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Low-temperature aging mechanisms of commercial graphite/LiFePO₄ cells cycled with a simulated electric vehicle load profile – A post-mortem study

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Abstract

Reduced cycle life is one of the issues hindering the adoption of large lithium-ion battery systems in cold-climate countries. Thus, the aging mechanisms of commercial graphite/LiFePO₄ (lithium iron phosphate) cells at low temperatures (room temperature, 0 °C and –18 °C) are investigated here through an extended post-mortem analysis. The cylindrical 2.3 Ah cells were cycled with a simulated battery electric vehicle load profile, and the aged cells were then disassembled inside an argon-filled glove box. A non-cycled cell was also dismantled as a reference. Half-cell testing was utilized to evaluate the degradation of the electrochemical performance of the electrodes, whereas X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, inductively coupled plasma optical emission spectroscopy and Raman spectroscopy were used to characterize the changes in the materials properties. The full-cell performance loss was mostly seen as capacity fade whereas significant changes in the cell impedance were not observed. Depending on the cycling temperature, loss of cyclable lithium due to solid electrolyte interphase growth and/or lithium plating on the graphite electrode were observed, and they are attributed as the main mechanisms responsible for the capacity loss. Furthermore, increased disordering of the graphite electrode was observed for the cell cycled at –18 °C. The graphite disordering was hypothesized to result from diffusion-induced stress and the mechanical stress caused by severe lithium plating. In contrast, the LiFePO₄ electrodes showed only minimal signs of degradation regardless of the cycling temperature.

Keywords: Lithium-ion battery; Battery electric vehicle load profile; Aging mechanism; Post-mortem analysis; Lithium plating; Graphite disordering

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1. Introduction

Lithium-ion batteries are currently utilized in increasingly large applications, such as battery electric vehicles (BEVs), hybrid electric vehicles (HEVs) and stationary energy storage systems. However, a major issue hindering the widespread adoption of these large battery systems in cold-climate countries is their poor low-temperature performance. Particularly the lifetime of the batteries can be significantly reduced as a result of low-temperature operation. To examine the mechanisms leading to the battery performance decline, several groups have studied the aging of commercial lithium-ion cells through post-mortem analyses [1–30]. However, to this date, studies done on cells cycled at low temperatures are scarce [11,12,14–22].

The aging processes of lithium-ion batteries are complicated. The capacity decrease and power fade seen during long-term operation are not caused by a single degradation process but rather result from several different processes and their interactions with each other [31]. Typically, side reactions at the electrode/electrolyte interfaces, loss of active material due to structural degradation or loss of electrical contacts, changes in the porosity and 3D structure of the electrodes as well as degradation of the non-active components (separators, binder materials or current collectors) are regarded as the most prevalent aging mechanisms [31–33]. To make the situation even more complicated, aging is affected by the operating conditions, such as cycling/storage temperature, state of charge (SoC), depth of discharge, current density and the applied voltage limits [31,32].

Waldmann et al. [12] have studied the effects of temperature on the aging of commercial 18650-type cells with a $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{Li}_y\text{Mn}_2\text{O}_4$ blend positive electrode and graphite/carbon negative electrode. They studied temperatures from -20 to 70 °C and found two different prevalent aging mechanisms depending on the cycling conditions. It was concluded that above 25 °C the cell performance decline is caused by both degradation of the positive electrode and a thickening of the passivating layer on the surface of the negative electrode [12]. This passivating solid electrolyte interphase (SEI) is formed because the operating potential of the carbonaceous negative electrode (around 0.1 – 0.2 V vs. Li^+/Li) is outside of the stability window of the commonly used organic electrolytes. The building of the SEI consumes active, cyclable lithium ions from the cell, thus leading to a decrease of cell capacity [31–33]. Moreover, the SEI formation reactions lead to gas evolution and can increase the impedance of the cell [31,34]. Ideally, this process occurs only during the formation cycle of the cell. However, small amount of SEI reformation and growth

occurs during cycling over the whole battery lifetime. This is due to the formation of small cracks in the SEI as a result of volume changes in graphite with lithiation and delithiation [31,32].

In the same study by Waldmann et al. [12], the authors suggested that below 25 °C the dominating aging mechanism is the plating of metallic lithium on the surface of the carbonaceous negative electrode. The potential of lithium-graphite intercalation compounds is close to the reduction potential of lithium (0 V vs. Li^+/Li). If the diffusion of lithium ions into the graphite lattice becomes hindered, e.g. due to charging at sub-zero temperature, the graphite electrode can polarize beyond the reduction potential of lithium and deposition of metallic lithium may occur [15,31,35]. In addition, lithium plating has been observed to take place even during cycling at higher temperatures (room temperature or above) as a result of high current densities or cell drying and gas formation caused by continuous electrolyte consumption [26,30]. Lithium plating adds to the capacity and power fade of the cell by two different mechanisms [31,35]. Firstly, irreversible lithium plating corresponds to a loss of cyclable lithium. Secondly, the potential of the plated lithium metal is outside of the electrochemical stability window of the organic electrolyte. Thus, more SEI will grow on its surface, consuming electrolyte from the cell. Moreover, lithium depositions can cause safety hazards by decreasing the thermal stability of the cells [8,36].

On the positive electrode, one of the most common aging mechanisms are structural changes of the active material during cycling, especially for layered transition metal oxides [37]. For example, a hexagonal-to-spinel transition has been reported for LiCoO_2 [38]. Other frequently reported aging mechanisms are e.g. transition metal dissolution and side reactions with the electrolyte leading to the formation of a cathode electrolyte interface (CEI) layer [33,37,39,40]. Recently, Li et al. [21] reported a loss of active material from the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ electrode of a commercial 2.2 Ah pouch cell after low-temperature operation at $-10\text{ }^\circ\text{C}$. They speculated that the degradation was caused by lithium plating on the graphite negative electrode and the associated lowered lithiation degree of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ positive electrode, which could be harmful to its layered crystal structure. Similarly, Wu et al. [41] have reported a higher loss of LiCoO_2 active material for pouch cells with a $\text{LiCoO}_2/\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ blend positive electrode after cycling at $10\text{ }^\circ\text{C}$ compared to $25\text{ }^\circ\text{C}$.

In contrast to the layered transition metal oxides, the LiFePO_4 (LFP) positive electrode material studied in this work is generally considered stable even during prolonged cycling. The operating potential of LFP lies inside the stability window of the organic electrolyte, and thus the CEI

formation is not expected to contribute significantly to the aging. However, due to volume changes of the material during lithiation and delithiation (6.8% difference in volume between LiFePO_4 and FePO_4 [42]), some loss of active material has been reported to take place due to particle cracking and the associated loss of electrical contacts [43–45]. Moreover, it has been suggested that the cracking of the particles [45] or HF (hydrogen fluoride) present in the LiPF_6 -based electrolyte could lead to iron dissolution from the material especially at elevated temperatures [26,46,47]. The dissolved metal ions migrate to the graphite negative electrode and reduce on the graphite surface. Thus, they are incorporated into the SEI structure, where they increase the conductivity of the SEI and thereby accelerate its growth [31,47].

The aging mechanisms described above are specific to each of the active materials, and therefore they cannot be extrapolated to other cell chemistries. The graphite/LFP material combination was chosen for this study, as it is interesting for many large-scale battery systems due to its favorable safety and cycle life properties. Furthermore, it is well suited for large-scale use because of its environmental friendliness and low cost due to the lack of cobalt and nickel in the positive electrode [48]. Thus, graphite/LFP cells have found applications in electric buses, EVs and HEVs [49], where exposure to low temperatures is unavoidable in cold-climate countries, and its effects on the cell aging should be understood better. Furthermore, the aging is affected by the cell design [16,31,45], and thus it is imperative to study the aging of different cell types separately. The cylindrical cell format chosen for this work can also be found in the EV batteries.

In the literature, most of the post-mortem studies conducted for low-temperature cycled cells have employed an accelerated aging scheme using constant currents in the cycle aging of the cells [11,12,14–19,21–23]. However, for example Klett et al. [26] have shown that constant current cycling (3.75C) in a wide SoC range results in significantly more severe degradation of the cell performance than a simulated HEV bus cycle (max. 15C/23C for charging/discharging) in a narrower SoC range. In their study, the authors investigated cylindrical 2.3 Ah graphite/LFP cells similar to the cells in this study, but only at a temperature of 22 °C. In contrast to the previous post-mortem studies for low-temperature cycled cells, in this work, we have chosen a simulated BEV cycle for the aging of the graphite/LFP cells to emulate the conditions in a real-life BEV battery at low temperature. Moreover, in the previous investigations on low-temperature aged cells, mainly materials characterization techniques have been used to identify the changes in the cell components. In this study, however, we have also included electrochemical characterization of the electrodes to

gain a more in-depth understanding of the aging effects on the cell performance on the electrode level.

To conclude, we present here a post-mortem analysis of commercial cylindrical 2.3 Ah graphite/LFP cells cycled at three different temperatures (room temperature, 0 °C and –18 °C) with a BEV cycle. The cycling performance of the cells has been published in ref. [50]. After electrochemical characterization of the full cells, the cells were disassembled inside an argon-filled glove box and samples were collected from the electrodes for further analysis. Electrochemical half-cell testing was used to evaluate the degradation of the electrochemical performance of the electrodes collected from the cells. In addition, these measurements were complemented with X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), inductively coupled plasma optical emission spectroscopy (ICP-OES) and Raman spectroscopy to identify the degradation mechanisms on each electrode.

2. Materials and Methods

2.1 Cycle aging and cell disassembly

The studied cells were high-quality commercial 26650 cylindrical format graphite/LFP cells with 2.3 Ah nominal capacity and 3.3 V nominal voltage. The cycle life results have been published in a previous article [50]. The cells had been cycled at three different ambient temperatures of –18 °C, 0 °C and room temperature (RT) using a cycle simulating the load profile in a BEV. The surface temperatures of the cells, measured with a thermocouple attached to the surface of each cell, were within 5 °C of the ambient temperatures during the cycling. Three cells were cycled at each of the temperatures. One representative cell per temperature and one non-cycled cell were then chosen for the post-mortem analysis.

