI film will generate a small amount of gas, H_2, CH_4, C_2H_6, and so on. According to Figure 5, it can be found that over discharge can significantly accelerate the aging of lithium-ion batteries. Aiming at the acceleration rate of aging, Chen et al. [42] set the over discharge cut-off voltage as a gradient of 0.25 V, and set it to 0.5 V, 0.75 V, and 1.0 V, respectively. The acceleration ratio coefficients of the energy storage battery decaying to 80% of the initial capacity were 3.8, 7.8, and 2.8, respectively.

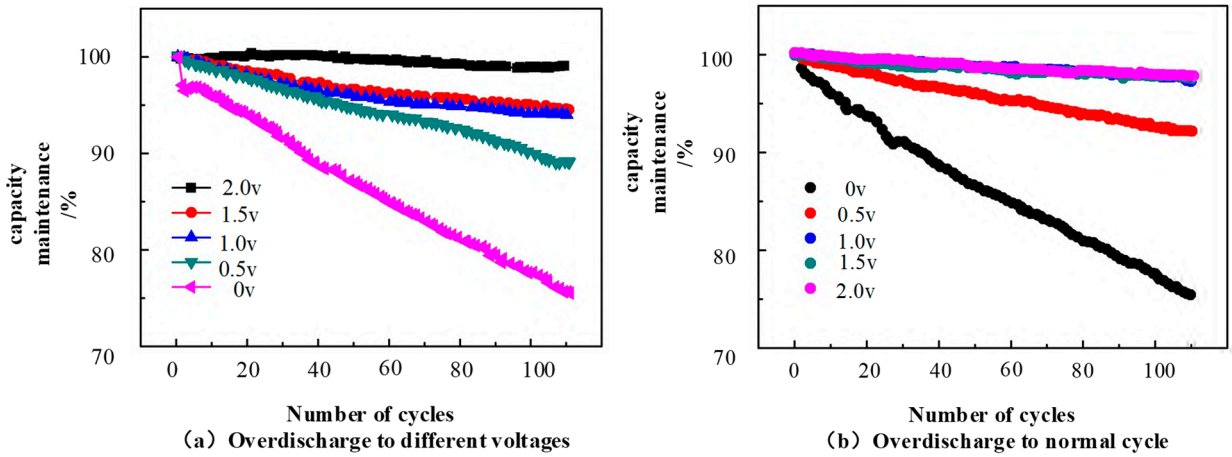


Figure 5. Relationship between the capacity of $LiFePO_4$/graphite battery and the number of cycles.

When the cut-off voltage of the battery is too low, it will accelerate the decomposition of the SEI film of the negative electrode and induce the potential to reach the dissolution potential of the copper electrode fluid. The dissolution of the copper fluid will lead to an increase in the internal resistance of the battery, and a large amount of gas will be generated to cause damage and deformation of the battery. This will affect the safe operation of the energy storage power station [43]. Excessive charging cut-off voltage will aggravate the attenuation of battery capacity and lead to the occurrence of the lithium evolution reaction. This will lead to lithium deposition and lithium ion loss. The precipitated lithium and electrolyte will reduce the efficiency of the battery by side reactions with the battery solvent, and the lithium deposited between the anode and the separator will increase the internal resistance of the battery. Therefore, lithium-iron phosphate batteries with a higher degree of fast charging will have a faster aging rate. The aging degree under the condition of fast charging to 100% is more serious than that under the condition of fast charging to 80% [44].

For the charging method, the charging efficiency of a pulse discharge is often higher than that of classical constant current (CC) charging or constant current constant voltage (CC-CV) charging, and the charging time is often shorter. However, the efficiency of pulse charging is not affected by the pulse frequency, and the increase in pulse frequency will not significantly improve the charging efficiency. The pulse charging method will greatly affect the battery's aging rate. According to the experimental results of Li [45], the pulse charging method will significantly increase the internal resistance of lithium-ion batteries, and the loss of negative active materials detected by technical means is also very obvious.

