Faculty for System and Process Engineering

Literature Survey

by

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Aging and degradation of lithium batteries

Lecture: Sustainability Assessment (LCA) for Biofuels

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Matrikel No.: 226036

Date: 22.05.2019

1. Abstract

Lithium-ion batteries are regarded as the key energy storage technology for both e-mobility and stationary renewable energy storage applications. Nevertheless, Lithium-ion batteries are complex energy storage devices, which are characterized by a complex degradation behavior, which affects both their capacity and internal resistance.

This paper primarily focuses on understanding different Aging Mechanisms of the Lithium ion Battery (LIB). The causes for the aging and degradation are provided here in detail. The types of aging such as cyclic aging and calendar aging are also discussed. How the operating condition of the battery affects its aging and degradation rate is a topic of immense interest. It is a very important to interpret how the battery functions under different conditions, the details on how to model the behavior of the battery are provided here. While discussing different battery models, their respective advantages and drawbacks are briefly discussed. Even the optimum conditions for their application of different models of the battery are provided here in a concise manner.

The materials with which different components of the battery are made of, play an important role. The ongoing transformation of battery technology has prompted many to learn about designing battery management systems as it measures and reports and also protects the battery from damage in a wide range of operating conditions. Finally, some insights on how the battery responds when it is subjected to different operating conditions are also discussed.

2. Introduction

In an effort to extend the battery cycle life, comprehensive understanding of the underlying ageing mechanisms that cause degradation in its energy storage performance such as capacity loss and cell impedance raise is necessary. As LIB ages it may be operated beyond its temperature and voltage stability windows, which accelerates the degradation of battery performance and may even results in catastrophic failures. A better understanding of the root causes of degradation processes offers a possible strategy to act on them, therefore, extends battery's lifetime and safety. However, the complexity of LIB system makes it challenging for the study of ageing. Capacity fade and cell impedance increase do not originate from one single cause but from several underlying processes which could be related to each other. This requires the investigation of various degradation processes in LIB during charge/discharge cycles in order to determine the predominant degradation mechanisms at different time scales.

The ageing of Li-ion batteries is a complex combination of a large number of electrochemical and mechanical processes, which are highly influenced by the operating conditions. The capacity fade and resistance increase (and subsequently power fade) do not originate from one single cause but from various ageing mechanism and their possible interactions. Furthermore, the aforementioned performance parameters degrade during both calendar and cycling ageing.

It is important to be aware of the battery degradation behavior with respect to the functionality of the LIBs. Batteries start to degrade as soon as they are assembled. Ageing will be different depending on battery materials and design, battery operation conditions and having an optimized Battery Management System (BMS) is very much importance in order to operate the battery at best possible conditions.

3. Origin of Aging

Aging first occurs at the interfaces between the electrolyte and the electrodes because of the chemical composition of the cell electrolyte. Aging mechanisms can be either mechanical or chemical and are strongly dependent on electrode composition. As a rule, two principal effects of battery aging can be identified: impedance rise and capacity fade. Performance loss results from various chemical-based mechanisms, which depend on the electrode materials. The consequences of these mechanisms for Li ion cells are as follows: A passivation layer forms around the anode, known as the solid electrolyte interphase (SEI), and its growth leads to an impedance rise at the anode. Typically, SEI formation occurs principally at the beginning of aging, but its growth proceeds throughout operation and storage. Simultaneously, loss of cyclable lithium occurs at both electrodes, as the SEI grows at the carbon anode as a result of electrolyte oxidation and/or changes in the oxide surface structure. The formation and growth of the SEI leads to gradual contact losses within the composite anode and thus increases the impedance in the cell. The loss of active electrode materials occurs, involving material dissolution, structural degradation, particle isolation, and electrode decomposition. With regard to battery performance, both the loss of active materials and the loss of cyclability lead to capacity fade. Moreover, the increase in the battery resistance can be directly associated with power fade. As a general rule, two aging mechanisms are often distinguished: calendar aging and cycle aging. Each term refers to the changes caused by different uses of the battery.