In short, the cycling procedure was as follows: the cells were charged at a constant current rate of 1C followed by a constant voltage period at 3.6 V until the current decreased to the cut-off value of 0.01C. After a 30 min rest period, the cells were subjected to a charge-depleting micro cycle, as

described in ref. [50], until the cut-off voltage of 2.0 V was reached. The highest charging current pulse rate applied during the charge-depleting micro cycle was 2C, and the highest discharge rate applied was 4C (Fig. S1 in the Supplementary materials). After the discharge, the cells were again charged at the rate of 1C, and the procedure described above was repeated. At every 50 cycles, the cells were brought to RT and the discharge capacities of the cells were checked by a capacity test conducted at 1C rate. The cycling was continued until the discharge capacity measured at 1C decreased below 80% of the initial capacity measured at 1C. More detailed information on the aging conditions and the cycling protocol can be found in ref. [50]. In addition to the cycled cells, a non-cycled cell was disassembled as a reference. The reference cell had been cycled only for a few cycles for characterization purposes. Due to differences in the cycle lives, the cells were stored for different periods of time between the termination of the cycling and the disassembling. The cells, including the reference, were stored at open circuit at room temperature for approximately 10–25 months.

Before disassembling, the cells were characterized electrochemically through galvanostatic charge-discharge cycling (2.0–3.6 V) and electrochemical impedance spectroscopy (EIS) at room temperature. The cycling was conducted with a Maccor 4300 battery testing station, and the EIS with a Metrohm Autolab potentiostat (PGSTAT100) and an Autolab frequency response analyzer. The impedance spectra were recorded after charging a capacity of 1.15 Ah at 0.05C rate to each of the cells, which corresponded roughly to the middle of the voltage plateau around 3.3 V (see Fig. 1). A voltage perturbation of 5 mV and a frequency range from 10 kHz to 10 mHz was used. Thereafter, the cells were discharged at a 0.1C rate to a voltage of 2.0 V, and one cell aged at each condition was opened inside an argon-filled glove box (<10 ppm O₂). The cell casings were carefully opened next to the terminals on both ends of the cells using a pipe-cutting tool, and the jellyrolls were unrolled. No indications of a short circuit caused by the disassembling procedure (e.g. heating of the cells) were observed. Samples were then cut out from the electrode jellyroll and washed three times in dimethyl carbonate (DMC, anhydrous, ≥99%, Sigma-Aldrich) in order to remove the electrolyte salt residues. After the washing, the electrodes were left to dry in the argon atmosphere of the glove box.

2.2 Structure and morphology analysis

All of the structural and morphology analyses were made on samples collected from the middle parts along the lengths of the electrode strips (see Fig. S2 in the Supplementary materials for further details). SEM images of the electrodes were taken using a JEOL JSM-7500FA field emission SEM equipped with an energy dispersive X-ray spectrometer (JEOL). All the samples were stored under argon until exposing them to air approximately 24 h before the imaging in order to prevent the reactive species on the sample surface from reacting inside the SEM. The acceleration voltage used for imaging was 5 kV, and 15 kV was used for EDX analysis.

XRD experiments were conducted with a PANalytical X'Pert Pro MPD Alpha-1 diffractometer using Cu $K\alpha_1$ radiation. The measured 2θ range was $5 - 120^\circ$ with a 0.0131° step size. The samples were exposed to air 1 h before the XRD measurements. Rietveld refinement program Fullprof [51] was used to estimate the relative amounts of lithiated (LiFePO_4) and delithiated (FePO_4) phases from the XRD data of the positive electrodes.

To acquire more surface-specific data, the graphite electrodes were also characterized with grazing incidence X-ray diffraction (GI-XRD) using PANalytical X'Pert Pro MPD diffractometer with Cu $K\alpha$ radiation. The measured 2θ range was $10-100^\circ$ with a 0.04° step size. In addition, ICP-OES (Perkin Elmer 7100 DV) experiments were conducted on the graphite samples. For the ICP-OES analysis, the graphite coatings of unwashed samples (size 150 x 58 mm) from the middle parts of the jellyrolls were dispersed in deionized water, and both the liquid and solid phases were then analyzed for the amount of iron.

Raman spectra were recorded with a Renishaw inVia Raman microscope to study the surface properties of the graphite electrodes. An excitation wavelength of 633 nm was used. For the Raman measurements, the samples were sealed in a specially built container with a glass window to prevent contact with air.

2.3 Electrochemical half-cell characterizations

For the electrochemical testing, samples were cut from both the inner and outer parts of the electrode jellyrolls (Fig. S2). The coating on one side of the current collector was removed by wetting the side of the electrode to be removed with N-methyl-2-pyrrolidone (NMP, Micropure™, Ashland) and gently rubbing with a cotton bud. Care was taken not to allow the NMP to wet the

other side of the electrode sheet during the process. Electrodes with diameters of 14 and 18 mm were then punched out of the one-sided electrode foil. The smaller electrodes were used for rate capability testing in coin cells and the larger ones for EIS and cyclic voltammetry (CV) measurements in a three-electrode setup. All of the rate capability results given in Section 3 present the average of two to three samples. The EIS and CV results presented in Section 3 are the results of one measurement representative of the behavior seen in two measurements. It should be noted here that although care was taken not to damage the electrodes, especially the graphite sheets were somewhat brittle and the preparation process could have caused minor changes to the samples. This is a problem commonly encountered in post-mortem analyses of aged cells and is widely reported in the literature [24–26,52].

The rate capability tests were conducted in coin cells (standard 2016-type, Hohsen) with a Li metal foil (thickness 0.38 mm, Sigma-Aldrich) as the counter electrode and 1 M LiPF₆ in a 1:1 mixture of ethylene carbonate and dimethyl carbonate (Selectilyte LP30, BASF) as the electrolyte. A 260 μ m thick glass fiber filter (GF/A, Whatman) was used as the separator. Galvanostatic charging and discharging of the cells was conducted using a Neware battery cycler in a voltage range of 0.01 to 1.0 V vs. Li⁺/Li for graphite and 2.8 to 4.0 V vs. Li⁺/Li for LFP. The discharge C-rates were varied from 0.05C to 4C while the charging rate was kept constant at 0.05C. Throughout this work, charging refers to lithiation of the graphite electrode and delithiation of the LFP electrode, consistent with the directions of the reactions in a full cell. The currents were approximated from the nominal capacity of the full cells and the geometric area of the electrodes measured during the disassembly of the cells (Table 1). The rate capability measurements were conducted at room temperature.

Table 1. The C-rates and corresponding current densities applied during the rate capability tests of the half-cells.

C-rate	0.05C	0.1C	0.2C	0.5C	1C	2C	4C
Current density (mA cm ⁻²)	0.07	0.14	0.27	0.68	1.36	2.73	5.45

CV and EIS measurements were performed in a three-electrode setup (EL-CELL) using a 1.55 mm glass fiber separator (EL-CELL) and Li metal as counter and reference electrodes. A Metrohm Autolab potentiostat (PGSTAT302N) was used for the measurements. CVs were recorded within a potential range of 0.005–1.0 V vs. Li⁺/Li for graphite and 2.8–4.0 V vs. Li⁺/Li for LFP. EIS for both the LFP and graphite electrodes was measured at a SoC of 41% determined from a low rate (0.05C)

capacity measurement. This SoC corresponded roughly to the SoC of the graphite electrodes in the full-cell EIS measurements prior to disassembling, and it was determined from the staging potential behavior of the graphite electrode. EIS was measured using a potential perturbation of 5 mV inside a 200 kHz to 10 mHz frequency range. The temperature during CV and EIS measurements was controlled with a temperature chamber (Vötsch) to 23 °C, and the cells were let to stabilize to the temperature for 2 h before the measurements.

3. Results and discussion

3.1 Full-cell condition before disassembling

A summary of the cycle aging parameters and the cycle life results for the full cells is presented in Table 2. To review the detailed cycling performance of the cells, the reader is again referred to the article by Omar et al. [50]. In short, all of the cells were cycled at the studied temperature (room temperature, 0 °C or –18 °C) using a simulated BEV cycle until the capacity, measured during a capacity test cycle (25 °C, 1C) that was conducted every 50 cycles, decreased to 80% of the original value. The cycle life of the cells at room temperature was 2071 equivalent cycles [50], which is well in line with the specifications given by the manufacturer. The equivalent cycles correspond to the total net discharge capacity accumulated during the cycle life of the cell divided by the discharge capacity measured at the beginning of life at 1C and 25 °C. A significant reduction of the cycle life at –18 °C was observed: the cycle life at –18 °C was less than 10% of the value at room temperature [50]. On the other hand, the reduction in cycle life at 0 °C was not very significant, and the cells could still deliver roughly 90% of the number of cycles at room temperature [50]. Accordingly, it can be said that cycling at a sub-zero temperature has a significant negative effect on the lifespan of the cells, and that especially charging at sub-zero temperatures should be avoided in all applications where the batteries are utilized.

Table 2. A summary of the aging parameters and cycle life results of the full cells.

	Ref	RT	0 °C	−18 °C
Cycling temperature (°C) [50]	–	23–25	0	−18
End-of-cycle-life capacity at 1C (%) [50]	–	80	80	80
Cycle life [50]	–	2600	2070	195
Number of equivalent cycles ¹ [50]	–	2071	1850	185
Storage time before opening (months)	~25	10–18	10–18	~25
Storage SoC (%)	~80	~60	~25	~95
Capacity before opening at 0.05C (%) ²	94	89	91	86

Although the cells were cycled until the discharge capacity at 1C decreased to 80% of the initial value, differences between the end capacities of the cells measured at 0.05C before disassembling are seen in Table 2. This is because the 1C current rate used in the determination of the end-of-cycle-life condition during the cycle aging is rather high. At 1C, the cell resistance has an effect on the measured discharge capacity, whereas the low current of 0.05C represents the electrochemically available capacity in the cells more accurately.

