Impact of Bracing on Large Format Prismatic Lithium-Ion Battery Cells during Aging

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To reduce the ecological footprint and to increase the lifetime of lithium-ion batteries (LIBs), it is necessary to understand aging phenomena inside the cells during cycling. In this study, the positive effect of external pressure through bracing the cells on aging is investigated for automotive battery cells with more than 7000 cycles. After cycling, the aged cells are studied by using post-mortem analysis. It is shown that bracing does not affect the anode and cathode in the same manner. A lack of external pressure results in lithium plating due to contact losses on the anode. Such a loss of lithium inventory plays only a small role in the braced cells. However, the structural and morphological degradation, such as particle cracking at the cathode, is significant. Half-cell tests of aged and unaged anode samples extracted from the automotive cells confirm the post-mortem findings, where only minimal differences can be seen for the braced cell. In contrast, the aged cathodes from braced cells demonstrate substantial capacity fade in half-cell measurements as compared to the cathodes extracted from the unbraced cell. Finally, a new concept of the mechanical state of health (mechanical SOH) is introduced to correlate mechanical effects with electrode degradation.

1. Introduction

The change from conventional internal combustion engines (ICE) to electric motors in battery electric vehicles (BEV) or in some hybrid electric vehicles (HEV) is underway due to the lower emissions and higher efficiency of the electric drive trains (30–66% lower emissions over lifetime depending the source of the electricity used). Lithium-ion batteries (LIB) play a key role in the electromobility because of their high specific energy and high efficiency (well-to-wheel efficiency: BEV ≈70% compared to ICE ≈25%). Nonetheless, there remain several limitations such as the high initial costs, the limited recycling scheme, material bottlenecks, particularly for cobalt and lithium, and the safety concerns. Due to these economic and ecological reasons, a long battery cell lifetime is essential for the widespread acceptance by the society and to reduce the ecological footprint and the costs.

Today, there are different cell geometries used in BEV or HEV. The three most common cell types are the pouch cell, the round or cylindrical cell (e.g., 18 650- or 21 700 type) and the prismatic cell. The pouch cell has the highest specific energy of all cell types, but has a low mechanical stiffness of the laminate casing. However, this low mechanical stiffness is compensated with the use of external bracing, which is known to reduce aging.

Pouch cells are part of the battery system of, e.g., the VW ID.3 or the Porsche Taycan. The battery of the Tesla Model S/3 contains round/cylindrical cells while other BEVs use prismatic cells in their battery packs such as BMW i3 or Mazda MX-30. The advantages of prismatic cells are the dense packaging, the simple module design and the high energy density in modules. However, they age faster than cylindrical cells due to a number of reasons including the lower pressure or mechanical stability inside the cell. As a result of reversible and irreversible volume changes of the anode and the cathode during cycling, low compression can result in insufficient contact between the components within an electrode stack.

There are several publications that have examined the influence of external mechanical pressure on cell aging. Most of the studies deal with either cylindrical or pouch cells with a small nominal capacity of 6 Ah. Hahn et al. investigated the effect of different types of bracing on automotive lithium-ion pouch cells with a capacity of 40 Ah, respectively 37 Ah. There are a few reports about the aging effects in prismatic cells but only little about the impact of bracing on the cells’ cycling performance.
In this study, the impact of mechanical bracing on the lifetime of large format 94 Ah prismatic cells during an accelerated aging test is examined. In the first part, the electrochemical results of the aging tests, where the cells were cycled for more than 7000 cycles under different bracing conditions, are presented. In the second part, the degradation of the cells using different post-mortem analysis techniques is examined. Furthermore, a new concept, the “mechanical state of health” (mechanical SOH) is introduced and discussed. The mechanical SOH is used to demonstrate the impact of mechanical forces, for example, external pressure or cell casing, on the performance of the cell or electrodes.

2. Results and Discussion

Figure 1 shows the master chart of all tests conducted in this study. Physical and electrical tests of the large format prismatic LIBs (with and without external pressure, i.e., bracing) are shown in Section 2.1. After the tests on the prismatic cells, the cells were opened and a post-mortem analysis was conducted (Section 2.2). This included an optical inspection (Section 2.2.1) and a physicochemical characterization to examine the morphology, the thickness, the chemical composition, and the structure of the electrodes as discussed in Section 2.2.2. Finally, the electrodes harvested electrodes after cell opening are characterized with electrochemical measurements in laboratory cells as in Section 2.2.3. In addition to the master chart in Figure 1a, Table S1, Supporting Information, has been included with a summary of the measurements and the main result from each one.

2.1. Accelerated Aging Test of the Prismatic Automotive Cells

The cell performance during the accelerated aging test of the different cells is shown in Figure 2. All the cells show similar aging in the beginning with a significant capacity loss in the first 700 cycles followed by a plateau at ≈84 Ah, which corresponds to 90% state of health (SOH), for up to 3000 cycles (Figure 2a). Starting at ≈3000 cycles, the unbraced cells show a larger drop in capacity compared to the braced cells. The critical threshold of 80% SOH was reached for the unbraced cells at ≈3800 cycles and at ≈4700 cycles for the braced cell. After ≈7420 cycles for the unbraced cells and after ≈7170 cycles for the braced cells, the cycling of the cells was paused for five weeks to see the relaxation behavior of the cells. The unbraced cells showed no capacity recovery after the break. In contrast, the braced cells regained ≈12% of the discharge capacity when comparing the last five cycles before and the first five cycles after the break. These observations indicate...
a reversible capacity loss in the braced cell and an irreversible capacity loss in the unbraced cell. After the pause step, the cells were cycled for \(\approx\) 80 cycles and then one of each unbraced and braced cells was used for post-mortem analysis while the other cells were cycled until 8500 cycles (unbraced cell) and 13 000 cycles (braced cell), with nearly linear capacity fading.