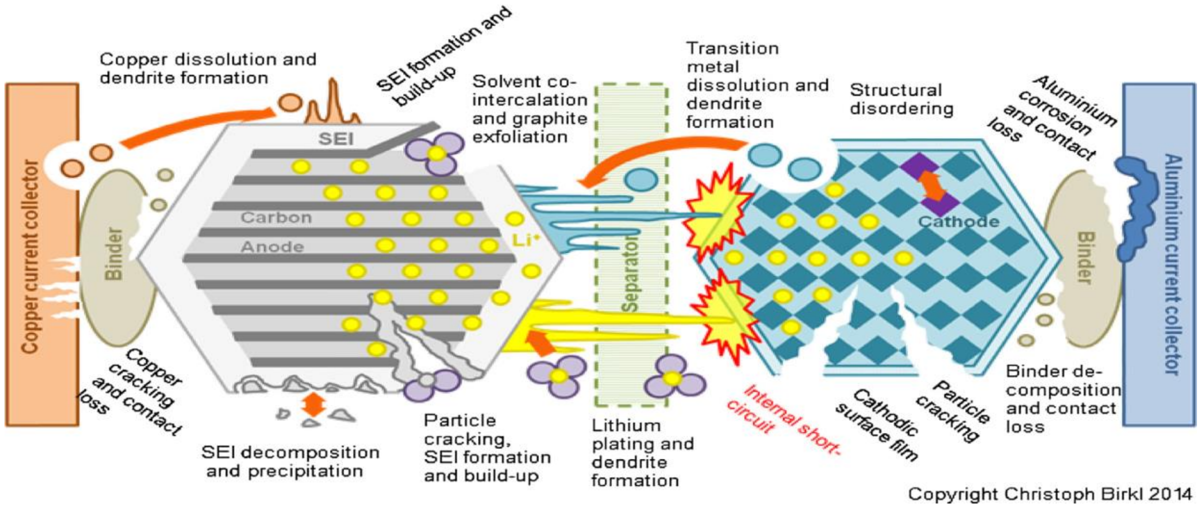


Figure. 1: Degradation of Li-ion batteries [1]

3.1. Calendar aging: Calendar aging occurs while the cell is in storage. In other words, it is the irreversible damage to the cell's capacity caused when the battery is not in use. The main stipulations regarding calendar aging are the storage temperature and the (SOC). When the temperature is high, side reactions such as metal dissolution are more rapid and the loss of capacity is more marked than under ambient-temperature conditions. The other main variable in calendar aging studies is the SOC level during storage.

3.2. Cycle aging: Cycle aging occurs as the cell is operating, either charging or discharging. In most cases, high temperatures will cause even greater charge capacity loss and impedance rise than those observed at ambient temperatures because of amplified aging effects. In addition, it is crucial to account for the effects of very low temperatures. The principal aging effect occurring at such temperatures is the plating of metallic lithium on the anode which is responsible for the loss of active material and growth of the SEI under cold conditions. The initial SOC is an important factor as it can yield to very fast aging. The utilization mode of the battery is also an influencing function in cycle aging and it can be interpreted indifferent ways: charging/discharging current rate, depth-of discharge, state-of-charge variation, charging/discharging voltage limit. The current scale is known to play a significant role in cycle aging. SOC variation during a cycle is also known as DSOC. Under dynamic conditions, DSOC (%) is the difference between the minimum SOC and the maximum SOC induced during cycle life testing. There is usually a loss of battery power for high DSOC values. Also, high charging voltage leads to accelerated aging phenomena, and a discharge voltage lower than the manufacturer recommendations also induces more rapid aging via augmentation of the cell's resistance.

3.3. Aging effect: Rationally, when a cell is below 0 C, the aging mechanisms described above are slowed or not dominant. However, these conditions create another problem due to the high polarization of the anode: lithium plating. Based on measurements of pouch cells with reference electrodes, the authors of [1] revealed a negative polarization with respect to Li/Li+ in the low-temperature range. This polarization is close to the potential of lithium metal (100 mV), and therefore, under these conditions, metallic lithium is deposited on the anode surface This lithium plating leads to capacity loss by interfering with the intercalation of lithium between the anode and electrolyte and a loss of lithium (electrolyte decomposition),which leads to capacity loss and, in turn, dramatically affects the cell's lifetime. In the case of low-temperature charging, the dendritic growth of metallic lithium has also been reported. Dendrites can reach the positive electrode by penetrating the separator, which causes an internal soft shorting of the cell and poses a potential safety risk. Therefore, the mechanisms of metallic lithium plating and lithium dendrite growth must be considered as parasitic side reactions during charging. Thus far, the principal solution to this lithium plating problem is to use anodes that operate at a higher working voltage vs. Li/Li+, such as lithium titanate, at the expense of energy density.

4. Predicting the complex behavior a Li–ion battery

Extensive studies have been conducted by the authors of [2] on the degradation of cell components in LIB with experimental and modelling approaches. For the experimental approach, characterization techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD) and neutron scattering techniques are used. These techniques are mostly ex-situ and destructive because the investigations are conducted by cross-checking fresh and aged cells and compare their positive and negative electrodes in order to find out the morphological, electrical, and structural changes that occur during ageing.

