

SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA
Faculty of Electrical Engineering and Information Technology



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Dissertation Thesis Abstract

**Diagnostics and analysis of degradation mechanisms
in Li-ion batteries with Ni-based cathodes**

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Understanding the degradation processes in Li-ion batteries is integral for further development of new battery technologies and for improving currently used batteries and battery management systems. This work focuses on the degradation analysis of both commercial and experimental cells. The first part of this work was conducted at the Slovak University of Science and Technology in Bratislava (STU), and it provides a comprehensive electrochemical analysis of degradation in commercial NCA-based Li-ion batteries while their degradation was elevated by various stress-inducing scenarios. To the best of the authors' knowledge, this is the first work analysing stress-induced degradation of NCA batteries simultaneously by electrochemical impedance spectroscopy (EIS), incremental capacity analysis (ICA), and galvanostatic intermittent titration technique (GITT). The second part of this work was conducted at the Norwegian University of Science and Technology (NTNU). These experiments utilize degradation analysis of experimental Ni-rich NMC/graphite cells on electrode level cycled at room (25 °C) and elevated (50 °C) temperatures in order to study LiFSI-based electrolytes as an alternative to commonly used LiPF₆-based electrolytes in carbonate solvents. This dissertation provides a cornerstone of EIS characterisation for future experiments focused on adjusting LiFSI-based electrolytes in order to support their implementation in high-voltage Ni-rich Li-ion batteries.

Keywords: Li-ion battery, degradation mechanisms, electrochemical characterisation, Ni-based cathodes, NMC, NCA

OBJECTIVES OF THIS DISSERTATION

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- To obtain new knowledge in the field of Li-ion batteries with Ni-based cathodes and their advanced characterisation in order to understand methods of battery ageing and degradation analysis.
- Analyse battery ageing and degradation mechanisms of selected Li-ion batteries with Ni-based cathodes via methods of electrochemical characterisation, where the manifestation of degradation is elevated by abusive battery-usage protocols.
- Characterise experimental Li-ion battery cells with Ni-based cathodes containing LiPF₆- and LiFSI-based electrolytes via methods of electrochemical characterisation with an aim to support the development of batteries with improved parameters.

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1 INTRODUCTION

Li-ion batteries have become a leading technology for grid-level large-scale electrical energy storage devices [1][2] as well as for energy storage systems in electric vehicles [3][4][5]. Nevertheless, currently used batteries and battery management systems (BMS) face many challenges related to their maximum capacity, longevity, safety, charging capability and cost [6]. Both performance- and safety-issues are mostly related to developing degradation occurring inside the batteries [1]. To address battery degradation, it is essential to correctly identify and analyse these degradation processes in order to evaluate the battery's State-of-Health (SOH) for its further effective and safe employment. Moreover, understanding these mechanisms enables battery scientists and engineers to further improve currently used batteries and BMSs as well as to develop new battery technologies [6][7]. To analyse degradation mechanisms in Li-ion batteries is not an easy task since these are complex electrochemical processes occurring at different parts and/or interfaces of the batteries [8]. Various degradation processes manifest themselves differently, depending mainly on the battery's chemistry, usage protocols, temperature conditions and manufacturing [9][10][11].

This work focuses on the identification and analysis of ongoing degradation mechanisms in Ni-based Li-ion batteries by methods of electrochemical characterisation without a need for post-mortem analysis, and hence, without a need for disassembling the studied battery. These methods allow the study of degradation mechanisms such as the thickening of the solid electrolyte interface (SEI) layer, graphite exfoliation, particle cracking, lithium plating or corrosion of current collectors [11]. The research work of this dissertation is divided into two stand-alone parts, each realized at a different workplace. The first set of experiments was conducted at the *Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava (ÚEF FEI STU)*. The main idea of these experiments is to provide a comprehensive electrochemical analysis of degradation in commercial 18650 NCA-based Li-ion batteries while their degradation is elevated by various stress-inducing scenarios, such as over-charging or charging with high currents. The second set of experiments was conducted at the *Department of Materials Science and Engineering, Faculty of Natural Sciences, Norwegian University of Science and Technology (IMA NV NTNU)*. In these experiments, electrochemical characterisation supported by scanning electron microscopy is used to study LiFSI-based electrolytes as an alternative to commonly used LiPF₆-based electrolytes for experimental NMC-based full-cell batteries operating at elevated temperatures. Contrary to the experiment performed at STU on commercial cylindrical cells, the construction of these experimental cells enables three-electrode analysis, which provides a better distinction between processes occurring at individual electrodes.

2 THE STATE OF THE ART

This chapter provides a brief overview of the current state of academic discussion regarding the non-destructive electrochemical characterisation of degradation of Ni-based cathodes for Li-ion batteries, whose understanding is integral part of the second objective of this dissertation. Also, challenges of LiPF₆- and promises of LiFSI-based electrolytes are discussed in this chapter, to provide a knowledgebase for the third objective of this dissertation.

2.1 Ni-based cathodes

The most dominant cathode materials on the market for Li-ion batteries for electric vehicles and power grid storage units are Ni-based cathodes, where the most successful representants are NCA (LiNi_xCo_yAl_{1-x-y}O₂; lithium nickel cobalt aluminium oxide) and NMC (LiNi_xMn_yCo_{1-x-y}O₂; lithium nickel manganese cobalt oxide) [12][13]. A radar chart comparison of the main characteristics of NCA and NMC cathodes with other notable cathode materials is shown in [Figure 1](#). Despite the success of NMC and NCA, these Ni-based batteries are still prone to degradation, which can hinder their performance upon cycling. The degradation of NCA cathodes is a fundamental part of this dissertation. Various usage protocols can lead to various sources of degradation, making NCA batteries overly sensitive to undesirable operating conditions [14][15]. These troublesome degradation tendencies raise questions regarding the safety of their usage. Hence, it is vital to understand and monitor the degradation of NCA batteries via methods applicable in onboard systems [9][16]. For this purpose, studying batteries stressed by various conditions that might induce degradation of different origins and/or magnitudes is crucial. Techniques such as electrochemical impedance spectroscopy (EIS), incremental capacity analysis (ICA), and galvanostatic intermittent titration technique (GITT) are suitable methods for the non-destructive on-board analysis of ongoing battery degradation [17][18][19][20]. Many noteworthy studies have been published in this area. In 2018, *Cabañero et al.* [21] demonstrated the applicability of the GITT for the analysis of Li⁺ diffusion of commercial batteries, including NCA. In 2021, *Su et al.* [22] used GITT-like measurements to study the effects of a wide range of conditions, such as various charge/discharge currents, cut-off voltages, and ambient temperatures. In 2020, *Sebastian et al.* [23] compared GITT and EIS for a study of the impact of fast-charging protocols on the battery's SOH and performance. *Devie and Dubarry* [24] demonstrated simulation-based ICA for the first time for the analysis of footprints of degradation modes for NCA batteries, and in 2020, *Zhang* [25] used this technique together with EIS, to study the influence of high-current charging. Over-charge conditions have been studied by EIS by *Kong et al.* [26] and by *Togasaki et al.* [27]. SOH for both over-charge and over-discharge scenarios was analysed by EIS by

Li et al. [28]. The influence of depth of discharge on the degradation of NCA batteries was studied by Preger et al. [29] by cyclic tests, by Watanabe et al. [30] by EIS, and by Pastor-Fernández et al. [31] by EIS and ICA. There are other notable studies on NCA batteries that used the EIS [32][33], GITT [34][35], or ICA [36][37] methods. These techniques provide a unique approach to battery analysis, yet the singular use of one of these methods does not provide an extensive or confirmatory degradation analysis. These methods have been used in battery research for years, however, there is a lack of studies which would analyse the degradation of NCA batteries by simultaneous usage of these methods, which is essential for a comprehensive and confirmatory understanding of battery degradation.

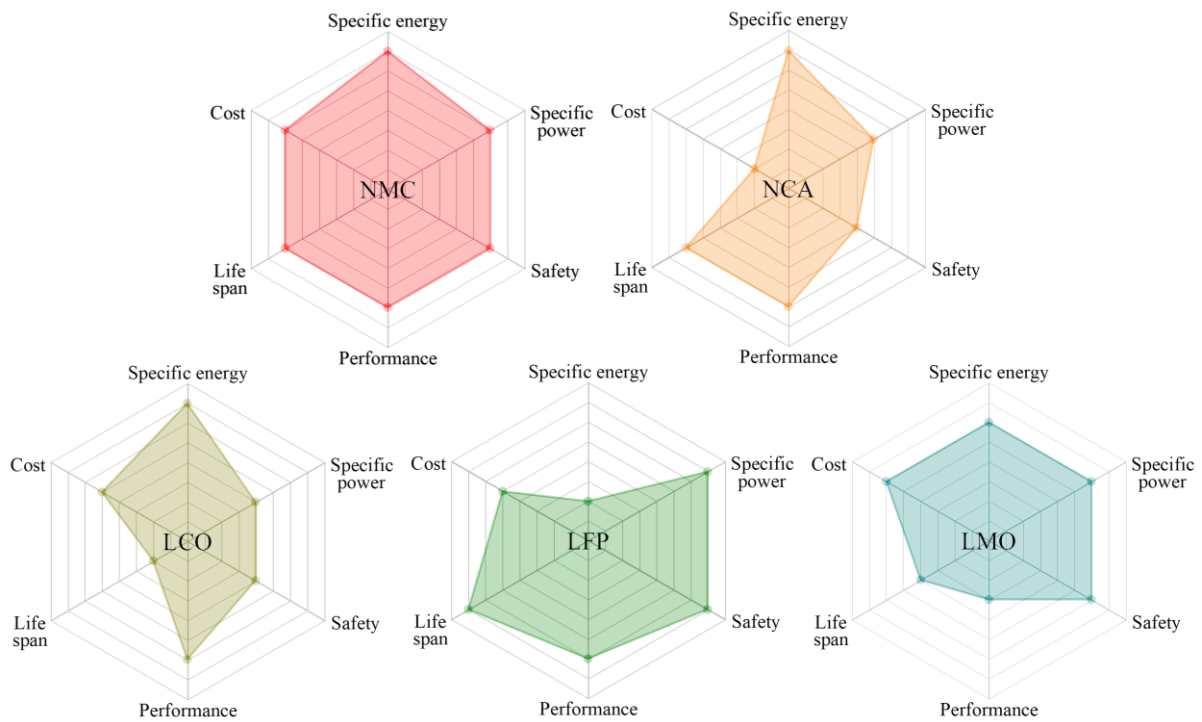


Figure 1 Graphic comparison of the main characteristics of the NMC, NCA, LCO, LFP and LMO cathodes for Li-ion batteries [38][39].

Regarding NMC-based cathodes, currently, the most commercially successful representatives of this category are NMC111, NMC442 and NMC532 cathodes. Different ratio of these composition elements influences the battery’s capacity, safety and kinetic properties [40]. To further improve the performance of NMC-based batteries, mainly their discharge capacity, Ni-rich NMC-based cathodes are being studied and developed, while the most promising adepts are NMC622 and NMC811, mainly for their use in electromobility [40][41]. However, with increasing content of Ni, these batteries suffer from severe capacity fade upon cycling and have lower thermal stability. Ni-rich cathodes are prone to the processes such as the formation of rock salt, cationic mixing, particle cracking, phase transformations, dissolution of transition metals or parasitic reactions on CEI interface [40].

