

A review on the key issues of the lithium ion battery degradation among the whole life cycle



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ABSTRACT

The lithium ion battery is widely used in electric vehicles (EV). The battery degradation is the key scientific problem in battery research. The battery aging limits its energy storage and power output capability, as well as the performance of the EV including the cost and life span. Therefore, a comprehensive review on the key issues of the battery degradation among the whole life cycle is provided in this paper. Firstly, the battery internal aging mechanisms are reviewed considering different anode and cathode materials for better understanding the battery fade characteristic. Then, to get better life performance, the influence factors affecting battery life are discussed in detail from the perspectives of design, production and application. Finally, considering the difference between the cell and system, the battery system degradation mechanism is discussed.

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1. Introduction

The lithium-ion battery is one of the most commonly used power sources in the new energy vehicles since its characteristics of high energy density, high power density, low self-discharge rate, etc. [1] However, the battery life could barely satisfy the demands of users, restricting the further development of electric vehicles [2]. So, as shown in Fig. 1, the battery aging mechanism and the impact of battery degradation should be considered to optimize the battery design and management.

From the perspective of the battery design, in the cell level, the battery aging mechanism and the degradation model need to be studied, especially the influence of the battery key parameters on the battery on battery life and other key characteristics parameters such as energy density and power density needs to be discussed. Here the key parameters include the anode and cathode active material thickness, porosity, particle size, cell scale, cell shapes, etc. Then, these parameters could be optimized based on the multi-objective optimization algorithms to design better cells with

improved life. In the battery system level, the battery aging mechanism and the degradation model are also very important. The influence of the electrical, mechanical and/or thermal factors on the battery life needs to be analyzed based on the aging mechanism and degradation models. Then to guarantee the battery system's life, the design of the battery system could be optimized including cell preload, battery thermal management system (TMS).

From the perspective of battery management, the battery aging mechanism and the degradation model are also very important to do the estimation of the battery health influenced by the history, optimization of working condition in the present, and predication of the performance in the future.

(1) Generally, estimation of the battery health influenced by the history is also called as state of health (SOH) estimation. Usually the battery performance, such as available capacity, available energy and available power, will degrade with the battery ages. So the BMS (battery management system) needs to estimate the battery SOH based on the aging mechanism and the battery degradation model. The result is very important for the other estimation algorithms in the BMS as an important input. Based on the SOH result, the battery could be used properly without abuse and safety accidents. (2) Generally, optimization of working condition in the present means the SOP(state of power) estimation and the thermal management. Of course, different operating conditions have different effects on

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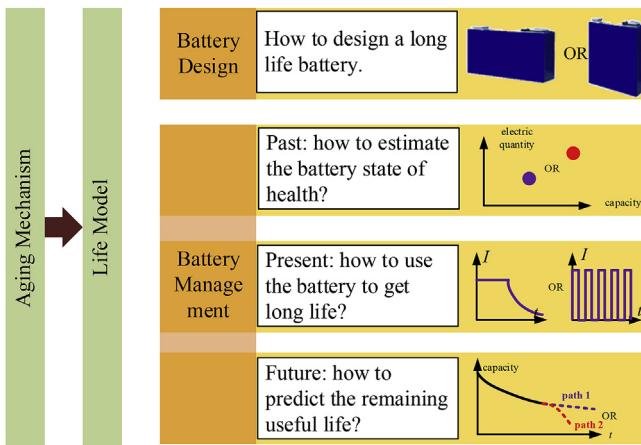


Fig. 1. Battery design and management issues based on the aging mechanisms and life model.

the battery future life. Therefore, based on the aging mechanism under different working conditions and the corresponding battery degradation model, the BMS could predict the damage caused by different working conditions. Then the BMS could coordinate the charging, discharging and the temperature of the batteries based on the life and performance analysis using online optimization methods. (3) Generally, predication of the performance in the future means the RUL (remaining useful life) prediction. The RUL is very useful for the battery online management, used car evaluation and battery echelon use, especially important for the battery residual value evaluation. Considering the nonlinear fading characteristics of the battery, the conventional extrapolation method cannot accurately predict the remaining life of the battery. It is necessary to realize the reliable prediction based on the dominant aging mechanism and corresponding battery life model under various working conditions and different fading stages.

It can be seen from a systematic perspective that, to solve a series of battery design and management problems related to the battery aging, the current researches related to battery degradation need to be reviewed, summarized and analyzed, including the influencing factors, aging mechanisms, degradation models and diagnostic methods. However, the existing review papers are mainly focus on a typical point. Some papers focus on the mechanism. Vetter [3] gives a comprehensive review on the ageing mechanisms of lithium ion batteries with carbonaceous anodes and lithium metal oxide cathodes, mainly lithium manganese oxides (LiMn_2O_4) and lithium nickel cobalt mixed oxides [$\text{Li}(\text{Ni},\text{Co})\text{O}_2$]. Li [4] gives a comprehensive review on one typical aging mechanism: lithium deposition. Some focus on the model. Santhanagopalan [5] gives a review of models for predicting the cycling performance of lithium ion batteries. Wang [6] gives a detailed review on the modeling of solid electrolyte interface (SEI) film. And some focus on the management method, Farnmann [7] and Berecibar [8] give some critical reviews on the state of health estimation methods of the batteries.

The battery whole life cycle includes battery design, production, EV application and second life application, as shown in Fig. 2. The battery performance degradation should be considered in the earliest battery design steps. And in the different stage, the battery degradation phenomena and the internal aging mechanisms may be very different.

From a systematic perspective, we would like to give a comprehensively review on the key issues related to the battery degradation in this paper including the following items: the battery internal aging mechanisms and external characters, the influence

factors affecting battery life from the perspectives of design, production and application, battery degradation models, and the aging mechanism as well as aging model of battery systems.

Generally, the battery aging analysis should be carried out on several levels including the influence factors, internal side reactions, degradation modes and external effects as shown in Fig. 3 [9]. The most intuitive external characters of battery degradation are capacity fade and/or power fade [10,11]. At present, most of the papers still focus on these two points to do the battery aging investigation and modeling. It should be noticed that usually the power fade is more difficult to investigate and the internal resistance would be investigated instead [12].

About the degradation modes, for battery management and online diagnosis, the aging mechanism of the battery can be summarized as [13–15]: loss of lithium ion inventory (LLI) and loss of anode/cathode active materials (LAM). As shown in Fig. 4, the dual-tank model could be used to describe the corresponding aging mechanism [16]. Generally, the battery charging and discharging processes are essentially related to the lithium ion intercalation and deintercalation on the anode and cathode active materials. So, the battery capacity is directly determined by the amount of the active materials and the available lithium ions. The active material is just like the tank, and the lithium ions are just like the water in the tank as shown in Fig. 4. Therefore, the main aging mechanisms of lithium ion batteries are LAM which is just like the change of the tank itself, and LLI which is just like the loss of water in the tank [14]. In addition, the battery degradation mode also includes the internal resistance increase (RI) and loss of electrolyte (LE). The internal resistance increase may directly lead to the battery power fade of the battery, and the battery available capacity would also decrease as the charge and discharge cut-off voltage stay constant. The loss of electrolyte, including the loss of the additives, is also a very important degradation mode. A small amount of electrolyte loss may have little effect on the battery performance. However, too much electrolyte loss may directly lead to the capacity diving at the end of the battery life.

And inside the battery, those degradation modes are caused by some internal physical or chemical side reactions. And it could be found that the aging related side reactions are very complicated and maybe even coupled. The LAM may be caused by: graphite exfoliation; metal dissolution coupled with the electrolyte decomposition; active materials loss of contact due to the current collector corrosion, binder decomposition and LE. And the LLI may be caused by SEI(solid electrolyte interface) film formation and continuous thickening, CEI (cathode electrolyte interface) formation, lithium deposition, etc. The LE may be caused by electrolyte consumption due to the side reactions like SEI film thickening, electrolyte decomposition due to the high potential, etc. And the RI may be caused by SEI formation and continues thickening, LE, etc.

And it could be found that there are many factors affecting the side reactions inside the battery, including factors during the battery design, production and work conditions. All these factors could influence the battery internal side reaction rate, then affect the battery life characteristics. Thus those factors should be discussed in detail.

The following parts of this paper are as follows: In section 2 the internal aging mechanism would be discussed, section 3 will focus on the battery degradation characteristics and the influencing factors, then the specific aging mechanism of the battery pack would be shown in section 4 and the chapter 5 is a summary.

2. Battery aging mechanisms

To clearly describe the battery degradation characteristic and the corresponding internal aging mechanism, this section will first

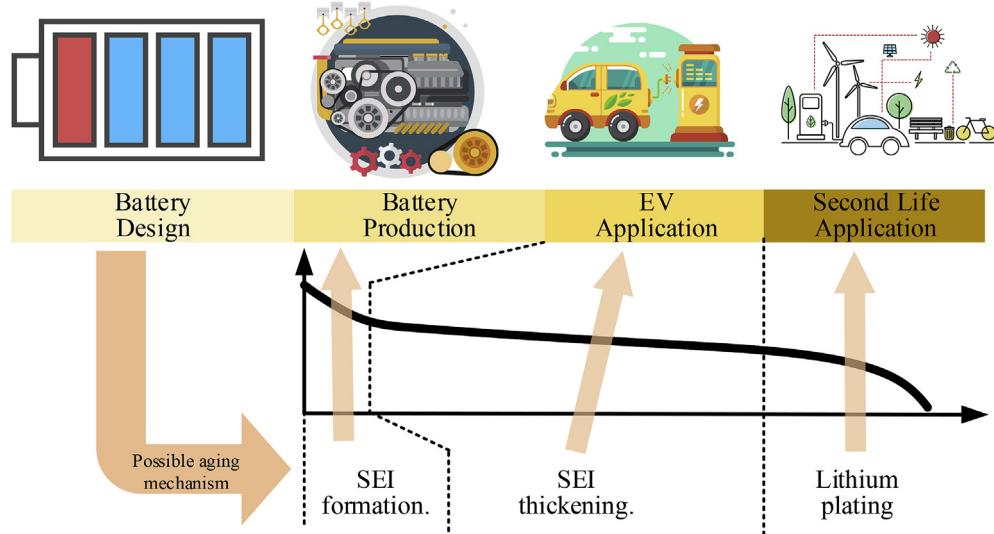


Fig. 2. Battery whole life cycle: design, production, EV application and second life application.

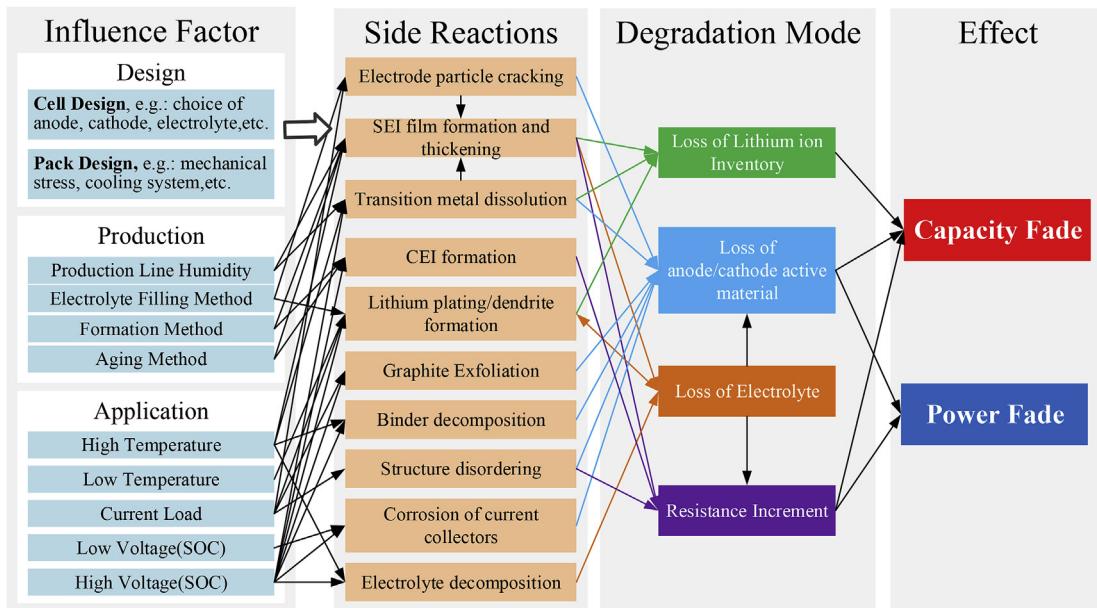


Fig. 3. Cause and effect of degradation mechanisms and associated degradation modes [9].

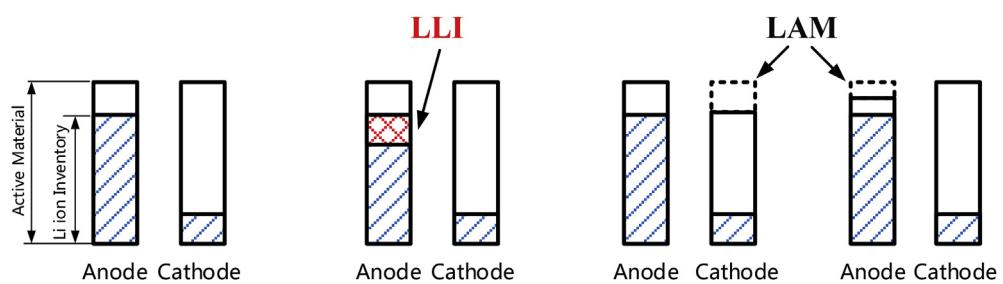


Fig. 4. Dual-tank model.

briefly introduce the cathode and anode materials commonly used in the lithium ion power batteries. Then the main physical and chemical side reactions inside the battery would be analyzed in

detail. An overview of these main side reactions is shown in Fig. 5. Since the side reactions are highly related to the materials, in section 2.1 and 2.2 the side reactions occurring at anode and cathode

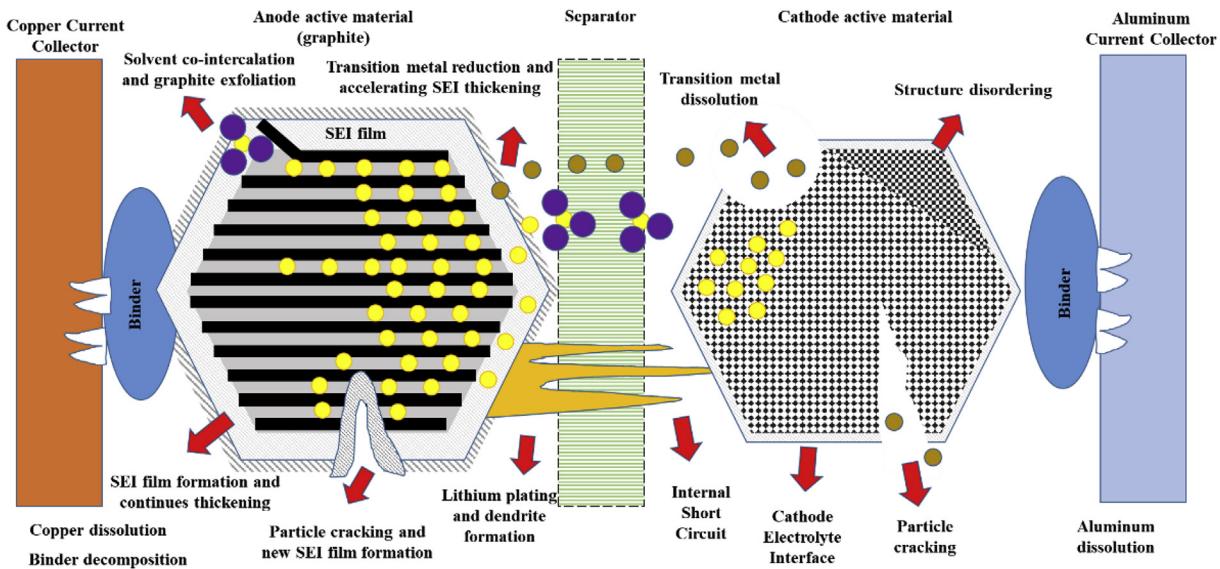


Fig. 5. Overview of main degradation mechanisms in Li-ion cells [9].

would be introduced respectively. The side reactions of the other parts like electrolyte and separator mainly occur on the surface of the electrode, thus could be covered in the corresponding sections.