The modelling approach is considered as in-situ non-destructive techniques (NDT) and very useful for prognosis and diagnosis. It can be concluded that particular inputs to the system can affect capacity fade and internal resistance increase of LIB. Some parameters and their relations are summarized from a principle point of view in Figure. 2.

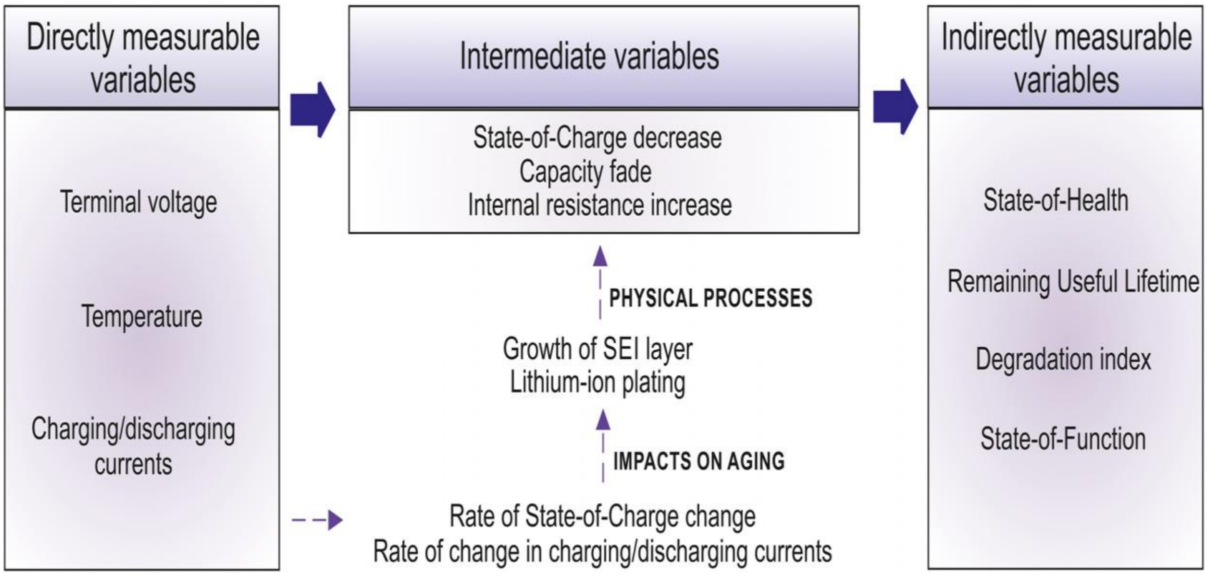


Figure. 2: Measurable and immeasurable variables and their relation to aging indicators. [3]

4.1 Modeling a Li–ion battery

General organization: Battery models are necessary to describe the features of the Li-ion battery. They are also the first step in the conceptualization of algorithms or management schemes for the implementation of a battery management system (BMS). They mathematically describe the parameters that influence the efficient use of the battery, such as voltage, load current, and temperature.

4.2. <u>Electrical behavior</u>:

4.2.1 *Electrochemical models*: Lying at the interface of chemistry and physics, electrochemical models can be used to identify factors that limit cell performance. This type of model is the most accurate for optimizing aspect of physical battery design, but it is also the slowest in producing predictions (high computational demand). However, because they specify and simulate the electro-thermal phenomena inside a cell, electrochemical models employ lists of parameters that must usually be acquired through data exploration, which can be time-consuming.

4.2.2 *Empirical model*: When an electrochemical model cannot be used, an empirical model is created instead because it simply consists of general equations representing the battery behavior with parameters suited to match experimental data. They are mainly descriptive and simple to configure, but their computational results are the least accurate, and they provide no knowledge regarding the real structure of the model.

4.2.3. *Electrical model*: Electrical models reproduce a battery's behavior by means of a simple electrical circuit. They use passive components such as impedances, polarization resistances, and capacitances as well as active elements such as controlled battery sources. Because this is a parametric approach, it can be used to model any battery, regardless of its chemistry, configuration, and rate of discharge, given a suitable combination of parameters. Therefore, electrical models are the most commonly employed for EV/HEV applications.

4.3. Thermal behavior: All of the challenges facing the cold-temperature operation are linked to thermal effects on the battery system: low performances, voltage drop, etc. Therefore, a proper means of establishing a new strategy for battery thermal management begins with the establishment of a detailed thermal battery model.

