Insights into Cycling Aging of LiNi$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$ Cathode Induced by Surface Inhomogeneity: A Post-mortem Analysis

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Abstract

A comprehensive post-mortem study is conducted on the power-optimized LiNi$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) cathode material harvested from large-format commercial pouch cells with different aging conditions. Uneven degradation phenomena are observed in the harvested NCA electrode during the post-mortem analysis. A schematic model, which is associated with the surface inhomogeneity, is proposed to interpret the formation of uneven degradation phenomena. Based on the model, the detrimental impact caused by an elevated cycling temperature is related to the fact that the high cycling temperature facilitates the local overcharge reaction, and further accelerates the
uneven degradation of the NCA electrodes. This work provides experimental evidence and an in-depth discussion concerning the cycling aging induced from the surface heterogeneity of the electrode material. Additionally, we also emphasize the necessity of carrying out a reliable aging study on thin-coated battery electrodes.

Introduction

After a few decades of continuous development of lithium-ion battery (LIB) technology, related industries have been greatly boosted in recent years due to the on-going revolution of vehicles electrification. Comparing to traditional LIB systems for consumer electronics, batteries for vehicle industries require better energy density, power density, stability and safety. LiNi$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA), which is one of the promising Nickel-rich layered cathode materials for LIB systems, will play a key role in the coming decade. A comprehensive understanding of degradation mechanisms is important to optimize battery management systems in order to prolong the lifespan of NCA-based LIBs or achieve further improvements on material aspects.

The degradation of NCA electrode materials during Li$^+$ extraction/insertion has been extensively studied. Abraham et al.\textsuperscript{2,3} found the formation of a NiO-like (rock-salt structure) surface layer on power-faded LiNi$_{0.80}$Co$_{0.2}$O$_2$ cathodes. They attributed the power fade and the impedance rise to the growth of a NiO-like surface layer on the cathode material since pure NiO presented both poor electronic and ionic conductivity. Later, a similar degradation scenario was observed on NCA cathode material. Several studies\textsuperscript{4-6} revealed that the capacity-fading mechanism of NCA cathode material was associated with the formation of an inactive NiO-like phase at grain boundaries and grain surfaces of primary/secondary particles. The amount of NiO-like phase displayed a correlation to the capacity loss. The origin of the surface NiO-like phase was attributed to instabilities of crystallographic and electronic structure induced by over-delithiation. These instabilities led to cation mixing accompanied with loss of oxygen and formation of a rock-salt structure.\textsuperscript{7-10} Zhang et al.\textsuperscript{11} characterized
low-rate (C/10) cycling NCA electrodes and observed rock-salt phases in the bulk instead of surface regions of primary particles. They suggested a mechanism in which oxygen migrated from the bulk to the surface domain due to an oxygen concentration gradient created between oxygen-deficient surface domains (rock-salt phase) and original bulk domains. The loss of oxygen finally led to the rock-slat phase formation in the bulk domains.

Morphological changes of NCA particles have been studied in-depth. Micro-cracks were observed on NCA secondary particles during cycling aging, especially with unfavorable cycling conditions such as elevated temperature and broad operating state-of-charge range ($\Delta$DoD).\textsuperscript{12,13} The generation of micro-cracks was attributed to changes of the crystal lattice during Li$^+$ extraction/insertion and the accumulation of micro-strains, particularly cycled at extended $\Delta$DoD.\textsuperscript{8,14} These micro-cracks were considered as one of the major causes of NCA cathode material degradation due to the formation of NiO-like inactive layer on the newly formed interface.\textsuperscript{14} Recently, rock-salt growth-induced (003) cracks were observed and suggested as a major cracking mechanism of NCA primary particles.\textsuperscript{15}

NCA particles with non-uniform SoC distribution were revealed by Raman microscopy.\textsuperscript{16-18} Lately, synchrotron-based techniques\textsuperscript{19-22} and Atomic Force Microscope (AFM)-based Kelvin Probe Force Microscope (KPFM)\textsuperscript{23} have been applied to inspect the non-uniform SoC distribution on a particle level. The researchers argued that the non-uniform SoC implied uneven local current distribution during charge/discharge steps resulting in local degradation. Forouzan et al.\textsuperscript{24} reported a comprehensive modeling study about the effects of electrode heterogeneity on LIB performance and lifetime. Their modeling results indicated that the electrode heterogeneity introduced non-uniform charge capacity, current-density, SoC and temperature, resulting in electrode degradation, especially during charging pulses. The non-uniformity could be further enhanced by elevated cycling current. Other works reported the inhomogeneity induced by the porous structure of composite electrodes. The inhomogeneities were distributed from the electrode surface perpendicularly towards the current collector (through-plane),\textsuperscript{25-27} resulting in an uneven through-plane degradation.\textsuperscript{24,26,28} It is
important to point out that surface-focused characterizations play a major role in LIB aging studies. Ignoring the through-plane heterogeneity can lead to spurious conclusions due to the deviations from actual aging scenarios.