Currently, there are many kinds of commercial intercalation materials which can be used in lithium ion power batteries for electric vehicles [18]. Some typical cathode materials include Lithium manganese oxide (LMO, LiMn_2O_4), Lithium iron phosphate (LFP, LiFePO_4), layered metal oxide like $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]_2$ (NCM) and Li rich materials. And the anode materials include graphite (C), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), and some alloy anode materials such as Si. The specific capacity and potential of some cathode and anode materials are different as shown in Fig. 6. In order to improve the battery energy density, the developing trend of cathode electrode materials is to find materials with high specific capacity and potential, such as Ni-rich layered-oxide materials and Li rich material. And for anode is the silicon/carbon composite anode materials, pure silicon anode, and lithium anode in the future.

At present, there are only several kinds of Li-ion cells with specific anode and cathode combinations including LFP/C, LMO/C, NCM/C, NCM/LTO, etc. LFP/C cell has long life and high safety, but low energy density and low power density. LMO/C cell has higher energy density and power density, but poor life characteristics. NCM/C cell has high energy density and poor safety; and it is mostly

used in pure electric vehicles, especially for passenger cars. NCM/LTO cell has high power performance, high safety and long life, but low energy density due to the low voltage; and it is often used in fast charging vehicles and hybrid vehicles [1].

2.1. Aging mechanisms on the anode materials

Currently, most of the commercial lithium ion battery use the carbonaceous anodes, generally graphite based materials. As shown in Fig. 6, the electrochemical stabilized voltage window of conventional liquid organic electrolyte is around 1V-4.5V [17,19], while the working voltage of graphite anode is about 0.05V [6,20], which is outside the stabilized voltage window of common electrolytes. Therefore, the graphite anode of lithium ion battery is theoretically unstable. During the charging and discharging process, there will be lithium ion consumption coupled with the electrolyte decomposition, forming a passivation protective layer on the surface of graphite anode electrode which is usually called as the SEI (solid electrolyte interface) film [21-23]. Theoretically, the SEI film only transports lithium ions and prevents electrons transportation. Thus further degradation of the electrolyte could be prevented and the lithium ion batteries with carbonaceous anodes could be stably cycled. The SEI film is mainly formed during the first few charging processes, especially during the first cycle, causing the fast degradation of the battery capacity [24]. With the battery charging and discharging, the graphite anode material would have a volume change of about 10% due to the lithium ions intercalation and deintercalation [3]. Because of the volume change [25], the SEI film may crack, leading to the contact and reaction between the lithiated graphite and electrolyte resulting in the electrolyte and lithium ions inventory consumption [26]. This lead to the continuous generation and thickening of SEI film, continuous reduction of the battery available capacity, as well as continuous increase of the battery internal resistance [27]. This formation and continuous thickening of the SEI film on the surface of graphite anode is widely accepted as one of the major reasons for lithium ion battery aging [28,29]. Besides, the lithium deposition due to the low temperature charging, fast charging or overcharging may lead to loss of electrolyte and lithium ions inventory [4,30]. Co-intercalation of Li ions with solvent molecules may lead to exfoliation of the graphite particles, leading to the loss of active material. The current collector

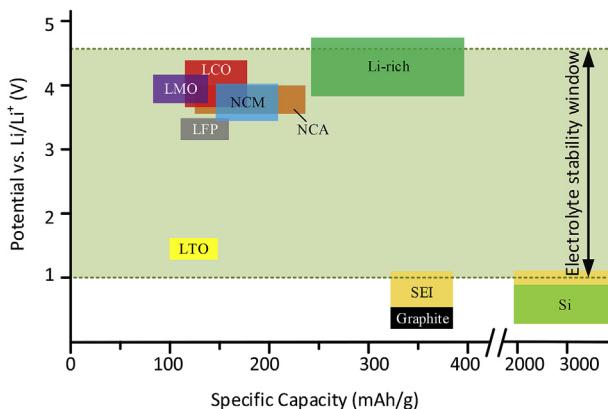


Fig. 6. Potential and specific capacity of active materials in Li ion batteries [16,17].

corrosion and binder decomposition may result in loss of active material [3]. These side reactions could possibly lead to battery degradation.

The spinel lithium titanium oxides (LTO) anode material is another widely used anode materials, which have been applied in HEV, 12V system, and 48V systems due to its high power density and long life. Since the electric potential is located in the electrolyte stabilized window as shown in Fig. 6 (approximately 1.5V vs. Li/Li⁺) [19], there would be no SEI film formation. And due to the relatively high potential, there would also be no reduction of the ions like Li⁺, resulting in no metal deposition. Moreover, LTO is a zero strain material with basically no volume change during the intercalation and deintercalation of lithium ions [31], which means there is almost no structure damage to the material. Therefore, the LTO battery has excellent cycle life [32]. The LTO anode also shows excellent low temperature performance, high C-rate charge-discharge performance and great safety performance. However, due to the high anode potential of LTO, lithium ion battery may have low voltage and low energy density compared to the battery with the same cathode material and graphite anode.

The silicon (Si) based anode batteries are developing very fast in recent years. Due to the high specific capacity (up to 4200mAh/g, much higher than graphite's 372mAh/g), low cost and low intercalation potential, the Si based anode material is one of the most promising anode material to be used in the next generation lithium ion batteries with high specific energy. Because its potential is outside the electrolyte stabilized voltage window, there would also be SEI film formation, resulting in the low coulombic efficiency of the first cycle. And the continuous thickening of SEI film would also lead to irreversible loss of lithium ion inventory. Moreover, during the lithiation process, the silicon would show dramatic expansion of 300%-400%, and the huge swelling may lead to subsequent SEI film creation and active material pulverization resulting in contact loss with the current collector [33,34]. And because of its poor electric conductivity, the capacity cannot be fully utilized and the power density is not good. For these reasons, many researcher focus on the Si/C composite anode material with silicon and carbon to improve the life and C-rate performance [33].

A degradation modes comparison of the different anode materials is shown in Table 1.

2.2. Aging mechanisms on the cathode materials

At present, most of the commercial power lithium ion battery in EV use cathode materials of spinel LMO anode, olivine LFP anode or layered NCM anode.

The spinel LMO cathode material has the advantages of low price, high energy density, nontoxic and is currently one of the widely used lithium ion battery cathode materials. The main aging mechanisms related to LMO are the structural deformation caused by Jahn-Teller distortion and dissolution of manganese [35,36]. In LMO cathode materials, the manganese is usually in two oxidation states, Mn⁴⁺ and Mn³⁺. In case of discharging, especially discharging under high current, the diffusion rate of lithium ions in the electrolyte is much faster than in LMO particles. As a result, lithium ions accumulate on the surface of the LMO particles, and LMO

spinel may insert additional lithium, then Jahn-Teller distortion happens, causing a phase transition from cubic to tetragonal. The volume of the LMO cathode material changes dramatically (approximately 16%), and the structure of the cathode material would be damaged, leading to the loss of the active material [37,38]. And the manganese dissolution may be caused by two reasons. One reason is that Mn³⁺ is unstable and may disproportionate into Mn²⁺ and Mn⁴⁺. This disproportionation reaction happens especially at low potentials. The Mn²⁺ are soluble in the electrolyte, and the lost manganese ions on the particles may be replaced by lithium ions. Another reason is the HF in the electrolyte which may cause the acid dissolution of manganese and generates insoluble LiF on the electrode surface. The dissolution of manganese in the electrolyte results in the LAM of cathode and loss of electrolyte. The insoluble LiF on the electrode surface may cause the resistance increase. For batteries with low potential anode like graphite, the manganese ions may move through the separator and be reduced on the anode surface; which may catalyzes the SEI thickening reaction, resulting in accelerated battery LLI and resistance increase [39]. However, for batteries with higher potential anode like LTO, the manganese ions will not be reduced, and the battery cycle life can be effectively improved [40].

The olivine LFP cathode has low voltage and high resistance, resulting in low energy density. However, it also has the advantages of long cycle life, long storage life, low price, and safety. Currently, it is one of the most widely used lithium ion battery cathode materials, especially in commercial vehicles [41]. During cycling, the volume change of LFP is only about 6.77% [42]. The iron ions are relatively stable, but similar to LMO, there would be also slight iron ions dissolution in the electrolyte, resulting in little LAM of cathode. The iron ions may also be reduced on the anode surface and catalyze the SEI formation, resulting in increased internal resistance and LLI. Compared to the LMO cathode, the life of lithium ion battery with LFP cathode would be much longer. Batteries composed of LFP cathode and LTO anode will show very low voltage, with very low energy density but have a very long cycle life [43].

The layered NCM cathode has high energy density and low price, and it is currently one of the promising materials for lithium ion batteries. It has been widely used in passenger vehicles. The proportion of Ni, Co and Mn may greatly influence the battery performance. Generally speaking, Ni may offer high capacity but poor cycle life and thermal stability, while Mn may provide good cycle life and safety. And Co could increase the electronic conductivity, resulting in lower resistance and excellent power performance. The Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cathode materials have been commercialized and widely used in the electric vehicles. For next generation lithium ion batteries, the content of Ni needs to be further increased to Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂, Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O₂ or even Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ [44,45]. The main aging mechanisms for NCM cathode may include: (1) volume change during the charging and discharging cycle, (2) dissolution of transition metal ions, (3) generation of CEI film by side reaction between cathode materials and electrolyte [46-49]. For Ni rich layered oxide cathodes, the specific capacity and energy density may increase while the safety and durability problems would arise as shown in Fig. 7 [45]. (1) since

Table 1

Degradation mode comparison of different anodes.

	Carbon	LTO	Si-C
LLI	★★ SEI formation and continuous thickening.	★★★ No SEI.	★ SEI and cracking
LAM	★★ Volume change of 13%, especially in low SOC region	★★★ Zero strain materials.	★ Huge volume change up to 300%.
LE	★★ LE caused by SEI formation and cracking.	★★★ No SEI.	★ LE caused by SEI formation and cracking.
RI	★★ SEI	★★★ No SEI.	★ SEI

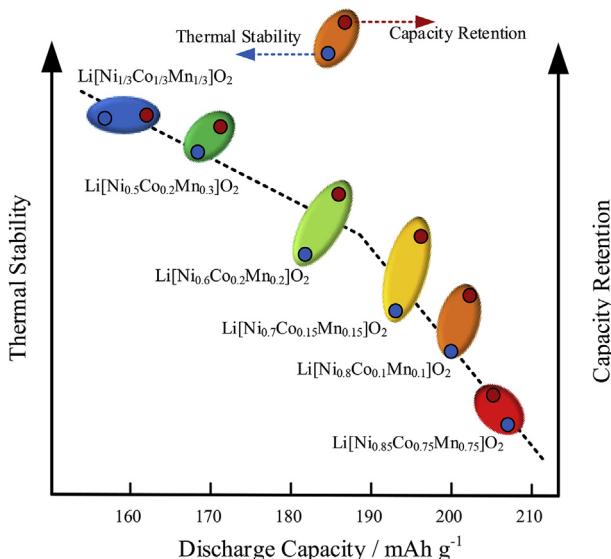


Fig. 7. Relationship between discharge capacity, and thermal stability and capacity retention of $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$.

the atomic radius of Ni^{2+} is close to Li^+ , with the increasing Ni content, the cation mixing phenomena would be more likely to happen, influence the battery performance and life. (2) The phase transformation would be more likely to happen in Ni rich cathode materials, causing the particle surface structural degradation. (3) The thermal stability of the Ni rich materials is worse, which means under higher temperature, the cathode is more likely to decompose, release oxygen and influence the battery safety and life.

A degradation modes comparison of different cathode materials is shown in Table 2.

3. Battery degradation characteristics and the influence factors

3.1. Battery degradation characteristics

From the perspective of the vehicle, the most important and relevant things for battery system are the capacity and power performance, which needs to be precisely estimated by the BMS as SOH. Thus as shown in Fig. 3, the battery degradation effects are usually represented by the change of the battery electric performance, especially the capacity and power. And this section would focus on this part. Generally, the useable capacity and available power fade with the aging of the battery.

For energy applications like BEV (Battery Electric Vehicle), usually the high energy type batteries are used, and the basic function of the battery is capacity storage. Thus, the battery degradation could be evaluated by the capacity fade. And for power

applications like HEV (Hybrid Electric Vehicle), usually the high power type batteries are used, and the battery's basic function is to satisfy the high pulse power requirement. So more attention needs to be paid to the power fade. For PHEV (Plugin Hybrid Electric Vehicle), both capacity fade and power fade should be considered. Usually, the main reasons of battery capacity fade is the LAM and LLI. And the battery internal resistance increases will also affect the battery capacity in case of the same charge and discharge cut-off voltage and C-rate. And the main reason of battery power fade is the increase of the internal resistance.

At present, for high energy battery, when the battery capacity decreases to the 80% of the initial capacity, the battery is considered to reach the end of life since the battery can't meet the requirement of the vehicles. For high power battery, the end of life is usually defined based on the point when the available power reaches 50% of the initial value (i.e., 100% impedance increment).

Basically, the battery life could be considered as two parts: calendar life and cycle life. Calendar life refers to the battery degradation caused by storage without cycling; while cycle life considering the battery degradation caused by charge and discharge cycles, which corresponds to the battery cycling in vehicle. For actual EV, the batteries may charge and discharge while driving or in the charging station; and while parking, the battery may just pause. So both calendar life and cycle life should be considered.

Generally speaking, for most batteries currently used in EV, the battery usually shows a nonlinear aging characteristic [50,51], which can be roughly divided into three stages as shown in Fig. 8. In the first stage, because of the SEI formation on the anode, LLI happens, resulting in a fast decrease of the battery capacity during the first several cycles, especially the first charging process. The battery may show a very low first coulombic efficiency. The problem of first coulombic efficiency is very important for the researches of battery design and production. In the second stage, the battery performance fades steadily due to the various side reactions inside the battery. In the third stage, there would be a rapid capacity drop [52] and resistance rise [50] near the end of life. The reason may be the rapid lithium ion inventory loss due to lithium deposition [50,52], and/or the active material loss due to the loss of electrolyte [53], failure of binder and volume change [54]. This rapid capacity drop phenomenon greatly influences the potential for battery second life application and need to be further studied in detail.