4.4. Aging: For the assessment of aging, several concepts have not yet been implemented in BMSs to quantify the battery degradation level. Indeed, cell aging is a complex mechanism. Two principal changes are observed in a cell as it degrades: it loses capacity and its impedance increases. Many methods of quantifying these characteristics of aging have been reported in the literature. They can be classified into three types: electrochemical models, performance-based models, and equivalent-circuit-based models

5. Materials Used in a Lithium Ion Battery:

The lithium nickel manganese cobalt oxide (NMC) chemistry is considered to be one of the major battery cathode materials due to its comparatively excellent energy density, long cycle life, and high safety performance. They usually consist of a carbon/graphite based anode, a lithium transition metal oxide or phosphate cathode (($LiMO_2$ or $LiMPO_4$, M = e.g., Co, Ni, Mn, Fe, Al, in varying contents) and with a liquid electrolyte (a mixture of linear and cyclic organic carbonates with 1 M of $LiPF_6$ as conducting salt) soaked polyolefin-based separator. A picture of the NMC cell lying on a sheet of A4 paper is shown in Figure 3.

Figure 3. Picture of the nickel manganese cobalt oxide (NMC) cell, lying on a sheet of A4 paper [4]

6. Thermal Management Strategies for Li-ion Batteries

Li-ion cells, under varying operation conditions, require elaborate battery thermal management strategies to guarantee ideal operation in terms of performance and lifespan. This is achieved via a battery thermal management system (BTMS). A BTMS is composed of systems that may be either active (external or internal sources of heating and/or cooling) or passive (natural convection) and can also be categorized into systems based on air, liquid, and phase-change materials (PCMs). They are: a) Air management, b) Liquid management, c) Phase-change materials, d) Heating strategies.

7. Battery Behavior in Different Operating Conditions

7.1 Due to fast charging:

In addition to a fast rise in the battery system temperature, the high current-rate condition of the fast-charging profile further deteriorates the LIB performance. Indeed, aging of LIBs, defined as the irreversible loss of their energy storage capability and power, is one such challenge.

7.2 Due to dynamic mechanical loading

To directly investigate the electrochemical failure of LIB induced by mechanical abusive loading, experiments were designed and conducted to characterize the mechanical properties of battery cell in terms of structure and its components in quasi-static and dynamic loading conditions, where basic loadings include tension, compression, bending, indentation, penetration and drop-weight.

Two groups of experiments were designed in this study by the authors of [5], namely large-deformation compression tests and drop-weight experiments. The specifications of the battery used for these experiments. There are two key factors dominating the mechanical behaviors of battery, i.e., SOC status and loading rate.

LIB parameters	Values
Charge cutoff voltage/V	4.2
Discharge cutoff voltage/V	2.7
Cathode/Anode materials	$LiCoO_2$/graphite
Nominal voltage/V	3.7
Nominal capacity/mAh	1250
Max charge/discharge current/C	10/10

Table 1: Specifications of lithium-ion pouch battery test samples. [5]

Generally, the stiffness of high SOC batteries is larger than that of low SOC batteries, Thus, different types of LIBs share similar SOC hardening behaviors. It is noteworthy that this SOC-hardening effect also existed in dynamic loading tests. Apart from that, the loading rate is a more decisive factor. The batteries exhibit high structural stiffness with loading rate. This loading rate dependent “hardening effect” is more obvious than SOC-dependent hardening.

The maximum peak forces of the drop-weight impact tests increase with SOC and loading rate. High loading rate leads to considerable changes in peak force after increasing SOC. The component deformation and materials failure state of battery determine the electrochemical discharging (voltage drop) behavior during short- circuit process of battery. Higher loading rate, causes a faster voltage-drop and more severe internal short circuit. This short-circuit discharging process in turn affects the force response in dynamic loading. Results of the experiments in [5] indicate remarkable differences of mechanical behavior, electrochemical behavior and failure mechanisms of LIBs in dynamic impact and provide useful insights for the mechanical integrity of LIBs and their crash-safety design.

7.3 The role of cations on LIBs performance

Cations and their chemistries play a major role in aging processes and mechanisms of LIBs. On the one hand, transition metal cations which derive from the cathode (i.e., transition metal dissolution (TMD)) and subsequently deposit on the surface of the anode and SEI are supposed to have a significant impact on aging and thus cell performance. During the charge/discharge processes, the lithium can be “lost” or immobilized and is therefore no longer available as an electrochemically active cation.