All of the cells were acquired at the same time and disassembled roughly at the same time. Because the time taken by the cycle aging varied according to the cycling temperature and the cycle life of the cells, there were differences in the storage times between the termination of the cycle aging and the disassembling. Accordingly, the cells were stored at room temperature for a period of approximately 10–25 months prior to disassembling, as seen in Table 2. However, the effect of the storage on the cell components can be assumed small compared to the effects of the cycle aging. It has been shown in several studies [13,53–55] that the capacity fade and impedance increase of graphite/LFP cells are small during storage at room temperature. Moreover, the same studies show that the capacity decline is more strongly dependent on the storage temperature than on the SoC. For example, Kassem et al. [53] measured a 5% decrease in the low-rate capacity after 8 months of storage at 30 °C and 30% SoC, whereas the value was 6% for cells stored at SoCs of 65% and 100%. The cell impedance increase was around 10% after the same storage period, regardless of the cell SoC [53]. In a post-mortem study by the same group it was shown that the performance decline due to storage is mostly caused by loss of cyclable lithium in the passivating layer on graphite,

¹ Total net discharge capacity accumulated during the cycle life of the cell divided by the measured discharge capacity at 25 °C at the beginning of life [50].

² Relative to the nominal capacity.

whereas other aging mechanisms are less significant [13]. Furthermore, it should be noted that calendar aging occurs also during the cycling of the cells [56]. Consequently, as the time between cell manufacture and disassembling was the same for all of the cells in this study, including the reference cell, the differences seen between the cells can be assumed to originate from the cycle aging at different temperatures.

Voltage profiles measured at a low current rate of 0.05C prior to dismantling the full cells are presented in Fig. 1a. Differences between the voltage characteristics of the cells cycled at different conditions are seen at the high-voltage plateau around 3.35 V, whereas other parts of the voltage profiles appear unaffected by the aging. The length of the high-voltage plateau is largest for the non-cycled reference cell, and varying levels of narrowing of the plateau are observed for the cycled cells. As the potential profile of the LFP positive electrode is known to be extremely flat [42], the voltage plateaus seen in the full-cell voltage profiles can be assigned to the potential behavior of the graphite negative electrode [57,58]. The narrowing of only the high-voltage plateau could result either from a loss of cyclable lithium from the cells or a reduction of the amount of LFP active material in the positive electrode. In previous studies, LFP has been found rather persistent towards both cycle aging and calendar aging [13,14,26], and thus the narrowing of the high-voltage plateau most likely originates from a loss of cyclable lithium from the cells. Major loss of graphite active material from the negative electrodes would be seen as narrowing of all of the voltage plateaus in Fig. 1a. Thus, the similarity of the voltage profiles below 3.35 V can be taken as an indication that loss of graphite active material was not a major contributor to the full-cell capacity loss. However, further examination of the discharge curves through differential voltage analysis, shown in Fig. S3 in the Supplementary materials suggests a minor loss of graphite active material for the RT and 0 °C cells.

Fig. 1. Electrochemical characterizations of the full cells prior to disassembling. (a) The voltage profiles measured at 0.05C current rate; (b) Nyquist plots recorded at 50% SoC (determined from the nominal capacity).

The impedance spectra recorded at 50% SoC (determined from the nominal capacity; 1150 mAh was charged to each cell) are shown in Fig. 1b as Nyquist plots. The impedance responses of all the cells consist of a high-frequency semicircle and a low-frequency tail, which are similar for all of the aging conditions. The high-frequency semicircle can be ascribed to the charge-transfer reactions and interfacial processes on both of the electrodes, whereas the low-frequency tail can be attributed to diffusion. The differences in the high-frequency semicircles are small, which indicates a similar charge-transfer resistance for all of the cells. The high-frequency intercepts with the real axis, corresponding to the cell ohmic resistances, are also very similar; the differences are within the experimental error. Moreover, it should be noted here that estimating from the positions of the voltage plateaus on the capacity axis in Fig. 1a, the lithiation degrees of the graphite electrodes (corresponding to the charged capacity of 1150 mAh) can be assumed roughly similar in all of the EIS measurements. However, the lithiation degrees of the LFP electrodes may vary according to the amount of cyclable lithium loss from the cells, which could have a minor effect on the EIS response of the cells. Accordingly, small differences in the lithiation degrees of the electrodes could cause the slightly smaller high-frequency semicircle measured for the 0 °C cell. Overall, Fig. 1 suggests

that the full-cell performance loss was dominated by a decrease in the reversible capacity caused by a loss of cyclable lithium from the cells, whereas the contribution of power fade due to impedance rise was secondary. The result is consistent with the ones reported by for example Liu et al. [14] for 2.2 Ah cylindrical graphite/LiFePO₄ cells.

3.2 Disassembly and visual analysis of the cell components

After discharge at 0.1C rate to a voltage of 2.0 V, the cells were disassembled inside an argon-filled glove box. All of the cells still had electrolyte left at the time of opening. Photographs of both the positive and negative electrodes taken during the disassembly of the full cells are presented in Figs. S4 and S5 in the Supplementary materials.

The LFP electrodes in all of the cells appeared visually undamaged by the aging (Fig. S4). The electrodes had a glossy black surface and the coating was still well attached to the current collector. No visual differences could be observed between the LFP electrodes cycled at different temperatures. For the graphite electrodes, the situation was different (Fig. S5). Even the graphite electrode of the reference cell showed differences in color between the edge and middle parts along the width of the electrode. The edges had a brownish gray color indicating a different degree of lithiation compared to the middle of the electrode strip, which showed a blue color. Similar differences were observed for the 0 °C and RT electrodes, which are described more specifically in the Supplementary materials. Especially the RT graphite electrode was brittle; small parts of the graphite coating detached from the current collector when the separator was removed during the disassembling. The delamination of the graphite coating was more severe towards the core of the cell.

Especially at approximately 1 cm from the edge of the 0 °C graphite electrode, light gray areas were observed (Fig. S5c). These were presumed to be metallic lithium. The amount of the deposits appeared to increase towards the core of the cell. Furthermore, small light grey deposits could be seen in the areas close to the current collecting tabs in all of the cells, even in the reference cell. These deposits appeared more prominent in the outermost parts of the jellyroll. These deposits, as well, were most likely metallic lithium, and they were probably formed already during the formation cycles of the cells. The graphite electrode of the -18 °C cell had a uniform silvery metallic color, which was most likely caused by severe lithium plating. The assumption that the

above described deposits were plated lithium metal was further supported by the observation that the graphite electrodes from the $-18\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$ cells reacted more vigorously (forming gas bubbles) compared to the RT and reference electrodes when brought into contact with water. As all of the graphite electrodes were delithiated prior to disassembling, the contribution of the residual intercalated lithium to the gas formation could be assumed small. Therefore, it can be concluded that during charging at the low temperature of $-18\text{ }^{\circ}\text{C}$, the graphite electrode polarized well beyond the reduction potential of lithium, whereas at $0\text{ }^{\circ}\text{C}$, the polarization was not as significant.

3.3 Analysis of the graphite negative electrodes

3.3.1 SEM, EDX, XRD and Raman analyses

SEM images of the graphite electrodes are presented in Fig. 2. As seen in the figure, the electrodes consist of graphite flakes of roughly 1 to 20 μm in diameter. The surfaces of the graphite particles in all of the cells are covered by a grainy surface film, which appears thicker in the cycled cells, especially the one cycled at RT (Fig. 2b). The surface of the $-18\text{ }^{\circ}\text{C}$ electrode (Fig. 2d) is covered by larger particles of an unknown material that partly cover the graphite flakes. These particles are assumed to be oxidation products of the plated lithium, formed in reactions with air prior to the SEM analysis (the samples were exposed to air, as described in Section 2.2). The EDX analysis of the particles showed higher oxygen content when compared to the graphite flakes, which supports the assumption that these particles are oxidation products of species deposited on the electrode surface. In the visual analysis of the cells during the disassembling, severe lithium plating was observed on the graphite electrode of the $-18\text{ }^{\circ}\text{C}$ cell, which explains the large amount of lithium oxidation products on its surface after air exposure.

In low-magnification SEM images (Fig. S6 in Supplementary materials), some loss of graphite active material is observed as small craters where the lower layers of the graphite coating are visible. These graphite flakes have probably detached from the electrode when the separator was removed during the disassembly of the full cells. Especially, small parts of the graphite electrode from the inner part of the cell cycled at RT were observed to stick to the separator when the cell was dismantled. This loss of graphite appeared more significant for the RT and $0\text{ }^{\circ}\text{C}$ cells (compared to the reference cell), which is in line with the electrochemical analysis of the full cells in Section 3.1.

As described above, the presumed oxidation products of lithium covered the surface of the $-18\text{ }^{\circ}\text{C}$ graphite electrode, and thus the integrity of the coating could not be analyzed from the SEM images.

Fig. 2. SEM images of the graphite electrodes disassembled from the full cells. (a) Reference; (b) RT cell; (c) $0\text{ }^{\circ}\text{C}$ cell; (d) $-18\text{ }^{\circ}\text{C}$ cell.

Table 3 shows the results of the EDX analysis of the graphite electrodes, which were taken as an average over a surface area of roughly $80 \times 110\text{ }\mu\text{m}^2$. The amount of oxygen relative to the amount of carbon was observed to be slightly higher for the cycled electrodes compared to the non-cycled reference, which is consistent with the thicker appearing surface film seen on these samples in Fig. 2. Fluorine and phosphorus were present in similar amounts in all of the samples. Both elements are expected for a SEI formed in a LiPF_6 -based electrolyte [40]. Furthermore, some of the fluorine detected in the EDX could arise from the binder material. A small signal arising from the copper current collector was also measured for all the samples but is not listed in Table 3. However, the copper signal indicates that the EDX measurement probed the whole thickness of the graphite electrode, and it can therefore be considered here as a bulk technique.

As the samples were exposed to air prior to the EDX measurements, a detailed analysis of the SEI composition is not possible here. However, the slightly stronger oxygen signal and the lower carbon signal of the electrodes cycled at RT and 0 °C (compared to the reference) are considered to result from a higher amount of reduction products of the carbonate-based electrolyte. In addition, the oxidation products of plated lithium (due to contact with air) on the surface of the 0 °C electrode are expected to contribute to the amount of oxygen on the surface of the electrode. The significantly higher amount of oxygen in the –18 °C electrode, in turn, most likely arises primarily from the reaction products of the plated lithium with air. Iron that might have migrated from the LFP electrode could not be indisputably detected on the surface of any of the graphite electrodes. It should be noted that the fluorine K α signal partly overlaps with the iron L α signal, which makes the standard error of the EDX analysis rather high for these elements, as shown in Table 3. To obtain a more reliable analysis of the iron amount in the SEI, ICP-OES analyses of non-rinsed graphite electrodes were conducted as well, and the results are presented in Section 3.4.1.

