

Holistic Approach to Understanding Battery Degradation

Richard Stocker^a, Asim Mumtaz^b, Neophytos Lophitis^c

Abstract-Li-ion cell degradation has a strong impact on electric vehicle performance both directly, through performance reduction, and indirectly through deviating behavior away from initial control system calibration. This necessitates a process for evaluating degradation causes and quantifying corresponding behavioral changes. This paper shows a holistic approach for achieving this, giving both an insight into the causes of cell degradation and emulation of the resultant performance changes through a virtual tools platform which can be used for degradation algorithm development. Additionally, the paper is an overview of the novel methodology developed within the process including testing, data evaluation, modelling and electrical and chemical validation. The process makes use of electrical cycling and electrochemical impedance spectroscopy (EIS) data to evaluate cell stoichiometry and individual impedance features to achieve a much more comprehensive ageing behavioral adaptation than is typically present in Li-ion cell equivalent circuit models. This is achieved while maintaining the versatility and computational efficiency of compact model approaches. The outlined process also gives a resolution of performance changes that allow for conclusions to be drawn on the root causes of ageing only through evaluation of electrical data, which is itself significant. Chemical analysis results are shown to verify the validity of the ageing cause conclusions shown by the process.

Index Terms Li-ion, Battery cell, degradation, ageing, modelling.

I. INTRODUCTION

The automotive industry is in rapid technological transience with vehicle driving, ownership models and powertrain philosophy undergoing significant disruptive changes [1]. For vehicle powertrains the Internal Combustion Engine (ICE) is declining in popularity due to vehicle emissions legislation [1,2]. Zero emission powertrain alternatives are Battery Electric Vehicles (BEVs) [3] and Fuel Cell Electric Vehicles (FCEVs) [4]. While battery cells are a clear requirement for BEV's, they also provide benefits as part of a fuel cell powertrain by allowing for regenerative braking as well as smoothing load demand to allow optimal operation of the fuel cell stack.

Automotive battery cell usage comes with many stringent targets and associated challenges including cost, energy

density and lifetime. Li-ion battery costs project a strong decreasing predicted trend over the next 5-10 years [5,6] with energy density continually increasing [7], with economies of scale and new cell chemistries/designs enabling improvements in the latter areas. Degradation, however, is a much more challenging problem to solve, due to its inherent complexity and dependency on cell design and usage conditions [8,9]. It is however important for vehicle usage, with manufacturers typically providing warranty conditions of 5 years and above [10–13] or related mileage utilization. It is also important to quantify degradation during usage as it changes several aspects of cell behavior in complex and nonlinear ways as explained in section II. If this is not understood, the continued achievement of vehicle requirements throughout life, such as power capability and driving range, cannot be predicted at the design stage. In the usage stage, the complex behavioral changes will make the Battery Management System (BMS) uncalibrated relative to the real cell performance. This affects the ability of the BMS to estimate changes in State-of-Charge (SoC) during usage due to mis-estimation of capacity and therefore relative capacity throughput, as well as mis-estimation of initial SoC through unrecognized changes in cell Open Circuit Voltage (OCV). Unaccounted changes in resistance can also lead to inaccurate forecasting of power limits which can compromise vehicle power and create issues from a usage perspective. For this reason, battery cell ageing must be fully understood and quantified.

A complex problem such as battery cell degradation estimation requires a sophisticated solution. A range of degradation estimation approaches have been created ranging from simple empirical measurements to data driven methods [14,15]. No approach thus far gives a completely satisfactory solution. Direct measurements are simple to implement and compatible with the limited computational power of a battery management system. The downside to simple methods however such as counting current throughput during charge, or measuring instantaneous voltage drop, give a simplified perspective of ageing. This simplified perspective does not inform of ageing cause, is sensitive to sensor error and does not account for variations with parameters such as temperature. As a result, data driven methods are increasingly popular, made possible by the additional computational capability of cloud based off-board analysis. These methods use machine learning techniques, for example Neural Networks [16] or Support Vector Regression [17]. Data driven approaches can give very powerful and accurate estimation of cell performance changes however they are often 'black box'

Richard Stocker is with the Horizon Scanning department, HORIBA MIRA, Nuneaton, CV10 0TU, United Kingdom. He is also with Coventry University, Coventry, CV1 2JH, United Kingdom.

Asim Mumtaz is with University of Liverpool, Department of Physics/EPRSC Centre for doctoral training in New & Sustainable PV, L69 7ZX.

Neophytos Lophitis is with Nottingham University Faculty of Engineering, University Park, Nottingham, NG7 2RD, United Kingdom

in their nature i.e. they do not reveal their internal correlation model. This is important as a key advantage of monitoring degradation is being able to react to it effectively, which requires understanding of its cause. Data driven approaches also require a significant amount of datapoints which depending on vehicle usage patterns may not give a full set of possible conditions. Between these are model based approaches, which still rely on vehicle data but have an underlying structure with which to infer physical meaning. In every case, to develop and validate algorithms a large amount of testing is required which is not physically realizable due to time and cost. For this reason, an accurate yet computationally efficient battery emulation and an understanding of underlying ageing is required from a relatively small dataset as tools for training BMS algorithms. This paper shows an approach to create such tools.

This paper outlines a holistic approach to understanding and quantifying the multiple aspects of Li-ion cell degradation. Section II introduces the aspects of cell ageing. Section III introduces the overall approach designed to quantify ageing, and the remaining sections explain the individual aspects of the process.. Some aspects of the patent applications as cited in [18,19] which apply to the impedance evaluation and the incremental capacity analysis (ICA) capacity and Open Circuit Voltage approach. This paper shows how the testing approach, data analysis algorithms and modelling approach combines to give a coherent and effective Li-ion cell ageing evaluation process to identify the ageing root causes and to quantify and model the changes in cell performance.

II. LI-ION FUNDAMENTALS AND AGEING

Lithium ion cells store and transport cells electrochemically. While the cell functions as a complete device, it is made up of multiple components shown in Figure 1. Li-ion cells work via intercalation of lithium between each electrode, with lithium moving from the positive electrode (cathode) to the negative electrode (anode) during charging of the cell and the reverse when discharging. In each case, the Li-ion must move from its current electrode and flow through the electrolyte, crossing the separator. The separator plays an important role,

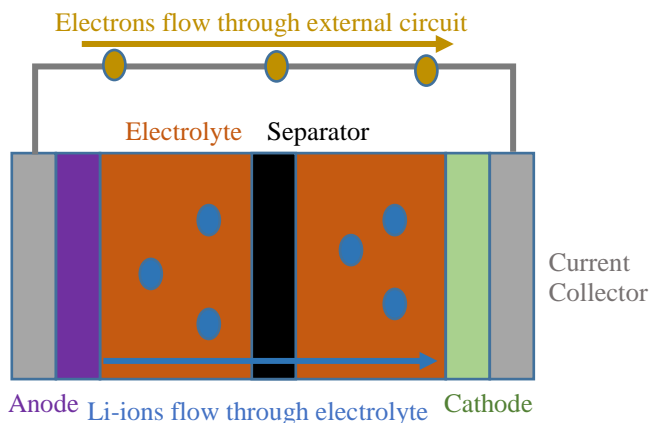


Figure 1 Cross-section of a Li-ion cell and its internal components

permitting flow of Li-ions while being electrically isolating. Li-ions have a positive charge and therefore when moving between electrodes create a charge imbalance. To resolve this, negatively charged electrons also move between the electrodes however they cannot go through the separator. Instead, they travel through the metallic current collectors and around an external circuit, giving or receiving work in the process. The rate of electron flow defines the current. Each electrode has a capacity for accepting lithium and its own electrical potential as a function of its relative amount of lithium contained and the resistance to any current applied. The full cell voltage measurable at the cell terminals is then given by the difference between the electrode potentials as shown in Figure 2.