Moreover, sometimes the battery capacity may increase abnormally [55,56]. This phenomenon is often observed in the early stage, or the cycling test is interrupted and after a long time storage there may be a capacity increase [57]. The reasons for this phenomenon still need further analysis and discussion. One possible explanation is the passive electrode effect [58,59], which considers the geometric excess anode may provide additional capacity (lithium ions actually) after storage and cause the capacity increase. Another possible reason is related to the charge redistribution where no charge or discharge force acting on them [60,61]. That

Table 2
Comparison of different Cathodes.

LMO	LFP	NCM
LLI ★ Mn^{2+} may accelerate the SEI growth side reactions.	★★★ Little dissolution of Fe ions	★★ Transition metal dissolution may accelerate the SEI growth
LAM ★ Dissolution of Mn^{2+} and Jahn-Teller effect	★★★ Stable structure. Less volume change	★★ Less volume change and no Jahn-Teller effect.
LE ★ High potential caused CEI formation. Mn^{2+} may accelerate the SEI growth and consume electrolyte	★★★ Low potential, less CEI formation.	★★ High potential caused CEI formation.
RI ★ SEI and CEI cause clear RI.	★★★ Less RI, however the resistance of LFP is large	★★ SEI and CEI cause clear RI.

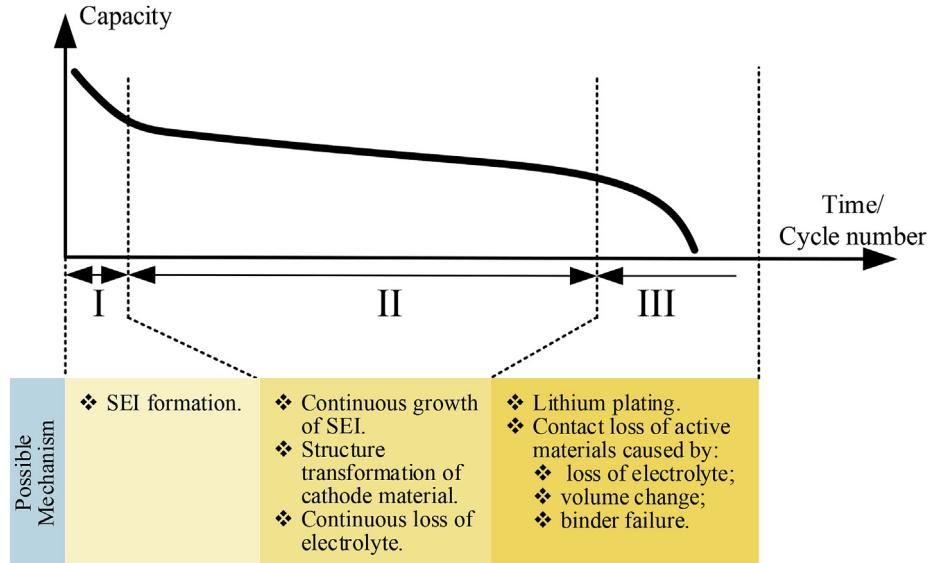


Fig. 8. Battery capacity fade and possible internal mechanism in different stages.

may be caused by improved electrolyte wetting of the electrode [62]. And the lithium plating and stripping process could also result in abnormal improvement of the battery performance [63].

Besides the electric characteristics, the mechanical and thermal characteristics of the battery will also change. For example, the thickness of the battery may increase due to gas generation and other reasons; the heat transfer coefficient, entropic potential may also change during the battery degradation. Considering that the change of mechanical and thermal characteristics does not directly affect the battery system function in real vehicles, this part will be analyzed and discussed in section 5.

It is clear that the battery degradation may be influenced by the battery design, production and application, and the effects of each part will be discussed in detail in next sections 3.2, 3.3 and 3.4 respectively.

3.2. Influence of the battery design

It is clear that battery design may directly influence its life. From the perspective of vehicles, the battery design can be summarized as several levels: material level, electrode level, cell level and system level. Each level may affect the battery life in vehicle

application, as shown in Fig. 9. It should be noted that the battery design needs to consider many factors and their influence to each other, and the factors are very complicated and coupled. Many factors such as heat generation and dissipation, SEI formation, etc., need to be considered in different levels.

3.2.1. Design in the material level

From vehicle engineers' perspective, here design in material level mainly refer to the rough selection of key materials inside the battery including anode and cathode active materials, electrolyte, separator and so on, but not to develop new materials. Definitely, the materials inside the battery may have a great impact on the battery life. A proper design may efficiently reduce the side reactions inside the battery, prolonging the battery life.

The effect of anode and cathode materials has been discussed in Section 2 as shown in Tables 1 and 2, thus will not be repeated here. Besides, by coating, doping and other methods to improve the stability and reduce the side reactions, the battery life performance can be further enhanced. For example, for Ni-rich cathode materials, the lifetime can be greatly improved through full concentration gradient design of the lithium transition-metal oxide cathode materials [44].

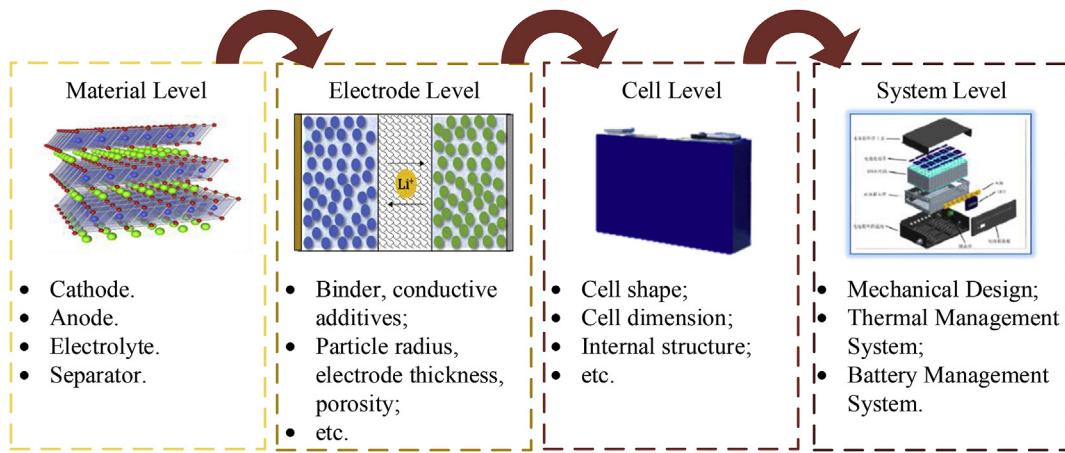


Fig. 9. Battery design on different level.

The electrolyte is also very important. There are many kinds of electrolyte including the aqueous electrolytes, polymer electrolytes, all solid state electrolytes, and the commonly used organic electrolyte. Now for almost all the batteries in EV just using the non-aqueous organic electrolyte. In this kind of electrolyte is usually some lithium salt dissolved in organic carbonates with some additional additives to improve the battery performance like the film-formation quality, electric conduction, flame retardant.

The lithium salt used as solute includes LiClO₄, LiAsF₄, LiPF₆, etc. LiClO₄ is a strong oxidant which is easy safety problems, while the toxicity of As in LiAsF₄ limits its application. Therefore, the main solute used in EV power batteries is LiPF₆, which have good performance of high conductivity but relatively poor stability. Especially it may react with water, generating various byproducts like HF and influence the battery life. Thus, the lithium salt solute still need to be further improved and developed, and many researchers have paid attention to the other salt like the organic lithium salt, e.g. LiODFB [64].

At present, the solvents used in EV lithium ion battery electrolyte are usually organic including EC (Ethylene carbonate), PC(Propylene carbonate), DMC(Dimethyl carbonate), DEC(Diethyl carbonate), EMC(Ethyl methyl carbonate) and so on. Some basic physicochemical properties of these common solvents are compared in Table 3 [65]. EC has higher dielectric constant and better conductivity, while EC could help to form stable SEI layers with higher quality and improve the battery life. However, EC is in the solid phase at room temperature (melting point 37°C) and it cannot be used alone for traditional Li ion batteries. PC also has a high dielectric constant and low melting point (-49°C), so the electrolyte including PC would have better performance at low temperature. However, PC may decompose on the anode surface, the formed SEI layer quality is not so good, and the PC solvent co-intercalation phenomenon may happen with the lithium ion insertion, causing graphite exfoliation and graphite particle cracking, and resulting in poor cycle performance. DMC has low viscosity and good cycling performance, but the dielectric constant and the flash point is low. In order to ensure the battery performance, usually a mixture of different solvents would be used. And some various electrolyte additives could also help to improve the electrolyte conductivity, SEI film quality, etc.

The separator may also influence the battery performance, especially the battery safety, resistance and so on [66,67]. From the perspective of life, some studies point out that the Al₂O₃ of the ceramic separator can improve the battery life since the separator may react with acid-spices and absorb harmful impurities (such as HF) in the electrolyte, thereby improving the battery life [67,68].

3.2.2. Design in the electrode level

Electrodes design is very important and could significantly influence the battery life. Here design in electrode level mainly refers to the design optimization of key parameters of battery electrode including the ratio of anode and cathode active materials, electrode particle size, porosity, electrode thickness and so on [69]. Usually, the Newman's battery mechanism P2D(Pseudo 2 dimensional) model [70] is used in the optimization to simulate the battery

performance under different electrode parameters. Considering the P2D model is a kind of mean-field model, some more complicated models are also developed and used to do the design optimization [71,72]. These models based optimization methods are currently the main battery electrode design methods [73]. The optimized design in the electrode level could reduce the impact on the life of mechanical factors (like stress), electrical factors (like polarization), thermal factors (like temperature) and other factors. There are many coupled parameters and they may influence various battery performance including durability as well as safety and power performance. So, only some key parameters affecting the battery life would be briefly discussed in this part.

One of the most important parameters at the electrode level is the ratio of the negative electrode capacity and positive electrode capacity, i.e., the N/P ratio. Generally speaking, the N/P ratio is usually designed to be slightly larger than 1, which means the anode active material would be slightly excessive [74]. If this N/P ratio is too small, which indicates that the anode active material is insufficient, the battery capacity may be severely limited by the anode capacity. Moreover, decreasing the N/P ratio would dramatically increase the risk of lithium plating, leading to fast capacity fade and safety problems [4]. And the N/P ratio design needs to consider the problem of SEI formation which may lead to lithium ion loss, capacity fade and low coulombic efficiency of the first cycle. If the N/P ratio is too large, there would be too much negative electrode (i.e., anode) active material, resulting in low energy density. And there would be additional SEI film formation on the excessive anode material surface, consuming the available lithium ions carried by the cathode active material. Especially for some anode materials with low first cycle coulombic efficiency like SiC composite, the irreversible capacity loss in the first several cycles needs to be compensated by adding different lithium sources to the anode or cathode. The anode involving methods like adding particular lithium powder or lithium foil in the anode. Then during the cycling, the excess lithium in the powder may become cyclable lithium by diffusion to the anode or migration to the cathode [74]. This method has been commercialized by the FMC Lithium Corp. However, the lithium is very active and dangerous, therefore the production process needs to be well controlled. Thus, some other lithium sources like Li_xSi could be used as the prelithiation reagent [75]. Another method is to form an SEI on the anode active material before assembling, which may bring additional processing step [74]. In the cathode side, some high capacity cathode materials like Li_{1+x}Ni_{0.5}Mn_{1.5}O₄ [76] and Li₅FeO₄ [77] could be added as the lithium source additive. Then during cycling, the excess lithium ions could insert in to the anode and compensate the irreversible capacity loss of the first cycle. In laboratory, the cyclable lithium ions could also be added by the third electrode, which is seldom used in the commercial cells.

The particle size of the anode and cathode active materials may also influence the battery life. On the one hand, as the particle radius decreases, the specific surface area per unit volume increases, which means that the electrochemical reactions, including side reactions like SEI formation and CEI formation, would be easier to take place on the particle surface. Though battery specific power

Table 3

Comparison of some common Electrolyte Solvents.

	Dielectric constant	Viscosity(25°C) mPa s	Flash Point °C	Boiling Point °C	Melting Point °C
EC	90	1.9(40°C)	143°C	238°C	36°C
PC	65	2.5		242°C	-49°C
DMC	3.1	0.59	17°C	90°C	5°C
DEC	2.8	0.75	25°C	127°C	-74°C
EMC	3	0.65	23°C	108°C	-53°C

would increase, the increased SEI film formation area and SEI formation rate may reduce the battery life. On the other hand, as the particle radius decreases, the stress on the particle surface as well as the induced crack would be reduced during the lithium-ion insertion and extraction. Thus, the battery life would be improved. In addition, the tap density of the active material may decrease as the particle radius decreases, which may affect the battery energy density. Therefore, the active material particle size needs to be comprehensively optimized.

The porosity of the electrodes is another important adjustable design parameters [73]. A large porosity may be caused by low compaction density of the electrode. Although the ionic conductivity in the electrolyte phase would be improved, the electric conductivity would be poor due to the loose contact between the particles. And the particles are easy to get mechanical disintegration within the electrode, especially for materials with large volume changes during cycling such as Si based anode. A small porosity may represent high compaction density of the electrode materials, which mean tight contact between particles. The contact resistance between particles would be better, leading to high electric conductivity and usually high energy density. However, the ionic conductivity of the electrolyte would be reduced, leading to poor lithium ion transportation in the electrolyte phase, and the battery available power would be reduced. Currently it was reported that, by graded porosity design, i.e., with varying porosity across the electrode, the battery performance could be improved. Generally, the porosity on the collector side should be reduced to get a higher energy density. And the porosity on the separator side should be increased to enhance the lithium ion transportation rate [78-80].

The electrode thickness is very important for the battery design [73]. It may directly influence the battery energy performance and power performance. With a smaller electrode thickness, the lithium ion transport path is shorter, resulting in high power density but low energy density. Correspondingly, to increase the battery energy density, usually the simplest way is to increase the electrode thickness. But the lithium ion transport path would also be longer and the battery impedance increases, causing poor power performance of the battery. The distribution of the solid phase and electrolyte phase potential of the porous electrode is shown in Fig. 10. Generally speaking, the solid phase conductivity is much better than that of the electrolyte phase. Therefore, only considering the influence of the electrolyte phase potential, the over potential distribution of the electrode is shown in Fig. 10 (b). It could be easily found that the activation over potential is much higher in the separator side, indicating that the electrochemical reactions are mainly take place in this part of the active materials. Meanwhile,

the activation over potential in the current collector side is very low, leading to little contribution to the whole current. Therefore, from the perspective of the electrochemical mechanisms, although the battery theoretical capacity increases with the increasing electrode thickness, the available capacity is limited. However, the polarization of the particles on the separator side increases dramatically, leading to side reactions like lithium plating and decreasing the battery life. In addition, if the thickness is too high, the battery impedance may be increased, leading to increasing heat generation and poor heat dissipation performance. Therefore, the battery temperature will increase during charging and discharging, which also has a negative impact on the battery life.

It should be mentioned that, some additives such as conductive agents and binders also have a great impact on the battery life. These additives may affect the key parameters and properties including the electric conductivity, porosity, safety performance of the anode and cathode materials. For example, the graphene can greatly improve the electrical conductivity and thermal conductivity of the electrode materials. Therefore, it could reduce the battery internal resistance and temperature, thus improve the battery life.

3.2.3. Design in the cell level

Here design in the cell level mainly refers to the optimal design of the cell internal structure, shape and size. Generally, the cell design would be restricted by the production equipment, process development, standards, design of the battery system, vehicle requirement, etc. Thus, all these requirements need to be considered and satisfied. And through the cell design, the cell could get a more uniform internal current distribution, less temperature rise and less temperature rise inconsistency, then the battery life could be improved.

