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Dependence of Cell Failure on Cut-Off Voltage Ranges and Observation of Kinetic Hindrance in LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$

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The dependence of differential capacity versus voltage (dQ/dV) of Li/NCA half cells on temperature and testing current (C-rate) was studied. Kinetic hindrance of lithium diffusion at both low (∼3.5 V vs Li/Li$^+$) and high states of charge (∼4.17 V) was observed. In-situ X-ray diffraction measured the volume changes of the NCA lattice versus state of charge. NCA/graphite pouch cells were cycled in various voltage ranges to explore the impacts of depth of discharge (DOD) ranges and the kinetic hindrance regions in NCA on cell failure. dV/dQ analysis, full cell impedance and symmetric cell impedance analysis as well as half-cell studies of recovered electrodes were performed after 0, ∼400 and 800 charge-discharge cycles. The contributions of active mass loss and shift loss (from loss of Li inventory) to the capacity fade of NCA/graphite cells under various testing conditions were determined. The increase in positive electrode charge transfer impedance with cycle number was proportional to the increase of positive electrode active mass loss. There was no strong correlation between positive electrode active mass loss and voltage range change. NCA active mass loss during cycling can be minimized when the dQ/dV peaks at ∼3.5 and 4.17 V (vs. Li/Li$^+$), that show kinetic hindrance, are partially or completely avoided.

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LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA), as a derivative of LiNiO$_2$, has been considered as one of the most promising cathode materials for lithium-ion batteries to be used for portable electronics and electric vehicles due to its high specific capacity. The partial substitution of Ni by Co and Al were reported to improve both thermal stability and structural stability. LiNiO$_2$ has been shown to have a phase transition from H1 to H2 to H3 phases during intercalation and deintercalation of Li$^+$, while these phase transitions were not observed in NCA. However, lithium ion cells with NCA as the positive electrode material were reported to show capacity fade during storage and cycling. Capacity loss in lithium ion cells can be caused by the loss of lithium inventory to the negative electrode solid electrolyte interphase (SEI). Capacity loss can also be caused by active material loss due to electrical disconnection at the particle/electrode level as well as structural degradation at the crystallite level in the active materials. Additionally, internal impedance or polarization increase is another major contributor to capacity loss under high rate testing conditions. At high potentials and/or elevated temperatures, accelerated unwanted reactions with the electrolyte such as electrolyte oxidation can ultimately lead to cell failure.

One cause of deterioration of NCA during charge-discharge cycling has been attributed to the generation of micro-cracks in secondary particles. Generation of micro-cracks can lead to poor electric and ionic contact between primary particles which leads to loss of active material and contributes to capacity loss. The failure mechanisms of NCA materials have been studied previously in the literature, however, a fundamental understanding of the cause of particle cracking in NCA has not reached a clear conclusion. S. Watanabe et al. showed that the deterioration of NCA is highly dependent on the depth of discharge (DOD) range. The presence of an upper or lower cutoff voltage is not significant. S. Watanabe et al. showed that severe capacity loss and large impedance increase in NCA/graphite cells, associated micro-cracks generation in NCA particles, were observed after cycling between 0–100% DOD region (4.2–2.5 V) at 1 C for 1500 cycles at 25°C. Conversely, no significant differences in fade, impedance rise and micro-crack generation in NCA particles were observed from cells cycled in ranges of 0–60% DOD (4.2–3.54 V), 10–70% DOD (4.05–3.48 V) and 40–100% DOD (3.78–2.5 V). It was thought that the volume changes in NCA are responsible for the generation of micro-cracks.