The distribution of lithium, as a capacity determining species in LIBs, is of great importance in order to understand cell performance. The content of mobile lithium, which is transferable between the anode and cathode, is responsible for the cell capacity. However, due to formation of protective layers like the SEI and CEI and the continuous growth and reformation of both, parts of the active lithium are immobilized. This directly results in capacity fading and loss of available specific discharge energy of the LIB cell. It is crucial to quantitatively determine the lithium in all parts of the cell in dependency of the cell type, C-rate and temperature. The aging mechanisms at anode and cathode can be well understood from the Figure 4.

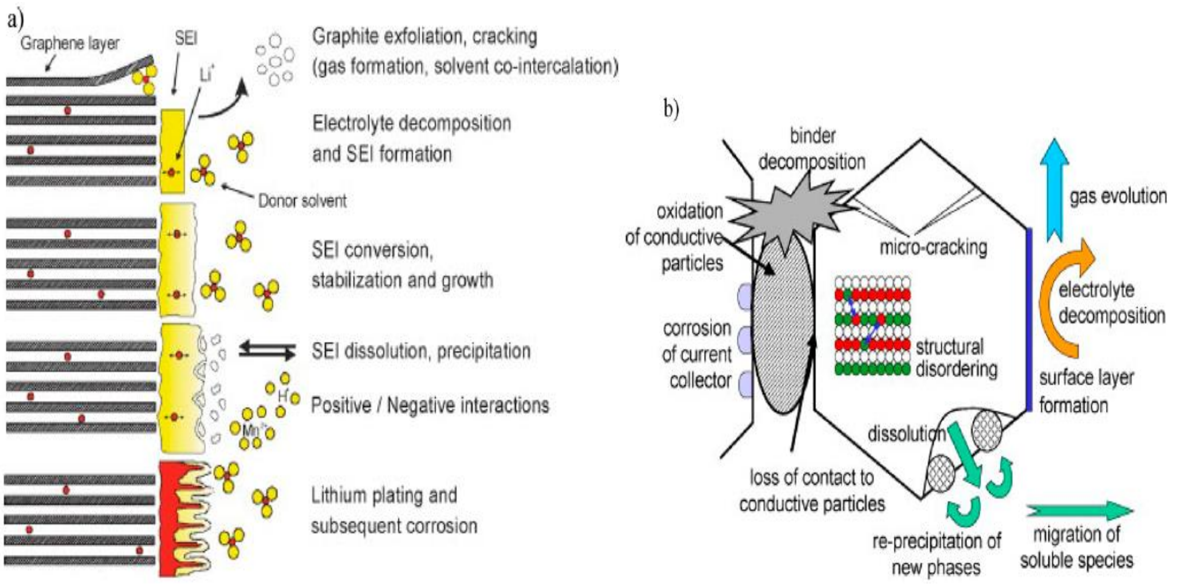


Figure 4. Aging mechanisms on the (a) anode and (b) cathode [6]

7.4 <u>Impact of different aging mechanisms on the thickness change and the quick-charge capability of lithium-ion cells</u>

The authors of [7] conducted an experiment whereby they analyzed the voltage and thickness change of lithium ion cells after degradation by calendar aging, cycling processes and due to lithium plating. The cell thickness is measured with a dial indicator mounted on a shaft support (Figure 5). With regard to the various aging types, characteristics of the cell thickness change and voltage are presented, which allows the determination of the aging type.

