Calendar aging of lithium-ion cells is investigated by storing commercial 18650 cells with NCA cathode and graphite anode at different states of charge and temperatures. The resulting capacity fades are analyzed by differential voltage analysis (DVA) and coulometry. DVA reveals that the capacity fade results mainly from a shift in the electrode balancing due to a reduced inventory of cyclable lithium. Moreover, DVA confirms that the capacity fade strongly correlates with the anode potential. The observed loss of cyclable lithium is further analyzed by coulomb tracking, which stands for creating a continuous ampere-hour balance from all individual measurements performed with an examined cell and tracking the slippage of charging and discharging endpoints. It reveals the extent of anodic and cathodic side reactions during the storage periods and their effect on the inventory of cyclable lithium. Anodic side reactions, which are related to electrolyte reduction and passivation layer growth, can be identified as the main driver of capacity fade. Coulomb tracking also discloses that increasing cathodic side reactions can reduce the irreversible capacity fade, particularly for storage at very high SoC, which is likely to be misinterpreted as decelerated aging reactions. Evaluating also the reversible capacity fade prevents such a misconception.

Calendar aging comprises all aging processes that lead to a degradation of a battery cell independent of charge-discharge cycling. It is an important factor in many applications of lithium-ion batteries where the operation periods are substantially shorter than the idle intervals, such as in electric vehicles.\(^1\)

Parasitic side reactions at the electrode-electrolyte interfaces are considered to be the predominant degradation processes of calendar aging.\(^2\),\(^3\) They cause electrolyte reduction at the negative electrode and electrolyte oxidation at the positive electrode.\(^4\),\(^5\) The electrolyte reduction at the anode is generally associated with a growth of the solid electrolyte interphase (SEI), the passivation layer which separates the anode active material from the electrolyte.\(^6\) In addition to electrolyte decomposition, transition metals are dissolved from the cathode at higher voltage and get deposited at the anode, which in turn increases anodic side reactions.\(^7\),\(^8\)

There are many studies on calendar aging of lithium-ion batteries which present the capacity fade of the cells over time but do not provide explicit investigations on anodic or cathodic side reactions causing the capacity fade.\(^9\)–\(^17\) Furthermore, calendar aging is mostly examined only for a few SoCs: Refs.\(^11\)–\(^17\) examine three SoCs or fewer. By contrast, this paper presents investigations on calendar aging with a large number of SoCs examined to obtain a comprehensive understanding of the dependency of the capacity fade on SoC. Moreover, side reactions are analyzed.

In this paper, two experimental studies on calendar aging of nickel cobalt aluminum oxide (NCA) lithium-ion batteries are presented and evaluated. Differential voltage analysis (DVA) and coulometry are employed to gain a deeper understanding of the degradation mechanisms and side reactions leading to calendar aging. These two methods are introduced in the following sections and allow to identify predominant aging mechanisms without opening the cells to insert reference electrodes or the need for post-mortem analyses.

**Differential Voltage Analysis**

DVA is an advanced technique for electrical characterization of battery cells. From a constant current charging or discharging sequence, the derivative \(dV/dQ\) is computed, which represents a linear superposition of the derivatives of the anode and cathode potential.\(^18\)

\[
V_{\text{cell}} = V_{\text{cathode}} - V_{\text{anode}}
\]

\[
dV_{\text{cell}}/dQ = (dV_{\text{cathode}}/dQ) + (-dV_{\text{anode}}/dQ)
\]

Figure 1a illustrates how the full-cell voltage of an NCA lithium-ion cell results from the difference of cathode and anode potential. For the four curves, Figure 1b presents the corresponding derivatives. The various slopes and peaks in the derivatives of the full-cells and half-cells demonstrate the linear superposition of both electrodes. As the individual contributions of both electrodes can be identified in the full-cell derivative, DVA can be used to determine the balancing and the utilization of the two electrodes without inserting a reference cell.
In aging studies, DVA is employed to separate different aging mechanisms, such as anode degradation, cathode degradation, and shifts in the electrode balancing. As the peaks in the differential voltage spectrum appear more pronounced with lower currents, charging and discharging currents of C/20 and below are typically used.

Based on the superposition of anode and cathode derivative depicted in Figure 1b, the characteristic slopes at 0% and 100% SoC can be assigned to the individual electrodes. The marked potential drop in the full-cell voltage indicating 0% SoC is linked to the rising potential of the delithiated graphite anode, which is represented by the steep slope in the differential voltage spectrum. Hence, an empty anode determines the discharging end point, which represents the lower end of the available capacity window of the full-cell. The upper end of the capacity window is not determined by the graphite anode since the anode is generally oversized and the anode potential is constant in the high SoC region. Thus, the charging end point is determined by the increasing potential of the cathode approaching its maximum permissible degree of delithiation, which is limited to ca. 55% for NCA cathodes to avoid substantial deformations in the lattice structure. The discharging and charging endpoints are also of special importance for the coulometry evaluations, which will be described later.

Figure 2 shows the complete assignment of slopes and peaks to both electrodes. From this assignment, the three characteristic capacities \( Q_1 \), \( Q_2 \), and \( Q_3 \) can be derived which are used in this paper to determine aging contributions from anode degradation, cathode degradation, and changes in the electrode balancing. As illustrated in Figure 2, \( Q_1 \) represents the distance between 0% SoC and the central graphite peak at about 1.6 Ah. The central graphite peak indicates the transition from the medium to the low voltage plateau of the anode potential, which occurs when the graphite anode is lithiated more than 50%. Since \( Q_1 \) bases solely on characteristic anode markers, it provides information about changes in the storage capabilities of the graphite anode. Similarly, \( Q_1 \) provides information about the storage capabilities of the NCA cathode, as it bases solely on characteristic cathode markers. \( Q_2 \) represents the distance between the central graphite peak and 100% SoC. Hence, it combines an anode and a cathode marker. It sums up together with \( Q_1 \) to \( Q_{\text{actual}} \) and provides information about the balancing of the two electrodes. A change in \( Q_2 \) without a change of the anode capacity \( Q_1 \) and the cathode capacity \( Q_3 \) indicates a sole shift in the electrode balancing, which changes the inventory of cyclable lithium and thus alters the operating window of the two electrodes.