A difference in the thickness change between the unbraced and braced cells can be seen in Figure 2b and Figure S1, Supporting Information. The unbraced cells have a relatively linear thickness increase during the aging test with a total increase of 22\% \(\approx\) 10 mm at end of life (EOL). This might be attributed to lithium plating on the anode, electrode swelling, delamination, and/or layer depositions on the electrodes. After the 5 week cycling pause after \(\approx\) 7420 cycles, no decline in thickness is observed, which might be related to irreversible lithium plating and thus an irreversible loss of capacity. It should be noted that a plastic deformation of the aluminum housing might also be a reason for the unchanged thickness after the pause. The braced cells show only a small thickness increase of \(\approx\) 2.5\% \(\approx\) 1.1 mm after 7000 cycles compared to the initial thickness of the cell. Interestingly, the thickness change decreased by \(\approx\) 45\% \(\approx\) 0.5 mm after the cycling pause compared to the thickness change before the break. This might be related to reversible lithium plating on the surface of the anodes which intercalates into the graphite structure at steady state conditions.

The corrected direct current internal resistance (DCIR) was determined every 500 cycles for Cell 2 (braced) and Cell 3 (unbraced) (Figure 2c). The initial resistance (after initial charging) of the unbraced cell is comparable to the braced cell (i.e., 0.65 and 0.64 m\(\Omega\), respectively). After the initial cycles, the DCIR decreases for both cells as the formation reactions are completed and then remains, more or less, stable until 3000 cycles. The larger increase of the resistance of the unbraced cell between 3500 and 4500 cycles (Figure 2c inset) is related to the increased capacity loss compared to the braced cell (Figure 2a inset). After the cycling break, the DCIR of the braced cells decreases by \(\approx\) 5.0\%, while the drop is negligible for the unbraced cell. This is a further indication that reversible lithium plating or capacity loss occurs in the braced cell.

The unbraced cells show increased aging during cycling compared to the braced cells. The unbraced cells reach the threshold of 80\% SOH, which is a typical value for the minimum usable capacity for BEV/HEV cells\[52–54] \(\approx\) 900 cycles earlier than the braced cells with the same aging procedure.

### 2.2. Post-Mortem Analysis of Three Different Aged Cells

For a deeper understanding of the different degradation mechanisms within the cells and to examine the cause of the thickness increase, post-mortem investigations were conducted on three of the cells. The first cell (Cell 1) is the reference cell without being cycled (only formation cycles), the second cell is the braced cell (Cell 2), and the third cell is the unbraced cell (Cell 3).

#### 2.2.1. Cell Opening

Figure 3 shows photographs of the electrodes and separators after cell opening inside the glovebox. The unaged electrodes of Cell 1 (Figure 3a: Cell 1: Reference cell [unaged]) show no visible degradation (e.g., depositions, delamination, or cracks) and the electrode layers appear homogeneous. The appearance of separator indicates no visible degradation and no electrode material sticks to the separator. The components extracted from Cell 2 (Figure 3b: Cell 2: aged cell, braced) shows only little visible degradation. Overall the anode looks homogeneous except at some spots adjacent to the current collector. Some windings (area at the edge of a jelly rolls [JR], where the electrodes are wrapped around) indicate minor lithium plating and delamination. Next to the current collector, the current is higher due to the ohmic potential drop along the negative current collector. Therefore the current is higher, which promotes lithium plating. At the windings, the inhomogeneous pressure distribution...
leads to a reduction of the separator porosity and thus, high exchange currents drive lithium plating.\textsuperscript{[57]} The cathode looks homogeneous with no visible deposition layers, for example, due to electrolyte decomposition, and only some cracks are found at the winding of the electrodes. This might be an artefact resulting from unwinding and separation of the electrodes and not from electrochemical aging effects. The appearance of the separator is consistent with the results from the electrodes and shows no obvious alteration, except for few spots adjacent to the current collector where anode material can be found sticking on the separator. The electrodes and separator of Cell 3 (Figure 3c: Cell 3: aged cell, unbraced) show significant degradation. Lithium plating is visible over a large area of the anode, mainly at windings, next to current collector and also in some areas spread over the flat face of the electrode sheet. Next to the current collector, there are also areas with crumbled coating and even small holes/perforations of the anode. The cathode shows little visible degradation in terms of deposition layers or cracks, but ripple formation is found in some stretches of the cathode. These ripples become more pronounced when moving from the outside layers to the inner layers of the JR. Extensive lithium plating can be found on the anodes facing those rippled areas (see Figure S2, Supporting Information). The peaks and troughs of the rippled areas demonstrate contact losses between anode, separator, and cathode and/or local separator deformation. This favors lithium plating on the anode due to high exchange currents. It remains unclear if the ripples initiate the areal contact losses and thus the lithium plating on the anode or vice versa. The obvious degradation and loss of lithium inventory also becomes evident when examining the separator. Here pieces of plated lithium are found as well as anode material (imprints of the ripples). Furthermore, melted areas of the separator are found close to material deposits.

These results show that for the braced cell there are only few areas showing visible degradation, such as lithium plating at some windings. In contrast, lithium plating in unbraced Cell 3 is pronounced and seems to be the predominant cause of degradation in the unbraced cells. At areas with high pressure inhomogeneity (e.g., windings) and high currents (close to current collector), lithium plating is even more pronounced. The external bracing leads to a more homogeneous pressure distribution over the cell which reduces the contact losses between the electrodes (e.g., cathode ripples) and hence also the degradation (e.g., lithium plating). The small amount of lithium plating also supports the theory of reversible lithium plating. During the 5 week pause in cycling (described in Section 2.1), plated lithium can re-intercalate into the graphite structure during steady-state conditions in the braced cell, which increases the capacity and decreases the thickness and the internal resistance of the cell.