Lithium-ion batteries also have the risk of thermal runaway, combustion, and explosion under micro-overcharge working conditions. According to the research viewpoint of K. Qian [46], a slight overcharge will deteriorate the decay of lithium-ion batteries (LiNi1/3Co1/3Mn1/3O2,NCM/C), and the cycle life will decrease from 1500 to 500 times. J. L. Liu et al. [47] found that both a high-rate charging environment and a high ambient temperature will induce the risk of thermal runaway through qualitative research on the influence of charging rate and ambient temperature on overcharge thermal runaway. L.L. Zhang et al. [48] found that a slight overcharge also increased the aging rate of the battery through the study of overcharge reactions.

Many current studies focus on the relationship between battery aging performance and the safety issues associated with overcharging. There is relatively little research on the relationship between mild overcharging and the rate of battery aging. Yet, the variability in batteries within energy storage systems makes the occurrence of slight overcharging inevitable, rendering the study of the relationship between slight overcharging and battery aging rate both necessary and significant.

3.3. The Effect of Charge–Discharge Rate on Battery Aging

Excessive current rates have detrimental effects on the active materials of lithium-ion batteries, such as fracture and dissolution of binders. These internal side reactions in batteries can be characterized using Peukert's law [49]. The specific principle is as follows:

$$\frac{da}{dN} = C(\Delta k)^m \tag{2}$$

In the above formula, a is the size of the porous particles in the positive and negative electrode materials of the lithium-ion battery; N is the number of cycles, and its size is often related to the charge and discharge cycle of the battery; k is the amplitude of the stress intensity factor, also known as the current ratio, C; and m is the correlation coefficient of the positive and negative active materials.

The capacity attenuation of a lithium-ion battery caused by an excessive current rate is mainly reflected in its influence on its internal resistance. An excessive current charge and discharge rate lead to an increase in ohmic internal resistance and polarization internal resistance. In these two kinds of internal resistance, the growth rate of polarization resistance is higher than that of ohmic resistance. The effect of the charge–discharge rate on the aging of the battery pack is often related to the battery capacity. Generally, for small-capacity batteries, the number of cycles at high charge and discharge times will be more than that of large-capacity batteries. More cycles lead to extremely frequent charging and discharging processes, which in turn accelerate the capacity decay of the battery. Excessive power consumption caused by excessive replay will also make the heat problem more prominent, resulting in safety problems.

Dubarry [50] changed the charge–discharge rate to carry out an aging test of a load cathode lithium-ion battery. The test results showed that a high rate of charge–discharge will indeed accelerate the decline of battery life. The aging process can be summarized in two stages. The first is the loss of active lithium ions from the surface of the negative electrode, and the second stage is the loss of active electrode materials. Cheng et al. [51] found that the capacity loss will increase with an increase in the number of cycles by studying the aging characteristics of lithium-ion batteries, and structural damage of the cathode material to the SEI film formation of the anode often occurs during the aging process. Barcellona and Piegari [52] used Peltier to suppress the change in the charge and discharge temperature and found that when the current rate and SOC were constant, the battery rate was not directly related to battery aging. Yang et al. [53] discussed the relationship between battery performance degradation and cycle times by establishing an electrochemical thermal coupling model considering side reactions. They believed that the increase in cycle times would not blindly change linearly, and the later nonlinear accelerated aging was due to the lithium evolution phenomenon generated inside the battery. Wang et al. [54] studied the capacity decay and impedance changes of two groups of lithium-ion batteries at different charging rates (0.5 C and 1.0 C). He selected four groups of batteries with a nominal capacity of 0.56 Ah and a rated voltage of 3.7 V, and numbered them 1, 2, 3, and 4. Cycle experiments were performed in pairs at 0.5 C and 1 C charging rates. It was found that a high charge rate made the reduction reaction time longer. It also increased the consumption of active lithium (Figure 6), accelerated the formation of an SEI film on the surface of the negative electrode, increased the internal resistance of the battery, and obviously accelerated capacity attenuation.