This work aims to provide a comprehensive aging study of NCA cathode materials harvested from large-format commercial cells that were aged according to a variety of aging conditions such as temperature, current rate and number of cycles. Previous studies and their post-mortem analysis were mainly conducted on aged cells at the end-of-life (EoL) criteria, normally 80% state-of-health (SoH). However it is important to note that the non-linear capacity decay was often observed at an extended number of cycles, but the behaviors were seldom discussed. We believe that valuable information can be achieved at intermediate aging conditions. So, in our approach, the evolution of the aging phenomena is tracked by performing post-mortem analysis on not only the EoL cells but also the intermediate degraded cells with the same cycling conditions. The cycling aging was conducted on NCA/LTO (Li$_4$Ti$_5$O$_{12}$) commercial cells. LTO anode was deliberately selected since it is known as the "SEI (solid electrolyte interface)-free" and "degradation-resistant" anode material. Accordingly, it allows us to fully focus on the aging phenomena on the NCA cathode material. Using large-format commercial cells allows us to age the NCA electrodes in a condition similar to the practical utilization scenario. Furthermore, the cells were power-optimized with thin-coated electrodes design, so that the through-plane inhomogeneity is subtle and can be neglected. It guarantees consistent aging conditions from the surface down to the bulk of the investigated electrodes. Based on the proposed approach, we obtained consistent post-mortem results, which provide some new and critical insights into the mechanism of the cathode material degradation.
Experimental

Sample preparation

The power-optimized pouch cells with thin electrode coating design are commercially available. The batteries were composed of NCA cathodes and Li$_4$Ti$_5$O$_{12}$ (LTO) anodes. Table 1 presents the specification of the cells provided by the manufacturer. The Battery Tester (PEC-SBT 0550) was used to conduct the cycling aging at varied conditions specified in Table 2. The five cells were concisely addressed based on their aging conditions, and summarized in Table 2 as well. Particularly, electrode materials harvested from the non-cycled cell were addressed as BoL (begin-of-life), and had been already preconditioned by the manufacturer.

Table 1: General specifications of the commercial pouch cells

<table>
<thead>
<tr>
<th>Item</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal capacity</td>
<td>5 Ah</td>
</tr>
<tr>
<td>Nominal voltage</td>
<td>2.2 V</td>
</tr>
<tr>
<td>Standard charge method</td>
<td>Constant current: 5 A to 2.8 V</td>
</tr>
<tr>
<td>Standard discharge method</td>
<td>Constant current: 5 A to 1.5 V</td>
</tr>
<tr>
<td>Specific energy</td>
<td>42 Wh/kg</td>
</tr>
<tr>
<td>Energy density</td>
<td>90 Wh/L</td>
</tr>
<tr>
<td>Cell dimension (at SoC 50%)</td>
<td>276 mm × 173 mm × 4 mm</td>
</tr>
<tr>
<td>Weight</td>
<td>Approx. 262 g</td>
</tr>
</tbody>
</table>

Table 2: Aging conditions of the five pouch cells

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Temperature</th>
<th>C-rate Charge/Discharge</th>
<th>Cycles</th>
<th>ΔDoD (SoC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BoL</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C25-2000</td>
<td>25°C</td>
<td>1C/1C</td>
<td>2000</td>
<td>5%-95%</td>
</tr>
<tr>
<td>C45-1100-0.5C</td>
<td>45°C</td>
<td>0.5C/2C</td>
<td>1100</td>
<td>5%-95%</td>
</tr>
<tr>
<td>C45-1100</td>
<td>45°C</td>
<td>1C/1C</td>
<td>1100</td>
<td>5%-95%</td>
</tr>
<tr>
<td>C45-1900</td>
<td>45°C</td>
<td>1C/1C</td>
<td>1900</td>
<td>5%-95%</td>
</tr>
</tbody>
</table>

The pouch cells were disassembled using well established procedures: the cells were opened at discharged state inside the argon-filled glove box (Jacomex GP); the NCA electrode
sheets were collected and rinsed with dimethyl carbonate (DMC) to remove the electrolyte residual; one side of the electrode material coating was removed from a two-side coated sheet by cotton swabs soaked with N-methyl-2-pyrrolidone; 8 mm diameter round electrodes (i.e. 0.5 cm$^2$) were cut from the one-side coated electrode sheets. For C45-1100 and C45-1900 cells, two kinds of electrodes were cut out separately from dark and shiny regions. All the cut electrodes were rinsed again with DMC and dried under vacuum overnight.

**Electrode characterization**

The digital photos were taken by a normal reflex camera through the glove box window where the electrode sheets were stored. The contrast level of the photos was adjusted in GIMP software. The SEM images were obtained using a JSM-IT300 (JEOL) electron microscope at 15 kV accelerating voltage. SEM images at a ×500 magnification were used for the particle size distribution analysis. The images were processed and analyzed through ImageJ software (NIH) with Phansalkar local thresholding method.\(^{36}\)

The electrochemical experiments were performed with commercial test cells (EL-CELL, ECC-ref) with a compact sandwich cell design. The galvanostatic capacity tests were done in the three-electrodes cell configuration with 8 mm diameter NCA electrode as working electrode (WE), lithium metal as counter electrode (CE) and reference electrode (RE). A piece of 1.55 mm thickness glassy-fiber separator and 0.5 mL commercial LP30 electrolyte (1 M LiPF6 in ethylene carbonate and dimethyl carbonate with 1:1 ratio by volume, Ube industries) were used in each cell. The assembled cells were galvanostatically charged/discharged at room temperature with 0.2C (0.11 mA cm$^{-1}$) using a VMP3 potentiostat (Bio-Logic). Five cycles were performed for each cell, and in the last discharge cycle the cells (or NCA electrodes) were discharged to 50% state-of-charge (SoC) relative to the capacity value of the previous discharge pulse.

