Interplay of Operational Parameters on Lithium Deposition in Lithium-Ion Cells: Systematic Measurements with Reconstructed 3-Electrode Pouch Full Cells

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Measurements of Eanode in full cells would allow detection of Li deposition. The results from the reconstructed 3-electrode cells are compared with independently performed aging tests of the original 16Ah cells.

Deposition of metallic Li is a severe aging mechanism in Lithium-ion cells. This study evaluates the influence of the main operating parameters leading to deposition of Li: temperature, charging C-rate, and end-of-charge voltage. Therefore both, graphite anodes and NMC cathodes from commercial 16Ah pouch cells are reconstructed into 3-electrode full cells. The position of the reference electrode between anode and cathode allows acquiring anode potentials vs. (Li/Li+) (see Figure 1). Extensive evaluations of data reveal critical combinations of operating parameters to avoid Li deposition. The results from the reconstructed 3-electrode cells are compared with independently performed aging tests of the original 16Ah cells.

It is known that Li deposition mainly depends on (i) charging C-rate, 8,14,16 (ii) temperature, 8,9,12,14,16-18 and (iii) end-of-charge voltage/state-of-charge. 8,14,17 Several authors reported trends for variation of only one of these parameters respectively. E.g. low temperatures during charging are reported to lead to Li plating on graphite anodes. 8,9,14-16 Due to the high chemical reactivity of metallic Li, it readily reacts with electrolyte leading to capacity loss of the cell. 8,9,14,16

Due to their comparably high energy and power densities, Lithium-ion batteries are currently used in state-of-the-art electric cars. 1-3 In automotive applications, battery life-times of 10 years are expected for customer acceptance. However, it is known that life-time of Lithium-ion batteries is limited by aging mechanisms. 4-11 One of these aging mechanisms is deposition of metallic Li on anodes. 8,9,14-16 Due to the high chemical reactivity of metallic Li, it readily reacts with electrolyte leading to capacity loss of the cell. 8,9,14-16

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The reason for deposition of Li on anodes are negative anode potentials Eanode vs. (Li/Li+) 8,12,14,20. Unfortunately, in commercial cells only the cell voltage

\[ E = E_{\text{cathode}} - E_{\text{anode}} \]  

and not the anode potential vs. (Li/Li+) can be measured. The reason is that commercial cells do not contain a third reference electrode. Measurements of Eanode in full cells would allow detection of Li deposition on anodes (condition: Eanode vs. (Li/Li+) < 0 V). Indeed, by introducing an additional reference electrode, such as metallic Li, the electrode potentials are accessible. 8,12,14,20,22,24

We note that such measurements are also not possible in a half-cell configuration with e.g. either only a graphite anode vs. a Li counter electrode or only a NMC cathode vs. a Li counter electrode, since the interaction between anode and cathode is not taken into account. Instead, 3-electrode full cells with the following electrodes are required to detect Li deposition correctly: (i) anode (e.g. graphite), (ii) cathode (e.g. NMC), and (iii) reference electrode (e.g. metallic Li).

Furthermore, it is well-known that the reference electrode has to be positioned near the anode in order to minimize the Ohmic drop and to measure its potential accurately. 24 For example, in aqueous systems, this is achieved by a Luggin-Haber capillary. 24 Simulations by Dees et al. also showed that the best position for a reference electrode in Lithium-ion cells is between anode and cathode. 25 The same was recently found in experiments by Hogg and Wohlfahrt-Mehrens. 20 In contrast for a reference electrode outside the electrode stack, the potential is not necessarily related to Li deposition on the anode. 20,25,26

We recently performed a reconstruction of both, graphite anode and NCA cathode from commercial 3.25Ah 18650-type cells into 3-electrode full cells with an additional Li reference electrode and verified this method. 14 Using this reconstruction technique, we were able to measure the anode potential vs. (Li/Li+) for different charging currents at 25 °C. 14 The results from these reconstructed 3-electrode full cells are promising, since they allowed optimizing the charging strategy of the original 18650 cells and to extend their cycle life significantly. 14 A similar approach using 3-electrode full cells with Li reference electrode was also helpful to explain faster aging of commercial 18650 cells with graphite anodes and NMC/LMO blend cathodes with decreasing temperature due to Li plating. 8

In the present study, we perform reconstruction of both, graphite anodes and NMC cathodes from a commercial 16Ah pouch cell into 3-electrode full cells with an additional Li reference electrode in between (see Figure 1). The anode potential vs. (Li/Li+) is measured by systematic variation of temperature, charging C-rate, and end-of-charge voltage. This allows drawing conclusions on general trends and on parameter sets that can exclude Li deposition. Finally, the results from the reconstructed 3-electrode cells are compared with aging tests of the original 16Ah pouch cells.