The cell internal structure could be basically divided into two types: stacked type and wound type, as shown in Fig. 11. The comparison between two types of cells is shown in Table 4. The production process of wound type jelly roll is relatively simple and the production efficiency is very high, however, the production efficiency of stacked type electrode is relatively low. During production, the wound jelly roll may have large deformation in the folded region on the edge, which may lead to durability and safety problems, while the stacked type would have very uniform deformation during production. And during the charging and discharging process, the lithium ion intercalation and deintercalation may cause the active materials volume change. For the wound jelly roll there would be high stress concentration, while for the stacked type there would be a more uniform stress distribution. Generally, for the stacked type electrode there would be one tab for every

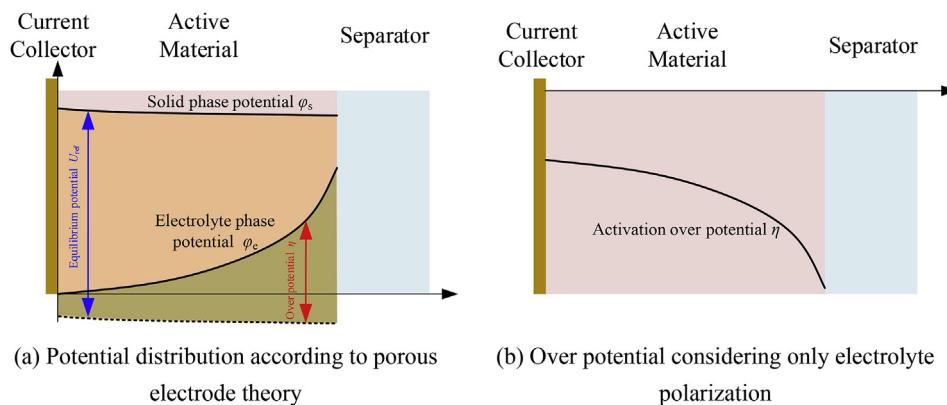


Fig. 10. Activation over potential η

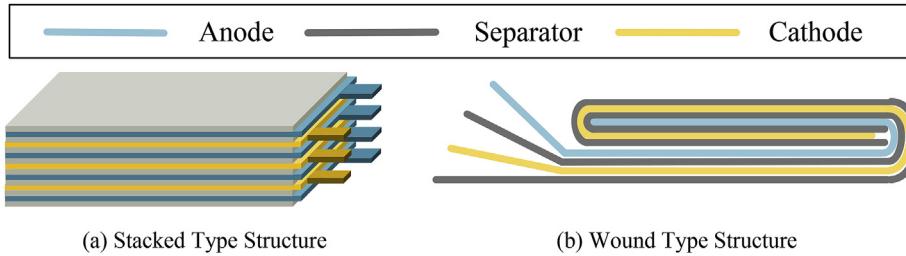


Fig. 11. Different types of cell internal structure.

Table 4
Comparison of Different types of cell internal structure.

	Stacked Type Structure	Wound Type Structure
Power Performance	★★★ Low resistance since usually every plate has one tab.	★ High resistance since usually only one tab for each electrode.
Capacity Density	★★★ Full use of the volume.	★★ Little waste in the arc position on the edge
Life	★★★ Long life since less deformation	★ Short Life since inconsistency of deformation
Production Efficiency	★ Relatively low efficiency	★★★ High efficiency
Application	High power application. HEV, PHEV, BEV	PHEV, BEV

plate, so the battery internal resistance is usually lower and the current distribution is more uniform. However, sometimes the wound jelly roll may be designed to have only one tab, then the battery internal resistance may be larger and have inconsistent current distribution, and it may easily lead to excessive local polarization induced lithium plating and other side reactions, affecting the battery life. And this problem could be solved by adding more tabs. Overall, the life of battery with stacked type structure would be slightly better than that of the wound type structure.

The cell shape used in commercial EV is usually one of the three types: cylindrical cell, prismatic cell or pouch cell. The comparison between different shape of cells is shown in Table 5. Generally, the cylindrical cell has a relatively small heat dissipation area due to the low specific surface area, so the internal temperature would be higher during charging and discharging, affecting the battery life. The heat dissipation area of prismatic cell would be larger. Because of a large surface area and usually thin thickness, the pouch cell could dissipate heat more efficiently. And the cylindrical cell is usually wound tightly, resulting in very high internal stress during charging and discharging, affecting the battery life. The pouch cell and prismatic cell usually have little margin for deformation, and the material stress is acceptable, especially for the prismatic cells. And also because the cylindrical cell is wound tightly, usually there is relatively less electrolyte in the cell. If the electrolyte loss to a certain level, due to lithium deposition and other reasons, the cell capacity may drop very fast, affecting the battery life. And the pouch cell and prismatic cell usually have relatively more electrolyte.

The cell size will also affect the life. The main purpose of the cell size optimization is to make the current flow through the active materials inside the battery more uniform, to prevent side reactions caused by excessive local current and excessive local polarization voltage; and to decrease the temperature rise as well as temperature difference under certain heat dissipation conditions. In order to achieve these targets, the following items are usually considered: (1) Use thicker copper foil and aluminum foil as the current collector of the anode and cathode, which can reduce the battery internal resistance and then reduce the heat generation. It could also improve the current flow consistency through the active materials, preventing local overcurrent. However, thick current collector may lead to energy density decrease. (2) Increase the thickness and width of the tabs or adding more tabs, place the tabs on the opposite sides of the battery rather than the same side. These methods could uniform the internal current flow and temperature rise of the battery. (3) Reduce the thickness of the battery and optimize the other dimensions of the battery to improve the battery heat dissipation or make the battery internal temperature more uniform.

3.2.4. Design in the system level

Generally speaking, the system level design mainly refers to a series of mechanical, electrical, and thermal related issues of integrating cells into a battery system. The design objective is to ensure that each cell could work within a suitable temperature and voltage interval. And the design in system level should include design of mechanical structure, thermal management system (TMS), and battery management system (BMS). Usually, TMS would be

Table 5
Comparison of Different type of cell shape.

	Cylindrical cell	Prismatic cell	Pouch cell
Design for manufacture	★★ Easy for cell manufacture; Hard for pack manufacture	★★★ Hard for cell manufacture; Easy for pack manufacture	★★★ Easy for cell manufacture, Little hard for pack manufacture
Thermal characteristic	★ Poor heat dissipation since relatively low specific surface area	★★ Specific surface area related to the capacity	★★★ Usually large surface area.
Capacity Density	★★ High.	★★ Depends on cell capacity	★★★ High.
Life	★ Usually less deformation but huge stress and less electrolyte.	★★★ Usually more electrolyte.	★★★ Usually poor electrolyte, uniform deformation.
Safety	★★ Usually little capacity.	★ Usually large capacity and easy to explode.	★★★ Usually no explosion.
Cell to Module Efficiency	★ Low efficiency, hard to design TMS.	★★★ High efficiency, Easy to design TMS.	★★ Low efficiency, easy to design TMS.

considered as part of BMS. However, considering that TMS and BMS mainly influence the way to use the batteries, thus their influence would be discussed in the section 3.4.

First of all, the cells configuration in the battery system is very important. Using series-parallel, parallel-series or other hybrid configuration will affect the current distribution of each cell in the system, and will also influence the BMS algorithm. For example, the system design based on the symmetrical loop circuit structure could provide great convenience for the internal short circuit diagnosis [81]. At present, considering the cost and reliability issues, the configuration of most battery system is the parallel-series structure. The cells are firstly parallel connected to reach the required capacity. This unit would be the minimum controllable unit by the BMS. And then these units would be connected in series to the desired voltage. In these processes, reducing the resistance of the bus bar, reducing the resistance of the welding spot and improving the welding quality, the system performance could be guaranteed, especially the current through each cell would be more uniform.

Another important factor is the compressive pressure load to the cells. For system design, the cells need to be compressed and constrained tightly to ensure that all the components are in a reasonable position, maintain good thermal contact, no tearing under the complex vibration environment on the real EV. The effect and mechanism of external compressive pressure on the battery life have not been fully revealed yet. Some researchers believe that the battery in a free state may have a longer life by some measures [82]. However, most literature state that the battery with certain external pressure could help to improve its life [83]. But if the pressure is too high, the battery life will be reduced [84,85], showing the existence of optimal pressure for the battery life as shown in Fig. 12. In addition, considering that the battery thickness may increase with the battery aging due to the gas generation or other reasons, the structure design must reserve enough space for this requirement.

3.3. Influence of the battery production

The battery production process will also have a great impact on the battery life. To obtain a long-life and high-performance battery, the production technology needs to be developed and detailed production processes need to be optimized rationally. Here, it should be noted that it is difficult to clearly distinguish the design

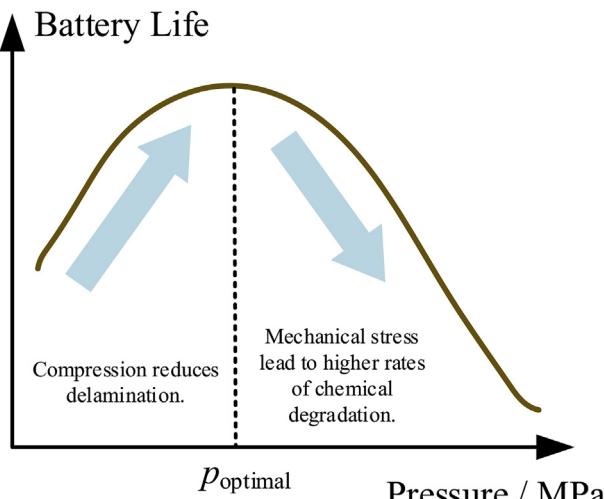


Fig. 12. Relationship between pressure and battery life.

and production. In many cases, production technology development is also considered as part of the battery design, namely process design. In this paper, "design" will mainly refer to the battery design in theory, and "production" mainly considers how to achieve it. In this section, the key process related to the battery life in the battery production would be focused and briefly discussed.

Generally speaking, the manufacturing processes of Li-ion batteries are shown in Fig. 13 [86], which roughly include mixing, coating, drying, calendering, cutting, stacking, welding, sealing, electrolyte filling, formation, aging, testing, sorting and so on. Different batteries with different structures, shapes or chemistries may have different production process, while the basic processes are very similar.

It should be pointed first that water may greatly influence the battery life. The water in the electrolyte may react with the lithiated graphite anode, and may generate HF which would attack the cathode material, leading to the transition metal dissolution of the cathode. Therefore, the humidity of the production environment is very important, and must be strictly controlled before formation. Generally speaking, the air dew point needs to be below -50°C , otherwise the water in the electrolyte may clearly influence the battery life.

And the influence of the production processes could be analyzed respectively.

- (1) The electrode fabrication process basically includes mixing, coating, drying and calendering. The main purpose of these steps is to make the anode and cathode electrode. These steps are generally traditional chemical engineering process.

Mixing, to be precise, the slurry preparation is to mix the active material powders, conductive additive powders, binder and some solvent through stirring or grinding by the dispersing equipment [87]. The mixing process has a great influence on the particle radius distribution of the active material and the conductive additive distribution inside the battery. As discussed in former sections, the particle radius and solid phase conductivity may influence the

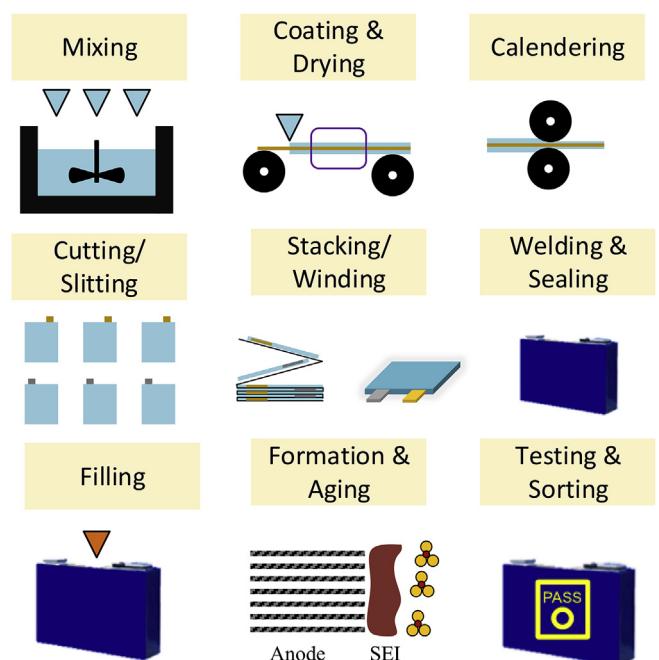


Fig. 13. Manufacturing processes of Li-ion batteries.

battery life. Therefore, it is very important to design the key parameters of mixing process, including the ratio of different components, tip speed of the mixer and so on [88,89].

The coating and drying process mainly refers to coating the slurry onto the current collector, and then removing the organic solvent in the slurry by drying [89,90]. In this process, the solvent evaporation and the active material particle sedimentation may affect the distribution of conductive additives, binders through the electrode. Therefore, the key parameters needs to be carefully designed, including the drying temperature, air flow speed and so on.

Calendering, also known as pressing, is the compaction process for battery electrodes and has a substantial impact on the electrode key parameters, including electrode thickness, porosity, compaction density and so on [88,91,92]. The key operation parameters include the roller speed, rolling force, and so on. The consistency of the active material thickness is very important. If the active material distribution uniformity is poor, it would be easy to have excessive or insufficient local anode or cathode active materials. The uneven electrode thickness tends to cause wrinkles and deformation which affect the battery performance, and local lithium deposition may occur in the wrinkled area. And the insufficient local anode materials would also easily cause the local lithium deposition during the charging and discharging process, which greatly affects the battery life. In order to guarantee the battery life, during the electrode fabrication process, the electrode thickness and uniformity need to be tracked carefully using the microscope or the laser based equipment.

(2) The next process is the cell fabrication from the electrodes, and for stacked type structure it basically includes cutting, stacking, welding, sealing and so on. For wound type structure, there would be little difference, usually including slitting, winding, welding, sealing and so on. The main purpose of these steps is to assemble the coated anode and cathode electrodes and separators into jelly roll, and make it into a cell. These steps are generally close to the traditional mechanical process. And local insufficient anode materials should be prevented during the production, which may lead to lithium deposition and influence the battery life.

For the cutting and slitting steps, the size control is very important. Generally speaking, the anode active materials should be slightly larger than cathode, otherwise there would be lithium deposition in the edge of the anode. And during cutting process, the burrs in the edge needs to be avoided. The burrs may penetrate the separator and lead to high self-discharge rate or internal short circuit, influencing the battery life and safety. And during the cutting process, there may be some metal debris on the electrode surface, which may also cause local metal deposition, dendrite growth, separator penetration, resulting in life and safety problems.

For battery with stacked type structure, the production efficiency of stacking is low, but this process usually has little influence on the battery life. For battery with wound type structure, the winding process has high production efficiency, however, the production process may bring in negative effects on battery life. As discussed in the section 3.2, during the winding process, the deformation of the electrode is not uniform, and there would be wrinkles and material cracks in the bending position, affecting the battery life. The tightness of the winding process also has an obvious effect on the battery life. Generally speaking, winding too tight may lead to lower internal resistance and improve the battery performance. However, it may also lead to difficulty of complete electrolyte wetting of the electrodes and separator pores; and it may destroy the mechanical structure of the anode and cathode

particle, influencing the battery life. Winding too loose may lead to insufficient constraint of the active materials, and during charging and discharging, the volume change may lead to the increase of internal resistance and contact loss of active materials.