In addition, a high-rate charging and discharging process also promotes the rapid expansion and contraction of the electrode volume, which can aggravate the structural rupture and aging of the electrode material.

By studying the capacity, AC impedance and open-circuit voltage characteristics of lithium-iron phosphate batteries at different discharge rates, Tang Jin [55] et al. obtained the variation law of each characteristic under different discharge rate cycles: the open-circuit voltage of the battery is greatly affected by the discharge rate of the battery at the later stage of the cycle, and the higher the discharge rate, the faster the open-circuit voltage

decreases. There is a significant correlation between the discharge rate and the discharge energy and heat of the battery. At high rates, the battery emits less energy, generates more heat, accelerates aging, and reduces service life.

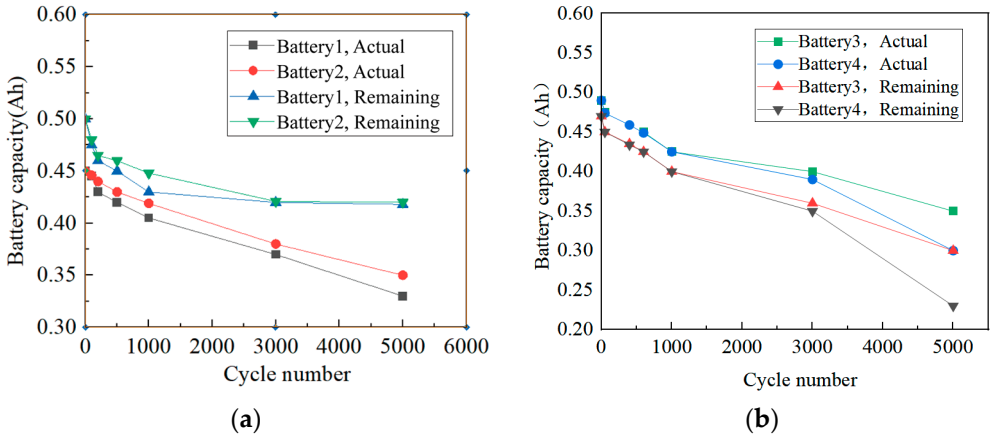


Figure 6. Attenuation curves of actual capacity and residual capacity of lithium batteries at 0.5 and 1.0 C aging rates. (**a**) 0.5 C. (**b**) 1 C.

3.4. Influence of Internal Differences on Battery Aging

An energy storage system is composed of a large number of lithium-ion batteries in series and parallel. Due to the difference in the manufacturing process and material in the manufacturing process, the battery cell will experience a difference in battery voltage, internal resistance, and capacity. Under the complex working conditions faced by the entire energy storage system, these differences in impedance, capacity, and cut-off voltage will accelerate the life attenuation of the battery. Therefore, the safety and stability of the energy storage system will be reduced.

When the cut-off voltage is inconsistent, a cell with a lower voltage at the discharge end will reach the cut-off voltage earlier and be completely empty, while other cells that do not reach the cut-off voltage will still have a certain capacity that does not reach the empty state. Studies have shown that the discharge behavior in low SOC states has a significant effect on battery life. The aging rate of the battery under full discharge will be much higher than that of other batteries. There is a strong correlation between the system differences and monomer differences of lithium-ion batteries. The life of the entire system depends on the service life of the single cell with the shortest life. The inconsistency of these designs and the complexity of the operating conditions lead to different physical capacities for each cell. Long-term, deep discharge life will be significantly shorter. According to Ziberman et al.'s differential voltage method, the aging characteristics of a series lithium-ion batteries were studied. The results showed that a temperature gradient of 5 °C will lead to a difference in battery aging speed, resulting in an obvious attenuation of battery capacity and performance degradation [56].