### Coulometry

Coulometry is a useful method for analyzing side reactions and battery aging. In conventional coulometry studies, the lithium-ion cells are cycled continuously with low currents of C/10 and below; the charged and discharged ampere-hours are recorded together with the cell voltage. From these cycling data, coulombic efficiencies are computed and their absolute values and changes over cycle number or time are evaluated. Furthermore, the slippage of the charging and discharging endpoints is analyzed, which provides explicit information about anodic and cathodic side reactions. Performing coulometry with the low-current cycling approach requires high-precision battery test systems which feature highly precise current measurements that exhibit no offset errors causing drifts in the ampere-hour integration.

In contrast to the conventional low-current cycling approach, we perform coulometry evaluations with the data from our calendar aging studies, in which the cells are not cycled continuously but are stored in open circuit condition. We only perform occasional checkups at the battery test systems to determine the actual capacities of the cells and bring them back to their respective storage SoCs before they are disconnected from the test system again and returned to the storage compartments.

**Coulomb tracking method.**—The coulometry method we present in this paper is named ‘coulomb tracking’ and consists of two steps. At first, the measurement data of all tests performed at the battery test system with the cell under test are ordered chronologically and a continuous ampere-hour balance is generated. To obtain this continuous charge balance, the last ampere-hour value of each measurement run is used as an offset for the charge balance of the subsequent measurement. During the time in which the cell is stored, the cell is disconnected from the battery test system. This is an important prerequisite of this coulometry method, as it ascertains that no charge can flow into or out of the cell during the storage periods. Thus, the charge balance remains unchanged. In the second step, the continuous charge balance is used to track the slippage of representative charging and discharging endpoints. To evaluate comparable endpoints, one specific sequence of the checkup procedure is selected from which the charging and discharging endpoints are determined and changes are monitored. The advantage of this method is that it can be performed with conventional battery test systems, as no long-term measurements have to be performed during the storage periods, where the current integration is prone to drifts owing to small offset errors in the current measurement. As the cells are stored in open circuit condition, the change in the charge balance always remains zero, independent of the storage duration lasting several weeks and months.

Figure 3 illustrates the coulomb tracking method. Figure 3a shows the periodic sequence of checkups (blue), test protocols bringing the cells to storage SoC (red), and the actual storage periods in open circuit condition (gray). During the checkups, charge-discharge cycles are performed to determine the actual capacity under reference conditions. Figure 3b shows the individual charge balances recorded for each measurement run at the battery test system. From these data, the continuous charge balance is generated as described above and illustrated in Figure 3c. The dotted lines represent the constant ampere-hour values during the storage periods, in which the cells are disconnected from the battery system. The crosses represent the discharging and charging endpoints of one specific sequence of the checkup where the current is low; and the dashed lines illustrate the slippage of the endpoints over time. The shifts of the charging and discharging endpoints provide information about anodic and cathodic side reactions. The interpretation of these shifts is similar as for the conventional coulometry approach, based on continuous low-current cycling.

**Interpretation of the coulometry results.**—In principle, coulometry can detect such side reactions that alter the degree of lithiation of one or both of the electrodes. For lithium-ion batteries, these side reactions can be categorized in the three cases which are illustrated schematically in Figure 4: Anodic side reactions, cathodic side reactions, and coupled side reactions, which represent a combination of the two previous cases.
altering degree of lithiation of the anode, the operating point shifts

Metals or electrolyte shuttle reactions. \cite{31,39} Although transition-metal dissolution is typically expected for manganese-based electrodes, \cite{8,40} post-mortem studies have also revealed a deposition of cobalt and nickel at the anode of aged NCA cells. \cite{41} Furthermore, reaction
to the left during the storage periods, as illustrated by the blue arrow and the cross marker in Figure 4a. As the ampere-hour value of the continuous charge balance does not change during storage, because the cells are always stored in open circuit condition, the side reactions can be interpreted as an internal shift of the anode half-cell curve to the right. The resulting degree of lithiation after the storage period is located at the ampere-hour value of the charge balance at the beginning of the storage period. This is illustrated in Figure 4d. The right-shift of the anode curve also entails a right-shift of the discharging end point, represented by the violet arrow, whereas the charging end point remains unaffected. This decreases the inventory of cyclable lithium and the utilization of both electrodes, which represents an irreversible capacity fade.

Anodic side reactions.—Figures 4a, 4d show side reactions that only affect the negative electrode. These anodic side reactions are generally related to electrolyte reduction and SEI growth, which consume intercalated lithium of the anode during storage.\cite{31,34,35} With the altering degree of lithiation of the anode, the operating point shifts

to the left during the storage periods, as illustrated by the blue arrow and the cross marker in Figure 4a. As the ampere-hour value of the continuous charge balance does not change during storage, because the cells are always stored in open circuit condition, the side reactions can be interpreted as an internal shift of the anode half-cell curve to the right. The resulting degree of lithiation after the storage period is located at the ampere-hour value of the charge balance at the beginning of the storage period. This is illustrated in Figure 4d. The right-shift of the anode curve also entails a right-shift of the discharging end point, represented by the violet arrow, whereas the charging end point remains unaffected. This decreases the inventory of cyclable lithium and the utilization of both electrodes, which represents an irreversible capacity fade.