(3) Filling and formation are the key steps in the battery manufacturing processes. The main purpose of these steps is to form stable SEI film. These steps are generally electrical engineering process.

Filling, also known as electrolyte injection, determines the amount of the electrolyte inside the battery. Too much electrolyte may lead to waste, result in lower battery energy density, and affect the battery sealing. However, if the electrolyte is insufficient, the battery internal active materials and separator cannot be completely wetted, resulting in high internal resistance, unstable SEI film, and lithium deposition may easily occur. As mentioned in the former section 3.1, due to the continuous electrolyte consumption, if the electrolyte amount is insufficient, the battery capacity may drop very fast. After the electrolyte injection is the absorption of the electrolyte into the electrode and separator. This electrolyte wetting process is time consuming, especially for electrode with low porosity. Vacuum could accelerate this process by a factor of two [93] and obviously improve the production efficiency. Incomplete wetting of the whole electrode may influence the battery performance, while parts of the active materials cannot involve in the charging and discharging process, and lithium deposition may occur, influencing the battery life. The wetting process could be visualized and evaluated by methods such as ultrasonic or neutron imaging [93] to ensure the battery life.

Formation is the key process to guarantee the battery life and performance. As discussed in section 3.1, for the first several charging and discharging cycles of the battery after injection, the electrolyte (including the additives and solvents) reacts with lithium ions on the anode particle surface, forming the SEI film [94,95]. Meanwhile, similar reactions may also occur on the cathode particle surface, forming the CEI film on the cathode, as shown in Fig. 14 [96,97]. The loss of available lithium ions, the consumption of the electrolyte and the increase of battery resistance due to the film formation may lead to the rapid drop of battery capacity during the formation process. And this irreversible capacity loss could be compensated by adding different lithium sources to the anode or cathode as discussed in section 3.2.

The SEI film quality has a significant impact on the battery life. SEI film with high stability can effectively prolong the battery life [98,99]. The SEI film quality is related to many factors, such as

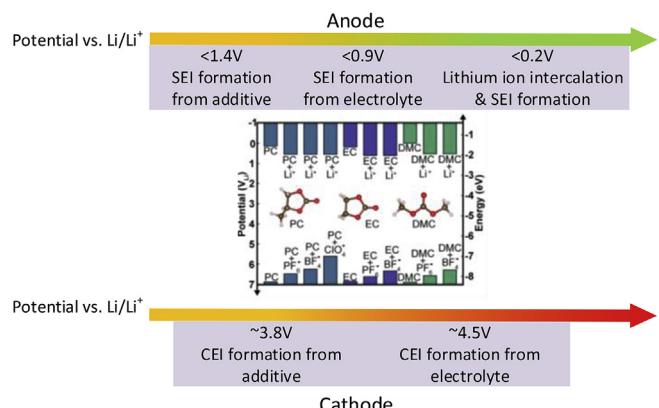


Fig. 14. SEI and CEI formation during the formation process.

anode (including the material structure, surface treatment), electrolyte (including solvents, lithium salts and additives) and the formation protocol used in the this process [99].

At present, in the formation process, the cells are usually charged and discharged at a very small rate (e.g. the first formation cycle at C-rate like C/20, followed by the second formation cycle at higher C-rate like C/10 under a higher temperature, then a third formation cycle with ever higher C-rate, and so on). And during the formation process, the cells may also need to take several aging processes at high temperature and high pressure. The whole process is time consuming. It is pointed that electrolyte wetting and SEI formation process are the most expensive processes in the lithium ion battery manufacturing [62]. The temperature, current, voltage and pressure will directly affect the SEI film quality and the battery performance. If the current is too large or the voltage is too high, it may cause rapid gas generation which would not be easy to exhaust, resulting in poor contact of the electrode and separator, which will lead to lithium deposition and low efficiency. If the current is too small, the production cost would be too high. Fast formation methods like multi-stage current formation method could help to solve this problem [100,101]. In order to ensure the SEI film quality, the formation process should be carefully optimized considering the specific battery characteristics and production cost.

During the formation, the generated gas need to be exhausted, and the cells need to be completely sealed. The battery life would also be influenced if it is not sealed properly. The continuous leakage of the electrolyte is directly related to the loss of electrolyte, leading to the lithium decomposition and loss of active materials. The water in the air may also react with the electrolyte, affecting the battery life.

- (4) Battery testing and sorting are the final step in battery production. In this step, appropriate indicators and threshold values should be set, filtering out unqualified cells and classifying qualified cells. Reasonable sorting method could find the cells with low quality, thus the battery life could be guaranteed. Generally speaking, the key performance indicators include the cell appearance, size, impedance, capacity, self-discharge rate, etc. From the perspective of durability, the key indicators mainly include the impedance, capacity and self-discharge rate. Setting reasonable thresholds for these indicators can effectively guarantee the cell life.

Usually, the cell manufacturers test the battery 1 kHz AC impedance at the end of line. Sometimes the DC impedance would also be tested, such as 5S or 10s DC impedance. It is easy to know that the impedance mainly affects the battery power performance. In case of the same cut-off voltage, the battery available current and available power are smaller under large impedance. From the perspective of life, the battery with larger impedance may generate more heat and makes the temperature higher under the same working condition, affecting the battery life. And high impedance may indicate some manufacture defects inside the cells, such as incomplete electrolyte wetting process, poor uniformity of the conductive additive distribution, which may affect the battery life due to the high polarization inside the battery. For the parallel connected cells, the inconsistency of the cell impedance may directly influence the current distribution through the cells. Thus the battery life would be influenced. The test efficiency of the cell impedance is very high, usually several seconds would be enough for each cell.

Both capacity and self-discharge rate have an obvious impact on battery consistency. It is widely accepted that the larger cell

capacity is, the better. However, according to the pack consistency theory, the battery pack capacity is limited by the smallest cell capacity, so the performance of the cells with larger capacity cannot be fully utilized [102]. And excessive self-discharge rate may indicate that obvious side reaction inside the cell, which will affect the battery energy storage efficiency. And it also represents that there may be some internal manufacturing defects such as the internal short circuit caused by metal debris, separator breakage or other reasons. Meanwhile, in a battery pack, the inconsistency of the various cells will continue to increase due to the inconsistency of the self-discharge rate. The cell consistency inside the pack will significantly affect the performance of the whole pack. This part would be discussed in section 6 in detail. The capacity could be derived during the formation process, and the self-discharge rate could be calculated after a long time storage.

3.4. Influence of the battery working condition

Same batteries under different working conditions, their life would be totally different. The main factors affecting the battery life include: high temperature [103–106] (accelerate the inside side reactions); low temperature [4,107,108] (metal ions would be easily reduced, lithium deposition, and the crystal structure of the active material would be easily damaged); high SOC or overcharge [109–111] (electrolyte decomposition, side reactions between the electrolyte and the cathode, lithium-ion deposition); low SOC or over discharge [112] (the anode copper current collector would be easily corroded, and the crystal structure of the active material would be easily collapsed); high charge and discharge rate [108] (crystal structure of the active material would be easily fatigued and damaged, and high rate causes the temperature rise, accelerating the internal side reactions). Generally speaking, the battery has a reasonable operating window, as shown in Fig. 15. The primary purpose of the BMS and TMS is to make the battery working within the long-life and high-performance operating area, and prevent it from working in the dangerous zone, which should be alerted and take measures timely.

(1) Influence of temperature

The temperature is one of the most important factors affecting the battery life. Both high and low temperatures can lead to accelerated degradation of the battery [113]. Generally, for most commercial lithium ion batteries, the appropriate working temperature interval is 15–35°C. The rate of various reactions inside the

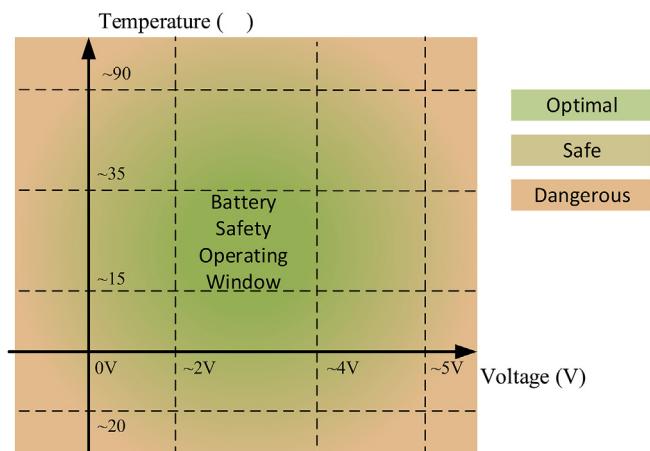


Fig. 15. Battery operating window.

battery, including main reactions and side reactions, are all related to temperature. If the temperature is higher, the side reaction rate is higher. Moreover, if the battery exceeds a certain temperature, it may further trigger self-heating, resulting in battery thermal runaway. Under low temperature, the polarization will increase due to the increase of the internal resistance, which may lead to additional side reactions. In particular, charging under low temperature may lead to lithium deposition, which may cause battery rapid degradation and even lead to safety problems. And the material embrittlement under low temperature may also influence the battery life. Consequently, ensuring that the battery works within a suitable temperature interval is the key to improving the battery life.

The battery temperature is determined by many factors, including environment temperature, battery heat capacity, battery thermal conductivity, battery heat generation, heating and cooling system in TMS, etc., as shown in Fig. 16. All the factors may have a greater impact on the battery temperature.

The environment temperature has a huge influence on the battery life. For power batteries in most real EVs, the most common state is actually the storage state, which corresponds to the vehicle parking state. At this time, all the vehicle electric systems are powered off, and the battery temperature is basically determined by the environment temperature. And the key factors affecting the battery calendar life are the temperature and SOC. In these areas with high environment temperature, the capacity loss is large under the storage state. In addition, the cycle life of the battery is also related to the temperature. The environment temperature is principally decided by the factors such as the climate, weather and season, which may be related to the geographical location of the vehicle. It is widely accepted that the lower the latitude is, the higher the temperature is. The data show that the battery capacity loss rate at lower latitudes is significantly higher than that at higher latitudes for Leaf cars in the United States [114]. In the high latitude area, since the temperature may be lower than 0°C in winter, it is necessary to utilize the heating system to prevent lithium deposition caused by low-temperature charging, which may lead to the

safety and durability problems.

During the battery charging and discharging process, there would be significant ohmic heat generation. The battery temperature change caused by this part depends on the battery thermal characteristics (heat capacity, thermal conductivity, etc.), resistance (battery internal resistance as well as the resistance of wire, busbar and welding spot), and the current intensity flowing through the battery. The battery thermal characteristics and resistance could be improved by reasonable cell and system design. However, the current may be influenced by many factors, especially the vehicle design. In BEV, usually the battery discharge rate is low, and the battery temperature rises slowly; while in HEV, the battery charge and discharge rate is respectively higher, and the battery temperature may rise very fast. The vehicle road conditions and driver's driving habits may directly determine the battery working condition; and the current under severe working conditions would be more extreme, leading to large battery temperature rise. And a reliable BMS can reasonably estimate the battery SOP consider the safety and life issues, limiting the current through the battery. Besides, the charging system will greatly influence the battery temperature. For example, the future 350 kW ultra-fast charger would have a much higher charging rate than the discharging rate during driving. Then the charging process will lead to severe battery temperature rise, which may influence the battery life.

In addition, TMS design, including function of heating at low temperatures, cooling at high temperatures and thermal insulation measures, can ensure that the battery works within appropriate temperature range [115]. According to the cooling medium, the cooling system can be generally classified into air cooling (including natural convection and forced convection, usually used in BEV with low battery temperature rise), liquid cooling (usually used in HEV due to higher thermal conductivity) and phase change cooling. And the heating system can be classified into internal heating and external heating methods. The external heating methods include heating plate, heating film, Peltier heating and so on [116]. The external heating method is easy to implement, however, the energy loss is higher and the battery temperature uniformity is poor. Then

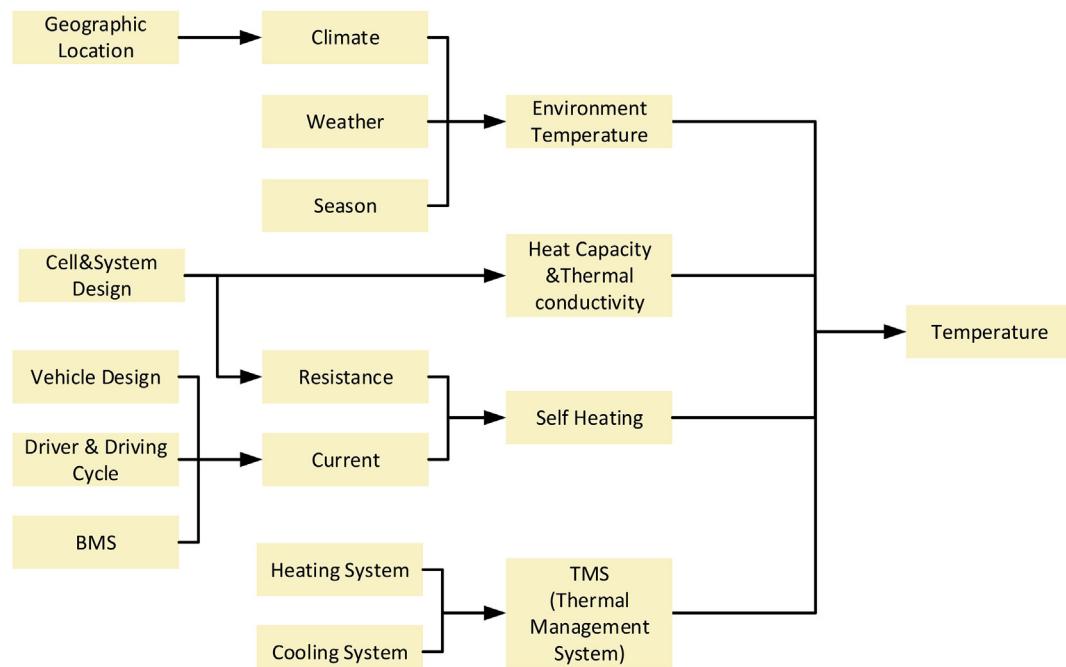


Fig. 16. Factors influencing the battery temperature.

the indirect heating method which heating the thermal medium to heat the battery could help to heat the battery evenly [117]. The internal heating methods include the built-in nickel chip method [118], the alternating current heating [119], the echelon internal heating method [120], etc. These methods can uniformly heat the battery with less heat loss and high efficiency [121,122]. With a reliable TMS in EV, the battery temperature can be effectively maintained and the battery life can be extended. For the second-used battery working in an energy storage station, the temperature is usually well controlled due to the high performance air conditioner.

(2) Influence of SOC

The battery SOC also has significant influence on the battery life. It should be noted that the battery SOC and the battery voltage are dependent. Given the battery SOC and current, the battery voltage could be derived, and this relationship could be described as the battery model. SOC indicates the available capacity stored in battery, which is more meaningful for the vehicle. Accordingly, in this section, the influence of the voltage would not be discussed alone. As shown in Fig. 17, the battery SOC is mainly determined by the vehicles.