3.5. Analysis of Accelerated Aging of Life under Multiple Factors

Up to now, there is still a lack of unified related concepts for an accelerated aging test. In various studies, accelerated life testing often includes various experiments that reduce the experimental life and promote product degradation. Extremely harsh experimental conditions are used to obtain product information faster. Therefore, in a relatively short period of time, it should be ensured that the high stress conditions used in the test of the product are consistent with the attenuation principle under low stress conditions.

Jia and Li [57] considered the influence of the dual effects of current and temperature on the life of lithium-ion batteries. After the current model was constructed, the temperature was modified, and a two-factor acceleration model of temperature and current coupling was established. According to the related research, heating and increasing the discharge

current play a positive feedback role in the accelerated aging of the battery. Ecker et al. [58] studied the attenuation of battery capacity with storage time under different SOC (20%, 50%, 80%, and 100% SOC) and different ambient temperatures (25 °C, 35 °C, 50 °C, and 65 °C). The results show that SOC and storage environment temperature are related to battery capacity attenuation and have a linear relationship. Wu et al. [59] studied the acceleration effect of charge and discharge cut-off voltage, charging current and temperature on battery attenuation. They used 106,495 commercial 5 Ah soft-packed lithium-ion batteries in a single cell cycle life experiment. The reason for the rapid decay of the worst single cell life in the battery pack was analyzed. They carried out battery cycle life experiments at different charge and discharge cut-off voltages (3.00 V, 2.50 V, and 2.20 V), different temperatures (0 °C, 20 °C, and 60 °C), and different charge and discharge rates (1.0 C, 1.10 C, 1.30 C, and 1.50 C). The results showed that the charge–discharge cut-off voltage accelerates the battery life attenuation by 200%, the temperature accelerates the battery life attenuation by 140%, and the charge–discharge rate accelerates the battery life attenuation by 115%. That is, the higher the charging cut-off voltage, charging current and temperature, the lower the discharge cut-off voltage and the faster the battery capacity decays.

Kassem et al. [60] investigated the impact of ambient temperature on the capacity fade of batteries at various states of charge (SOC). When stored at approximately 30 °C for eight months, the capacity fade of the batteries was not significant. However, at around 45 °C, the coupling relationship between SOC and capacity change became more evident, though the overall fade remained minimal. At 60 °C, the capacity fade became markedly more pronounced, with a reduction to 80% of the nominal capacity after six months of storage. Wang et al. [61] studied the degradation of lithium-ion batteries subjected to cycling aging under different ambient temperatures, depths of discharge, and discharge rates, finding that at lower charge rates, the degree of capacity fade is highly correlated with cycle time and ambient temperature. Su et al. [62] utilized the orthogonal experimental method to examine 18 experiments, elucidating the relationships between environmental temperature, constant current charge current, charge cut-off voltage, constant voltage charge time, constant current discharge current, and discharge cut-off voltage with the aging rate of lithium-ion batteries. They compared the main effects of each influencing factor and weighted them to identify the primary cause of battery aging. Cui et al. [63] concluded from orthogonal experiments that temperature is the predominant factor in the degradation of lithium battery life. Li [64] delved deeper into the coupled effects of multiple influencing factors. He integrated environmental temperature, charge and discharge rates, and charge and discharge cut-off voltages into a comprehensive consideration, designing experiments with single and pairwise combinations of these stress conditions and applying them to lithium iron phosphate batteries. By comparing the aging effects of single and dual stress factors, he found that any two aging factors exhibit some coupling phenomena, but with varying intensities and no discernible pattern. The coupling mechanism of dual factors is highly complex and has not yielded quantitative results. A comparison of different aging models is shown in Table 1.

Table 1. Comparison of different aging models.