Cathodic side reactions.—Figures 4b, 4e depict side reactions that only affect the positive electrode. Cathodic side reactions include electrolyte oxidation and transition-metal dissolution, which provoke a reinsertion of the lithium into the positive electrode that can be observed in form of a potential decrease.\cite{36,37} The changing degree of lithiation and the potential drop are illustrated by the red arrow and cross marker in Figure 4b. Comparable to the shift of the anode curve in Figure 4d, Figure 4e demonstrates that cathodic side reactions lead to a right-shift of the cathode half-cell curve. The violet arrow shows that this shift entails a right-shift of the charging end point, while the discharging end point remains at the same location, as long as the cathode is not fully utilized. This expands the inventory of cyclable lithium and the utilization of both electrodes. Thus, cathodic side reactions can increase the actual capacity of the full-cell. However, the stored amount of charge decreases during the storage periods due to the reinsertalitarian of lithium into the cathode. Hence, cathodic side reactions cause a reversible self-discharge.\cite{38}

Coupled side reactions.—Figures 4c, 4f illustrate the effects of coupled side reactions, which combine side reactions at the positive and negative electrode. In Figure 4c, the arrows and cross markers represent the changes in the degree of lithiation of both electrodes. Coupled side reactions occur when reaction products generated at one electrode migrate or diffuse to the other electrode and cause additional side reactions there, such as deposition of dissolved transition metals or electrolyte shuttle reactions.\cite{31,39} Although transition-metal dissolution is typically expected for manganese-based electrodes,\cite{8,40} post-mortem studies have also revealed a deposition of cobalt and nickel at the anode of aged NCA cells.\cite{41} Furthermore, reaction
products from electrolyte oxidation at higher cell voltage were identified to diffuse to the anode and increase side reactions there.\footnote{These reactions include electrolyte decomposition, anodic decomposition of the electrolyte, and side reactions at the anode or cathode.} In this paper, coupled side reactions are such combinations of anodic and cathodic side reactions where the amount of lithium that is intercalated at the cathode and the amount of lithium consumed at the anode are identical. As illustrated in Figure 4f, this leads to an identical right-shift of both half-cell curves and results in an identical shift of the discharging and charging end point. As a consequence, these side reactions cause a fully reversible self-discharge without a change in the actual capacity of the cell.\footnote{These side reactions can be modeled as a combination of the reactions at the anode and cathode.} Hence, there are no changes in the inventory of cyclable lithium, as long as there is no considerable degradation of the electrodes.

The side reaction mechanisms presented above all base on a delithiation of the anode and/or a delithiation of the cathode. They all have in common that they reduce the energy content of the battery cell – even if the actual capacity of the cell remains unchanged or even increases. In those cases, the energy loss occurs in form of reversible self-discharge which can be recovered during the next charging sequence. Other hypothetical side reactions which cause a lithiation of the anode or a delithiation of the cathode are not taken into consideration. They do not appear feasible, as they would increase the energy content of a battery cell during storage, which is considered as thermodynamically unfavorable. An increase in the energy content during storage periods can only be expected when there was a previously generated inhomogeneity of the lithium distribution in the electrodes, e.g., in the “overhang areas” of the anode, which have no opposed cathode counterpart.\footnote{These regions are typically caused by manufacturing processes.} In these cases, the equalization process of previously generated concentration gradients can appear as an increasing energy content during storage. As such effects are not aging-related side reactions, the three side reaction mechanisms presented in Figure 4 were sufficient to reproduce and explain the capacity fades and end point shifts which occurred in the two calendar aging studies evaluated in this paper.

**Experimental**

In this paper, two studies on calendar aging of lithium-ion batteries are evaluated. In these experimental studies, commercial high-energy cells of type Panasonic NCR18650PD were examined. The cells of 18650 format had a capacity of ca. 2.8 Ah and featured an NCA cathode and a graphite anode. Both studies examined the same cell type, but the respective cells were from different production lots. The 18650 format had a capacity of ca. 2.8 Ah and featured an NCA cathode and a graphite anode. Both studies examined the same cell type, but the respective cells were from different production lots. The CTS battery test system with 32 independent 5V/5A channels was used. For all measurements at the battery test system, the cells were placed in thermal chambers at 25°C with temperature variations of less than 0.2°C to obtain identical environmental conditions for all checkup measurements.

**Checkup routines.—**The checkup procedures of the two aging studies are presented in Table I and Table II. To determine the actual capacity, the cells were discharged with a constant current constant voltage (CCCV) sequence until the amplitude of the discharging current decreased below 100 mA. These discharging steps are marked with \([\text{CAP}]\). Before the capacity measurements, the cells were fully charged to 4.2 V until the charging current dropped below 100 mA. These steps provide the ampere-hour values of the discharging and charging endpoints. The low-current charging sequence of the second checkup is also marked with \([\text{DVA}]\) as it is also used for DVA.

**Storage conditions.—**To obtain a detailed understanding of the dependency of calendar aging on the SoC, the entire SoC range from 0 to 100\% was examined with 8 and 16 storage SoCs. This provided a fine resolution of the aging results with respect to SoC. Figure 5 shows the various storage conditions examined. In both studies, the cells were charged to the respective storage SoC with a charging current of 700 mA. However, the definition of the storage SoC (except for 0\% and 100\% SoC) was different. In the first study, the storage SoCs were established based on the cell voltage. Six charging voltages were defined at which the charging procedure was terminated. In the second study, the storage SoCs were established by coulomb counting. The storage SoCs were defined as percentage of the actual capacity, which was determined in each checkup. Figure 5 also illustrates the approximate SoCs for the different charging voltages specified in the first calendar aging study. For each SoC, different temperatures were examined. In both aging studies, cells were stored at 25°C. Moreover, cells were stored at elevated temperatures to accelerate the tracking analyses. The beginning and the end of these two charging steps provide the ampere-hour values of the discharging and charging endpoints. The low-current charging sequence of the second checkup is also marked with \([\text{DVA}]\) as it is also used for DVA.