### 2.2.2. Physicochemical Analysis

After cell opening, the surface of the electrodes was examined with scanning electron microscopy (SEM) (Figure 4 and Figure S3, Supporting Information). The morphology of the anode surface of Cell 1 (reference cell) shows a uniform Al\textsubscript{2}O\textsubscript{3} particle coating on the graphite. This particulate surface layer is also observed
for Cell 2 (braced), but shows additional spots of deposition which can be decomposition products of the electrolyte. The anode surface of Cell 3 (unbraced) shows extensive areas with deposits, which can be attributed to plated lithium.

The SEM investigations of the cathode surfaces (Figure S3, Supporting Information) show no significant differences between Cells 1, 2, and 3. There is evidence of particle segregation with aging (Cells 2 and 3), which is not as pronounced for the cathode of the reference cell (Cell 1). However, neither major cracks nor delamination are found. The cathode samples from Cell 3 extracted from regions with and without ripple peaks and ripple troughs (Figure 3c: cathode) show no difference in surface morphology in the SEM images. Overall, there is neither formation of additional layers on the cathode surface due to aging nor delamination, indicating that the capacity reduction of the cell during cycling is largely associated with the anode and, for example, lithium plating. This aspect is discussed in more detail in the following sections.

For a closer analysis, the cross section of the electrodes is examined. The anodes of all cells consist of non-spherical graphite particles with a 2–6 µm thick Al₂O₃ particle coating. The total thickness of the double-sided graphite anodes ranges between ≈151 µm for Cell 1 and ≈177 µm for Cell 3, which includes the ≈7 µm thick Cu current collector (Table 1). The analysis of the cross section (Figure S4, Supporting Information) reveals only marginal morphological changes, if any, between the reference cell (Cell 1) and the aged cells (Cells 2 and 3) in terms of cracks inside the particles. Nevertheless, the total thickness of the graphite electrode increases during aging (Table 1), which might be attributed to partial exfoliation and solid electrolyte interphase (SEI) formation. Most of the anode surfaces are covered by a uniform Al₂O₃ particle coating. Only for Cell 3, the unbraced aged cell, defects in the coating can be detected. It is at these locations that there is direct contact with the graphite particles and thus lithium plating occurs (Figure S4(d), Supporting Information). This finding is confirmed by the SEM-energy dispersive X-ray

![Figure 4. SEM pictures of anode surfaces of the reference and aged cells.](image)

### Table 1. Mean thickness and standard deviation of double-sided coated electrodes and separators. The copper current collector (anode) is ≈7 µm thick and the aluminum current collector (cathode) ≈12 µm.

| Cell       | Anode thickness [µm] | Separator thickness [µm] | Cathode thickness [µm] |
|------------|----------------------|--------------------------|------------------------|
| Cell 1: unaged, reference | 150.7 ± 0.7          | 20.1 ± 0.4               | 131.2 ± 0.3            |
| Cell 2: aged, braced         | 168.5 ± 1.9          | 20.0 ± 0.8               | 134.6 ± 1.3            |
| Cell 3: aged, unbraced       | 176.8 ± 6.5          | 19.7 ± 0.7               | 142.3 ± 1.8            |
(EDX) measurements (Figure 5). Oxygen is detected over the complete surface of the graphite electrode, but aluminum, associated with the Al₂O₃ coating layer, is only detected in the center of the image. This indicates that there is lithium plating at the edges of the picture as the metallic lithium reacts with the oxygen of the air (e.g., Li₂O) during the cross-section polisher (CSP) sample preparation. Lithium plating starts at a defect site within the Al₂O₃ coating layer, which then further destroys the layer in adjacent areas and directly deposits on the graphite particles.

The SEM cross-sections of the cathodes are shown in Figure 6. The double-sided cathode is ≈131 µm, including the ≈12 µm Al current collector, for Cell 1 and expands up to ≈142 µm for Cell 3 (Table 1). The cathode consists of secondary particles with diameters up to ≈12 µm. The secondary particles of the reference cell (Figure 6a) exhibit only few cracks, whereas the secondary particles of the aged Cells 2 and 3 show significant particle cracking along the grain boundaries. These cracks are accompanied by volumetric changes in combination with external pressure on the electrodes. By cracking, “fresh” cathode/NCM active material comes into contact with electrolyte, which can cause undesirable side reactions along with the loss of ionic and electronic pathways within the electrode.[58–60]

The amount of cracks in the case of Cell 2 is only slightly higher than Cell 3: without ripples (Figure 6b,c). In contrast, the amount of visible cracks is significantly higher in areas of the Cell 3 cathode with ripples compared to areas without ripples (Figure 6c,d). For Cell 3: with ripples (Figure 6d), there is a gradient where the gap size between the cracks increases from the current collector towards the surface of the electrode. These cracks can lead to contact losses between the particles especially at the surface of the electrode resulting in enhanced morphological degradation or increased overpotentials of the electrode in those areas. Additionally, the cracks cause a volumetric expansion of the particles, what can be seen in a thickness increase of the cathode (Table 1). The smaller cathode thickness of Cell 2 compared to Cell 3 (134.6 to 142.3 µm) may be related to the presence of external pressure, which might hinder the expansion of the particles to a certain degree. Another reason for the increased cathode thickness for Cell 3 is delamination, but this might also be an artifact from CSP preparation.

Overall, it can be concluded that the anode suffers from aging phenomena such as lithium plating, rather than from morphological changes. In contrast, the cathode shows significant morphological degradation along the grain boundaries (cracking), which probably contributes to the loss of cell capacity. The cathodes of the unbraced cell in the area of the ripples show enhanced particle cracking close to the surface. Although the SEM surface images suggested that the anode made a more significant contribution to cell aging, the SEM cross sections revealed as the cathode particles also shows significant morphological degradation during cycling. The negative impact of these cathode morphological changes on the cell performance is discussed in Section 2.2.3.