Figure 1. Schematic cross-section of the reconstructed 3-electrode pouch full cells. The Li reference electrode (Ref.) is positioned between anode (--) and cathode (+).
Figure 2. Scheme of the reconstruction: After disassembly, both, anodes and cathode are reconstructed together with a Li reference electrode into 3-electrode full cells to measure anode potentials \( E_{\text{anode}} \) vs. \( \text{(Li/Li}^+ \) \).

**Experimental**

The commercial pouch cells (‘original cells’) used in this study have a specified minimum capacity of 16Ah, a voltage range of 2.7 V–4.2 V, and a maximum specified charging rate of 3C. Anodes and cathodes of the original 16Ah cells consist of graphite and NMC, respectively.

Reconstruction into 3-electrode cells was performed similar to our previous study\(^{14}\) where this method had been verified and is illustrated in Figure 2. For the reconstruction, fresh 16Ah cells were used as received from the manufacturer. These original fresh cells had been subject to formation cycles by the manufacturer, but to no other cycling tests in our lab. For safety reasons, the original 16Ah pouch cells were discharged via a Basytec CTS system with a rate of C/10 (= 1.6A) until the end-of-discharge voltage of 2.7 V was reached prior to disassembly. The cells were transferred into an Ar-filled glove box \((\text{O}_2 < 0.1 \text{ ppm}, \text{H}_2\text{O} < 0.1 \text{ ppm})\), where they were carefully opened. Anode and cathode were separated and dipped three times in DMC (each time fresh DMC was used), before they were dried in vacuum for 30 min. Similarly to Itou and Ukyo\(^{27}\) and to previous experiments in our lab,\(^{15}\) the reconstruction was carried out in a dry room with a dew point of \(-64 \text{ C}\). Transfer of the glove box to the dry room was accomplished by sealing the electrodes separately in pouch foil.

The reconstructed 3-electrode full cells are pouch-type and each cell contains two one-side coated NMC cathodes and one double-side coated graphite anode (see Figure 1). Since the cathodes from the original 16Ah cells were coated on both sides, the coatings on the back of the cathodes were removed by laser blanking. In order to create an area for welding, coating was removed in an area of \(0.5 \times 1 \text{ cm}^2\) by laser blanking for anodes and cathodes. For building the reconstructed 3-electrode full cells, a fresh separator (Celgard separator type 2325) as well as EC:DMC = 1:1 (wt%) / 1 M LiPF\(_6\) electrolyte were used in combination with the graphite anode and the NMC cathode from the commercial cell and an additional Li reference electrode. A previous study had shown that exchange of electrolyte and separator results only in minor effects regarding the anode potential.\(^{14}\)

Similar to our previous studies\(^{8,14,20}\) and as recommended by Dees et al.,\(^{25}\) the Li metal reference electrode was positioned between anode and cathode (anode side of separator). Contact of anode and reference electrode was prevented by an additional layer of separator in between. Before building the reference electrode, the surface of Li metal was scraped off to remove oxidized parts. 3 mm of Li metal was wrapped around a Ni tab (130 \(\mu\)m thickness). After pressing the Li metal onto the Ni tab, the overlaying Li metal was removed to reduce the size of the reference electrode.

The reference electrode was positioned near the current collecting tab of the anode. The reason is that the current density is most likely highest in this region. Therefore, this position reflects the most critical region for the anode potential inside the cell.

