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TABLE OF CONTENTS

1	Overview	3
2	Need	3
3	Objectives	3
4	Results	4
4.1	Metrologically sound life cycle tests and impedance measurement procedures	4
4.1.1	Background	4
4.1.2	Definitions and workplan	4
4.1.3	Metrological characterisation	7
4.1.4	Measured capacity (SoH) evolution and GEIS data sets	8
4.1.5	Finding correlations between the EIS response of a battery and its SoH	10
4.1.6	Repeatability (reproducibility) of SoH-EIS evolution	12
4.1.7	Repeatability (reproducibility) of SoH-NFRA evolution	13
4.1.8	Conclusion	16
4.2	Development and characterisation of impedance-based procedures to measure the	
res	idual capacity and detect accelerated aging	17
4.2.1	Background	17
4.2.2	General method to identify aging parameters	17
4.2.3	Impedance-based methods for residual capacity prediction	19
4.2.4	LCTs and EIS of 18650 cells under various cycling conditions	23
4.2.5	Validation of the impedance-based aging parameters	40
4.2.6	Accelerated aging	46
4.2.7	Conclusion	48
4.3	Low impedance standards and calibration procedures	49
4.3.1	Background	49
4.3.2	Design of low impedance standards	49
4.3.3	Characterisation of impedance standards	55
4.4	Validated test protocol to characterise modules based on impedance measurements	58
4.4.1	LCT of modules	59
4.4.2	Conclusion	61
5	Impact	61
6	List of publications	62
7	Contact details	63



1 Overview

Li-ion batteries have useful applications ever after removal from their first use in electric vehicles, such as low-cost energy storage media in conjunction with photovoltaic systems. However, their uptake is hampered by the lack of accurate and cost-effective characterisation techniques. This project has developed robust measurement procedures and paved the way for a supporting metrological infrastructure to measure the residual capacity of li-ion batteries using fast and non-destructive impedance-based methods and investigate the feasibility to predict premature failure. Such procedures will enable the economical and sustainable re-use of the multitude of Li-ion batteries, which become more and more available in the meanwhile.

2 Need

Once Li-ion batteries have reached their end of life in an electric vehicle (EV), these batteries can be used for many years in a wide range of applications. For instance, they can be used as reserve power in electricity grids or for local energy storage in conjunction with photovoltaic systems. Such batteries are called second-use (or second-life) batteries. 8.5 million electric vehicles were globally sold until 2020. It is estimated that up to 150 million second-use batteries will be available by 2030. The sale of repurposed batteries could therefore provide considerable economic opportunities for the European market, and it would improve the environmental footprint of electric vehicle Li-ion batteries.

Hence, the optimisation of battery reprocessing is urgently required, otherwise, the application of second-use batteries will be too expensive to be economically viable. In particular, validated impedance-based procedures to measure the residual capacity need to be significantly faster and more accurate compared to existing methods. Furthermore, a robust measurement procedure to assess the risk of premature failure, at least qualitatively, does not yet exist. Impedance-based measurement and evaluation methods could serve this purpose however, the underpinning metrological framework, including traceability, quantified measurement uncertainties and defined measurement procedures in order to guarantee comparability of the results, is currently lacking. Consequently, standardised protocols for life cycle testing and impedance measurements as well as practical calibration concepts and standards for impedance measurement devices must be developed. In the broader, environmental context, the EU has declared the need to reduce greenhouse gas emissions on several occasions. Hence, actions to implement second-use batteries in conjunction with renewable energy sources need to be supported, instead of wasting enormous amounts of storage capacity and buying new storage systems, primarily imported from Asia, for that purpose.

3 Objectives

The overall objective of this project was to establish an accurate, fast and practical measurement procedure for European industry to measure the residual capacity and to study feasibility to detect premature failure of Li-ion batteries of electric vehicles (EVs) for second use applications using impedance based methods. The specific objectives of the project were:

- 1. To develop protocols for life cycle testing of different types of Li-ion- battery cells and modules in terms of capacity, chemistry and geometry, at different temperatures, currents and cycling patterns. The life cycle tests will include both impedance-based methods (e.g. EIS, EC, DRT, NFRA and TDM) and conventional methods e.g. open circuit voltage (OCV) measurement and current integration.
- To develop validated impedance-based measurement procedures to measure the residual capacity of Li-ion battery cells and modules with a target relative uncertainty of better than 3 %. In addition, to assess the feasibility of detecting the premature sudden death of Li--ion batteries based on impedance-based measurements.
- 3. To establish traceable impedance measurements in the m□ and sub-m□ range in the full complex plane in the frequency range between 10 mHz and 5 kHz, with a target relative uncertainty of 1 %. This will include the development of low impedance standards with arbitrary phase angles and a calibration method for impedance meters.
- 4. To develop a validated protocol for the application to Li-ion battery modules of the traceable impedance measurements in the m□ and subm□ range in the full complex plane in the frequency range between 10 mHz and 5 kHz.
- 5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g. batteries manufacturers and the automotive industry)



standards developing organisations (e.g. IEC-TC21 and input to IEC 62660-1) and end users (e.g. the transport sector).

4 Results

This section summarises the main technical results of the LiBforSecUse project. The main sections (second level headings) are structured according to the scientific objectives as stated in section 3. The respective subsections summarise main activities and results achieved to address the objectives in a logical order, even though the activities have partly been conducted in different work packages, at various institutes and in another timely order.

4.1 Metrologically sound life cycle tests and impedance measurement procedures

4.1.1 Background

The aim of this work was to create an empirical database of impedance-based measurement results of aged Li-ion battery cells and modules on sound metrological grounds. NIC and PTB in cooperation with all consortium partners prepared strategy for establishing feasible advanced measurement procedures and selection of tested cells that were shaped to a definite working version after discussions with involved partners. Robust measurement procedures for life cycle tests (LCT) and impedance-based measurements were defined based on the experience of the partners involved in the project. Different types of Li-ion battery cells and modules in terms of capacity, chemistry and geometry, were within the LCTs tested at different temperatures, state-of-charge (SOC) ranges, current loads and cycling profiles. The LCTs included impedance measurement and evaluation methods. The final aim was to provide a database for the assessment of the feasibility of detecting the premature sudden death of Li-ion batteries established by employing impedance-based measurements.

4.1.2 Definitions and workplan

The main aim of this task was to devise a consistent measurement plan and to create partners-agreed measurement procedures for the subsequent tasks and work packages. The measurement procedures provided the basis for the standardisation of impedance measurements.

4.1.2.1 Batteries under investigation

NIC together with PTB, JRC, NPL, (first TUBS) then KIT, Aalto, Li.plus and ACE defined the type of battery cells and modules to be used in systematic sets of measurements. Defined were: cell chemistry, housing, nominal capacity, and physicochemical characteristics. The main decision regarding the testing battery cell type was to use high-energy Ni-rich NMC-based batteries since this type of battery cell is one of the most important candidates for the use in automotive applications for powering electric vehicles (that is primary/first industrial life of a Li ion battery use) and as such would enable to study cell parameters after reaching end of "first life" thus effectively probing correlations during second use of a Lithium-ion battery. Further it was planned to perform comparison study of larger format prismatic cells that include high-energy Ni-rich NMC cathode and with cell nominal capacity in the range 40-60 Ah. The measurements on individual prismatic cells were (due to multiple technical issues at JRC and NPL) realized in practice only at PTB by testing 50 Ah NMC-Graphite cells. Measurements on alternative high-energy NMC and LMO-NMC prismatic and pouch batteries were planned in order to extend the study more in a broader battery field and verify whether the trends and correlations observed for high-energy NMC-based cells are applicable more in general for Li ion batteries. Due to Covid-19 pandemic related situation that for some of the included institutions (NPL, NIC) partially reduced the accessibility to the laboratories and copyright matters (JRC) the testing for other types of cells/chemistry was mostly cancelled or it cannot be included in the results of present project. Regarding the variation of cell chemistry LCTs together with impedance evolution were conducted on LFP-Graphite cells (NIC) that demonstrated major impact of cell chemistry on battery long-term performance and corresponding impedance development. Within WP2 it was planned to combine individual 40-60 Ah prismatic cells and build modules with individual cells connected in series, parallel (or both) to obtain total nominal capacity ranging 500-600 Ah and total power up to 120 V/70 A. Realization of the building of modules was partial due to technical issues during module fabrication and delays in the commissioning of module cycler (NPL). The operating modules were successfully constructed at PTB (4 units with each unit including five 50 Ah NMC-Graphite prismatic cells connected in series, nominal voltage 18 V) and LCTs together with impedance measurements were performed.



4.1.2.2 Workplan

In the first stage PTB, NIC, NPL, Aalto, JRC and TUBS prepared detailed information about their measurement and life cycle test facilities available for the project before the kick-off meeting and provided them to NIC. Based on this information NIC developed a work plan, particularly including allocation of LCTs to partners. After considering both research and practical aspects of the implementation of the measurements strategies it was jointly decided to introduce the concept of a "reference battery cell". Type of cell chosen for reference battery cell was such that it enabled: a) simple and direct inter-lab comparison of parallel measurements conducted at several partners using different measurement instruments and temperature chambers with cells tested at "reference conditions", b) versatile options for systematic variation of testing conditions. As the reference cell it was chosen cylindrical 18650 high-energy NMC-Graphite cell based on Nickel-rich 811 NMC cathode with nominal capacity of about 3 Ah. Subsets of tests with reference cells were defined to be used for LCTs until cell failure, for post-mortem analysis, and capacity measurements. Furthermore, it was jointly decided in between the partners that the cell type for impedance comparison measurement would be "reference battery cell".

During joint discussion of the partners life cycle test parameters (C-rate, temperatures, rest time, charge/discharge sequence pattern, stop criterion) for reference conditions as well as for majority of other LCTs were discussed and accepted. The obtained testing protocol is presented further below. The central electrochemical measurements under reference conditions for inter-lab comparison that served for building of baseline long-term cycling and impedance database were performed in parallel at 6 institutions (PTB, JRC, NPL, KIT, NIC, Aalto). The inter-lab comparison between 6 partners was conducted on reference cells by performing LCTs with the same experimental conditions – but at different institutions and with different measurement equipment as listed in Table 4.1-1.

Partner	Measurement equipment	Number of cells	Cell code (identifier)
PTB	Cycling: BasyTec XCTS EIS: Gamry Reference 3000 Multiplexer: BasyTec EIS Mux Climate chamber: Vötsch VT3 4060	4	PTB-15 PTB-16 PTB-17 PTB-18
JRC	Cycling: Maccor Series 4000 coupled with Modulab XM ECS (Solatron Analytical) for EIS Climatic chamber: BiA MTH 4.46	3	JRC-04 JRC-05 JRC-06
NPL	Cycling: BioLogic VMP3/VMP3-B10 EIS: BioLogic VMP3/VMP3-B10 Climatic chamber: Binder MK115 & ED56	2	NPL-11 NPL-12
KIT	Cycling: BasyTec XCTS, EIS: Zahner Zennium, NFRA: Zahner Zennium + Zahner PP241 Climate chamber: Weiss WK3-340/70	2	KIT-06 KIT-07
NIC	Cycling: BioLogic MPG-205, EIS: BioLogic SP-200 Climatic chamber: Binder KB 240	2	NIC-01 NIC-02
Aalto	Cycling: Maccor series 4300 EIS: BioLogic MPG-205, Climatic chamber: Vötsch VC3 4018	2	Aalto-03 Aalto-04

Table 4.1-1: Measurement equipment, number of cells and cell codes for the LCTs done for the Interlab comparison task.

In addition to Inter-lab comparison task reference cells were used for performing several other experimental tasks:

Aging under calendaric conditions;

Checking of effect of Temperature during long-term cycling;

Checking of effect of DoD range during long-term cycling.



Comparison of LCT evolution of State-of-Health (SoH) and corresponding evolution of impedance of prismatic cells was done at PTB. At PTB the 50 Ah NMC-Graphite prismatic cells were configuried into modules and tested.

The overview of the initially planned and eventually performed electrochemical LCTs in the present project is presented in Table 4.1-2.

Table 4.1-2: Summary of planned and performed electrochemical tests on batteries and modules within WP2.

Activity (task)	LCT #	Partner	Testing conditions	Status/Comment	
	1.01	PTB			
	1.02	JRC			
Interlab comparison	1.03	NPL			
	1.04	KIT	T = 45 °C, DoD = 0-100	Completed	
	1.05	NIC			
	1.06	Aalto			
	1.07	PTB	<i>T</i> = 45 °C, SoC = 100		
Calendaric	1.08	JRC	<i>T</i> = 45 °C, SoC = 80	Completed	
conditions	1.09	KIT	$T = 45 ^{\circ}\text{C}, \text{SoC} = 50$		
	1.10	JRC	<i>T</i> = 35 °C, DoD = 0-100		
	1.11	JRC	<i>T</i> = 45 °C, DoD = 25-75		
	1.12	NIC	<i>T</i> = 45 °C, DoD = 50-100		
	1.13	NIC	<i>T</i> = 23 °C, DoD = 0-100		
Effect of T and	1.14	NPL	<i>T</i> = 45 °C, DoD = 0-50	Completed	
DoD	1.15	кіт	<i>T</i> = 45 °C, DoD = 30-100, DoD = 10-80		
	1.16	КІТ	<i>T</i> = 45 °C, DoD = 60-90, DoD = 25-55		
	1.17	Aalto	<i>T</i> = 10 °C, DoD = 0-100		
Time domain measurements	1.18	PTB Li.plus		Cancelled	
De tra Caller	1.19	PTB		Cancelled	
Potentially additional LCTs	1.20	KIT		Cancelled	
	1.21	Aalto		Cancelled	
	2.01	РТВ	<i>T</i> = 23 °C, DoD = 0-100 Current = 25 A	Completed	
Comparison of	2.02	JRC		Testing could not be initiated due to multiple issues with the chamber and tester_allocated to higher currents.	
prismatic cells	2.03	NPL		Testing could not be initiated because of delays due to cell holder fabrication high current channels commissioning	
	2.04	PTB	<i>T</i> = 45 °C, DoD = 0-100	Completed	
	2.05	NPL		Cancelled	
Alternative high- energy batteries	2.06	JRC		Will not be included in D4. We decided not to include them as the data belong to other project and it was not easy to sort out the copyright matters.	



Activity (task)	LCT #	Partner	Testing conditions	Status/Comment
	2.07	NIC		Cancelled
Modules	2.08	РТВ	<i>T</i> = 45 °C (initial), <i>T</i> = 35 °C (cycling), DoD = 0-100	Completed LiBforSecUse - Dokumente\Workpackages\WP3\Parsed EIS-SOH Data (Matlab)
	2.09	NPL		Cancelled due to issues with module fabrication and delays in the commissioning of module cycler
Other batteries	2.10	NPL		Cancelled
	2.11	KIT		Cancelled
	2.12	NIC		Cancelled
	2.13	NIC	<i>T</i> = 23 °C, DoD = 0-100	Completed
	2.14	NIC	LFP-Graphite 3 Ah battery $T = 24 ^{\circ}$ C, DoD = 0-100	Completed
	1.15	PTB		Cancelled

4.1.2.3 Capacity test measurements

The measured capacity of a Li-ion battery is not an independent quantity, but depends on the C-rate (i.e. the current) at which it was measured. The higher the C-rate, the higher the overpotential of the battery and the lower the measured capacity. In preliminary tests, it was tested how reproducible the measured capacity is at different C-rates for different cells in order to define ideal measurement parameters. This resulted in high standard deviations for high and low C-rates. A C-rate of 0.5 was chosen for determining the capacity of the batteries in the LCTs. In addition, a rate of 0.05 was chosen because it has the advantage of being largely unaffected by the overpotential.

4.1.2.4 Protocol for LCT and EIS measurements+6

Impedance measurements and, in particular, electrochemical impedance spectroscopy (EIS) of Li-ion batteries are very sensitive to a variety of measurement conditions. Results can hardly be reproduced and are subject to misinterpretation if the measurement parameters are ill-defined. This fundamental issue, that is often not adequately addressed, applies particularly to its use in life cycle tests (LCT). Impedance results of LCTs are correlated in one or the other way with the aging of the battery under investigation. Thus, it is of crucial importance to define adequate reproducibility conditions for impedance measurements and LCTs. Well defined measurement conditions will guarantee their metrological comparability, will provide stable results and will avoid misinterpretation of LCT observations. Therefore, a number of preparatory tests and crucial measurement parameters and have been defined to establish reproducibility conditions for interlaboratory collaboration. These include wiring, device calibration, capacity measurement, impedance measurement parameters, cycling conditions and many others. The protocol has been published as a best practice guide¹.

4.1.3 Metrological characterisation

4.1.3.1 Uncertainty of EIS measurements

One aim of the project was to develop measurement procedures that allow impedance measurements with a relative standard measurement uncertainty of less than 3 %. Impedance spectroscopic measurements are influenced by various external factors. In addition to measurement setup related aspects such as cable routing and contacting, the following three influencing variables mainly determine the result of the measurement:

- SOC
- Relaxation to OCV
- Temperature

The measurement uncertainty of the impedance resulting from these factors is given by:

¹ DOI 10.5281/zenodo.6407810



$$u_{rel}(Z')_T = \frac{\Delta Z'/\Delta x_i}{Z'_{23^\circ C}} \cdot u(x_i)$$

$$4.1-1$$

The uncertainty u(x) is given by the accuracy of the deployed measuring device. The influence of the individual factors on the measured impedance was determined experimentally by measuring under reference conditions and under deviating conditions. In this way, the measurement uncertainty resulting from the individual factors for the impedance measurement was determined. The relative measurement uncertainty resulting from deviating from the individual factors in temperature is plotted in Figure 4.1-1 for the real and imaginary parts of the impedance.