After the charge/discharge cycles, the cells were relaxed for two hours at open-circuit condition, after which the electrochemical impedance spectroscopy (EIS) tests were con-
ducted. More specifically, EIS measurements were performed in an in-house developed EIS setup, odd random phase EIS (ORP-EIS).\textsuperscript{37} The setup consists of a Wenking Potentiostat POS 2 (Bank Elektronik), a PCI-4461 DAQ-card (National Instruments), a MATLAB-based software with a fitting toolbox. A frequency range of 5 mHz - 10 kHz and amplitude of 5 mV RMS were chosen for the experimental conditions. The equivalent electrical circuit (EEC) modeling was done by the fitting toolbox that uses a Gauss-Newton algorithm followed by a Levenberg Marquardt minimization scheme.\textsuperscript{38}

KPFM experiments were performed using a commercially available Atomic Force Microscope (XE7, Park Systems), which was installed inside the glove box and connected with a lock-in amplifier (SR-830, Stanford Research Systems). The KPFM was operated in non-contact mode with frequency modulation. An AC voltage, 17kHz and 2 V amplitude, was extracted from the lock-in amplifier and fed to the KPFM controller. A DC voltage, used to compensate electrical static forces induced from the contact potential difference, was applied on the tip. A topography image and a potential image were obtained simultaneously owing to the single-pass scanning approach. Conductive Cr/Au-coated Si tips (NSC36-Cr/Au, MikroMasch) were used in the tests.

X-ray photoelectron spectroscopy (XPS) images were recorded using a PHI5600 photo electron spectrometer (Physical Electronics) with an Al K\textsubscript{α} monochromatic X-ray source (1486.71 eV photon energy). Ar\textsuperscript{+} sputtering with 3 keV energy ions and with duration of 24s (0.4 minutes) of sputtering time for each sputtering step. The harvested electrode were rinsed twice with DMC solvent inside glove box and dried under vacuum overnight before the XPS characterization. The electrode samples were introduced into the XPS with a short exposure (< 1 min) towards the ambient environment.
Results and discussion

Post-mortem analysis

Figure 1(a) shows four complete NCA electrode sheets harvested from four cycling aged pouch cells. The electrode sheets cycled at 1C rate and 45 °C (C45-1100 and C45-1900) display some shiny areas with distinctive optical reflectance compared to the rest of the sheets. The number of cycles has an impact on the appearance of the sheets: C45-1900 exhibits less shiny areas than C45-1100. On the other hand, the sheets cycled at 25 °C with 1C rate (C25-2000) and 45 °C with 0.5C (C45-1100-0.5C) exhibit no observable macroscopic inhomogeneity. It is important to mention that the results are consistent with all the electrode sheets harvested from the same pouch cell. Additionally, as shown in Figure 1(b), three sheets harvested from the same C45-1100 cell show randomly distributed shiny patterns. This means that the origin of the shiny and dark regions are neither associated to external mechanical influences nor to the macroscopic uneven current distribution from the current collector tab towards the unconnected end. Otherwise, the sheets should present a consistent pattern similar to the results reported previously by other researchers.

The electrodes harvested from different cells and regions (dark or shiny) were examined by SEM (Figure 2). Figure 2(a) shows the cross section of a BoL electrode with a coating of active material of less than 20 μm. Such a thin-coating design is the key to conduct a consistent aging study of electrode materials without deriving spurious correlations from inhomogeneous reactions through-plane. Figure 2(b) shows the morphology of a fresh NCA electrode. Spherical-like NCA secondary particles are composed of smaller size primary particles. Figure 2(c) and Figure 2(d) generally exhibit similar morphologies as the fresh electrode even though they have been aged for more than 1000 cycles. Nevertheless, it is barely noticeable that the inter-particle distance between primary particles is slightly enlarged. Figure 2(e) and (f) display the morphologies of the shiny area and the dark area of C45-1100 electrode, respectively. Micro-cracks are clearly formed and present on secondary
Figure 1: Photographs of harvested NCA electrode sheets. (a) electrode sheets from four different aged cells; (b) electrode sheets from C45-1100. The physical size of the sheets is 19 cm × 15 cm.

particles shown in Figure 2(f). On the contrary, in the shiny area the secondary particles are densely packed as demonstrated in Figure 2(e). Similar observations are also obtained on the C45-1900 shown in Figure 2(g) and (h): the dark area presents secondary particles with micro-cracks while the shiny areas exhibit densely packed secondary particles. Accordingly, the "shiny" and "dark" visual effects are possibly associated with the morphological conditions: the micro-cracks increase the roughness of the particle surface and reduce the light reflectance of electrodes in the macroscopic scale.
Figure 2: SEM images of the harvested NCA electrodes. (a) BoL (cross section); (b) BoL; (c) C25-2000; (d) C45-1100-0.5C; (e) C45-1100-shiny; (f) C45-1100-dark; (g) C45-1900-shiny; (h) C45-1900-dark. (i) box plot of the particle size distribution of the seven harvested NCA electrodes.