Electrochemical tests with the reconstructed 3-electrode full cells were performed with a Maccor System 4200 including temperature chambers (temperature accuracy: \(\pm 1 \text{ C}\)). The cells were charged three times at each C-rate (0.2C, 0.5C, 1C, 2C, 3C) and discharged with 1C using a standard CC protocol and the same cell voltage range as for the original 16 Ah pouch cell (2.7 V–4.2 V). For better understanding, the experiment at 20 \(\text{ C}\) is exemplarily shown in Figure 3. For evaluation, the 3rd cycle of the respective charging C-rate was used to reduce the influence of previous cycles at other C-rates. In a previous study,\(^{15}\) we found that the constant CV-phase is not lowering the anode potential. Therefore, the CV-phase was neglected in the present study.

For reproduction, all measurements were repeated with an additional reconstructed cell which showed very good reproducibility for temperatures in the range of 15 \(\text{ C}\)–45 \(\text{ C}\). We note that in case of 5 \(\text{ C}\), the reproducibility was not as good as for the higher temperatures however, as discussed below it was acceptable.

**Results and Discussion**

**Measurement of anode potentials vs. \((\text{Li/Li}^+)\) in reconstructed 3-electrode full cells.**—Figure 4 shows the measurement of \( E_{\text{anode}} \) vs. \((\text{Li/Li}^+)\) for exemplary ambient temperatures of 5 \(\text{ C}\), 20 \(\text{ C}\), and...
45°C as a function of the cell voltage U. For each temperature, two reconstructed 3-electrode full cells were tested and each cell was charged with rates of 0.2C, 0.5C, 1C, 2C, 3C.

According to the measured $E_{\text{anode}}$ values, the reproduced reconstructed 3-electrode full cells are in very good agreement for both 20°C and 45°C (compare solid and dashed lines in Figures 4b, 4c). For 5°C (especially at higher charging C-rates) the difference between the two reproduced reconstructed cells are stronger (Figure 4a) compared to the measurements at 20°C and 45°C. Therefore, the measurements at 5°C / 1C-3C are similar within the error range. The generally stronger tendency for Li plating at 5°C and high C-rates might be the reason for the scattering. We note that we had previously proven Li plating for the same cells after charging at 5°C and 3C by glow discharge optical emission spectroscopy (GD-OES) depth profiling.13

Clear trends were observable for $E_{\text{anode}}$ vs. (Li/Li$^+$) in Figure 4 for all three tested temperatures. In particular, the following tendencies were found:

1. Comparing different ambient temperatures, it is found from the measurements with the reconstructed 3-electrode full cells that lower temperatures lead to lower $E_{\text{anode}}$ vs. (Li/Li$^+$) values in the range of 3.8 V–4.2 V.
2. $E_{\text{anode}}$ vs. (Li/Li$^+$) is decreased with higher charging C-rates in the range of 3.8 V–4.2 V.
3. $E_{\text{anode}}$ vs. (Li/Li$^+$) is monotonically decreasing with increasing cell voltage U and therefore with increasing SOC.

These findings regarding low temperatures, high charging C-rate, and high SOC are discussed in the following using Figures 5a–5c, respectively. Please note that in Figure 5, the numbering corresponds to the argumentation order.

A model for the temperature behavior of $E_{\text{anode}}$ vs. (Li/Li$^+$) is shown in Figure 5a. For a given diffusion barrier, low temperatures lead to slower kinetics of Li diffusion in the anode. This can be demonstrated by the diffusivity $D$ given by the following equation:

$$D = D_0 \cdot \exp \left( - \frac{E_D}{k_B T} \right)$$

with the diffusion coefficient $D_0$, the diffusion barrier $E_D$, the Boltzmann constant $k_B$, and the absolute temperature $T$. Under the reasonable assumption that the temperature dependency of $D_0$ is negligible, the ratio of the diffusivities at two different temperatures $T_1$ and $T_2$ is
The lower Li diffusivity in graphite at low temperatures hinders the Li ions to intercalate. Furthermore, the low Li diffusivity in graphite is likely to lead to an accumulation of Li at the border of the graphite particles, hindering the intercalation process additionally.30 Therefore, Li is accumulated in front of the anode surface leading to Li plating (see Figure 5a). This is consistent with recent measurements of the Li$^+$ activity in 4-electrode full cells with two reference electrodes.8,14,16