Table 3. EDX results of the graphite electrodes recovered from the full cells.

Element	Ref	Content (atomic %)		
		RT	0 °C	–18 °C
Carbon	80.4 $\pm$ 0.1	78.0 $\pm$ 0.2	78.1 $\pm$ 0.2	65.8 $\pm$ 0.1
Oxygen	11.4 $\pm$ 1.0	13.0 $\pm$ 1.0	14.0 $\pm$ 1.1	25.9 $\pm$ 0.5
Fluorine	8.1 $\pm$ 4.2	8.8 $\pm$ 4.6	7.8 $\pm$ 5.0	8.2 $\pm$ 3.2
Phosphorus	0.1 $\pm$ 0.4	0.2 $\pm$ 0.4	0.1 $\pm$ 0.4	0.1 $\pm$ 0.3
Iron	0.0 $\pm$ 2.2	0.1 $\pm$ 2.4	0.1 $\pm$ 2.6	0.0 $\pm$ 1.5

In XRD analysis of the graphite electrodes, no significant changes in the graphite bulk structure were observed. Most of the reflections seen in the diffractograms (Fig. S7 and S8 in the Supplementary data) belong to bulk graphite and the copper current collector. However, some additional peaks are also seen, which are considered to originate from the SEI components and the oxidation products of the plated lithium. These include small reflections caused most likely by LiOH, Li₂CO₃ and LiF. For example, an increase in the amount of LiF on the graphite surface as a result of cycling especially at higher temperatures has been reported in the literature [7,26,40]. Other common inorganic SEI components include Li₂O and Li₂CO₃ [26,40]. Furthermore, as stated earlier, the oxidation of the plated lithium on the surface of the low-temperature cycled graphite electrodes as well as remaining intercalated lithium inside the graphite particles can also result in

the formation of species such as LiOH and Li₂CO₃ on the electrode surface [59]. The detected intensities of these supposed lithium oxidation products are again highest for the -18 °C electrode. However, many of the peaks overlap with each other, which makes quantitative analysis unreliable. Moreover, amorphous components possibly present in the SEI cannot be detected with XRD.

Raman spectra recorded for the graphite electrodes are presented in Fig. 3. For the Raman measurements, the samples were sealed inside a glovebox into a container with a glass window to prevent contact with ambient air. The graphite D, G and D' bands at 1330 cm⁻¹, 1580 cm⁻¹ and 1620 cm⁻¹, respectively, are clearly visible for all of the samples [60–63]. In the spectrum of the -18 °C sample, three extra bands are seen at 1090, 1480 and 1850 cm⁻¹. The first two bands can be ascribed to Li₂CO₃ [64,65], whereas the band at 1850 cm⁻¹ has previously been ascribed to Li₂C₂ present in the SEI of lithium metal [66] or formed as a decomposition product of Li₂CO₃ due to local laser heating during the Raman measurement [67,68]. The presence of Li₂CO₃ likely results from the SEI on the graphite particles as well as on the surface of the plated lithium, which was observed in substantial amounts on the surface of the -18 °C sample during the disassembling. A slightly increasing amount of disordered carbon is indicated for the cycled electrodes; the ratio of the integrated D and G band intensities (I_D/I_G) increases from 0.39 for the reference sample to 0.42 for the RT electrode, 0.45 for the 0 °C electrode and 0.56 for the -18 °C sample. As the XRD results indicated that the bulk structure of the graphite did not change significantly, the disordering of graphite seen in the Raman analysis most likely occurs only on the surfaces of the particles. An increased carbon disordering as a result of prolonged cycling at higher temperatures of 25–30 °C has been reported before for graphitic materials [69,70]. However, based on the above results it appears that low-temperature cycling also promotes the disordering of graphite. The possible causes for the phenomenon are discussed further in the next section.

Fig. 3. Raman spectra of the graphite electrodes disassembled from the full cells.

3.3.2 Electrochemical properties

The rate capability performance of the graphite electrode samples recovered from the inner and outer parts of the jellyrolls are presented in Fig. 4a and b, respectively. The values presented in the figures are averages of two to three samples. The standard deviation of the rate capability results obtained for the parallel samples was 0.03 mAh cm⁻² or less. The slight scattering of the results was most likely caused by small differences in the areas of the punched electrode samples. Furthermore, the reproducibility of the rate capability behavior was good.

Fig. 4. Electrochemical properties of the graphite electrodes recovered from the full cells.

The rate capability performance of the graphite electrodes collected from (a) inner part of the jellyroll and (b) outer part of the jellyroll; (c) CVs recorded at a scan rate of $20 \mu\text{V s}^{-1}$ in a potential range of 0.005–1.0 V vs. Li⁺/Li; (d) The impedance spectra at a SoC of 41%. The samples for CV and EIS measurements were collected from the outer parts of the electrode jellyroll.

The first step of the rate capability measurement was a discharging step (delithiation) at a C-rate of 0.05C to see if measurable amounts of lithium had remained intercalated in the graphite structure after the 0.1C discharge of the full cells before disassembling. However, none of the graphite electrodes showed a measurable amount of residual lithium in the half-cell testing.

The capacities measured at the low current rate of 0.05C in Fig. 4a and b can be taken to represent the amount of electrochemically active graphite available in the electrodes, since at this low current the electrode polarization can be considered to have a negligible effect on the measured capacity. Thus, it is seen from Fig. 4a and b that the discharge capacities of all of the cycle-aged electrodes are somewhat smaller compared to the non-cycled reference, which indicates a slight loss of active material from the graphite electrodes. The result is consistent with the electrochemical analysis of

the full cells prior to disassembling (Section 3.1) which suggested a minor loss of electrochemically active graphite for the RT and 0 °C cells. Furthermore, the results are similar for samples from both the inner and outer parts of the electrode jellyrolls.

The loss of graphite active material during full-cell cycling could be caused by e.g. excessive build-up of the SEI, cracking of the graphite particles due to diffusion-induced stress or degradation of the binder. The loss of graphite active material can also explain why brownish gray or blue color was observed in the graphite electrodes but lithium could not be deintercalated from the electrodes in the half-cell tests. If some of the lithium has been trapped inside the graphite and lost electrical contact during the charging steps, differences in color could be seen but the lithium would not be active in electrochemical testing. Moreover, some detachment of graphite particles was seen also in the SEM images (shown in Fig. S6 in Supplementary materials). This also contributes to the loss of electrochemically active graphite in the half-cell testing and is proposed to result from the degradation of the binder properties with cycling.

The 0 °C electrode has suffered from loss of graphite active material the most, whereas the area capacities of RT and –18 °C samples are more similar to the reference sample. The 0 °C cell had undergone a significantly higher amount of charge-discharge cycles during the cycle aging of the cells compared to the reference and –18 °C cells (see Table 2). Thus, it is not surprising that the 0 °C graphite electrode has lost more of its reversible capacity. However, the difference between the RT and 0 °C samples is more unexpected: the RT cell could be cycled for 2071 equivalent cycles compared to the 1850 cycles for the 0 °C cell before the cells met the end-of-cycle-life condition of 80% remaining capacity at 1C. The larger loss of active graphite of the 0 °C cell could be affected by differences in the mechanical properties of the binder at low temperatures as well as the properties of the SEI formed on the surface of the graphite electrode at 0 °C. In a recent study by Friesen et al. [71], the authors found that the ability of the SEI to protect the underlying graphite is strongly dependent on the cycling temperature, especially if the temperature is outside of the optimized range of the electrolyte mixture. Thus, the degradation of the 0 °C graphite electrode could be affected by the poorer ability of the SEI to passivate the surface.

It can be seen from Fig. 4a and b that there is also a difference in the area capacities between the inner and outer parts of the 0 °C graphite electrode. This most likely arises from a non-uniform current density during the cycle aging at 0 °C. A temperature gradient is expected to form between the inner and outer parts of the electrode jellyroll when cycling a cylindrical cell. A higher

temperature for the inner parts is expected due to limited heat transfer rate of the cells, as will be discussed further in Section 3.4.2. A higher temperature would cause the current density to be higher in the inner parts of the jellyroll during cycling, which is expected to accelerate the aging of the inner parts. The adverse effect of increasing current density on the studied cells is demonstrated in the previous work by N. Omar et al. [50]. Furthermore, in the visual analysis of the 0 °C electrode, the presumed lithium deposits appeared more prominent in the inner parts of the jellyroll compared to the outer parts. Accordingly, the higher current density appears to promote the lithium plating more strongly than the lower temperature of the skin parts of the cell.

In Fig. 4a and b, it can further be noted that when the C-rate is increased, the discharge capacity decreases similarly for the graphite electrodes of the reference, RT and 0 °C cells. However, a surprisingly small decrease in discharge capacity with increasing C-rate is observed for the graphite electrodes disassembled from the -18 °C cell. Again, the behavior is similar for samples from both the inner and outer parts of the jellyroll. It is suggested here that the enhanced performance results from an increase in the accessible graphite particle surface area of the -18 °C electrode. This could be caused by graphite particle cracking due to diffusion-induced stress and the mechanical stress caused by the lithium plating. At low temperatures, lithium diffusion in the graphite lattice is slow, and significant concentration gradients can form inside the particles. As the lithium insertion/extraction causes a volume change (approximately 10% change in the graphene layer spacing from pristine graphite to LiC_6 [72]), the concentration gradients can lead to diffusion-induced stress and eventually cracking of the graphite particles or the particle surfaces [73–75]. For example, in a study by Takahashi et al. [75], graphite particle cracking was detected by SEM after 100 cycles at -10 °C temperature (10C current rate). On the other hand, in a study by Burow et al. [20], the authors observed that in lithium-ion cells pulse charged (8C current rate) at a -15 °C temperature lithium plating occurs not only on the graphite particle surfaces but also on the inner surfaces of pores inside the graphite particles. The authors proposed that this could lead to cracking of the graphite particles. Also Petzl et al. [15] saw a loss of graphite active material in their study of commercial graphite/LFP cells after cycling the cells at a temperature of -22 °C (1C current rate). They attributed the loss of active material to the volume stresses caused by continuous lithium plating and stripping.