**Figure 5.** Storage conditions of the two calendar aging studies.

| Table I. Checkup sequence of aging study I. |
| --- | --- | --- |
| Step | Parameters | Termination |
| (1) Cyc. Volt.* | \(dV/dt = 3 \text{ mV/min} \) | \(V > 4.2 \text{ V} \) |
| (2) Charge CV | \(V = 4.2 \text{ V} \) | \(I < 0.1 \text{ A} \) |
| (3) Cyc. Volt.* | \(dV/dt = -3 \text{ mV/min} \) | \(V < 3 \text{ V} \) |
| (4) Cyc. Volt.* \([\text{CT}]\) | \(dV/dt = 3 \text{ mV/min} \) | \(V > 4.2 \text{ V} \) |
| (5) Pause | | \(t > 30 \text{ min} \) |
| (6) Charge CCCV | \(I = 700 \text{ mA}, V = 4.2 \text{ V} \) | \(I < 0.1 \text{ A} \) |
| (7) Pause | | \(t > 15 \text{ min} \) |
| (8) Discharge CCCV \([\text{CAP}]\) | \(I = -3 \text{ A}, V = 2.75 \text{ V} \) | \(I > -0.1 \text{ A} \) |
| (9) Pause | | \(t > 15 \text{ min} \) |
| (10) Charge CC | \(I = 700 \text{ mA} \) | SoC > 50\% |

*Slow-rate cyclic voltammetry.*

| Table II. Checkup sequence of aging study II. |
| --- | --- | --- |
| Step | Parameters | Termination |
| (1) Discharge CCCV | \(I = -1 \text{ A}, V = 2.5 \text{ V} \) | \(I > -0.1 \text{ A} \) |
| (2) Pause | | \(t > 15 \text{ min} \) |
| (3) Charge CC \([\text{DVA} \& \text{CT}]\) | \(I = 100 \text{ mA} \) | \(V = 4.2 \text{ V} \) |
| (4) Pause | | \(t > 15 \text{ min} \) |
| (5) Discharge CCCV \([\text{CAP}]\) | \(I = -2 \text{ A}, V = 2.5 \text{ V} \) | \(I > -0.1 \text{ A} \) |
| (6) Pause | | \(t > 15 \text{ min} \) |
| (7) Charge CC | \(I = 700 \text{ mA} \) | SoC > 50\% |

Downloaded on 2018-07-19 to IP 207.241.231.80 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
Results and Discussion

Two calendar aging studies are evaluated which were performed with commercial high-energy 18650 cells. Both studies examined the same NCA cell type, but the cells stemmed from different production lots. The cells examined in the first aging study were produced ca. 6 months earlier than the cells examined in the second study. In both studies, the lithium-ion cells were stored more than 9 months at different SoCs and temperatures. From the two studies, the capacity fade is shown with respect to SoC for two different temperatures. In addition to that, the results from DVA and coulomb tracking are presented to provide additional insights into the predominant aging reactions responsible for the capacity fade.

Capacity fade after 9 months of storage.—The capacity fade after ca. 9 months of storage is shown in Figure 6 for the two aging studies. In both studies, cells were stored at 25°C. In addition to that, the capacity fade for an elevated temperature of 55°C or 50°C is shown. Comparing the results of the two studies shows that the order of the capacity fade in the low and medium SoC range (<60% SoC) is similar for the cells of the two studies, which stemmed from different production lots. In the high SoC range (>80% SoC), however, the two groups of cells differ. In general, the capacity fade of lithium-ion cells is expected to increase with higher SoC. As it can be seen in Figure 6a, the capacity fade in the first aging study increases for storage SoCs from 0% to 80%, but decreases again toward 100% SoC. Such a decrease is not observed in Figure 6b for the cells of the second aging study. Hence, it is assumed that the cells of the two production lots were not 100% identical, as the aging mechanisms at high SoC differ considerably. Since the different trends at high SoC are observed at different SoCs and temperatures. From the two studies, the capacity fade is shown with respect to SoC for two different temperatures. In addition to that, the results from DVA and coulomb tracking are presented to provide additional insights into the predominant aging reactions responsible for the capacity fade.

Insights from differential voltage analysis.—To identify the dominant degradation mechanisms, DVA is performed with the checkup data from the second aging study. For DVA, constant-current charging curves with a low charging current of 100 mA have been evaluated to determine the characteristic capacities \( Q_1, Q_2, \) and \( Q_3 \), which were defined in Figure 2. Figure 7 shows the fade of \( Q_{\text{actual}} \) for six selected cells and also presents the changes in \( Q_1, Q_2, \) and \( Q_3 \) of these cells after 9.5 months of storage.

Origin of capacity fade.—For the cells presented in Figure 7, the actual capacities have faded between 60 mAh and 150 mAh for storage at 25°C and between 140 mAh and 310 mAh for storage at 50°C. This corresponds to a capacity fade of ca. 2–5% at 25°C and 5–11% at 50°C. The analysis of \( Q_1, Q_2, \) and \( Q_3 \) enables us to determine the origin of the capacity fade. The \( Q_1 \) capacities have remained rather unchanged for all cells after the 9.5 months of storage. This demonstrates that there has been zero degradation of the anode itself, as no changes of the storage capabilities of the graphite active material are observed. For \( Q_3 \), which represents the storage capability of the cathode active material, there are also zero or very minor changes detectable. In contrast to \( Q_1 \) and \( Q_3 \), substantial changes are observed for \( Q_2 \). The absolute reductions in the \( Q_2 \) capacities are similar to the reductions in \( Q_{\text{actual}} \). As the changes in the \( Q_2 \) values indicate a shift in the electrode balancing and as the individual electrodes exhibit no considerable degradation, the utilization of both electrodes has decreased: The anode remains less lithiated at 100% SoC, where the cathode approaches its maximum permissible degree of delithiation; and the cathode becomes less lithiated at 0% SoC, where the anode is fully delithiated. This reduces the inventory of cyclable lithium. Overall, the analysis of \( Q_1, Q_2, \) and \( Q_3 \) has shown that the capacity fade from calendar aging results predominantly from a shift in the electrode balancing related to a loss of cyclable lithium.