Ageing in Li-ion cells is complex due to the multitude of mechanisms that occur across the different cell components as a function of usage and time. The evolution rate of each mechanism can depend on cell design conditions, such as electrode surface area. It can also depend on usage conditions such as temperature. For detail on cell ageing, there are many high quality reviews explaining the mechanisms in detail [8,20–22]. This section gives a high-level overview with a focus on the implications on cell performance.

A dominant degradation mechanism for Li-ion cells is the formation and growth of the Solid Electrolyte Interphase (SEI) layer due to anode-electrolyte surface reactions [22,23]. This SEI layer is formed by design, as it forms a barrier for further reactions. It cannot however completely prevent all further reactions with a small rate of reactions persisting throughout lifetime. These reactions consume lithium, reducing cell capacity, and the resultant SEI surface layer increases cell impedance. This mechanism causes a steady degradation

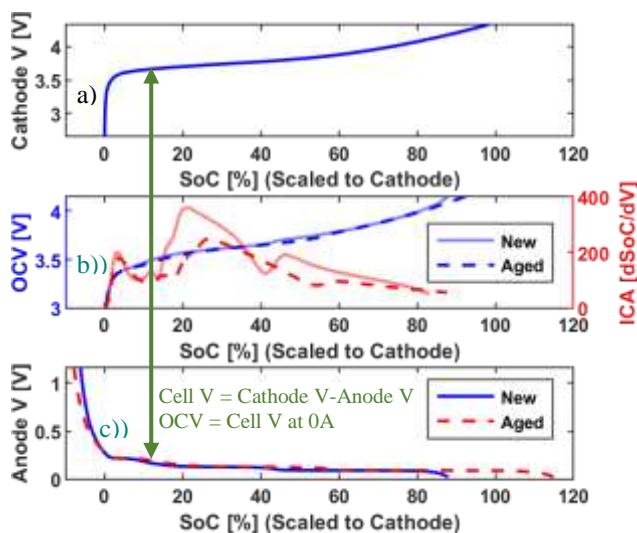


Figure 2 Illustration of Li-ion cell stoichiometry through the interaction of the Cathode, a, the Anode, c) and the full cell Open Circuit Voltage (OCV) b). Cell b) shows the Open Circuit Voltage through the difference between the cathode and anode at a given SoC, In b) it is also shown the Incremental Capacity Analysis (ICA) curve which shows the relative differential capacity to differential voltage across the SoC range. In each case, the difference due to ageing in each curve is shown due to a reduction of cathode capacity and subsequent rescaling of 0-100% SoC

throughout the cell life which is accelerated by higher temperatures and higher cell potentials.

Another significant mechanism is lithium plating. This mechanism is avoidable but has large consequences when it occurs. If anode potential drops below 0V Li/Li⁺, or 0V relative to the lithium standard potential, then lithium deposit's on the anode surface rather than intercalating into it's bulk structure [24–26]. In cases where there is high thermal gradients in the cell, such as fast charging, the threshold for lithium plating can even be several mV higher than 0V [27]. Plated lithium can be recovered by stripping during discharge however if the lithium becomes electrochemically disconnected this is no longer possible and the plated lithium and associated capacity is permanently lost. This can also pose a safety risk as the lithium deposits on the surface and repeated deposition can form dendrites that can eventually pierce the separator, causing a short circuit in the cell [28,29]. The occurrence of this mechanism depends on the anode overpotential, which makes it more prevalent at low temperatures and high current dendrites [30].

Aside from SEI formation and lithium plating, there are also several additional mechanisms that occur such as mechanical damage from anode volume change at low SoC [21,31], cathode damage from lithium intercalation/deintercalation [32–34] and cathode surface layer formation [35–37]. These combine to cause a map of different condition sensitivities, an example of which is shown in Figure 3 that uses temperature and SoC as examples.

Multiple ageing causes each with complex evolution profiles makes tracing individual ageing mechanisms difficult. A reduced framework grouping ageing into important features and locations helps simplify the problem while retaining useful information. To do this, the key performance changes must be known and included.

A common ageing consequence is a reduction in the cells ability to store charge which is known as capacity fade. Capacity fade is caused by changes in cell stoichiometry, and what is often neglected is these changes also cause alterations in the Open Circuit Voltage (OCV) profile with SoC, and affect sensitivity to further ageing [38,39]. With the OCV curve typically used to define initial SoC, changes in the SoC-OCV relation are important to understand for effective control recalibration. An example change in electrode stoichiometry with ageing and the corresponding subtle change in SoC-OCV is shown in Figure 2.

The other important aspect of battery cell performance change with ageing is its ability to give and receive charge i.e. impedance change. Cell impedance itself is very complex,

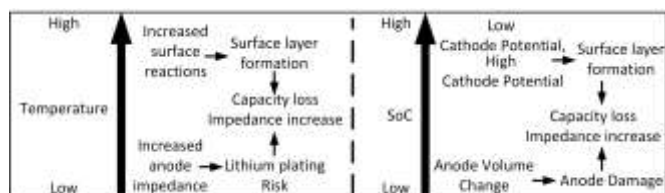


Figure 3 The influence of temperature and State-of-Charge (SoC) on the types of cell ageing that occur, as illustrated by the physical effect and resultant ageing symptoms that occur at the high and low ends of temperature and SoC.

being made up of ohmic, charge transfer (CT) and diffusion contributions with each contribution occurring in multiple regions of the cell [40]. Ohmic resistance arises from material resistances within the cell, particularly the electrode materials and electrolyte [40,41]. Ohmic resistance acts instantaneously, and arises from material properties that are not dependent on current or SoC [42,43], although the electrolyte resistance has some temperature dependence [40]. Charge transfer impedance occurs due to the resistance at the electrode/electrolyte interface to Li-ion transfer into the electrodes. Charge transfer impedance has a fast acting time constant of <1s, decreases significantly with temperature rise [42–44] and current magnitude increase [40], and is also sensitive to SoC dependent on the electrode stoichiometry of individual cells. Diffusion impedance arises from the buildup of concentration gradients within the electrolyte and electrodes due to continued current application and Li-ion transfer. The time taken to build up these gradients gives diffusion relatively long time constants (up to 100s of seconds) relative to the other impedance aspects. Diffusion impedance strongly decreases at higher temperature [43] due to improved electrode intercalation kinetics. It can also have a strong relationship with SoC as the electrodes undergo phase changes at different levels of lithiation which also affect electrode kinetics particularly for graphite anodes [45].