The observed temperature behavior of E$_{\text{anode}}$ vs. (Li/Li$^+$) as measured in the reconstructed 3-electrode full cells (Figure 4) is also in agreement with recent degradation studies using commercial 18650 cells.8,14,16 These studies showed that the aging rate is increased by cycling at lower temperatures.8,14,16 Furthermore, Burns et al. found by Post-Mortem analysis of cycled commercial pouch cells that the tendency of Li deposition is increased at lower temperatures for a given charging C-rate.16

A model for the behavior of E$_{\text{anode}}$ vs. (Li/Li$^+$) with regard to charging C-rates is shown in Figure 5b. The high current density leads to activity gradients of Li ions in the electrolyte.20 Although the intercalation into graphite leads to a depletion of Li ions near the anode surface, high charging C-rates lead to an accumulation of Li ions in front of the anode and therefore favoring Li deposition on the anode surface.20 Additionally, intercalated Li might be accumulated at the border of the graphite particles, leading to hindering of intercalation.

The result regarding the influence of charging C-rate is consistent with measurements at 25°C using 3-electrode full cells reconstructed from high-energy 18650 cells.14 For similar charging C-rates, the absolute values of E$_{\text{anode}}$ vs. (Li/Li$^+$) of those cells14 are lower compared to the present study. The reason is most likely the higher electrode thickness and lower porosity of the high-energy cells from the former study14 leading to stronger polarization. However, the observed trend of lower E$_{\text{anode}}$ values with higher charging C-rate observed in the present paper in the temperature range of 5°C–45°C was similar in measurements at 25°C14 and in calculations by Tippmann et al. at 0°C.17 Furthermore, this result is in agreement with recent results from Dahn’s group.16 The authors found Li deposition occurs at a given temperature, if a certain value of the charging C-rate is exceeded.16

A model for the behavior of E$_{\text{anode}}$ vs. (Li/Li$^+$) with regard to high end-of-charge voltages / high SOCs is described in Figure 5c. With increasing SOC, the amount of intercalated Li increases, leading to a blocking of diffusion paths in the graphite particles. Persson et al. showed by ab-initio calculations that the higher amount of intercalated Li leads to repulsive Li-Li interactions and therefore to an increased effective migration barrier for Li in graphite.30,31 More specifically, the diffusion barrier is increased from E$_{\text{D1}}$ = 0.308 eV (Li$_{0.33}$C$_6$) to E$_{\text{D2}}$ = 0.4 eV (LiC$_6$).30 According to Equation 2, one can derive a factor

$$ D_1 / D_2 = \exp \left( \frac{E_{D2} - E_{D1}}{k_B T} \right) $$

for calculating how the diffusivity is decreased with higher diffusion barrier. For example at 20°C, an increase of E$_{\text{D1}}$ = 0.308 eV to E$_{\text{D2}}$ = 0.4 eV results in a decrease of the diffusivity of Li in graphite by a factor of 0.05. Since this factor is about one order of magnitude lower than that calculated for a temperature change from 20°C to 5°C (see discussion above), high SOC has most likely a larger effect on Li deposition compared to low temperature.

The observations from the measurements with the reconstructed 3-electrode full cells in the present study agree very well with literature. However, to best of our knowledge, the results presented in literature so far neither give a quantitative view nor an overall picture of the operating parameters and their interplay leading to negative anode potentials/Li deposition. This full picture is developed in the following section.

**Interplay of operational parameters leading to negative anode potentials.—** Figure 6 shows a 3-dimensional plot of those combinations of end-of-charge voltage, charging C-rate, and temperature leading to zero-crossings of E$_{\text{anode}}$ vs. (Li/Li$^+$). In this plot data from Figure 4 as well as additional temperatures (5°C, 20°C, 30°C, 35°C, and 45°C) were included.

The voltage values of the data points in Figure 6 correspond to 3.98 V, 4.022 V, 4.08 V, 4.136 V, and 4.2 V which were chosen for practical reasons. We note that for some combination of operating parameters, no zero-crossings were found.

In Figure 6, negative anode potentials vs. (Li/Li$^+$) indicating Li deposition are found for combinations of operating parameters which are in front of the data points. In contrast, operating conditions leading to positive anode potentials vs. (Li/Li$^+$) indicating the absence of Li deposition are related to parameter sets behind the data points (shaded areas).