Type	Theoretical Basis	Advantage	Shortcoming	Ref
Mechanism model	Porous electrode theory Matter conservation equation Current conservation equation Side reaction mechanism	The principle is clear and helps to understand the nature of battery aging	There are many parameters and comp-licated calculations, and the correctness and accuracy of the model are difficult to verify	Doyle [65] Safari [66–68]
Semi-empirical model	SEI film growth mechanism speed control theory	The model is simple, the model parameters are few and easy to understand, and can describe the main mechanism of the internal aging of the battery	The rationality of the hypothesis lacks verification, and the accuracy of the model is reduced to some extent	Ramadass [69] Polehn [70]
Empirical model	Research experience Statistical method Experimental design method	With few parameters, the model is simple and easy to use to estimate the variation of off-cell characteristics	The variation of out of pool char-acteristics requires the support of a large amount of experimental data	Wright [71] Bloom [72–74]

4. Real Data and Life Prediction Research Model Research Technology

The relationship between the influencing factors and the aging characteristics of lithium-ion batteries is called the accelerated aging model of the battery. The modeling of the aging characteristics of the battery's full-cycle life fading mechanism is the essence of predicting the battery life. In the process of establishing the model, it is necessary to consider the differences in battery characteristics under different aging conditions and analyze the change mechanism of its internal parameters. So far, there are three lithium-ion aging models, namely an empirical model, data-driven model and electrochemical model [75,76]. The flow chart for model construction is shown in the following figure (Figure 7).

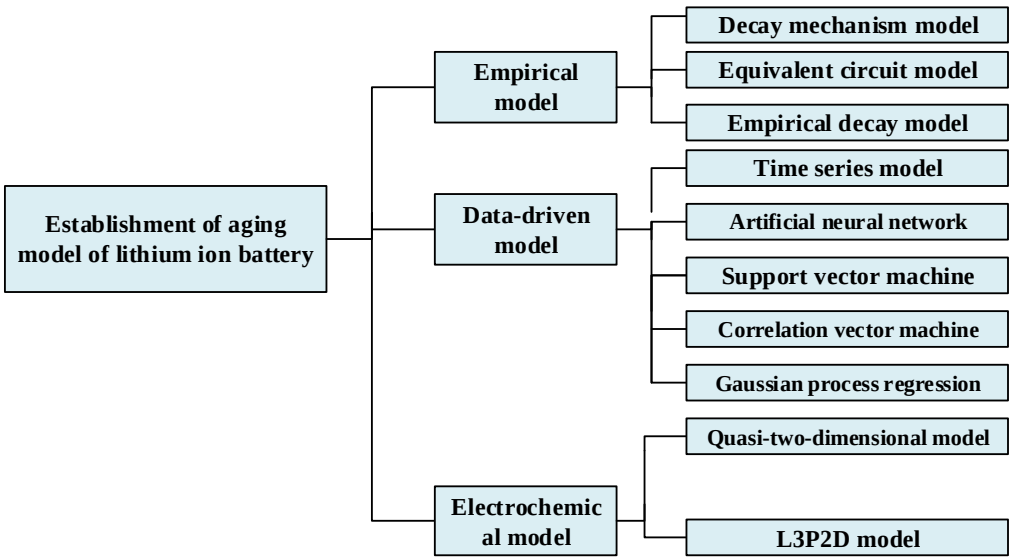


Figure 7. Flow chart of lithium-ion battery aging model construction.

The construction of the empirical model first needs to fit the actual attenuation curves of a large number of lithium-ion batteries under different aging paths to accurately predict the remaining life of the battery [77]. However, the accuracy and environmental adaptability of the model are relatively poor. In the fitting process, the aging process inside the lithium-ion battery and the lithium-ion change process from the microscopic perspective cannot be considered, so it is generally only applied to the online operation of the embedded system. The data-driven method is similar to the empirical model method. The difference is that the data-driven method uses a large database to extract aging features, and then realizes the aging state estimation of lithium-ion batteries. The accuracy is relatively high, but its implementation requires the construction of a full life cycle database. The dependence of the test data, experimental data, and driving data is very high. A series of mathematical partial differential equations are needed to describe it to achieve microscopic parameter evolution [78] to achieve life prediction.