A statistical particle size distribution analysis is conducted and shown in Figure 2(i). The bottom and top of the box represent the first and third quantiles. The band (or the notch) inside the box is the median. The bars indicate the highest and lowest datum within 1.5 interquartile range, and the dots are the outliers. The particles with less than 1 μm radius are most likely the fragments of primary particles, and therefore are excluded from the analysis. It is clear that the tendency of the mean values and the width of the distributions is in good agreement with the local morphological conditions of the secondary particles:
the formation of the micro-cracks enlarges the size of secondary particles. \textit{C45-1100-dark} and \textit{C45-1900-dark} present larger secondary particles than the other electrodes. \textit{C45-1100-shiny} and \textit{C45-1900-shiny} exhibit very similar distributions as that of BoL. The particle size distributions of \textit{C25-2000} and \textit{C45-1100-0.5C} are in between the fresh electrode (BoL) and the electrodes obtained from the dark areas (\textit{C45-1100-dark} and \textit{C45-1900-dark}).

The formation of micro-cracks, which leads to deteriorations of the battery performance, has been previously reported in several studies.\textsuperscript{12-14,40} It is mainly attributed to the volume expansion and contraction of NCA particles during lithium ions intercalation and deintercalation.\textsuperscript{8} A high cycling temperature favors the micro-cracks formation,\textsuperscript{14} which agrees with the observations in this post-mortem analysis. Apart from that, there are much less micro-cracks observed on \textit{C45-1100-0.5C}, indicating that applying a lower charging current might effectively suppress the micro-cracks formation.

The electrodes harvested from the shiny and dark regions of \textit{C45-1100} were characterized by AFM-based KPFM. Figure 3 shows the topographies and the surface potential maps of a shiny region (Figure 3(a) and (b)) and a dark region (Figure 3(c) and (d)) that were harvested directly from the same electrode sheet without further cycling. The potential maps correspond well to their topographies. Particles in the shiny region present higher surface potential than the particles in the dark region. Notably, the adjacent spaces between secondary particles display significantly higher potentials than that of the secondary particles. It is attributed to the artifacts induced by the drastic changes of the topography, where the Z-direction scanner is out of the range and cannot obtain correct the feedback response.\textsuperscript{41} According to our previous work,\textsuperscript{23} where we revealed a direct correlation between the measured surface potential and the SoC on the same batch of NCA electrodes, the particles from the shiny region are thus at a higher SoC level than the particles from the dark region. It is important to mention that the cathode-electrolyte interface (CEI) layer and other kinds of passivation layer can potentially affect the surface potential by, in general, increasing the surface potential.\textsuperscript{23} Nevertheless, the dark region with cracked secondary NCA particles,
which might have more significant passivation effect (i.e., a higher surface potential),\textsuperscript{14,42} still present distinctively lower potential values than that of densely packed particles from the shiny region. Therefore, the co-existence of the shiny and dark areas surely indicates an unevenly distributed SoC on the same electrode sheet despite that the sheet was already discharged to the cut-off voltage. In addition, the SoC inhomogeneities are present in a microscopical scale between secondary particles, or even between primary particles as indicated in Figure 3(b) or Figure 3(d). This has been discussed in-depth in our previous work.\textsuperscript{23}

Figure 3: KPFM measurements of NCA electrodes harvested from C45-1100. (a) topography of the shiny region; (b) surface potential map of the shiny region; (c) topography of the dark region; (d) surface potential map of the dark region.
Figure 4: XPS spectra of the NCA electrodes harvested from C45-1100. (a)-(f) shiny region: (a) C 1s XPS spectra according to sputtering time; (b) F 1s XPS spectra according to sputtering time; (c) O 1s XPS spectra according to sputtering time; (d)-(f) O 1s XPS spectra after 0 min, 0.4 min and 4 min sputtering time. (g)-(l) dark region: (g) C 1s XPS spectra according to sputtering time; (h) F 1s XPS spectra according to sputtering time; (i) O 1s XPS spectra according to sputtering time; (j)-(l) O 1s XPS spectra after 0 min, 0.4 min and 4 min sputtering time.
The surface chemistry of the cathode-electrolyte interface is characterized by XPS. Figure 4 displays the C 1s, F 1s and O 1s spectra of NCA electrodes harvested from a shiny region (Figure 4(a)-(f)) and a dark region (Figure 4(g)-(l)) of a C45-1100 electrode sheet. Minor differences are observed from the spectra between the two regions. Major peak components are labeled in C 1s and F 1s spectrum which are consistent with literature. The O 1s spectrum is the most informative part, and therefore is in-depth analyzed. The peak can be deconvoluted to three major components, i.e., ROCO$_2$Li, Li$_2$CO$_3$ and oxygen in the lattice structure of NCA. ROCO$_2$Li and Li$_2$CO$_3$ are the compositions of cathode-electrolyte interface film formed by electrolyte decomposition.