From Figure 6, it can clearly be seen that all three investigated operational parameters – temperature, charging C-rate, and end-of-charge voltage – have significant influence on the zero-crossing of the anode potential vs. (Li/Li$^+$) and therefore on Li deposition. Furthermore, these operational parameters are not independent but strongly related to each other.

In Figure 6, the parameter space which does not lead to Li deposition gets smaller with decreasing temperature. This is fully consistent with the fact that Li plating is often observed during charging at low temperatures.8,9,12–14,16 However, Figure 6 clearly shows that it is possible to avoid Li plating at low temperatures, for instance by limiting the end-of-charge voltage (in the present case for >5°C) or by lowering the charging C-rate.

On the other hand it is possible to avoid Li deposition during charging with high C-rates by limiting the end-of-charge voltage in the range of 5°C–45°C. This is fully consistent with our recent study on optimized charging strategies developed for commercial 18650 cells at an ambient temperature of 25°C.14 In that previous study, high charging C-rates were applied at the beginning of charging until a
certain end-of-charge voltage was reached, followed by a lower charging C-rate.\textsuperscript{14} In long-term cycling tests, the cyclability as well as the total charge throughput was enhanced significantly at 25°C.\textsuperscript{14} The results from the present study indicate that it should be possible to derive optimized charging protocols also for a wider temperature range.

It is noted that the operating parameters in Figure 6 represent charging starting from the specified end-of-discharge voltage. For cells which are charged starting from higher charge levels, more experiments are required however this is out of scope of the present study.

It is further noted that the parameter sets obtained in the present study are only valid for the cells under investigation. However, the observed trends are very likely to be generally valid for most types of Lithium-ion cells.

**Transferability of results from reconstructed 3-electrode full cells to aging behavior of the original 16Ah cells.—**In a first attempt to test the transferability of the results from the reconstructed 3-electrode full cells to the original 16Ah cells, a comparison of the cell voltage U of the 16Ah cell and the reconstructed cells are shown in Figure 7 for charging at rates of 0.2C, 0.5C, 1C, 2C, and 3C.

The differences in the voltage curves are comparably small. The reason for the observed difference is most likely the different heating behavior of the 16Ah cells and the reconstructed 3-electrode full cells during charging.\textsuperscript{14,32} However, for high SOCs (high end-of-charge voltages), which are most interesting in the case of Li deposition,\textsuperscript{14} a good agreement of U between the 16Ah cells and the reconstructed 3-electrode full cells was found. Especially, at higher C-rates we find a better agreement than in our previous study, where 3-electrode full cells were reconstructed from 18650-cells.\textsuperscript{14} Therefore, it is very likely that the anode potentials and their trends measured in the 3-electrode cells are similar to those in the original 16Ah cells.

Figure 8 shows a comparison of the capacities during CC charging until 4.2 V at 20°C. The capacities of the reconstructed 3-electrode full cell and the 16Ah cell are correlated linearly. A second reproduced pouch cells with those of reconstructed 3-electrode full cells at an ambient temperature of 20°C. Filled and open squares correspond to reproduction of reconstruction of 3-electrode full cells.

The data in Figure 8 show the clear trend of decreasing capacities with increasing charging C-rate. This is behavior is in agreement with results of other Lithium-ion cells.\textsuperscript{14,16,33} For instance, Burns et al. observed a decrease to \(\sim 75\%\) of the charged capacity of commercial 18650 cells when increasing the C-rate from C/10 to 1C.\textsuperscript{16}

The linear correlation of the data in Figure 8 shows that the decrease of charged capacity with higher C-rates decreases for both, the reconstructed 3-electrode full cells and the original 16Ah cells in the same manner. The difference in the capacities for both cell types can be explained by the different electrode areas. Therefore, the charged capacities of the reconstructed 3-electrode full cells and the original 16Ah cells are comparable.

It is highly likely that the measurements of anode potentials in the reconstructed 3-electrode full cells allow conclusions on the Li deposition behavior in the original 16Ah cells at the beginning of their life-time. We would like to note that the measurements with the reconstructed 3-electrode full cells resemble the features of the electrodes, whereas influence of electrolyte was found to be rather weak.\textsuperscript{14} Smart and Ratnakumar discussed that the electrolyte has influence on the solid electrolyte interface (SEI) and therefore on Li plating.\textsuperscript{34} In our study this is different, since the initial SEI on the anodes had already been formed at the manufacturer of the original cell.