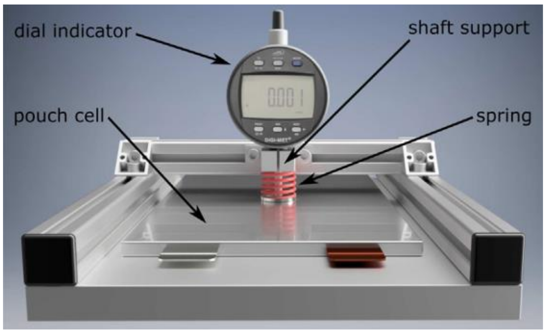
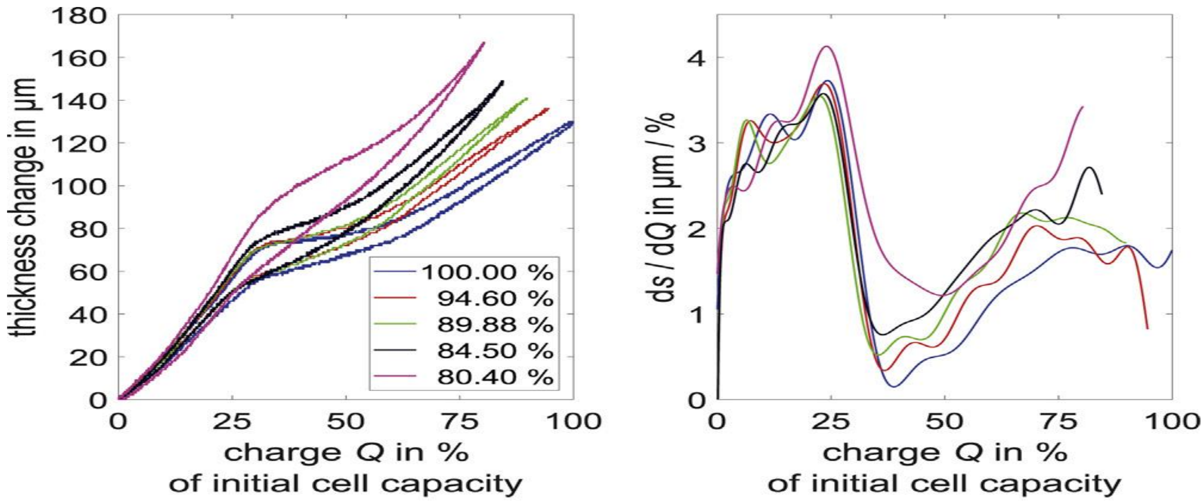


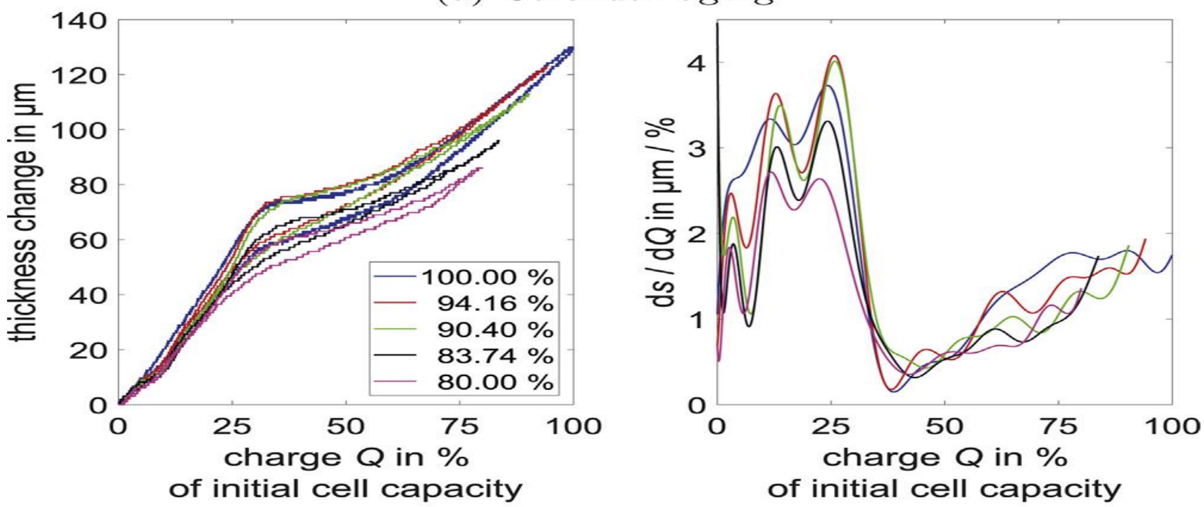
Figure 5. Setup for the measurement of the cell thickness change [7]

Cell Aging procedure: To carry out tests on aged cells and compare the different aging types, new cells are submitted to calendar aging, cycled aging and lithium plating in steps of 5% capacity loss until the end of life (EOL) criterion (80% remaining cell capacity). For each aging type, we obtain four cells with 95%, 90%, 85% and 80% remaining cell capacity.