The method based on the data-driven model often constructs the relationship model of lithium-ion aging for the environmental factors of lithium-ion battery aging, which avoids the complexity of model construction to a certain extent and is a hot topic in the research of lithium-ion batteries in recent years. Long et al. [79] proposed a method for predicting the remaining useful life of lithium-ion batteries based on an improved autoregressive (AR) model based on particle swarm optimization (PSO). Liu et al. [80] proposed the use of a nonlinear degradation autoregressive model when predicting the cycle life of the battery where the particle filter (PF) algorithm is integrated. When verifying this method, the experimental results of lithium-ion battery test data from NASA and CALCE (University of Maryland Life Cycle Engineering Center, College Park, MD, USA) were used. The results

showed that the proposed fusion prediction method can effectively predict the remaining life of the battery, and the prediction results are more accurate.

For the electrochemical model that uses an electrochemical mechanism to describe the aging process of lithium-ion batteries, due to the limitation of the calculation method and accuracy of the model, various types of partial differential equations are usually included. Aiming at the problem that the SEI film is formed by the deposition of the product of the reaction between pure lithium and electrolyte in the sub-electrochemical reaction of the negative electrode, Pang et al. [81] proposed a simplified model for the formation of SEI film on the surface of electrode materials. First, according to the internal situation of the lithium ion, it is assumed that the growth rate of the SEI film follows a quadratic curve. With an increase in the number of cycles, his mathematical model is as follows (3). Singh et al. [82] also proposed a similar equation to analyze the growth process of SEI. Based on the particle model, LIU et al. [83] constructed a calculation model of SEI film overpotential (4) as follows:

$$\frac{d\delta_f}{dt} = -\frac{J_s^- M_f}{\rho_f} \tag{3}$$

$$\eta_i = \frac{RT}{0.5F}\text{asinh}\left(\frac{j_i}{2d_{0,i}}\right) \tag{4}$$

$$d_{0,i}(t) = Fk_i\sqrt{C_e(t)C_{s,i}(t)(C_{max,i} - C_{s,i}(t))} \tag{5}$$

In the above formula, δ_f is SEI film thickness; J_s is the growth current density; M_f is the molar mass of SEI film product; ρ_f is the average density of the SEI film; R is the ideal gas constant; T is the temperature; F is Faraday's constant; j_i is the reaction current density; k_i is the reaction rate constant; C_e is the ion concentration in liquid phase; C_s is the concentration of ions in solid phase; and a is the exchange current density.

In view of the lithium evolution aging factors of the negative electrode, especially the lithium evolution reaction caused by the mild super-rate fast charge during fast charge, Koleti et al. [84] constructed an equivalent model to obtain the spatial state model of lithium evolution reaction, which can predict the occurrence of lithium evolution reactions based on the embedded system. Von Lüders [85] obtained the equation of lithium dendrite growth and ablation based on the lithium evolution potential and studied the precipitation and decomposition of lithium in detail. The core calculations are shown in Equations (6) and (7). The model and its extended model are widely used [86,87]. In addition, incremental capacity analysis and voltage difference analysis can also be used for lithium evolution detection and aging prediction [88,89].

$$i_{1pl} = i_{0,pl}(exp(\frac{\alpha_{a,1pl}F}{RT}\eta_{1pl}) - exp\left(-\frac{\alpha_{c,1pl}F}{RT}\eta_{1pl}\right)) \ (\eta_{1pl} \le 0) \tag{6}$$

$$i_{1pl} = i_{0,pl}\left(exp\left(\frac{\alpha_{a,1pl}F}{RT}\eta_{1pl}\right) - exp\left(-\frac{\alpha_{c,1pl}F}{RT}\eta_{1pl}\right)\right)\frac{q_{1pl} - q_{1st}}{q_{1pl,max}} \ (\eta_{1pl} > 0) \tag{7}$$

In the formula, α is the charge transfer coefficient; η_{1pl} is the lithium overpotential; q_{1pl} is the number of reversible lithium depositions; and q_{1st} is the number of free lithium ions.