2.2 LiFSI- vs LiPF₆-based electrolytes

To further improve the performance of Li-ion batteries with Ni-rich cathodes, mainly their longevity and thermal stability, improving or replacing currently used electrolytes is vital. Various electrolytes and/or additives are being studied as an alternative to the most commonly used LiPF₆-based electrolytes [40][41]. The main disadvantages of LiPF₆-based electrolytes are their instability at high voltages and high temperatures, and extreme sensitivity to moisture, leading to the generation of hazardous HF [42][43]. LiPF₆ is thermally unstable at temperatures above ~55 °C, where it decomposes and produces LiF and PF₅ [43][44]. If traces of water are present, hydrolysis of PF₅ with H₂O leads to the generation of HF and POF₃ [42][45], and hence, HF generation is catalysed by moisture [46]. Also, the interaction of PF₅ with carbonate solvents such as EC or DEC can shift the equilibrium of the reaction to the right, increasing the amount of produced HF [46]. Moreover, carbonate solvent molecules can oxidise at voltages above 4.2 V, producing reactive species, which can also hydrolyse LiPF₆ and produce even higher amounts of HF [47]. Hence, conventional LiPF₆-based electrolytes with organic carbonates are generally considered to be stable up to 4.2 V [48] and under ~55 °C [43], which hinders their usage for high-voltage cathodes [48]. Principally, the thermal decomposition of LiPF₆ precedes HF generation, while high voltages accelerate this generation [45]. However, it is worth mentioning that in 2020, *Metzger et al.* reported [49] that traces of H₂O can hydrolyse EC and produce EG, which can then be oxidized at ~4.0 V vs Li⁺/Li and create H⁺, which then reacts with PF₆⁻ and produces PF₅ and HF, and therefore, HF is being generated without a need of prior thermally-induced decomposition of LiPF₆. The generation of HF is one of the main bottlenecks of LiPF₆-based electrolytes [50][45]. One of the very promising alternatives to LiPF₆ salt for high-voltage Li-ion batteries is LiFSI [43][51]. The LiFSI salt, contrary to LiPF₆, does not lead to the generation of HF [42] and is thermally stable up to 200 °C [52]. LiFSI-based electrolytes benefit from higher conductivity than LiPF₆ [42][43]. A disadvantage of these electrolytes is that they can lead to corrosion of aluminium current collectors in high-voltage operations [48][52], while the onset of this corrosion is ~3.8 V [42]. Regarding this corrosion, LiPF₆-based electrolytes have a clear advantage against LiFSI-based electrolytes because they can spontaneously repassivate the Al current collector. This happens by advantageous reaction of otherwise problematic HF, where HF localized at the surface of Al metal reacts with a native protective layer of Al₂O₃ and transforms it into AlF₃. The native Al₂O₃ layer provides protection against corrosion up to ~3.8 V vs Li/Li⁺, while it is prone to decomposition at higher voltages. This layer is labelled as “native” since it is formed after Al-metal exposure to the air during manufacturing. The AlF₃ layer is stable up to 6.0 V vs Li/Li⁺; therefore, its formation is beneficial for high-voltage batteries [53].

3 RESEARCH CONDUCTED AT THE ÚEF FEI STU

The research objective addressed in this chapter is: *Analyse battery ageing and degradation mechanisms of selected Li-ion batteries with Ni-based cathodes via methods of electrochemical characterisation, where the manifestation of degradation is elevated by abusive battery-usage protocols.* These experiments were conducted at the *Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava.* This study intends to fill this research gap by analysing the degradation of NCA Li-ion batteries via simultaneous usage of EIS, GITT, and ICA methods for common stress-inducing operating conditions (over-charge, over-discharge, and high-current charging). This work aims to demonstrate that only simultaneous usage of these methods can lead to a comprehensive and more profound understanding of ongoing degradation processes. Moreover, this study shows that to avoid making assumptions arising from two-electrode measurements of full-cell batteries and to determine the correct origin of degradation with confidence, several complementary methods of characterisation should be used. To the best of the authors' knowledge, this is the first work that provides a comprehensive degradation analysis of full-cell NCA batteries (NCR18650B) via EIS, GITT, and ICA methods for various stress-inducing scenarios (over-charge, over-discharge, and high-current charging). This chapter is based on the authors' published work [54][55][56][57].

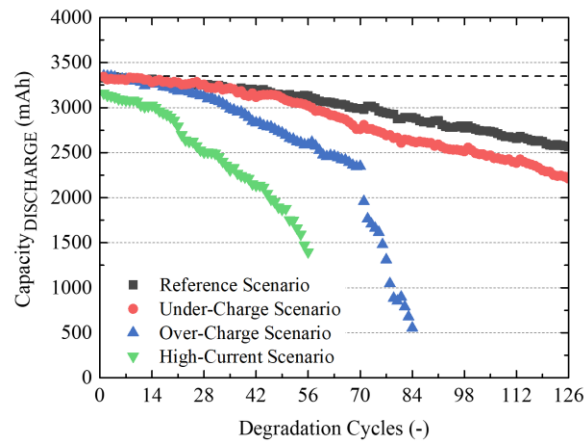


Figure 2 Discharge capacity of the NCA 18650B batteries.

For the purposes of the experiments, commercially successful NCA 18650B batteries by Panasonic were chosen. Three scenarios of cyclic degradation were studied, labelled as *High-Current Charging Scenario*, *Over-Charge Scenario*, and *Under-Charge Scenario*. The fourth set of measurements was carried out by the optimal-operating conditions for comparison purposes, labelled as *Reference Scenario*. The *High-Current Charging Scenario* was based on charging with the above-recommended current, corresponding to 1 C. The *Over-Charge Scenario* charges the battery up to

4.3 V, instead of the recommended 4.2 V. The *Under-Charge Scenario* discharges the battery to 2.3 V instead of 2.5 V. The *Reference Scenario* maintains the recommended voltage window, charges the battery with the maximum allowed current corresponding to 0.7 C, and discharges with 1 C. Between all degradation cycles, 10 min of relaxation was allowed. After each 7th degradation cycle, all batteries were charged by 0.7 C and relaxed for 1 h, followed by EIS. After each 2nd EIS, GITT discharging took place (after each 14th degradation cycle). The EIS was performed galvanostatically and for 20 kHz – 20 mHz. The GITT was done by C/20 discharging, $t_{on} = 10$ min, and $t_{rest} = 10$ min. The ICA was realized via the GITT.

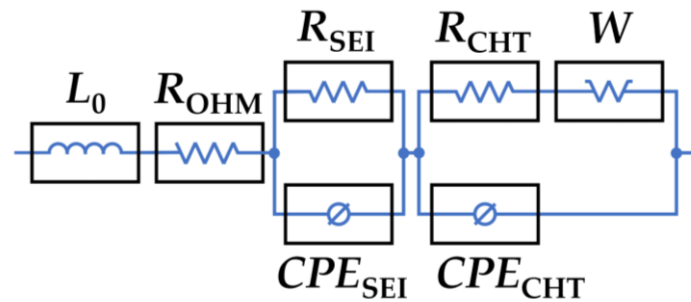


Figure 3 Equivalent electric circuit model used in this study.

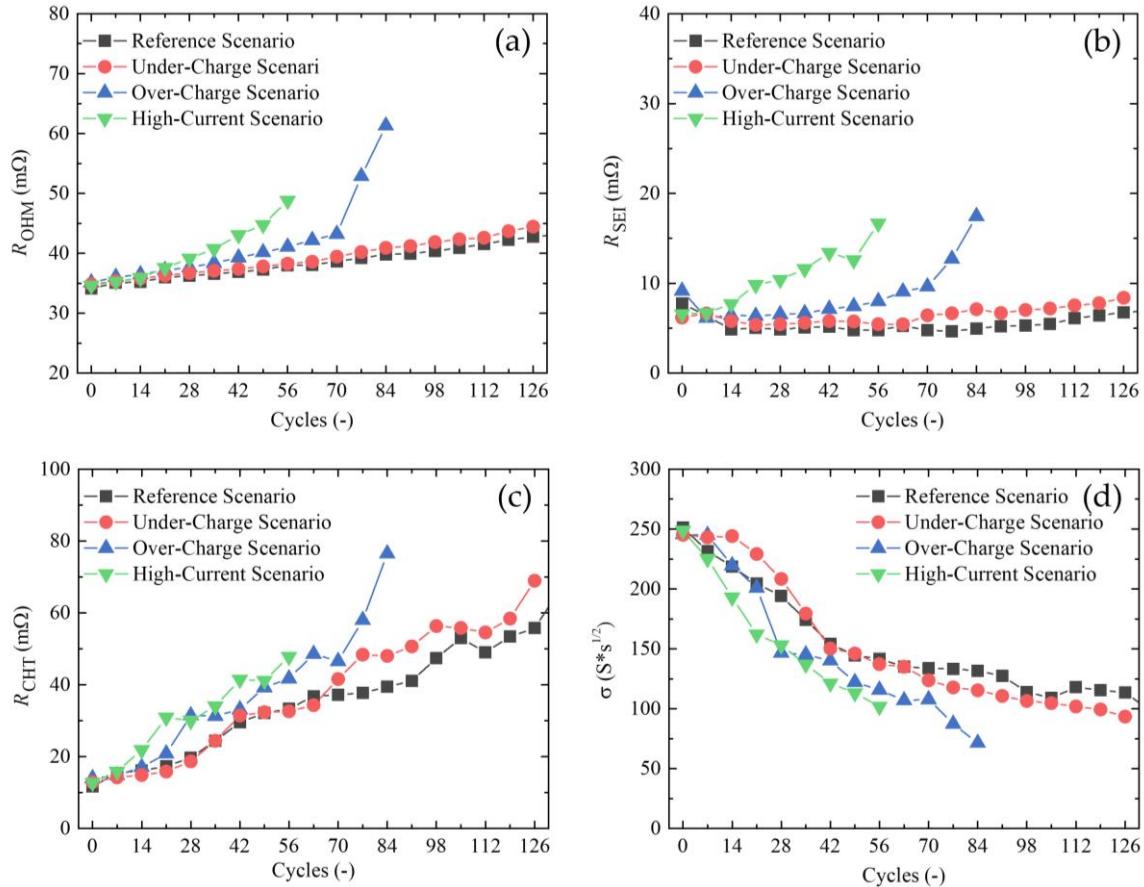


Figure 4 Results of the EIS data fitting via the equivalent electric circuit model.

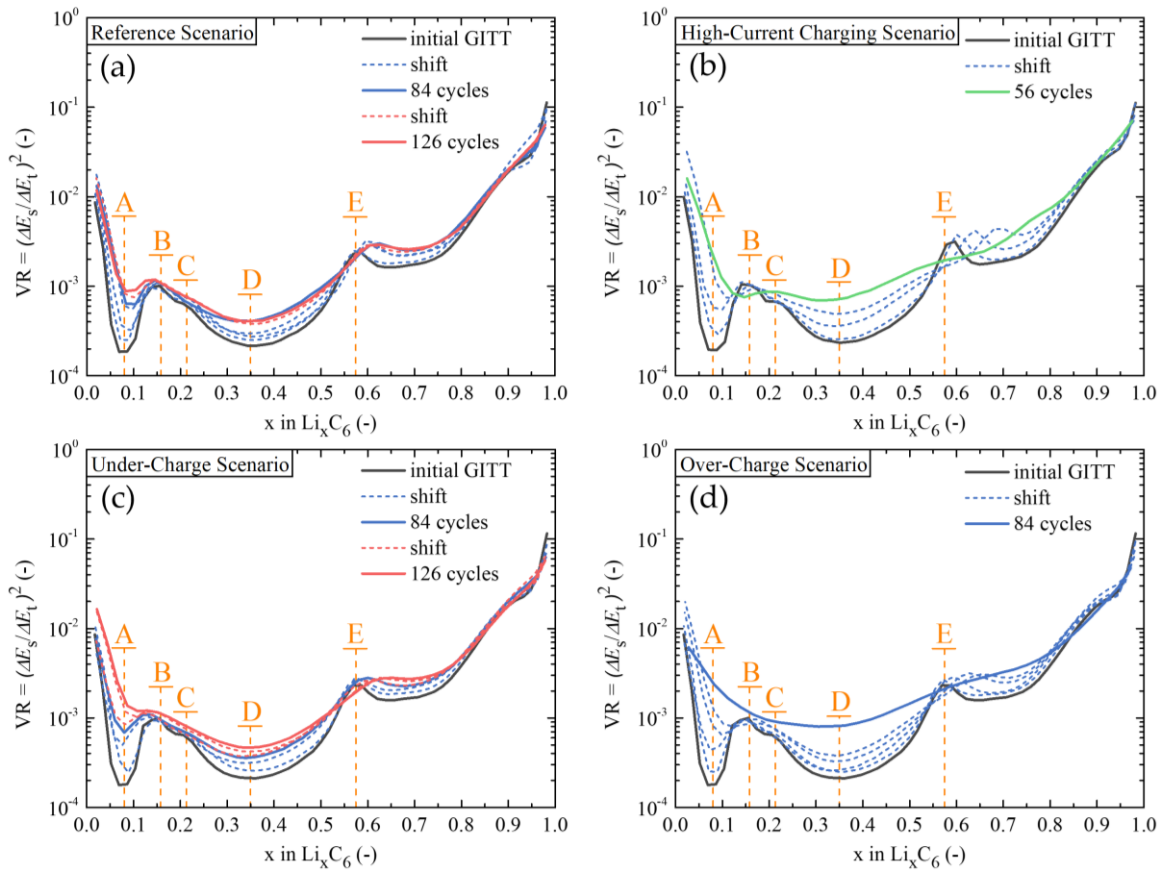


Figure 5 VR parameters as a function of x in Li_xC_6 .