Correlation between capacity fade and anode potential.—Figure 8 presents the capacity fade over time for the cells from the second aging study. It clearly shows the SoC regions in which the capacity fade is similar. As presented in Ref. 1, the capacity fade from calendar aging strongly correlates with the anode potential. As illustrated in Figure 1, the central graphite peak in the differential voltage spectrum...
to reduce calendar aging, i.e., electrolyte reduction and SEI growth, are the main driving forces of these observations, it can be concluded that anodic side reactions, capacity fade. Moreover, Figure 8a shows a continuously decreasing graphite peak also separates the plateau regions of medium and high anode potential. The differential voltage spectrum represents the transition from the plateaus of medium anode potential to a square-root-of-time behavior for the capacity fade. Based on passivation layers as dominant aging mechanism, as this usually leads to the electrode balancing which reduces the inventory of cyclable lithium. As the electrode materials remain largely intact, side reactions are expected to occur which affect the degree of lithiation of the electrodes and thus alter the balancing of the electrodes. Coulomb tracking enables us to analyze these aging processes.

From the checkup data of the first aging study, Figure 9 shows representative charging curves after different storage periods. Cells stored at different SoCs and temperatures are compared. The ampere-hour value at the beginning of each charging curve represents the ampere-hour value of the discharging end point in the continuous charge balance and the ampere-hour value at the end of the curve is the ampere-hour value of the charging end point. For all six cells presented, the discharging endpoints shift considerably to the right; and these shifts enlarge with higher SoC and temperature. The shifts of the charging endpoints also increase with SoC and temperature, but they remain substantially smaller than the shifts of the discharging endpoints. As described in the method section on coulomb tracking, only right-shifts of the endpoints occur as a result of the side reactions during the storage periods. From the varying end point slippage for different storage SoCs and temperatures, characteristics of anodic and cathodic side reactions are derived.

Minimal cathodic side reactions at low SoC.—For storage at 10% SoC (Figures 9a, 9b), a considerable slippage of the discharging endpoints is observed, whereas the charging endpoints change only marginally. The stable charging endpoints indicate that the extent of cathodic side reactions is very low. Thus, coupled side reactions must also be very low as they always include cathodic side reactions. Consequently, solely anodic side reactions are the predominant aging mechanism at low SoC. These side reactions, which are related to electrolyte reduction and SEI growth, are known to cause right-shifts in practical applications, the lithium-ion cells should preferably be stored at SoCs which lie below the SoC location of the central graphite peak. This avoids storage periods at lowest graphite potential, which leads to fastest capacity fade. The location of the central graphite peak typically lies between 55% and 80% SoC, depending on the balancing between anode and cathode.

Insights from coulomb tracking.—As determined by DVA, the capacity fade from calendar aging results predominantly from a shift in the electrode balancing which reduces the inventory of cyclable lithium. As the electrode materials remain largely intact, side reactions are expected to occur which affect the degree of lithiation of the electrodes and thus alter the balancing of the electrodes. Coulomb tracking enables us to analyze these aging processes.

Figure 8. (a) Capacity fade over SoC for different storage periods. (b) Differential voltage spectrum of a cell in new condition. The dotted vertical line represents the SoC location of the central graphite peak.

Figure 9. Charging sequence after different storage durations at 25°C and 55°C used for coulomb tracking. The shifts of the ampere-hour value of the beginning and of the end of each voltage curve represent the slippage of the discharging and the charging end point, respectively.
of the discharging endpoints and this agrees well with the observed transformations of the charging curves.

**Increasing anodic side reactions with higher SoC.**—Figure 9 demonstrates that with higher SoC, the slippage of the discharging end point increases markedly. Hence, the consumption of intercalated lithium of the anode due to electrolyte reduction and SEI growth aggravates. This can be caused either by solely anodic side reactions or by coupled side reactions, which simultaneously alter the degree of lithiation of the anode and the cathode. For three SoCs from 45% to 100% SoC, Figure 10 illustrates the overall capacity fade over time and the respective contributions of both end point shifts. The shifts of the discharging endpoints, presented in Figures 10g–10i, exhibit that the rate of the end point slippage decreases with time. This is in good agreement with the supposed passivation layer growth, which slows down successively over time. As the anode potential decreases from 45% SoC to 75% SoC (see Figure 1), increasing anodic side reactions occur as expected. If the slippage of the discharging end point was caused by solely anodic side reactions, it should depend directly on the anode potential. Then, the end point shifts for 75%, 80%, and 100% SoC should be similar, as the anode potential remains constant for these SoCs. Instead, considerably larger shifts of the discharging endpoints are observed at 100% SoC. Consequently, there must be increasing coupled side reactions toward 100% SoC.

**Side reactions at very high SoC.**—In addition to the slippage of the discharging end point, Figures 10d–10f show the slippage of the charging end point. It is moderate or small for storage SoCs up to 80%. For storage at 100% SoC, however, increased shifts of the charging endpoints are observed at all temperatures. This indicates aggravating cathodic side reactions. As described above, there are also larger shifts of the discharging endpoints for storage at 100% SoC. This supports the assumption of coupled side reactions, e.g., from transition metal dissolution at the cathode and a reduction of the dissolved transition metal ions at the anode. As it can be seen in Figures 10f, 10i for the shifts of the charging and the discharging endpoints of the cells from the second aging study, the differences between the curves for 80% and 100% SoC are similar. This confirms the assumption of a crosstalk between both electrodes which leads to coupled side reactions that alter the degree of lithiation of both electrodes. In Ref. 30, interactions between the side reactions at both electrodes were reported: A lithium-ion cell with the electrolyte additive vinylene carbonate (VC) exhibited lower anodic as well as cathodic side reactions than a reference cell without VC in the electrolyte. The authors suggest that reaction products from anodic side reactions migrate to the cathode and intensify cathodic side reactions. From our observations, the opposite direction appears more likely: As the anode potential remains constant in the high SoC regime between 70% and 100% SoC, the amount of reaction products from anode-initiated side reactions can be regarded as similar. Thus, there is no source for intensified crosstalk behavior toward 100% SoC. At the cathode, however, side reactions—comprising electrolyte oxidation and transition-metal dissolution—aggravate with higher potential. Hence, the successively increasing cathode potential toward 100% SoC is regarded as a source of intensified crosstalk, because an increasing amount of reaction products is generated at the cathode, which can migrate or diffuse to the anode and consume intercalated lithium there. This causal relationship also accords well with the above-mentioned reductions in anodic and cathodic side reactions when adding VC to the electrolyte, as VC was reported to inhibit cathodic side reactions.17,47