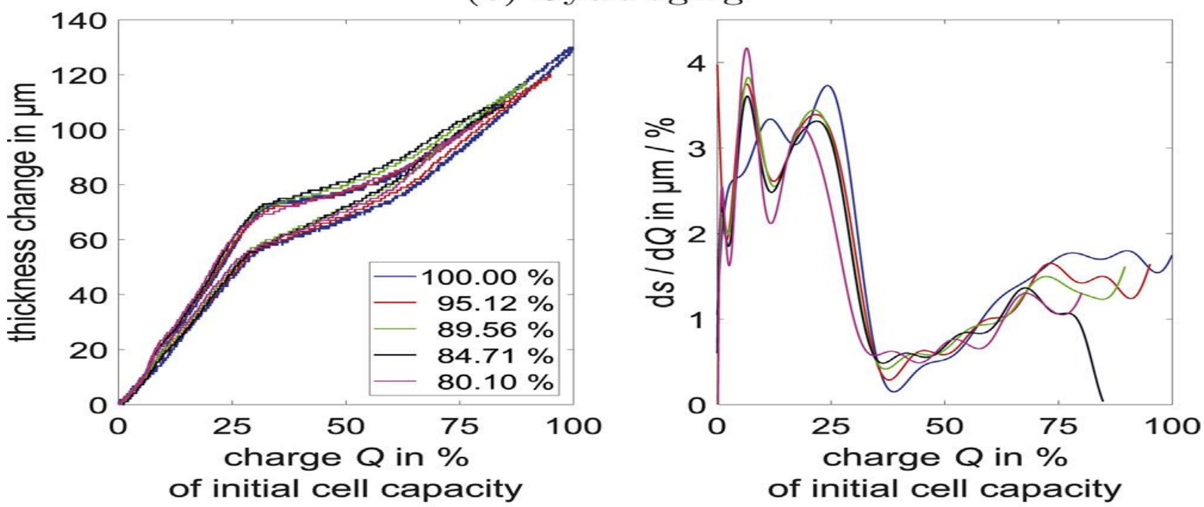
The comparison of the thickness graphs of the three aging types with a remaining cell capacity of approx. 85% is shown in Figure 6. The three aging types exhibit very different thickness graphs. The calendar aging amplifies the thickness increase, the cycling aging reduces the thickness increase and there is almost no change after aging due to lithium plating.



(a) Calendar aging



(b) Cycle aging



(c) Aging due to lithium plating

Figure 6. Cell thickness curves at a charging and discharging current of 0.5 A in the voltage range of 3 V up to 4.15 V of different aging types and aging degrees including the derivative of the discharge curves. [7]

7.5 Under Different Charging Stresses

It becomes necessary to identify the battery aging mechanisms and quantify the effects that different charging stresses introduce to the battery. A high-quality charging pattern of lithium-ion battery will achieve the balance between the charging speed and battery lifespan.

To investigate the aging mechanisms of lithium-ion battery and establish life degradation model under different charging stresses, cycle life tests were conducted by the authors of [8] under different conditions including varied charging current rates and cut-off voltages. The tested batteries are commercial 18650 batteries whose parameters are listed in Table 2.

Item	Specification
Cathode material	$LiCoO_2$
Anode material	Graphite
Nominal capacity	2.4Ah
Max. charging current	1C
Charging cut-off voltage	4.20 ± 0.05 V
Max. discharging current	3C
Discharging cut-off voltage	3 V

Table 2: Nominal specifications of battery [8]

The batteries were subjected to various cycle aging conditions by using a multichannel Arbin battery tester, and in the process of cycle life test, the batteries were placed in an environment chamber to maintain a constant ambient temperature of 25 C. To investigate the effects of different charging stresses on battery cycle life, the maximum available capacity degradation along with cycles under varied charging current rates and cut-off voltages were compared, which is illustrated in Figure 7. To exclude the effects of random factors, the mean capacity of three tested batteries is used for comparison.