Each impedance aspect arises from different components and causes and is therefore sensitive to different ageing mechanisms. The consequence of ageing therefore is not just a change in absolute resistance, but a changing profile with usage parameters and a change in dynamic response to current. An evolution of dynamic response with ageing at a consistent temperature, SoC and current magnitude is shown in Figure 4. It can be seen that the absolute resistance value changes with month but also that the response-time profile changes, with the aged cells responding over a longer time period than when new. This effect is important, because changes in voltage evolution can affect heat generation and available power during the highly transient automotive drive

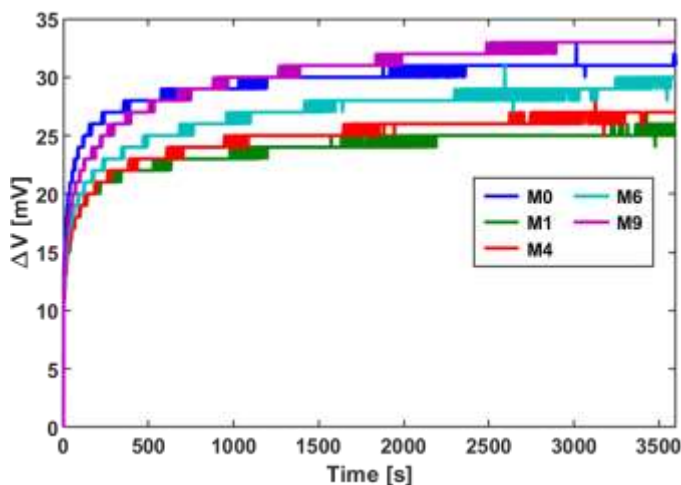


Figure 4 Cell Voltage Response to step current at identical temperature and SoC conditions, with ageing month. In this figure it is shown that the voltage response to current changes in its overall magnitude, but it also changes in the evolution of that response with time after the change in current application.

cycles as well as the waiting period after loading before the cell is sufficiently relaxed for OCV measurements.

The complexity of the combined changes in cell stoichiometry and impedance necessitate a process combining multiple aspects and algorithms, explained in section III.

III. HOLISTIC APPROACH TO BATTERY DEGRADATION

The complexity of battery degradation and the resulting effects on cell performance make a solution both essential and challenging. Outlined in this section is a holistic process to understand, quantify and model Li-ion cell ageing. This process must provide a reliable and informative evaluation of ageing and its behavioral impact. To be practically applicable, the approach is also required to be versatile across different Li-ion cell designs and electrode chemistries, functional using only data accessible from electrical cycling, and intuitive in its process without strong domain knowledge user requirements.

The elements of the developed approach are shown in Figure 5. To quantify ageing, 3 main aspects are required: characterization testing, data evaluation, and modelling of resultant cell performance. It is critical that these aspects are designed to be optimal together. The testing approach defines the input data available for the analysis algorithms, which in turn defines the results available for the model. It is therefore important that the entire approach is designed to achieve the objective of understanding the root causes of ageing and to quantify/model the behavioral differences described in section II. It is also important to be able to validate the approach. It is important to both evaluate the underlying ageing causes and model the resultant ageing symptoms. These must be validated using separate approaches as described later in section VII.

IV. CHARACTERIZATION & AGEING TESTING

A fundamental aspect of the evaluation process is acquisition of representative data. This process achieves this through electrical characterization testing. Electrical testing is practically accessible in a way that cell dismantling, and chemical evaluation is not and does not need as significant adaption across different electrode chemistries and designs. The objectives of the electrical characterization are to characterize new cell behavior and acquire data on cell performance changes with ageing.

For new cell characterization it is important to acquire data that depicts all behavior including capacity, OCV and dynamic

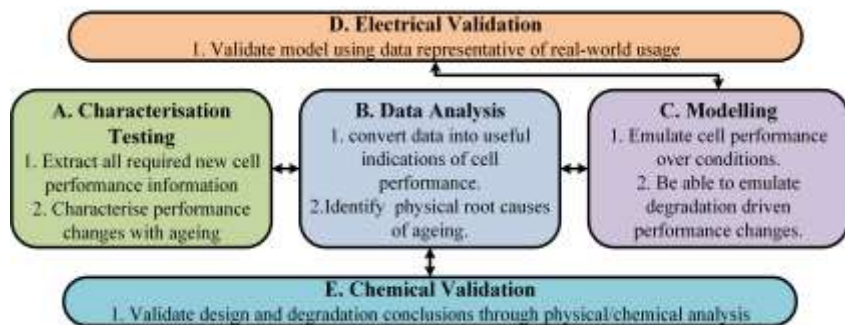


Figure 5 Overall holistic process that incorporates all of the required steps to evaluate ageing in Li-ion cells.

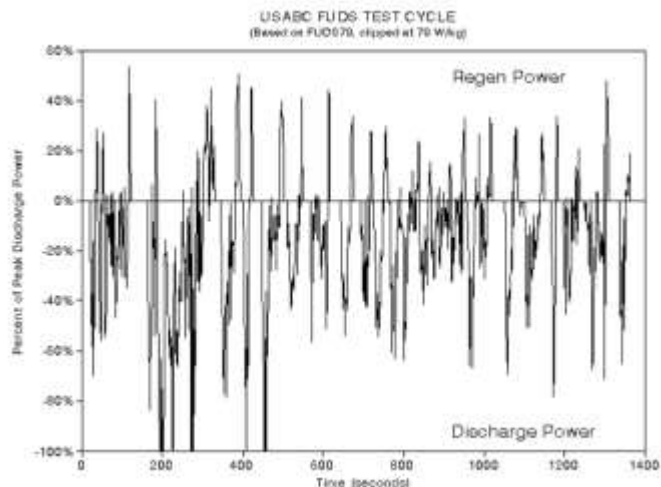


Figure 6 FUDS profile as defined in [53], chosen for its dynamic profile spanning the full range of cell usage, and its inclusion of charge pulses representing regenerative braking

impedance evolution. This is required across the usable range of cell conditions, such as temperature, SoC and current [40]. It is not necessary to emulate real automotive cycle profiles during characterization, instead optimizing cycling for key data acquisition and ease of analysis. Many methods exist for this, such as Electrochemical Impedance Spectroscopy (EIS), Incremental Capacity Analysis (ICA) and Time based pulse relaxation analysis [46–52]. Each gives unique information; therefore, a combination of methods is recommended and applied during this process.

It is not practically realizable to quantify ageing comprehensively across usage conditions due to the associated time and cost. Ageing characterization therefore must be efficient in giving informative data. This requires defining two aspects of ageing testing, the ageing cycles and the characterization cycles. The ageing cycles must be closely representative of the target use case. For automotive conditions when a cycle is not already known, the Federal Urban Driving Schedule (FUDS) [53] is generally representative due to its inclusion of transient profiles, scalability to different cell designs, large current magnitude range and inclusion of regenerative braking. It is shown in Figure 6.

The ageing characterization profiles can be based on the new cell characterization, but the range of tests and conditions must be condensed. Hybrid Pulse Power Characterization (HPPC) tests are useful for this, giving a wide range of information in a compact test profile [54].

Cell degradation cause and effect is highly sensitive to cell usage conditions, as discussed in section II. For this reason a design of experiments approach to cell ageing testing is used to evaluate the impact of different parameters [9,55,56]. The choice of variables can vary, but overall the most significant usage parameters on cell performance are temperature, cyclable SoC range and charge current [30,57,58]. When formulating a design-

of-experiments approach, the experimental matrix should consider that these parameters have both higher order and interaction effects, so multiple levels should be used [55]. Close control of the conditions, particularly temperature, is also crucial due to high sensitivity. For modern Li-ion cells lifetime performance is very high therefore even with continual 24-hour high temperature cycling it can take at least 9 months to approach end-of-life conditions, although this varies significantly with cell chemistry and design.

V. DATA ANALYSIS

The data analysis stage uses the available characterization data to generate model parameters quantifying changes in cell performance and to inform on the underlying ageing causes. The cell performance results must also be output in a way that can be used in a modelling platform such as in section VI.

Section II explained the complex landscape of Li-ion cell ageing and subsequent performance changes. To evaluate this several algorithms must be applied, each targeting a specific aspect of cell characteristics. The strategy taken in this holistic approach is summarized in Figure 7.