The results of the reconstructed cells are most likely limited by high C-rates, since their heating behavior gets more different compared to the larger original cells.\textsuperscript{15} In consistence with our previous measurements,\textsuperscript{14} the reconstructed cells did not show a significant temperature increase during charging.

The 3-electrode full cells in the present study were reconstructed from fresh commercial cells after formation cycles which were not subject to a specific aging procedure. Therefore, the results obtained in the present paper allow conclusions only on the behavior of fresh cells as obtained from the manufacturer, since the main degradation mechanism may change during aging. Especially at elevated temperatures, drying of the cells\textsuperscript{15,35} or gas evolution\textsuperscript{15} can happen due to acceleration of side reactions. For instance, Jalkanen et al. suggested that such effects can lead to Li deposition in aged cells even at elevated temperature. On the other hand it is often difficult to reconstruct electrodes from aged cells, since they often show inhomogeneities\textsuperscript{10} or adhesion loss of the coated material.\textsuperscript{36} In this sense, the results gained in the present study are related to the initial aging mechanisms rather than for later degradation states.

Table I shows original 16Ah cells cycled under different conditions. In order to be more complementary to the results of the 3-electrode cells, the cycling tests were conducted independently at different research institutes. In particular, six conditions (#1 to #6) were tested and each condition was reproduced with three 16Ah cells. In order to account for the initial aging mechanism as discussed above,
only the capacity loss after the first 1000 cycles was considered. Further evaluation of the aging behavior of these cells is out of scope of the present study and will be discussed in detail later.37

The following comparison between measurements of anode potentials via reconstructed 3-electrode cells and aging behavior of the original 16Ah cells is based on the observation that cells with Li deposition show faster capacity fade.3,13,14,16 Therefore, negative anode potentials are correlated to stronger capacity loss after the same amount of charge/discharge cycles.

In test #1 and #2 of Table I, 16Ah cells are cycled at an ambient temperature of 5°C with end-of-charge voltages of 4.08 V. The rise of the charging C-rate from 1C to 2C for test #1 to 2C for test #2, results in a decrease of from 88% to 82% after 1000 cycles, respectively. This is consistent with the decrease of the anode potential vs. (Li/Li+) as measured in the reconstructed 3-electrode full cells. In particular, the anode potential is decreased from −55 mV to −69 mV when the charging C-rate is increased from 1C to 2C at 5°C.

In tests #3 and #4 of Table I, 16Ah cells are cycled at an ambient temperature of 25°C with end-of-charge voltages of 4.08 V and 4.20V, respectively. The capacity after 1000 cycles is decreased from 96.5% to 92% for tests #3 and #4, respectively. In full consistency with Figure 6, an increase of both, end-of-charge voltage and C-rate leads lower anode potentials. In the respective case, the minimum anode potential during charging is decreased from 0 V (test #3) to −57mV (test #4) as measured by the reconstructed 3-electrode full cells.

In tests #5 and #6 of Table I, 16Ah cells are cycled at an ambient temperature of 45°C with end-of-charge voltages of 4.20 V. Again, the increase of charging C-rate from 1C to 3C lowers the capacity after 1000 cycles from 87% to 80%, respectively. This is consistent with a change of the sign of the anode potential from (Li/Li+) to −69 mV (test #5) to −13 mV (test #6) as measured by the reconstructed 3-electrode full cells.

We conclude that the cycling aging tests with the original 16Ah cells which were performed independently at other research institutes are in full agreement with the results of anode potential measurements of the reconstructed 3-electrode full cells.

When considering the operating conditions leading to Li deposition in large cells, it must be discussed, in which area of the cell Li deposition is expected to be preferred. The reason is that large cells, develop temperature gradients32,38,39 and differences in current density39,40 during charging or discharging.

For example in case of cylindrical cells, it was found that the temperature rise inside the jelly roll is usually significantly higher compared to the cell surface.41,42 In case of charging at low ambient temperatures, this leads presumably to a higher amount of Li plating on the outside of the jelly roll of cylindrical cells.5 Similarly, temperature gradients inside pouch cells35 are likely to lead to higher tendencies of Li deposition in regions with locally lower temperatures.