**Additional cathodic side reactions in the first aging study.**—The comparison of both aging studies also confirms that the cathodic side reactions do not rely on reaction products from anodic side reactions. According to Figures 10b–10i, the shifts of the discharging endpoints at 25°C are similar in both aging studies, which represents similar anodic side reactions. The shifts of the charging endpoints, however, are only similar for SoCs up to 80% and differ considerably for storage at 100% SoC. At 100% SoC, the shifts of the charging endpoints are substantially larger in the first aging study, which indicates

![Figure 10](https://example.com/figure10.png)

**Figure 10.** (a)-(c) Capacity fade, (d)-(f) shift of the charging (top) end point, and (g)-(h) shift of the discharging (bottom) end point for different storage SoCs. Different temperatures are shown for study I (left and center column); and cells from different production lots are compared for the storage temperature of 25°C (center and right column).
intensified cathodic side reactions, although the anodic side reactions are similar. Consequently, there must be additional, solely cathodic side reactions. As introduced in the method section on the effects of solely cathodic side reactions, they increase the actual capacity as they cause a reversible capacity fade together with a right-shift of the charging end point. Since the actual capacity corresponds to the difference between charging end point and discharging end point – which confines the inventory of cyclable lithium – it is directly affected by the slippage of both endpoints. The double arrows in Figure 10 illustrate the changes in the actual capacity resulting from the end point shifts. The arrows demonstrate that the irreversible capacity fade during storage is mainly caused by the slippage of the discharging end point, ascribable to electrolyte reduction and SEI growth, which reduces the inventory of cyclable lithium. Solely cathodic side reactions, which cause a reversible self-discharge, can relieve this reduction by right-shifting the charging end point. These side reactions are supposed to be oxidative processes which generate no reaction products affecting the anodic side reactions. Such solely cathodic side reactions explain why a lower capacity fade is observed in the first aging study for storage at 100% SoC than for storage at 75% SoC (see Figure 6), independent of the storage temperature. As these cathodic side reactions are not observed in the second study, it is assumed that slight changes in the functional materials, such as modifications of the electrolyte and its additives, have reduced the cathodic side reactions of the cells examined in the second aging study, which were produced several months later.

Conclusions

Our investigations on calendar aging of lithium-ion batteries, based on two experimental aging studies examining commercial NCA cells, have shown that the capacity fade from calendar aging results predominantly from side reactions which reduce the inventory of cyclable lithium. DVA has disclosed that there is zero or very minor degradation of the storage capabilities of the individual electrodes, but a substantial shift in the electrode balancing. A strong correlation between the capacity fade and the anode potential has been shown. Coulomb tracking has confirmed that anodic side reactions are the main driver for the capacity fade, as they lead to a slippage of the discharging end point which reduces the inventory of cyclable lithium and the utilization of the electrodes. These results confirm that electrolyte reduction and SEI growth at the anode are the predominant aging mechanisms responsible for the irreversible capacity fade of calendar aged cells. At high SoCs, additional cathodic side reactions occur, which cause a reversible self-discharge. Moreover, a crosstalk between both electrodes is observed, where cathodic side reactions entail intensified anodic side reactions. Our newly introduced method of coulomb tracking has also enabled us to determine the reason for a decreasing capacity fade observed in one of the calendar aging studies for cells stored above 80% SoC: Additional, solely cathodic side reactions at very high SoC caused a larger slippage of the charging end point which extended the inventory of cyclable lithium. This relieved the diminishing inventory of cyclable lithium and, thus, reduced the irreversible capacity fade, although the overall aging reactions increased in that case due to the reversible self-discharge caused by the cathodic side reactions. Consequently, the reversible capacity fade – as an indicator for cathodic side reactions – should also be evaluated in battery aging studies to avoid misinterpreting a lower capacity fade toward 100% SoC as decreasing side reactions.

To reduce calendar aging in practical applications, lithium-ion cells should preferably be stored at low temperature and at a low or medium SoC. The SoC should remain below the SoC location of the central graphite peak, which represents the transition from the plateau of medium to low anode potential. This avoids storage periods at lowest graphite potential, which causes fastest capacity fade owing to increasing anodic side reactions. Furthermore, avoiding high SoCs also minimizes cathodic side reactions. Since the SoC location of the central graphite peak depends on the balancing of the electrodes and varies from cell type to cell type, a DVA measurement should always be performed to determine this characteristic SoC location of an unknown lithium-ion cell. Storing the cells below this SoC can prolong the battery life substantially.