Figure 4.1-1: relative uncertainty of the frequency dependent impedance due to temperature deviation. Real and imaginary parts are plotted individually.

The measurement uncertainty of the impedance resulting from the three impedance spectra is frequency dependent. For better comparability and quantification, the uncertainties for the real and the imaginary part of the impedance at 0.5 Hz are given in Table 4.1-1. The frequency was chosen because impedance parameters used as predictors for the SOC estimation lie in this frequency range.

	u _{rel} (Z') / %	u _{rel} (Z ["]) / %
SOC	0.176	0.269
Relaxation	0.160	0.194
Temperature	1.620	1.660
Σ	1.956	2.123

Table 4.1-2: relative uncertainties for the different contributions to the overall uncertainty.

The sums of the various contributions to the measurement uncertainty of the impedance show that the project goal of being able to carry out impedance measurements with an uncertainty of less than 3 % has been clearly achieved.

4.1.3.2 Interlaboratory Reproducibility

An important emphasis was given to repeatability (reproducibility) of the electrochemical tests. It is important to stress that properties/performance of battery cells in general are affected by various factors. Even the conditions before the first battery usage (for example the previous warehouse storage temperature) in addition to the starting industrial production variance between the cells can somewhat affect the cell performance. Within the inter-lab comparison, the selected LCTs on 15 cylindrical 18650 NMC-Graphite cells were performed by the 6 partners.

4.1.4 Measured capacity (SoH) evolution and GEIS data sets

In order to check general repeatability of the electrochemical cycling tests together with the corresponding impedance measurements, a comparative analysis of the obtained data for the 15 selected cells (Table 4.1-1) was performed. Firstly, the dependence of SoH vs. cycle number of the cells (Figure 4.1-1) was compared with each other in order to observe general trends and deviations.





Figure 4.1-2: Evolution of SoH of the 15 reference cells during the LCTs for the Inter-lab comparison task.

The main general trend observed for all of the cells is the rather fast decrease of SoH in the initial stage of cycling (typically during about 200 cycles) which is probably linked with the fast degradation of performance of Si particles in the anode. In the following (second) stage one observes a close-to-linear decrease of SoH with cycle number, SoH/Cycle. The latter rate of SoH decrease is observed to be quite comparable for most of the cells which is found to be about -1% per 100 cycles. The largest deviation from these trends is observed for the two cells tested at NPL. A possible reason could lie in the calendar aging effect that these two tests started significantly later (about 1 year) than the others due to Covid-19 related restrictions. In addition, these two cells might have aged more when the LCT was terminated at late night, weekend or holidays then cells were stored longer at the elevated temperature of 45°C than the design of experiment which ideally requires that the cells transfer promptly to the ambient 23°C climatic chamber for the periodic health check point. On the other hand, all the cells tested at PTB show a comparable second-stage "linear" decrease of SoH (i.e. the same value of SoH/Cycle) as the other cells. At the same time, it seems that their measured SoH is somewhat larger compared to the cells tested at the other institutions. In the third stage a transition to more rapid decrease of SoC (a higher value of - SoH/ Cycle) is observed. The evolution of SoH in this third stage of testing was found to be the least reproducible, that is, it depended the most on individual properties of cells. For example, one of the cells tested at PTB (PTB-17) exhibited this third stage already before ca. 1500 cycles while the other three cells continued the linear (second) stage of SoH decrease beyond 2000 cycles.

The onset of the third stage and further SoH (capacity) evolution is very important for the second-life use of a battery cell. The possibility of prediction of this onset would be of major importance, especially as in some cases an accelerated decrease of battery SoH was observed. Here, it is important to note that the conditions during the Inter-lab comparison LCTs were quite harsh (charging with a maximal recommended current of 1.33C, and at the elevated temperature of 45°C). Consequently, the observed evolutions of SoH showed a relatively short cycle life (1200 – 1800 cycles) when reaching the EoL condition. In real applications standard Li-ion battery cells (with standard electrolytes) are almost never exposed to such constant elevated temperatures. Accordingly, the SoH evolutions obtained in the Interlab comparison task (figure 4.1.1) should be considered as the results of slightly accelerated degradation tests. This was done due to the limited project duration within which we not only wanted to reach EoL of a battery but also to obtain the evolution of SoH beyond EoL, thus covering effectively the actual "second life" of a battery.

The periodic measurements of EIS and NFRA determination for the Inter-lab comparison task produced a large data set with more than 5000 EIS spectra and around 300 NFR spectra obtained. For that reason only part of the data is shown in the present report for the selected SoC = 100%. The sets of EIS spectra measured at other SoCs exhibit comparable information and are thus not shown in the report. Most importantly, already a fast checking of the data demonstrates that there was a natural spread in EIS of the cells with slightly different initial SoH evolution and furthermore the data sets varied more significantly between the partners in the SoH at the end of tests. Because of those two reasons the EIS data sets needed to be compared using a simplified approach as described in continuation.



4.1.5 Finding correlations between the EIS response of a battery and its SoH

For the purpose of being able to estimate the repeatability of the evolution of the sets of measured impedance spectra during the long-term LCTs Figure 4.1-1), a proper correlation between the EIS spectrum and SoH of the cell had to be found. The procedure of finding of such a correlation is demonstrated on typical examples of measurements obtained at NIC (LCT 1.05). Figure 4.1-2shows the evolution of SoH of two cells (NIC-01 and NIC-02) as a function of cycle number. In Figure 4.1-3 the corresponding set of the EIS spectra measured on cell NIC-01 at several SoCs is presented.



Figure 4.1-3: Typical example of evolution of SoH of the reference cells during 4 A cycling at 45°C in full DoD range and CV step at the upper cut off voltage (Interlab comparison test LCT 1.05, NIC-01 and NIC-02) as a function of cycle number.





d)



Figure 4.1-4: Typical measured set of the EIS spectra obtained in the Inter-lab comparison tests. Presented are the results of LCT 1.05 for cell NIC-01 obtained at SoC: a) 100 %, b) 65 %, c) 50 %, and d) 20 %. In the legends the cycle numbers at which the particular EIS spectrum was measured are shown.

It can be observed in Figure 4.1-3 that, at all SoCs the EIS spectra show a gradual increase of impedance values with increasing cycle number. Furthermore, it can be seen that the impedances at the same cycle number are the largest at SoC = 100 % and gradually became smaller with reducing SoC down to 20 %. At all the SoCs a gradual increase in the high-frequency intercept and interfacial impedance arc can be seen. Moreover, the increase (increment) of the interfacial impedance arc prevails over the increase of the high-frequency intercept; and this effect is the strongest at the highest SoC. Plainly such a direct comparison of the EIS spectra gives some information, but it does not provide any further direct insight into the corresponding SoH evolution of the compared cells. Obviously, the SoH evolution and related impedance responses need to be represented in such a way that a direct SoH-EIS correlation could be plotted. One of the simplest possibilities to do so is presented in Figure 4.1-4, and is based on the so-called minimal-frequency-impedance assumption, as explained in continuation.

Instead of applying elaborated analysis techniques for disentangling the impedance data and relating them to the output of the SoH evolution, we here proceed with a simple approach. This simplification is particularly justified due to the very large amount of the EIS data and, additionally, due to the fact that some spectra exhibit peculiar trends. Thus, the so-called minimal-frequency-impedance assumption is presented in Figure 4.1-4 where 3 typical EIS spectra from a set of Inter-lab comparison LCTs is shown (specifically, NIC-0001 in Figure 4.1-3). We assume that the impedance response obtained at the lowest measured frequency (f_{min}) includes - from the point of view of impedance magnitude - all the contributions measured down to that frequency. In other words, when attempting to relate the results of galvanostatic cycling (e.g. discharge capacity or equivalently SoH evolution) with a magnitude of impedance at a single measured frequency, the lower the frequency the more reasonable is to expect that a reasonable correlation could be found. Here it is needed to note that one important practical restriction has to be satisfied: f_{min} must be lower than the transition from the interfacial do diffusional part of a battery cell impedance spectrum. A simple observation of the spectra in Figure 4.1-4 shows that this is definitely true for a pristine cell while in the case of considerably degraded cells f_{min} gradually reduces to get closer to 10 mHz. Thus, it seems that the sets of EIS spectra with f_{min} = 10 mHz could be expected to exhibit some reasonable correlation with SoH - at least in the cases when severe degradation of the interfaces has not yet taken place.





Figure 4.1-5: Representation of the minimal-frequency-impedance assumption shown for the case of three typical EIS spectra from a set of measured EIS data in the Inter-lab comparison LCT (shown is an example of cell NIC-01 from **Error! Reference source not found.** a for SoC = 100 % after 500, 2000 and 3200 cycles).

4.1.6 Repeatability (reproducibility) of SoH-EIS evolution

The methodology of simple analysis of EIS evolution based on the *minimal-frequency-impedance assumption* was applied to the results of Inter-lab comparison LCTs (see table 4.1-1) for the case of sets obtained at SoC = 100%. Figure 4.1-5 shows the obtained results of the experimental correlation SoH-EIS where on *x*-axis the values of impedance magnitude (|*Z*|) for EIS measurements at $f_{min} = 10$ mHz are plotted. At first glance, the SoH-EIS dependence shown in figure 4.1-5 is very much resembling the SoH dependence upon cycle number (figure 4.1-1) so that the resemblance of the two relations is also expected. Even more, the general observation of the similarity of the relations gives a strong direct support to the main aim of this project – it clearly proves that impedance can be used as a tool to directly track SoH of a Li-ion battery cell during its life time.

A more detailed comparison of the relations in figure 4.1-1 and figure 4.1-5 reveals that during the initial stage of cycling (with probable degradation of Si in the anode being the main mechanism) is also directly reflected in the SoH-|Z| relation. It seems that the probable initial degradation of Si in the anode (resulting in the rather rapid loss of capacity in the initial \Box 200 cycles) does not produce more rapid increase of impedance (|Z|) at 10 mHz for SoC = 100%. In other words, |Z| at 10 mHz for SoC = 100% seems not to be directly sensitive to the degradation of Si particles. This observation is not surprising since both NMC cathode and Graphite anode exhibit a strong dependence of EIS upon SoC.





Figure 4.1-6: Obtained SoH-EIS dependence for the Inter-lab comparison task where SoH is plotted as a function of impedance magnitude (|Z|) for EIS spectra measured at $f_{min} = 10$ mHz and SoC = 100%.

In 4.1-5 it is observed that in the 2nd stage the close-to-linear rate of SoH decrease with cycle number is aligned with a close-to-linear rate of SoH decrease with increase in impedance magnitude, |Z|. Accordingly, we can relate the observed Δ SoH/ Δ Cycle rate with Δ SoH/ Δ |Z| rate. For the compared cells in the SoH range between 0.7 and \Box 0.9 the average Δ SoH/ Δ |Z| decrease is found to be about -0.17% per 1 m Ω . By comparing the two rates (Δ SoH/ Δ Cycle and Δ SoH/ Δ |Z|) we find that the cell in the Interlab comparison task showed in the second stage of cycling in average about 6 m Ω increase in |Z| per 100 cycles (for the selected SoC = 100%). The results obtained at NPL clearly deviate from this relation similarly as already described above for the dependency of SoH with cycle number. We attribute the reasons for this deviation to the same fact – namely that the tests at NPL started later than the other tests with about 1 year delay (due to Covid-19 related restrictions) including additional temperature effect aforementioned which probably resulted in somewhat worse initial condition of the two cells.

In the third stage of testing (in most of the cases below SoH = 0.7) the cells exhibited the individual-cell-dependent evolutions. Practically for all of the cells in the third stage the rate of SoH decrease (i.e. the value of $-\Delta SoH/\Delta|Z|$) became larger compared to the second stage. Regarding the second use ("life") of a Li ion battery, it can be speculated that a reliable determination of $-\Delta SoH/\Delta|Z|$ could play an important role in estimation of practical useful remaining life of a battery cell.

4.1.7 Repeatability (reproducibility) of SoH-NFRA evolution

NFR measurements were additionally conducted on cells that were cycled at KIT: KIT-06 and KIT-07. These two cells had been aged under the same conditions (DoD = 0 - 100% and 45 °C) and we see in Figure 4.1-2 that the aging progression in both cells are very similar. The nonlinearities of the cells are analysed based on the second (Y₂) and third (Y₃) harmonic signals. Unlike the EIS measurements, where the spectra at SoC 100% were analysed, the analysis for NFR was carried out on at SoC 80%, 65%, 50%, 35% and 20%. The NFRA was not recorded at SoC 100% in order to avoid a drift in the system due to the high excitation amplitude of 5 A.

In Figure 4.1-7, we see that the increase in the nonlinear signals in the lower frequency range (< 2 Hz) can be well correlated to the increase in the impedance as shown in the semicircle at the lower frequency (1 - 10 Hz) in the impedance spectrum. This shows that the process that underlies in the frequency range is highly nonlinear and we attribute this nonlinear process as the charge transfer process at the electrode/electrolyte interface. As the cells age, the semicircle specifically at this frequency range increases significantly, so do the nonlinear signals that arise from this process. This signifies that not only the charge transfer process becomes



more impeded (Y_3 increases) but also the symmetrical behaviour of the charge transfer process is violated (Y_2 increases).



Figure 4.1-7: Impedance (a) and NFRA (b) of KIT-06 from LCT 1.04. Simultaneous increase in impedance and nonlinearities with increasing cycle numbers.

This similar aging behaviour with increasing Y_2 and Y_3 can be observed at other SoCs (Figure 4.1-8). However, the nonlinear signals seem to be stronger at high SoC and at low frequency and this SoCs dependency is in consistent with the impedance spectra as shown in Fig. 4-1.4. With this in mind, we have selected 0.1 Hz at SoC 80% for the subsequent analysis.





Figure 4.1-8: NFR spectra of KIT-06 at different SoCs that was measured at 5 A, 23°C and between 10-1 – 103 Hz.

Looking at Figure 4.1-9, we can see that the constant increase in nonlinear signals Y_2 and Y_3 correlates well to a SoH decrease. With this NFRA method, we are also able to distinguish the three different stages of aging by analysing the quotient of the nonlinear signals Y_3/Y_2 . The results obtained are very much comparable to the EIS technique shown in Figure 4.1-6. During the first stage of aging, we have a decrease in the Y_3/Y_2 , which means that the increase in Y_2 is greater than Y_3 in this stage. One reason for the great increase in Y_2 could be the increased overpotential in diffusion process, which resulted in greater asymmetry of this process. In the second stage, where we have a linear SoH decrease, the increase in Y_3 surpassed Y_2 . This indicates that the kinetic of the charge transfer process decreases, possibly due to the loss of active material or inhibition of the active surface area on the electrode. In stage three, again we have a decrease in the Y_3/Y_2 . This is possibly due to the transition from symmetrical to asymmetrical charge transfer process. On the whole, we can say that NFR results on both cells are very similar, and the analysis based on the Y_2 and Y_3 signals can deliver good reproducibility.





Figure 4.1-9: Three stages of aging can be distinguished by analysing the quotient of Y3 to Y2 signal (SoC 80%, 0.1 Hz). The value of Y3/Y2 (in b) can be correlated to the SOH progression (in a).

4.1.8 Conclusion

The Inter-lab comparison tasks (together with that described and 4.2.7.3) was planned and performed in order to realize the *Objective 1* of this project: provide and verify metrologically sound life cycle test and impedance measurement procedures. For this purpose, the joint designing of experimental LCT procedures that were cleverly combined with impedance determination and the following measurement effort of 6 involved partners (PTB, JRC, NPL, KIT, NIC, Aalto) produced impressively large database of impedance and NFR data obtained during the conducted long-term cycling testing. Just from the point of view of database the Inter-lab comparison LCT task on reference high-energy 811 NMC-Graphite battery cell produced more than 2100 EIS and about 300 NFR spectra.

In order to check repeatability of the LCTs at different institutions (with different measurement equipment) we introduced a simple methodology based on the so-called *minimal-frequency-impedance assumption*. The latter allows for the large experimental data sets of SoH and corresponding EIS evolutions to be simply analysed by finding direct SoH-EIS correlation. We found that SoH-IZI dependencies of reference cell during long-term cycling for minimal measured frequency $f_{min} = 10$ mHz of the impedance response often exhibit a close-to linear relationships (in large cycle range). This is a very important observation since it directly supports the validity of the correlation analysis methodology based on the *minimal-frequency-impedance assumption*. Moreover, it directly supports (what was one of the main starting assumptions of this project) that properly conducted impedance measurements do provide direct information about the internal state of a lithium-ion battery. It has to be empathized that SoC of a Li ion battery is the most important parameter that has to be clearly defined and controlled in order to be able to obtain reliable and repeatable EIS and NFR data.

