Considering Li-Ion Battery Cell Ageing in Automotive Conditions

車載リチウム・イオン電池の劣化についての考察

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This paper explores how to understand and use knowledge of cell ageing in automotive conditions. The key problems and considerations of ageing are considered, followed by an explanation of their causes. This is then used to discuss the tools and understanding required for including this in context of electrified vehicles design and control. What is shown is that ageing is complex, and the dominant underlying causes depend on cell design and usage throughout lifetime. To characterize this, testing, simulation and control approaches must combine, with methods for each of these discussed and evaluated. With future industry trends to higher energy density chemistries, longer pack usage and second life applications, sufficient degradation tools will become even more important in future.

本稿では，車載時の電池劣化の知識をどのように理解し使用するかについてその方法を説明する。劣化の主要な課題とその原因について説明し，劣化を考慮した電動化車両の設計と制御に求められるツールと考え方について議論する。ここで明らかにしたいことは，劣化の複雑さと，その根本的な原因が電池設計とライフサイクルを通した使用法に依存しているということである。劣化を特徴づけるためには，試験，シミュレーション，および制御アプローチを組み合わせて，これらを議論し評価する必要がある。高エネルギー密度の電気化学の進歩に伴って，電池の長寿命化，生活電源への応用，劣化度評価ツールは今後ますます重要になると考えられる。

Introduction

With vehicle electrification being a key contemporary engineering concern[1, 2], it is of great importance to understand the performance, efficiency and longevity of Li-ion cells used in automotive battery packs. Li-ion cell durability is essential to understand for development of pack architectures, battery management systems (BMS) and warranty condition criteria. Unfortunately battery cell ageing is very complex[3, 4], being dependent on cell chemistry, design and usage conditions[5, 6]. This is further complicated by the fact degradation occurs within a battery cells chemically active materials invisible to the user during operation, making the cells effectively a ‘black box’. Instead, any BMS must rely on inferring a cells current health through indirect means such as its voltage response to current, and its temperature behavior on the surface and terminals. This makes battery cell ageing estimation a difficult challenge, which requires a multitude of tools to effectively estimate, predict and mitigate.

The performance of a Li-Ion cell can change in several different ways as it evolves through its usable life. A common and important aspect of degradation is reduction in the cells ability to store charge, also known as ‘capacity fade’, effectively reducing vehicle range and energy density, as well as causing mis-estimation in a BMS that does not account for this effect.

A battery cells charge transfer impedance can also change with time and usage, affecting voltage response to a given current. This can limit power capability through earlier reaching of voltage limits, reduces energy transfer efficiency, and increases demand of any pack cooling system present. This change in impedance can be harder to quantify than capacity. Impedance itself is a function of cell states, such as State-of-Charge (SoC) /temperature, and the relative change in impedance may not be uniform across the range with ageing. It can be further complicated by the fact there are several contributions to impedance which do not necessarily change in the same way[7].