Figure 7 shows how one algorithm is applied to evaluate cell stoichiometry and subsequently OCV and cell capacity changes. This algorithm infers information about the cell underlying behavior, specifically changes in individual electrode capacities and lithium distribution within the cell.

ICA is a powerful technique for achieving this through calculating the change of SoC relative to the change in voltage across the cell capacity range [39]. The resultant profile is dependent on the relative lithiation state of each electrode, as voltage change with lithiation is sensitive for each electrode to points in the lithiation curve at which phase changes occur [59]. This trait makes the ICA curve shape very sensitive to

ageing, as shown by *Figure 2* which compares a subtle change in OCV with ageing to a very pronounced change in the ICA profile. The ICA curve features change uniquely based on the cause of degradation being Loss of lithium, anode capacity reduction or cathode capacity reduction [60]. The sensitivity of the ICA curve to cell internal stoichiometry means it can first acquire the baseline cell relationships. With the baseline established, changes in ICA curves at a consistent current can be used to track specific degradation modes within the cell. The subsequent knowledge of cell stoichiometry can then be used directly to give expected changes in OCV and cell capacity.

Impedance is a very complex aspect to analyze due to the combination of ohmic, charge transfer and diffusion impedance acting across both electrodes, the electrolyte and current collectors [40,43,61,62]. The accumulation of these features span a large range of characteristic time constants with ohmic resistance being instantaneous and diffusion resistance acting over 1000s of seconds (see *Figure 4*). No one method can reliably evaluate the entire impedance range, so the high and low frequency aspects are evaluated separately.

EIS is effective at ascertaining high and medium frequency impedance aspects such as ohmic and charge transfer [63]. It is fast to perform allowing coverage of a range of SoC and temperature values quickly. It is not however good at identifying low frequency effects such as diffusion [63,64]. EIS requires a net zero current to be valid, and at lower frequencies the longer current application causes sufficient OCV oscillation for the corresponding voltage change to appear on the resulting impedance estimate. As the frequencies get slower, the time of the test also elongates to the point of impracticality. For the generation of the analysis and modelling in this work, a range of 1mHz to 10kHz was used.

Current interrupt through methods such as time pulse relaxation provide a good alternative for low frequency evaluation [63,64]. By applying a fixed current until cell impedance is fully evolved then allowing the cell to relax for an extended time period, the cell impedance behavior can be evaluated through the voltage-time profile as OCV is approached [52]. The high frequency aspect due to their fast characteristic time constants are difficult to separate using this method, but the zero current during relaxation allows for the slower diffusion behavior to be quantified well. This method can also be applied across multiple load currents, with the relaxation behavior reflecting the current magnitude before relaxation.

The combination of frequency and time domain methods can be used to ascertain baseline impedance values and ageing changes in each contribution. These can be translated into virtual tools through the model platform in section VI. The remaining cell behavioral changes are completed by the cell stoichiometry algorithm altering cell rest parameters.

The combined knowledge of individual impedance contributions and cell stoichiometry also allows for the root cause of ageing to be evaluated. The understanding of how and why the cell ages can be used to predict lifetimes and adapt the cell usage and control approach, demonstrated in *Figure 8*.

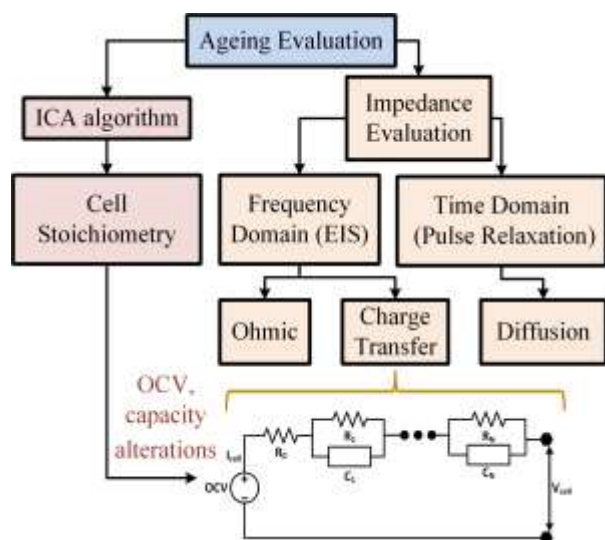


Figure 7 Schematic showing the different aspects of cell behavior that need to be incorporated and the different range of techniques incorporated for quantification including Incremental Capacity Analysis (ICA), Electrochemical Impedance Spectroscopy (EIS) and time domain pulse relaxation. The schematic also shows how each aspect quantifies information for the resultant equivalent circuit.

VI. MODELLING PLATFORM

The modelling platform is required to emulate cell performance under a range of conditions and to effectively model performance changes with ageing identified by the analysis methods in section V. The interaction between the algorithms and modelling platform is shown in Figure 7. An Equivalent Circuit Model (ECM) approach was used for the model structure, implemented within Matlab/Simulink [65]. This was chosen due to a wide range of possible cell and usage conditions combined with a requirement for emulation of cell behavior over the highly transient drive cycles. An ECM allows for a more accurate emulation of transient performance relative to empirical models while having versatility and ease of data population physical-chemical models lack. The approach also allows the structure to be flexible to incorporate the amount of impedance features shown as significant across the usage range by the ageing algorithms. The electrical ECM is combined in a closed loop format with a thermal model that calculates the irreversible ohmic and reversible entropic losses. This paper talks about the model structure as part of the overall ageing evaluation process. For more information on the model structure specifically and underlying theory see the authors previous papers [51,52].

VII. VALIDATION APPROACH

The dual purposes of the holistic ageing process are to identify root causes of cell ageing and emulate resultant performance changes in virtual tools. Both aspects required separate validation roots. Model performance was verified by comparing outputs with test data variations on electrical profiles and ageing month. In addition to model outputs, the ageing algorithms also give conclusions on degradation cause. These cannot be proven by electrical testing and therefore must be validated via physical and chemical investigation of the aged cells as described in the second half of this section.

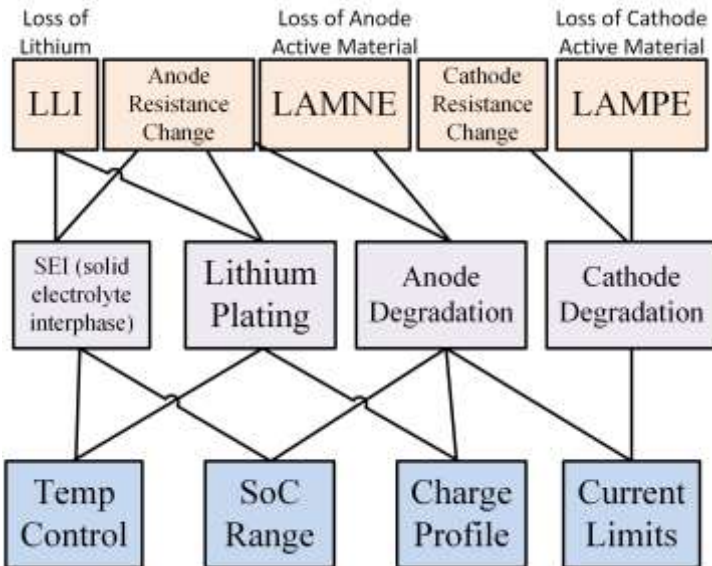


Figure 8 Link between ageing modes, mechanisms, and control aspects. The top row shows types of degradation modes, the middle row their underlying cause, and the bottom row the sensitivities of those mechanisms in terms of controllable usage conditions.