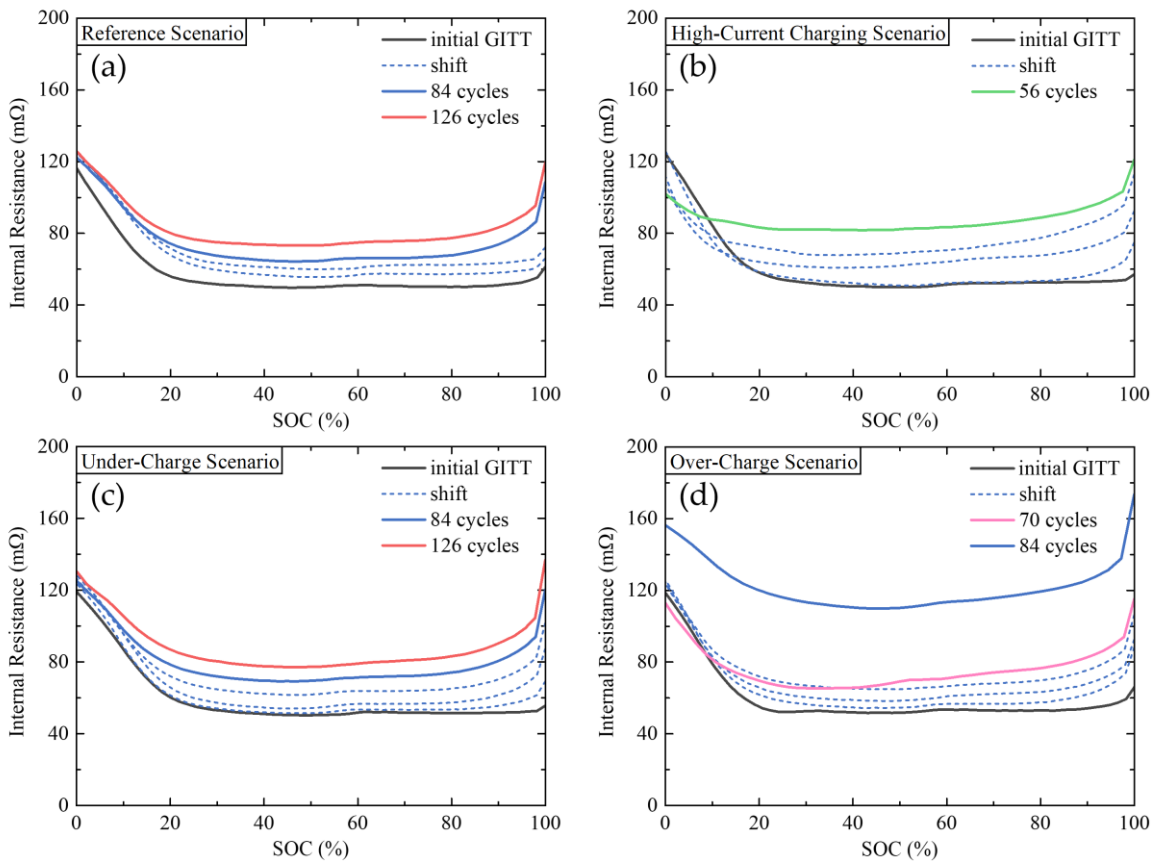


Figure 6 Internal resistance (IR) obtained via GITT measurements.

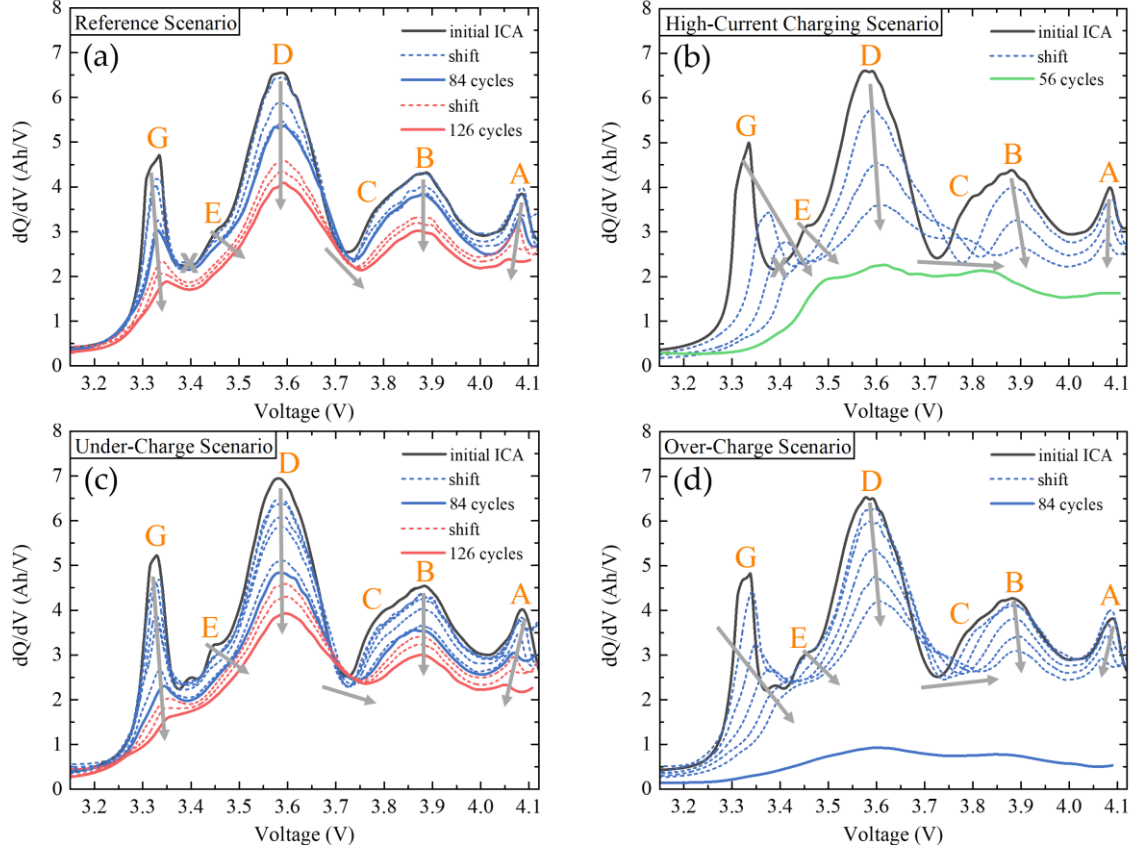


Figure 7 The cyclic development of the ICA curves of studied NCA 18650 cells.

3.1 The Reference Scenario

For the *Reference Scenario*, a slight linear decrease in capacity was observed, where capacity decreased from an initial 3350 mAh to 2563 mAh after 126 cycles. Authors believe that this decrease was induced preliminarily by DOD 100% and by the extensive amount of analytical measurements, as discussed above. Especially high DOD is known to lead to micro- and phase-changes of the NCA cathode material. Analysis via EIS measurements revealed that R_{OHM} and R_{SEI} are increasing negligibly with cycling. From this, it can be assumed that the SEI layer remains stable throughout the experiment. Quasi-stable R_{OHM} values point to irrelevant conductivity losses. Values of R_{CHT} are increasing quasi-linearly for the entire duration of experiments, pointing to the presence of microstructural and/or phase changes, while this change in active materials is also supported by decreasing diffusion of lithium ions. The disadvantage of the two-electrode EIS measurements is its inability to distinguish between the influences of individual electrodes, and therefore, the origin of increasing R_{CHT} has to be found by other methods. Analysis via GITT enabled the analysis of the behaviour of lithium-ion diffusion as a function of x in Li_xC_6 . This analysis showed that even reference measurements lead to certain stress disparities in the graphite's lattice, primarily in the surface region of graphite's bulk, upon formation of *Stage IV* - Phase LiC_{72} . It is assumed that the formation of this phase is being suppressed with

cycling. The GITT also enabled the study of the internal resistance, which confirmed the thermodynamic stability of the battery. The footprint of the ICA suggests LAM_{LiPE} as the dominant source of degradation, while mild LLI is also present. The ICA also contains a hint of a minor occurrence of LAM_{deNE} , which would be in accordance with the GITT study, although this mode is not considered to have an influential role in the degradation of the studied battery. By combining results from ICA and GITT, it can be said that the origin of increasing R_{CHT} is in the degradation of cathode active material. This confirms the initial hypothesis that the degradation of this battery would be induced primarily by cycling between SOC 0% and SOC 100%.

3.2 The Under-Charge Scenario

This scenario has the same capacity-decrease trend as the *Reference Scenario*, which has slightly lower capacity values from the $\sim 50^{\text{th}}$ cycle onwards. Higher DOD arguably induces this higher degradation due to over-discharging. Values of R_{OHM} and R_{SEI} obtained via EIS are in close to absolute overlap with the *Reference Scenario* measurements. Values of R_{CHT} are increasing at an almost negligibly higher pace than the *Reference Scenario* values, hence, microstructural and/or phase changes on one or both electrodes are considered to be the dominant source of degradation. Regarding D_{Li+} analysis via GITT, the only notable difference is in higher $VR_{\text{Stage IV}}$ values. As an explanation for this difference, more profound delithiation leading to higher intercalation/deintercalation stress onto graphite electrodes is suggested. A comparison of the internal resistance of the *Under-Charge Scenario* and the *Reference Scenario* points only to a single noticeable difference in the close-to-100% SOC region, where the *Under-Charge Scenario* shows slightly more increasing values. Analogously to the *Reference Scenario*, the ICA suggests primarily LAM_{LiPE} and LLI modes as dominant degradation modes. It can be argued that additional stress onto graphite lattice due to over-discharging might lead to observable LAM_{deNE} . Nevertheless, evidence for this degradation mode is not persuasive, hence, it is not considered to have a determining effect on the battery's State-of-Health.

3.3 The Over-Charge Scenario

Uniquely for the *Over-Charge Scenario*, capacity fade occurs in two stages, where linear capacity fade occurs for the first 70 cycles, subsequently followed by a rapid capacity fade, leading to the death of the battery in just another 14 cycles. This two-stage capacity fade was observed only for this scenario, and therefore, it is directly ascribed to over-charging up to 4.3 V. R_{OHM} slowly increases up to 70 cycles, pointing to conductivity losses. Its values have almost doubled in the last 14 cycles. R_{SEI} is stable up to the 49th cycle and increases moderately up to the 70th cycle, from where it increases dramatically, showing gradual changes in the SEI layer. Values of R_{CHT} initially have a similar trend

as the *Under-Charge Scenario*, while from the 70th cycle onwards, its values increase dramatically, having the same trend as R_{OHM} and R_{SEI} , suggesting that R_{CHT} is connected to SEI layer changes and conductivity losses. It is known that NCA batteries are high-current and high-voltage sensitive and that the above-recommended voltages might lead to transition metal decomposition and deposition onto the SEI. This phenomenon is in good agreement with the presented results here. From the D_{Li^+} study via GITT, it is clear that *Stage IV* - Phase LiC_{72} is being suppressed at a higher pace than for the reference measurements. The battery's internal resistance develops moderately up to the 70th cycle, after which its values increase dramatically, where IR of the plateau region of SOC almost doubles, displaying a similar trend as R_{OHM} . This is an indicator of dying battery. The ICA suggests LLI and LAM_{LiPE} as dominant degradation modes. The *Peak A* shift possibly points to very moderate LAM_{deNE} .