The SoH-EIS and SoH-NFRA correlations could potentially provide additional insights into the degradation mechanisms taking place in this type of battery cells. We observed for the case of the reference cells that both the SoH vs. cycle number as well as the corresponding SoH- evolution exhibit 3 distinct stages. In the first stage of cycling a rather fast decrease of SoH was observed that could probably be related to the rapid initial degradation of Silicon particles in the anode, which might cause larger Y₂ contribution than Y₃ in NFRA due to increased diffusional overpotential or asymmetrical behaviour of charge transfer process. In the second stage of cycling we observed that the close-to-linear rate of SoH decrease with cycle number is aligned with a close-to-linear rate of SoH decrease with cycle number is aligned with a close-to-linear rate of SoH decrease with cycle number is aligned with a close-to-linear rate of SoH decrease with Δ SoH/ Δ [Z] rate. We found that for the reference cells in the SoH range between 0.7 and ~0.9 that in the average there was about 6 m Ω increase in [Z] per 100 cycles (for the selected SoC = 100%, cycling at 45 °C). The NFRA in this aging stage shows an increased Y₃ over Y₂, which suggests the typical aging behaviour due to impediment in charge transfer process. In the third stage of cycling (roughly below SoH = 0.7) the cells exhibited more diverse behaviour where both SoH vs. cycle number and SoH-[Z] relations showed larger Cell-to-Cell variations. In NFRA, it is again shown that the contribution of Y₂ overtakes Y₃, indicating that the charge transfer asymmetry again dominates in this aging stage.



It was demonstrated that it is possible in first and second stage of cycling to achieve good reproducibility and comparability of the results of internal state (SoH) evolution of Li ion batteries by employing EIS and NFRA technique – if well-defined testing protocols on metrological basis are utilized. It appears that further evolution of SoH in third stage of cycling is dominated by individual Cell-to-Cell variations. Further research is needed in order to provide additional answers whether full power of EIS and NFR-based approach could be realized in practice by e.g. physical-based analysis of the EIS and NFR data measured in more broad frequency range(s) with the lowest frequency of ≤ 1 mHz.

4.2 Development and characterisation of impedance-based procedures to measure the residual capacity and detect accelerated aging

4.2.1 Background

KIT, PTB and NPL, advised by all consortium partners, led development of impedance-based state-of-health (SOH) estimation models to characterise the residual capacity of Li-ion cells. All models were based on a common data set of correlated EIS and capacity measurement on LCTs conducted under reproducibility conditions on 18650 format cells from a single supplier; KIT additionally utilised correlated NFRA and capacity measurements. The purpose of the models is to demonstrate that data gathered through controlled cycling tests can be used empirically to evaluate residual capacity from a much more rapid experiment. Uncertainty of all models was quantified and used for model comparison. Models were extended as far as data allowed to assess accelerated aging risk.

4.2.2 General method to identify aging parameters

KIT, PTB and NPL, advised by all consortium partners, proposed a general method to identify aging parameters. As the impedance and NFR spectra comprise a set of discrete data points that are highly correlated to each other, reliable model training may require excessive quantities of input data. To resolve this challenge, different data reduction methods were applied to the impedance and NFR data. The simplest approach is to limit the analysed data to specific frequencies. An alternative is to use EC or DRT analysis to represent the raw impedance data as a smaller set of uncorrelated coefficients that are suitable as inputs to an empirical model.

Following data reduction, suitable aging parameters that correlate with the SOH fade are identified from each of the impedance- and NFRA-based methods. The strength of the correlation between the aging parameters and the SOH fade was assessed via Spearman rank correlation. Spearman rank correlation evaluates the monotonic relation (linear or nonlinear) between the aging parameter and SOH fade. The Spearman rank coefficient ρ_s can be computed via Equation 4.2-1, where *d* is the difference between the ranks of the aging parameter and SOH fade and *m* is the number of experiments.

$$\rho_{\rm s} = 1 - \frac{6\sum_{i=1}^{m} d_i^2}{m(m^2 - 1)} \tag{4.2-1}$$

Once aging parameters were selected with the support of the correlation coefficient information, an empirical model was developed using the training data set. Models were trained using stepwise linear regression to coefficients of a quadratic function of SOH on aging parameters x_i , combined with binary crosswise terms as the product of pairs of aging parameters x_i and x_j (Equation 4.2-2).

$$SOH = a_0 + \sum_{i=1}^m a_i x_i + \sum_{i=1}^m \sum_{j=1, j \neq i}^m b_{ij} x_i x_j + \sum_{i=1}^m c_i x_i^2$$
(4.2-2)

Once a model is trained, there exists an uncertainty for the predicted SOH when new test data are input to the model. The uncertainty for SOH prediction was assessed using cross-validation and uncertainty propagation. Cross-validation is used to empirically assess model fit quality when only one training data set is available – the data are repeatedly divided into one portion of training data used to establish fit coefficients, and independent test data which are used to quantify the accuracy of the fit. Here, a four-fold cross-validation



procedure to each of the models was applied, by partitioning at random the data set of experiments (in the form of aging parameters computed for each experiment) into four subsets (approximately 25 % of input in each). Four regression models were then trained for each method; each model successively uses one of the four subsets as test data for validation, while the model is trained on the combination of the three remaining subsets. Root mean square error (RMSE) is computed for the model SOH predictions on the test data, by comparison to the corresponding measured SOH values. The mean of the RMSE for all four trained models gives an estimate of the combined uncertainties for SOH estimation.

Uncertainty propagation is used to estimate the likely proportion of the empirically observed RMSE attributable to experimental uncertainty. Specifically, identified experimental input uncertainties are propagated through the trained model to a resulting (partial) SOH prediction uncertainty. This propagated uncertainty does not include the contributions from cell-to-cell variation in the original data set, or model quality, and so it is not a unique value for SOH uncertainty that is directly usable with model predictions; rather, the goal of this analysis is to assess whether experimental contributions are a negligible or substantial proportion of the overall empirical RMSE.

Three influencing factors from the experiments were identified: temperature (inhomogeneities in the temperature distribution in the measurement chamber and in the cell), SOC (the desired SOC can only be adjusted with a certain degree of accuracy), measurement time (cells never fully equilibrate) and the calibration of the impedance meter. For the EIS-based models, the uncertainties due to SOC adjustment are disregarded, since all aging parameters were selected from data at SOC 100 %, which occurs at a well-defined voltage level (end-of-charge cut-off at 4.2 V). Also, after 30 min rest time, complementary testing was not able to yield quantitative information on impedance variation due to ongoing further cell equilibration, so this effect was discounted for the purpose of uncertainty quantification. In this work, for EIS-based models, the quantitative uncertainty estimation was confined to the impact of variable measurement temperature and instrument calibration. For the NFRA-based models, NFR data at SOC 80% was considered; as such, besides temperature, the partial uncertainty due to SOC adjustment needs to be considered.

For the simpler cases of the direct impedance- and NFRA-based models, which use raw data points as aging parameters, the estimation of each uncertainty contributions was calculated on the basis of the 'Guide to the expression of uncertainty in measurement'. A partial uncertainty for the aging parameter Z' (at a defined frequency and SOC) due to the input uncertainty, e.g., temperature (*T*) is shown as an example in Equation 4.2-3:

$$u(Z')_T = \frac{\Delta Z'}{\Delta T} \cdot u(T) \tag{4.2-3}$$

where $\Delta Z'/\Delta T$ is the experimentally determined sensitivity coefficient of Z' with respect to temperature, and u(T) is the input uncertainty for temperature. The uncertainties of Z'' for EIS, and Y₂ and Y₃ for NFRA, are calculated analogously by replacing the sensitivity coefficients in Equation 4.2-3. The partial uncertainty due to SOC adjustment was quantified analog to the equation above. The partial uncertainty for the aging parameter is then propagated to the estimated SOH via the law of propagation of standard uncertainties:

$$u(\text{SOH}) = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u(x_i)^2}$$

(4.2-4)

where f is the SOH estimation model (given by Equation 4.2--4) and the xi are the aging parameters (raw impedance or NFR values) from the SOH estimation model.

For the models using processed data (EC-based and DRT-based), the aging parameters in equation above are no longer simply discrete impedance values whose uncertainties are given by Equation 4.2-3; hence, a more complex Monte Carlo approach is required. In this approach, a large number (m) of values for the input temperature are determined at random, within the estimated probability distribution for the temperature. From these, m impedance spectra were calculated using the appropriate sensitivity coefficients, using Equation 4.2-3. Model-specific aging parameters were then calculated for each spectrum, resulting in m sets of aging parameter values. Each instance from this set of values is then used in Equation 4.2-2 to yield a set of m SOH values, from which a standard uncertainty for predicted SOH due to the varied input quantities can be extracted as the standard deviation.



4.2.3 Impedance-based methods for residual capacity prediction

4.2.3.1 Direct impedance-based method

KIT developed a SOH prediction model based on raw impedance data. To establish a reduced set of frequencies at which raw impedance data show good correlation to SOH, the impedance data at all measured SOCs and frequency points were analysed against the SOH fade via Spearman rank correlation. Figure 4.2-1 (a) and (b) show the correlation coefficients: light colours indicate that the absolute magnitude of the correlation coefficient is close to 1, which means that impedance values at this region are strongly correlated to the SOH fade.



Figure 4.2-1: Absolute value of Spearman correlation coefficients for the spectral parameters of (a) Z' and (b) Z" to SOH as function of frequency and SOC.

In general, Z' shows strong correlation across a larger frequency and SOC range. This shows that Z' is strongly correlated to the SOH fade at most frequencies, but the correlation is the strongest for Z' at high SOC and low frequency. Similarly, Z" at high SOC and low frequency also shows strong and linear correlation to the SOH fade. From the correlation analysis, the following four spectral features were identified as the best correlated aging parameters to the SOH fade for the direct impedance-based SOH model:

- Z' at SOC = 100 % and 0.03 Hz,
- Z' at SOC = 100 % and 0.01 Hz,
- Z" at SOC = 100 % and 0.2 Hz, and
- Z" at SOC = 100 % and 0.5 Hz.

All identified aging parameters are at SOC 100 %, due to the high sensitivity towards the degradation behaviour of the cell. This is especially helpful in consideration of practical implementation of the impedance-based SOH estimation, due to the straightforward experimental accessibility of the SOC 100 % state. Instead of taking the absolute value of the selected impedance data points as the model predictors, the model takes as input the difference between the impedance at a certain aged state and the initial value at pristine state. This is to avoid the systematic error that could possibly arise from the measurement setup, as the LCTs were conducted with different devices at different institutions.

Based on the reference data sets, the direct impedance-based approach could achieve RMSE of 0.75 % SOH units from four-fold cross-validation. Furthermore, a propagated input uncertainty due to the temperature fluctuation is less than 0.5 % SOH units. This suggests that a full impedance spectrum is not required, instead only few selected impedance points, i.e., at low frequency and high SOC range, are needed to achieve a promising SOH prediction accuracy.

4.2.3.2 DRT

At PTB an SOH estimation model using impedance parameter derived by the distribution of relaxation times (DRT) method was developed. An error-free DRT calculation requires the subtraction of inductive and diffusive components from the impedance spectra. For this so-called pre-processing, the respective parts of the spectrum were partially fitted by means of equivalent circuit fitting. For the subsequent DRT calculation and evaluation, the software *DRTtools* was extended. A typical DRT plot of an 18650 cell is shown in Figure 4.2.





Figure 4.2-2: DRT plot of an impedance spectrum measured at SOC 100 after 200 cycles. Five time constants can be differentiated in it.

The qualitative information from the DRT analysis is identical to the plot shown in Figure 4.2 for the vast majority of spectra measured at SOC 100: five different time constants can be identified (t1 - t5, numbering is from left to right in the DRT plot). From each of these time constants, the underlying resistance and associated capacitance was calculated, so that a total of 15 impedance parameters were derived from each spectrum. Spearman Rank correlation analysis was used to examine the correlation of the parameters with the SOH. Especially the parameters from the low-frequency part of the spectrum could be identified as suitable predictors for the SOH estimation model. Based on the lowest time constant (t5) and the derived resistance (R5), a regression model was parameterized. In a four-fold cross-validation approach, the predictive ability of the model was validated: with the reference data set, the RMSE was about 1.1 %.

In further investigations, it was found that impedance parameters derived from the high-frequency part of the spectrum by DRT analysis are also suitable for SOH estimation. Despite the disadvantage of less accurate estimates (RMSE ~ 3 %), this approach has promising advantages: due to the higher frequencies at which these parameters are measured measurement times are significantly lower. Moreover, these parameters are largely independent of the SOC of the battery. The approach is therefore suitable for a much faster estimation of the SOH.

4.2.3.3 Equivalent circuit (EC)-based model

NPL, supported by Aalto and NIC, developed an equivalent circuit (EC, Figure 4.2-3 (a)) capable of accurately representing the impedance response observed for cells, across the studied SOH and SOC range. NPL used coefficients from the EC fit were used to prepare an EC-based SOH model.

An example fit is shown in figure 4.2-3(c). The equivalent circuit achieves data reduction of the EIS data by mathematical representation in terms of angular frequency (ω) and 12 equivalent circuit coefficients, as expressed mathematically in Equation 4.2-5. The choice of equivalent circuit followed the state-of-the-art established in the literature² during the course of the project; its suitability was confirmed empirically as > 95% of spectra were successfully fit with a normalised residual < 5 × 10⁻³. Comprehensive details on the fitting algorithm will be given in a subsequent paper (submitted).

$$Z = R_{\rm s} + \frac{1}{\frac{1}{i\omega L_{\rm s}} + \frac{1}{R_{\rm p} + i\omega L_{\rm p}}} + \left(\sum_{k=1}^{2} \frac{R_{{\rm ct},k}}{1 + (i\omega R_{{\rm ct},k} C_{{\rm dl},k})^{\alpha} {\rm dl},k}\right) + \frac{(i\omega)^{\alpha} {\rm diff}}{Q_{{\rm diff}}}$$

$$4.2-5$$

² <u>https://iopscience.iop.org/article/10.1149/2.1051908jes</u>





Figure 4.2-3: (a) Equivalent circuit used to represent EIS data. CPE: constant phase element. (b) Example equivalent circuit fit superimposed on experimental data (cell at SOC 100 %, after 250 cycles corresponding to SOH ≈ 90 %). (c) Cumulative distribution function of fits sorted by normalised residual of fit quality, indicating that only a small fraction (< 5 %) of fits exhibit relatively low-quality normalised residuals.

The degree of correlation of each EC coefficient to SOH was analysed using Spearman rank correlation analysis, which revealed the strongest correlations for the low frequency semiarc coefficients $R_{ct,2}$ and $C_{dl,2}$, and the series resistance R_s . Correlations for other EC coefficients, representing inductive contributions, the high-frequency semiarc, and the diffusive tail; excepting the diffusive tail, the more weakly correlated coefficients include those for which strong hardware-specific dependence is expected, such that they would not be suitable as inputs to a generic SOH model. Series resistance may also have strong hardware-specific dependence.

On this basis, 5 coefficients ($R_{ct,2}$, $C_{dl,2}$, $\alpha_{dl,2}$, Q_{diff} , α_{diff}) were selected as aging parameters and used as training data for an SOH model; of these, only $R_{ct,2}$ and $C_{dl,2}$ were retained after stepwise regression. On the reference data set, the EC-based model had a RMSE of 1.21 % SOH units from four-fold cross-validation. A propagated input uncertainty for the EC-based model, using Monte Carlo uncertainty analysis, suggested that the partial SOH standard uncertainty due to experimental temperature fluctuation in the training data is generally less than 0.1% SOH units. From this result, it was concluded that suggesting that it is a relatively small contribution to the model error, which is thus dominated by intrinsic cell-to-cell variation in the data set.

4.2.3.4 NFRA

KIT developed a SOH prediction model based on the raw NFR data. Similar to the direct impedance-based model, sensitivities with respect to SOH of the raw data (in this case, higher harmonic voltage magnitudes Y_2 and Y_3) were evaluated for data across all characterised SOCs and frequencies via Spearman rank correlation as described previously to obtain aging parameters for the NFRA-based model. The correlation coefficients are shown in Figure 4.2-4 (a) and (b).





Figure 4.2-4: Absolute value of Spearman correlation coefficients for the spectral parameters of (a) Y2 and (b) Y3 to SOH as function of frequency and SOC.

It can be concluded that the NFR signals at low frequency and high SOC show the strongest correlation to the SOH fade, whereas also in the range around 80 Hz a good correlation can be seen; the latter may be especially interesting for fast measurement. The following most strongly correlated aging parameters were identified:

- Y₂ at SOC 80 % and 8.13 Hz,
- Y₂ at SOC 80 % and 0.25 Hz,
- Y_3 at SOC 80 % and 5.89 Hz, and
- Y₃ at SOC 80 % and 0.25 Hz.

The four selected aging parameters were then differenced from their fresh-cell values and used as predictors for model training/validation. The mean RMSE for SOH estimation with the NFRA-based model from four-fold cross-validation is approximately 1.11 % SOH units, which is in the same range of prediction accuracy as the three impedance-based approaches described above. Using this method would thus be feasible to estimate the SOH from a cell. Adjustment of 80% SOC would mean that the battery needs not be fully charged for the measurement; yet it would imply additional uncertainty would be incurred on the predicted SOH due to inaccuracies SOC adjustment, which is less than 0.6 % SOH units. Similarly, the uncertainty arises from the temperature fluctuation was quantified for NFRA-based method. Here, it is noted that the temperature uncertainty for the NFRA-based SOH prediction is in the same range as for the EIS-based prediction. However, at SOH < 82 %, the uncertainty impact of temperature is stronger for the NFRA-based approach – nonetheless it is still below 2 % SOH units. The higher partial uncertainty with respect to temperature fluctuation of the NFRA-based model below SOH 82 % may arise because due to the smaller quantity of low SOH data available in training the SOH prediction model. At lower SOH range, it should be noted that the uncertainties due to the temperature are larger and ought no longer to be neglected. Therefore, when applying NFR measurements for SOH estimation at SOH < 80 %, temperature-control is beneficial for high accuracy.