Generally speaking, higher SOC indicates higher terminal voltage, which suggests lower anode potential and higher cathode. For the graphite anode with lower potential, the side reactions rate such as the SEI thickening will be higher, resulting in battery higher aging rate [6]. And in case of abnormal charging like overcharging or low temperature charging, the anode potential may be too low and may reach the lithium deposition potential, then the side reaction of lithium deposition may occur to accelerate the battery aging [4]. Meanwhile, for the cathode with higher potential, there would be electrolyte oxidation and the cathode decomposition [123,124]. Lower SOC indicates higher anode potential and lower cathode potential, which generally benefit the battery life. However, if the battery SOC is too low, the corrosion of the anode copper current collector and the cathode active material structure disordering would dramatically affect the battery life [112]. The battery calendar life under different SOC

is shown in Fig. 18 [125]. Hence, in case of battery storage mode, the battery would be better in a low SOC state, e.g., around 20% SOC, which is beneficial to the battery life. And the safety performance at low SOC would be also better than that at a higher SOC.

For BEV mode, usually the battery would be fully charged and then discharged to a certain DOD (depth of discharge). Here the definition of DOD is shown in Fig. 17, DOD of 80% would generally mean battery is cycled within the range of 20%-100% SOC. Under this case, the battery life is greatly influenced by the DOD. The influence of DOD on the battery life is very complicated. In Fig. 19 an experiment result is shown [126]. With the DOD increases, first the battery life would be better since the average SOC decreases as well as corresponding anode potential, leading to lower side reaction rate; then the battery life would be worse since the cathode and anode materials will undergo multiple phase change regions

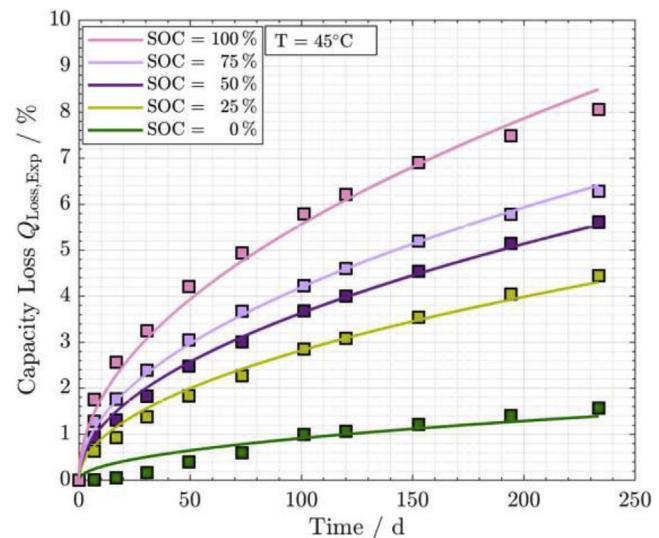


Fig. 18. Capacity loss vs. SOC.

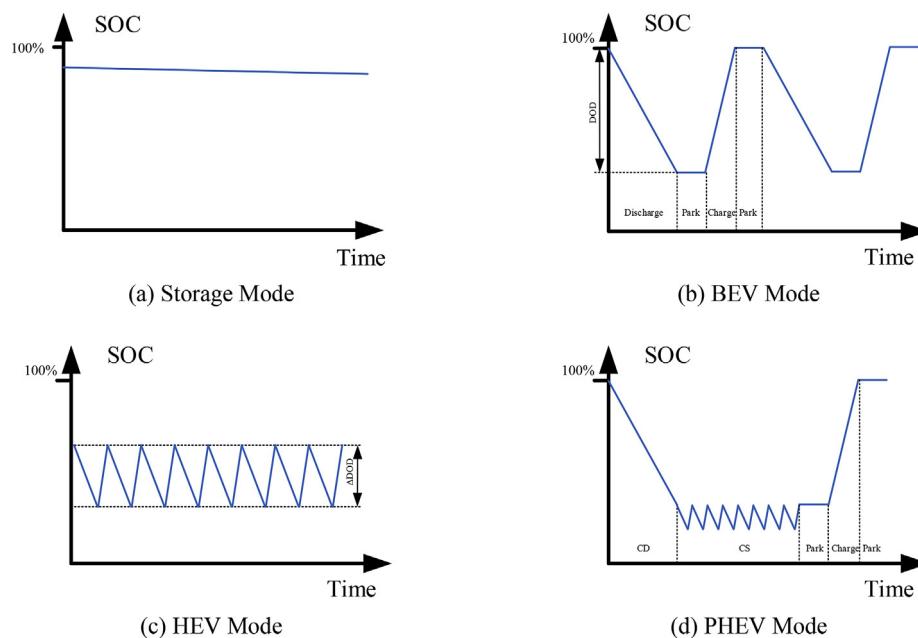
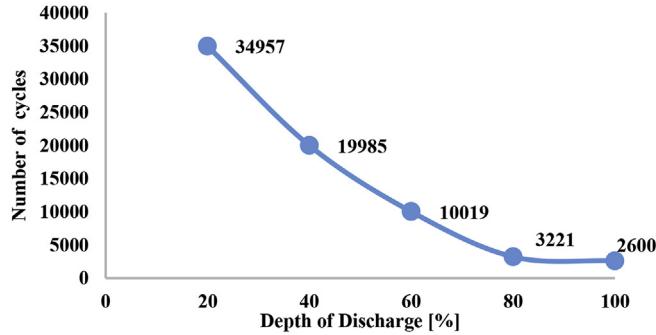
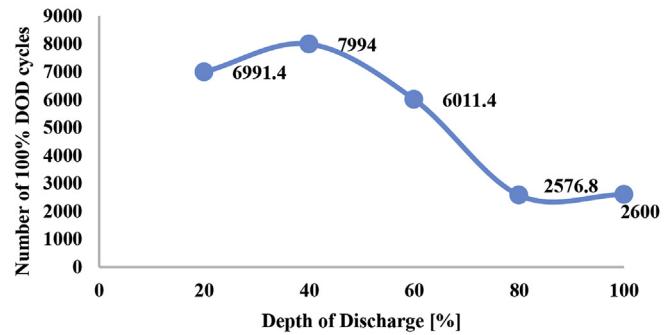


Fig. 17. Battery working SOC in different vehicles.



(a) Cycle life



(b) 100% DOD equivalent cycle life

Fig. 19. Cycle life vs. DOD.

because of high DOD, leading to severer structure and volume change. Thus, the battery life would be significantly reduced under higher DOD. Overall, there seems to be an optimal DOD considering the battery life, however this DOD is usually too small to meet the driving range requirements. Consequently, in the real EV, the battery capacity should be carefully designed and should not be used with high DOD under the premise of satisfying the customer's need.

For the HEV mode, the battery would be cycling in a certain SOC interval with high frequency. And the magnitude of this SOC interval is generally called as Δ DOD as shown in Fig. 17. Cycling under lower SOC range could extend the battery life, as shown in Fig. 20 [127]. Meanwhile, it would be better for the battery to cycle away from the phase change region of the active material. Considering the requirements of vehicle, this working SOC interval needs to ensure sufficient discharging and regeneration capability. Generally speaking, in HEV the batteries are often cycled in the SOC range within 30% - 80%. For PHEV, as shown in Fig. 17, the battery usually works in CDSC mode. The CD (charge depleting) stage is similar to the EV mode, where the battery SOC decreases steadily. And the CS (charge sustaining) stage is similar to the HEV mode, where the battery SOC is basically stable with fluctuating. As aforementioned, it is necessary to design a reasonable working range for the battery, considering both the battery life and the requirements of the driving range. And for the second-used battery working in an energy storage station, the battery cycling profile is usually similar to the HEV mode, and it also needs to be carefully designed.

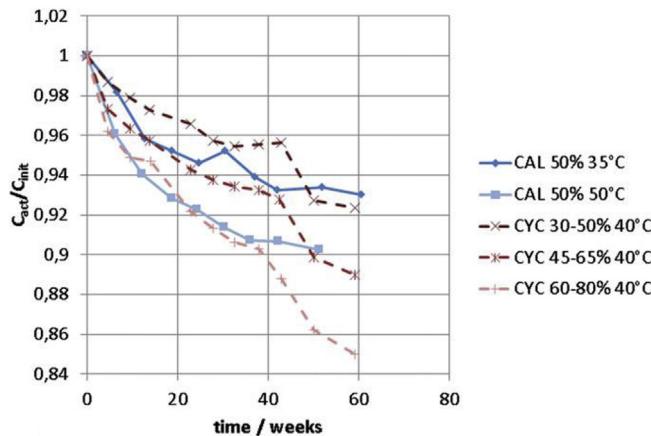


Fig. 20. Battery aging under different SOC.

(3) Influence of current

The battery current also has an obvious impact on the battery life. On one hand, the current flowing through the battery will produce Joule heat, which affects the battery temperature. Especially the large charge and discharge rates may cause a dramatic temperature rise, influencing the battery life. On the other hand, the current also influences the battery terminal voltage and the internal potential, which results in the related side reactions to reduce the battery life. Especially for charging process, there exists a boundary current of lithium deposition [128]. Besides, excessive current represents a rapid lithium-ion intercalation and deintercalation process on the particle surface, which may cause the active material structure fatigued and damaged. The excessive current may also lead to poor uniformity of the current distribution inside the battery, resulting in local lithium plating or inconsistent structure deformation. And in case of fast charging, the limited lithium-ion migration rate may cause lithium deposition and influence the battery life. In summary, under most cases, the smaller the current flowing through the battery is, the longer the battery life would be. However, considering the demands of power, charging time, etc., in real EV usually the current cannot be simply reduced.

It is clear that the battery current rate is primarily determined by design of the energy storage station or the vehicle including the battery system, motor system, etc. Generally, the charge and discharge rate in HEV is much higher than that in BEV and PHEV. For BEV or PHEV, installing battery system with more energy would make longer pure electric range and relatively small discharging rate. It is beneficial to the battery life, but the cost of the vehicle would be very high. In addition, with a reasonable BMS with efficient algorithm, the battery system can be effectively managed, and the current through the battery could be controlled, partially prolonging the battery life.

Specifically, considering the discharging, the two key functions of BMS are SOP estimation and SOE estimation. The purpose of SOP estimation is to predict the short-term behavior of the battery, such as the available current within 10s~30s. And the aim of SOE estimation is to predict the long-term behavior of the battery, which indicates the total available energy stored in the battery under a specific power. With accurate SOP and SOE estimation results, the vehicle could optimize its driving behavior, especially the battery system output can be limited in case of low SOC, low temperature or high temperature to prevent abuse like over discharge. However, the current is usually directly determined by the driving demands, and usually the BMS could not directly control the output current.

The battery charging process is usually carried out on a charger,

and the charging current could be controlled by BMS. Hence the charging could be easily optimized. For charging, the main problems are the temperature rise and lithium deposition, as shown in Fig. 21. Based on a control oriented electrochemical model and stable reference electrode technology, a close-loop observer of lithium deposition status is built, then Chu et al. [129] proposed a battery fast charging method considering the lithium deposition. In the case of low temperature charging, the battery charging capability is greatly restricted due to the low lithium ion transportation rate. A self-heating battery is developed by Wang, et al. [118], which could warm the cell up very fast to solve the low temperature charging problem. And based on the impedance analysis, Li, et al. [130,131] also propose a method combined of alternating current heating and optimal charging considered the lithium deposition boundary.

In short, the design, production and working condition of the battery may influence the battery life. To solve this problem, on one hand, the battery aging mechanism related to different factors should be deeply analyzed. On the other hand, battery aging model needs to be developed considering the aging mechanism. Then, based on this Degradation Model, it is believed that the optimized battery design, production and management could effectively improve the battery life.

4. The aging mechanism of battery system

At present, there are relatively more studies focus on the aging of a single cell, while there are few studies on the aging of the battery system. On one hand, the performance of the system is directly determined by the performance of each single cell, which means the cell aging may directly lead to the system aging; on the other hand, the battery system performance is greatly affected by the inconsistency between the cells.

For the parallel connected systems, due to differences of the internal resistance, capacity, etc., there may be a large difference of the current flowing through each cell [132]. And the nonuniform current distribution may affect the temperature distribution of each cell. Conversely, the temperature distribution between the cells also affects the cell internal resistance as well as the current distribution [133]. Especially under extreme conditions, the currents flowing through different cells may have great difference, up to several times. Due to the different current and temperatures, the life of the cells and system would also be significantly affected [134]. Qualitatively speaking, the current flowing through a cell with small internal resistance would be large, which may accelerate the cell degradation and its internal resistance may increase faster. Such a negative feedback mechanism will lead to the convergence

trend of the capacity and internal resistance of each cell in the parallel system [135]. In an actual battery system, usually only one current sensor is used to measure the total current, and for several cells connected in parallel, only one voltage can be measured. Therefore, in practice, cells connected in parallel are often regarded as one cell.

For the series connected system, due to the difference between the battery capacity and the SOC, the available charging and discharging capacity of each cell are significantly different. But the current flowing through the individual cells are the same, therefore the available charging and discharging capacity are limited and could not be fully used. More specifically, assuming that the capacity of i_{th} cell is C_i , and the electric quantity, which means the available discharge capacity is Q_i , the cell SOC can be defined as $SOC_i = Q_i/C_i$. And the available discharge capacity of the total system is $\min(Q_i)$, while the available charge capacity is $\min(C_i - Q_i)$. Therefore, the capacity of the total system is following this equation:

$$C_{\text{pack}} = \min(Q_i) + \min(C_i - Q_i) = \min(SOC_i C_i) + \min((1 - SOC_i) C_i) \quad (1)$$

Since the capacity and SOC of each cell are different, the capacity of the system is very complicated, not equal to the minimum capacity cells.

To better describe the system's state, usually a histogram as shown in Fig. 22(a) could be used. However, such diagram is not convenient, and could not reflect the system's capacity and SOC conditions adequately. So, the electric quantity - capacity scatter diagram could be used instead as shown in Fig. 22(b) [102,136]. The horizontal axis is the capacity axis, while the vertical axis is the electric quantity. Then the state of each cell could be represented by a dot in the figure. Then the state of the system can be obtained based on two cells as shown in Fig. 22(b).

As shown in Fig. 23, it can be seen that the system capacity fade may be caused by the aging of single-cell as shown in case A. This case represents the irreversible system capacity fade. The system capacity fade could also be caused by the system consistency deterioration as shown in case B. This case represents the reversible system fading process. The loss of the system capacity could be recovered by balancing. And of course in most cases, there would be both irreversible and reversible loss of system capacity, as shown in case C.

Based on the scatter diagram and model simulation, it could be easily found that without an efficient balancing system, the system performance loss is mainly affected by coulomb efficiency, self-discharge rate, and so on. Usually, the reversible capacity loss

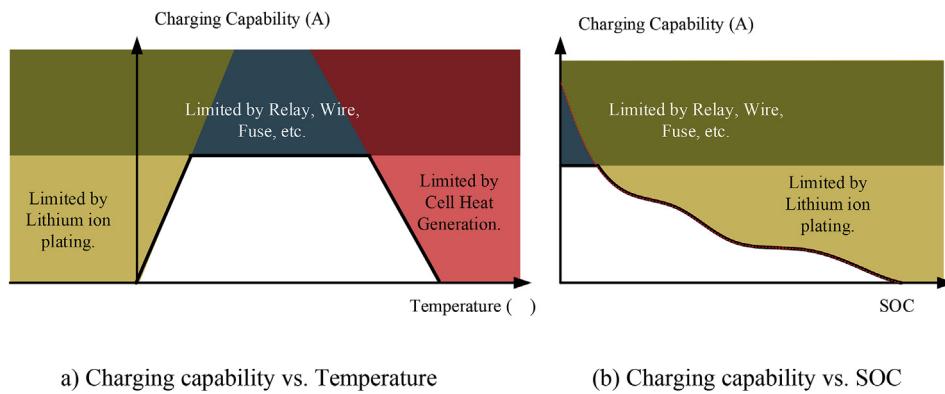


Fig. 21. Analysis of the charging capability.