3.4 The High-Current Charging Scenario

All analytical tools proved that this scenario led to the most severe degradation, preliminarily on the cathode side of the battery. The ICA recognizes LLI and LAM_{LiPE} as dominant and decisive degradation modes. D_{Li^+} recognises the increasing influence of the cathode region with an increasing number of degradation cycles. Gradually increasing R_{OHM} indicates high-current charging induced generation of CO_2 and O_2 gasses, leading to increased internal pressure, electrolyte depletion, and hence, conductivity loss. This is due to the reversible Li_2CO_3 surface film. The EIS measurements were performed at SOC 100%, thus, R_{OHM} values correspond to the fully charged and relaxed battery. Another resistance-related phenomenon was observed from the internal resistance study performed via GITT: decreasing resistance values for low-SOC regions. This can be attributed to the continuously decreasing pace of Li_2CO_3 decomposition during charging. Authors suggest that high-current charging led to disproportional Li_2CO_3 decomposition to Li_2CO_3 formation. R_{SEI} increases quasi-linearly, suggesting the thickening of the SEI layer, which can be considered a partial source of LLI. Quasi-linearly increasing values of R_{CHT} and decreasing Li^+ diffusion point to cationic mixing of the layered NCA structure also result in LLI. All ongoing NCA degradation was strengthened by DOD 100%, which leads to more intense structural microcracking, resulting in a loss of active cathode material and an increase in parasitic-reaction sites. Regarding the graphite anode, high-current charging led to more severe $VR_{Stage IV}$ suppression than reference charging. This might have been induced by local accumulation of Li^+ in the surface regions of the anode, leading to higher stress disparity and structural changes, however, similar suppression was observed for over-charging, and therefore, several origins can induce this suppression. Out of all four scenarios, anode-related changes were the most profound for the *High-Current Charging Scenario*. Nonetheless, characterisation via EIS, GITT, and ICA suggests only insignificant degradation of graphite anode.

4 RESEARCH CONDUCTED AT THE IMA NV NTNU

The research objective addressed in this chapter is: *Characterise experimental Li-ion battery cells with Ni-based cathodes containing LiPF₆- and LiFSI-based electrolytes via methods of electrochemical characterisation with an aim to support the development of batteries with improved parameters.* These experiments were conducted at the *Department of Materials Science and Engineering, Faculty of Natural Sciences, Norwegian University of Science and Technology.* The aim of the experiment presented in this chapter is to conduct electrochemical characterisation of the influence of high-voltage and high-temperature on NMC622/graphite Li-ion cells containing LiFSI-based electrolyte as a substitution for commonly used LiPF₆-based electrolytes in carbonate solvents, in order to provide a characterisation “base stone” for further research in this area.

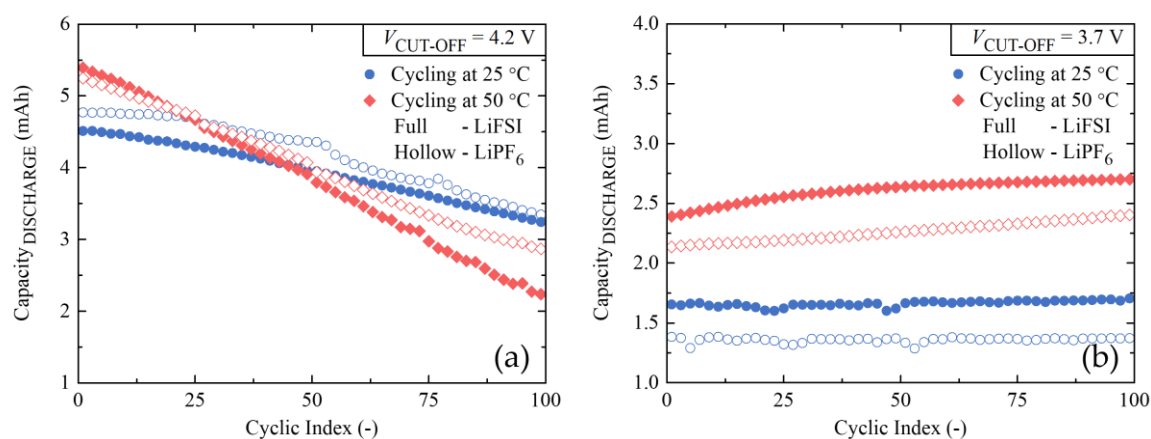


Figure 8 Discharge capacities of NMC622/graphite cells cycled with different $V_{\text{CUT-OFF}}$, where (a) represents cells with $V_{\text{CUT-OFF}} = 4.2 \text{ V}$, and (b) cells with $V_{\text{CUT-OFF}} = 3.7 \text{ V}$.

For the purposes of this experiment, three-electrode experimental NMC622/graphite cells containing either LiFSI- or LiPF₆-based electrolyte in carbonate solvents were assembled. The cyclic experiment was conducted at room temperature (25 °C) and elevated temperature (50 °C). The influence of the high-voltage operation (up to 4.2 V) was compared with the operation up to 3.7 V, which is expected to maintain the stability of the protective Al₂O₃ layer. The electrochemical characterisation was conducted via EIS, while it was supported by post-mortem characterisation via SEM. The cycling was conducted at the ambient temperature of the temperature-controlled laboratory at 25 °C with a temperature fluctuation of $\pm 0.5 \text{ °C}$ and in an environmental chamber at stable 50 °C. After an entry/removal of the samples into/from the chamber, cells were allowed to rest for 5 hours to ensure sufficient and even heating/cooling of the studied PAT-Cells since these cells are robust. These resting periods were also allowed for cells cycled at 25 °C to maintain high comparability. For samples cycled up to 4.2 V, electrochemical characterisation was performed via EIS at SOC 80% after each

25th cycle up to 100 cycles, while the EIS was realized in galvanostatic fashion and for the frequency range 100 kHz – 10 mHz. The SOC 80% was chosen to prevent a high concentration gradient during the measurements at high voltages. For samples cycled up to 3.7 V, EIS was performed for the same frequency range after the 100th cycle at SOC 100%. All cells were relaxed for 1 hour prior to EIS. All impedance measurements were performed at ambient temperature of the laboratory.

4.1 EIS characterisation of the cathode side of the studied cells

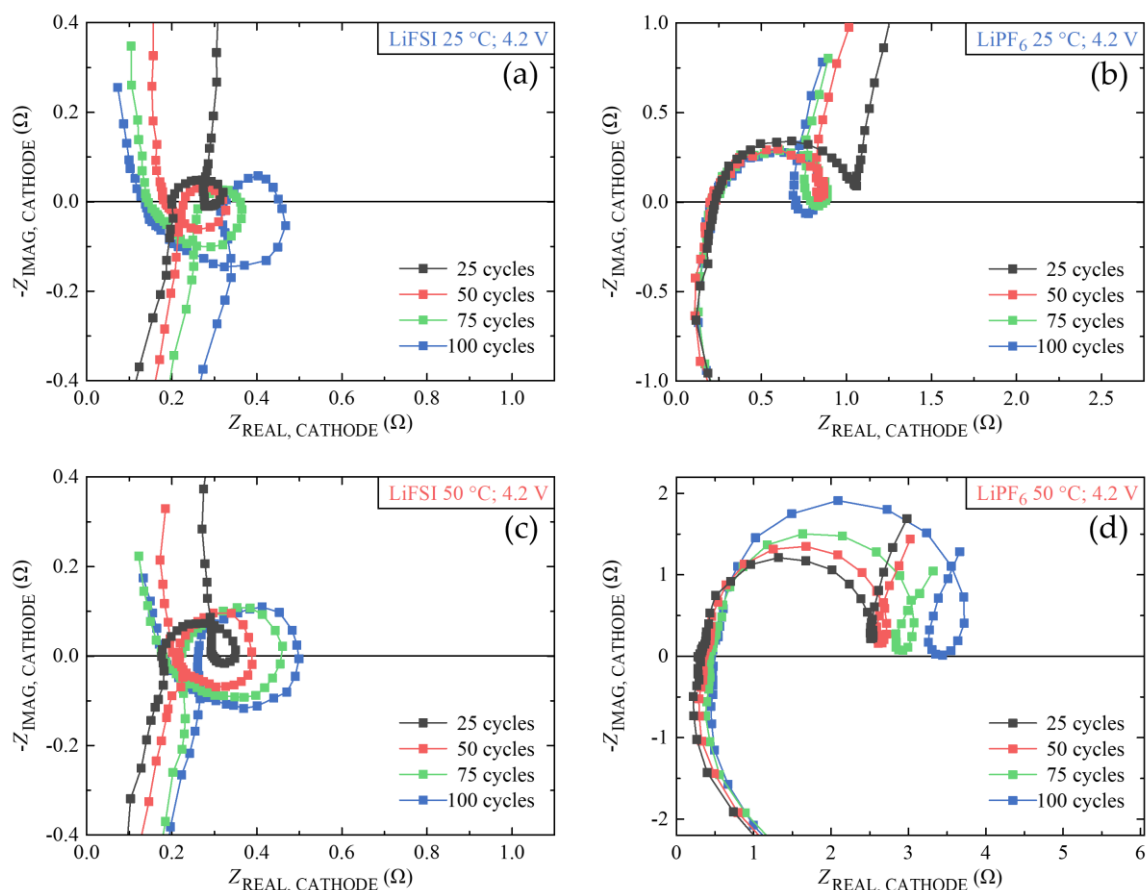


Figure 9 EIS data for the cathode side of studied cells cycled with $V_{\text{CUT-OFF}} = 4.2$ V, where (a) and (c) represent LiFSI-based cells cycled at 25 °C and 50 °C, respectively, and (b) and (d) represent LiPF₆-based cell cycled at 25 °C and 50 °C, respectively.

Figure 9a and Figure 9c display EIS data for the cathode side of LiFSI-based cells cycled up to 4.2 V at 25 °C and 50 °C, respectively. In both cases, small capacitive semi-circles at high- to mid-frequencies and severe induction loops at mid- to low-frequencies are observed. Given that these induction loops may strongly influence and overshadow the capacitive features of studied electrodes, parametrisation of these capacitive semi-circles by an equivalent electric circuit model is not included in this study to prevent any false conclusions. Nevertheless, by visual characterisation, it can be seen

that induction loops for cells cycled at 50 °C are slightly wider than those cycled at 25 °C. These induction loops can be ascribed to the corrosion of Al current collectors. The presence of this corrosion was confirmed by SEM (Figure 10). This corrosion is induced by the LiFSI-based electrolyte with carbonate solvents, which at high voltages can lead to the decomposition of the native Al₂O₃ layer and subsequently to the pitting corrosion of aluminium. Given the slightly wider nature of induction loops for cells cycled at 50 °C, it can be suspected that this corrosion occurs with a higher intensity.

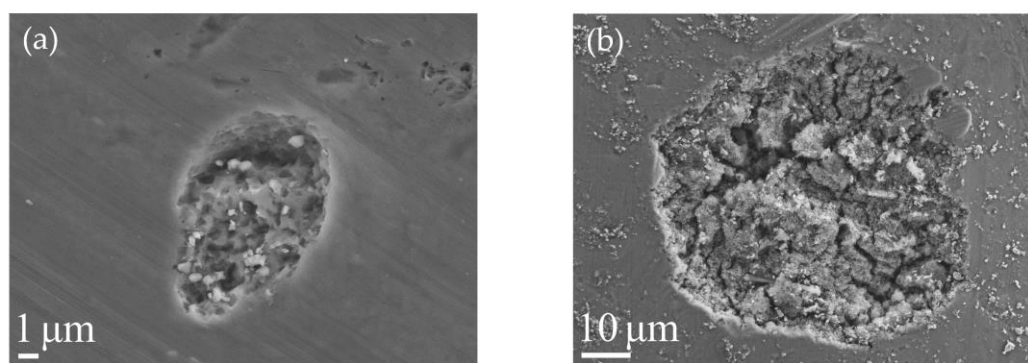


Figure 10 Selected SEM images revealing pitting corrosion of aluminium current collector for cells containing 1.0 LiFSI in EC:DMC 1:1 electrolyte, were (a) corresponds to the cell cycled at 25 °C and (b) to the cell cycled at 50 °C.