4.2.3.5 Assessment of the methods

All models have a standard prediction uncertainty < 1.5 % SOH units, as assessed by cross-validation on the reference data set within the range 70 % < SOH < 95 %. This performance falls within the project objective of 3 %, across the SOH range of interest for second-life applications. Achieving this performance is contingent on the availability of a consistent experiment data set for training, gather under reproducibility conditions as described in section 4.1. In absolute terms, for the specific data set used, the direct impedance-based SOH model is most accurate; its performance is relatively similar, however, to the other models, suggesting that all methods successfully represent the underlying correlation of SOH to frequency response (EIS or NFRA).

While all models give comparable SOH prediction performance for the given data set, the choice between different experimental methods (EIS vs NFRA) and different data analysis approaches (raw data use vs EC fitting vs DRT fitting) may prove advantageous for other combinations of cycling condition, cell format and/or cell chemistry. Methods based on processed data (EC- and DRT-based models) require more numerical effort and require a full spectrum to be recorded rather than specific frequencies, implying longer measurement time;



however, these methods also exhibit lower propagated uncertainty from experimental condition than for the methods based on raw data, and did not require differencing with respect to fresh cell values.

For all models assessed at fixed SOC (SOC 100 % for EIS, SOC 80 % for NFRA), aging parameter selection showed the strongest SOH correlation for spectral features in the low frequency part of the spectrum (f < 100 Hz). The natural attribution is that the aging parameters quantify the progressive slowing of the charge transfer (Li insertion or de-insertion) process in one of the insertion electrodes of the cell, with strong correlation during aging (albeit not necessarily causative connection) to the cell's SOH fade. The supplementary DRT-based SOH model developed at PTB demonstrated that high-frequency features can show correlation to SOH independently of SOC – the developed model had predictive performance below the project objective (RMSE of 3.37 % SOH units) but also would offer extremely simple practical implementation due to its SOC independence, eliminating the need for cell charging before measurement for SOH determination. Relative advantages and disadvantages can be balanced in decisions around future exploitation of the project.

The project has identified the strong dependence of predictive performance on a sufficient quantity of training data, gathered under relevant cycling conditions. Rapid characterisation of residual capacity for cell second life depends on data provision by primary cell producers, prospectively working in concert with measurement institutes and/or with measurement service suppliers following a defined standard methodology for model development. Thus, it is recommended that metrology institutions charged with implementing the CIPM-MRA establish respective metrological services for battery manufacturers and companies implementing such batteries in their products, based on the methodology developed in this project.

KIT, PTB, NPL, NIC, JRC and Aalto co-authored and submitted the manuscript "Comparison of methodologies to estimate state-of-health of commercial Li-ion cells from electrochemical frequency response data" to *Journal of Power Sources*, in order to disseminate the overall methodology established within the project for residual capacity prediction for second life.

4.2.4 LCTs and EIS of 18650 cells under various cycling conditions

For the case of cylindrical LG18650 NMC-Graphite battery cells two additional types of systematic testing were conducted. In the first, the effect of the temperature during galvanostatic cycling at 1.33C (using standard procedure with CC-CV charge and CC discharge) was checked by performing tests at 35 °C, 23 °C, and 5 °C. In the second type of testing galvanostatic cycling at 1.33C was performed in several defined DoD ranges and at the selected temperature of 45 °C. During the cycling periodical measurements of EIS were conducted at selected predetermined SoCs (in accordance with the testing protocol). For more detailed description of the testing procedure and to compare obtained impedance spectra and observed specific impedance features between various testing conditions please see D4 (and appendixes in D4).

4.2.4.1 Effect of Temperature on full DoD range cycling

The effect of temperature on battery SOH and the corresponding impedance evolution during long-term full DoD range cycling was checked by performing measurements at 3 institutions: JRC (at 35 °C, LCT 1.10), NIC (at 23 °C, LCT 1.13), and Aalto (at 10 °C, LCT 1.17). In figure 4.2-5 the evolution of SoH of the cells with cycle number is shown. It appears that the two trends for the cells cycled at 35 °C and 23 °C cannot be distinguished. While on the other hand the cells cycled at Aalto at 5 °C show a strong deviation from that trend, with a very rapid decrease of SoH. Interestingly, it can be observed that for the cells cycled at 35 °C and 23 °C the rate of SoH decrease is reduced after passing the SoH = 60 % (corresponding to about 2800 cycles in average). This is quite important observation for the activities related with the second use ("life") of lithium-ion batteries.





Figure 4.2-5: Evolution of SoH of the 9 reference cells with cycle number where the effect of temperature during cycling was monitored.

In order to get a full insight into the actual effect of temperature during cycling, the data obtained in the tests conducted at 35 °C, 23 °C and 5 °C (figure 4.2-5) need to be compared with the data obtained at the elevated temperature of 45 °C (shown in figure 4.2-6). In fact, the latter are the very tests that were conducted during the Inter-lab comparison task. In figure 4.2-6 we show all the 24 sets of SoH evolutions needed to perform an analysis of SoH-EIS correlations obtained during cycling at different temperatures. In 4.2-7 it can be seen that some of the cells cycled at 35 °C and 23 °C tend to show somewhat extended cycle life (when reaching SoH = 80 %) compared to the cells cycled at 45 °C. On the other hand, the two cells cycled at Aalto at 5 °C clearly show a strong deviation of the SoH trend with observed extremely fast degradation of capacity.



Figure 4.2-6: All the sets of data needed to perform analysis of the effect of temperature during cycling on the evolution of the SoH-EIS correlation.

Overall, an analysis of the SoH-Cycle trends shown in figure 4.2-6 and figure 4.2-7 suggests a rather difficult decoupling of the effects of temperature during cycling on one hand and cell-to-cell variations between the individual cells on the other (exception being cells cycled at 5 °C). In other words, additional parameters are needed to give us enough information to be able to differentiate between the various degradation modes going



on in the cells. For this purpose, the methodology of analysis of impedance evolution based on the minimal-frequency-impedance assumption was applied.



Figure 4.2-7: All the sets of data needed to perform an analysis of the effect of temperature during cycling on the evolution of the SoH-EIS correlation (magnified part of figure 4.2-6 at higher SoH).

The corresponding sets of EIS spectra were measured periodically during the LCTs. It is interesting to note that, for example, in the two tests conducted at JRC (JRC-10 and JRC-11) there were about 100 impedance spectra measured for each cell during the LCT. An example of evolution of the measured EIS spectra during cycling at 35 °C is shown in figure 4.2-8 (cell JRC-11). In the following we present results of SoH-EIS correlation analysis for all the 24 cells included in the analysis of the effect of temperature on the cycling evolution.



Figure 4.2-8: Example of evolution of EIS during full DoD range cycling of reference cylindrical LG18650 cell at 35 °C conducted at JRC. The EIS data were measured at 23 °C. The cell used was JRC-11.



In figure 4.2-9 we show the results of the SoH-EIS correlation analysis for all of the 24 tested cells that were used for monitoring of the effect of temperature on the cycling evolution. It can be clearly seen figure 4.2-9 that the groups of cells cycled at different temperatures are definitely separated in the rate of SoH decrease with increasing IZI(10 mHz). This is a very important observation since it directly supports the validity of the correlation analysis methodology based on the minimal-frequency-impedance assumption. Moreover, it provides additional insights into the degradation mechanisms going on in this type of battery cells. Namely, in figure 4.2-9 it can be clearly seen that there is a definite trend of SoH with the cycling temperature: the lower the temperature the larger is the rate of the capacity decrease. Moreover, in some ranges the SoH-IZI dependencies are rather close to linear. This fact gives a direct affirmation that impedance-based techniques could indeed be used for monitoring and possibly even predicting of the future SoH evolution in the second use ("life") of lithium-ion batteries.

From the variation of the evolution of SoH-IZI relations with temperature shown in figure 4.2-9 it can be reasoned that lowering of temperature is extremely detrimental for this particular cell - possibly due to strongly enhanced metal Lithium plating on the anode particles during (relatively) large charging current (4 A \approx 1.33 C rate). The latter reasoning further suggests that, for this particular cell, at temperatures below 35 °C the cycle life is probably strongly affected by the dominant mechanism of solid electrolyte interface (SEI) degradation on graphite anode (and other related effects) as a consequence of lithium metal plating.



Figure 4.2-9: Sets of SoH-IZI correlations for the groups of reference cells cycled at different temperatures. The impedance magnitudes IZI were collected at f_{min} = 10 mHz for the spectra measured at SoC = 100 %.

Furthermore, it can be deduced that the degradation damage developed during cycling at 35 °C, 25 °C and 5 °C is less pronouncedly observed in EIS spectra in frequency range until 10 mHz. And oppositely, the degradation processes at the elevated temperature of 45 °C lead to a relatively larger impedance (IZI) increase at 10 mHz compared to cycling at lower temperatures. The reason for this observation could probably be found by further studying the trends and analyzing the EIS spectra in such a way that it would be possible to attribute the actual physical phenomena to the impedance features.

Effect of used DoD range during cycling

The effect of used DoD range on battery SOH and the corresponding impedance evolution during long-term cycling at the selected temperature of 45 °C was checked by performing measurements at 4 institutions: JRC (LCT 1.11 DoD = 25-75), NIC (LCT 1.12 DoD = 50-100), NPL (LCT 1.14 DoD = 0-50), KIT (LCT 1.15 DoD = 30-100 and DoD = 10-80, LCT 1.16 DoD = 60-90 and DoD = 25-55). We define here full equivalent cycle (FEC) by simply normalizing the cycle number (N) by a factor F that represents the fraction of the full DoD range used during cycling:



(4.2-6)

$$FEC = N \times F = N \times \frac{\Delta DoD}{100}$$

In figure 4.2-10 we show the evolution of SoH of the cells with FEC. It appears that the cells tested at NIC have better stability compared to other cells. This is partially due to the real effect of the testing conditions where by applying DoD in the range of 50-100 one avoids the degradation processes at high-voltages. In addition to that, the periodic evaluation (PE) done at NIC was conducted at a lower current (0.5 A = C/6 C-rate) compared to the other partners (1.25 A). Consequently, the SoH values obtained at NIC are more stable (dropping slower) compared to the tests done at the other partners.



Figure 4.2-10: Evolution of SoH with FEC of the 13 reference cells where the effect of DoD range during cycling was monitored.

In order to perform a full comparison of the effect of DoD range on SoH and the related impedance evolution, also the results obtained with the cells from Inter-lab comparison task should be included. In figure 4.2-11 SoH evolution of 4 selected (representative) cells from Inter-lab comparison are added (black lines). It can be seen in figure 4.2-11 that the cycling stability of cells from the Inter-lab comparison (DOD = 0-100 %) is the worst of all the tested DoD ranges (only exception being cell KIT-10). And this trend is observed already from the beginning in the 1st stage of cycling. Interestingly, the KIT cells (KIT-11 and KIT-13) that were cycled in the central part of DoD range with small DoD span (\Box DoD = 30 %) seem to be showing the best stability with FEC. On the other hand, the cells tested at JRC (JRC-13, JRC-17, JRC-19) were cycled in the central DoD range as well – but the DoD span was larger (\Box DoD = 50 %). This observation is suggesting that small DoD span might be favourable for long-term cycling stability. Of course, it is questionable how practical would this kind of cycling be for real-use applications.





Figure 4.2-11: Evolution of SoH with FEC of the reference cells where the effect of DoD range during cycling was monitored (black lines correspond to 4 cells from Inter-lab comparison task).

The most stable SoH evolution in the 1st stage (figure 4.2-11) was observed for the cells cycled at NPL (DoD = 0-50 %) but are latter on at about 1000 FECs surpassed by the mentioned two KIT cells with narrow DoD span of cycling (KIT-11 and KIT-13). It is important to note that the cells from Inter-lab comparison are the only cells that were cycled in full DoD range, while all the other cells were cycled in partial ranges. It appears that for obtaining more insight about the long-term cycling stability larger number of cells should be tested at the same testing condition. The latter would help to identify the "outliers" and enable selecting the cells that show repeatable behaviour – thus effectively reducing the effect of cell-to-cell variations (at the same testing condition).

During the cycling of the cells in different DoD ranges periodic measurements of EIS responses were conducted. In figure 4.2-12 we show sets of obtained SoH-IZI correlations for 10 mHz at SoC = 50 %. Overall, the trends seem to be rather comparable. The evolutions for the cells tested at NIC seem to somehow deviate, the reason for the latter fact is not clear. It interesting to observe that the cell KIT-10 that was found to deviate from other cells with partial DoD cycling ranges also deviates in the corresponding SoH-IZI correlations. Namely, it appears to follow trend that is non-distinguishable from the full DoD range cycling results.



Figure 4.2-12: Sets of SoH-IZI correlations for the groups of reference cells cycled within different DoD ranges at 45 °C. The impedance magnitudes IZI were collected at f_{min} = 10 mHz for the spectra measured at SoC = 50 %.



From the data shown in figure 4.2-12 it is not possible to unambiguously extract definite conclusions regarding the most preferred DoD range to achieve stable long term cycling. Moreover, it is not straightforward to obtain clear reasoning about the observed trends in the SoH-IZI correlations. Partially this is due to the fact that effect of DoD cycling range on stability is rather complex and furthermore this fact is in the experiments additionally blurred by the individual cell-to-cell variations. As mentioned above – larger number of cells should be tested at the same testing condition. The latter would help to identify the "outliers" and enable selecting the group of cells that show repeatable behaviour.

Additionally, NFR measurements were also carried out on cells that were aged at different conditions as mentioned above: KIT-10 (DoD: 30-100), KIT-11 (DoD: 60-90), KIT-12 (DoD: 10-80), KIT-13 (DoD: 25-55). The effect of DoD cycling range and the SoH-|Z| correlations have been discussed previously. In this section, we shall look at the effect of DoD and cycling range on the NFRA results, along with the EIS.

The impact of DoD can be observed in figure 4.2-13. Although all four cells had been aged to SoH 80%, however their EIS and NFR spectra showed different development. In comparison to KIT-10 and KIT-12, which have a cycle depth of 70 %, KIT-06 and KIT-07, which were cycled with a DoD of 100 % showed an overall higher Y2 and Y3-signals as well as a greater semicircle in the EIS. Cycling at a larger DoD could result in greater volume changes in the silicon-graphitic anode due to the greater volume fraction of the de-/intercalated lithium ions. The continuous expansion and shrinkage of the anode induce mechanical stress within the active material particles, causing cracks on the electrode particle surface. The freshly generated surface area from the cracks that expose to the electrolyte will react with the electrolyte and form new SEI layer on the electrode surface. On the cathodic side, the active material in cathode will experience greater extent of the phase transformations at larger DoD cycling (especially at higher value of upper cut-off voltage), which could cause transition metal dissolution into the electrolyte.



Figure 4.2-13: NFR spectrum (left) and EIS (right) of cells measured at SoH 80 %, SoC 50 % and 23°C. Impact of difference in DoD can be observed in the spectra. Cell KIT-06 and KIT-07 have a DoD of 100 %, whereas DoD of KIT-10 and KIT-12 is 70 %.

Despite being cycled with the same cycle depth, cell KIT-10 experienced accelerated degradation after 1000 equivalent full cycles. Aging in cell KIT-12 remained somewhat insignificant. As cell KIT-10 was generally cycled at higher voltage niveau than cell KIT-12, this promotes a greater extent of transition metal dissolution from the cathode side and leads to greater loss of active materials or capacity fade when compared to cell KIT-12. The dissoluted transition metal will be then transported from the cathode to the anode side, which favours and accelerates the SEI growth. This results in a greater inhibition of the active surface area and thus, impedes the charge transfer process at the anode. Hence, greater nonlinear signals and impedance can be observed for cell KIT-10 as shown in figure 4.2-14.





Figure 4.2-14: NFR spectra (in a, c) and EIS (in b, d) of cell KIT-10 (top) and KIT-12 (bottom) after different number of equivalent full cycles and the respective SoHs. The measurements were carried out at SoC 50% and 23°C.

In figure 4.2-14 (b) and (d), we can see from impedance spectra that the ohmic resistance in cell KIT-10 increased significantly in comparison to KIT-12. This is because cycling at higher voltage niveau is always accompanied not only by the dissolution of the transition metal but also the electrolyte oxidization at the cathode side.

Likewise, the impact of cycling range can be observed in the EIS and NFR spectra (figure 4.2-15) of cell KIT-11 and KIT-13. Despite having the same cycle depth, the increased in nonlinearities signals, especially Y2 in greater in cell KIT-13, which corresponds to the impedance increase of the charge-transfer reaction. Here, the results show that cell KIT-11 that was cycled at higher voltage niveau aged less significant than cell KIT-13, which is the reverse case for the previous scenario. This actually can be explained by the different intercalation stages at the graphitic anode. It is expected that there is no change in intercalation stage between DoD 30 % - 90 % as the anodic potential level is relative flat within this region while cycling between DoD 25 % - 55 % could experience at least two intercalation stages, which could result in greater mechanical stress (eventually cracks) within the particles, forming new SEI layer and creating greater impedance for the charge transfer process.





Figure 4.2-15: NFR spectra (in a, c) and EIS (in b, d) of cell KIT-11 (top) and KIT-13 (bottom) after different number of equivalent full cycles and the respective SoHs. The measurements were carried out at SoC 50% and 23°C.

4.2.4.2 Application of the methods to the results

KIT applied the direct impedance-based method, PTB applied DRT analysis and NPL applied EC fitting as described above to EIS under other cycling conditions. Additionally, KIT applied the NFRA-based method to the NFRA data under other cycling condition.