To examine the impact of lithium plating and cathode degradation, inductively coupled plasma optical emission spectroscopy (ICP-OES) is performed (in duplicate) on a sample from each electrode and each cell. The amount of lithium in the anode, in mole per square centimeter, is converted into milliamp hour per square centimeter to provide a value that is more tangible and thus easier to relate to the capacity losses. The areal lithium content increases in the anode during cycling as shown in Figure 7a. The anode of the unaged reference cell has a lithium content of 0.5 ± 0.01 mAh cm⁻², which is 4.9% of the total lithium in the anode and cathode. This lithium is associated with the SEI and any remaining lithium ions inside the graphene layers. The share of lithium in the anode is 13.9% for Cell 2 (aged, braced) and 15.6% for Cell 3 (aged, unbraced). One possible reason for the lithium gain is the lithium plating on the anode during the aging test. Additionally, the growth of the SEI during aging consumes lithium which further increases the amount in the anode. These results demonstrate the loss of lithium inventory inside the battery cell due to lithium plating and SEI growth, which causes capacity reduction. A small amount of the lithium increase can be explained by a different degree of lithiation at cell opening due to different overpotentials, although an extensive CV step at 2.7 V at the end of discharge is intended to minimize this effect. The unbraced Cell 3 shows the highest lithium loss due to increased plating, which coincides with the results from analytical investigations discussed in the previous sections. It should be noted that for ICP-OES, anode samples with excessive visible lithium plating were not chosen in order to obtain representative values for Cell 3.

Based on the ICP-OES results, the composition of the cathode active material of Cell 1 (reference cell) is estimated as Li₁₋₀.₀₄ Ni₀.₄ Co₀.₃ Mn₀.₃ O₂, where the oxygen content is inferred from the crystal structure. The cathode active material composition of aged Cell 2 (braced) is estimated to be Li₀.₈₆ Ni₀.₄ Co₀.₃ Mn₀.₃ O₂, while that of Cell 3 (unbraced) is estimated to be Li₀.₈₆ Ni₀.₄ Co₀.₃ Mn₀.₃ O₂. For Cell 3, areas with and without ripples were studied but no notable differences in the metal ion contents were observed. It should be noted that the seemingly higher stoichiometric amount of lithium in the cathode...
unbraced cell as compared to the braced is related to the calculation of the value itself. This is because the stoichiometric amount of lithium is based on the ratio of lithium to the sum of nickel, cobalt, and manganese. Since the amount of transition metals decreases more in the cathode of the unbraced cell than in the braced cell, the resultant proportion of lithium is higher in the unbraced cell.

The transition metal content in the anode is shown in the Figure 7b. The manganese content is higher in the anode after cycling and follows the lithium content in the anode. This gain is related to the enhanced SEI formation on the anode during aging.\textsuperscript{[61–63]} Mn disproportionation (2Mn\textsuperscript{3+} → Mn\textsuperscript{4+} + Mn\textsuperscript{2+}) may occur, which would accelerate the formation of complexes between the Mn\textsuperscript{2+} ions and the carbonate-based electrolyte. The Mn\textsuperscript{2+} ions are transported to the anode and subsequently can trap further lithium ions in the SEI.\textsuperscript{[61,64–66]} This causes a further loss of lithium inventory. The amount of cobalt and nickel in the anode also increases but not as much as for manganese. The ICP-OES results mirrors the data presented in the previous sections and underscores the positive effect of the bracing on the cell performance. The lithium and the transition metal content in the anode is slightly higher for the cell without external bracing (Cell 3), which can be related to lithium plating and SEI growth. Only the Mn content is slightly higher for the

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure6.png}
\caption{SEM cross sections of the differently aged cathodes. a) Cell 1, reference, b) Cell 2, braced, c) Cell 3, unbraced, w/o ripples, d) Cell 3, unbraced, w/ ripple. On the pictures on the left side the current collector can be seen at the top, and the electrode area near the surface at the bottom.}
\end{figure}
braced cell, albeit with a higher error. This result might be related to increased cracking of the particles, and thus also to the increased disproportionation of Mn$^{3+}$ ions and subsequent trapping of lithium ions in the SEI.

X-Ray diffraction (XRD) analyses were performed (Figure 8) to further investigate the structural degradation of the aged cathodes. Rietveld analysis was used to perform the structure refinement. No significant phase changes due to aging could be detected. Previous studies showed changes from $R$-$3m$ layered to $Fd-3m$ spinel and to $Fm-3m$ rock salt structure during aging.$^{[64,67]}$ A closer examination of the lattice parameters obtained from the Rietveld analysis, for example, $a/c$ (lattice parameter), $R$ (intensity ratio), crystallite size, and lattice strain (Table 2) indicates an increased structural degradation of the layered cathode materials for the aged braced cell (Cell 2) and for the aged unbraced cell in the areas with ripples (Cell 3: with ripples). The unbraced cell in the area without ripples (Cell 3: without ripples) shows less structural degradation.

A high $I(003)/I(104)$ ratio represents a “well-layered” structure and low level of Ni$^{2+}$ and Li$^+$ cation mixing in the crystal structure.$^{[64,68]}$ The reference Cell 1 and Cell 3: without ripples have a higher $I(003)/I(104)$ ratio than Cell 2 and Cell 3: with ripples. It should be noted that the intensity ratio should only be used as an indication for degradation of the active material, rather than quantitative measure as the ratio can be affected by the variations in the experimental setup.$^{[68]}$ A better indication of Ni$^{2+}$ and Li$^+$ cation mixing of is the intensity ratio $R ((I(006) + I(102))/I(101))$, introduced by Dahn.$^{[69]}$ High $R$ values, as observed for Cell 2 and Cell 3 with ripples, indicate increased cation mixing as the intensity peak of (101) is lower when Ni atoms occupy Li sites in the layered structure.$^{[70]}$ The broadening of the peaks in the XRD pattern is a further indication of structural damage within the cathode active material lattice from the aged cells and can be correlated with the crystallite size and the lattice strain of the particles.$^{[71,72]}$ The cathode particles of the aged cells show decreased crystallite size and slightly increased lattice strain for Cell 2 and Cell 3: with ripples. The active particles of Cell 3: without ripples have enhanced crystallite size compared to the particles of the other aged cells and also slightly lower lattice strain compared to the particles of the reference cell.
The XRD results suggest a correlation of the crystallite size and applied pressure on the electrodes. Higher pressure on the electrodes (Cell 2 and Cell 3: with ripples) increase the damage of the layered structure and the cation mixing compared to the electrodes which were not subjected to such high pressure (Cell 3: without ripples or Cell 1). The increased pressure arises from the external bracing or from the internal volume changes through ripples on the cathode and hence lithium plating on the anode. Moreover, cathodes with smaller crystallite size show an increased lattice strain and also more pronounced Ni$_{2+}$ and Li$^+$ cation mixing. External pressure seems to increase the aging of the cathode (particle cracking). Without external pressure, (Cell 3) different areas of the electrodes exhibit different characteristics: areas without ripples show only minor aging (Cell 3: without ripples), while areas with ripples shown much more significant aging (Cell 3: with ripples).