Figure 4(d)-(f) show the O 1s spectrum of the shiny region after 0 min, 0.4 min, and 4 min Ar$^+$ sputtering, respectively. Figure 4(j)-(l) show the O 1s spectrum of the dark region after 0 min, 0.4 min, and 4 min Ar$^+$ sputtering, respectively. Before sputtering, the O 1s spectrum is dominated by ROCO$_2$Li and Li$_2$CO$_3$. ROCO$_2$Li in Figure 4(d) shows lower intensity than that of Figure 4(f), indicating that more ROCO$_2$Li component presents on the dark region. After the first sputtering cycle (0.4 min), ROCO$_2$Li peak is significantly reduced for both regions. In Figure 4(f) and Figure 4(l), the lattice oxygen peak dominates the O 1s spectrum after 4 min sputtering. Li$_2$CO$_3$ peak in Figure 4(l) demonstrates a slightly higher intensity than that of Figure 4(f). It could be attributed to the cathode-electrolyte interface layer formed on the interior of the particles in the dark region due to the micro-cracks formation on the secondary NCA particles. The overall sputtering profile of O 1s is demonstrated in Figure 5. The shiny and dark regions show an almost identical profile, indicating a very similar thickness of CEI layer. Moreover, this conclusion further validates the assumption that the CEI layer has minor effects on the KPFM results.
Figure 5: Ratios of peak intensity of RO\textsubscript{CO}2Li or Li\textsubscript{2}CO\textsubscript{3} to NCA (lattice oxygen) in O\textsubscript{1}s core level spectra as a function of Ar\textsuperscript{+} sputtering time.

The harvested NCA electrodes were further characterized electrochemically. The charge/discharge curves (0.2C) of the NCA/Li half cell are displayed in Figure 6(a). NCA electrodes harvested from different aged cells or different areas display distinctive capacity values. The cell polarization, which is substantially affected by the cell impedance, increases with the decrease of the capacity values during both charge and discharge.

Figure 6(b) shows the electrode capacities relative to the value of BoL electrode. C25-2000 maintains 96.9% capacity retention even after 2000 cycles. At the elevated cycling temperature, C45-1100-0.5C shows 70.5% capacity retention after 1100 cycles. It is worth to mention that C45-1100-0.5C was charged with 0.5C and discharged with 2C rate. 2C discharge rate was not an extreme condition for the power-optimized NCA electrode material. It might contribute to the electrode degradation but in a minor way. In Figure 1, different regions of C45-1100 and C45-1900 are shown. Therefore, the NCA electrodes were harvested separately from the shiny areas and the dark areas and characterized individually. As shown in Figure 6, the shiny areas present full capacity retention, on the contrary, the dark areas show much lower capacity retention. The significant difference indicates that the dark and shiny area aged differently, although they were harvested from the same electrode sheet. The capacity results are in good agreement with the SEM images: the electrodes
obtained from the dark areas present cracked NCA particles indicating a severe degradation;\textsuperscript{14,46} in contrast, the shiny areas, showing full capacity retention, display a BoL-like surface morphology without micro-cracks. Additionally, the capacities of \textit{C45-1100-shiny} and \textit{C45-1900-shiny} are slightly higher than \textit{BoL}, which can be attributed to newly-formed active surfaces resulting from the volume expansion or contraction of secondary particles during charge or discharge.\textsuperscript{12,13}

EIS characterization was conducted on the same cells after the capacity tests. Figure 6(c) shows the Nyquist plot of the EIS data consisting of two semicircles and a diffusion tail. An electrical equivalent circuit (EEC) model,\textsuperscript{38} displayed in Figure 6(c), is applied to model the EIS data for quantitative interpretation. \( R_s \) is the ohmic resistance. The parallel connected \( R_p \) and the constant phase element (CPE1) represent, respectively, the resistance and capacitance of the CEI layer. They correspond to the small arc as shown in the Nyquist plots. The parallel \( R_{ct} \) and CPE2 are related to the charge-transfer process, which is seen as the dominating arc in the Nyquist plots. The generalized finite-space Warburg (GFW) describes the diffusion behavior. More related impedance discussions can be found in our previous work,\textsuperscript{38} studying the same batch of NCA electrodes. Here, we only focus on the charge transfer resistance \( R_{ct} \), which is essentially associated with the kinetic and the polarization behavior shown in Figure 6(a). According to the correlation,\textsuperscript{47}

\[
R_{ct} = \frac{RT}{nFA_0i_0} \quad (1)
\]

where \( R \) is the gas constant, \( T \) is the absolute temperature in Kelvin, \( n \) is the number of electrons, \( F \) is the Faraday constant, \( A_0 \) is the active surface area and \( i_0 \) is the exchange current density.