References

1. P. Keil, S. F. Schuster, J. Wilhelm, J. Travi, A. Hauser, R. C. Karl, and A. Jossen, “Calendar Aging of Lithium-Ion Batteries,” J. Electrochem. Soc., 163, A1872 (2016).
2. M. Kassem, J. Bernard, R. Revel, S. Péllissier, F. Duclouët, and C. Delacourt, “Calendar aging of a graphite/LiFePO4 cell,” Journal of Power Sources, 208, 296 (2012).
3. A. J. Smith, J. C. Burns, and J. R. Dahn, “A High Precision Study of the Coulombic Efficiency of Li-Ion Batteries,” Electrochem. Solid-State Lett., 13, A177 (2010).
4. P. Arora, R. E. White, and M. Doyle, “Capacity Fade Mechanisms and Side Reactions in Lithium-Ion Batteries,” J. Electrochem. Soc., 145, 3647 (1998).
5. J. Vetter, P. Novák, M. R. Wagner, C. Veit, K.-C. Möller, J. O. Besenhard, M. Winter, M. Wolfhard-Mehrens, C. Vogler, and A. Hammouche, “Aging mechanisms in lithium-ion batteries,” Journal of Power Sources, 147, 269 (2005).
6. E. Peled and D. Golidońska, “SEI on lithium, graphite, disordered carbons and tin-based alloys,” in: P. B. Balbuena and Y. Wang (Eds.), Lithium-ion batteries: Solid-electrolyte interphase and electrolyte, Academic Press, London, 2013.
7. I. Buchberger, S. Seifalmayer, A. Pokharel, M. Piana, J. Hattendorf, F. Kudjojova, R. Gilles, and H. A. Gasteiger, “Aging Analysis of Graphite/LiNi0.8Mn0.1Co0.1O2 Cells Using XRD, PGAA, and AC Impedance,” J. Electrochem. Soc., 162, A2737 (2015).
8. M. Wohlfahrt-Mehrens, C. Vogler, and J. Garcke, “Aging mechanisms of lithium cathode materials,” Journal of Power Sources, 127, 58 (2004).
9. M. Ecker, N. Nieto, S. Kabitz, J. Schmalstieg, H. Blanke, A. Warnke, and D. U. Sauer, “Calendar and cycle life study of Li-NiMnO2-based 18650 lithium-ion batteries,” Journal of Power Sources, 248, 839 (2014).
10. S. Kabitz, J. B. Gerschler, M. Ecker, Y. Yurdagel, B. Emmermacher, D. André, T. Mitsch, and D. U. Sauer, “Cycle and calendar life study of a graphite/LiNi0.8Mn0.1Co0.1O2 high energy system. Part A: Full cell characterization,” Journal of Power Sources, 239, 572 (2013).
11. E. Saraseta-Zabala, I. Gandiga, L. M. Rodriguez-Martinez, and I. Villarreal, “Calendar aging analysis of a LiFePO4/graphite cell with dynamic model validation: Towards realistic lifetime predictions,” Journal of Power Sources, 272, 45 (2015).
12. B. Suany, J. C. Ziegler, M. Zhang, J. P. Schmieder, and P. Henrissat, “Electrochemical characterization and post-mortem analysis of aged LiNi0.8Mn0.1Co0.1O2/NMC/graphite lithium ion batteries part II: Calendar aging,” Journal of Power Sources, 258, 61 (2014).
13. S. Grolleau, A. Delaillie, H. Gualous, P. Gyan, R. Revel, J. Bernard, E. Redondo-Iglesias, and J. Peter, “Calendar aging of commercial graphite/LiFePO4 cell – Predicting capacity fade under time dependent storage conditions,” Journal of Power Sources, 255, 450 (2014).
14. D. Li, D. L. Danilov, J. Xie, L. Rajmakkers, L. Gao, Y. Yang, and P. H. Notten, “Degradation Mechanisms of C/6LiFePO4 Batteries: Experimental Analyses of Calendar Aging,” Electrochimica Acta, 190, 1124 (2016).
15. J. Belt, V. Ugíkar, and I. Bloom, “Calendar and PHEV cycle life of high-energy, lithium-ion cells containing high level of spincal and layered-oxygen cathodes,” Journal of Power Sources, 196, 10213 (2011).
16. I. Bloom, B. Cole, J. Sohn, S. Jones, E. Polzin, V. Battaglia, G. Henrikson, C. Motloch, R. Richardson, T. Unkelhaeuser, D. Ingersoll, and H. Case, “An accelerated calendar and cycle life study of Li(NiMnCo)O2-based 18650 lithium-ion batteries,” Journal of Power Sources, 258, 61 (2014).
17. M. Safari and C. Delacourt, “Aging of a Commercial Graphite/LiFePO4 Cell,” J. Electrochem. Soc., 158, A1123 (2011).
18. I. Bloom, A. N. Jansen, D. P. Abraham, J. Knuth, S. A. Jones, V. S. Battaglia, and G. L. Henrikson, “Differential voltage analyses of high-power, lithium-ion cells,” Journal of Power Sources, 139, 295 (2005).
19. H. M. Dahn, A. J. Smith, J. C. Burns, D. A. Stevens, and J. R. Dahn, “User-Friendly Differential Voltage Analysis Freeware for the Analysis of Degradation Mechanisms in Li-Ion Batteries,” Journal of Power Sources, 159, A1405 (2012).
20. M. Dubarry, C. Truchot, and B. Y. Liaw, “Synthesise battery degradation modes via a diagnostic and prognostic model,” Journal of Power Sources, 219, 204 (2012).
21. K. Honkura and T. Horiba, “Study of the deterioration mechanism of LiCoO2/graphite cell: Charge/discharge cycles using the discharge curve analysis,” Journal of Power Sources, 264, 140 (2014).
22. I. Bloom, L. K. Walker, J. K. Basco, D. P. Abraham, J. P. Christophersen, and C. D. Ho, “Differential voltage analyses of high-power lithium-ion cells. 4. Cells and batteries,” Journal of Power Sources, 191, 238 (2001).
23. J. Wang, J. Purewal, P. Liu, J. Hicks-Garner, S. Soukazian, E. Sherman, A. Sorenson, L. Yu, H. Tataria, and M. W. Verbrugge, “Degradation of lithium ion batteries employing graphite negatives and nickel–cobalt–manganese oxide + spinel manganese oxide positives: Part I, aging mechanisms and life estimation,” Journal of Power Sources, 269, 937 (2014).