In general, the predictive performance for all impedance-based as well as NFRA-based model trained on the reference LCT conditions worsened with increasing deviation from those conditions (lower temperature, reduced DoD). The RMSE of all SOH prediction models exceeded the project objective of 3 % SOH units. Also, it could be observed that the prediction RMSE for all SOH models for cells that were cycled under lower temperature is larger as compared to the cells that were cycled under reduced DoD.

Table 4.2-1: RMSE of all SOH prediction models under different cycling conditions (lower temperature and reduced DoD) given in SOH units. No NFRA data is available for cycling experiment at lower temperature.

	Lower temperature	Reduced DoD
Direct impedance-based method	4.41 %	3.10 %
DRT	3.98 %	2.56 %
EC	5.10 %	3.10 %
NFRA	-	3.01 %

This study shows that impedance- and NFRA-based SOH estimation models do not incorporate intrinsic information about physical mechanisms. In other words, with respect to operating condition, they interpolate but do not extrapolate. It is possible that a more mature machine learning approach could increase the model robustness; however, the relatively similar performance under validation of all four models, developed using diverse methods, suggests that the limitation is probably intrinsic to the data.



Table 4.2-2: RMSE of the retrained SOH prediction models given in SOH units. The direct impedancebased, DRT- and NFRA-based SOH model were retrained on data set at all DoD and temperatures, the ECbased SOH model was retrained on data set at all DoD and fixed temperature at 45°C.

	Retrain
Direct impedance-based method	1.92 %
DRT	2.24 %
EC	1.77 %
NFRA	2.36 %

Retrained models show improved prediction accuracy overall, i.e., within the project objective 3 % SOH units. Therefore, it is concluded that SOH estimation models trained using only data from the reference LCTs suffer significant accuracy loss when applied to frequency response data from LCTs under different cycling conditions. The general methodology for preparing SOH estimation models from frequency response data should begin with a consideration of target cycling conditions, and that LCTs are carried out under a range of cycling conditions relevant to the target use case. Only through this process will it be possible to validate the application of the model to cells with diverse cycling history.

LCTs and EIS of other cell types

Prismatic NMC-Graphite cells

Prismatic cells with a capacity of 50 A (Delta, P/N P140) were subjected to LCT. Four cells were galvanostatically cycled for over 2000 cycles and capacity and impedance measurements were conducted at intervals of 50 - 250 cycles. The results are summarized in Figure 4.2.16.

In part (a) of the figure, the SOH of the cells is plotted as a function of cycle number. All cells show a linear decrease in residual capacity, which becomes lower after about 1500. In part (b) of the figure, a selection of the impedance spectra measured during the LCT is shown for one of the investigated cells: the impedance increases with increasing cycle number. Consequently, it can be assumed that the impedance spectra contain information related to the ageing of the cells.



Fig. 4.2-16: SOH as function of cycle number for the four cells (a), impedance spectra at different cycle numbers (b), resistance of the lowest time constant as function of the SOH (c) and results of the fourfold cross validation of the SOH prediction model.



To further investigate the relationship between the impedance of the cells and their residual capacity, the spectra were subjected to DRT analysis. Therein, three different time constants could be identified for all spectra measured at SOC = 100%. Like the LCTs on 18650 cells, the lowest time constant and the derived resistance had the most pronounced correlation with the SOH. In part (c) of the figure, the resistance determined from this time constant is plotted as a function of SOH. Analogous to the procedure for the 18650 cells, this resistance and the associated time constant were selected as predictors for a regression model for SOH estimation. The results of the four-fold cross-validation of the model are shown in part (d) of the figure. The estimates show high agreement with the actual values - the mean RMSE of the four iterations of cross-validation is 1.35% (in SOH units).

Thus, the method for SOH estimation based on DRT-generated impedance parameters developed previously for 18650 cells is transferable to delta-type cells.

4.2.4.3 LFP-Graphite cells

Within the LCT task 2.14 performed at NIC cycling testing together with periodic measurements of EIS were conducted on two cylindrical LFP-Graphite battery cells (NIC-15, NIC-16) with nominal capacity of 3 Ah. The cells were cycled in galvanostatic mode with +2.85 A charge followed by voltage hold (current limit C/30) and -4.95 A discharge cycling in the voltage range of 2 V - 3.6 V at 24 °C. Periodic evaluation of SoH was performed by measuring discharge capacity in galvanostatic cycle with applied current of +/- 0.4 A and with voltage hold at the upper cut-off voltage (3.6 V, current limit C/30). Periodic measurement of EIS was performed at 6 selected SoC's (in a similar manner as in all the other LCTs). The evolution of SoH with cycle number is shown in figure 4.2-17 where it is plotted together with the SoH evolution of some selected sets of NMC-Graphite cells at comparable cycling conditions. It is evident from figure 4.2-17 that the LFP-based battery cells exhibit superior cycling (SoH) stability compared to the batteries with 811-NMC cathode. The initial loss of SoH for the LFP-based cells in the first stage of cycling is much smaller compared to the 811-NMC-based. Moreover, in the second stage of cycling the LFP-based cells show very small rate of - Δ SoH/ Δ Cycle decrease of about - 0.15% per 100 cycles – compared to found about -1% per 100 cycles for 811-NMC-based cells. In fact, the LFP-based cells do not enter into the third stage cycling even after 5000 cycles.



Figure 4.2-17: Evolution of SoH with cycle number of the two LFP-Graphite cells (NIC-15, NIC-16) cycled at 24 °C. The evolutions are shown together with evolution of some selected sets of NMC-Graphite cells at comparable cycling conditions.

The superior cycling stability of the LFP-based cells is expectedly reflected in the corresponding SoH-EIS correlations shown in figure 4.2-18 and figure 4.2-19. There is striking difference between the evolution of SoH-|Z| correlations when comparing reference NMC-based cell and the LFP-based cells. For example, the two NMC-based cells tested at JRC at 35 °C (JRC-10 and JRC-11) that were cycled beyond 5000 cycles showed large increase of |Z| compared to the pristine state, final |Z| being larger than 150 m Ω . Somewhat



smaller |Z| could be anticipated at 5000 cycles from the extrapolation of the data for the NMC-based cells cycled at 23 °C (in the range of about 125 m Ω). On the contrary, the LFP-based cells showed negligible impedance growth (during the initial 100 cycles |Z| was even decreasing).



Figure 4.2-18: Comparison of SoH-IZI correlations of LFP-based cells (SoC = 50%) and 811-NMC-based cells (SoC = 100%) cycled at comparable cycling conditions. The impedance magnitudes IZI correspond to $f_{min} = 10 \text{ mHz}.$

Thus, one more time we found that the cycling (SoH) stability is directly reflected in the corresponding impedance evolution. The change of impedance magnitude for NMC-based cells is large due to continuous and severe degradation processes taking place during long-term cycling. On the other hand, LFP-based cells are intrinsically more stable due to very stable structure of LFP active material that additionally exhibits superior chemical stability compared to Ni-rich NMC cathode materials. Moreover, the operating voltage range of LFP cathode is within the electrochemical stability window of electrolytes. Consequently, in non-severe operating conditions the progression of the degradation processes.



Figure 4.2-19-: Enlarged part of comparison of SoH-IZI correlations of LFP-based cells (SoC = 50%) and 811-NMC-based cells (SoC = 100%) at high values of SoH.



in LFP-Graphite cells at room temperature is very slow. This low degradation tendency was observed as very slow increase of |Z| during cycling of the two tested LFP-based batteries.

Post-mortem analysis

Protocols for sample harvesting and analysis

Fresh and cycled 18650 cells were disassembled with the aim to perform post-mortem analyses of electrode materials and to understand the effect of cycling process on anodic and cathodic compounds. The goal was to perform investigation on materials using several analytical techniques and to compare results for a better understanding of the whole system.

The disassembling process was performed by the partner JRC in Petten. Before removal of the metallic case, the cells were discharged at constant current of 0.6 A down to 2.0 V.

In order to remove the metallic case, a groove (depth 0.11-0.12 mm) was performed with a lathe machine.

The final opening, disassembling and sampling processes were executed inside an argon-filled Glove Box (O2 < 0.1 ppm; H2O < 0.1 ppm). A dedicated tool for the opening of 18650 cells was developed by JRC-Petten workshop. Anode and cathode foils were separated carefully and both electrodes were cut in two halves. The most exterior aliquots of the electrode foils were rinsed in DMC in two separate vials for 20 minutes and afterwards subjected to dynamic vacuum for one hour.

The process above reported was performed only for cells JRC-1 and JRC- 4 (as received and cycled @ 45 °C untill reaching 80% SoH). For all other cycled cells, neither rinsing, nor dynamic vacuum steps were executed due to the severe damages and degradation of active materials on electrode foils, in particular for graphite in anodes.

Partners of the project involved in Post-mortem analyses received aliquots of electrode foils of circa 60x50 mm. Each aliquot was stored in a transparent plastic bag and loaded inside a stainless-steel vacuum tube to guarantee protection against moisture and air during transport.

4.2.4.4 Methods

Below the performed techniques by different partners are listed:

- Scanning Electron Microscopy (SEM)
- Energy Dispersive X-ray Spectroscopy (EDX)
- X-Ray Diffraction (XRD)
- X-Ray Photoelectron Spectroscopy (XPS)
- Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)
- Raman Spectroscopy
- Electrochemical cycling

SEM and SEM-EDX

Samples from anode and cathode electrodes were prepared in a glovebox in argon atmosphere. Squares sized roughly 4 mm x 4 mm were cut and mounted on SEM stubs using double-sided adhesive carbon tape. Samples were transferred to SEM stage directly from the glovebox in a home-made vacuum stage to avoid air exposure of the samples.

The surface morphology was observed using scanning electron microscope (SEM) (Zeiss, Germany). A SEM accelerating voltage of 20 kV and a current of 400 pA were used. A secondary electron detector (SE) was employed. The elemental composition and distribution on the surface of the samples were measured using a



scanning electron microscope (SEM) (Zeiss, Germany), equipped with energy dispersive spectrometer (EDX) SDD EDX UltimMax 100 Premium (Oxford UK). SEM accelerating voltage of 7 kV or 20 kV and a current of 400pA were used, with a process time (PT) 5 and live image time 60 s. A backscatter detector (analytical distance 8.5 mm) was used. Calibration was performed using reference standards X-Ray microanalysis No. 1457 (Micro- Analysis Consultant LTD, UK). Data analysis was performed using advanced software Spectrum Processing Equipment with Large Area Mapping Add-on - AZTEC 5.0 (Oxford, UK).

FIB-SEM

Samples for analysis were sent from JRC to NIC in a hermetically sealed container. The container was opened in an argon-filled glovebox and samples were mounted onto SEM aluminum stubs using double-sided adhesive (electrically conductive) carbon tape. Samples were additionally firmly fixed to an aluminium stub using silverconductive cement and sputtered with 50 nm of a carbon conductive layer using a PECS 682 (Gatan, US). Prior to the data acquisition, regions of interest (ROI) with dimensions of $15 \square m^2$ were protected with a 1.5 $\square m$ platinum layer by inducing the Pt-organo-metallic precursor with a FIB (30 kV @2.5 nA). Parallel and diagonal lines were then briefly milled into the protective layer and covered with 100 nm-thick carbon bands by in situ inducing the organic precursor with the FIB (30 kV @0.23 nA). An additional platinum layer (1 Im) was deposited on top of the ROI to embed high-contrast carbon reference markers within the protective layer. The ROI was finalized by milling away a U-shaped trench to enable direct cross- sectional imaging with a SEM and prevent shadowing of the imaging signals. The sample was then sectioned using a slicing procedure with an active drift-correction algorithm and auto-focusing routine to obtain BSE images. With FIB a vertical cut was performed in order to prepare cross section of the NMC agglomerates in the cathode from an aged cell. FIB-SEM analysis of a cathode sample was performed by using Field emission SEM (Carl Zeiss, FE-SEM SUPRA 35 VP, equipped with energy dispersive spectroscopy Inca 400, Oxford Instruments. For SEM and EDX 7 kV and 20 kV voltage was used respectively.

The main purpose of the analysis was to determine chemical composition of cathode and anode active materials, further on to observe morphological features of both the electrodes, and to find potential peculiarities (e.g. addition of silicon in anode, traces of electrolyte additives, impurities), as well as compositional homogeneity of the electrodes in general. Furthermore, we have verified the relevance of sample (electrode) rinsing on the results of SEM and EDX compositional analysis. In order to investigate the morphology of the cathode active material further, another pristine LG18650 cell was opened at NIC Ljubljana in an argon-filled glovebox and after rinsing with Diethyl carbonate a sample was obtained for FIB-SEM analysis. With FIB a vertical cut was performed in order to prepare cross section of the NMC agglomerates in the cathode. This procedure enables us to get direct insight in the state of the agglomerates and potential damage produced during electrode processing. EDX elemental analysis within the FIB-SEM instrument was used to check uniformity of chemical composition along the radius of the sphere-like NMC agglomerates.

XRD

Laboratory XRD patterns were collected using an Empyrean PANalytical diffractometer. Its configuration was set in Bragg-Brentano geometry, using Copper (Cu K α 1,2) and Molybdenum (Mo K α 1,2) X-ray sources in combination with PIXCell And GaliPIX detectors, respectively. The X-ray generator operated at 45 kV and 40 mA, and 60 kV and 40 mA for Cu K α 1,2 and Mo K α 1,2 sources, respectively. Pulse height distribution values of detector were set at 42-70 % for Cu K α 1,2 XRD measurements collected in reflection geometry. The X-ray diffraction campaign was expanded performing 2D-XRD measurements for all samples and only in one case, the diffractometer configuration was changed from reflection to transmission setting in combination with Copper X-ray radiation.

Samples were subjected to wide-angle X-ray diffraction data collection in 20 angular range 5°- 145° and 5°- 150° for Mo K α 1,2 and Cu K α 1,2 X-ray sources, respectively. Instrumental function (IF) was determined using LaB6 standard (SRM 660 NIST). Temperature inside XRD cabinet was 26.0 ± 0.1 °C.



X-ray sourc e	Wavelengt h	Voltage [kV] Current [mA]	Detecto r type	Step size [°]	Time/step [s/°]	Soller slit [°]	Angular Range [°]	Geometry
Cu Kα _{1,2}	1.54059	45-40	PIXCell 1D	0.026 3	72.165 10X*	0.02	5-150	Reflection Transmission
Mo Κα _{1,2}	0.70932	60-40	GaliPIX 1D & 2D	0.028 6	75.150 7X*	0.04	5-145	Reflection

Table 4.2-3: XRD technical details

The XRD samples preparation was executed inside a dedicated argon filled glove-box (conc. O_2/H_2O below 1.0 ppm, typically < 0.1 ppm). Electrode foils were cut to obtain squared aliquots of average dimension ca. 1.5x1.5 cm. Each sample was place on sample holder and covered with Kapton foil for protecting it against air/moisture during diffraction experiments. For measurements in transmission geometry, scratched electrode material was loaded inside a glass capillary and sealed with wax to protect material against air/moisture.

4.2.4.5 XPS

- To preserve the air sensitive surface chemistry of the anode and cathodes, samples should be prepared under an inert Ar atmosphere and transferred to the XPS instrument by means of some inert atmosphere transport system.
- Careful consideration of the surface charging should be applied at each measurement area. The appropriate charge neutralizer parameters may differ between areas on the same sample and/or at differing depths during Ar+ ion sputtering, therefore a charge neutralisation check should be carried out at each new area or after every change to the sample surface.
- It is recommended that the samples are disconnected from ground during an XPS measurement; this allows the entire sample to charge to the same potential, mitigating differential charging and allowing finer control with the charge neutralizer.
- Due to significant variability in assignment of chemical species in the literature, it is recommended to use either trusted sources of reference spectra (e.g. Surface Science Spectra) or conduct XPS measurements on reference materials.

Inside an argon-filled glovebox, two 9 mm \times 9 mm pieces of NMC cathode material (rinsed and not rinsed) were mounted onto an XPS sample holder using adhesive carbon tape. The samples transferred from the glovebox to the XPS load lock chamber, which involved exposing them transiently to atmospheric conditions for a controlled period of 1 minute.

X-ray photoelectron spectroscopy (XPS) was carried out in ultra-high vacuum using a Kratos Axis Ultra DLD instrument (Kratos Analytical, Manchester, UK) equipped with monochromatic AI K α X-rays (15 kV, 5 mA emission). All spectra were acquired in the hybrid lens mode using the slot aperture. Each analysis area was approximately 700 µm x 300 µm, and the depth of information in XPS is less than 10 nm. Survey spectra in the range 1350 eV to -10 eV binding energy were taken at an emission angle of 0° to the surface normal from three areas of each sample.

After the initial XPS measurements were acquired on the cathode materials, sputtering was performed (in one region for each sample) by employing a monoatomic Ar+ ion source operated at 5 kV over an area of $2 \text{ mm} \times 2 \text{ mm}$ for a total of 1500 seconds (5 cycles of 300 seconds).

The software CasaXPS (Version 2.3.19) was used to analyse the XPS spectra. Each spectrum was intensitycorrected using the NPL transmission function (intensity) calibration (Most recent calibration with respect to measurement: 20th June 2019). The binding energy of all spectra were shifted to align the C 1s peak to 285 eV. Minimum detectable concentrations in XPS are usually between 0.1 atomic % and 0.5 atomic % for elements, excluding H and He which are not measurable.



ToF-SIMS

- In this study, it was not possible to transfer electrodes to the SIMS instrument without exposure to the laboratory atmosphere. It is recommended that a method of inert transport is devised for SIMS measurements, similar to XPS.
- The SIMS field-of-view is relatively narrow and due to the inhomogeneous nature of these electrode materials, a single measurement may not appropriately represent the entire surface. It is recommended that multiple areas on the samples are analysed and correlated.
- Mass spectra must be acquired in both positive and negative ion modes as ions with similar elemental composition may originate from different materials in the electrodes, e.g. Li⁻ and Li⁺.