Figure 6(d) shows the best-fit \( R_{ct} \) values and their standard deviation of the harvested NCA electrodes as calculated using the EEC shown in Figure 6(c). \textit{BoL} presents the lowest \( R_{ct} \) value. For the aged electrodes, there is a general trend that \( R_{ct} \) increases as the mea-
sured electrode capacity (Figure 6(b)) decreases. This is due to the fact that the electrode capacity is proportional to the active surface area $A_0$, while $R_{ct}$ is inversely proportional to $A_0$ (Equation 1). The drop of the capacity and the active surface area can be partially correlated to the morphological changes, where some primary NCA particles lose electrical contact with the electrode matrix due to the formation of micro-cracks on the secondary particles, shown in Figure 2.\textsuperscript{16,46}

Furthermore, $C45-1100$-$dark$ and $C45-1900$-$dark$ show an approximately ten times higher $R_{ct}$ than $C45-1100$-$shiny$ and $C45-1900$-$shiny$, while their capacity difference is only a factor of two. In this case, the exchange current density $i_0$, which corresponds to the interface kinetics, must have a dominant effect on $R_{ct}$. The decrease of the interfacial kinetics (i.e., $i_0$), resulting in $R_{ct}$ raising, can be attributed to the formation of NiO-like (rock-salt) surface structures on NCA particles.\textsuperscript{2,42} Besides, more cathode-electrolyte interface layer is generated on $C45-1100$-$dark$ and $C45-1900$-$dark$ due to the micro-cracks formation as shown in Figure 2(f) and (h). The newly-formed interfaces thus lead to the growth of the NiO-like structure on the NCA primary particles, which contributes to the significant rise of $R_{ct}$.\textsuperscript{14} This argumentation is also supported by comparing $R_{ct}$ of $C45-1100$-$dark$ and $C45-11000.5C$. There is nearly a three times difference in $R_{ct}$, but their capacity retention is very close, i.e., 67.4\% and 70.5\%, respectively. Additionally, as shown in Figure 2, the formation of micro-cracks on $C45-1100$-$dark$ is much more severe than that of $C45-11000.5C$.

It is worth noting that $C45-1900$-$dark$ shows slightly lower $R_{ct}$ but much lower capacity than $C45-1100$-$dark$. According to the equation Equation 1, $C45-1100$-$dark$ electrode has much lower kinetics ($i_0$) than $C45-1900$-$dark$, though $C45-1100$-$dark$ experienced less cycles. This discrepancy could be attributed to the non-uniform degradation within the dark region. For the further investigation, four electrodes harvested from four regions of $C45-1100$ are characterized and shown in Figure S1. Position1 and position2 cut from the shiny region, show similar capacity and impedance results. Position3 and position4 cut from the dark region display a small difference on their capacity values but a significant difference on
This complementary data suggests non-uniform degradation within the dark area. Additionally, the results of position 1 and position 4 in Figure S1 are the same set of data of C45-1100-shiny and C45-1100-dark, respectively.

Figure 6: Electrochemical characterizations of the harvested NCA electrodes from different aged cells and dark or shiny regions. (a) charge and discharge curve (0.2C and room temperature); (b) capacity retention; (c) Nyquist plot of EIS results and the proposed electrical equivalent circuit; (d) the fitted charge transfer resistance $R_{ct}$ (error bars indicate the fitting errors).

In addition to the post-mortem analysis of the NCA cathode, the LTO anode from the same cells is also harvested and analyzed. These results are shown in the supporting material. Similar pattern is observed on the harvested LTO electrode sheets. The positions of the pattern are aligned with that of the NCA electrode sheet, obtained from the same cell compartment as shown in Figure S2. Here "shiny" and "dark" are also used to address
different regions on the LTO sheet, which corresponds to the "shiny" and "dark" regions of the NCA sheet in the same cell compartment. SEM and XPS were applied to characterize the surface of the LTO electrodes. In figure S3, the SEM morphologies are identical between shiny and dark regions. As shown in the XPS survey spectra (figure S4), no significant differences are noticed between different regions. Moreover, color differences can be visually observed within a shiny region on LTO sheets. LTO materials are selected and cut from the different positions of a electrode sheet shown in Figure S5, and electrochemically characterized. In Figure S6, no significant difference on the capacity value is observed among these areas. Besides, it is important to clarify that the non-uniform aging is not initiated by LTO anode since the non-uniform aging behavior is only seen at elevating temperature. If LTO causes the inhomogeneity, increasing cycling temperature would rather inhibit inhomogeneous reactions due to the enhanced kinetics and mass transport. Nevertheless, the origin of the visual pattern observed within a shiny region remains unclear. A further investigation is out of the scope of this work, but will be carried out in the future.

Moreover, the slippage of the SoC window between two electrodes as a result of side reactions (i.e., passive-film formation) is one of the major cause of reversible capacity loss. It is even more severe in LiFePO₄/graphite system due to the flat potential curve of LiFePO₄ cathode material. The slippage of SoC window could lead to unfavorable lithiation states for both cathode and anode material, which increases the risk of thermal run-away. Since LTO anode material also presents a flat potential curve, the slippage issue for NCA/LTO system is in-depth discussed in the supporting materials (Figure S7), where we conclude that the slippage of the SoC window in NCA/LTO system is unrelated to the degradation of the NCA cathode material.

The results of the post-mortem analysis show consistent aging behavior. The uneven degraded regions are observed on the cells aged at 45 °C. For any other electrode sheets harvested from C45-1100 or C45-1900, the electrode materials of the dark regions are much more degraded than the shiny regions, showing micro-cracked NCA particles, low capacity
retention and greatly increased charge transfer resistance. This typical aging behavior can be ascribed to the elevated cycling temperature. More interestingly, by comparing the electrode sheets harvested from C45-1100 and C45-1900, it was found that the dark regions propagate as the cycle number increases, and a reduced amount of shiny areas is seen in C45-1900 compared with C45-1100. The uneven degradation behavior and the material deterioration can be suppressed when the cell is charged at a lower C-rate. When the cycling temperature is kept at 25 °C, the NCA electrode material shows an excellent cycling stability without any sign of uneven aging.