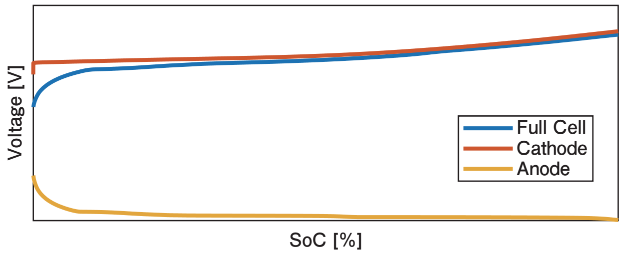

Figure 1 Example Cell Stoichiometry OCV-SOC Relation

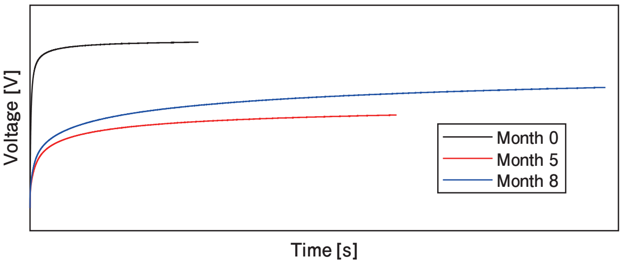

Figure 2 Evolution of relaxation from discharge example horiba mira cell data

While capacity and impedance changes dictate the strongest changes in cell performance, more subtle changes also occur which can affect a BMS's ability to estimate and control cell behavior. When new, each cell has a defined relationship between its Open Circuit Voltage (OCV) and SoC. This relationship is a function of its positive and anode chemistries but is also a relationship of cell design, through their relative sizes and lithiation balance[8], as shown in Figure 1. While electrode chemistries do not significantly change with degradation, the balance between electrodes does, affecting OCV. If this is not accounted for, then errors can develop in a system through mis-calculation. Another aspect that can change with ageing is the cells time taken to relax after current is applied, as shown in Figure 2. If this is not accounted for, then algorithms using open circuit voltage may drift due to incorrect assumption of cell relaxation. What is inferred by this, is that simple estimation of cell ageing symptoms is not sufficient to fully adjust control strategy with ageing, but more complex analysis is required, linked with an understanding of the underlying causes.

Li-Ion Degradation Causes and Usage Factors

As mentioned previously, cell ageing depends on both the design and manufacture of the battery cells, as well as the conditions they are exposed to during their lifetime. The reason for this, is that there are a multitude of ageing mechanisms within a battery cell, each with different causes and effects. In this section, the main effects are discussed along with their influences and impacts. A diagram summarizing the interactions and sensitivity of degradation mechanisms to usage is shown in Figure 3.

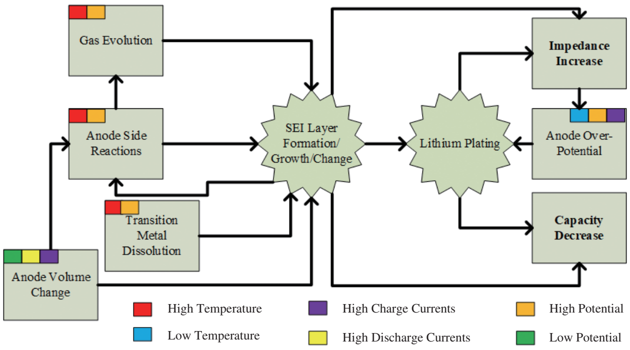

Figure 3 Illustration of ageing mechanism interactions in Li-Ion cells

Solid Electrolyte Interphase (SEI) layer formation is regarded as the main ageing mechanism in Li-Ion battery cells for capacity loss[9, 10]. At the potentials in which a cell operates, the electrolyte and anode are inherently unstable[3, 11], causing reduction reactions to occur. The reaction products form an SEI layer on the anode, providing a barrier to further damaging reactions[12,13]. This layer primarily forms in specially designed 'formation' cycles used to ensure a safe and reliable cell during the manufacturing process. It is however, never completely protective, slowly growing during cycling and even during storage conditions[14-16]. This growth consumes cyclable lithium and adds extra impedance to Li-Ion intercalation at the electrolyte-anode interface.

For conventional Li-Ion cells, forming of this layer is unavoidable, leading to gradual cell deterioration through loss of cyclable lithium and increase in cell impedance[17, 18]. The rate at which it develops however is influenced by cell design and usage. Increasing temperature accelerates reaction rates, increasing the formation of the layer[10, 15, 19-21]. High SoC values increase the potential difference to the anode also increasing the rate of layer formation[4], particularly at very high SoC[14]. Cell design also has an influence, with higher anode porosity providing a larger surface area necessitating more SEI to form[3, 17]. Cell chemistry is also important, particularly of the anode. While graphite electrodes will always see this mechanism, Lithium Titanate Oxide (LTO) operate at higher potentials, making them immune to this mechanism[22-24]. The higher potential of the LTO anode however comes at the expense of lower cell voltage and therefore energy density, limiting their use in full electric vehicle applications.