### 2.2.3. Electrochemical Testing

To substantiate the results related to cathode and anode electrode degradation, electrochemical tests were performed in three electrode laboratory cells with electrodes from selected areas of the prismatic cells. Electrical impedance spectroscopy (EIS) was conducted after 5 cycles (2 × 0.1 and 3 × 0.2 C) at 100% state of charge (SOC) to correlate the morphological and structural changes with electrochemical phenomena. The results are shown in Nyquist plots presented in Figure 9. The individual spectra of the anode and cathode half cells consist of several features which can be described as follows: a high-frequency intercept due to ohmic resistances in the cell (R$_{\text{ct}}$ and R$_{\text{c:f}}$) and a semicircle at high frequencies related to the surface film on the particles (R$_{\text{SEI}}$ and R$_{\text{c:s}}$). The a and c in the subscripts refer to the anode and cathode half cells, respectively. For the anode half cells, a second semicircle at medium frequencies is related to the charge transfer resistance (R$_{\text{c:e}}$) and a third semicircle at low frequencies is detected (R$_{\text{c:f}}$). The third semicircle has been reported to appear only for high and low SOCs,[2] where solid-state diffusion in the electrode plays a role but may not be detectable. For the cathode half cells, the second semicircle at medium frequencies is related to the electrical conductivity of the active material along with the metallic lithium/electrolyte interface (R$_{\text{c:f}}$) and the third semicircle at low frequencies is correlated to the charge transfer resistances (R$_{\text{c:e}}$).[23-25] The inclined line is related to solid-state diffusion for both electrodes. These features were fitted with an appropriate model (Figure 9c).

The EIS study of the anode half cells revealed an increase of the impedances (Table S2, Supporting Information) between the reference cell and the aged cells as can be seen in Figure 9a. For instance, the SEI resistance (R$_{\text{SEI}}$) increases from 6.0 Ω cm$^2$ in the reference cell to >19.0 Ω cm$^2$ in the aged cells. This is consistent with the findings of the ICP-OES analysis, which showed a pronounced TM content on the anode after cycling that is likely associated with a thicker SEI, due to transition metal dissolution. The resistances dramatically increase, a factor of ≈5 (R$_{\text{SEI}}$ by a factor of ≈10), for the anodes of Cell 3 containing visible lithium plating. This is in agreement with the results from previous sections, showing lithium plating as the main cause of performance degradation.

The results of the EIS of the cathode half cells (Figure 9b and Table S3, Supporting Information) are also in accordance with the data presented in previous sections, as the cathodes from Cell 2 and Cell 3: with ripples show increased resistances than Cell 1 and Cell 3 without ripples. For instance, R$_{\text{ct}}$, which is correlated with the electrical conductivity of the active material and the lithium metal/electrolyte interface resistance, is higher in the aged cells than the reference cell. As the lithium metal/electrolyte interface resistance should be more or less the same for all cells, the change in the resistance can be attributed to the electrical conductivity of the active material particles. For the cathode of Cell 3: with ripples, the resistance is the highest. These electrode areas exhibited significant particle cracking and separation between the particles (Figure 6d), which would result in the most inhibited conductivity inside the secondary particles. The charge transfer resistance (R$_{\text{ct}}$) is expected, as lowest in Cell 1 (reference cell) and increases in the aged cells. R$_{\text{ct}}$ is larger for the cathodes with the high applied pressure (Cell 2 and Cell 3: with ripples) as compared to Cell 3: without ripples. This might also be related to the lower crystallite size (Table 2) and hence to the more pronounced cracking of the active particles due to higher internal and external pressure on the particles. For the surface film resistance R$_{\text{c:f}}$ and the ohmic resistance R$_{\text{c:f}}$, no clear trend is visible indicating little relationship with the aging processes. The incomplete first semicircle and also the variation of R$_{\text{c:e}}$ in some measurements might be related to cable resistances.

The results from half-cell EIS measurements enable a better understanding of the resistances inside the prismatic cells. The anode likely makes the most significant contribution to the resistance of the full cell. The higher resistances in the unbraced cell can be attributed to lithium plating. The increase of the surface layer resistance in the aged cells compared to the reference cell is probably mainly caused by the anode, whereas the larger the charge transfer resistance probably can be attributed to both electrodes.