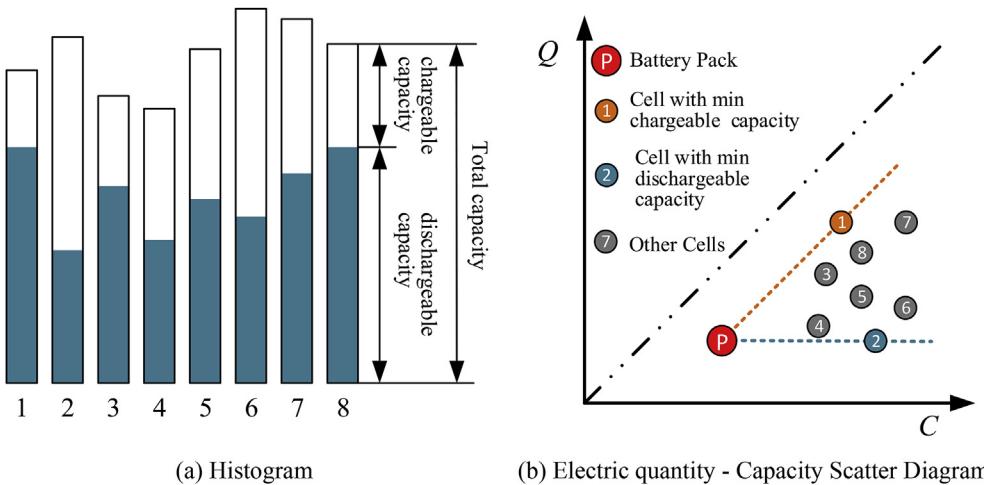


Fig. 22. Pack status diagram.

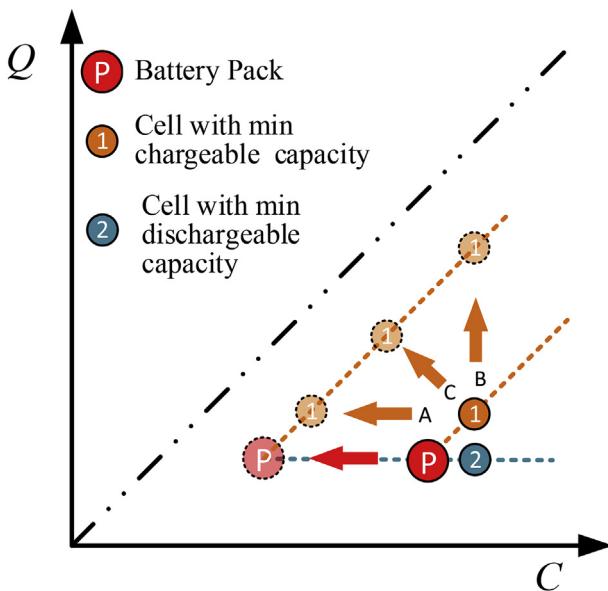


Fig. 23. Capacity fade of the system.

would have a large proportion. Through reasonable dissipation equalization system design, this part of capacity loss can be effectively compensated. However, with a dissipation equalization system, the optimal capacity of the battery system would be only equal to the minimum cell capacity. With a non-dissipative equalization system, the battery system could get a higher available capacity, however, it would have a much higher cost, poor reliability as well as relatively limited benefit [137].

5. Summary

Lithium ion batteries are very complicated systems with many different degradation mechanisms. The research on the battery degradation is very important. The battery aging mechanism and its modeling is the key scientific problem in the battery research area. The capacity and power fade may be caused from multiple and complex side reactions. And the side reactions may be influenced by many factors including the battery design, production and the way to use the battery. This article provides a comprehensive review on the battery degradation along the whole cycle life.

However, the battery degradation problems still need further research, especially for the high energy density battery with new chemistry including the Ni-rich cathode, Li-rich cathode, lithium sulfur battery, all solid state battery, and so on.

The battery aging effects could be considered as capacity fade and power fade, and the internal aging mode could be classified as LAM, LLI, LE and RI. The related internal side reactions have been summarized according to different anode and cathode. Those side reactions may be directly influenced by various factors including the battery design, production and application. To enlarge the life expectancy, the battery need to be carefully designed. The model based optimization method could be used to reduce the internal side reactions. And during production, the battery quality should be guaranteed, especially the homogeneity in each process is very important and should be simultaneously controlled. While using the battery, the temperature and voltage need to be well controlled in the optimal working range by design of the vehicle, battery pack, TMS and BMS algorithm. And the charging current need to be carefully controlled based on the internal anode potential to avoid the lithium plating side reactions.

And the battery system degradation is complicated, which is determined by the aging of single cells and the evolution of the system consistency. The electric quantity - capacity scatter diagram could be used to visually analyze the battery system state. Optimal design of the cell pressure, battery balancing algorithm could help to enlarge the system's life.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] Lu L, Han X, Li J, et al. A review on the key issues for lithium-ion battery

- management in electric vehicles. *J Power Sources* 2013;226:272–88.
- [2] Barré A, Deguilhem B, Grolleau S, et al. A review on lithium-ion battery ageing mechanisms and estimations for automotive applications. *J Power Sources* 2013;241:680–9.
- [3] Vetter J, Novák P, Wagner MR, et al. Ageing mechanisms in lithium-ion batteries. *J Power Sources* 2005;147(1–2):269–81.
- [4] Li Z, Huang J, Yann Liaw B, et al. A review of lithium deposition in lithium-ion and lithium metal secondary batteries. *J Power Sources* 2014;254:168–82.
- [5] Santhanagopalan S, Guo Q, Ramadass P, et al. Review of models for predicting the cycling performance of lithium ion batteries. *J Power Sources* 2006;156(2):620–8.
- [6] Wang A, Kadam S, Li H, et al. Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. *Npj Computational Materials* 2018;4 (UNSP 15).
- [7] Farnham A, Waag W, Marongiu A, et al. Critical review of on-board capacity estimation techniques for lithium-ion batteries in electric and hybrid electric vehicles. *J Power Sources* 2015;281:114–30.
- [8] Berecibar M, Gandiaga I, Villarreal I, et al. Critical review of state of health estimation methods of Li-ion batteries for real applications. *Renew Sustain Energy Rev* 2016;56:572–87.
- [9] Birk CR, Roberts MR, Mcturk E, et al. Degradation diagnostics for lithium ion cells. *J Power Sources* 2017;341:373–86.
- [10] Bloom I, Cole BW, Sohn JJ, et al. An accelerated calendar and cycle life study of Li-ion cells. *J Power Sources* 2001;101(2):238–47.
- [11] Wright RB, Christophersen JP, Motloch CG, et al. Power fade and capacity fade resulting from cycle-life testing of Advanced Technology Development Program lithium-ion batteries. *J Power Sources* 2003;119–121:865–9.
- [12] Belt J, Utgikar V, Bloom I. Calendar and PHEV cycle life aging of high-energy, lithium-ion cells containing blended spinel and layered-oxide cathodes. *J Power Sources* 2011;196(23):10213–21.
- [13] Pop V, Bergveld HJ, Regtien PPL, et al. Battery aging and its influence on the electromotive force. *J Electrochem Soc* 2007;154(8):A744–50.
- [14] Dubarry M, Truchot C, Liaw BY. Synthesize battery degradation modes via a diagnostic and prognostic model. *J Power Sources* 2012;219:204–16.
- [15] Sarasketa-Zabala E, Aguesse F, Villarreal I, et al. Understanding lithium inventory loss and sudden performance fade in cylindrical cells during cycling with deep-discharge steps. *J Phys Chem C* 2015;119(2):896–906.
- [16] Han X, Ouyang M, Lu L, et al. A comparative study of commercial lithium ion battery cycle life in electrical vehicle: aging mechanism identification. *J Power Sources* 2014;251:38–54.
- [17] Scrosati B, Garche J. Lithium batteries: status, prospects and future. *J Power Sources* 2010;195(9):2419–30.
- [18] Nitta N, Wu F, Lee JT, et al. Li-ion battery materials: present and future. *Mater Today* 2015;18(5):252–64.
- [19] Yi T, Jiang L, Shu J, et al. Recent development and application of Li₄Ti₅O₁₂ as anode material of lithium ion battery. *J Phys Chem Solids* 2010;71(9):1236–42.
- [20] Endo M, Kim C, Nishimura K, et al. Recent development of carbon materials for Li ion batteries. *Carbon* 2000;38(2):183–97.
- [21] Verma P, Maire P, Novák P. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochim Acta* 2010;55(22):6332–41.
- [22] Aurbach D. Review of selected electrode–solution interactions which determine the performance of Li and Li ion batteries. *J Power Sources* 2000;89(2):206–18.
- [23] Aurbach D, Zinigrad E, Cohen Y, et al. A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions. *Solid State Ionics* 2002;148(3–4):405–16.
- [24] Arora P, White RE, Doyle M. Capacity fade mechanisms and side reactions in lithium-ion batteries. *J Electrochem Soc* 1998;145(10):3647–67.
- [25] Lin N, Jia Z, Wang Z, et al. Understanding the crack formation of graphite particles in cycled commercial lithium-ion batteries by focused ion beam – scanning electron microscopy. *J Power Sources* 2017;365:235–9.
- [26] Koltypin M, Cohen YS, Markovsky B, et al. The study of lithium insertion-deinsertion processes into composite graphite electrodes by in situ atomic force microscopy (AFM). *Electrochim Commun* 2002;4:17–23 (PII S1388-2481(01)00264-81).
- [27] Christensen J, Newman J. Effect of anode film resistance on the charge/discharge capacity of a lithium-ion battery. *J Electrochem Soc* 2003;150(11):A1416–20.
- [28] Deshpande R, Verbrugge M, Cheng Y, et al. Battery cycle life prediction with coupled chemical degradation and fatigue mechanics. *J Electrochim Soc* 2012;159(10):A1730–8.
- [29] An SJ, Li J, Daniel C, et al. The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon* 2016;105:52–76.
- [30] Perkins RD, Randall AV, Zhang X, et al. (2292)Controls oriented reduced order modeling of lithium deposition on overcharge. *J Power Sources* 2012;209(0):318–25.
- [31] Ouyang CY, Zhong ZY, Lei MS. Ab initio studies of structural and electronic properties of Li₄Ti₅O₁₂ spinel. *Electrochim Commun* 2007;9(5):1107–12.
- [32] Lu W, Liu J, Sun YK, et al. Electrochemical performance of Li₄/3Ti₅/3O₄/Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}O₂ cell for high power applications. *J Power Sources* 2007;167(1):212–6.
- [33] Shen X, Tian Z, Fan R, et al. Research progress on silicon/carbon composite anode materials for lithium-ion battery. *J Energy Chem* 1 July 2018;27(4):1067–90.
- [34] Heubner C, Langlotz U, Michaelis A. Theoretical optimization of electrode design parameters of Si based anodes for lithium-ion batteries. *J Energy Storage* 2018;15:181–90.
- [35] Wohlfahrt-Mehrens M, Vogler C, Garche J. Aging mechanisms of lithium cathode materials. *J Power Sources* 2004;127(1–2):58–64.
- [36] Du Pasquier A, Huang CC, Spitzer T. Nano Li₄Ti₅O₁₂–LiMn₂O₄ batteries with high power capability and improved cycle-life. *J Power Sources* 2009;186(2):508–14.
- [37] Chung KY, Kim K. Investigations into capacity fading as a result of a Jahn–Teller distortion in 4V LiMn₂O₄ thin film electrodes. *Electrochim Acta* 2004;49(20):3327–37.
- [38] Li X, Xu Y, Wang C. Suppression of Jahn–Teller distortion of spinel LiMn₂O₄ cathode. *J Alloy Comp* 2009;479(1–2):310–3.
- [39] Amine K, Liu J, Belharouak I, et al. Advanced cathode materials for high-power applications. *J Power Sources* 2005;146(1–2):111–5.
- [40] Belharouak I, Koenig JRGM, Amine K. Electrochemistry and safety of Li₄Ti₅O₁₂ and graphite anodes paired with LiMn₂O₄ for hybrid electric vehicle Li-ion battery applications. *J Power Sources* 2011;196(23):10344–50.
- [41] Wang Y, He P, Zhou H. Olivine LiFePO₄: development and future. *Energy Environ Sci* 2011;4(3):805–17.
- [42] Zhang W. Structure and performance of LiFePO₄ cathode materials: a review. *J Power Sources* 2011;196(6):2962–70.
- [43] Zaghib K, Dontigny M, Guerfi A, et al. Safe and fast-charging Li-ion battery with long shelf life for power applications. *J Power Sources* 2011;196(8):3949–54.
- [44] Sun Y, Chen Z, Noh H, et al. Nanostructured high-energy cathode materials for advanced lithium batteries. *Nat Mater* 2012;11(11):942–7.
- [45] Noh H, Youn S, Yoon CS, et al. Comparison of the structural and electrochemical properties of layered Li[NixCoyMnz]O₂ (x = 1/3, 0.5, 0.6, 0.7, 0.8 and 0.85) cathode material for lithium-ion batteries. *J Power Sources* 2013;233:121–30.
- [46] Kim J, Chung H. The first cycle characteristics of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ charged up to 4.7 V. *Electrochim Acta* 2004;49(6):937–44.
- [47] Huang Y, Chen J, Ni J, et al. A modified ZrO₂-coating process to improve electrochemical performance of Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂. *J Power Sources* 2009;188(2):538–45.
- [48] Shaju KM, Subba Rao GV, Chowdari BVR. Performance of layered Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ as cathode for Li-ion batteries. *Electrochim Acta* 2002;48(2):145–51.
- [49] Burns JC, Kassam A, Sinha NN, et al. Predicting and extending the lifetime of Li-ion batteries. *J Electrochem Soc* 2013;160(9):A1451–6.
- [50] Schuster SF, Bach T, Fleder E, et al. Nonlinear aging characteristics of lithium-ion cells under different operational conditions. *J Energy Storage* 2015;1:44–53.
- [51] Bach TC, Schuster SF, Fleder E, et al. Nonlinear aging of cylindrical lithium-ion cells linked to heterogeneous compression. *J Energy Storage* 2016;5:212–23.
- [52] Yang X, Leng Y, Zhang G, et al. Modeling of lithium plating induced aging of lithium-ion batteries: transition from linear to nonlinear aging. *J Power Sources* 2017;360:28–40.
- [53] Park J, Appiah WA, Byun S, et al. Semi-empirical long-term cycle life model coupled with an electrolyte depletion function for large-format graphite/LiFePO₄ lithium-ion batteries. *J Power Sources* 2017;365:257–65.
- [54] Leng F, Wei Z, Tan CM, et al. Hierarchical degradation processes in lithium-ion batteries during ageing. *Electrochim Acta* 2017;256:52–62.
- [55] Richardson RR, Osborne MA, Howey DA. Gaussian process regression for forecasting battery state of health. *J Power Sources* 2017;357:209–19.
- [56] Chen L, Lin W, Li J, et al. Prediction of lithium-ion battery capacity with metabolic grey model. *Energy* 2016;106:662–72.
- [57] Reichert M, Andre D, Rösmann A, et al. Influence of relaxation time on the lifetime of commercial lithium-ion cells. *J Power Sources* 2013;239:45–53.
- [58] Lewerenz M, Münnix J, Schmalstieg J, et al. Systematic aging of commercial LiFePO₄ |Graphite cylindrical cells including a theory explaining rise of capacity during aging. *J Power Sources* 2017;345:254–63.
- [59] Gynies B, Stevens DA, Chevrier VL, et al. Understanding anomalous behavior in coulombic efficiency measurements on Li-ion batteries. *J Electrochim Soc* 2014;162(3):A278–83.
- [60] Eddahech A, Briat O, Bertrand N, et al. Behavior and state-of-health monitoring of Li-ion batteries using impedance spectroscopy and recurrent neural networks. *Int J Electr Power Energy Syst* 2012;42(1):487–94.
- [61] Eddahech A, Briat O, Vinassa J. Lithium-ion battery performance improvement based on capacity recovery exploitation. *Electrochim Acta* 2013;114:750–7.
- [62] Wood DL, Li J, Daniel C. Prospects for reducing the processing cost of lithium ion batteries. *J Power Sources* 2015;275:234–42.
- [63] Epding B, Rumberg B, Jahnke H, et al. Investigation of significant capacity recovery effects due to long rest periods during high current cyclic aging tests in automotive lithium ion cells and their influence on lifetime. *J Energy Storage* 2019;22:249–56.
- [64] Wu F, Zhu Q, Chen R, et al. Ionic liquid electrolytes with protective lithium difluoro(oxalate)borate for high voltage lithium-ion batteries. *Nano Energy* 2015;13:546–53.
- [65] Li Q, Chen J, Fan L, et al. Progress in electrolytes for rechargeable Li-based