Another important mechanism is lithium plating on the surface of the anode during charge, as shown in Figure 3. Unlike SEI, this can be avoided because it is only occurring if the potential of the anode reaches 0 V vs Li/Li^{+}[25]. The consequences if it occurs however are more damaging to cells, leading to rapid capacity fade and impedance increase. As anode potential under load is proportionally dependent on its impedance, this ageing mechanism becomes much more likely at low temperatures where impedance increases[4]. For the same reason, it is also more likely at higher SoC, with higher impedance conditions and lower anode resting potential conditions exist, making exceeding the threshold for lithium plating more likely. Increasing charge current also increases likelihood, due to the associated higher drop in anode potential. Overall, chance and extent of lithium plating depends on a combination of temperature, SoC and charge current. Cell design also plays a role, with larger anode surface area decreasing average current density, thus decreasing lithium plating[26, 27]. Oversizing the anode relative to the positive also reduces likelihood of lithium plating, by limiting the maximum lithiation of the anode[28, 29]. As with SEI, changing the anode chemistry can mitigate this effect, with LTO cells being much less susceptible[30].

Several other ageing mechanisms can occur based on extreme conditions of the usage range. Below 20% SoC, the anode can shrink by 10%, which can cause cracks to form[26]. On subsequent expansion, this can create gaps in the SEI layer, encouraging further reduction reactions to occur[15, 17, 26, 31]. At high SoC, the positive electrode can oxidize with the electrolyte, particularly for modern high nickel compounds[32, 33]. These oxidization products can then migrate to the anode, increasing SEI layer resistance[3, 9] and encouraging further layer growth[31]. Permeable layers can also form on the positive electrode due to oxidization reactions, having a strong contribution on resistance[9, 15]. The electrolyte can also degrade, increasing ohmic resistance[34] and increasing internal pressure through gas evolution[35].

What can be shown from this, is that while there are two main ageing considerations, SEI layer formation and lithium plating, there are several other degradation aspects, which all have separate and unique contributions to cell performance changes such as capacity, impedance, stoichiometry and dynamic response. This creates a complex ageing landscape which due to interactions with cell design and usage conditions will manifest different degradation symptoms in each cell. The degradation symptoms in each cell, deriving each from multiple ageing mechanisms, cannot always be correlated, and therefore require their own metrics for monitoring and predicting. Decisions in how the cell is designed and used are not always clear, requiring compromise and consideration of target application. As an example, electrode surface area is a compromise between energy density (high volume) and power density (high surface area) but when considering ageing, it is also a direct compromise between SEI layer formation and lithium plating susceptibility. Cell temperature itself is also an important consideration. In general, higher temperatures promote accelerated ageing through accelerated chemical reactions of both electrodes. Low temperature however present's its own challenges, particularly during charging. For this reason, 10-35 ºC is cited as ideal over a usage profile depending on the cell used[20, 36-38] but this would be less for storage and likely to be higher during charging.

Developing Tools for Ageing Analysis

In previous sections, it was shown that ageing in cells gives a complex change in cell performance with a large amount of hidden states, each dependent on multiple factors. A problem such as this requires a range of different tools to be applied, combining testing and simulation to develop methods for powertrain design, BMS control and state estimation strategy development.

For modelling Li-Ion cells electrical behavior there are 3 main approaches: empirical, equivalent circuit, and physical[39]. High level attributes of each is shown in Table 1. With enough test data, empirical models can give a good representation of the symptoms of cell degradation, particularly when dealing with simple metrics such as capacity fade and simple resistance increase, with some ability to estimate specific mechanisms through known equations[40]. Where empirical models would not be suitable however, is when attempting to model complex physical behavior, or when separating multiple ageing symptoms. Physical models are more suitable for this, based on fundamental chemical principles[41-44] and extended to incorporate various ageing mechanisms[13, 45]. These models are suitable if a good detail of knowledge about cell internal chemistry and construction is known, as they can be very powerful optimization and prediction tools. Without this information however, they do not perform, making them difficult to adapt to different cells particularly when considering degradation, although work is being done on solving this problem[46]. They are also very computationally expensive and could be more in-depth than is required for typical control and system optimization