In the present study, the hypothesis of graphite particle cracking either due to diffusion induced stress and/or lithium plating is in line with the Raman spectra (Fig. 3) where indications of an increased amount of disordered carbon were observed for the -18 °C electrode. The XRD data,

however, implied that the bulk structure of the graphite remained unchanged after cycling at $-18\text{ }^{\circ}\text{C}$. Thus, the suggested cracking and disordering of the graphite most likely occurs along the grain boundaries or only on the particle surfaces. It is well known that the insertion of lithium into graphite is highly anisotropic and occurs only through the prismatic surfaces or defects in the basal planes [58]. Accordingly, it is suggested that the disordering of the graphite creates more sites for the (de)insertion of lithium ions, thereby leading to the improved rate capability performance. Moreover, the above described graphite particle cracking and subsequent loss of electrical contacts could also contribute to the loss of graphite active material observed for the $0\text{ }^{\circ}\text{C}$ electrodes.

The cyclic voltammograms in Fig. 4c are in line with the rate capability results. The integrated area of the anodic peaks (delithiation) corresponding to the capacity of the graphite electrode is slightly higher for the reference cell compared to the cycled ones. Furthermore, the separation between the anodic and cathodic peaks is smaller compared to the cycled electrodes, indicating faster kinetics or a lower resistance for the reference sample. The samples for the CV measurement were collected from the outer part of the electrode jellyroll. Thus, the significant loss of graphite material seen for the $0\text{ }^{\circ}\text{C}$ sample from the inner part of the jellyroll is not seen in the CVs.

The impedance spectra measured for the outer parts of the graphite electrodes are presented in Fig. 4d. The Nyquist presentations consist of three semicircles and a low-frequency tail related to diffusion. The semicircles are heavily depressed due to the porosity of the graphite electrodes. The high frequency semicircle has previously been ascribed to interfacial impedance related to the current collector [26,76]. The mid-frequency and low-frequency semicircles are ascribed to the interfacial properties of the porous electrodes and the charge-transfer reactions. It should be noted that the high-frequency semicircle and the high-frequency intercept with the real axis in the Nyquist plots can be affected by the sample preparation procedures and by minor differences in the position of the reference electrode in the three-electrode setup used in the measurement. Therefore, the high-frequency intercept with the real axis representing the ohmic resistance of the cell cannot be taken to reflect the differences in the ohmic resistances of the graphite electrodes reliably. Thus, it is omitted from the analysis of the EIS data.

In the Nyquist plots in Fig. 4d, it can be seen that the impedances of the reference graphite electrode and the $0\text{ }^{\circ}\text{C}$ and RT electrodes are similar. However, the $-18\text{ }^{\circ}\text{C}$ electrode presents a notably higher impedance, which is most likely caused by the lithium plating on the graphite surface. As the potential of metallic lithium is outside of the stability window of the carbonate-based electrolyte,

the significant amount of lithium plating observed visually during the cell disassembly is expected to cause the formation of a thick passivating layer on its surface. Accordingly, a significant amount of Li_2CO_3 was observed on the $-18\text{ }^\circ\text{C}$ electrode with Raman spectroscopy. This result seems to contradict the result of the surprisingly good rate capability performance of the electrode. However, also in the rate capability tests of the $-18\text{ }^\circ\text{C}$ electrode, a higher polarization compared to the reference was observed, which is in line with the EIS result. Therefore, it is hypothesized that the most likely explanation for the surprisingly good rate capability performance is a lowered diffusion distance within the particles caused by the increased surface area rather than, for example, an increased conductivity of the SEI due to the lithium plating.

3.4 Analysis of the LFP positive electrodes

3.4.1 SEM and XRD analyses

The SEM images of the LFP electrodes are shown in Fig. 5. All of the LFP composite electrodes consist of particles of approximately 10–100 nm in diameter forming agglomerates of roughly 0.2–1 μm in size. No changes in the morphologies of the samples aged at different temperatures can be identified. Furthermore, surface layer formation or cracking of the LFP particles are not visible.

Fig. 5. SEM images of the LFP electrodes disassembled from the full cells. (a) Reference; (b) RT cell; (c) 0 °C cell; (d) -18 °C cell.

In the XRD analysis of the positive electrodes, only LiFePO_4 and FePO_4 phases were detected (Fig. S9 in the Supplementary materials), indicating that structural changes of the LFP material or formation of new crystalline phases had not taken place. Small additional reflections belonging to the aluminum current collector were also seen. The degree of lithiation (corresponding to the $\text{LiFePO}_4/[\text{LiFePO}_4 + \text{FePO}_4]$ mole ratio) was estimated from the XRD diffractograms through Rietveld refinement, and the obtained values were in line with the results from the half-cell testing (Fig. 6d).

The stability of the LFP material was studied also indirectly by analyzing the amount of iron impurities on unwashed graphite electrodes by ICP-OES. The amount of iron detected on the graphite was low for all samples: the concentration of iron on the graphite electrodes was lowest for the reference sample and the sample cycled at -18 °C (60–100 $\mu\text{g/g}$), and slightly higher for the samples cycled at RT and 0 °C (around 150 $\mu\text{g/g}$ for both of the samples). Therefore, the dissolution of iron from the LFP electrodes was not a significant contributor to the aging of the full cells.

3.4.2 Electrochemical properties

The discharge capacities as a function of C-rate measured for the LFP electrodes recovered from cells cycled at different temperatures are presented in Fig. 6a and b. Again, the values presented in the figures are averages of two to three samples. The standard deviation of the results obtained for the parallel samples was 0.04 mAh cm^{-2} or less. It is seen that the discharge capacities for all the samples are similar. Therefore, significant loss of LFP active material had not occurred during the cycling of the full cells. At the lowest current rates of 0.05C and 0.1C, however, the average discharge capacity of the reference sample is slightly higher compared to the cycled electrodes, but the differences are smaller compared to the graphite electrodes in Section 3.3.2. In the CVs in Fig. 6c, the peaks of the cycled electrodes are slightly sharper and the peak separation is somewhat smaller compared to the reference sample. However, the differences are very small, and can be affected by the sample preparation and small variations in the sizes or alignment of the electrodes in the cells. Nevertheless, slightly improved kinetics and minor loss of active material from the cycled electrodes could have been caused by diffusion-induced stress and electrochemical milling also for the LFP electrodes.

The impedance spectra of the LFP electrodes in Fig. 6e further highlight the similarity between the electrodes from the cells cycled at different temperatures. The Nyquist plots show one slightly depressed semicircle related to the charge-transfer reactions on the LFP electrode and a low-frequency diffusion tail. Again, the high-frequency intercepts with the real axis cannot be taken to reflect the differences in the ohmic resistances of the LFP electrodes reliably, even though the LFP electrodes were less brittle than the graphite electrodes.

Fig. 6. Electrochemical properties of the LFP electrodes recovered from the full cells. Rate capability performance of the LFP electrodes recovered from (a) inner part of the jellyroll and (b) outer part of the jellyroll; (c) CVs recorded at a scan rate of $20 \mu\text{V s}^{-1}$ in a potential range of 2.8–4.0 V vs. Li^+/Li ; (d) The lithiation degrees of the LFP determined from the half-cell measurements and XRD data; (e) The impedance spectra at a SoC of 41%. The samples for CV and EIS measurements were collected from the outer parts of the electrode jellyroll.

The lithiation degrees of the LFP electrodes determined from the capacities of the first two charge-discharge cycles in the half-cell tests as well as from the XRD data through Rietveld refinement are presented in Fig. 6d. As there was some variation in the results of parallel samples, the standard deviations of the lithiation degrees determined from the half-cell tests are also plotted in Fig. 6d. As

the cells were fully discharged before disassembling and there was no residual lithium in the graphite electrodes (see Section 3.3.2), the lithiation degrees of the LFP electrodes correspond to the amount of cyclable lithium left in the cells. It can be seen from Fig. 6d that the lithiation degree of the LFP electrode of the reference cell is roughly 84% on average, which is higher compared to the cycled electrodes. The average lithiation degree from the different techniques is 74% for the RT electrode, 79% for the 0 °C electrode and 76% for the -18 °C electrode. It should be noted, however, that some of the lithium from the LFP electrode is lost in building the SEI on the graphite electrode during the formation cycle of the cells, and therefore a lithiation degree of 100% is not expected even for unaged cells. It is also seen in Fig. 6d that the lithiation degrees of the LFP electrodes in the outer parts of the electrode jellyroll are lower compared to the inner parts for all of the studied cells. The values obtained from XRD are similar to the electrochemical results from the inner parts or intermediate of the values determined from the inner and outer parts of the jellyroll. As the XRD samples were collected from the middle parts of the jellyroll, the values are in agreement with the electrochemical results.

The lower lithiation degree of the outer part of the -18 °C electrode can be explained by differences between the temperatures and pressures of the outer and the inner parts of the electrode jellyroll during the cell cycling. For example, Petzl et al. [15] have reported a higher area mass of plated lithium on the outer parts of the graphite negative electrode of a commercial 26650-type graphite/LFP cell cycled at -22 °C (1C current rate) compared to the inner part of the jellyroll. They attributed the difference in the amount of plated lithium to differences in the cell pressure and related variations in the current and potential distributions in the cell. According to the authors, a higher pressure in the inner parts of the cell, caused by the smaller winding radius of the jellyroll, causes a mechanical hindrance to lithium plating. Ghanbari et al. [19] also reported similar results for the same cell type using glow discharge optical emission spectroscopy and attributed the difference in the amount of lithium plating to temperature gradients within the cells. They measured a 1.5 °C higher temperature in the inner parts of the jellyroll compared to the surface of a cell operating at -20 °C. This could explain the observed difference in the amount of deposited lithium, as the rate of lithium diffusion into the graphite lattice is strongly dependent on the temperature.

A lower lithiation degree of the LFP electrode in the outer parts of the jellyroll was also observed for the 0 °C and RT cells. Furthermore, even the reference cell showed variation in the lithiation degree, although the difference was smaller. This is likely affected by the lithium plating observed in the areas close to the current collecting tabs in all of the cells, which appeared more prominent in

the outermost parts of the jellyroll. Furthermore, non-uniform surface film formation on the graphite electrode and corresponding differences in the lithiation degree of the adjacent positive electrode after cycling at room temperature or above have been reported by Klett et al. [26]. They assigned this phenomenon, as well, to gradients in the temperature and pressure of the cells, leading to non-uniformities in the current density and utilization of the electrodes. In any case, the observation that the lithiation degree of the LFP electrode from the reference cell was also not constant throughout the cell suggests that the underlying cause of the phenomenon is not the aging of the cells, but rather it is inherent to the cell type or design. Moreover, the effects of the tab locations should be studied further.