The electrical validation of the model as applied to new cells is shown in [51,66] therefore the focus here is on the consistency of the results with ageing. The approach to validate the model was to use a variety of cycle data to show its accuracy in a range of conditions. In this work, the model was validated against constant current (CC) discharge and charge tests at 1/3 of the rated cell capacity to evaluate steady state performance across the SoC range with ageing as shown in Figure 9. In addition, it was explained in section II and Figure 4 that ageing can give a significant difference in the time based voltage response to current change through evolving resistance. This is not easily visible through constant current testing therefore time based current and relaxation pulses were applied through the Hybrid Pulse Power Characterization (HPPC) profiles. These tests were conducted at 25°C with temperature control through cooling plates connected to the cell, being performed prior to the ageing testing and then repeated once per month subsequently.

The objective of the validation is not to see absolute model error but to see changes in model error at relative states of ageing therefore evaluating the effectiveness of the ageing model. Figure 10 shows the mean absolute error (MAE) of the ageing model relative to original Reference Performance Test (RPT) data for the monthly HPPC, C/3 discharge and C/3 charge tests. It can be seen that the error stays within a similar order of magnitude throughout life. Figure 9 compares the model to the validation test data at early, mid and late life. It can be seen the profile is followed well during the dynamic HPPC and CC tests. The main regions of error are the very low SoC regions and around 60% SoC where a phase change is occurring in the anode [59]. This is due to linear interpolation of insufficient datapoints in the model for the

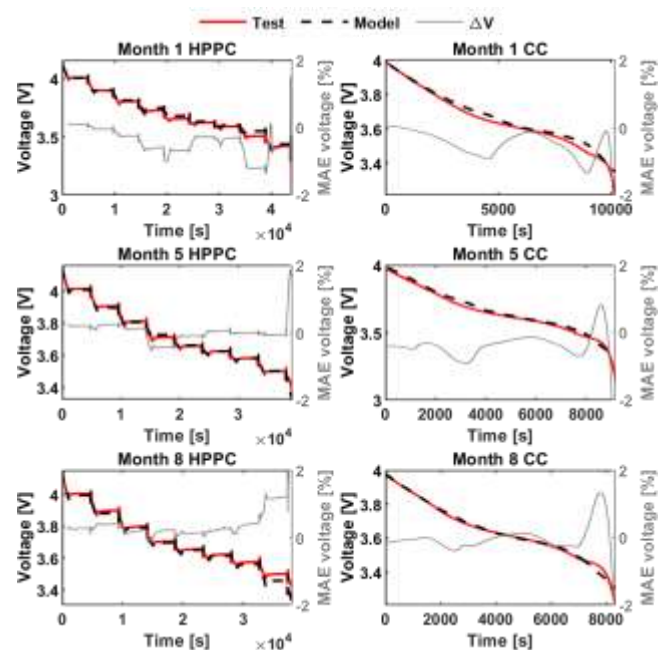


Figure 9 Validation of ageing model against reference test profiles of a hybrid pulse power characterization (HPPC) and a constant current (CC) discharge. Shown at beginning of life (Month 0), Mid-Life (Month 5) and near end of life (Month 8)

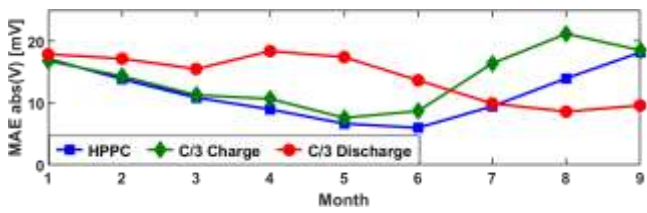


Figure 11 mean absolute error of ageing model relative to test data at monthly intervals for Hybrid Pulse Power Characterization (HPPC) testing, C/3 charge and C/3 discharge tests, 5-90% SoC range

highly transient impedance and OCV behavior in these regions and can be resolved through more targeted RPT profiles.

The chemical evaluation was performed based on a range of techniques. The stoichiometry changes involve changes in lithium distribution and active material capacity degradation. This is resolved by half-cell analysis of the electrodes in the new and aged cells, and techniques such as Nuclear Magnetic Resonance (NMR) [67] to investigate the lithium consumed in surface layer formation. The impedance changes can be due to surface and structural changes in the electrode and electrode/current collector interfaces therefore surface and cross-sectional surface imaging through Scanning Electron Microscopy (SEM) [68] is required.

The key conclusions from the presented case study is a significant loss of lithium and loss of cathode capacity. In addition to this, there was a noticeable decrease in the cathode

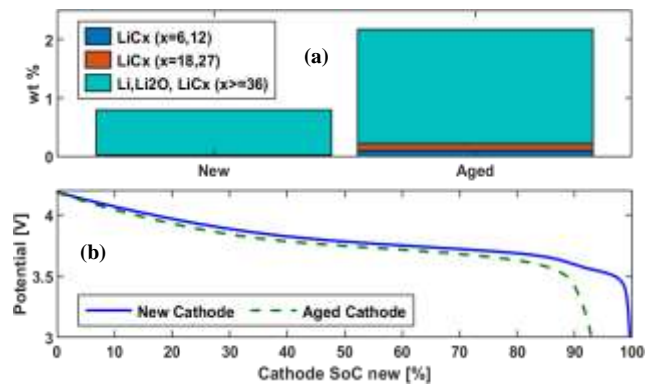


Figure 10 Chemical evaluation of new and aged Li-ion cells showing (a) Nuclear Magnetic Resonance (NMR) results showing increased surface layer formation and (b) cathode half-cell curves for new and aged cells showing noticeable reduction in cathode capacity,

charge transfer impedance. The loss of lithium is confirmed by Figure 12 (a), which through NMR shows a larger quantity of lithium within the SEI meaning it is no longer contributing to cell charge storage [69]. The loss of cathode active material is confirmed by cycling of active material extracted from new and aged cell samples, showing a reduction of capacity within the cyclable cathode limits in Figure 12 (b). The SEM results in Figure 11 compare an example new and aged (end of 9-month cycling) cell for the anode and cathode surface. The graphite anode shows only minor changes in surface condition

however the cathode shows significant deterioration and both inter-granular and intra-granular cracking. This increases cathode surface area, which in turn reduces its charge transfer impedance [70]. It is important to apply a range of chemical analysis methods when proving out an ageing evaluation approach to verify the conclusions are physically accurate. Once this is proven to be robust, the chemical analysis in future case studies is not essential.

VIII. CONCLUSIONS

This paper shows a holistic approach for evaluating ageing in Li-ion cells and emulating the complex performance changes through virtual tools. Li-ion ageing is complex both in terms of multitude of ageing conditions and the resultant combined performance changes however the metrics for evaluating and expressing this are often over-simplified. This approach resolves that issue by more fully evaluating ageing impact and in particular by expressing individual performance changes in capacity, OCV and individual impedance features.