- batteries and beyond. *Green Energy & Environ* 2016;1(1):18–42.
- [66] Li J, Daniel C, Wood D. Materials processing for lithium-ion batteries. *J Power Sources* 2011;196(5):2452–60.
- [67] Arora P, Zhang ZJ. Battery separators. *Chem Rev* 2004;104(10):4419–62.
- [68] Banerjee A, Ziv B, Luski S, et al. Increasing the durability of Li-ion batteries by means of manganese ion trapping materials with nitrogen functionalities. *J POWER Sources* 2017;341:457–65.
- [69] Doyle M, Newman J. The use of mathematical modeling in the design of lithium/polymer battery systems. *Electrochim Acta* 1995;40(13):2191–6.
- [70] Doyle M, Fuller TF, Newman J. Modeling of galvanostatic charge and discharge of the lithium polymer insertion cell. *J Electrochim Soc* 1993;140(6):1526–33.
- [71] García RE, Chiang Y, Craig Carter W, et al. Microstructural modeling and design of rechargeable lithium-ion batteries. *J Electrochim Soc* 2005;152(1):A255.
- [72] Joos J, Carraro T, Weber A, et al. Reconstruction of porous electrodes by FIB/SEM for detailed microstructure modeling. *J Power Sources* 2011;196(17):7302–7.
- [73] Newman J. Optimization of porosity and thickness of a battery electrode by means of a reaction-zone model. *J Electrochim Soc* 1995;97–101.
- [74] Christensen J, Newman J. Cyclable lithium and capacity loss in Li-ion cells. *J Electrochim Soc* 2005;152(4):A818–29.
- [75] Zhao J, Lu Z, Wang H, et al. Artificial solid electrolyte interphase-protected lix Si nanoparticles: an efficient and stable prelithiation reagent for lithium-ion batteries. *J Am Chem Soc* 2015;137(26):8372–5.
- [76] Gabrielli G, Marinaro M, Mancini M, et al. A new approach for compensating the irreversible capacity loss of high-energy Si/C|LiNi 0.5 Mn 1.5 O 4 lithium-ion batteries. *J Power Sources* 2017;351:35–44.
- [77] Su X, Lin C, Wang X, et al. A new strategy to mitigate the initial capacity loss of lithium ion batteries. *J Power Sources* 2016;324:150–7.
- [78] Ramadesigan V, Methkar RN, Latinwo F, et al. Optimal porosity distribution for minimized ohmic drop across a porous electrode. *J Electrochim Soc* 2010;157(12):A1328–34.
- [79] Golmon S, Maute K, Dunn ML. A design optimization methodology for Li+ batteries. *J Power Sources* 2014;253:239–50.
- [80] Dai Y, Srinivasan V. On graded electrode porosity as a design tool for improving the energy density of batteries. *J Electrochim Soc* 2016;163(3):A406–16.
- [81] Zhang M, Ouyang M, Lu L, et al. Battery internal short circuit detection. *ECS Transactions* 2017;77(11):217–23.
- [82] Barai A, Tangirala R, Uddin K, et al. The effect of external compressive loads on the cycle lifetime of lithium-ion pouch cells. *J Energy Storage* 2017;13:211–9.
- [83] Zhao Y, Patel Y, Hunt IA, et al. Preventing lithium ion battery failure during high temperatures by externally applied compression. *J Energy Storage* 2017;13:296–303.
- [84] Cannarella J, Arnold CB. Stress evolution and capacity fade in constrained lithium-ion pouch cells. *J Power Sources* 2014;245:745–51.
- [85] Mussa AS, Klett M, Lindbergh G, et al. Effects of external pressure on the performance and ageing of single-layer lithium-ion pouch cells. *J Power Sources* 2018;385:18–26.
- [86] Smekens J, Gopalakrishnan R, Steen N, et al. Influence of electrode density on the performance of Li-ion batteries: experimental and simulation results. *Energies* 2016;9(2):104.
- [87] Krytsberg A, Ein-Eli Y. Conveying advanced Li-ion battery materials into practice—the impact of electrode slurry preparation skills. *Adv Energy Mater* 2016;6(21):1600655.
- [88] Westphal BG, Mainusch N, Meyer C, et al. Influence of high intensive dry mixing and calendering on relative electrode resistivity determined via an advanced two point approach. *J Energy Storage* 2017;11:76–85.
- [89] Bauer W, Nötzel D, Wenzel V, et al. Influence of dry mixing and distribution of conductive additives in cathodes for lithium ion batteries. *J Power Sources* 2015;288:359–67.
- [90] Westphal B, Bockholt H, Gunther T, et al. Influence of convective drying parameters on electrode performance and physical electrode properties. *ECS Transactions* 2015;64(22):57–68.
- [91] Meyer C, Bockholt H, Haselrieder W, et al. Characterization of the calendering process for compaction of electrodes for lithium-ion batteries. *J Mater Process Technol* 2017;249:172–8.
- [92] Haselrieder W, Ivanov S, Christen DK, et al. Impact of the calendering process on the interfacial structure and the related electrochemical performance of secondary lithium-ion batteries. *ECS Transactions* 2013;50(26):59–70.
- [93] Weydanz WJ, Reisenweber H, Gottschalk A, et al. Visualization of electrolyte filling process and influence of vacuum during filling for hard case prismatic lithium ion cells by neutron imaging to optimize the production process. *J Power Sources* 2018;380:126–34.
- [94] Verma P, Maire P, Novák P. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochim Acta* 2010;55(22):6332–41.
- [95] An SJ, Li J, Daniel C, et al. The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon* 2016;105:52–76.
- [96] Abe K, Ushigoe Y, Yoshitake H, et al. Functional electrolytes: novel type additives for cathode materials, providing high cycleability performance. *J Power Sources* 2006;153(2):328–35.
- [97] Gauthier M, Carney TJ, Grimaud A, et al. Electrode–electrolyte interface in Li-ion batteries: current understanding and new insights. *J Phys Chem Lett* 2015;6(22):4653–72.
- [98] Shi Q, Liu W, Qu Q, et al. Robust solid/electrolyte interphase on graphite anode to suppress lithium inventory loss in lithium-ion batteries. *Carbon* 2017;111:291–8.
- [99] Agubra VA, Fergus JW. The formation and stability of the solid electrolyte interface on the graphite anode. *J Power Sources* 2014;268:153–62.
- [100] An SJ, Li J, Du Z, et al. Fast formation cycling for lithium ion batteries. *J Power Sources* 2017;342:846–52.
- [101] Lee H, Wang Y, Wan C, et al. A fast formation process for lithium batteries. *J Power Sources* 2004;134(1):118–23.
- [102] Zheng Y, Ouyang M, Lu L, et al. Understanding aging mechanisms in lithium-ion battery packs: from cell capacity loss to pack capacity evolution. *J Power Sources* 2015;278:287–95.
- [103] Takei K, Kumai K, Kobayashi Y, et al. Cycle life estimation of lithium secondary battery by extrapolation method and accelerated aging test. *J Power Sources* 2001;97–98:697–701.
- [104] Amine K, Liu J, Belharouak I. High-temperature storage and cycling of C-LiFePO₄/graphite Li-ion cells. *Electrochim Commun* 2005;7(7):669–73.
- [105] Zhang Q, White RE. Calendar life study of Li-ion pouch cells. *J Power Sources* 2007;173(2):990–7.
- [106] Ramasamy RP, White RE, Popov BN. Calendar life performance of pouch lithium-ion cells. *J Power Sources* 2005;141(2):298–306.
- [107] Ouyang M, Chu Z, Lu L, et al. Low temperature aging mechanism identification and lithium deposition in a large format lithium iron phosphate battery for different charge profiles. *J Power Sources* 2015;286:309–20.
- [108] Fan G, Pan K, Canova M, et al. Modeling of Li-ion cells for fast simulation of high C-rate and low temperature operations. *J Electrochim Soc* 2016;163(5):A666–76.
- [109] Choi SS, Lim HS. Factors that affect cycle-life and possible degradation mechanisms of a Li-ion cell based on LiCoO₂. *J Power Sources* 2002;111(1):130–6.
- [110] Ouyang M, Ren D, Lu L, et al. Overcharge-induced capacity fading analysis for large format lithium-ion batteries with LiyNi_{1/3}Co_{1/3}Mn_{1/3}O₂ + LiyMn₂O₄ composite cathode. *J Power Sources* 2015;279:626–35.
- [111] Ohsaki T, Kishi T, Kuboki T, et al. Overcharge reaction of lithium-ion batteries. *J Power Sources* 2005;146(1–2):97–100.
- [112] Guo R, Lu L, Ouyang M, et al. Mechanism of the entire overdischarge process and overdischarge-induced internal short circuit in lithium-ion batteries. *Sci Rep* 2016;6.
- [113] Waldmann T, Wilka M, Kasper M, et al. Temperature dependent ageing mechanisms in Lithium-ion batteries – a Post-Mortem study. *J Power Sources* 2014;262:129–35.
- [114] Leaf N. Battery capacity loss[EB/OL] [2019.03.01], <http://www.electricvehiclewiki.com/wiki/battery-capacity-loss/>.
- [115] Xia G, Cao L, Bi G. A review on battery thermal management in electric vehicle application. *J Power Sources* 2017;367:90–105.
- [116] Liu H, Wei Z, He W, et al. Thermal issues about Li-ion batteries and recent progress in battery thermal management systems: a review. *Energy Convers Manag* 2017;150:304–30.
- [117] Yang L, Tai N, Fan C, et al. Energy regulating and fluctuation stabilizing by air source heat pump and battery energy storage system in microgrid. *Renew Energy* 2016;95:202–12.
- [118] Wang C, Zhang G, Ge S, et al. Lithium-ion battery structure that self-heats at low temperatures. *Nature* 2016;529(7587):515–8.
- [119] Ge H, Huang J, Zhang J, et al. Temperature-adaptive alternating current preheating of lithium-ion batteries with lithium deposition prevention. *J Electrochim Soc* 2016;A290–9 {163}(2).
- [120] Guo S, Xiong R, Wang K, et al. A novel echelon internal heating strategy of cold batteries for all-climate electric vehicles application. *Appl Energy* 2018;219:256–63.
- [121] Ji Y, Wang CY. Heating strategies for Li-ion batteries operated from subzero temperatures. *Electrochim Acta* 2013;107:664–74.
- [122] Andreas Vlahinos AAP. Energy efficient battery heating in cold climates. *SAE Technical Papers* 2002 (2002-01-1975).
- [123] Hausbrand R, Cherkashinin G, Ehrenberg H, et al. Fundamental degradation mechanisms of layered oxide Li-ion battery cathode materials: methodology, insights and novel approaches. *Mater Sci Eng, B* 2015;192:3–25.
- [124] Ren D, Feng X, Lu L, et al. An electrochemical-thermal coupled overcharge-to-thermal-runaway model for lithium ion battery. *J Power Sources* 2017;364:328–40.
- [125] Schimpke M, Von Kuepach ME, Naumann M, et al. Comprehensive modeling of temperature-dependent degradation mechanisms in lithium iron phosphate batteries. *J Electrochim Soc* 2018;2(165):A181–93.
- [126] Omar N, Monem MA, Firouz Y, et al. Lithium iron phosphate based battery – assessment of the aging parameters and development of cycle life model. *Appl Energy* 2014;113:1575–85.
- [127] Ecker M, Gerschler JB, Vogel J, et al. Development of a lifetime prediction model for lithium-ion batteries based on extended accelerated aging test data. *J Power Sources* 2012;215:248–57.
- [128] Burns JC, Stevens DA, Dahn JR. In-Situ detection of lithium plating using high precision coulometry. *J Electrochim Soc* 2015;162(6):A959–64.
- [129] Chu Z, Feng X, Lu L, et al. Non-destructive fast charging algorithm of lithium-ion batteries based on the control-oriented electrochemical model. *Appl*

- Energy 2017;204:1240–50.
- [130] Ge H, Huang J, Zhang J, et al. Temperature-adaptive alternating current preheating of lithium-ion batteries with lithium deposition prevention. *J Electrochim Soc* 2016;163(2):A290–9.
- [131] Zhang J, Ge H, Li Z, et al. Internal heating of lithium-ion batteries using alternating current based on the heat generation model in frequency domain. *J Power Sources* 2015;273:1030–7.
- [132] Dubarry M, Devie A, Liaw BY. Cell-balancing currents in parallel strings of a battery system. *J Power Sources* 2016;321:36–46.
- [133] Yang N, Zhang X, Shang B, et al. Unbalanced discharging and aging due to temperature differences among the cells in a lithium-ion battery pack with parallel combination. *J Power Sources* 2016;306:733–41.
- [134] Shi W, Hu X, Jin C, et al. Effects of imbalanced currents on large-format LiFePO₄/graphite batteries systems connected in parallel. *J Power Sources* 2016;313:198–204.
- [135] Pastor-Fernández C, Bruen T, Widanage WD, et al. A study of cell-to-cell interactions and degradation in parallel strings: implications for the battery management system. *J Power Sources* 2016;329:574–85.
- [136] Ouyang M, Gao S, Lu L, et al. Determination of the battery pack capacity considering the estimation error using a Capacity-Quantity diagram. *Appl Energy* 2016;177:384–92.
- [137] Zhou L, Zheng Y, Ouyang M, et al. A study on parameter variation effects on battery packs for electric vehicles. *J Power Sources* 2017;364:242–52.