3.5 Discussion on full-cell aging based on the characterizations of the electrodes

The full-cell performance loss was mostly seen as a decrease of the cell capacity, whereas the impedance responses of all of the cells remained very similar (Fig. 1b). Thus, it can be said that while the capacity decreased as the cells aged, the power performance and energy efficiency were not significantly affected by the cycling at any of the studied temperatures. However, it should be noted that the cell impedance is intrinsically higher at low temperatures due to the low rate of the electrochemical processes in the cells at low temperature. The lithiation degrees of the cycled LFP electrodes, corresponding to the amount of cyclable lithium in the cells, were smaller compared to the non-cycled reference (Fig. 6d). On the other hand, major loss of active material was not detected on any of the electrodes. Therefore, it can be concluded that the full-cell capacity loss was primarily caused by loss of cyclable lithium from the cells. The dominant mechanism causing the loss of active lithium varied according to the cycling temperature. Indications of significant lithium plating were found on the surface of the graphite electrodes from the cells cycled at temperatures of $-18\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$. On the other hand, the SEM images and EDX analysis of the cells cycled at room temperature and $0\text{ }^{\circ}\text{C}$ suggested a thickening of the surface films on the graphite electrode (Fig. 2 and Table 3).

Even though it was not major, some loss of graphite active material was observed for the cycled cells. The charge-discharge curves of the full cells and the corresponding differential voltage analysis conducted prior to disassembling indicated minor graphite active material loss for the RT and $0\text{ }^{\circ}\text{C}$ cycled cells. In the half-cell measurements, the discharge capacity in the most degraded area of the graphite electrodes, the inner parts of the $0\text{ }^{\circ}\text{C}$ jellyroll, was 9% smaller than the

capacity of the reference sample (Fig. 4). Moreover, a less pronounced loss of graphite active material was observed for the RT and $-18\text{ }^{\circ}\text{C}$ cells, too. The loss of electrochemically active graphite was most likely caused by the mechanical stresses related to continuous cycling due to diffusion-induced stress and lithium plating as well as due to the thickening of the SEI. Moreover, degradation of the properties of the binder probably affected the graphite loss, as well, since some detachment of graphite particles was observed with SEM. However, due to safety reasons, the capacity of the graphite negative electrode is always higher than the capacity of the positive electrode in commercial cells. Thus, the contribution of the graphite active material loss to the capacity decline of the full cells was likely not significant. However, if the loss of graphite active material had occurred while the graphite was in a lithiated state, it could have also contributed to the loss of cyclable lithium from the cells.

Interestingly, a better rate capability performance was observed for the graphite electrode disassembled from the cell cycled at $-18\text{ }^{\circ}\text{C}$ when compared to the non-cycled reference cell (Fig. 4). This is suggested to result from graphite particle cracking due to diffusion-induced stress and the mechanical stress caused by the lithium plating. Furthermore, this conclusion is supported by the Raman spectroscopy results, which indicated a higher amount of disordered carbon on the surface of the graphite electrodes from the cells cycled at low temperatures. In the full-cell tests prior to disassembling, however, improved performance was not observed for the cell cycled at $-18\text{ }^{\circ}\text{C}$. The improved rate capability performance of the graphite electrode could be canceled out by the degradation of the other cell components, such as the electrolyte, the current collector and the separator. Furthermore, the electrode pretreatments during the cell disassembling (e.g. washing with DMC) could have an effect on the performance in the half-cell tests. Nevertheless, it is an interesting phenomenon, which has not been reported earlier for low-temperature cycled commercial cells.

Despite the improved rate capability, a higher impedance was measured for the graphite electrode in the outer part of the jellyroll of the cell cycled at $-18\text{ }^{\circ}\text{C}$. However, a higher impedance was not detected for the $-18\text{ }^{\circ}\text{C}$ cycled full cell. This is most likely affected by the non-uniformity of the degradation throughout the jellyroll. The lithiation degree of the $-18\text{ }^{\circ}\text{C}$ cycled LFP electrode was observed to be smaller in the outer parts. This can be taken as an indication that the amount of lithium plating on the graphite was likely higher in the outer part of the jellyroll compared to the other parts. From the full-cell impedance spectra, it is difficult to distinguish between the responses of the different parts of the jellyroll as well as the individual electrodes. The impedance responses

of both of the electrodes were severely overlapped for the cells in this study. Therefore, the increased impedance of the outer part of the graphite electrode could be masked by the contributions from the positive electrode as well as the graphite electrode in other parts of the jellyroll. Non-uniform lithiation degrees were measured for the LFP electrodes of the other cells as well, which indicates that the aging is not uniform throughout the cells. This is, however, difficult to verify from non-destructive full-cell measurements, which should be taken into account when developing state-of-health estimation procedures.

Finally, the results also demonstrate the stability of LFP during cycling at room temperature or below, in contrast to other common positive electrode materials. For example, phase transitions on the surface, transition metal dissolution and surface modifications due to reactions with the electrolyte are commonly reported especially for the layered transition metal oxides [31,37]. On the contrary, the LFP material in this study did not show significant loss of active material, impedance increase or changes of material properties due to the low temperature operation. Thus, the negative electrode side was the primary contributor to the full-cell performance loss.

4. Conclusions

In this work, the low-temperature cycle aging of commercial graphite/LFP cells was studied through post-mortem analysis. Prior to disassembly, the cells were cycled at three different temperatures (room temperature, 0°C and –18 °C) with a load profile simulating the battery behavior in a battery electric vehicle. The electrochemical characteristics of the full cells measured before disassembling were very similar, showing mainly a shrinking of the high-voltage plateau in the voltage profiles. Accordingly, a loss of cyclable lithium could be identified as a likely cause of the capacity decrease of the cells, but the mechanisms causing it could not be determined without disassembling the cells.

When the cells were dismantled, the main causes of the loss of cyclable lithium were observed to be lithium plating and SEI growth on the graphite negative electrode. Which of the mechanisms was dominating, depended on the cycling temperature. On the graphite electrode of the cell cycled at –18 °C, significant lithium plating was observed, and it is considered the main mechanism causing

the full-cell capacity loss at sub-zero temperatures. There were some indications of lithium plating on the surface of the graphite electrode in the cell cycled at 0 °C, as well, but it was significantly less severe compared to the –18 °C cell. Furthermore, indications of a thickening of the graphite SEI were found on the surface of the 0 °C graphite electrode, as well. Thus, it appears that there were two significant aging mechanisms at 0 °C; the lithium plating and the SEI thickening. At room temperature, in turn, the loss of cyclable lithium was primarily caused by a thickening of the SEI on the graphite electrode.

Some loss of graphite active material was also observed for the negative electrodes of the cycled cells. This was not, however, considered a significant contributor to the full-cell performance decline, due to the oversizing of the negative electrode in commercial cells. In addition, an improvement of the rate capability performance accompanied by a higher amount of disordered carbon was observed for the graphite electrode disassembled from the cell cycled at –18 °C. This was hypothesized to result from the cracking of the graphite particles or particle surfaces caused by the mechanical stresses related to lithium plating and to diffusion-induced stress at low temperature. The LFP positive electrodes, in turn, did not show significant signs of degradation at any of the studied temperatures, highlighting the stability of LFP in low-temperature operation.

Finally, the different aging mechanisms could not have been distinguished without the post-mortem analysis. For example, lithium plating, which is a significant safety hazard, could not have been discovered without dismantling the cells or predicted without knowing their thermal histories. This should be taken into account when considering the large-scale use of lithium-ion batteries in second life applications, especially for cells operated in cold-climate countries.

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References

- [1] D. Aurbach, B. Markovsky, A. Rodkin, M. Cojocaru, E. Levi, H.-J.J. Kim, An analysis of rechargeable lithium-ion batteries after prolonged cycling, *Electrochim. Acta.* 47 (2002) 1899–1911. doi:10.1016/S0013-4686(02)00013-0.
- [2] D.P. Abraham, J.L. Knuth, D.W. Dees, I. Bloom, J.P. Christophersen, Performance degradation of high-power lithium-ion cells - Electrochemistry of harvested electrodes, *J. Power Sources.* 170 (2007) 465–475. doi:10.1016/j.jpowsour.2007.03.071.
- [3] E. Sarasketa-Zabala, F. Aguesse, I. Villarreal, L.M. Rodriguez-Martinez, C.M. López, P. Kubiak, Understanding lithium inventory loss and sudden performance fade in cylindrical cells during cycling with deep-discharge steps, *J. Phys. Chem. C.* 119 (2015) 896–906. doi:10.1021/jp510071d.
- [4] D. Li, D.L. Danilov, J. Xie, L. Raijmakers, L. Gao, Y. Yang, et al., Degradation Mechanisms of C6/LiFePO₄ Batteries: Experimental Analyses of Calendar Aging, *Electrochim. Acta.* 190 (2016) 1124–1133. doi:10.1016/j.electacta.2015.12.161.
- [5] D. Li, D. Danilov, L. Gao, Y. Yang, P.H.L. Notten, Degradation Mechanisms of C6/LiFePO₄ Batteries: Experimental Analyses of Cycling-induced Aging, *Electrochim. Acta.* 210 (2016) 445–455. doi:10.1016/j.electacta.2016.05.091.
- [6] K. Kleiner, P. Jakes, S. Scharner, V. Liebau, H. Ehrenberg, Changes of the balancing between anode and cathode due to fatigue in commercial lithium-ion cells, *J. Power Sources.* 317 (2016) 25–34. doi:10.1016/j.jpowsour.2016.03.049.
- [7] M. Lang, M.S.D. Darma, K. Kleiner, L. Riekehr, L. Mereacre, M. Ávila Pérez, et al., Post mortem analysis of fatigue mechanisms in LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ - LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ - LiMn₂O₄/graphite lithium ion batteries, *J. Power Sources.* 326 (2016) 397–409. doi:10.1016/j.jpowsour.2016.07.010.
- [8] M. Börner, A. Friesen, M. Grützke, Y.P. Stenzel, G. Brunklaus, J. Haetge, et al., Correlation of aging and thermal stability of commercial 18650-type lithium ion batteries, *J. Power Sources.* 342 (2017) 382–392. doi:10.1016/j.jpowsour.2016.12.041.
- [9] V. Ruiz, A. Kriston, I. Adanouj, M. Destro, D. Fontana, A. Pfrang, Degradation Studies on Lithium Iron Phosphate - Graphite Cells. The Effect of Dissimilar Charging – Discharging Temperatures, *Electrochim. Acta.* 240 (2017) 495–505. doi:10.1016/j.electacta.2017.03.126.
- [10] S. Sun, T. Guan, B. Shen, K. Leng, Y. Gao, X. Cheng, et al., Changes of Degradation Mechanisms of LiFePO₄/Graphite Batteries Cycled at Different Ambient Temperatures, *Electrochim. Acta.* 237 (2017) 248–258. doi:10.1016/j.electacta.2017.03.158.
- [11] M. Ouyang, Z. Chu, L. Lu, J. Li, X. Han, X. Feng, et al., Low temperature aging mechanism identification and lithium deposition in a large format lithium iron phosphate battery for different charge profiles, *J. Power Sources.* 286 (2015) 309–320. doi:10.1016/j.jpowsour.2015.03.178.
- [12] T. Waldmann, M. Wilka, M. Kasper, M. Fleischhammer, M. Wohlfahrt-Mehrens, Temperature dependent ageing mechanisms in Lithium-ion batteries – A Post-Mortem study, *J. Power Sources.* 262 (2014) 129–135. doi:10.1016/j.jpowsour.2014.03.112.