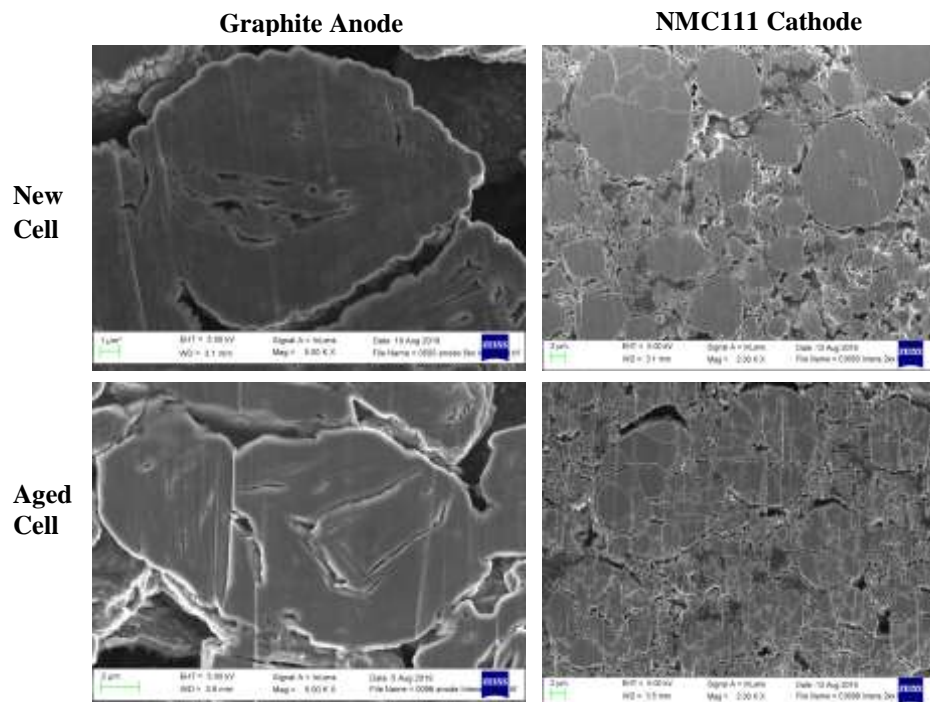


Figure 12 SEM images of anode and cathode samples under identical resolution for the new and both aged cells. All Graphite Anode images are at 5K magnification and NMC111 Cathode images are at 2k magnification. Images included to show clear deterioration of the cathode and minor deterioration of cathode at the aged cell condition of 9 months of cycling

The approach involves definition of representative testing, a suite of evaluation algorithms to cover the range of cell behavior and ageing, and a versatile equivalent modelling platform designed to be adaptable to the algorithm conclusions. The result was shown to be a model that retains consistency in accuracy over lifetime. It was also shown through chemical validation that it provides reliable conclusions on the root causes of cell ageing at least in high temperature cycling conditions.

IX. REFERENCES

- [1] The Roadmap Report Towards 2040 : a Guide To Automotive Propulsion Technologies, Coventry, UK, 2020.
- [2] European Commission, Proposal for a Regulation of the European Parliament and of the Council: Setting emission performance standards for new passenger cars as part of the Community's integrated approach to reduce CO2 emissions from light-duty vehicles, Brussels, 2018.
- [3] K. Baes, F. Carlot, Y. Ito, M. Kolk, A. Merhaba, Future of batteries, 2018. https://www.adlittle.com/sites/default/files/viewpoints/adl_future_of_batteries-min.pdf.
- [4] B.G. Pollet, S.S. Kocha, I. Staffell, Current status of automotive fuel cells for sustainable transport, *Curr. Opin. Electrochem.* 16 (2019) 90–95. <https://doi.org/10.1016/j.coelec.2019.04.021>.
- [5] P. Cazzola, M. Gorner, L. Munuera, Global EV Outlook 2017: Two million and counting, 2017. <https://doi.org/10.1787/9789264278882-en>.
- [6] J. Yamaguchi, D. Galves, Tesla Gigafactory : heightened LiB competition from ESS market entry, Tokyo, Japan, 2015. <https://plus.credit-suisse.com/u/xcJY2U>.
- [7] A. Thielmann, A. Sauer, R. Isenmann, M. Wietschel, Technology Roadmap Energy storage for Electric mobility 2030, 2013.
- [8] J. Vetter, P. Novák, M.R. Wagner, C. Veit, K.-C. Möller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, Ageing mechanisms in lithium-ion batteries, *J. Power Sources.* 147 (2005) 269–281. <https://doi.org/10.1016/j.jpowsour.2005.01.006>.
- [9] W. Prochazka, G. Pregartner, M. Cifrain, Design-of-Experiment and Statistical Modeling of a Large Scale Aging Experiment for Two Popular Lithium Ion Cell Chemistries, *J. Electrochem. Soc.* 160 (2013) A1039–A1051. <https://doi.org/10.1149/2.003308jes>.
- [10] Ford Motor Company, 2016 Model Year Ford Hybrid Car and Electric Vehicle Warranty Guide, Detroit, Michigan, USA, 2016. http://www.ford.com/resources/ford/general/pdf/brochures/2016-Hybrid-Electric-Vehicle-Warranty-version-1_frdwa_EN-US_03_2015.pdf.
- [11] Nissan, Nissan Warranty, Nissan Off. Website. (2016). <https://www.nissan.co.uk/ownership/nissan-car-warranties.html> (accessed September 27, 2016).
- [12] Tesla, Infinite Mile Warranty, Tesla Off. Website. (2016). https://www.tesla.com/en_GB/blog/infinite-mile-warranty?redirect=no (accessed July 28, 2016).
- [13] J.-M. Timmermans, A. Nikolian, J. De Hoog, Rahul, Gopalakrishnan, Shovon, Goutam, Noshin, Omar, Thierry, V. Coosemans, J. Van Mierlo, Batteries 2020 - Lithium-ion battery first and second life ageing, validated battery models, lifetime modelling and ageing assessment of thermal parameters, in: 2016 18th Eur. Conf. Power Electron. Appl. EPE 2016 ECCE Eur., IEEE, 2016. <https://doi.org/10.1109/EPE.2016.7695698>.
- [14] R. Xiong, L. Li, J. Tian, Towards a smarter battery management system : A critical review on battery state of health monitoring methods, *J. Power Sources.* 405 (2018) 18–29. <https://doi.org/10.1016/j.jpowsour.2018.10.019>.
- [15] N. Noura, L. Boulon, S. Jemei, A review of battery state of health estimation methods: Hybrid electric vehicle challenges, *World Electr. Veh. J.* 11 (2020) 1–20. <https://doi.org/10.3390/wevj11040066>.
- [16] P. Li, Z. Zhang, Q. Xiong, B. Ding, J. Hou, D. Luo, Y. Rong, S. Li, State-of-health estimation and remaining useful life prediction for the lithium-ion battery based on a variant long short term memory neural network, *J. Power Sources.* 459 (2020) 228069. <https://doi.org/10.1016/j.jpowsour.2020.228069>.