5. Challenges in Lithium-Ion Battery Life Cycle Life Prediction Technology

As the capacity decay mechanism and life aging mechanism of lithium-ion batteries have been thoroughly studied by relevant researchers at home and abroad, a relatively complete theoretical system of lithium-ion battery degradation has been formed. However, there are still some difficulties to be solved in the related research on the structural damage and influencing factors of lithium-ion batteries.

5.1. Differences between Energy Storage Batteries and Other Batteries

The application of energy storage lithium-ion batteries is more and more extensive, and the difference between them and power batteries is becoming more and more obvious. There are great differences in the design capacity, volume, life and energy density of these batteries. Their specifications and battery safety prevention methods are also very different. Therefore, the life prediction model of a power battery has poor robustness in an energy storage system. Some comparisons between them are shown in Table 2.

Table 2. Comparison between power battery and energy storage battery.

Influencing Factor	Power Battery	Energy Storage Battery (User Side)	Energy Storage Battery (Power Side)	Energy Storage Battery (Grid Side)
Cooling mode	Liquid cooling	Nature	Natural/air cooled	Air cooled
Consistent regulation	Harder	Easiness	Difficult	Difficult
Unit price of capacity	Middle rank	Low	High	High
Placement position	Move	Immobilization	Immobilization	Immobilization
Decommissioning capacity	80%	60%	60%	60%
Energy density	High	Middle rank	Low	Low

5.2. SEI Membrane Composition Problem

Current research on the solid electrolyte interphase (SEI) membrane remains somewhat limited, particularly in terms of the membrane's composition and the quantification of lithium-ion consumption during its formation and decomposition processes. The SEI membrane comprises inorganic components such as Li_2CO_3, LiF, Li_2O, LiOH, and organic components like $ROCO_2Li$, ROLi, $(ROCO_2Li)_2$, among others. The proportions of these components, their formation mechanisms, and the chemical reaction processes involved are not yet well understood. This lack of clarity hinders the realization of SEI membrane formation, control, and thickness prediction.

5.3. Differences between Actual Operation Data and Theoretical Cycle Data

The current research work has data defects that cannot be ignored. The quality of the data and the lack of verification data have a decisive impact on the life cycle life prediction of the ion battery. In real working conditions, operating stress conditions can change throughout the life cycle of the battery, such as seasonal temperature differences and differences between the batteries in the battery pack. Different SOC windows, charging and discharging current and power will affect the battery's aging more or less. In addition, the differences between batteries in the battery pack or module, low sensor accuracy, noise, data loss or error, and rapidly changing current make it very challenging to extract battery features or fitting parameters. These factors also limit the identifiability of physical models and data-driven models.

6. Conclusions

In this paper, the aging mechanism of energy storage lithium batteries in energy storage systems is systematically analyzed. Starting from the failure mechanism of the internal structure of the battery such as positive and negative electrodes, separators, and electrolytes, and then moving to environmental factors such as temperature, charge and discharge rate, charge and discharge cut-off voltage, charge and discharge rate, and charge and discharge methods, the aging rate of energy storage lithium batteries is introduced in detail. It can be seen that energy storage lithium batteries are still constrained by cycle life and safety issues. It is necessary to make breakthroughs in the reliability, safety, and extended use of energy storage lithium batteries from the time scale of production, work and scrap. Some environmental factors corresponding to the specific failure structure of energy storage lithium batteries were found. Research on the aging mechanism of the battery and the analysis of the coupling relationship between the aging of the internal

material structure and the environmental factors have far-reaching significance for the establishment of an accurate capacity degradation model of energy storage lithium batteries and a prediction model of the remaining life and aging rate. It provides an important theoretical reference for an optimization strategy to improve the safety and stability of energy storage power stations.

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