Nyquist plots of cathode sides of LiPF₆-based cells cycled up to 4.2 V at 25 °C and at 50 °C are displayed in Figure 9b and Figure 9d, respectively. Similarly to LiFSI-based cells, induction loops are observed. However, it can be seen that these loops have different shapes and follow different patterns. Mainly, inductive loops for LiFSI-based cells are circular, their onsets begin at positive values of Z_{IMAG} and at lower frequencies, and diffusion tails follow the circular pattern of the induction loops. For LiPF₆-based cells, induction loops are ellipsoidal, their onsets are in negative values of Z_{IMAG} and at higher frequencies, and diffusion tails turn towards higher values of Z_{REAL}. For the LiPF₆-based cell cycled at 25 °C, the Nyquist plot after the 25th cycle does not show any inductive loop, however, it has several data points for different low frequencies at approximately the same spot, which can be considered as an indication or precursor of possible future induction loop. At the 50th cycle, an induction loop appears, while it increases its magnitude for the duration of this experiment. Capacitive semi-circles for the 50th, 75th and 100th cycle show close-to-identical values, while the semi-circle for the 25th cycle is slightly wider. This supports the assumption that induction loops partially overshadow capacitive semi-circles, which can hinder their correct analysis via fitting. The occurrence and development of this induction loop can be ascribed to the presence of adsorbed inhibitors, which, in this case, create a protective AlF₃ layer. When this protective layer thickens, the capacitive semi-circle

increases its values. This is in agreement with Nyquist plots for the LiPF_6 -based cell cycled at $50\text{ }^\circ\text{C}$, where induction loops of similar magnitude and shape are observed, however, capacitive semi-circle increases dramatically with cycling. This can be explained by the thermally-induced decomposition of LiPF_6 and subsequent generation of HF , which can result in a thicker AlF_3 layer or in the formation of the LiF layer. As a reflection to these findings, a new batch of cells was prepared, while in this case, $V_{\text{CUT-OFF}}$ was decreased from 4.2 V to 3.7 V in order to maintain the protective Al_2O_3 layer, which is stable up to $\sim 3.8\text{ V}$ vs Li/Li^+ . The aim is to confirm (or disprove) the above-presented results and explanations. Nyquist plots after 100 cycles with $V_{\text{CUT-OFF}} = 3.7\text{ V}$ for LiFSI-based cells are displayed in [Figure 11a](#) and for LiPF_6 -based cells in [Figure 11b](#).

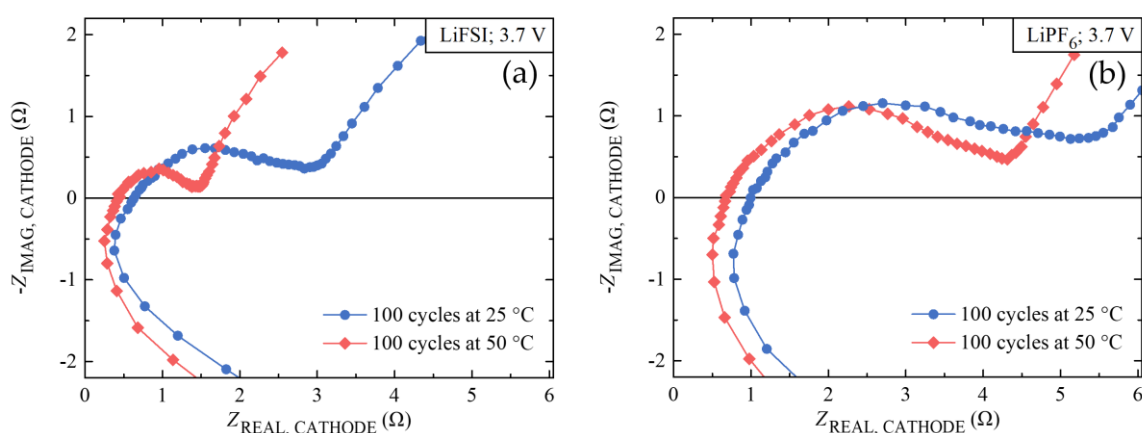


Figure 11 EIS data for the cathode side of studied cells cycled with $V_{\text{CUT-OFF}} = 3.7\text{ V}$, where (a) represents LiFSI-based cells and (b) LiPF_6 -based cells.

For LiPF_6 -based cells cycled up to 3.7 V at $25\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$, EIS shows Nyquist plots with almost identical shape and magnitude and with a mild shift towards lower Z_{REAL} for $50\text{ }^\circ\text{C}$ which can be ascribed to better conductivity of the system at higher temperatures. Based on this, it can be stated that thermally-induced decomposition of LiPF_6 -based electrolyte did not take place or was insignificant. These Nyquist plots do not show any induction loops, suggesting that under these circumstances, repassivation of Al_2O_3 with AlF_3 did not occur. For LiFSI-based cells cycled up to 3.7 V , induction loops are not present, suggesting that corrosion of the aluminium current collector is suppressed. The presence of the pitting corrosion of aluminium current collectors for LiFSI-based cells cycled up to 4.2 V and the absence of this corrosion for LiFSI-based cells cycled up to 3.7 V and for all LiPF_6 -based cells were confirmed by SEM.

4.2 EIS characterisation of the anode side of the studied cells

This subchapter discusses EIS data for the anode sides of the studied cells. Parametrisation by an equivalent electric circuit model was performed, and its results are displayed in Figure 12.

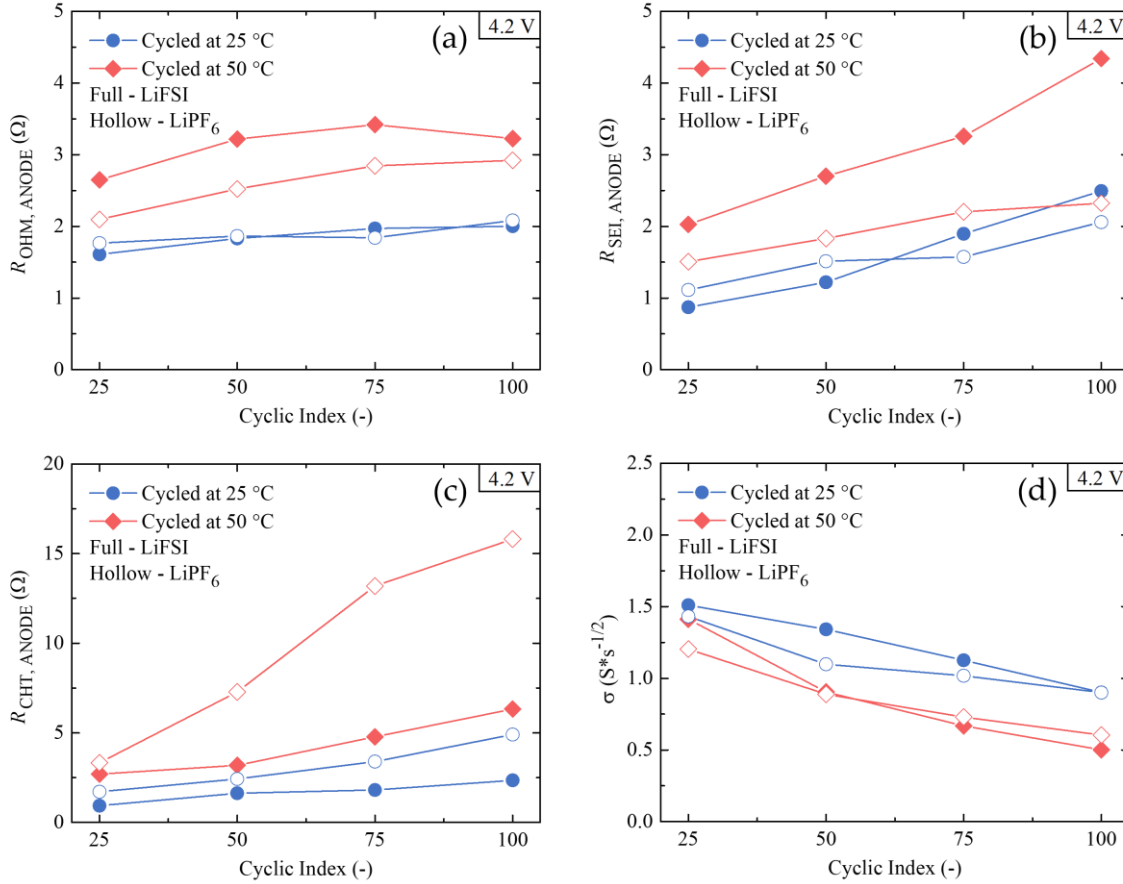


Figure 12 Results of the anode side EIS data fitting via equivalent electric circuit model.

Figure 12a shows ohmic resistance for the anode side of the studied cells for an increasing number of cycles. For the LiPF₆-based cell at 25 °C, $R_{OHM, ANODE}$ increases only slightly with cycling. These changes are more profound at 50 °C, where $R_{OHM, ANODE}$ increases quasi-linearly and at a higher pace. This can be ascribed to conductivity losses caused by thermally-induced decomposition of electrolytes. For the LiFSI-based cell at 25 °C, $R_{OHM, ANODE}$ remains stable and shows almost identical values and behaviour as it does for its LiPF₆ counterpart. However, at 50 °C, $R_{OHM, ANODE}$ of the LiFSI-based cell increases significantly. In the case of the LiFSI-based electrolyte, thermally-induced decomposition at 50 °C is unlikely, and therefore, it is necessary to look for another explanation. Given the presence of the corrosion of the aluminium current collector at the cathode side, it can be speculated that this corrosion led to electrolyte composition changes, which, under the elevated temperature, led to conductivity loss. Figure 12b shows the development of SEI layer resistances of studied cells. At 25 °C, $R_{SEI, ANODE}$ develops quasi linearly for both LiFSI- and LiPF₆-based cells, however, SEI layer

resistance of the LiFSI-based cell increases at a slightly higher pace. The LiPF₆-based cell shows slightly higher values when cycled at 50 °C than at 25 °C, while their development follows a similar trend. On the contrary, the LiFSI-based cell at 50 °C shows much higher values of $R_{\text{SEI, ANODE}}$ than at 25 °C, while this suggests unstable development of the SEI layer. This explanation is in agreement with the findings of *Su et al* [48], in which the authors conclude that 1.0 M LiFSI in regular carbonate solvents cycled at high voltages suffers from a low aggregation level, which results in an unstable SEI layer. Values of the charge-transfer resistance of the anode side of studied batteries ($R_{\text{CHT, ANODE}}$) are displayed in Figure 12c. The LiFSI-based cell cycled at 25 °C shows very low values of $R_{\text{CHT, ANODE}}$ with only slight increments with cycling, while these increments are more profound at 50 °C. The LiPF₆-based cell at 25 °C shows higher values of $R_{\text{CHT, ANODE}}$ as its LiFSI counterpart, however, this development can still be considered stable. This is not the case for the LiPF₆-based cell cycled at 50 °C. In this scenario, $R_{\text{CHT, ANODE}}$ increases dramatically with cycling. To find the limiting factor of the charge-transfer process, it is necessary to consider all its dominant contributors. It is known that the charge-transfer of lithium ions covers several processes, starting from the de-solvation of the solvated Li⁺ as it enters the SEI, followed by the migration of de-solvated Li⁺ through the SEI layer and its subsequent intercalation into the graphite lattice, ending with its acceptance of an electron and becoming a lithium atom [58]. To distinguish between the impact of individual impedance contributors, several assumptions have to be made. Given the moderate cycling conditions that are not expected to cause any significant structural changes to graphite anodes, intercalation into the graphite lattice and formation of Li atoms are not considered as limiting factors of the charge-transfer process. If such structural damage had occurred, significant increments of $R_{\text{CHT, ANODE}}$ would be expected in all cells. This leaves the influence of de-solvation of solvated Li⁺ and migration of Li⁺ via the SEI layer to be considered. The contribution of both may be non-negligible [59][60][61][62], and selecting one of them as a limiting factor of the charge-transfer process may lead to a faulty oversight of the second one, and therefore, both of these processes are considered as dominant contributors to $R_{\text{CHT, ANODE}}$. Considering these assumptions, as a possible explanation of dramatically increasing values of $R_{\text{CHT, ANODE}}$ of the LiPF₆-based cell cycled at 50 °C authors propose a gradual evolution of SEI layer upon cycling as de-solvation of solvated Li⁺ takes place, while these newly grown SEI layer compounds suffer from low ionic conductivity. Figure 12d displays values of Warburg coefficients of anode sides of studied cells. This plot shows that LiFSI- and LiPF₆-based cells at 25 °C follow the same decreasing trend and display highly comparable values. The same is true for cells cycled at 50 °C. This indifference between Warburg coefficients of cells with various electrolytes suggests that neither of these electrolytes led to significant morphological changes of active anode material.