ToF-SIMS measurement of rinsed and not rinsed electrode materials, prepared in the same way as for XPS measurements in the previous section, were performed using a ToF-SIMS IV instrument (ION-TOF Gmbh, Germany) at a base pressure $<5 \times 10-9$ mbar. Each depth profile was acquired by analyzing a 150 µm × 150 µm surface area (128 × 128 pixels, randomly rastered) centered within a 400 µm × 400 µm sputtered region in a noninterlaced mode (alternating data acquisition and sputtering cycles). Elemental analysis was carried out using 25 keV Bi³⁺ ions from a liquid metal ion gun (LMIG), with a spot size less than 5 µm in spectroscopy mode, a cycle time of 100 µs, and an ion current of 0.1 pA. For sputtering, 10 keV Cs+ ions with a current of 20 nA oriented at 45° to the sample were employed.

Raman

Postmortem Raman spectroscopy was performed on rinsed and not rinsed uncycled NMC electrodes. Samples $(5 \text{ mm} \times 5 \text{ mm})$ were cut from the electrodes and mounted in an air-tight sample holder (EL-Cell ECC-Opto-Std) equipped with a sapphire window. A holed glass fibre spacing separator (1 mm uncompressed thickness) was placed between the sample and the window to avoid Raman signal from the sapphire window.

Raman spectroscopy was performed using a Horiba LabRAM HR Evolution spectrometer equipped with a 532 nm laser and a 50x super-long working distance objective lens. The laser power was attenuated to approximately 0.8 mW at the sample, and the DuoScan beam rastering feature used to delocalize the laser spot to a diameter of 10 μ m and thus minimize sample damage. A 600 lines/mm grating was used, and a 100 μ m slit and a 150 μ m hole. Spectra presented are the sum of 3 x 20 s acquisitions, with background subtraction applied. For each sample, 25 spectra were taken spaced across a 50 μ m x 50 μ m area.

Electrochemical cycling

Half-cell assembly, coin cell assembly and EL-Cell assembly were carried out on harvested samples. The electrochemical properties of anode and cathode materials (both rinsed and not rinsed) were analyzed by: galvanostatic measurements and Cyclic voltammetry.

4.2.4.6 Results

Bellow, a brief summary of results obtained by various characterisation techniques is presented.

Structure	Anode	Cathode
SEM	Graphite flakes with micron and submicron size additives, particle cracking.	5 -15 micron spherical secondary particles consisting of micron size primary particles. Particle cracking.
FIB-SEM		Secondary particle cracking in the surface layer due to the calendaring.
XRD	Crystallographic phases identification & Mass fraction [wt-%]: Graphite, Si, Al ₂ O ₃ and LiF Crystallite size 2500-320 Å	Crystallographic phases identification & Mass fraction [wt-%]: NMC-811, NiO, Li ₂ O, Zr, Zr ₃ O, ZrO ₂ Crystallite size 2500-200 Å
Chemical composition		

Table 4.2-4 Summary of results obtained by various characterisation techniques



Structure	Anode	Cathode
EDX	Carbon with silica and alumina particles, remains of P, F and S containing electrolyte.	NMC85 with separate NiOx or LNO particles, remains of the electrolyte, Zr coating or dopant, F form the PVDF binder and C from the binder and conductive additives.
XRD	See above	See above
XPS	Elemental composition of surface obtained. Could not detect metals, potentially below detection limit. Chemical environment of anode surface studied through high-res. scans	Elemental composition of surface obtained. Ar ⁺ ion sputtering required to reveal low-concentration metals in active material (i.e. Mn, Co) Chemical environment of anode surface studied through high-res. scans
ToF-SIMS	Secondary ion signal from species including phosphorous (PO ₃ ⁻ , mainly on the surface), fluorine species (F ⁻ , deeper into the bulk of the sample), carbon active material, and lithium species. Location of the different species identified can be resolved in the images.	Presence of metal oxide ion signal from manganese, cobalt and nickel and their spatial distribution. Phosphorous (PO ₃ ⁻), fluorine (F ⁻), boron, and boron oxide species also detected in specific areas of the sample. Other species detected.
Raman	N/A	Inhomogeneous NMC with diagnostic D and G of carbon from conducting agent in micrometer scale

In this work, the aging mechanisms of NMC positive electrode and graphite negative electrode materials were investigated. Based on characterization results of commercial NMC811/graphite battery cells cycled at 45°C several aging mechanisms have been found. Microcracking of aged samples was observed from SEM images in both positive and negative electrodes suggesting that active materials experience loss of electrical contacts which increases resistance. The particle size of the positive and negative electrodes decreased after aging. Additionally, we found particles deposited on graphite electrodes after aging which can be Al oxide or Li carbonate agglomerates. EDX shows slightly increased electrolyte element concentration on the surface of the aged positive and negative electrodes indicating SEI and CEI growth. XRD diffraction shows that aged positive and negative electrodes are suffering from exfoliation which is hindering the lithium mobility in the material thus causing capacity fade. According to XRD, there is a decrease in the size of the crystals in both NMC and graphite electrodes. Peaks related to new extra phases are found for the aged samples. Rate capabilities tests demonstrates that at low C-rates the capacity decreases which is related to degradation of the samples. At high C-rates the capacity firstly increases and then linearly decreases which is related to "training" improving the diffusion of samples and following capacity fade. Rinsing of both positive and negative electrode materials decreases the capacity related to the CEI/SEI destruction and particle contact loss. Also, both positive and negative electrode materials degrade slower than the whole Li-ion battery and negative electrode suffers less than positive electrode from capacity fade. In the CV experiments, the H2 - H3 phase transformation occurred in the aged positive electrode is observed to shrink in comparison to the fresh electrode. This phenomenon is connected to capacity fade due to excluding phase transitions from charge/discharge processes. Peak position movement indicates diffusion difficulties rising with SoH decreasing. There are flattening and disappearance of phases, the samples became more disordered, some elements were washing out.

The results indicate that the positive electrode degradation limits the performance of the NMC811/graphite battery system. Graphite is observed to sustain moderately aging at 45 °C even though microcracks were observed and lithium plating was suspected. Positive electrode NMC811 was facing a severe amount of microcracking, cation mixing, CEI growth, TM leaching and extra phase formation. Negative electrodes are



suffering from microcracking, SEI growth, TM contamination and extra phase formation and Li plating. All these effects lead to the capacity fade and diffusion difficulties resulting in performance of the full battery cell.

4.2.5 Validation of the impedance-based aging parameters

4.2.5.1 Physicochemical simulation of EIS under degradation: qualitative comparison

Physicochemical modelling of cell impedance response provides one route to increased insight into the likely physical causes for observed correlations between EIS data (raw or processed) and measured SOH. Purely empirical correlations expressed by the EIS-based SOH models derived in the project can then be interpreted in terms of physical causes; such interpretation rests also on experimental evidence from comparative *post mortem* analysis of fresh and aged cells.

NPL, in consultation with KIT, established a representative physicochemical model of an NMC811silicon/graphite cell and implemented it COMSOL Multiphysics (COMSOL AB, Stockholm). The model was used to understand qualitatively the respective SOH and impedance sensitivities to prospective aging mechanisms indicated from the *post-mortem* analysis.

The physicochemical model is based upon the "Newman model", which is widely used for spatially resolved lithium-ion cell modelling. From *post-mortem* indications, Aalto recommended the following shortlist of aging processes of interest:

- Loss of active material at the positive electrode, due to Mn leaching and disconnection of active particles
- Gradual increase in secondary particle size at both electrodes
- Progressive growth of solid-electrolyte and cathode-electrolyte interfaces, potentially leading to:
 - Loss of lithium inventory (LLI)
 - Slower Li insertion kinetics

Of these, LAM_{PE}, LLI and slower electrode kinetics were selected as candidates for further investigation. Comparative EIS (SOC 100%) and galvanostatic discharge responses were predicted by solving the model with progressively altered coefficients away from the fresh cell condition. The best qualitative correlation to observed behaviour from the LCTs was associated with LAM_{PE}, in which SOH decrease is correlated with increase in the impedance of a low-frequency semicircle in the EIS; other candidate processes show a predicted EIS-SOH relation which is qualitatively distinct from experimental observations.

The correlation of decreased SOH to the increased impedance of a lower frequency EIS arc suggests a role for loss of active material at the positive electrode, in the 70% < SOH < 95% range; this is one of the candidate degradation processes also suggested by *post-mortem* analysis and is a known degradation process for NMC811 electrodes. Further study beyond this limited qualitative study would be needed to give more specific or quantitative interpretation of the SOH models determined in this project.

4.2.5.2 Physicochemical simulation of EIS and NFRA under degradation: parameter fitting

KIT performed physicochemical simulation of EIS and NFRA using the representative "Newman model" (in consultation with NPL), which was mentioned in the previous section. In this "Newman model", KIT implemented additional interfacial reaction that describes the de-/solvation at the interface of SEI/electrolyte.

At selected interval of elapsed cycle (Figure 4.2-20), the aging behaviour of the cell were assessed based on the "Newman model". Based on these states of interest, the discharge behaviour, electrochemical impedance spectroscopy (EIS) and nonlinear frequency response analysis (NFRA) were simulated and compared with the experimental results. By fitting the discharge behaviour, EIS and NFRA over the life cycle test using the aforementioned battery model, the fitted parameter quantifies the evolution of the battery internal state, thus the aging behaviour of the Li-ion battery can be better understood.





Figure 4.2-20: SOH fade of KIT-06 from LCT 1.04 with five selected points of interest (red diamond) for model assessment. Table on the right-hand side shows the cycle number and the corresponding SOH of the selected points of interest.

As the cell ages, the capacity reduces. By fitting the discharge behaviour, the result identifies that there is a significant loss of active material on the cathode side as compared to the anode side (Figure 4.2-21). The initial maximum Li⁺ ions concentration at the cathode side has decreased more significantly as compared to the anode side. Possible causes for this significant loss at the cathode side could be the manganese dissolution that is in qualitative good agreement with the *post-mortem* analysis.



Figure 4.2-21: The experimental (dashed) and simulated (solid) discharge behaviour of KIT-06 (LCT 1.04) at the five selected points of interest (LHS) with the fitted active material losses on anode and cathode respectively (RHS)Using the EIS, the losses from the underlying individual processes in the lithium-ion cell can be better identified and quantified. As cell ages, the semicircle at high frequency which is subjected to the transport losses in SEI layer increase insignificantly as compared to the semicircle at low frequency. Instead, a shift of the spectrum at the high frequency is more significant (inset of Figure 4.2-22). By fitting the impedance at the high frequency range, the result suggests that the thickness of the SEI layer has increased about six times larger as compared to the pristine state. Meanwhile, the ionic conductivities of the SEI drastically decreases by one order of magnitude mainly at the later stage of the aging, which could be the reason of for the significant shift as observed earlier (Figure 4.2-23). Nevertheless, there could be some other reason such as the increase in contact resistance between electrode and current collector or the decrease in ionic conductivity of the electrolyte. However, these contributions cannot be uniquely and separately identified via EIS. In this simulation case, both contributions were assumed to remain constant, and all the impedance increase at high frequency is attributed to the SEI effect. It is important to consider the contact resistance into the cell aging in the future.





Figure 4.2-22: Experimental (dashed) and fitted (solid) EIS of KIT-06 (LCT 1.04) at the five selected points of interest over the life cycle test. Ohmic shift is observed at the higher frequency range of the EIS.



Figure 4.2-23 The fitting results of the high frequency range of EIS that indicates the evolution of physical properties of the SEI.

The growth of the semicircle in the lower frequency (< 1 Hz) is attributed to the charge transfer reaction at the cathode side according to the post-mortem analysis, i.e., three electrode set-up measurement by KIT. Possible reasons for the impedance increase in the cathodic charge transfer reaction (Figure 4.2-24 left) could be the reduction in the reaction rate due to the loss of active material loss, e.g., the dissolution of manganese, or reduction in active surface area (Figure 4.2-24 right) due to the formation of rock-salt structure on the cathode surface. The fitting result indicates that exponential reduction in either reaction rate or active surface area could lead significant growth of the semicircle as observed in the experimental results. Principally, the impedance increase in the lower frequency range could also be the combination of both effects from the reduction in specific surface area and charge transfer rates. However, this cannot be easily identified purely based on only one type of experiment. Additional post-mortem measurement like measuring the remaining available specific surface area is needed in order to aid in identifying the contribution of one factor, so that the other parameter can be quantified via impedance fitting.





Figure 4.2-24: Impedance increase in the lower frequency range of EIS is mainly attributed to the reduction in the kinetic of the cathodic charge transfer process (left - simulation case 1) as well as the reduction in the active surface area (right - simulation case 2).

Based on the parameter set that obtained from the previous fitting of discharge curves and EIS, the NFR spectra was simulated. The result (Figure 4.2-25 left) shows that with the exiting parameter set, a good match between experimental and simulated Y3 can be obtained. However, discrepancies between experimental and simulated Y3 can be obtained. However, discrepancies between experimental and simulated Y2 were observed. To improvise the fitting for NFR spectra, charge transfer coefficients were additionally taken into account. There are in total two sets of transfer coefficients that give a good fit to both experiment and simulation (Figure 4.2-25 right). Both of these two parameter sets show that the charge transfer coefficient deviates from the symmetrical value, i.e., 0.5, either more preference in oxidation or reduction direction. This indicates that the assumption with constant symmetrical charge transfer process throughout the cycling experiment might not be true, or in other context, the charge transfer process might has transitioned from symmetrical to asymmetrical behaviour as the cell ages.



Figure 4.2-25: Left - the fitted NFR spectra based on the parameter set that is obtained from the fitting of discharge behaviour and EIS with no change in the charge transfer coefficient (α =0.5); Right - the improvised NFR fitting by considering the change in charge transfer coefficient during the aging study (α ≠0.5).

From this model-based assessment, it is shown that through NFR-spectrum fitting, additional information, e.g., the symmetry of charge transfer process, can be attained. Especially at the late aging stage, the symmetrical charge transfer coefficient no longer holds, i.e., $\alpha \neq 0.5$. As an outlook, the degradation in the electrolyte chemistries or properties as well as the contact resistance should be considered, whereby these contributions were assumed to be remains constant throughout the aging study in this model-based assessment.



4.2.5.3 Validation with comparison measurements

A comparison measurement has been conducted to investigate the reproducibility of impedance measurements of Li-ion battery cells. Results are described in more detail in deliverable D8 of this project. Four institutes participated (JRC, KIT, NPL and PTB). The participants have been asked to measure the capacity and an impedance spectrum of a commercial 18650 cell (Si-graphite anode/NMC cathode) at full state-of-charge (SOC100) and half charge (SOC50). The cell and the fixture have been provided by NPL. The measurement conditions have been thoroughly defined in a technical protocol that was based on the best practice guide for impedance and life cycle tests mentioned in section 4.1.2.4. Basically, these conditions have been the same as defined for the life cycle tests (LCT) of the 18650 cells conducted for the LiBforSecUse project. Therefore, NPL had provided one of the aged cells of their LCT (state-of-health (SOH) around 70%) with respect to the nominal capacity.

Figure 4.2-26 shows exemplarily the degrees of equivalence (DoE) of the real parts of the measured spectra in dependence of frequency at SOC50 (imaginary parts are comparable). The dashed lines show the minimal and maximal expanded (k=2) uncertainties of the DoEs of three institutes (NPL data had to be removed because of inconsistencies). The arithmetic means of the impedances have been used as comparison reference values. The uncertainties of the DoEs considered the measurement uncertainties of the individual results and the standard deviation of the results of the three institutes. On average the (mean) uncertainty of the measurement results is roughly twice the spread of the results of the institutes (expressed by the standard deviation). At high frequencies above 1 kHz, the impedances begin to differ significantly. This is due to the large uncertainties introduced by mutual inductive coupling of the various parts of the measurement set-up, which is typical for low-impedance measurement. The slightly increased, but still acceptable, difference seen at the low frequency end is due to instabilities of the diffusive properties of the cell, which is presumably affected by timely and spatially inhomogeneous temperature variations during the measurement. It must however be mentioned that the difference is much larger at SOC100. Obviously, the sensitivity of an impedance spectrum is much larger at SOC 100 compared to lower SOCs.



Fig. 4.2-26: Degrees of Equivalence of the real parts of the impedance spectra in dependence of frequency at SOC50.

As a final validation of the methods described in section 4.2.3, the impedance spectra measured in the comparison have been used as input data for the models and the SOH values have been calculated with all three models. Residual capacities have been calculated from the SOH values with respect to a capacity value of 2723 mAh, which has been the measured average capacity of the 18650 cells at the beginning of the life cycle tests of the project. Finally, the predicted values have been compared with the actual residual capacity values. The participating institutes have therefore also measured the capacity of the 18650 by integrating the discharge current of a full discharge cycle.