Figure 10 shows the C-rate capability test of the electrodes harvested from the prismatic cells. Anode and cathode samples obtained from the prismatic cells are tested either individually in half cells or together in full cells (laboratory cells). After the

| Cell | $a$ [Å] | $c$ [Å] | $I(003)/I(104)$ | $R_c/(R_{i006} + I(102))/I(101)$ | Crystallite size [Å] | Lattice strain [%] |
|------|--------|--------|-----------------|--------------------------|----------------|----------------|
| Cell 1: unaged, reference | 2.857 | 14.250 | 2.03 | 0.74 | 1357 | 0.08 |
| Cell 2: aged, braced | 2.849 | 14.308 | 1.52 | 0.92 | 388 | 0.11 |
| Cell 3: aged, unbraced, without ripples | 2.849 | 14.304 | 2.23 | 0.73 | 994 | 0.06 |
| Cell 3: aged, unbraced, with ripples | 2.848 | 14.327 | 1.26 | 0.88 | 387 | 0.10 |
initial 0.1 C (referring to the reference cell) charge and discharge cycles, the cells are charged with 0.2 C and discharged as described in the experimental section. No significant capacity deviations occur between samples taken from different regions of the JR, for example, inner and outer part of the JR or between different locations in one electrode sheet (Figure S6, Supporting Information). Therefore, only the mean values are shown. Only for Cell 3, a distinction between different areas of the electrodes (areas with and without ripples) has been made. For the full cell tests (laboratory scale), large capacity variations between the reference cell (Cell 1, for example, 2.6 mAh cm$^{-2}$ at 0.2 C) and the aged cells (Cell 2 + 3, for example, 1.9 and 1.8 mAh cm$^{-2}$ at 0.2 C) are observed, which are comparable to the differences in the long-term cycling test described in Section 2.1. The anode and cathode half cells have smaller capacity differences between the reference cell and the aged cells than is evident in the full cell test. This indicates little degradation of the electrodes, in terms of a capacity reduction, during cycling.

During the full cell test, the reference cell has a ≈28% higher capacity compared to the braced cell and ≈32% higher capacity compared to the unbraced cell, for example, 2.6 mAh cm$^{-2}$ for Cell 1 compared to 1.9 mAh cm$^{-2}$ for Cell 2 and 1.7 mAh cm$^{-2}$ for Cell 3 at 1.1 C. This loss reflects the capacity difference between the aged prismatic BEV cells with its nominal capacity before the cycling of ≈24% for the braced prismatic cell and ≈33% for the unbraced prismatic cell (Figure 2). As it remains unclear if the capacity loss of the cells in the full-cell test is initiated by the cathode, anode, or both of them, the half-cell tests are examined to study the impact of the individual electrodes.

For the anode half cell tests, no capacity fading is detected up to 7.4 mA (1.1 C); the capacity decreases only with further increasing currents. For the highest current rate of 2.2 C, the capacity shows the largest drop among all currents, which is partly related to the diffusion limitations of the lithium counter electrode in combination with the carbonate-based electrolyte.[76] The electrodes from the braced cell (e.g., 2.6 mAh cm$^{-2}$ at 1.1 C) have only a slightly lower capacity of 3% compared to the reference cell (e.g., 2.7 mAh cm$^{-2}$ at 1.1 C). This reveals only little degradation in terms of capacity reduction for the anodes from the braced cell. The electrodes from the unbraced cell show the lowest capacity (e.g., 2.4 mAh cm$^{-2}$ at 1.1 C), that is, 11% lower capacity compared to the reference cell, and the highest standard deviation over the whole test. This demonstrates the pronounced degradation of the anode in the unbraced cell due to the increased lithium plating.

The cathode half cells test show a linear discharge capacity fading until 11 mA (1.6 C), with an increased capacity drop at 14.7 mA due to the high current. Interestingly, the cathodes from the unbraced cell (6% lower capacity compared to reference cell, for example, 2.3 to 2.5 mAh cm$^{-2}$ at 1.1 C) have a slightly higher capacity compared to those of the braced cell (11% lower capacity compared to reference cell, for example, 2.2 mAh cm$^{-2}$ at 1.1 C) confirming that the applied external pressure along with the rising internal pressure results in

![Figure 9. Nyquist plot of anode- (a) and cathode half cells (b) obtained from different prismatic cells. EIS measurements performed at 100% SOC. The markers correspond to the measured data and the line presents the fit of the data. The individual spectra are shifted along the y-axis for better visibility. Data shown from 1 MHz to 10 mHz. c) Equivalent circuit model used for fitting.](image-url)
pronounced structural cathode degradation. The areas from the cathode of Cell 3: with ripples (unbraced) show more significant capacity fading than the other cathode half cells, which supports the hypothesis that the electrical conductivity and the charge transfer inhibit the performance.

The results of the C-rate test show that the capacity fade of the full cells is primarily attributed to the loss of lithium inventory and to a smaller extent, by the individual electrodes. The loss of lithium for the intercalation into the electrodes is mainly caused by lithium plating and increased SEI formation, as is shown in Figures 3 and 4. The examination of the laboratory electrodes from the braced cell show that the anode suffers only little from capacity reduction compared to the reference cell, whereas the cathode suffers from significant mechanical degradation through the high pressure. In comparison, the laboratory cells derived from the unbraced cell reveal that the capacity fading is also related to the loss of lithium inventory and structural cathode degradation, but the aging of the anode plays a more significant role due to the substantial lithium plating. It can be concluded that external pressure is beneficial for the overall performance in prismatic cells, as it leads to decreased anode degradation even if the cathode suffers more from the high pressure. The bracing also results in a more homogeneous degradation over the complete cell, in terms of morphological and structural changes, lithium plating, and capacity reduction compared to the unbraced cell. In the unbraced cell a variety of different local aging mechanisms, for example, ripples on the cathode, widespread lithium plating, or crumbled coatings, occur.

2.3. Mechanical State of Health

The new concept of the mechanical SOH is introduced in this section. It shall correlate the capacity reduction with the mechanical degradation of, for example, the electrode particles or other cell components. Although these aspects also play a role in the more general term “state-of-health”, the concept of mechanical SOH is intended to focus more on the mechanical characteristics of the materials and cell components and their influence on the capacity loss. Compared to temperature and current, the mechanical effects on the cycle life of a battery cell are rather unexplored, but play a vital role in the lifetime of batteries, particularly as the volumetric energy density (related to the space for the battery) is continually increased. The mechanical SOH is derived from the processes inside the battery cell/electrodes (particle cracking or volumetric expansion/contraction, to name a few). Electrodes with a good mechanical SOH should have low structural and irreversible volume changes and also a low capacity reduction. In comparison, electrodes with a poor mechanical SOH have large structural changes, for example, particle cracking, high irreversible volumetric growth in combination with a significant capacity fading. In this sense, changes in mechanical SOH are not directly initiated by external effects like applied pressure, etc., but are certainly affected by them. This work illustrates this point through the effect of fixed bracing, for example, on the particle cracking in the cathodes.