24. Y. Ito and Y. Ukyo, “Performance of LiNi0.8Co0.2O2 materials for advanced lithium-ion batteries,” Journal of Power Sources, 146, 39 (2005).
25. T. Ohsako, “Formation of Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell,” J. Electrochem. Soc., 140, 2490 (1993).
26. V. A. Suthuram, L. J. Hardwick, V. Srinivasan, and R. Kostecchi, “Surface structural disordering in graphite upon lithium intercalation/deintercalation,” Journal of Power Sources, 195, 3655 (2010).
27. S. R. Li, C. H. Chen, J. Camardese, and J. R. Dahn, “High Precision Coulometry Study of LiNi0.5Mn1.5Co1.5O4/Li Coin Cells,” Journal of the Electrochemical Society, 160, A1517 (2013).
28. J. C. Burns, D. A. Stevens, and J. R. Dahn, “In-Situ Detection of Lithium Plating Using High Precision Coulometry,” Journal of the Electrochemical Society, 162, A959 (2015).
29. D. Y. Wang, J. Xia, L. Ma, K. J. Nelson, J. E. Harlow, D. Xiong, L. E. Downie, R. Petibon, J. C. Burns, A. Xiao, W. M. Lamanna, and J. R. Dahn, “A Systematic Study of Electrolyte Additives in Li[Ni0.5Mn1.5Co1.5]O2 (NMC)/Graphite Pouch Cells,” Journal of the Electrochemical Society, 161, A1818 (2014).
30. R. D. Deshpande, P. Redgwney, Y. Fu, W. Zhang, J. Cai, and V. Battaglia, “The Limited Effect of VC in Graphite/NMC Cells,” Journal of the Electrochemical Society, 162, A330 (2014).
31. J. Xu, R. D. Deshpande, J. Pan, Y.-T. Cheng, and V. S. Battaglia, “Electrode Side Reactions, Capacity Loss and Mechanical Degradation in Lithium-Ion Batteries,” J. Electrochem. Soc., 162, A2026 (2015).
32. A. J. Smith, J. C. Burns, S. Trussler, and J. R. Dahn, “Precision Measurements of the Coulombic Efficiency of Lithium-Ion Batteries and of Electrode Materials for Lithium-Ion Batteries,” J. Electrochem. Soc., 157, A196 (2010).
33. T. M. Bond, J. C. Burns, D. A. Stevens, H. M. Dahn, and J. R. Dahn, “Improving Precision and Accuracy in Coulombic Efficiency Measurements of Li-Ion Batteries,” Journal of the Electrochemical Society, 160, A521 (2013).
34. D. A. Stevens, R. Y. Ying, R. Fathi, J. N. Reimers, J. E. Harlow, and J. R. Dahn, “Using High Precision Coulometry Measurements to Compare the Degradation Mechanisms of NMC/LMO and NMC-Only Automotive Scale Pouch Cells,” Journal of the Electrochemical Society, 161, A3364 (2014).
35. R. Fu, S.-Y. Cho, Y. Agubra, and J. Fergus, “Development of a physics-based degradation model for lithium ion polymer batteries considering side reactions,” Journal of Power Sources, 278, S06 (2015).
36. N. N. Sinha, A. J. Smith, J. C. Burns, G. Jain, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, “The Use of Elevated Temperature Storage Experiments to Learn about Parasitic Reactions in Wound LiCoO2/Graphite Cells,” J. Electrochem. Soc., 158, A1194 (2011).
37. D. Y. Wang, J. C. Burns, and J. R. Dahn, “A Systematic Study of the Concentration of Lithium Hexafluorophosphate (LiPF6) as a Salt for LiCoO2/Graphite Pouch Cells,” Journal of the Electrochemical Society, 161, A1278 (2014).
38. J. C. Burns, N. N. Sinha, D. J. Coyle, G. Jain, C. M. Vandelzen, W. M. Lamanna, A. Xiao, E. Scott, J. P. Gardner, and J. R. Dahn, “The Impact of Varying the Concentration of Vinylene Carbonate Electrolyte Additive in Wound Li-Ion Cells,” J. Electrochem. Soc., 159, A85 (2012).
39. A. J. Smith, J. C. Burns, D. Xiong, and J. R. Dahn, “Interpreting High Precision Coulometry Results on Li-ion Cells,” J. Electrochem. Soc., 158, A1136 (2011).
40. T. Waldmann, N. Ghanbari, M. Kasper, and M. Wohlfahrt-Mehrens, “Correlations between Electrochemical Data and Results from Post-Mortem Analysis of Aged Lithium-Ion Batteries,” Journal of the Electrochemical Society, 162, A1500 (2015).
41. S. Watanabe, M. Kinoshita, and K. Nakura, “Comparison of the surface changes on cathode during long term storage testing of high energy density cylindrical lithium-ion cells,” Journal of Power Sources, 196, 6906 (2011).
42. M. Metzger, B. Strehele, S. Solchenbach, and H. A. Gasteiger, “Origin of H2 Evolution in LIBs: H2O Reduction vs. Electrolyte Oxidation,” J. Electrochem. Soc., 163, A798 (2016).
43. K. Nakura, Y. Ohstugi, M. Imazaki, K. Ariyoshi, and T. Ohsaku, “Extending Cycle Life of Lithium-Ion Batteries Consisting of Lithium Insertion Electrodes: Cycle Efficiency Versus Ah-Efficiency,” J. Electrochem. Soc., 158, A1243 (2011).
44. B. Gyenes, D. A. Stevens, V. L. Chevrier, and J. R. Dahn, “Understanding Anomalous Behavior in Coulombic Efficiency Measurements on Li-Ion Batteries,” Journal of the Electrochemical Society, 162, A278 (2014).
45. H. J. Ploehn, P. Ramadass, and R. E. White, “Solvent Diffusion Model for Aging of Lithium-Ion Battery Cells,” J. Electrochem. Soc., 151, A456 (2004).
46. A. J. Smith, J. C. Burns, X. Zhao, D. Xiong, and J. R. Dahn, “A High Precision Coulometry Study of the SEI Growth in Li/graphite Cells,” J. Electrochem. Soc., 158, A447 (2011).
47. J. C. Burns, G. Jain, A. J. Smith, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, “Evaluation of Effects of Additives in Wound Li-ion Cells Through High Precision Coulometry,” J. Electrochem. Soc., 158, A255 (2011).