- [17] S. Li, H. He, J. Li, Big data driven lithium-ion battery modeling method based on SDAE-ELM algorithm and data pre-processing technology, *Appl. Energy.* 242 (2019) 1259–1273. <https://doi.org/10.1016/j.apenergy.2019.03.154>.
- [18] R. Stocker, P. Mathur, Li Battery Degradation Analysis, GB2101761, 2021.
- [19] R. Stocker, Power Unit Analysis, GB2101761, 2021.
- [20] A. Barré, B. Deguilhem, S. Grolleau, M. Gérard, F. Suard, D. Riu, A review on lithium-ion battery ageing mechanisms and estimations for automotive applications, *J. Power Sources.* 241 (2013) 680–689. <https://doi.org/10.1016/j.jpowsour.2013.05.040>.
- [21] M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, R.J. Staniewicz, Main aging mechanisms in Li ion batteries, *J. Power Sources.* 146 (2005) 90–96. <https://doi.org/10.1016/j.jpowsour.2005.03.172>.
- [22] C. Lin, A. Tang, H. Mu, W. Wang, C. Wang, Aging Mechanisms of Electrode Materials in Lithium-Ion Batteries for Electric Vehicles, *J. Chem.* 2015 (2015). <https://doi.org/10.1155/2015/104673>.
- [23] R.. S. M Broussely , S Herreyre, P Biensan, P Kasztejna, K Nechev, Aging mechanism in Li ion cells and calendar life predictions, *J. Power Sources.* 97–98 (2001) 13–21. [https://doi.org/10.1016/S0378-7753\(01\)00722-4](https://doi.org/10.1016/S0378-7753(01)00722-4).
- [24] P. Keil, A. Jossen, Aging of Lithium-Ion Batteries in Electric Vehicles : Impact of Regenerative Braking, *EVS28 Int. Electr. Veh. Symp. Exhib.* (2015) 1–11. <https://doi.org/10.13140/RG.2.1.3485.2320>.
- [25] C.H. Lin, C.L. Chen, Y.H. Lee, S.J. Wang, C.Y. Hsieh, H.W. Huang, K.H. Chen, Fast charging technique for Li-Ion battery charger, in: *Proc. 15th IEEE Int. Conf. Electron. Circuits Syst. ICECS 2008*, St. Juliens, Malta, 2008; pp. 618–621. <https://doi.org/10.1109/ICECS.2008.4674929>.
- [26] B. Suthar, P.W.C. Northrop, R.D. Braatz, V.R. Subramanian, Optimal Charging Profiles with Minimal Intercalation-Induced Stresses for Lithium-Ion Batteries Using Reformulated Pseudo 2-Dimensional Models, *J. Electrochem. Soc.* 161 (2014) F3144–F3155. <https://doi.org/10.1149/2.021141jes>.
- [27] H. Wang, Y. Zhu, S.C. Kim, A. Pei, Y. Li, D.T. Boyle, H. Wang, Z. Zhang, Y. Ye, W. Huang, Y. Liu, J. Xu, J. Li, F. Liu, Y. Cui, Underpotential lithium plating on graphite anodes caused by temperature heterogeneity, *Proc. Natl. Acad. Sci. U. S. A.* 117 (2020) 29453–29461. <https://doi.org/10.1073/pnas.2009221117>.
- [28] V. Agubra, J. Fergus, Lithium ion battery anode aging mechanisms, *Materials (Basel).* 6 (2013) 1310–1325. <https://doi.org/10.3390/ma6041310>.
- [29] B. Moyer, A Dendrite-Free Lithium Anode, *Electron. Eng. J.* (2015). <http://www.eejournal.com/archives/articles/20150521-pnnl/> (accessed January 16, 2016).
- [30] S. Tippmann, D. Walper, L. Balboa, B. Spier, W.G. Bessler, Low-temperature charging of lithium-ion cells part I: Electrochemical modeling and experimental investigation of degradation behavior, *J. Power Sources.* 252 (2014) 305–316. <https://doi.org/10.1016/j.jpowsour.2013.12.022>.
- [31] P. Keil, S.F. Schuster, J. Wilhelm, J. Travi, A. Hauser, R.C. Karl, A. Jossen, Calendar Aging of Lithium-Ion Batteries, *J. Electrochem. Soc.* 163 (2016) A1872–A1880. <https://doi.org/10.1149/2.0411609jes>.
- [32] V. Gopalan, W.H. McClain, SEI: Yesterday, today and tomorrow, *RNA.* 21 (2015) 541–543. <https://doi.org/10.1261/ma.049759.115>.
- [33] Y. Itou, Y. Ukyo, Performance of LiNiCoO2 materials for advanced lithium-ion batteries, *J. Power Sources.* 146 (2005) 39–44. <https://doi.org/10.1016/j.jpowsour.2005.03.091>.
- [34] a. J. Smith, J.C. Burns, D. Xiong, J.R. Dahn, Interpreting High Precision Coulometry Results on Li-ion Cells, *J. Electrochem. Soc.* 158 (2011) A1136. <https://doi.org/10.1149/1.3625232>.
- [35] D. Aurbach, B. Markovsky, G. Salitra, E. Markevich, Y. Talyossef, M. Koltypin, L. Nazar, B. Ellis, D. Kovacheva, Review on electrode-electrolyte solution interactions, related to cathode materials for Li-ion batteries, *J. Power Sources.* 165 (2007) 491–499. <https://doi.org/10.1016/j.jpowsour.2006.10.025>.
- [36] R. Hausbrand, D. Becker, W. Jaegermann, A surface science approach to cathode/electrolyte interfaces in Li-ion batteries: Contact properties, charge transfer and reactions, *Prog. Solid State Chem.* 42 (2014) 175–183.