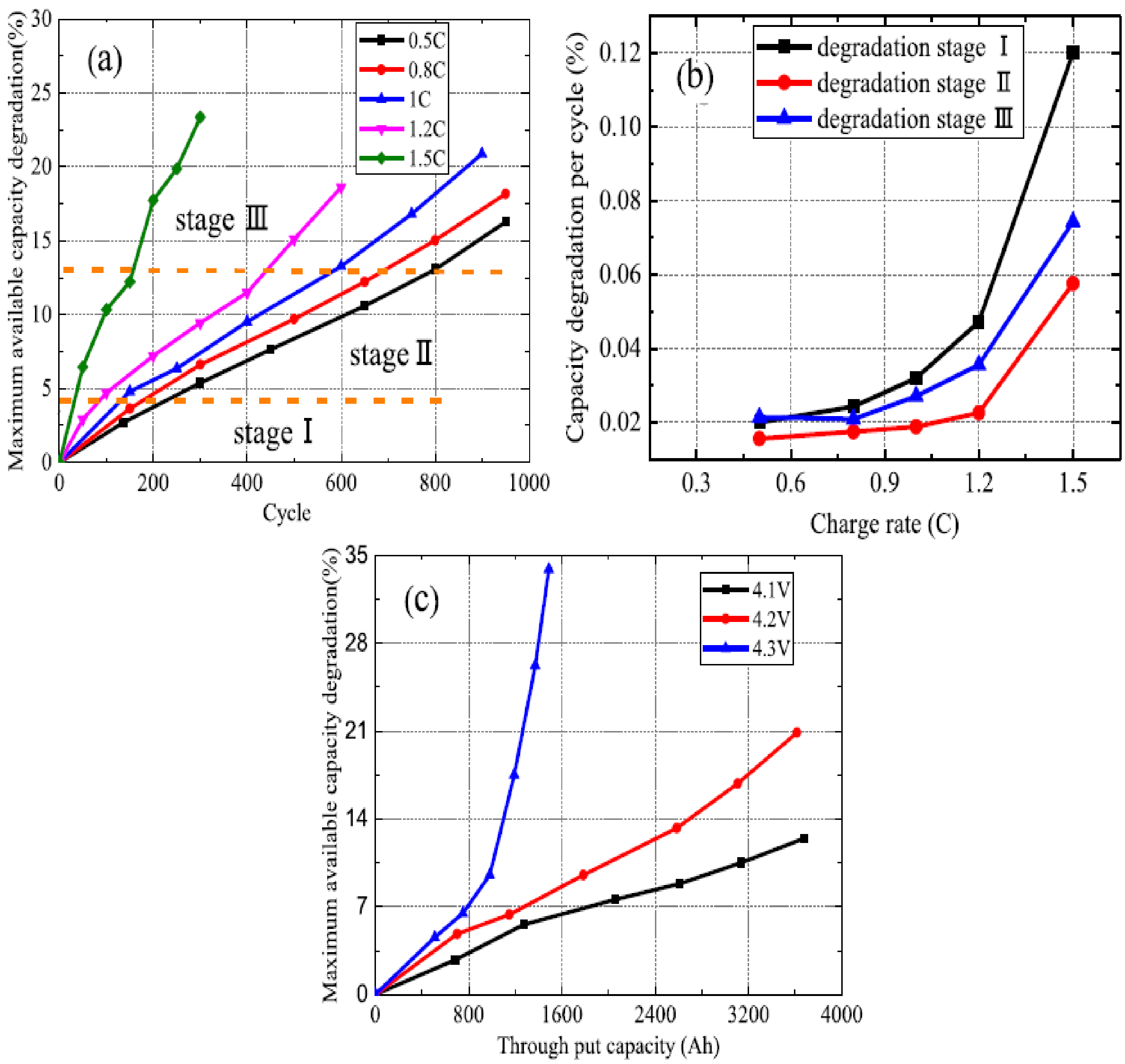


Figure. 7. (a) The maximum available capacity degradation under different charging rates. (b) The maximum available capacity degradation rate under different charging currents. (c) The maximum available capacity degradation under different charging cut-off voltages. [8]

The results show that there exist critical values for charging current rate and cut-off voltage. When the charging current or cut-off voltage exceed the critical values, the capacity degradation and resistance increase will be accelerated dramatically. For the tested batteries, the critical charging current rate is 1C and critical charging cut-off voltage is 4.2 V. When the charging stresses are less than the critical values, with the increase of charging stresses, the acceleration of battery capacity degradation and resistance increase is not significant.

However, after the battery suffers a certain number of cycles at 1C and 4.2 V, the charge acceptance capability of the battery gets weak, and as a result, reducing charging stresses in an appropriate aging stage is necessary to delay battery aging.

8. Conclusion:

A solution to mitigate the aging issues is to relay on accurate models which are able to predict accurately the performance and lifetime of the lithium-ion (Li-ion) batteries. Consequently, by using battery models, expensive and time-demanding field trials can be minimized. Li-ion battery performance models are used to predict mainly the short-term dynamic behavior (e.g., voltage, power, etc.) at different conditions [e.g., temperature, load current, state-of-charge (SOC)]. The battery lifetime models are used to estimate the long-term degradation behavior of the Li-ion battery performance parameters (e.g., capacity, internal resistance, etc.) during ageing (both calendar and cycle ageing). The determination of the cation migration and distribution is an important for a better understanding of reversible and irreversible reactions in LIB cells.

The most important factors discovered are:

1) Li-ion batteries can include different materials and thus exhibit different cell potential and capacity.

2) Battery degradation is unavoidable but can evolve at different paces depending on the design and operation conditions.

3) There are three main chemical processes responsible for ageing: electrolyte decomposition, lithium plating and transition metal dissolution.

4) Thorough experimentation coupled with modelling is crucial to understand and mitigate battery ageing

9. References.

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