Table 1 High level comparison of modelling approaches

Modelling Approach	Empirical	Equivalent Circuit	Physical
Testing Requirements	High	High	Medium
Ageing Insight	Low	Medium-High	High
Implementation Complexity	Low	Medium	Medium
Cell Information Requirements	Low	Low	High
Computational Requirements	Low	Low	High
Transfer to new cell design	Low	Medium-High	Medium

problems, being more suited to cell design and development. Equivalent circuit models give intermediate levels of practicality and information. If designed correctly, elements in the circuit can be linked to physical behavior and more complex aspects such as cell internal states can be represented practically[47]. These models can also be implemented in simple environments, and easily populated, making them suitable when versatile platforms are required to model performance and degradation across a range of cells.

Testing and data analysis methods must backup the chosen model platform. With section II showing usage factors impact not just the rate of degradation but its cause, it is important to get a test matrix range that covers all important degradation mechanisms and can allow for isolation and analysis of them. Bearing in mind the higher order and strong interaction effects between parameters[48] a factorial approach becomes preferred, in particular considering temperature, SoC window and charge current. It is also important to consider the complexity of ageing symptoms and develop reference performance tests that capture the more complex aspects, such as relaxation time and changes in individual impedance components as well as the influence of SoC and temperature in this. Accelerated ageing experiments should be performed with caution and limitations should be considered e.g. high temperature cycling will accelerate ageing, but may also change the profile and underlying causes, making it less representative of real automotive usage.

For ageing informed Battery-cell control, it is important to maintain current limits and adjust algorithms for estimating the available energy and power. As confidence is required in algorithms before they are implemented on-board, effective testing and accurate modelling approaches are a necessary pre-requisite. It is important to estimate changes in cell capability in succinct ways that are easy to calculate using low processor power, and do not interfere with vehicle usability. Reduced equivalent circuit models lend themselves to this purpose, as do methods that can infer changes directly from voltage profiles such as Incremental Capacity Analysis[49] and time domain relaxation analysis. It is necessary to have separate analysis methods at least for capacity and impedance, and possibly separation further for individual impedance components.

With the development of ageing understanding, evolving of chemistry and improvement in on-board control, the scope for Li-Ion cell degradation solution tools is evolving. In the short-medium term, the main trends in Li-Ion cells is high Nickel content NMC 811 cathodes, and incorporation of silicon doping in anodes[50]. NMC 811 cells, due to their high nickel content, have more severe issues with cathode oxidization and transition metal dissolution than previously, which mean more cathode degradation needs to be considered. Silicon anodes bring about larger volume change than currently used graphite, leading to more damage of the electrode structure. Both electrode changes expand the focus of which ageing models need to consider. New cell electrolytes, such as solid-state, will bring a step change in degradation behavior, for example with solid state interfacial surface contact degradation between the electrodes and electrolyte can be dominant. To anticipate this, techniques must be sufficiently versatile to adjust, and the key degradation mechanisms of each new chemistry must be understood. Because of this, when developing both modelling and control algorithms, focus should be on making the tools adaptive, versatile and importantly predictive.