As discussed above (Figure 6), the cathodes of the braced cell and of the unbraced cell in the areas of the ripples suffer, in particular, from cracking. These visible results are confirmed by XRD-measurements (Figure 8 and Table 2) and indicate a reduced mechanical SOH in those areas. The cathodes of the unbraced cell in the areas without ripples have a higher mechanical SOH, which is also confirmed by electrochemical investigations (Figures 9 and 10). The change in thickness (only considering the electrode material) compared to the reference cathode is lower for the braced cell compared to the unbraced cell, thus also contributing to the lower mechanical SOH.

The mechanical SOH of the anode of the aged cells is only slightly lower than that of the reference cell. There is negligible increase in cracking (Figure S4, Supporting Information) and only a small capacity loss (Figure 10). The higher capacity loss of the anode without external bracing is possibly related to lithium plating and not to effects which have an impact on the mechanical SOH. Nevertheless, the anodes of the braced prismatic cell show a lower change in thickness as the anodes of the unbraced prismatic cells at EOL.

In total, the mechanical SOH can be used as an indication for the degradation of an electrode material. In this work, the reduction of the mechanical SOH of the aged cathodes is associated with particle cracking and volumetric expansion, while for the anode, only the volumetric expansion may be contribute to the lower mechanical SOH. Further studies need to be conducted with specialized sensor technology, for example, ultrasound, to gain a deeper understanding of the correlation between changes in the mechanical characteristics of the materials and components and the capacity reduction. With this additional information, it may be possible...
to integrate the mechanical SOH into battery management systems.

3. Conclusion

The cycling tests of braced and unbraced automotive prismatic BEV cells for more than 7000 cycles reveal different aging phenomena, which are investigated using post-mortem analysis. The externally-braced prismatic cells exhibit an enhanced cycling performance during the aging test, reaching the threshold of 80% SOH 900 cycles later compared to the unbraced cells. This result demonstrates the importance of external bracing, and more specifically a homogeneous pressure distribution for lithium-ion cells. During this aging test, the change in cell thickness of the braced cell is ≈2.5% while the unbraced cell expanded ≈17.5%. This expansion is associated with lithium plating, electrode delamination, and electrode swelling. Further post-mortem studies revealed that the morphological and structural cathode degradation, for example, particle cracking and cation mixing, has a reasonable impact on the cell performance reduction for the braced cell, whereas the impact of the anode on the performance loss is small. For the unbraced cell the effect of the anode on the capacity loss is clearly increased as the anode suffers from lithium plating due to insufficient contact between the components within the electrode stack. Nevertheless, the C-rate test of the laboratory cells revealed that the main factor contributing to the capacity reduction of the prismatic BEV cells is the loss of lithium inventory.

The concept of a mechanical SOH as an indicator for electrode degradation due to mechanical effects is introduced in this work. The cathode suffers from a reduced mechanical SOH due morphological and structural degradation, whereas the anode exhibits a relatively stable mechanical SOH during aging. One explanation is the higher Young’s modulus of the polycrystalline NCM (≈200 GPa) as compared to graphite (≈100 GPa) in the lithiumated state.\(^{[77–79]}\) The high modulus in combination with the volumetric expansion leads to stress and hence cracking inside the particles. Thus, external bracing results in a reduced mechanical SOH for the cathode material, but a more uniform aging over the entire cell and less localized degradation.

4. Experimental Section

**Prismatic Cells:** Figure 11a shows the cells tested in this study and Table S4, Supporting Information, gives information about the cells. These prismatic cells are designed for BEV applications.

A total of 4 cells were cycled (Table S5, Supporting Information), whereby two cells were cycled without external pressure and the other cells were cycled under braced conditions. Two form-fitted metal plates are used to brace the front and back of the battery cell (Figure 11b). The pressure is applied with fixed bracing. At the beginning of the cycling experiment, the plates are positioned at the sides of the battery cell and the spacing of the plates corresponds to the thickness of the prismatic cell. With the plates in place, further expansion of the battery cell is severely limited. An exact pressure determination over the entire cell is not possible, since the cell has an additional housing at the top and bottom of the battery cell (Figure 11 and Figure S1, Supporting Information).

**Electrochemical Testing:** Table S5, Supporting Information, shows the parameters for the electrochemical testing of the prismatic cells. All cells were cycled (BaSyTec GmbH) at room temperature using an adapted aging protocol with elevated discharge currents of 188 A (2.0 C, related to nominal capacity). The discharging procedure used a constant current (CC) step with an end criterion of 2.7 V. The charging procedure used a constant current-constant voltage (CCCV) procedure with a current of 94 A and an end criterion of current \( | I < 0.1 \text{C} | \) at 4.15 V. Every 250 cycles, the cycling procedure was paused to measure the width (DIGI MET, HELIOS-PREISSER GmbH) in the center of the cell.

The DCIR is determined with the current switch method\(^{[80]}\) every 500 cycles. The DCIR is calculated by the difference in the voltage divided by the difference in the current. The difference is the result of the last charging voltage or current value at 100% SOC and the voltage or current value after 10 s of discharge. The DCIR has to be corrected with a temperature factor to account for the fluctuating temperature during cycling. The uncorrected DCIR value at 1000 cycles is set as the reference value for the correction, since the temperature is known to be \( \approx 25 \text{°C} \). This correction is based on the Arrhenius equation and the assumption that between cycle 1000 and 1500 the change of the DCIR is negligible. Figure S5, Supporting Information, visualizes the impact of the temperature on the DCIR.