- <https://doi.org/10.1016/j.progsolidstchem.2014.04.010>.
- [37] N. Schulz, R. Hausbrand, C. Wittich, L. Dimesso, W. Jaegermann, XPS-Surface Analysis of SEI Layers on Li-Ion Cathodes: Part II. SEI-Composition and Formation inside Composite Electrodes, *J. Electrochem. Soc.* 165 (2018) A833–A846. <https://doi.org/10.1149/2.0881803jes>.
- [38] J. Groot, State-of-health estimation of Li-ion batteries: cycle life test methods, Chalmers University of Technology, 2012. <http://komar.bitcheese.net/files/JensGroot.pdf>.
- [39] M. Dubarry, C. Truchot, B.Y. Liaw, Synthesize battery degradation modes via a diagnostic and prognostic model, *J. Power Sources*. 219 (2012) 204–216. <https://doi.org/10.1016/j.jpowsour.2012.07.016>.
- [40] S. Gantenbein, M. Weiss, E. Ivers-Tiffée, Impedance based time-domain modeling of lithium-ion batteries: Part I, *J. Power Sources*. 379 (2018) 317–327. <https://doi.org/10.1016/j.jpowsour.2018.01.043>.
- [41] J.P. Schmidt, S. Arnold, A. Loges, D. Werner, T. Wetzel, E. Ivers-Tiffée, Measurement of the internal cell temperature via impedance: Evaluation and application of a new method, *J. Power Sources*. 243 (2013) 110–117. <https://doi.org/10.1016/j.jpowsour.2013.06.013>.
- [42] J. Illig, M. Ender, A. Weber, E. Ivers-Tiffée, Modeling graphite anodes with serial and transmission line models, *J. Power Sources*. 282 (2015) 335–347. <https://doi.org/10.1016/j.jpowsour.2015.02.038>.
- [43] D. Andre, M. Meiler, K. Steiner, C. Wimmer, T. Soczka-guth, D.U. Sauer, Characterization of high-power lithium-ion batteries by electrochemical impedance spectroscopy. I. Experimental investigation, *J. Power Sources*. 196 (2011) 5334–5341. <https://doi.org/10.1016/j.jpowsour.2010.12.102>.
- [44] J.P. Schmidt, T. Chrobak, M. Ender, J. Illig, D. Klotz, E. Ivers-Tiffée, Studies on LiFePO₄ as cathode material using impedance spectroscopy, *J. Power Sources*. 196 (2011) 5342–5348. <https://doi.org/10.1016/j.jpowsour.2010.09.121>.
- [45] M. Hess, Kinetics and stage transitions of graphite for lithium-ion batteries, 2013. <https://doi.org/https://doi.org/10.3929/ethz-a-010000442> Rights.
- [46] C. Pastor-Fernández, K. Uddin, G.H. Chouchelamane, W.D. Widanage, J. Marco, A Comparison between Electrochemical Impedance Spectroscopy and Incremental Capacity-Differential Voltage as Li-ion Diagnostic Techniques to Identify and Quantify the Effects of Degradation Modes within Battery Management Systems, *J. Power Sources*. 360 (2017) 301–318. <https://doi.org/10.1016/j.jpowsour.2017.03.042>.
- [47] N. Lohmann, P. Weßkamp, P. Haußmann, J. Melbert, T. Musch, Electrochemical impedance spectroscopy for lithium-ion cells: Test equipment and procedures for aging and fast characterization in time and frequency domain, *J. Power Sources*. 273 (2015) 613–623. <https://doi.org/10.1016/j.jpowsour.2014.09.132>.
- [48] B. Wu, V. Yufit, Y. Merla, R.F. Martinez-Botas, N.P. Brandon, G.J. Offer, Differential thermal voltammetry for tracking of degradation in lithium-ion batteries, *J. Power Sources*. 273 (2015) 495–501. <https://doi.org/10.1016/j.jpowsour.2014.09.127>.
- [49] D. Klotz, M. Schönleber, J.P. Schmidt, E. Ivers-Tiffée, New approach for the calculation of impedance spectra out of time domain data, *Electrochim. Acta*. 56 (2011) 8763–8769. <https://doi.org/10.1016/j.electacta.2011.07.096>.
- [50] R. Amin, Y.-M. Chiang, Characterization of Electronic and Ionic Transport in Li_{1-x}Ni_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC 333) and Li_{1-x}Ni_{0.50}Mn_{0.20}Co_{0.30}O₂ (NMC 523) as a Function of Li Content, *J. Electrochem. Soc.* 163 (2016) A1512–A1517. <https://doi.org/10.1149/2.0131608jes>.
- [51] R. Stocker, A. Mumtaz, Paramjeet, M. Braglia, N. Lophitis, Universal Li-Ion Cell Electro-Thermal Model, *IEEE Trans. Transp. Electr. Early Acce* (2020) 1–1. <https://doi.org/10.1109/te.2020.2986606>.
- [52] R. Stocker, N. Lophitis, A. Mumtaz, Development and verification of a distributed electro-thermal Li-ion cell model, in: *Proc. IECON 2018 - 44th Annu. Conf. IEEE Ind. Electron. Soc., IEEE*, 2018: pp. 2044–2049. <https://doi.org/10.1109/IECON.2018.8591633>.
- [53] USABC, Electric Vehicle Battery Test Procedures Manual Revision 2, 1996.
- [54] J.P. Christopherson, Battery Test Manual for Plug-In Hybrid Electric Vehicles, 3rd ed., U.S. Department of Energy, Idaho Falls, 2015. <http://www.inl.gov/technicalpublications/Documents/3952791.pdf>.
- [55] R. Stocker, A. Mumtaz, N. Lophitis, Design-of-Experiments Analysis of Li-Ion Cell Capacity Fading in High Temperature Automotive Conditions, in: *2019 Electr. Veh. Int. Conf. EV 2019, IEEE Transactions*, Bucharest, 2019: pp. 2–7. <https://doi.org/10.1109/EV.2019.8893026>.
- [56] L. Su, J. Zhang, C. Wang, Y. Zhang, Z. Li, Y. Song, T. Jin, Z. Ma, Identifying main factors of capacity fading in lithium ion cells using orthogonal design of experiments, *Appl. Energy*. 163 (2016) 201–210. <https://doi.org/10.1016/j.apenergy.2015.11.014>.
- [57] M. Broussely, S. Herreyre, P. Biensan, P. Kasztejna, K. Nechev, R.J. Staniewicz, Aging mechanism in Li ion cells and calendar life predictions, *J. Power Sources*. 97–98 (2001) 13–21. [https://doi.org/10.1016/S0378-7753\(01\)00722-4](https://doi.org/10.1016/S0378-7753(01)00722-4).
- [58] J. Schmalstieg, S. Käbitz, M. Ecker, D.U. Sauer, A holistic aging model for Li(NiMnCo)O₂ based 18650 lithium-ion batteries, *J. Power Sources*. 257 (2014) 325–334. <https://doi.org/10.1016/j.jpowsour.2014.02.012>.
- [59] M. Heß, Kinetics and stage transitions of graphite for lithium-ion batteries, ETH Zurich, 2013. <https://doi.org/10.3929/ethz-a-010000442>.
- [60] M. Dubarry, M. Bercebar, G. Baure, N. Omar, I. Villarreal, State of Health Battery Estimator Enabling Degradation Diagnosis, *Meet. Abstr. MA2017-02* (2017) 85–85. <http://ma.ecsdl.org/content/MA2017-02/1/85.short>.
- [61] J. Illig, J.P. Schmidt, M. Weiss, A. Weber, E. Ivers-tiffée, Understanding the impedance spectrum of 18650 LiFePO₄ -cells, 239 (2013) 670–679. <https://doi.org/10.1016/j.jpowsour.2012.12.020>.
- [62] M. Schönleber, C. Uhlmann, P. Braun, A. Weber, E. Ivers-Tiffée, A Consistent Derivation of the Impedance of a Lithium-Ion Battery Electrode and its Dependency on the State-of-Charge, *Electrochim. Acta*. 243 (2017) 250–259. <https://doi.org/10.1016/j.electacta.2017.05.009>.
- [63] J. Illig, J.P. Schmidt, M. Weiss, A. Weber, E. Ivers-Tiffée, Understanding the impedance spectrum of 18650 LiFePO₄-cells, *J. Power Sources*. 239 (2013) 670–679. <https://doi.org/10.1016/j.jpowsour.2012.12.020>.
- [64] W. Waag, S. Käbitz, D.U. Sauer, Experimental investigation of the lithium-ion battery impedance characteristic at various conditions and aging states and its influence on the application, *Appl. Energy*. 102 (2013) 885–897. <https://doi.org/10.1016/j.apenergy.2012.09.030>.
- [65] I. The Mathworks, MATLAB and Simulink 2019a, (2019).
- [66] R. Stocker, P. Mathur, A. Mumtaz, N. Lophitis, Considering Li-Ion Battery Cell Ageing in Automotive Conditions, *HORIBA Readout*. 53 (2019) 90–96. <https://doi.org/10.1016/j.ocecoaman.2013.03.010>.
- [67] P. Verma, P. Maire, P. Novak, A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries, *Electrochim. Acta*. 55 (2010) 6332–6341. <https://doi.org/10.1016/j.electacta.2010.05.072>.
- [68] M. Börner, A. Friesen, M. Grützke, Y.P. Stenzel, G. Brunklus, J. Haetge, S. Nowak, F.M. Schappacher, M. Winter, Correlation of aging and thermal stability of commercial 18650-type lithium ion batteries, *J. Power Sources*. 342 (2017) 382–392. <https://doi.org/10.1016/j.jpowsour.2016.12.041>.
- [69] Y. Merla, B. Wu, V. Yufit, N.P. Brandon, R.F. Martinez-Botas, G.J. Offer, Novel application of differential thermal voltammetry as an in-depth state-of-health diagnosis method for lithium-ion batteries, *J. Power Sources*. 307 (2016) 308–319. <https://doi.org/10.1016/j.jpowsour.2015.12.122>.
- [70] M. Dubarry, C. Truchot, B.Y. Liaw, Cell degradation in commercial LiFePO₄ cells with high-power and high-energy designs, *J. Power Sources*. 258 (2014) 408–419. <https://doi.org/10.1016/j.jpowsour.2014.02.052>.