Machine learning tools have been adapted to predict key battery degradation states[51] and could aid in accurate SoH estimations. These tools must be used with caution however, as it is difficult to ensure their robustness and consistency. Their ‘black box’ nature also means that while they may be good at deriving performance changes and ageing symptoms, they may not reveal to the system the underlying ageing mechanisms. This creates limitations in situations where knowledge of ageing mechanisms could be used to improve longevity i.e. intelligent control strategies. It is important to use practical methods that also identify the actual root causes of ageing, and intelligently react the control system operation to specifically mitigate these. For this reason, black box tools must be integrated carefully as part of a larger system combined with chemically representative models. Significant progress should be made on making models that illuminate specific changes in battery cell behavior yet still be practical enough to use in optimization strategies or even on-board so that they can be paired with automatic parameterization and integration strategies. To identify the underlying ageing mechanisms, all symptoms of behavioral change must be observed and combined to isolate the contribution of each ageing mechanism, using a variety of strategies including differential voltage methods, relaxation curve analysis, cell heating signatures, coulombic efficiency and capacity analysis. This information can then be analyzed to correlate with ageing mechanisms matching the observed behavioral changes, subsequently adapting the strategy to avoid certain ageing mechanisms e.g. reducing low temperature charging when lithium deposition is identified as dominant. This would allow for BMS that were originally designed identical, to become individually adapted based on the unique usage profile and subsequent degradation of each specific pack. For this approach to be feasible, it must first be correlated with a high level of ageing information before being employed online. This requires the employment of a variety of techniques for enough validation information. As the on-board algorithms are approximating chemical changes in cell behavior, verifying through conventional electrical cycling is not sufficient. Cell dismantling and chemical analysis techniques such as Raman Spectroscopy, Scanning Electron Microscopy and X-Ray Diffraction are essential to illuminate the physical changes occurring in different parts of the cell, which can quantify the real physical/chemical ageing that has occurred to validate the adaptable approaches. A promising area of development is also in the form of in-operando degradation measurement techniques such as Ultrasound and Computed Tomography[52-56] that allow observation of cell chemical and thermal behavior in real time. This will allow for additional information to be gathered that can get the level of detail required for developing informed and verified models and algorithms. It will also give opportunity to develop strategies for correlation of observable on-board measurements with internal chemical features, removing the reliance on constructed states to estimate behavior.

The evolution of the industry must also be anticipated with developing ageing tools. With increased original range, automakers are expanding their allowable degradation rate to allow battery packs usable down to 70% of original capacity. In addition to this, second life applications are in growing demand for used battery packs. Considering this, degradation tools must consider a much deeper level of degradation going forward. For these tools to be effective, cells must be able to be categorized not just on capacity but matched on impedance and cell stoichiometry to ensure uniform performance through the next stage of cell lifetime. This also requires methods for quantifying cell degradation while being ignorant of usage history, which requires a different approach to on-board monitoring.

Conclusions

In this paper, the landscape of Li-Ion cell ageing was explored which considered the variety and nature of degradation mechanisms, and the tools required to incorporate this knowledge into system design and control optimization. Li-ion ageing is complex, nonlinear and has multiple dependencies on how a cell is designed and used. The ageing dominates from the anode, with SEI formation and lithium deposition, but there are several other contributing mechanisms, and new chemistry developments will further increase this. This ageing depends on many factors, but in particular electrode design and chemistry during manufacture, and temperature, SoC and charge current during usage.

To fully characterize, predict and mitigate ageing, a set of tools is required considering the testing, analysis, modelling and control aspects of the system design. Testing must reflect the nonlinear relationships with usage conditions, and their effect to change the underlying causes, to make sure all key condition combinations are covered, as well as capturing the more complex aspects of cell behavior change. Accelerated ageing tests could be helpful, but the effect on the realism of results must be considered. Modelling must be a balance between practicality and insight, but importantly must be linked to the real underlying physical/chemical features of the cells to analyze their specific evolutions. Control algorithms must be effective using only the information available to them, using machine learning only if the concerns with that approach are addressed by the rest of the system. An intelligent approach however has promise for developing adaptable BMS that can tune control behavior based on identification of ageing mechanisms. If combined with appropriate internal cell measurements and using chemical/physical analysis of aged cells for technique validation, it could create very powerful algorithms. What is clear, is that these approaches must consider metrics for each of the multiple degradation systems and should be accurate even down to relatively high levels of degradation to meet market trends. There is also a growing demand for tools which can analyze and classify the health level of used cells, without knowledge of their prior usage.

* This content is based on our investigation at this publish unless otherwise stated.

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