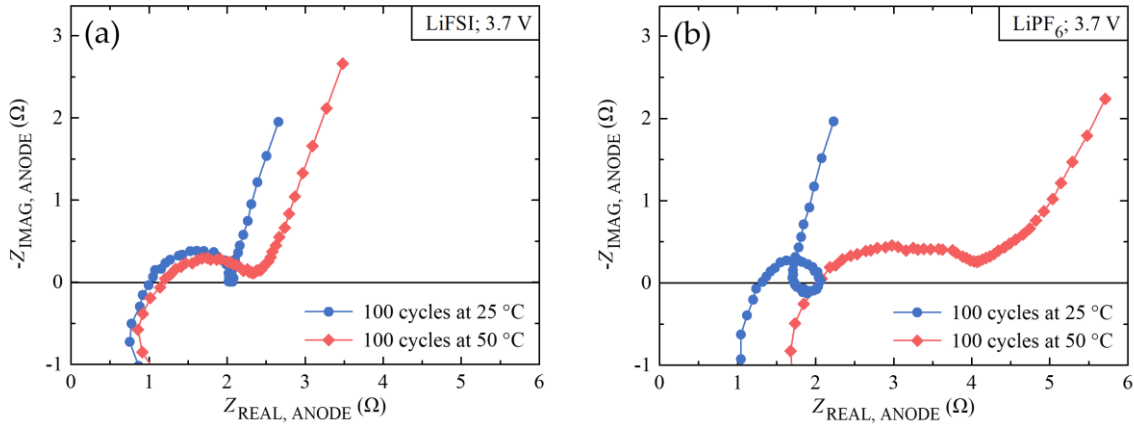


Figure 13 EIS data for the anode side of studied cells cycled with $V_{\text{CUT-OFF}} = 3.7$ V, where (a) represents LiFSI-based cells and (b) LiPF₆-based cells.

Nyquist plots for cells cycled for 100 cycles with $V_{\text{CUT-OFF}} = 3.7$ V are provided in Figure 13. At 25 °C, EIS spectra for both LiFSI- and LiPF₆-based cells contain induction loops, which hinder the parametrisation and evaluation of these spectra. These loops are not uncommon phenomena when it comes to three-electrode measurements of the anode side of the battery, however, their interpretation is troublesome. The current state of the scientific debate about these loops' origins is insufficient, and it attributes several contrasting origins to these features [63]. Since the here-presented experiment is not constructed in a way that would make it suitable to analyse such loops, it was decided not to include these measurements in the discussion of this work, however, they are displayed for completeness.

At 50 °C, the LiFSI-based cell outperforms its LiPF₆ counterpart in all EIS features. Ohmic resistance is 1.29 Ω for the LiFSI-based cell and 2.16 Ω for the LiPF₆-based cell, suggesting that under these new operating conditions, LiFSI-based electrolyte results in higher conductivity than LiPF₆-based electrolyte. The value of $R_{\text{SEI, ANODE}}$ is 0.48 Ω for the LiFSI-based cell, while it is 0.59 Ω for the LiPF₆-based cell. These results suggest that decreasing the $V_{\text{CUT-OFF}}$ from 4.2 V to 3.7 V enables NMC/graphite with LiFSI-based electrolyte to form a more stable SEI layer. The parametrisation of charge-transfer processes yielded $R_{\text{CHT, ANODE}}$ of 0.44 Ω for the LiFSI-based cell and 1.25 Ω for the LiPF₆-based cell. Such a significant difference shows that LiPF₆-based electrolyte at elevated temperatures keeps struggling with low ionic conductivity, regardless of the decreased $V_{\text{CUT-OFF}}$. Warburg coefficients are 2.65 S.s^{-1/2} for the LiFSI-based cell and 2.09 S.s^{-1/2} for the LiPF₆-based cell, which are significantly higher values than those for cells cycled up to 4.2 V. These high values are in agreement with results discussed in [64], where it is described that under certain situations cycling can increase d-spacing of the graphite anode, what leads to higher D_{Li^+} .

4.3 Conclusion of the research conducted at IMA NV NTNU

The LiFSI-based electrolyte led to the corrosion of aluminium current collectors in cells cycled up to 4.2 V. This corrosion was observed via induction loops for cells cycled at both 25 °C and 50 °C, while its presence was confirmed by SEM. When $V_{\text{CUT-OFF}}$ was decreased to 3.7 V, these induction loops were not observed. This shows that decreasing $V_{\text{CUT-OFF}}$ enabled the current collector to maintain its Al_2O_3 protective layer, and hence, it suppressed the corrosion of Al. Induction loops are also observed for LiPF_6 -based cells cycled up to 4.2 V, however, these loops have a different shape, magnitude and frequency on-set, and they are ascribed to the different origin - the repassivation of the Al current collector with AlF_3 layer. At 50 °C, capacitive semi-circle increases with cycling, which is ascribed to the thermally-induced decomposition of electrolyte and subsequent generation of HF, resulting in a thicker AlF_3 layer and/or LiF layer formation. When cycled up to 3.7 V, EIS indicates that the protective Al_2O_3 layer remains stable, and the decomposition of the LiPF_6 -based electrolyte does not take place or is insignificant. Regarding the anode side, several observations are made. The ohmic resistance of LiFSI- and LiPF_6 -based cells increases when cycled at 50 °C up to 4.2 V. This increase for the LiPF_6 -based cell is considered to originate in thermally-induced electrolyte decomposition, leading to conductivity loss. For the LiFSI-based cell, it is speculated that the Al corrosion leads to electrolyte composition changes, which negatively affect the conductivity of such electrolytes at elevated temperatures. Concerning the SEI layer, EIS measurements suggest that the LiFSI-based cell cycled up to 4.2 V forms an unstable SEI layer, while this instability is elevated when cycled at 50 °C. The SEI layer of LiPF_6 -based cells appears to be more stable, however, significantly increasing R_{CHT} with cycling at 50 °C suggests gradual evolution of the SEI layer as de-solvation of solvated Li^+ takes place, while these newly grown SEI layer compounds suffer from low ionic conductivity. When $V_{\text{CUT-OFF}}$ is decreased to 3.7 V, LiFSI-based electrolyte seems to form a more stable SEI layer than its LiPF_6 counterpart, while LiPF_6 keeps struggling with high R_{CHT} . The experiments conducted within the third objective suggest that NMC622/graphite cells containing experimental 1.0 M LiFSI in EC:DMC 1:1 electrolyte outperform cells containing commercial 1.0 M LiPF_6 in EC:DEC 1:1 in all studied features when cycled up to 3.7 V at both 25 °C and 50 °C, however, LiFSI-based electrolyte leads to the corrosion of Al current collector when cycled up to 4.2 V. In order to utilize LiFSI for high-voltage cathode Li-ion batteries, it is necessary to address this issue. This work provides a cornerstone of electrochemical characterisation of individual electrodes via EIS for future experiments focused on ways how to adjust LiFSI-based electrolytes in order to suppress the corrosion of Al current collectors, which hinders their usage for high-voltage Li-ion batteries capable of competitive operation at elevated temperatures.

5 SUMMARY OF THE DISSERTATION

The aim of this dissertation work, when put into one sentence, was to study degradation mechanisms in commercial and experimental Ni-based Li-ion batteries via methods of non-destructive electrochemical characterisation. This work is further summarized in the following paragraphs.

The first part of this work provides an overview of the principles of I. Li-ion batteries, II. their degradation mechanisms, and III. methods of their non-destructive electrochemical characterisation. Different ways of implementation of characterisation methods such as electrochemical impedance spectroscopy (EIS), incremental capacity analysis (ICA) and galvanostatic intermittent titration technique (GITT) were studied in order to successfully establish research in this area at the *Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava (ÚEF FEI STU)*. Aside from this, scientific literature dealing with LiFSI- and LiPF₆-based electrolytes in various carbonate solvents for Ni-rich Li-ion batteries operating at various temperatures was studied extensively in order to obtain a broad knowledgebase for experiments conducted at the *Department of Materials Science and Engineering, Faculty of Natural Sciences, Norwegian University of Science and Technology (IMA NV NTNU)*.

The set of experiments designed to tackle the second objective was conducted at the ÚEF FEI STU. This work aimed to provide a comprehensive electrochemical analysis of degradation in commercial 18650 NCA-based Li-ion batteries, while this degradation was elevated by various stress-inducing scenarios. These scenarios were over-charging, under-charging, and charging with above-recommended currents. Results of this work were published in the journal *Batteries* [54], while to the best of the authors' knowledge, this was the first work analysing stress-induced degradation of NCA batteries simultaneously by EIS, ICA, and GITT. This work demonstrates that each of these methods provides a unique set of information about the battery's condition, however, only joint usage of these methods leads to a comprehensive and more profound understanding of the battery's condition. Moreover, the simultaneous usage of various confirmatory techniques enables the assignment of the origin of degradation with higher certainty. Battery analysis performed in this fashion relieves experiments of the otherwise necessary assumptions arising from two-electrode measurements.

The set of experiments that aimed to address the third objective was conducted at the IMA NV NTNU. In these experiments, characterisations via EIS supported by SEM are used to study LiFSI-based electrolytes as an alternative to commonly used LiPF₆-based electrolytes for experimental NMC622/graphite cells operating at 25 °C and 50 °C. The construction of these cells made it possible to perform EIS in a three-electrode fashion, allowing the analysis of the impedance features of both electrodes separately. The results suggest that NMC622/graphite cells containing

experimental 1.0 M LiFSI in EC:DMC 1:1 electrolyte outperform cells containing commercial 1.0 M LiPF₆ in EC:DEC 1:1 in all features studied via EIS when cycled up to 3.7 V at both 25 °C and 50 °C, however, LiFSI-based electrolyte leads to the corrosion of aluminium current collector when cycled up to 4.2 V. The presence of this corrosion was suggested by EIS and confirmed by SEM. In order to utilize LiFSI-based electrolytes for high-voltage Li-ion batteries, it is necessary to address this issue. In the case of LiPF₆-based cells cycled up to 4.2 V, EIS points to the repassivation of the Al current collector, where HF transforms the native protective Al₂O₃ layer into a passivation AlF₃ layer. Moreover, measurements of the cell cycled at 50 °C suggest that the AlF₃ layer is getting continuously more robust. This can be ascribed to thermally-induced higher generation of HF, which can result in such development of this layer. When cycled up to 3.7 V, measurements indicate that the Al₂O₃ layer remains stable and fulfils its protective function. This work provides a cornerstone of electrochemical characterisation of individual electrodes via EIS for future experiments focused on adjusting LiFSI-based electrolytes to suppress the corrosion of Al current collectors. It is suspected that solving this issue will enable wide implementation of LiFSI-based electrolytes for high-voltage Ni-rich Li-ion batteries with superior characteristics when compared to commonly used LiPF₆-based electrolytes.

The main results of this work are: I. Published demonstration [54] of comprehensive degradation characterisation of commercial NCA Li-ion batteries via methods of electrochemical characterisation (EIS, ICA, GITT) for various stress-inducing scenarios. This study shows that simultaneous usage of various confirmatory techniques enables degradation analysis of Li-ion batteries with higher certainty while it can relieve the experiment of otherwise necessary assumptions. II. Experimental NMC622/graphite cells cycled up to 3.7 V at 25 °C and 50 °C containing 1.0 M LiFSI in EC:DMC 1:1 electrolyte outperformed cells containing commercial 1.0 M LiPF₆ in EC:DEC 1:1 electrolyte at both temperatures in all studied features. III. The LiFSI-based electrolyte in NMC622/graphite cells cycled up to 4.2 V at 25 °C and 50 °C led to the corrosion of the Al current collectors at both temperatures. IV. The LiPF₆-based electrolyte in NMC622/graphite cells cycled up to 4.2 V led to the repassivation of the Al current collector with AlF₃. Measurements suggested that the AlF₃ layer had become more robust when the cell was cycled at 50 °C. This was ascribed to the thermally-induced generation of HF. When cycled up to 3.7 V, measurements indicated that the native protective Al₂O₃ layer remained stable. V. The cornerstone of the electrochemical characterisation of individual electrodes via EIS was established for future experiments focused on adjusting LiFSI-based electrolytes in order to suppress the corrosion of Al current collectors. VI. The methods of electrochemical characterisation for the study of Li-ion batteries were successfully established at the ÚEF FEI STU.