**Table 3.** History of prismatic cells examined via post-mortem techniques.

| Bracing Condition | Cell 1 (Reference cell) | Cell 2 | Cell 3 |
|-------------------|-------------------------|--------|--------|
| Cycles\(^{[4]}\)   | None                    | 7250   | 7500   |
| EOL capacity\(^{[5]}\) [Ah] | 72.0                    | 63.2   |
| Actual capacity\(^{[6]}\) [Ah] | 97.0                    | 80.5   | 71.6   |

\(^{[4]}\)(1.0 C charge/2.0 C discharge); \(^{[5]}\)(0.05 C charge/0.05 C discharge).
Post-Mortem Analysis: Table 3 summarizes the history of the cells which were studied with post-mortem techniques. Two of the cells were electrochemically aged under different bracing conditions (Table S5, Supporting Information) and one unaged cell was used as a reference (Cell 1).

Prior to post-mortem characterization the cells were cycled for 2 cycles with 4.7 A (0.05 C) from 2.7 to 4.15 V to determine the actual capacity. Afterwards, the cells were discharged with a CCCV step with 4.7 A (0.05 C) in CC step until 2.7 V and then held at 2.7 V for 12 h to ensure that the lithiation state was similar for all cells. The prismatic cell casing was removed and the four JR were detached from the casing. For each JR, the anode, cathode, and separator were separated and examined inside the glovebox. Prior to the following investigations, the samples were washed with dimethyl carbonate (DMC).

Morphological analysis of the electrodes was done with a SEM (Auriga 60, Carl Zeiss Microscopy GmbH) and EDX analysis (Element SDD Detector, AMETEK/EDAX). The sample preparation and the transfer into the SEM were carried out in argon atmosphere without contact to the air with a custom-made sample holder. The cross-section preparation was conducted with a CSP (Ion Milling System IM4000Plus, Hitachi High-Tech Corporation). The samples for the CSP were handled in air and the visualization was done with the SEM.

The electrode and separator thickness were determined by a displacement sensor (GT2-H12K, KEYENCE Corporation). After washing the samples inside the glovebox and drying in the antechamber at room temperature under vacuum, the electrodes and the separators were handled in air for the thickness measurements. To calculate the mean and standard deviation of each sample (e.g., cathode thickness of Cell 2, aged, braced), measurements were taken on two different jelly rolls, where measurements were made on two different sheets and on different areas of the sheet. At least 24 measurements were made for each sample to calculate the mean values.

The chemical composition of the anode and cathode samples was determined with ICP-OES. The specimens were weighed after washing and drying, and then digested with aqua regia (mixture of hydrochloric acid and nitric acid, vol%/1.3). The dispersion was filtered and the filtrate was then characterized with ICP-OES (Vista-PRO radial, Varian Inc.). The graphite and the binder remained as a solid residue. A more detailed explanation of the ICP-OES procedure is described by Bach et al. The carbon and oxygen content of the solid residue was examined by C-Leco and ONH-Leco (LECO C744 and LECO ONH836, LECO Corporation).

XRD of the cathode material was performed with a SmartLab diffractometer (Rigaku Corporation) in the range of 2θ = 10–80° and at a scan rate of 0.5°/min. Powder samples were collected by carefully scratching the active material from the current collector with a scalpel, followed by drying and grinding by hand in a mortar and pestle.

For the electrochemical tests, laboratory test cells (PAT-Core, EL-Cell GmbH) with a three-electrode set-up were built from electrodes harvested at different areas of the JR. A drawing of the electrodes and the locations for sampling can be seen in Figure S6, Supporting Information. The electrodes were harvested from: 1) the center of the electrode sheet from the inner and outer part of the electrode; and 2) from the top, bottom, side and center from the middle part of the jelly roll. The selection of these positions was intended to provide a representative picture of the jelly roll electrode as a whole.

The active material was carefully removed from one side of the electrode to enable electrical contact with the current collector. The separator was a 220 μm thick double-layered separator made up of a nonwoven polypropylene (PP) cloth and a microporous PE membrane (FS-5P, EL-Cell GmbH). LP 57 (Gotion Inc.), a 1 M LiPF6 in EC/EMC = 30/70 wt% solution, was used as the electrolyte. Either half cells with a working electrode from the JR and lithium metal (380 μm thick, Merck KGaA) as counter electrode, or full cells with a cathode working electrode and an anode counter electrode from the JR were built. For the EIS measurements only cathode and anode half cells from the center part of an electrode sheet were used. The EIS was performed at 100% SOC due to the fact that the electrodes were at a state of maximum expansion resulting in the pressure inside the cell. The impedance spectra were recorded in a frequency range of 1 MHz to 10 mHz with a 5 mV root-mean-square perturbation. For all EIS measurements at least two cells were built. The rate capability test was applied to all cells with three initial charging and discharging (formation) cycles with a current density of 0.29 mA cm⁻². After formation, the cells were charged with 0.58 mA cm⁻² CCCV (I < 0.13 mA cm⁻²) and discharged with 0.58, 0.96, 1.45, 2.89, 4.33, 5.78, and 0.58 mA cm⁻² CC sequentially. It should be noted that the same current densities were applied for all cells and refer to the C-rate from the initial 0.1 C formation cycles of the electrodes harvested from the reference cell. The rate test consisted of the following:

2: C charging and 0.2, 0.4, 0.5, 1.1, 1.6, 2.2, and 0.2 C discharging. The full cells were cycled between 2.7 and 4.2 V, the cathode half cells between 3.0 and 4.3 V and the anode half cells between 0.01 and 1.0 V. At least 8 cells were built in different areas of the JR (Figure S6, Supporting Information) for the aged cells and at least 3 cells (only from the center part of the electrode sheets) for the unaged reference cell.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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