- [13] M. Kassem, C. Delacourt, Postmortem analysis of calendar-aged graphite/LiFePO₄ cells, *J. Power Sources*. 235 (2013) 159–171. doi:10.1016/j.jpowsour.2013.01.147.
- [14] P. Liu, J. Wang, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, et al., Aging Mechanisms of LiFePO₄ Batteries Deduced by Electrochemical and Structural Analyses, *J. Electrochem. Soc.* 157 (2010) A499. doi:10.1149/1.3294790.
- [15] M. Petzl, M. Kasper, M.A. Danzer, Lithium plating in a commercial lithium-ion battery – A low-temperature aging study, *J. Power Sources*. 275 (2014) 799–807. doi:10.1016/j.jpowsour.2014.11.065.
- [16] M. Ecker, P. Shafiei Sabet, D.U. Sauer, Influence of operational condition on lithium plating for commercial lithium-ion batteries – Electrochemical experiments and post-mortem-analysis, *Appl. Energy*. 206 (2017) 934–946. doi:10.1016/j.apenergy.2017.08.034.
- [17] A. Friesen, F. Horsthemke, X. Mönnighoff, G. Brunklaus, R. Krafft, M. Börner, et al., Impact of cycling at low temperatures on the safety behavior of 18650-type lithium ion cells: Combined study of mechanical and thermal abuse testing accompanied by post-mortem analysis, *J. Power Sources*. 334 (2016) 1–11. doi:10.1016/j.jpowsour.2016.09.120.
- [18] A. Friesen, S. Hildebrand, F. Horsthemke, M. Börner, R. Klöpsch, P. Niehoff, et al., Al₂O₃ coating on anode surface in lithium ion batteries: Impact on low temperature cycling and safety behavior, *J. Power Sources*. 363 (2017) 70–77. doi:10.1016/j.jpowsour.2017.07.062.
- [19] N. Ghanbari, T. Waldmann, M. Kasper, P. Axmann, M. Wohlfahrt-Mehrens, Inhomogeneous Degradation of Graphite Anodes in Li-Ion Cells: A Postmortem Study Using Glow Discharge Optical Emission Spectroscopy (GD-OES), *J. Phys. Chem. C*. 120 (2016) 22225–22234. doi:10.1021/acs.jpcc.6b07117.
- [20] D. Burow, K. Sergeeva, S. Calles, K. Schorb, A. Börger, C. Roth, et al., Inhomogeneous degradation of graphite anodes in automotive lithium ion batteries under low-temperature pulse cycling conditions, *J. Power Sources*. 307 (2016) 806–814. doi:10.1016/j.jpowsour.2016.01.033.
- [21] Y. Li, K. Qian, Y.-B. He, Y.V. Kaneti, D. Liu, D. Luo, et al., Study on the reversible capacity loss of layered oxide cathode during low-temperature operation, *J. Power Sources*. 342 (2017) 24–30. doi:10.1016/j.jpowsour.2016.12.033.
- [22] B.P. Matadi, S. Geniès, A. Delaille, C. Chabrol, E. de Vito, M. Bardet, et al., Irreversible Capacity Loss of Li-Ion Batteries Cycled at Low Temperature Due to an Untypical Layer Hindering Li Diffusion into Graphite Electrode, *J. Electrochem. Soc.* 164 (2017) A2374–A2389. doi:10.1149/2.0491712jes.
- [23] B.P. Matadi, S. Geniès, A. Delaille, T. Waldmann, M. Kasper, M. Wohlfahrt-Mehrens, et al., Effects of Biphenyl Polymerization on Lithium Deposition in Commercial Graphite/NMC Lithium-Ion Pouch-Cells during Calendar Aging at High Temperature, *J. Electrochem. Soc.* 164 (2017) A1089–A1097. doi:10.1149/2.0631706jes.
- [24] B. Stiaszny, J.C. Ziegler, E.E. Krauss, J.P. Schmidt, E. Ivers-Tiffée, Electrochemical characterization and post-mortem analysis of aged LiMn₂O₄-Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O₂/graphite lithium ion batteries part I: Cycle aging, *J. Power Sources*. 251 (2014) 439–450. doi:10.1016/j.jpowsour.2013.11.080.
- [25] B. Stiaszny, J.C. Ziegler, E.E. Krauss, M. Zhang, J.P. Schmidt, E. Ivers-Tiffée, Electrochemical characterization and post-mortem analysis of aged LiMn₂O₄-NMC/graphite lithium ion batteries part II: Calendar aging, *J. Power Sources*. 258 (2014) 61–75.

doi:10.1016/j.jpowsour.2014.02.019.

- [26] M. Klett, R. Eriksson, J. Groot, P. Svens, K. Ciosek Högstöm, R. Wreland Lindström, et al., Non-uniform aging of cycled commercial LiFePO₄/graphite cylindrical cells revealed by post-mortem analysis, *J. Power Sources*. 257 (2014) 126–137. doi:10.1016/j.jpowsour.2014.01.105.
- [27] M. Klett, P. Svens, C. Tengstedt, A. Seyeux, J. Światowska, G. Lindbergh, et al., Uneven Film Formation across Depth of Porous Graphite Electrodes in Cycled Commercial Li-Ion Batteries, *J. Phys. Chem. C*. 119 (2015) 90–100. doi:10.1021/jp509665e.
- [28] T. Waldmann, N. Ghanbari, M. Kasper, M. Wohlfahrt-Mehrens, Correlations between Electrochemical Data and Results from Post-Mortem Analysis of Aged Lithium-Ion Batteries, *J. Electrochem. Soc.* 162 (2015) A1500–A1505. doi:10.1149/2.0411508jes.
- [29] H. Zheng, L. Tan, L. Zhang, Q. Qu, Z. Wan, Y. Wang, et al., Correlation between lithium deposition on graphite electrode and the capacity loss for LiFePO₄/graphite cells, *Electrochim. Acta*. 173 (2015) 323–330. doi:10.1016/j.electacta.2015.05.039.
- [30] K. Jalkanen, J. Karppinen, L. Skogström, T. Laurila, M. Nisula, K. Vuorilehto, Cycle aging of commercial NMC/graphite pouch cells at different temperatures, *Appl. Energy*. 154 (2015) 160–172. doi:10.1016/j.apenergy.2015.04.110.
- [31] J. Vetter, P. Novák, M.R. Wagner, C. Veit, K.C. Möller, J.O. Besenhard, et al., Ageing mechanisms in lithium-ion batteries, *J. Power Sources*. 147 (2005) 269–281. doi:10.1016/j.jpowsour.2005.01.006.
- [32] M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, et al., Main aging mechanisms in Li ion batteries, *J. Power Sources*. 146 (2005) 90–96. doi:10.1016/j.jpowsour.2005.03.172.
- [33] P. Arora, R.E. White, M. Doyle, Capacity Fade Mechanisms and Side Reactions in Lithium-Ion Batteries, *J. Electrochem. Soc.* 145 (1998) 3647–3667. doi:10.1149/1.1838857.
- [34] R. Imhof, P. Novák, In Situ Investigation of the Electrochemical Reduction of Carbonate Electrolyte Solutions at Graphite Electrodes, *J. Electrochem. Soc.* 145 (1998) 1081–1087. doi:10.1149/1.1838420.
- [35] M. Petzl, M.A. Danzer, Nondestructive detection, characterization, and quantification of lithium plating in commercial lithium-ion batteries, *J. Power Sources*. 254 (2014) 80–87. doi:10.1016/j.jpowsour.2013.12.060.
- [36] M. Fleischhammer, T. Waldmann, G. Bisle, B.-I. Hogg, M. Wohlfahrt-Mehrens, Interaction of cyclic ageing at high-rate and low temperatures and safety in lithium-ion batteries, *J. Power Sources*. 274 (2015) 432–439. doi:10.1016/j.jpowsour.2014.08.135.
- [37] M. Wohlfahrt-Mehrens, C. Vogler, J. Garche, Aging mechanisms of lithium cathode materials, *J. Power Sources*. 127 (2004) 58–64. doi:10.1016/j.jpowsour.2003.09.034.
- [38] H. Gabrisch, R. Yazami, B. Fultz, Hexagonal to Cubic Spinel Transformation in Lithiated Cobalt Oxide, *J. Electrochem. Soc.* 151 (2004) A891. doi:10.1149/1.1738677.
- [39] K. Edström, T. Gustafsson, J.O. Thomas, The cathode-electrolyte interface in the Li-ion battery, *Electrochim. Acta*. 50 (2004) 397–403. doi:10.1016/j.electacta.2004.03.049.
- [40] S. Malmgren, K. Ciosek, M. Hahlin, T. Gustafsson, M. Gorgoi, H. Rensmo, et al., Comparing anode and cathode electrode/electrolyte interface composition and morphology using soft and hard X-ray photoelectron spectroscopy, *Electrochim. Acta*. 97 (2013) 23–32.

doi:10.1016/j.electacta.2013.03.010.