6 RESUMÉ IN SLOVAK LANGUAGE

Táto práca sa zameriava na identifikáciu a analýzu prebiehajúcich degradačných dejov v Li-ion batériách s katódami na báze niklu pomocou metód elektrochemickej charakterizácie, akými sú napríklad elektrochemická impedančná spektroskopia (EIS), galvanostatická prerušovaná titračná technika (GITT), a inkrementálna kapacitná analýza (ICA). Tieto metódy umožňujú skúmať degradačné deje, akými sú napríklad hrubnutie vrstvy na rozhraní elektrolytu a anódy (SEI vrstva), exfoliácia grafitu, tvorba lítiových dendritov, či korózia zberačov prúdu. Experimentálna práca realizovaná v rámci tejto dizertačnej práce pozostáva z dvoch samostatných celkov, pričom každý z nich bol realizovaný na inom pracovisku.

Prvý súbor experimentov riešených v tejto práci bol realizovaný na *Inštitúte elektroniky a fotoniky, Fakulty elektrotechniky a informatiky, Slovenskej Technickej Univerzity v Bratislave* (ÚEF FEI STU). Hlavným cieľom tohto celku bolo poskytnúť rozsiahlu elektrochemickú analýzu degradačných dejov v komerčných NCA Li-ion batériách, pričom ich degradácia bola umocnená viacerými scenármi urýchľujúcich degradáciu, akým je napríklad nabíjanie vysokým prúdom. Taktiež je dôležité spomenúť, že popri výskumnej práci boli úspešne implementované a rozvinuté metódy elektrochemickej charakterizácie Li-ion batérií na tomto pracovisku.

Druhý súbor experimentov bol realizovaný na *Oddelení materiálových vied a inžinierstva, Fakulty prírodných vied, Nórskej Univerzity Vedy a Techniky* (IMA NV NTNU). V tejto práci bola použitá elektrochemická charakterizácia podporená analýzou pomocou skenovacieho elektrónového mikroskopu (SEM) na skúmanie elektrolytov na báze LiFSI ako alternatívy k bežne používaným elektrolytom na báze LiPF₆ pre na-nikel-bohaté NMC Li-ion batérie operujúce pri vysokých teplotách. Na rozdiel od experimentov s komerčnými batériami realizovanými na ÚEF FEI STU, v prípade týchto experimentov boli použité experimentálne články, ktoré umožňujú použitie referenčných lítiových elektród, vďaka čomu je možné separovať a skúmať procesy prebiehajúce na jednotlivých elektródach.

V rámci experimentov realizovaných na ÚEF FEI STU bola analyzovaná degradácia komerčných 18650 NCA batérií prostredníctvom metód nedeštruktívnej elektrochemickej charakterizácie pri scenároch urýchľujúcich degradáciu, ktorými boli prebíjanie, podbíjanie, a nabíjanie vysokým prúdom. Na základe nadobudnutých poznatkov o aktuálnom stave problematiky a po vyčerpávajúcom štúdiu odbornej literatúry autori dospeli k záveru, že sa jedná o prvú prácu zaoberajúcu sa rozsiahlou analýzou takto urýchlených degradačných procesov v komerčných NCA Li-ion batériách pomocou simultánneho použitia metód EIS, GITT a ICA. Táto práca demonštruje, že každá z týchto metód poskytuje unikátne informácie o stave skúmanej batérie, avšak iba spoločné a komparatívne použitie týchto metód vedie ku komplexnejšiemu porozumeniu prebiehajúcich

degradačných procesov na elektródovej úrovni bez nutnosti rozobrať skúmanú batériu. Analýza batérií vykonaná takýmto spôsobom znižuje počet nevyhnutných domniek pri vyhodnocovaní dvojelektródových meraní.

Experimenty realizované na IMA NV NTNU poukazujú, že NMC622/grafit články cyklované do 3.7 V pri 25 °C a 50 °C obsahujúce experimentálny 1.0 LiFSI v EC:DMC 1:1 elektrolyt prekonávajú vzorky obsahujúce komerčný 1.0 M LPF₆ v EC:DEC 1:1 všetkých skúmaných parametroch, avšak elektrolyt na báze LiFSI vedie ku korózii hliníkového zberača prúdu pri cyklovaní do 4,2 V. Pre implementáciu elektrolytov na báze LiFSI pre vysoko-napäťové Li-ion batérie je nevyhnutné vyriešiť tento problém. Táto práca poskytuje širokú charakterizačnú bázu pomocou EIS pre budúce experimenty hľadajúce spôsoby ako potlačiť koróziu hliníkových zberačov prúdu pri použití takýchto elektrolytov, ktorá je limitujúcim faktorom pre uplatnenie LiFSI vo vysoko-napäťových Li-ion batériách schopných operácie aj pri vysokých teplotách.

Hlavnými prínosmi tejto práce sú: I. Publikovaná demonštrácia [54] rozsiahlej charakterizácie degradačných mechanizmov v komerčných 18650 NCA Li-ion batériách pomocou metód elektrochemickej charakterizácie (EIS, GITT, ICA) pre rôzne scenáre urýchľujúce degradáciu. Táto práca demonštruje ako simultánne použitie viacerých komplementárnych metód umožňuje analýzu degradácie s vyššou presnosťou, a odbremeňuje experiment od viacerých inak nevyhnutných domniek vyplývajúcich z dvoj-elektródových meraní. II. Experimentálne NMC622/grafit články cyklované do 3,7 V pri 25 °C a 50 °C obsahujúce experimentálny 1,0 M LiFSI v EC:DMC 1:1 elektrolyt prekonali vzorky s komerčným 1,0 M LiPF₆ v EC:DEC 1:1 elektrolytom vo všetkých skúmaných parametroch pri oboch teplotách. III. Elektrolyt na báze LiFSI v NMC622/grafit batériách pri cyklovaní do 4,2 V pri 25 °C a 50 °C viedol ku korózii hliníkových zberačov prúdu pri oboch teplotách. IV. Elektrolyt na báze LiPF₆ v NMC622/grafit batériách cyklovaných do 4,2 V viedol k repasivácii hliníkových zberačov prúdu vrstvou AlF₃. Merania nasvedčujú, že cyklovanie pri 50 °C viedlo k hrubnutiu AlF₃ vrstvy, pričom toto hrubnutie je možné označiť za dôsledok termálne-urýchlenej dekompozície elektrolytu a generácie HF. Pri cyklovaní do 3,7 V EIS merania poukazujú na stabilnú Al₂O₃ vrstvu. V. Práca poskytuje širokú charakterizačnú bázu pomocou EIS na elektródovej úrovni pre budúce experimenty zamerané na modifikáciu elektrolytov na báze LiFSI s cieľom potlačiť koróziu hliníkových zberačov prúdu. VI. V rámci procesu riešenia tejto práce boli zavedené a rozvinuté metódy elektrochemickej charakterizácie v oblasti Li-ion batérií na *Ústave elektroniky a fotoniky, Fakulty elektrotechniky a informatiky, Slovenskej Technickej Univerzity v Bratislave*.

7 REFERENCES

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8 PUBLICATION ACTIVITIES

Scientific works in foreign peer-reviewed journals

- ADC01 **KEMÉNY, Martin [70 %]** - ONDREJKA, Peter [10 %] - MIKOLÁŠEK, Miroslav [20 %]. Comprehensive degradation analysis of NCA Li-Ion batteries via methods of electrochemical characterisation for various stress-inducing scenarios. In *Batteries*. Vol. 9, Iss.1 (2023), Art. no. 33 [22] s. ISSN 2313-0105 (2022: 4.000 - IF, Q2 - JCR Best Q, 0.763 - SJR, Q2 - SJR Best Q). DOI: 10.3390/batteries9010033; SCOPUS: 2-s2.0-85146810055; WOS: 000916979500001; CC: 000916979500001.
- ADC02 **KEMÉNY, Martin [30 %]** - ONDREJKA, Peter [10 %] - WEIS, Martin [15 %] - HURAN, Jozef [5 %] - ANDOK, Robert [5 %] - HOTOVÝ, Ivan [5 %] - MIKOLÁŠEK, Miroslav [30 %]. Plasmonic enhanced photo-electrochemical water splitting on amorphous silicon structures. In *Optik*. Vol. 257, (2022), Art. no. 168769 [9] s. ISSN 0030-4026 (2022: 3.100 - IF, Q2 - JCR Best Q, 0.539 - SJR, Q2 - SJR Best Q). SCOPUS: 2-s2.0-85125587235; WOS: 000783890200001; CC: 000783890200001; DOI: 10.1016/j.ijleo.2022.168769.
- ADC03 ONDREJKA, Peter [50 %] - SOJKOVÁ, Michaela [15 %] - KOTOK, Valerii [5 %] - NOVÁK, Patrik [10 %] - HOTOVÝ, Ivan [5 %] - **KEMÉNY, Martin [5 %]** - MIKOLÁŠEK, Miroslav [10 %]. Tuning the electrochemical properties of NiS₂ 2D-nanoflakes by one-zone sulfurization for supercapacitor applications. In *Materials Research Express*. Vol. 10, iss. 6 (2023), Art. no. 065508 [10] s. ISSN 2053-1591 (2022: 2.300 - IF, Q3 - JCR Best Q, 0.401 - SJR, Q2 - SJR Best Q). DOI: 10.1088/2053-1591/acdfaa; WOS: 001019148200001; CC: 001019148200001; SCOPUS: 2-s2.0-85164226747.
- ADC04 SAHOO, Prangya [20 %] - MIKOLÁŠEK, Miroslav [20 %] - HUŠEKOVÁ, Kristína [10 %] - DOBROČKA, Edmund [5 %] - ŠOLTÝS, Ján [5 %] - ONDREJKA, Peter [10 %] - **KEMÉNY, Martin [10 %]** - HARMATHA, Ladislav [1 %] - MIČUŠÍK, Matej [9 %] - FRÖHLICH, Karol [10 %]. Si-based metal-insulator-semiconductor structures with RuO₂-(IrO₂) films for photoelectrochemical water oxidation. In *ACS Applied Energy Materials*. Vol. 4, Iss, 10 (2021), s. 11162-11172. ISSN 2574-0962 (2021: 6.959 - IF, Q1 - JCR Best Q, 1.613 - SJR, Q1 - SJR Best Q). CC: 000711236300077; WOS: 000711236300077; SCOPUS: 2-s2.0-85117754638; DOI: 10.1021/acsaem.1c02021.

Scientific works in domestic journals registered in WOS or SCOPUS databases

- ADN01 HOTOVÝ, Ivan [30 %] - ŘEHÁČEK, Vlastimil [20 %] - **KEMÉNY, Martin [15 %]** - ONDREJKA, Peter [10 %] - KOSTIČ, Ivan [10 %] - MIKOLÁŠEK, Miroslav [10 %] - SPIESS, Lothar [5 %]. Preparation and gas-sensing properties of very thin sputtered NiO films. In *Journal of Electrical Engineering*. Vol. 72, No. 1 (2021), s. 61-65. ISSN 1335-3632 (2021: 0.840 - IF, Q4 - JCR Best Q, 0.200 - SJR, Q4 - SJR Best Q). SCOPUS: 2-s2.0-85103272862; WOS: 000681642800009; DOI: 10.2478/jee-2021-0009.
- ADN02 MIKOLÁŠEK, Miroslav [30 %] - FRÖHLICH, Karol [10 %] - HUŠEKOVÁ, Kristína [10 %] - ONDREJKA, Peter [10 %] - CHYMO, Filip [15 %] - **KEMÉNY, Martin [10 %]** - HOTOVÝ, Ivan [10 %] - HARMATHA, Ladislav [5 %]. Development and characterisation of photoelectrochemical MIS structures with RuO₂/TiO₂ gate stacs for water oxidation. In *Journal of Electrical Engineering*. Vol. 72, No. 3 (2021), s. 203-207. ISSN 1335-3632 (2021: 0.840 - IF, Q4 - JCR Best Q, 0.200 - SJR, Q4 - SJR Best Q). DOI: 10.2478/jee-2021-0028; WOS: 000681684100008.

ADN03 ONDREJKA, Peter [55 %] - **KEMÉNY, Martin [10 %]** - DUBINA, Matúš [10 %] - NOVÁK, Patrik [10 %] - HOTOVÝ, Ivan [5 %] - MIKOLÁŠEK, Miroslav [10 %]. Supercapacitors and energy conversion structures based on WS₂ and MoS₂ disulfides. In *Journal of Electrical Engineering*. Vol. 72, No. 4 (2021), s. 256-261. ISSN 1335-3632 (2021: 0.840 - IF, Q4 - JCR Best Q, 0.200 - SJR, Q4 - SJR Best Q). WOS: 000696957400005; DOI: 10.2478/jee-2021-0035.