Institute	predicted SOH	predicted capacity	deviation	2 x RMS
		mAh	%	%
JRC	0.83	2248.58	3.96	1.5
KIT	0.82	2241.26	3.81	1.5
PTB	0.88	2393.93	10.17	1.5
NPL	0.87	2369.29	10.61	1.5

Table 4.2-5 a Model for SOH prediction: direct impedance analysis

Table 4.2-5 b Model for SOH prediction: DRT analysis

Institute	predicted SOH	predicted capacity	deviation	2 x RMS
		mAh	%	%
JRC	0.82	2225.16	2.87	2.3
KIT	0.81	2208.55	2.29	2.3
PTB	0.88	2389.45	9.96	2.3
NPL	0.87	2363.67	10.35	2.3

Table 4.2-6 c Model for SOH prediction: EC modelling

Institute	predicted SOH	predicted capacity	deviation	2 x RMS
		mAh	%	%
JRC	0.81	2212.46	2.29	2.4
KIT	0.81	2212.00	2.45	2.4
PTB	0.87	2357.98	8.51	2.4
NPL	0.87	2365.81	10.45	2.4

The predicted residual capacities of PTB and NPL deviate significantly from the actual values. For all SOH models, the deviation is significantly larger than the uncertainty assigned to the model. Just like in the comparison, the PTB and NPL life cycle test data of the 18650 cells have shown significant deviation from those of the other institutes. Therefore, they had not been used for model development. The results of this comparison seem to confirm that there is some kind of bias that must be evaluated. On the other hand, the comparison results of the DRT and EC analysis of KIT and JRC are reasonably consistent with the RMS values, which basically confirms the validity of the methods. The direct impedance analysis shows a deviation also for the JRC and KIT results. However, this method involves reference of the selected impedance aging-parameters of the aged cell, to the same aging-parameters of the fresh cell. The latter have not been available for the comparison, which explains the deviation.

The results of the comparison measurements basically confirm the results of the cross-validation analysis. The SOH of a battery cell can be predicted with an uncertainty of less than 3 %, which has been the target uncertainty of this project. However, using SOC100 as a reference for SOC adjustment should be reconsidered, because the measured spectrum is strongly sensitive to small uncertainties in the adjustment of SOC100, even though SOH prediction seems much less sensitive to this uncertainty.



4.2.5.4 Evaluation by industrial user

The Best Practice Guides (PBG) and procedures to predict residual capacity have been presented to the industrial partners and stakeholders of the project. The industrial partners have prepared a corresponding case study. They have pointed out the following benefits:

The BPG will enable battery manufacturers to have confidence that a measurement service being offered by multiple suppliers or developed internally will be equivalent and that the results achieved comparable. This gives a focus and clear drive and reliable benchmarking options for product development.

This also provides the value chain for lithium-ion batteries with increased confidence in the performance of the batteries on offer, if the measurements can be developed into a certified methodology this will further increase.

4.2.6 Accelerated aging

In addition to the remaining capacity, the rate at which a battery ages is another important factor for evaluating its suitability for second use applications. The decline in capacity due to cyclic aging is linear for lithium-ion batteries at an early stage and becomes faster as the number of cycles increases (see Figure 4.2-27). This phase is called accelerated aging. Whether a cell is already in the phase of accelerated aging allows conclusions about the future development of the cell capacity.



Figure 4.2-27 SOH decrease across the cycle number for (a) all the cells tested under LCT 1.1 and (b) specifically cells at KIT

KIT and PTB have examined the LCT data measured under reference conditions for parameters that can be used to determine accelerated aging. In the first step, the direct impedance method identifies that the magnitude at 1000 Hz correlates with the accelerated aging (Figure 4.2-28). It shows that a characteristic turning point can be seen at the cycle number, where the accelerated aging starts. Similar observation is also observed in other cells (Figure 4.2-29), which also show accelerated aging during LCT. It was concluded that the high-frequency range contains information about the occurrence of accelerated aging.





Figure 4.2-28 The development of (a) Z', (b) Z", (c) |Z| and (d) phase shift during aging for KIT-06 at selected frequency points. Insets show the development of the respective impedance components at frequency points except at 0.01 Hz and 0.1 Hz. The impedance values are all taken from SOC 100 %



Figure 4.2-29: |Z| at SOC 100 % and 1000 Hz for cells at both institution (a) KIT and (b) JRC show characteristic inflection point upon the onset of accelerated aging, i.e., 2000th cycle for KIT-07 and cell JRC-05 as well as 3000th cycle for JRC-06.

In a second step, the first derivative of the SOH with respect to the cycle number was formed to quantify the aging behaviour (see figure 4.2-30 (a)). It was found that the aging accelerates constantly when the aging rate falls below a threshold value of about -1.25 % / 100 cycles. Impedance parameters derived from the spectra using the distribution of relaxation times (DRT) method were examined for correlation with the aging rate. In accordance with the findings from the direct impedance analysis, it was found that especially the parameters derived from the high-frequency part of the spectrum have a pronounced correlation with the aging rate. The two parameters R1 (b) and C1 (c) show a clear correlation with the aging rate, especially below the threshold value, and are thus suitable predictors for the prediction of accelerated aging.





Figure 4.2-30 First derivation of the SOH with respect to the cycle number (aging rate) (a). Plot of the impedance parameters R1 (b) and C1 (c) determined by DRT as function of the aging rate.

In a further approach to investigate accelerated aging, it was shown that by means of NFRA aging features can also be derived from the low-frequency range. By comparing the Y3 to Y2 signals at SOC 80 % and 0.1 Hz, two distinctive turning points can be observed as indicated in Figure 4.2-29. These turning points indicate that the switching of the contribution between Y2 and Y3. When Y3/Y2 increases, this signifies that the contribution of Y3 surpasses Y2, which means that the reaction rate of the charge transfer processes is predominantly impeded and causes Y3 to increase more than Y2. This can be then correlated to the linear SOH degradation in the second region stage of cell aging as shown in Figure 4.2-30. When Y3/Y2 decreases, this indicates that the contribution of Y2 surpasses Y3, which means that the charge transfer process becomes more asymmetrical or the increase diffusive resistivity due to the porosity decrease in the electrode. This could be the reason to the accelerated SOH degradation not only in the third stage but also the first stage of cell aging as shown in Figure 4.2-31. Therefore, the turning point as observed in the Y3/Y2 has a potential to be further developed as an indicator for detecting the onset of accelerated aging.



Figure 4.2-31: (a) The three aging stages of KIT-06 and KIT-07 can be well correlated to (b) the distinctive turning points in Y3/Y2 at SOC 80 % and 0.1 Hz.

4.2.7 Conclusion

Objective 2 aimed at the development of validated, impedance-based measurement procedures to estimate the residual capacity of second-use battery cells with a target uncertainty of 3 %. It can be reasonably seen as the key objective of the project. Even though the other objectives are also goals in its own right, in this project, they have also served to prepare the metrological ground, such as the impedance measurement protocols and LCT results described in section 4.1, or they are extensions of objective 2, such as the investigation of modules (objective 4). In this more extensive section, we have shown that this key aim of the project has been achieved. Four methods have been successfully developed and validated. A methodology has been presented that can be applied to other cell types and will pave the way for respective metrological services in future.



4.3 Low impedance standards and calibration procedures

4.3.1 Background

Electrical Impedance Spectroscopy (EIS) of lithium-ion cells covers impedance range from sub-m Ω for large cells to over a 100 m Ω for smaller aged cells. In order to ensure metrological traceability in this area, it was necessary to cover this range with impedance standards and reference calibration setup able to characterise them. The battery EIS range is specific and differing from typical impedance metrology in three aspects. First, the impedances are quite low and furthermore with arbitrary phase angles. Second, it goes to sub-Hz frequencies, in our case down to 0.01 Hz. Finally, the measurements are performed in presence of DC bias voltage. None of these conditions is met by vast majority of impedance standards and bridges developed in NMIs before this project. Thus, the basic targets of this objective were to: (i) provide impedance standards covering the EIS-specific impedance range; (ii) provide reference impedance bridge (traceability); (iii) prepare calibration and measurement procedures of EIS meters; (iv) validate steps (i) to (iii) by interlaboratory comparison.

4.3.2 Design of low impedance standards

Several types of standards were developed, prototypes constructed and tested: (i) pure resistive; (ii) pure reactance; (iii) with arbitrary phase angles.

4.3.2.1 Current Shunt

LNE developed a passive resistive measurement standard (current shunt). The current shunt has been designed for electrical currents below 2 A and frequencies up to 5 kHz. The final structure is defined in a 4-terminal pair (4TP) configuration with BNC connectors suitable for direct connection to industrial impedance meters: for example, BT4560 impedance meters. The current shunt is based on a calculable structure defined in a 2-terminal pair (2TP) configuration using a resistive disk made of a resistive alloy placed on an insulating substrate and on a coaxial line made of an inner conductor and an outer conductor (shielding). The material of the resistive disk is Evanohm (copper alloy), and the resistive layer is placed on an insulating Macor substrate. The inner conductor is connected electrically to the inner and outer conductors. The resistance of the shunt is then defined by the resistive disk. This latter is perpendicularly arranged to the inner conductor of the shunt. This part of the structure defined in 2TP is illustrated in Fig. 4.3-1 (left). Two N-Type connectors are welded to the inner conductor at both sides of the coaxial line: the first connector is used for injecting the input current and the other for measuring the output voltage. An adapter box has been fabricated to convert the 2TP coaxial device (with N-type connectors) in 4TP configuration (with BNC connectors). The BNC connectors are electrically insulated from the metallic box. This structure is suitable for the calibration of the RLC-meter. The Fig. 4.3-1 (right) shows the final structure of the current shunt defined in 4TP (with BNC connectors).



Figure 4.3-1 – Structure of the current shunt defined in 2-terminal pair (left), final structure of the current shunt defined in 4-terminal pair (right).



The current shunt developed is characterized by its coaxial geometry. Its calculable design was made to obtain a low impedance variation (less than 1%) up to 5 kHz. The value of the DC resistance of the current shunt has been defined at 17.5 m Ω . The absolute values measured for of transposition deviation and phase angle are less than 1.4 m Ω/Ω and 1.1 mrad respectively for currents below 2 A and frequencies up to 5 kHz. These values obtained permit a current shunt impedance variation less than 0.23 % (for a target set at 1%). The drift and the temperature coefficient TC are the main parameters to be improved because of the non-homogeneity of the deposited thin film of the resistive disk. These parameters can be improved by optimizing the sputter deposition parameters.

4.3.2.2 Reactance standard based on mutual inductance

CMI developed "pure" reactance standard based on mutual inductance. The standard uses air-cored toroidal coil which enabled realization of small inductances well below 1 μ H with minimal phase angle error and with minimal magnetic coupling to surrounding objects. Thus, the standard is stable in value and linear with current. By swapping polarity of voltage coil by relays, the standard can simulate both polarities of reactance, i.e. it can present itself to EIS meter as either inductive or capacitive reactance. Furthermore, the standard was accompanied with unique tandem DC bias voltage source which is able to simulate DC bias voltage up to 5 V without affecting simulated impedance value. This unique DC bias technique allows to combine the DC bias source with any impedance standard. Thus, it is ideal solution for evaluating EIS meter's measurement error dependence on the applied DC bias, which is not possible by other means. The standard was designed with 4-terminal pair (4TP) connection using four BNCs, however it can be connected also in 4-terminal arrangement (4T) for EIS meters with minimal difference in value (below 1 nH). The prototype design was made openhardware design for further development.





Figure 4.3-2 – CMI reactance standard with DC bias simulator (left), practical realisation of mutual inductance coil.



4.3.2.3 Impedance simulator

METAS developed an impedance simulator able to generate impedance value with arbitrary phase and amplitude below 10 \Box . A simplified diagram as well as a picture of the setup are represented in Fig. 4.3-3.



Figure 4.3-3. Working principle (left) and setup (right) of the impedance simulator.

The LCR-meter (DUT) is measuring an impedance as the ratio of the complex voltage V_{HP} , applied to the HP port, to the complex current I_{LC} , entering the LC port. The working principle behind the impedance simulator is to applied to the HP port a signal which is independent to the current I_{LC} using an external voltage source S_v . A first digitizer is measuring the voltage V_v effectively applied to the port HP and a second digitizer is measuring the voltage drop generated by the current *I* flowing through the reference impedance Z_{CB} .

As represented in Fig. 4.3-4, changing the phase and the amplitude of S_v (and therefore the measured phase and amplitude of V_v) gives the ability to simulate any value of impedance using only one reference impedance Z_{CB} .





Figure 4.3-4. Calibration of the gain error of the LCR-meter (Keysight E4980AL) measured using the impedance simulator at 1~kHz. The polar plot on the right represents the different impedance values at which the gain error has been measured.

The impedance simulator has been successfully used to characterize a commercial LCR-meter (Keysight E4980AL) in the impedance range from 100 \Box to 10 \Box and with arbitrary phase angle. The k=1 uncertainty on the measured gain error is well below than the projects target uncertainty of 1 % for impedance of 1 m \Box and above. The impedance simulator has been validated at frequencies from 20 Hz to 10 kHz. Thought, it is supposed to work at lower frequencies, 20 Hz is the lowest allowed frequency of the E49080EL instrument.

It is worth to mention that to ensure the impedance simulator is working correctly, the external source Sv has to mimic perfectly (frequency and signal shape) the signal of the DUT's internal oscillator. Therefore, the impedance simulator cannot be used with EIS/LCR meters that do not provide a continuous, stable drive signal.

4.3.2.4 Active standards with fixed phase angles

The aim of this work was to try to construct a low impedance standard (Limp) in a range typical for Li-ion battery cells. The standard should work in a frequency range of 10 mHz - 5 kHz, at rms current up to 1 A, and it should be stable within 0.1 %.

The working principle behind the simulated standard is to utilize a general impedance converter design, as shown in the image below. The two OP-amps are active elements which ensure that the potentials at A, B and C remain equal. This results in an output impedance Z which can be controlled by appropriate choice of the different circuit impedances Z1-Z5. We constructed and tested three different standards, with simulated values of: 1 F, 10 F and 1 m \Box .





Figure 4.3-5 General impedance converter concept.

The paragraphs below will focus on the design and measurements taken on the 1 F, which was the one with the best performance. The standard is an active circuit which simulates a 1 F capacitor using ceramic capacitors of 1 μ F and a 106-factor scaling circuit. By using ceramic capacitors, we can achieve higher stability and linearity compared with electrolytic capacitors, and the ceramic capacitors are ambipolar in contrast to electrolytic ones. While this demonstrator has only a single impedance value, it is quite straightforward to realise other values. If the 1 μ F capacitor is replaced with a 1 k Ω resistor, the circuit will simulate 1 m Ω , a 10 μ F capacitor will simulate 10 F, etc. This can be implemented as a small one port impedance which plugs into an external connector.





Figure 4.3-6 Circuit design of 1 F standard.

The impedance of the Limp was measured by comparing it to a 100 A wideband current shunt with a nominal resistance of 8 m Ω in a digital complex impedance bridge. The voltage signals were measured with NI 5922 digitizers. Below are the results of these measurements. The current used was 0.8 A rather than 1 A, because at some low frequencies the circuit became unstable after a few minutes, probably because of self-heating. At 0.8 A this was not a problem.

In the graphs, the measurement results (red rings) are compared with a model impedance of a capacitor and a resistor in parallel (black x'es). The model capacitor was 0.9678 F and the resistor was 0.9508 Ω . This gave a good fit for the absolute Limp value and a reasonable fit for the phase, up to about 1 kHz. Above 1 kHz there is a notable deviation, particularly in the phase. One should note, however, that the sampled output signal above 1 kHz was less than 100 μ V, and we can expect a quite high uncertainty.

The parallel resistance of about 1 Ω comes from the fact that we connected the digitizer to the V2 output (see below), effectively putting the 1 M Ω input impedance of the digitizer in parallel to the 1 μ F capacitance of the Limp. This 1 M Ω resistance was then scaled to 1 Ω in the scaling circuit.





Figure 4.3-7 Measurement data (red) and theoretical data (black) for the 1 F standard.

4.3.3 Characterisation of impedance standards

4.3.3.1 Digital sampling impedance bridge

Developed impedance standards had to be characterised before they were used for EIS meter calibration. The higher frequency band starting from approx. 20 Hz to 5 kHz was achievable by traditional impedance bridges already available at NMIs. However, the frequencies down to 0.01 Hz and measurements in presence of DC bias required special approach. In order to get to the low frequencies, no transformer can be included in the bridge circuit. That condition discarded most of traditional designs. Thus, the new setup was developed. It is a complex voltage ratio sampling setup with no balancing circuits and thus no transformers involved. Two compared impedances Z1 and Z2 are connected in series and their voltage drops are digitized by a pair of digitizers. FFT signal analysis of the digitized voltage waveforms is used to calculate voltage vectors on the impedances and their ratio. The supply current is sourced by a transimpedance amplifier via coaxial cable. The current in the current path cable is returning via its shield, thus the current in the cable is balanced, so electromagnetic interference to the potential cables is minimised which allows accurate measurements even for sub-m Ω . The setup was tested with precision digitizers Keysight 3458A and low-cost National Instruments NI 9238 modules.



Figure 4.3-8– CMI digital sampling impedance bridge setup in 4T configuration (left), and 4TP configuration (right)

Several setup modifications were tested for different terminal arrangements. First, simple 4T setup with a pair of digitizers was tested. Circuit analysis showed that even this simple connection can achieve accuracies down to order of 0.001% at low frequencies, however even above 0.1% errors at 5 kHz because of current leakage via the high-side digitizer. Numerous passive and active guarding techniques were tested that reduced the errors down to order of 0.01% in full range of frequencies. Extension of the setup for 4TP measurements was made by adding another digitizer. For measurement in presence of DC bias voltage, the linearity of the digitizers in presence of DC bias was evaluated. The non-linearity reduced achievable uncertainty to order of 0.1%. Thus, DC bias compensator was designed in order to eliminate DC voltage component from the digitized waveform, which enabled measurements with uncertainty down to order of 0.001% - 0.01% even with DC bias for impedance in order of mΩ. This safely exceeded 1% uncertainty goal of the project. The bridge control SW is based on open-source digital sampling tool TWM developed in scope of EMPIR project TracePQM. Another open-source tool was developed for automatic measurement of impedance dependence on frequency and/or current. Both tools are freely available for replication of the setup at other labs. Good practice guide was prepared for the setups. It explains details of the bridge topologies, practices of low impedance measurements and use of the SW tools. Although the bridge is theoretically usable for direct EIS measurement of cells, its primary use is to characterise reference impedance standards.