On the other hand, differences in current density inside pouch cells,39,40 which are often observed near the current collecting tabs are likely to lower the anode potential locally. For critical ambient temperatures, this effect could also lead to localized Li deposition in such regions. However, since gradients of temperature and current density are not independent, a combination of both has to be considered.

Conclusions

In the present study, the main operational parameters leading to negative anode potentials vs. (Li/Li+) and therefore to Li deposition on graphite-based anodes during charging of Lithium-ion cells were investigated quantitatively and systematically. Therefore, a full picture of the relevant operating parameters leading to Li deposition was developed for the first time from experimental results.

For the purpose of anode potential measurements, both, graphite anodes and NMC cathodes from the original commercial 16Ah Lithium-ion cells were reconstructed into 3-electrode full cells with an additional Li reference electrode. The reconstructed 3-electrode full cells allowed to measure the anode potential vs. (Li/Li+) and therefore to determine the operating conditions leading to Li deposition on anodes (condition: anode potential vs. (Li/Li+) < 0 V).

The key operating conditions relevant for Li deposition are charging C-rate, temperature, and end-of-charge voltage. Systematic variation of these three most relevant operational parameters allowed gaining deeper understanding of their interplay. The main result is shown in Figure 6, from which it can easily be seen which combinations of operational parameters lead to Li deposition and how it can be avoided. For example, it is possible to charge Lithium-ion cells at rather high C-rates without Li deposition, if the end-of-charge voltage is lowered. However, this leads to a limitation of charged capacity. Furthermore, charging at low temperatures without Li deposition is possible, if either the charging C-rate or the end-of-charge voltage or both are reduced. In case that only the C-rate is reduced, this does not necessarily lead to reduced capacity. However, capacity will be decreased if the end-of-charging voltage is lowered. Another possibility would be to charge a cell at the beginning with a high C-rate and switch to a lower C-rate at higher SOC.14 However, we would like to note that the practicability of a charging strategy depends on the respective application.

The reason for negative anode potentials vs. (Li/Li+) and therefore for Li deposition/plating is explained by an accumulation of Li ions in front of the anode. This accumulation is mainly caused by:

1. low diffusivity of Li in graphite at low temperatures,
2. low diffusivity of Li in graphite at high SOC due to blocked diffusion paths,
3. Li activity gradients in the electrolyte due to high charging currents.

The effect of SOC on diffusivity was found to be most likely about one order of magnitude higher compared to that of temperature.

Evaluation showed that the results from the reconstructed 3-electrode cells can be transferred to the behavior of the original 16Ah cells. Most strikingly, the results from the reconstructed 3-electrode cells are in agreement with cycling aging tests of the original 16Ah cells performed independently at different research institutes. It is highly probable that for other types of Lithium-ion cells, the trends are very similar. However, the exact parametrization can be different due to differences in cell chemistry and design.

Extended cycling and calendar aging tests37 as well as post-mortem analysis43 with the original 16Ah cells used in the present study will be evaluated in further publications.

Table I. Capacity loss after the initial 1000 cycles of the original 16Ah cells (average of 3 reproduced cells).

| Test number | Temperature | End-of-charge voltage | Charging C-rate | Capacity retention after 1000 cycles | Eanode,min vs. (Li/Li+) | Test with original cells performed at institute |
|-------------|-------------|------------------------|----------------|--------------------------------------|------------------------|-----------------------------------------------|
| #1          | 5°C         | 4.08 V                 | 1C             | 88%                                 | −55mV                  | CIDETEC                                       |
| #2          | 25°C        | 4.08 V                 | 2C             | 82%                                 | −69mV                  | CIDETEC                                       |
| #3          | 25°C        | 4.08 V                 | 1C             | 96.5%                               | 0mV                    | CEA                                           |
| #4          | 45°C        | 4.20 V                 | 2C             | 92%                                 | −57mV                  | KIT                                           |
| #5          | 45°C        | 4.20 V                 | 1C             | 87%                                 | +43mV                  | VITO+EIGSI                                    |
| #6          | 45°C        | 4.20 V                 | 3C             | 80%                                 | −13mV                  | VITO+EIGSI                                    |
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