Published contributions at foreign scientific conferences

AFC01 MIKOLÁŠEK, Miroslav [60 %] - **KEMÉNY, Martin [30 %]** - ONDREJKA, Peter [10 %]. Analysis of Li-ion battery degradation mechanism by EIS, GITT and ICA and their possible utilization for SOH monitoring. In *ABAF 2022 : 23th International Conference on Advanced Batteries, Acumulators and Fuel Cells. Brno, Czech Republic. August 21-24, 2022*. Brno: Brno University of Technology, 2022, S. 77-79. ISBN 978-80-214-6088-1.

Published contributions at domestic scientific conferences

AFD01 **KEMÉNY, Martin [70 %]** - ONDREJKA, Peter [10 %] - MIKOLÁŠEK, Miroslav [20 %]. Incremental capacity analysis for prediction of Li-Ion battery degradation mechanisms: simulation study. In *ASDAM 2020 : 13th International conference on advanced semiconductor devices and microsystems. Smolenice, Slovakia. October 11-14, 2020*. 1. ed. Danvers: IEEE, 2020, S. 19-22. ISSN 2474-9737. ISBN 978-1-7281-9776-0. V databáze: SCOPUS: 2-s2.0-85104567707; WOS: 000669651600005; IEEE: 9393834; DOI: 10.1109/ASDAM50306.2020.9393834.

AFD02 **KEMÉNY, Martin [55 %]** - ONDREJKA, Peter [20 %] - MIKOLÁŠEK, Miroslav [25 %]. Impedance characterization of Li-ion batteries for ageing mechanism analysis. In *ADEPT 2021: 9th International conference on advances in electronic and photonic technologies. Podbanské, Slovakia. September 20-23.2021*. 1. vyd. Žilina : Publisher EDIS, 2021, S. 111-114. ISBN 978-80-554-1806-3.

AFD03 **KEMÉNY, Martin [60 %]** - ONDREJKA, Peter [10 %] - MIKOLÁŠEK, Miroslav [30 %]. Incremental capacity analysis (ICA) via galvanostatic intermittent titration technique (GITT) data for battery degradation study. In *ASDAM 2022 : 14th International conference on advanced semiconductor devices and microsystems. Smolenice, Slovakia. October 23-26, 2022*. 1. ed. Danvers: IEEE, 2022, S. 21-24. ISBN 978-1-6654-6977-7. DOI: 10.1109/ASDAM55965.2022.9966773; IEEE: 9966773; SCOPUS: 2-s2.0-85144596054.

AFD04 MIKOLÁŠEK, Miroslav [65 %] - **KEMÉNY, Martin [5 %]** - CHYMO, Filip [5 %] - ONDREJKA, Peter [20 %] - HURAN, Jozef [5 %]. Amorphous silicon PEC-PV hybrid structure for photo-electrochemical water splitting. In *Journal of Electrical Engineering: 19th Solid State Surfaces and Interfaces 2018. Smolenice, Slovakia. November 19-22, 2018*. Vol. 70, No. 7s (2019), s. 107-111. ISSN 1335-3632 (2019: 0.686 - IF, Q4 - JCR Best Q, 0.204 - SJR, Q3 - SJR Best Q). SCOPUS: 2-s2.0-85073789117 ; WOS: 000489301300015; DOI: 10.2478/jee-2019-0050.

AFD05 MIKOLÁŠEK, Miroslav [55 %] - **KEMÉNY, Martin [25 %]** - ONDREJKA, Peter [20 %]. Analysis of Li-ion battery degradation mechanism by advanced electrical characterization. In *ADEPT 2021: 9th International conference on advances in electronic and photonic technologies. Podbanské, Slovakia. September 20-23.2021*. 1. vyd. Žilina: Publisher EDIS, 2021, S. 25-28. ISBN 978-80-554-1806-3.

AFD06 MIKOLÁŠEK, Miroslav [55 %] - **KEMÉNY, Martin [25 %]** - ONDREJKA, Peter [10 %] - NOVÁK, Matej [10 %]. Electrical characterisation techniques for Li-ion battery degradation analysis and state of health estimation. In *ASDAM 2022: 14th International conference on*

advanced semiconductor devices and microsystems. Smolenice, Slovakia. October 23-26, 2022. 1. ed. Danvers: IEEE, 2022, S. 79-82. ISBN 978-1-6654-6977-7. DOI: 10.1109/ASDAM55965.2022.9966792; IEEE: 9966792; SCOPUS: 2-s2.0-85144594139.

- AFD07 ONDREJKA, Peter [50 %] - **KEMÉNY, Martin [10 %]** - ŘEHÁČEK, Vlastimil [10 %] - DUBINA, Matúš [10 %] - HOTOVÝ, Ivan [10 %] - MIKOLÁŠEK, Miroslav. MoS₂ supercapacitors for energy storage applications: Evaluation of morphological factor. In *ASDAM 2020: 13th International conference on advanced semiconductor devices and microsystems. Smolenice, Slovakia. October 11-14, 2020.* 1. ed. Danvers : IEEE, 2020, S. 23-26. ISSN 2474-9737. ISBN 978-1-7281-9776-0. SCOPUS: 2-s2.0-85104509052; WOS: 000669651600006 ; IEEE: 9393834; DOI: 10.1109/ASDAM50306.2020.9393838.
- AFD08 ONDREJKA, Peter [55 %] - **KEMÉNY, Martin [10 %]** - DUBINA, Matúš [10 %] - NOVÁK, Patrik [10 %] - HOTOVÝ, Ivan [5 %] - MIKOLÁŠEK, Miroslav [10 %]. MoS₂ disulfides based supercapacitors and water splitting structures. In *ADEPT 2021: 9th International conference on advances in electronic and photonic technologies. Podbanské, Slovakia. September 20-23.2021.* 1. vyd. Žilina: Publisher EDIS, 2021, S. 139-142. ISBN 978-80-554-1806-3.
- AFD09 ONDREJKA, Peter [55 %] - SOJKOVÁ, Michaela [10 %] - KOTOK, Valerii [5 %] - ZIMA, Oleksandra [3 %] - **KEMÉNY, Martin [5 %]** - NOVÁK, Patrik [10 %] - MIKOLÁŠEK, Miroslav [12 %]. Sulfurization of Ni-foam as a binder-free supercapacitor electrode. In *ASDAM 2022: 14th International conference on advanced semiconductor devices and microsystems. Smolenice, Slovakia. October 23-26, 2022.* 1. ed. Danvers: IEEE, 2022, S. 127-130. ISBN 978-1-6654-6977-7. DOI: 10.1109/ASDAM55965.2022.9966779; IEEE: 9966779; SCOPUS: 2-s2.0-85144598203.
- AFD10 CHYMO, Filip [40 %] - FRÖHLICH, Karol [10 %] - HARMATHA, Ladislav [5 %] - HUŠEKOVÁ, Kristína [10 %] - ONDREJKA, Peter [5 %] - **KEMÉNY, Martin [5 %]** - HOTOVÝ, Ivan [5 %] - MIKOLÁŠEK, Miroslav [20 %]. Development and characterization of photoelectrochemical MIS structures for hydrogen generation applications. In *ADEPT 2019 : 7th International conference on advances in electronic and photonic technologies. Štrbské Pleso, Slovakia. June 24-27, 2019.* 1. vyd. Žilina: Publisher EDIS, 2019, S. 103-106. ISBN 978-80-554-1568-0.

Abstracts of contributions from foreign conferences

- AFG01 MIKOLÁŠEK, Miroslav [30 %] - **KEMÉNY, Martin [10 %]** - ONDREJKA, Peter [20 %] - WEIS, Martin [10 %] - HURAN, Jozef [10 %] - ANDOK, Robert [10 %] - HOTOVÝ, Ivan [10 %]. Plasmonic enhanced photoelectrochemical water splitting. In *SURFINT - SREN VI : 6h Conference on Progress in applied surface, interface and thin film science. Extended abstract book. Florence, Italy. November 18-21, 2019.* Bratislava: Comenius University, 2019, S. 106. ISBN 978-80-223-4811-9.
- AFG02 SAHOO, Prangya P. [30 %] - **KEMÉNY, Martin [10 %]** - HUDEC, Boris [10 %] - MIKOLÁŠEK, Miroslav [10 %] - MÍČUŠÍK, Matej [10 %] - ŠIFFALOVÍČ, Peter [10 %] - STRAKOVÁ FEDORKOVÁ, Andrea [10 %] - FRÖHLICH, Karol [10 %]. Enhanced performance of LiFePO cathodes protected by atomic layer deposited ultrathin alumina films. In *ECS Meeting Abstracts, Volume MA2022-01: 242nd Electrochemical society Meeting. Atlanta, GA, USA. October 9-13, 2022.* Bristol: IOP Publishing, 2022, Art. no. 306 [2] s. ISSN 2151-2043. DOI: 10.1149/MA2022-023306mtgabs.

Abstracts of contributions from domestic conferences

- AFH01 **KEMÉNY, Martin [55 %]** - ONDREJKA, Peter [20 %] - MIKOLÁŠEK, Miroslav [25 %]. Advanced electrochemical characterisation and analysis of degradation mechanism in Li-ion battery. In *SURFINT - SREN VII : 7th Conference on Progress in applied surface, interface and thin film science. Extended abstract book. November 22-24, 2021*. Bratislava: Comenius University, 2021, S. 28. ISBN 978-80-223-5296-3.
- AFH02 MIKOLÁŠEK, Miroslav [40 %] - **KEMÉNY, Martin [15 %]** - CHYMO, Filip [15 %] - ONDREJKA, Peter [15 %] - HURAN, Jozef [15 %]. Amorphous silicon based structures for photo-electrochemical and photovoltaic energy generation. In *SSSI 2018: Extended abstract book : 10th International conference solid state surfaces and interfaces. Smolenice, Slovak Republic. November 19-22, 2018*. Bratislava: Comenius University, 2018, S. 55-56. ISBN 978-80-223-4606-1.
- AFH03 MIKOLÁŠEK, Miroslav [35 %] - FRÖHLICH, Karol [15 %] - CHYMO, Filip [10 %] - ONDREJKA, Peter [10 %] - **KEMÉNY, Martin [10 %]** - ŘEHÁČEK, Vlastimil [10 %] - HUŠEKOVÁ, Kristína [10 %]. Silicon based water splitting IMIS photoanode with thin TiO₂ protection layers: transport mechanism. In *Solid State Surfaces and Interfaces: 11th conference, November 23-26, 2020, Smolenice, Slovak Republic*. 1. vyd. Bratislava: Comenius University, 2020, S. 61-62. ISBN 978-80-223-5018-1.
- AFH04 ONDREJKA, Peter [55 %] - **KEMÉNY, Martin [10 %]** - DUBINA, Matúš [10 %] - NOVÁK, Patrik [10 %] - HOTOVÝ, Ivan [5 %] - MIKOLÁŠEK, Miroslav [10 %]. MoS₂ based structures for energy storage and conversion applications. In *SURFINT - SREN VII: 7th Conference on Progress in applied surface, interface and thin film science. Extended abstract book. November 22-24, 2021*. Bratislava: Comenius University, 2021, S. 41-42. ISBN 978-80-223-5296-3.

Abstracts of professional works from foreign events (conferences...)

- BFA01 MIKOLÁŠEK, Miroslav [30 %] - **KEMÉNY, Martin [10 %]** - CHYMO, Filip [10 %] - ONDREJKA, Peter [20 %] - WEIS, Martin [10 %] - HURAN, Jozef [10 %] - HOTOVÝ, Ivan [10 %]. Amorphous silicon based photocathodes with plasmonic Au and Ag nanoparticles for hydrogen generation. In *E-MRS 2019 spring meeting: Nice, France. May 27-31, 2019*. Strasbourg : EMRS, 2019, Art. no. H.P1.18 [1] s.

Statistics:

ADC	Scientific works in foreign peer-reviewed journals	4
ADN	Scientific works in domestic journals registered in WOS or SCOPUS databases	3
AFC	Published contributions at foreign scientific conferences	1
AFD	Published contributions at domestic scientific conferences	10
AFG	Abstracts of contributions from foreign conferences	2
AFH	Abstracts of contributions from domestic conferences	4
BFA	Abstracts of professional works from foreign events (conferences...)	1
Sum		25



Ing. Martin Kemény

Dissertation Thesis Abstract

Diagnostics and analysis of degradation mechanisms
in Li-ion batteries with Ni-based cathodes

Bratislava, 2023