Figure 4.3-9 – Digital sampling impedance bridge.



4.3.3.2 Characterisation results

The digital sampling setup was used to calibrate most of the impedance standards available in scope of this project. Characterisation covered 4TP resistance standard provided by Hioki, 4TP reactance CMI standard, high capacitance simulator by RISE, PTB cell impedance simulators with arbitrary phase angles and coaxial shunt from LNE. The measurement capability on all these standards was tested by interlaboratory comparison between CMI and RISE, where CMI used setup described above and RISE used their complex voltage ratio setup based on NI PXI 5922 digitizers. The comparison showed variety of problems. In some cases, the stability of the standards was not sufficient for comparison. However, in case of the stable standards, the match between RISE and CMI was mostly below $\pm 1 \ \mu\Omega$, in some cases even below $\pm 200 \ n\Omega$ on both real and reactance component of impedance. The comparison also showed importance of exactly prescribed wiring to the standards. In case of the simple 4TP Hioki resistors, very high deviation on reactance (26 nH) was achieved. It was caused by different terminal arrangement.



Figure 4.3-10 – Example of CMI – RISE bilateral comparison of low impedance with arbitrary phase angle. Blue lines are CMI ref. limits, green measurements are RISE absolute deviations with associated uncertainties.

4.3.3.3 Calibration concept

Characterised standards were used to calibrate EIS meters. Calibration concept was following:

- Perform SHORT correction: Connect test leads to short arrangement. Twist current and potential leads separately to minimize mutual coupling between them. Measure residual SHORT impedance Z_S of the SHORT arrangement. Subtract the Z_S from all subsequent measurements while trying to keep change in wiring geometry minimal between the SHORT and UUT measurement.
- 2. Evaluate EIS meter errors using measurement of characterised impedance standards. The standards should be chosen so some values are below and some above the cell impedance values. Calculate correction factors for these errors.
- 3. Use correction factors from (ii) to correct every subsequent measurement of UUT impedance (cell).

Practical measurements showed the steps (ii) and (iii) are applicable only when EIS meter allows to manually lock the measurement range, so its error can be evaluated at its bottom and top. For EIS meters without manual range function, this approach will likely not lead to reduction of errors. One the other hand, the SHORT correction (i) and proper wiring (twisted leads) is essential for any low impedance measurement.

4.3.3.4 Comparison of the calibration of impedance meters

Calibration concept and measurement practices for EIS meters was tested practically by interlaboratory comparison between CMI – PTB – NPL – KIT with CMI as reference lab. The comparison used Hioki 1 m Ω and 10 m Ω resistors for corrections of the EIS meters. The object of comparison was resistor Hioki 3 m Ω and PTB cell impedance simulator at two different ranges covering values from 1.5 to 4.5 m Ω in full complex plane. The deviations for frequencies below 1 kHz were below ±10 $\mu\Omega$ for both real and imaginary components, which was safely within specifications of all used EIS meters. At higher frequencies, the mutual coupling between the test leads resulted to higher deviations up to over ±50 $\mu\Omega$ on reactance. However, the SHORT correction confirmed to be essential to achieve these relatively low errors. The deviations without SHORT were up to ±1 m Ω on reactance and up to ±0.4 $\mu\Omega$ on real component. Thus, the SHORT correction reduced the errors about



10x. On the other hand, any effect of the EIS error corrections using known impedance standards was not observed, likely due to inability to lock the measurement range and due to significant standard deviation of repeated measurements. However, despite the inability to correct EIS errors by ref. standards, the calibration procedure ensured very good match among the participants mostly below target 1% error even for top frequency of 5 kHz.





Figure 4.3-11 – Example of comparison on EIS meter measurement of 3 m Ω resistor. The blue lines are CMI ref measurement uncertainties, all other measurements are absolute deviations of participants. The one with larger error bars are with just SHORT correction, whereas the ones with lower bars are with corrections using known ref. standards.

4.4 Validated test protocol to characterise modules based on impedance measurements

Background

Most lithium-ion batteries that are considered for secondary use come from automotive applications such as battery electric vehicles (BEV) and hybrid electric vehicles (HEV). For such applications, individual cells are usually electrically interconnected to form larger units called modules, which in turn are combined to form battery packs. Due to the rapidly increasing spread of electro mobility, it can be assumed that in the future large quantities of used modules and packs that are suitable for secondary use will accumulate. Secondary use of modules and packs is particularly attractive if the units can be used immediately and do not have to be disassembled into individual cells and reassembled subsequently. Therefore, quick estimation of the residual capacity of such units is required.

Consequently, another goal of the project was to transfer the impedance-based SOH estimation method, which was previously developed on cell level, to modules. The main question to be addressed was whether information about the condition of the cells installed in modules can be derived from impedance spectra measured on modules. To generate the voltages required in BEVs, battery cells are connected in series in modules. In the study, five prismatic cells (Delta, P/N P140) were connected in series to form a module.



4.4.1 LCT of modules

4.4.1.1 Set-up

Three such modules were galvanostatically cycled in an LCT. The charging process of the modules is controlled via balancers mounted on each cell. When a cell reaches the end-of-charge voltage of 4.15 V, the charging current is subsequently dissipated via the balancer. This prevents damage to the cells due to the application of excessive voltages. It also ensures that the cells of a module have a comparable state of charge at the end of the charging process and are thus balanced, since the total capacity of the module is affected thereby. Discharge is monitored by measuring the individual cell voltages. If a cell falls below the lower voltage limit of 2.7 V, the charging process of the entire module is terminated. This control system thus fulfills the function of a battery management system (BMS).

One objective of the study is to investigate which information can be derived from impedance spectra of modules about the cells interconnected within them. In addition to the impedance spectra measured on the modules, spectra were recorded on each individual cell. The parameterization of the impedance measurements on modules and cells are listed in the table 4.4.1 Cycling of the modules was interrupted after every 50 cycles to determine the residual capacitance and to measure the impedance spectra.

Table 4.4.1: Measurement parameters of LCT - cyclization and impedance measurements - on modules and cells.

Cycling			
	Upper cut-off voltage	20.25 V	
	Lower cut-off voltage	15.50 V	
	Current	66.5 A	
	Temperature	35 °C	
EIS		module	cell
	mode	GEIS	GEIS
	f _{max}	5,000 Hz	10,000 Hz
		0.05 Hz	0.01 Hz
	Amplitude	25 A	5 A
	Temperature	23 °C	23 °C

4.4.1.2 Results

The results of the LCT are summarized in figure 4.4.1. Part (a) shows the decrease in the measured capacity of the modules as a function of cycle number. The decrease in module capacity differs for the three modules. Moreover, the decrease is not continuous - the measured capacity increases at some points with increasing cycle number. In (b), the impedance spectra of one selected module are plotted for different cycle numbers. The overall impedance of the module increases continuously with cycle number. The impedance spectra of the individual cells of the module measured before the start of the cycling and after 500 cycles are shown in (c) and (d). The impedance of the individual cells also increases during the cycling. The increase in impedance differs for the different cells of the module, so it can be assumed that they contribute differently to the capacity decrease of the module.





Figure 4.4.1 Plot of SOH versus number of cycles for the different modules (a), impedance spectra of a module after different cycles (b), impedance spectra of the cells of a module before (c) and after aging (d).

The spectra of modules and cells were evaluated by the distribution of relaxation times (DRT) method. At least two time constants, i.e. two different electrochemical loss processes, could be identified. In figure 4.4.2 (a), the charge transfer resistances of the individual cells of a module are plotted as a function of cycle number. The plot illustrates the different characteristics of the aging of the individual cells of the module.



Figure 4.4.3: Plot the charge transfer resistances of the individual cells of a module against the number of cycles (a) and compare the two resistances of the module and the sum of the respective resistances of the cells (b).

In part (b) of the figure, the two resistances R1 and R2 of the module are plotted against the number of cycles and he sums of the corresponding resistances of the individual cells are displayed. A high level of agreement is observed for both parameters.

Qualitative discussion

The continuous increase of the impedance of the module spectra shows that they contain information about the decrease of the capacity and that it is generally possible to derive insight about the SOH. Furthermore, the detailed evaluation of the impedance spectra of modules and cells shows that the impedance parameters of a



module actually correspond to the sum of the parameters of the individual cells. This correlation is the basis for detecting failures of individual cells in the impedance spectra of the modules.

The temporary increase of the measured capacity with increasing number of cycles (figure 4.4-3 (a)) is probably due to the equalization of the state-of-charge of the cells of a module during an interruption of the LCT. It can be assumed that the amount of charge that can be taken from a module does not necessarily correspond to the actual remaining capacity and can be lower due to unequal states-of-charge of the individual cells.

Due to the low impedance of the cells used in the modules, it was not possible to achieve optimal results for the impedance measurements in some cases. In order to evaluate such impedance spectra error-free by DRT, the application of very high filters is required. This leads to a reduction in the resolution of the DRT plots, and consequently not all loss processes can be quantified independently.

4.4.2 Conclusion

It could be shown that impedance spectra measured on series-connected modules basically contain information related to the residual capacitance of the module. For further investigations, the concept of determining the SOH of modules should be reconsidered so that the actual residual capacitance is measured. One approach would be to measure the SOH of the individual cells individually and sum them to the module SOH. An improvement of the measurement quality of the impedance spectra would lead to an increase of the resolution of the DRT evaluation and enable a more differentiated correlation of impedance parameters with the residual capacitance.

5 Impact

The project presented at least 11 papers at various national and international conferences and workshops, such as the International Metrology Congress, COMSOL Conference, PRiME meeting of the Electrochemical Society, MoD Val, International Symposium on Electrochemical Analysis, Advanced Battery Power, Circusol workshop 2019, Battery reuse solutions seminar, Tulevaisuuden Akku ecosystem (a national workshop in Helsinki). Two of these workshops have been organised by the consortium. The presentations were aimed at representatives from industry and the scientific community. The project objectives and its progress have also been presented at relevant technical committee meetings of EURAMET (TCMC-SCEA/Bern 2020, TCEM-SCLF/Ljubljana 2019, TCMC-SCEA 2021 (online)) and the Electrochemical Working Group of the Consultative Committee for the Amount of Substance at the International Bureau for Weights and Measures (BIPM, 2021, online). Eight peer-reviewed, open access papers have been published and one submitted. The latter is an invited review paper on the impedance spectroscopy of commercial Li-ion cells in the highly recognised Journal of Power Sources.

Impact on industrial and other user communities

This project has, for the first time, realised SI traceability for m Ω and sub-m Ω impedance measurement results in the complete complex plane with a target uncertainty of less than 1%. Manufacturers of impedance measurement devices and end-users from industry and research institutions will be able to calibrate the devices to provide traceability to the SI in this challenging impedance range. Furthermore, the published calibration procedure will help end-users to identify and correct systematic measurement errors. As a result, the low impedance measurements in industry and research facilities; especially for Li-ion- batteries; will be more accurate and reliable.

In addition, by providing new and metrologically sound measurement procedures based on impedance measurement and evaluation methods, the characterisation of Li-ion battery cells and modules will be significantly accelerated in comparison to the current practice. Once established, the new procedures will enable test centres and companies to effectively test or reprocess Li-ion batteries for second-use applications and take fast and reliable measurements for residual capacity. Subsequently, these improvements will facilitate the development of economically viable business models for the reuse of Li-ion batteries salvaged from electrical vehicles. Furthermore, the preliminary results of a feasibility study investigating the potential of impedance-based measurements to predict premature accelerated ageing are promising. It might be possible to develop a method in future to detect if premature failure of second-use batteries has to be expected.

Impact on the metrology and scientific communities

This project has paved the way for primary calibration services in an impedance range that has not been covered so far in the metrological services provided by National Metrology Institutes (NMIs). It will provide a basis for pilot studies and key comparisons in relation to low impedances at arbitrary phase angles at the



relevant technical committees and working groups of EURAMET and the respective consultative committees of the BIPM. Corresponding entries in the databases of the Calibration and Measurement Capabilities of NMIs will be prepared. This objective has been presented at the EURAMET TC-EM and the EURAMET TC-MC meetings. The first comparison measurement on impedance measurements of Li-ion batteries has been approved by EURAMET TC-MC.

Furthermore, the identification and metrological validation of reproducibility conditions for impedance-based measurement methods and life cycle tests of Li-ion battery cells and modules will provide a sound metrological basis for these measurements. This will significantly improve their accuracy and increase confidence in a measurement method that has unrivalled potential to provide information about the internal processes of Li-ion batteries in a non-destructive measurement. Unfortunately, up to now, this method has been deemed to provide unreproducible and ambiguous measurement results. The guides published by this project will overcome this situation and will provide a common basis to make impedance measurements accepted as a fast and reliable tool in Li-ion- battery characterisation and research.

Eventually, results of 13 LCTs on 34 cells, with more than 6000 impedance data sets and corresponding capacity measurements have been created. The results have been made publicly available on the LiBforSecUse repository for further use by external users, with a steady increase of observed downloads (41 downloads by the time this report was submitted).

Impact on relevant standards

The consortium was involved in the development of new standards and guides under IEC TC 21/PT 63330 'Requirements for reuse of secondary batteries and IEC SC 21A/PT 63338 'General guidance on reuse and repurposing of secondary cells and batteries, which are currently in the committee draft stage. These documents were improved as a result of this project. Currently, the impedance-based methods to predict residual capacity are in a laboratory stage, not ready for direct practical use. However, once optimised for practical use, a new work item will be raised within IEC TC 21/JWG 69 Li leading to standardisation. First steps have been taken to establish traceability of low-impedance standards and measurements within the framework of the CIPM-MRA at EURAMET and respective consultative committees and working groups of the BIPM (i.e. in technical committees related to electrochemical and low-frequency, electrical measurements).

Longer term economic, social and environmental impacts

The energy supply in Europe is currently undergoing a dramatic transition from fossil fuels to renewable energy sources for several reasons. The most relevant renewable energy sources, wind and sun, are not permanently available. Therefore, reliable energy storage systems need to be established. Li-ion battery technology is one of the most important candidates to comply with the demands for such systems. In particular, the use of second-use batteries for this purpose would provide significant economic impact in the production of Li-ion batteries. The outcomes of this project will contribute to creating the necessary conditions to establish a market for second-use batteries salvaged from EVs. It has provided new metrologically sound measurement procedures to make the measurement of residual capacity significantly more efficient in terms of measurement time. The large amount of battery energy storage capacity that will come to the end of its EV life in the years ahead will either be recycled or repurposed for second-use applications. If recycled (or even worse incinerated as is often the current practice), new batteries will have to be imported from outside Europe for applications such as storage of intermittent renewable energy sources, since there is no relevant battery production facility in Europe. In contrast, a vibrant European second-use market for batteries from EVs would decrease costs for such systems and the investment capital would remain in Europe. Moreover, the life cycle impact of renewable energy systems would be significantly improved and would contribute to achieving the climate and air quality goals declared by the European Union.

The main social impact of the increase in uptake of EVs and second use applications of Li-ion batteries will be the increase in quality of life and health of European citizens due to improved air quality and reduced noise pollution. This will also manifest itself in reduced strain on health services, less need for regular cleaning of buildings. It is also anticipated that an increase in social awareness of electromobility will result from the increased visibility of both EVs and second-use applications as this new market develops.

6 List of publications

- 1. Nina Meddings, et al, "Application of electrochemical impedance spectroscopy to commercial Li-ion cells: A review, Journal of Power Sources", 2020, <u>https://doi.org/10.1016/j.jpowsour.2020.228742</u>
- Jože Moškon et al 'A Powerful Transmission Line Model for Analysis of Impedance of Insertion Battery Cells: A Case Study on the NMC-Li System', J. Electrochem. Soc., 2020, <u>https://doi.org/10.1149/1945-7111/abc769</u>



- Mašláň, Stanislav, "High capacitance simulation using mutual inductors", Proceedings of the 24th IMEKO TC4 Symposium, 2020 <u>http://doi.org/10.5281/zenodo.4630725</u>
- Mašláň, Stanislav. (2020) 'Design of digital sampling impedance bridge for battery impedance spectroscopy', Proceedings of the 24th IMEKO TC4 Symposium, <u>http://doi.org/10.5281/zenodo.4630641</u>
- 5. Klement Zelič, et al 'Derivation of Transmission Line Model from the Concentrated Solution Theory (CST) for Porous Electrodes', J. Electrochem. Soc, 2021, <u>https://doi.org/10.1149/1945-7111/ac1314</u>
- 6. Tanja Vidaković-Koch, et al, 'Nonlinear Frequency Response Analysis: A Recent Review and Perspective', Current Opinion in Electrochemistry, 2021, <u>https://doi.org/10.1016/j.coelec.2021.100851</u>
- 7. Benyamin Rusanto et al, 'Primary measurement method for the characterisation of impedance standard in the m Ω range, Measurement Science and Technology', 2022, <u>https://doi.org/10.1088/1361-6501/ac6a45</u>

This list is also available here: <u>https://www.euramet.org/repository/research-publications-repository-link/</u>

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