The presence of regions with different SoCs in the same electrode sheet, revealed from the KPFM measurements (Figure 3), are caused by the deviation of the capacities between dark and shiny regions. As indicated in Figure 6, C45-1100-dark only retains about 66% capacity compared to C45-1100-shiny. As a consequence, during the discharge pulse, C45-1100-dark reaches 0% SoC earlier than C45-1100-shiny. The cell reaches the cut-off potential before discharging C45-1100-shiny completely due to the fact that the cut-off potential depends on an average value of the whole electrode material rather than the local electrochemical potential. In the charge pulse, the electrode material of C45-1100-shiny with higher capacity is only partially charged. Restricting the ΔDoD can significantly improve the cycling performance. On the contrary, the electrode material from C45-1100-dark with a lower capacity goes through overcharge, which is detrimental for the material degradation.

Degradation of the NCA electrode induced from surface inhomogeneity

According to the post-mortem analysis results, a schematic model, illustrated in Figure 7, is proposed to understand the origin of the uneven degradation. On the microscopic scale, the composite electrode exhibits the intrinsic heterogeneous surface reactivities due to variations in local structure and composition. More specifically, three factors could be taken into account: 1) variations of the local electron conductivity due to the distribution of conductive
agent; 2) variations of the local ionic conductivity because of the local microstructure determined by agglomerate structures of secondary NCA particles and binder materials; 3) the intrinsic kinetic heterogeneity of primary NCA particles due to the anisotropic structure.\textsuperscript{52} Surface active sites with higher reactivity can reach higher delithiation level (i.e., SoC) than the other parts of the electrode in the charging pulse. During the open-circuit condition, thermodynamically speaking, overcharged particles could be re-lithiated (discharged) by the normal charged particles with lower Fermi level. However, kinetics plays a decisive role here. On the basis of the observations in our previous work,\textsuperscript{23} SoC inhomogeneity persisted after a reasonable relaxation period (i.e., 3 hours). In the discharging pulse, the active sites cannot be fully discharged or lithiated while the macroscopic potential reaches the cut-off limit. The active sites are further delithiated in the following charging pulse. The offset of the local delithiation level accumulates as the cycling continues. At a certain cycle (i.e., the critical cycle), the active sites reach an over-delithiated state during the charge pulse. The local microstructure of the electrode material goes through irreversible overcharge reactions, resulting in capacity loss, micro-crack generation, and NiO-like surface layer formation.\textsuperscript{7,8} In the following cycles, because of the capacity loss at the active sites, the local cycling C-rate on the active sites and the neighboring particles increases, as compared to the average current density. The degradation of the neighboring particles is advanced and the degraded region gradually propagates. Meanwhile, the active sites go through an even deeper overcharge reaction. The SoC (or capacity) offset between the aged region and the non-aged region decelerates the degradation of the non-aged region because the local ΔDoD is restricted. In addition, the aging model could be correlated to the non-linear capacity decay of electrodes or full cells (shown in Figure S8), which has been extensively observed in literature as well.\textsuperscript{30-34} Before the critical cycle, when the active sites still maintain their full capacity, the overall capacity decay is negligible. However, after the critical cycle, the active sites start losing their capacity and the aging regions propagate during further cycling aging. Accordingly, the overall capacity starts decreasing, and the decay is intensified with the increase of cycle
numbers, owing to the propagating phenomena, which display an exponential behavior. In addition, lowering the charging current can facilitate homogeneous current distribution, that can further restrain the uneven degradation of electrodes. This is in agreement with the experimental results obtained in $C_{45\cdot1100\cdot0.5C}$.

![Diagram](image)

Figure 7: Schematic illustration of the formation and propagation of unevenly degraded regions on thin-coated NCA electrode during charging pulse.

The proposed aging model is further justified in another work from our group, in which using redox shuttle electrolyte additives (RSAs) is proved to be an effective approach of improving the cycling stability of Ni-rich layered cathode materials. The redox molecules in the electrolyte can functionally balance the inhomogeneously distributed SoC by shuttling excess charges between overcharged particles and normal charged particles. The unfavorable local overcharging reactions are thus inhibited, and the cycling performance is improved about 30% with the same batch of NCA electrodes. The remarkable effectiveness of the RSA approach emphasizes the crucial role that the surface inhomogeneity plays in the cycling
The visual observation of uneven aged electrodes was rarely reported. Previously, Klett et al.\textsuperscript{30} reported a post-mortem study on the non-uniform aged graphite electrodes harvested from graphite/LiFePO$_4$ cylindrical cells. Their harvested electrodes presented a consistent uneven aging pattern owing to the cylindrical cell design. It is important to point out that their cylindrical cells were also power-optimized, and then presumably consisted of thin-coated electrodes.\textsuperscript{55} We argue that the thin-coated electrodes are the criteria of the direct observation of the uneven aging phenomena from post-mortem analysis. On a thick-coated electrode, the degraded region propagates three-dimensionally, which is less observable than on a thin-coated electrode with only two-dimensional propagation. Another possible reason can be related to the non-uniform aging from the surface to the bulk material (through-plane).\textsuperscript{24,26,28} The electrode surface can be aged in a more extreme conditions than the expected scenario, in which the surface uneven aging is not observable.