- [41] Y. Wu, P. Keil, S.F. Schuster, A. Jossen, Impact of Temperature and Discharge Rate on the Aging of a LiCoO₂/LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ Lithium-Ion Pouch Cell, *J. Electrochem. Soc.* 164 (2017) A1438–A1445. doi:10.1149/2.0401707jes.
- [42] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries, *J. Electrochem. Soc.* 144 (1997) 1188–1194. doi:10.1684/agr.2014.0700.
- [43] D. Wang, X. Wu, Z. Wang, L. Chen, Cracking causing cyclic instability of LiFePO₄ cathode material, *J. Power Sources.* 140 (2005) 125–128. doi:10.1016/j.jpowsour.2004.06.059.
- [44] H. Gabrisch, J. Wilcox, M.M. Doeff, TEM Study of Fracturing in Spherical and Plate-like LiFePO₄ Particles, *Electrochem. Solid-State Lett.* 11 (2008) A25. doi:10.1149/1.2826746.
- [45] M. Dubarry, C. Truchot, B.Y. Liaw, Cell degradation in commercial LiFePO₄ cells with high-power and high-energy designs, *J. Power Sources.* 258 (2014) 408–419. doi:10.1016/j.jpowsour.2014.02.052.
- [46] M. Koltypin, D. Aurbach, L. Nazar, B. Ellis, More on the performance of LiFePO₄ electrodes - The effect of synthesis route, solution composition, aging, and temperature, *J. Power Sources.* 174 (2007) 1241–1250. doi:10.1016/j.jpowsour.2007.06.045.
- [47] K. Amine, J. Liu, I. Belharouak, High-temperature storage and cycling of C-LiFePO₄/graphite Li-ion cells, *Electrochem. Commun.* 7 (2005) 669–673. doi:10.1016/j.elecom.2005.04.018.
- [48] L.-X. Yuan, Z.-H. Wang, W.-X. Zhang, X.-L. Hu, J.-T. Chen, Y.-H. Huang, et al., Development and challenges of LiFePO₄ cathode material for lithium-ion batteries, *Energy Environ. Sci.* 4 (2011) 269–284. doi:10.1039/C0EE00029A.
- [49] BYD Company Limited, Products and Services, (2017). <http://www.bydeurope.com> (accessed October 24, 2017).
- [50] N. Omar, M.A. Monem, Y. Firouz, J. Salminen, J. Smekens, O. Hegazy, et al., Lithium iron phosphate based battery - Assessment of the aging parameters and development of cycle life model, *Appl. Energy.* 113 (2014) 1575–1585. doi:10.1016/j.apenergy.2013.09.003.
- [51] J. Rodriguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Phys. B Condens. Matter.* 192 (1993) 55–69.
- [52] T. Waldmann, S. Gorse, T. Samtleben, G. Schneider, V. Knoblauch, M. Wohlfahrt-Mehrens, A Mechanical Aging Mechanism in Lithium-Ion Batteries, *J. Electrochem. Soc.* 161 (2014) A1742–A1747. doi:10.1149/2.1001410jes.
- [53] M. Kassem, J. Bernard, R. Revel, S. Pélissier, F. Duclaud, C. Delacourt, Calendar aging of a graphite/LiFePO₄ cell, *J. Power Sources.* 208 (2012) 296–305. doi:10.1016/j.jpowsour.2012.02.068.
- [54] S. Grolleau, A. Delaille, H. Gualous, P. Gyan, R. Revel, J. Bernard, et al., Calendar aging of commercial graphite/LiFePO₄ cell - Predicting capacity fade under time dependent storage conditions, *J. Power Sources.* 255 (2014) 450–458. doi:10.1016/j.jpowsour.2013.11.098.
- [55] P. Keil, S.F. Schuster, J. Wilhelm, J. Travi, A. Hauser, R.C. Karl, et al., Calendar Aging of Lithium-Ion Batteries I. Impact of the Graphite Anode on Capacity Fade, *J. Electrochem. Soc.* 163 (2016) A1872–A1880. doi:10.1149/2.0411609jes.

- [56] A.J. Smith, H.M. Dahn, J.C. Burns, J.R. Dahn, Long-Term Low-Rate Cycling of LiCoO₂/Graphite Li-Ion Cells at 55°C, *J. Electrochem. Soc.* 159 (2012) A705. doi:10.1149/2.056206jes.
- [57] J.R. Dahn, Phase diagram of Li_xC₆, *Phys. Rev. B.* 44 (1991) 9170–9177. doi:10.1103/PhysRevB.44.9170.
- [58] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novák, Insertion Electrode Materials for Rechargeable Lithium Batteries, *Adv. Mater.* 10 (1998) 725–763. doi:10.1002/(SICI)1521-4095(199807)10:10<725::AID-ADMA725>3.0.CO;2-Z.
- [59] S. Malmgren, K. Ciosek, R. Lindblad, S. Plogmaker, J. Kühn, H. Rensmo, et al., Consequences of air exposure on the lithiated graphite SEI, *Electrochim. Acta.* 105 (2013) 83–91. doi:10.1016/j.electacta.2013.04.118.
- [60] R. Baddour-Hadjean, J.-P. Pereira-Ramos, Raman Microspectrometry Applied to the Study of Electrode Materials for Lithium Batteries, *Chem. Rev.* 110 (2010) 1278–1319. doi:10.1021/cr800344k.
- [61] L.J. Hardwick, H. Buqa, P. Novák, Graphite surface disorder detection using in situ Raman microscopy, *Solid State Ionics.* 177 (2006) 2801–2806. doi:10.1016/j.ssi.2006.03.032.
- [62] F. Tuinstra, J.L. Koenig, Raman Spectrum of Graphite, *J. Chem. Phys.* 53 (1970) 1126–1130. doi:10.1063/1.1674108.
- [63] G.L. Doll, P.C. Eklund, J.E. Fischer, Raman scattering study of the high-frequency graphitic intralayer modes in Li-graphite and the stage dependence of the mode frequency in donor graphite intercalation compounds, *Phys. Rev. B.* 36 (1987) 4940–4945. doi:10.1103/PhysRevB.36.4940.
- [64] M.H. Brooker, J.B. Bates, Raman and Infrared Spectral Studies of Anhydrous Li₂CO₃ and Na₂CO₃, *J. Chem. Phys.* 54 (1971) 4788–4796. doi:10.1063/1.1674754.
- [65] N. Koura, S. Kohara, K. Takeuchi, S. Takahashi, L.A. Curtiss, M. Grimsditch, et al., Alkali carbonates: Raman spectroscopy, ab initio calculations, and structure, *J. Mol. Struct.* 382 (1996) 163–169. doi:10.1016/0022-2860(96)09314-3.
- [66] R. Schmitz, R. Ansgar Müller, R. Wilhelm Schmitz, C. Schreiner, M. Kunze, A. Lex-Balducci, et al., SEI investigations on copper electrodes after lithium plating with Raman spectroscopy and mass spectrometry, *J. Power Sources.* 233 (2013) 110–114. doi:10.1016/j.jpowsour.2013.01.105.
- [67] C. Naudin, J.L. Bruneel, M. Chami, B. Desbat, J. Grondin, J.C. Lasségues, et al., Characterization of the lithium surface by infrared and Raman spectroscopies, *J. Power Sources.* 124 (2003) 518–525. doi:10.1016/S0378-7753(03)00798-5.
- [68] T.A. Galloway, L. Cabo-Fernandez, I. Aldous, F. Braga, L. Hardwick, Shell Isolated Nanoparticles for Enhanced Raman Spectroscopy Studies in Lithium-Oxygen Cells, *Faraday Discuss.* 205 (2017) 469–490. doi:10.1039/C7FD00151G.
- [69] Y. Li, M. Bettge, B. Polzin, Y. Zhu, M. Balasubramanian, D.P. Abraham, Understanding Long-Term Cycling Performance of Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.10}O₂-Graphite Lithium-Ion Cells, *J. Electrochem. Soc.* 160 (2013) A3006–A3019. doi:10.1149/2.002305jes.
- [70] E. Markervich, G. Salitra, M.D. Levi, D. Aurbach, Capacity fading of lithiated graphite electrodes studied by a combination of electroanalytical methods, Raman spectroscopy and SEM, *J. Power Sources.* 146 (2005) 146–150. doi:10.1016/j.jpowsour.2005.03.107.

- [71] A. Friesen, X. Mönnighoff, M. Börner, J. Haetge, F.M. Schappacher, M. Winter, Influence of temperature on the aging behavior of 18650-type lithium ion cells: A comprehensive approach combining electrochemical characterization and post-mortem analysis, *J. Power Sources*. 342 (2017) 88–97. doi:10.1016/j.jpowsour.2016.12.040.
- [72] A.H. Whitehead, K. Edström, N. Rao, J.R. Owen, In situ X-ray diffraction studies of a graphite-based Li-ion battery negative electrode, *J. Power Sources*. 63 (1996) 41–45. doi:10.1016/S0378-7753(96)02440-8.
- [73] J. Christensen, Modeling Diffusion-Induced Stress in Li-Ion Cells with Porous Electrodes, *J. Electrochem. Soc.* 157 (2010) A366. doi:10.1149/1.3269995.
- [74] V.A. Sethuraman, L.J. Hardwick, V. Srinivasan, R. Kostecki, Surface structural disordering in graphite upon lithium intercalation/deintercalation, *J. Power Sources*. 195 (2010) 3655–3660. doi:10.1016/j.jpowsour.2009.12.034.
- [75] K. Takahashi, V. Srinivasan, Examination of Graphite Particle Cracking as a Failure Mode in Lithium-Ion Batteries: A Model-Experimental Study, *J. Electrochem. Soc.* 162 (2015) A635–A645. doi:10.1149/2.0281504jes.
- [76] M. Gaberscek, J. Moskon, B. Erjavec, R. Dominko, J. Jamnik, The Importance of Interphase Contacts in Li Ion Electrodes: The Meaning of the High-Frequency Impedance Arc, *Electrochem. Solid-State Lett.* 11 (2008) A170. doi:10.1149/1.2964220.