Last question that needs to be addressed is how the elevated temperature facilitates the uneven aging phenomena, only found in the cells cycled at 45 \textdegree C. It has been extensively reported\textsuperscript{5,6,14} that cycling temperature is a key operating parameter associated with the degradation of NCA electrodes. Yet the mechanism behind is still unclear.

KPFM was proved to be able to quantitatively correlate the measured surface potential with the SoC (or lithiation level) of the cathode material on the basis of its Fermi energy.\textsuperscript{23} For the further investigation, KPFM characterizations were conducted on two BoL NCA electrodes that were charged to 4.3 V vs. Li/Li$^+$ at different temperature (i.e., 25\textdegree C and 60\textdegree C). The potential maps correspond well to their topographies shown in Figure 8(a) and (c). The SoC inhomogeneity of the NCA secondary particles is also observed on the potential maps. It is important to point out that the particles shown in Figure 8(d) present higher surface potential compared to that of the particles in Figure 8(b). Despite the identical cut-off charging potential, the different cycling temperature can lead to a significant deviation of the surface potential measured by KPFM: which can be linearly correlated to
the SoC or delithiation state. In addition, the charging curve of these two BoL electrodes are demonstrated in Figure 8(e). The NCA electrode charged at room temperature clearly shows a higher polarization than the electrode charged at 60 °C.

This temperature impact can be correlated with the kinetics of the electrode during the temperature variation: according to the Arrhenius equation, the rate constant of a chemical reaction, i.e., \( k \), increases rapidly with elevating the temperature. The increased \( k \) further results in a lower \( R_{ct} \) (Equation 1) and a lower polarization in Figure 8(e). Due to the lower polarization at 60°C, the NCA electrode reaches a higher delithiation level than the NCA electrode charged at room temperature while a same cut-off potential value is used. Apart from the kinetics, thermodynamics could also play a role. Electrode potential (or cell voltage) is temperature dependent according to the Nernst equation; the potential decreases when the temperature rises. Therefore, with a higher cycling temperature the electrode is beyond its original delithiation level while keeping the same cut-off charging potential.

By combining this with the proposed aging model (Figure 7), elevating the cycling temperature and keeping the cut-off potential facilitate the active sites reaching the over-delithiation state with less cycles, and further advances the uneven aging behavior. Watanabe et al. reported that restricting the operating ΔDoD from 0% - 100% to 10% - 70% could significantly improve the cycling stability of the NCA cell at 60 °C. Their findings align with our discussion since application of a lower cut-off potential to restrict the ΔDoD can result in the suppression of the local overcharge reaction. Accordingly, we strongly recommend to integrate the operating protocol that automatically lowers the cut-off charging potential when the cycling temperature rises.
Figure 8: KPFM measurements of BoL NCA electrodes: (a) topography and (b) surface potential of a NCA electrode charged to 4.3 V vs. Li/Li$^+$ at room temperature; (c) topography and (d) surface potential of a NCA electrode charged to 4.3 V vs. Li/Li$^+$ at 60°C. (e) charging curves (1C) of the two NCA electrodes used for KPFM measurements.
Conclusions

Through this systematic post-mortem analysis on a batch of power-optimized commercial NCA electrodes with different aging conditions, we have gained new insights into the aging mechanism associated with surface inhomogeneity of NCA electrodes.

Uneven degradation phenomena are directly observed on the NCA electrodes aged at an elevated temperature. The post-mortem analysis revealed that the non-aged regions are randomly distributed over the harvested electrode sheets. The NCA material in the deteriorated region displayed micro-cracked NCA particles, low capacity and greatly increased charge transfer resistance. Lowering the charging rate can effectively suppress the uneven aging behavior. We also noticed that the degraded regions propagate along with the incremental of cycle number.

Accordingly, an aging model is proposed to describe the formation of the uneven degraded areas on the same electrode. The root cause is ascribed to the intrinsic surface heterogeneity of NCA electrodes. In addition, the post-mortem results clearly demonstrate that cycling temperature plays a crucial role on the cycling performance of NCA-based LIBs. The mechanism is further interpreted as the facilitation of local overcharge reactions due to the elevated temperature.

This work stressing the crucial role that electrode heterogeneity plays on the degradation of NCA electrodes. More research effort should be devoted to improve the surface homogeneity, such as surface modification methods or developing better synthesis routes. Besides, the successful observation of the uneven degradation and the consistent aging behavior was possible thanks to the thin-coated electrode design, which minimizes the porous inhomogeneity (through-plane). Hence, we strongly suggest to take this factor into account in future aging studies of electrode materials.
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Supporting Information Available

The supporting information concerning the complementary post-mortem analysis of C45-1100 and LTO anode material is available free of charge.

This material is available free of charge via the Internet at http://pubs.acs.org/.

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Table of Contents Graphic

>1000 cycles
High T
High C-rate

Post mortem analysis

Further cycling ageing

Normal charged particle
Over charged particle

random active site