Using X-ray photoelectron spectroscopy (XPS), S. Watanabe et al. showed that the observed amount of ROCO$_2$Li or Li$_2$CO$_3$ on the cycled NCA surface did not differ significantly for electrodes tested under different DOD conditions. It was concluded that the SEI film with about several nanometers in thickness did not influence any electrochemical performance. In addition to micro-crack generation, it was reported that a rocksalt type (NiO-like) surface layer can be formed in delithiated NCA and delithiated Ni-rich NMC materials when stored in air or in contact with electrolyte. It was thought that new surface layers (NiO-like) would be formed at the surfaces of micro-cracks within secondary particles, which can lead to impedance increase during cycling. However, the generation of micro-cracks within secondary particles can also lead to increased surface area for unwanted reactions with electrolyte. New positive electrode/electrolyte interphases can be formed on the surface of micro-cracks within the secondary particles that may not be observable by XPS, which could also lead to impedance growth during cycling.

It may also be the case that micro-cracks that are not accessible to electrolyte form entirely within particles. This possibility has been proven by McGrogan et al. in studies on LiMn$_2$O$_4$. Scheme 1, adapted from Figure 1 in Ref. 26, shows different scenarios for micro-crack formation to address the impact of micro-cracks on impedance growth. Scheme 1 shows electrode fragmentation with maintained electrical connection (a) and with electrical isolation (b). Scheme 1 shows micro-cracks at the surface with (c) and without (d) electrolyte access as well as micro-cracks within the bulk with that yield electrically and ionically isolated particles (e) and that yield electrical and ionic path disruption (f). Scenarios (a) and (c) will lead to an increased surface area in contact with electrolyte and shorter Li-ion diffusion paths, but they also would cause much unwanted reactions with the electrolyte. Due to the increased surface area in contact with electrolyte, scenarios (a) and (c) will lower the charge transfer resistance assuming the positive electrolyte interface has the same thickness and properties as the original surface. Scenarios (d), (e) and (f) can significantly reduce the contact surface area between...
neighboring primary particles and disrupt electronic and ionic transport, which leads to an increase in impedance. McGrogan et al. showed that the effects of these internal cracks can appear around the mid to low frequency range and increase the diameter of the “semicircle” in the Nyquist diagram as measured using impedance spectroscopy.

A few questions can be asked after reviewing these results. First, is it true that the deterioration of NCA is “closely related to: not the upper and lower limits of DOD or operation voltage but the width of DOD”?

Second: is the generation of micro-cracks solely related to the volume changes of NCA? Third: are there other mechanisms that are responsible for the capacity fade and micro-crack generation? Fourth: is it true that the deterioration of NCA is “closely related to: not the upper and lower limits of DOD or operation voltage but the width of DOD”?

The observation of micro-cracks through cross-sectional scanning electron microscope (SEM) images can be expensive and requires careful sample preparation. Therefore it is often difficult to obtain statistically meaningful results without analyzing a huge number of samples. Differential voltage analysis (dV/dQ vs. Q analysis) was used here to analyze the contribution of active material mass loss, which directly relates to the generation of micro-cracks, and shift loss, which reflects loss of lithium inventory, to the failure of NCA/graphite cells.

Differential voltage analysis is non-destructive and easy to perform. To demonstrate the impacts of positive electrode active mass loss and shift loss on Li-ion cell capacity, Figure 1 shows a typical capacity balance between the positive and negative electrodes in a full cell construction. Figure 1 shows the voltage-capacity (V-Q) curves of the positive electrode, negative electrode vs (Li/Li+), and full cell voltage in blue, red and black, respectively. Solid lines show the situation in a full cell before long-term cycling while the dashed lines show a possible situation after long term cycling. The zero point on the capacity axis is defined at the point where the full cell voltage reached the lower cutoff voltage. Arrows n and p show the shifts of the negative and positive electrode voltage-capacity curves relative to the zero point before long-term cycling, while arrows n and p show the corresponding shifts after the long term cycling. Arrows a, b and c show the difference between n and p, the difference between n and p, and the difference between p and p, respectively. During cycling, the positive curve usually shifts more than the negative curve toward the negative direction. As a result of these shifts, the full cell would reach the lower cutoff voltage earlier than it did before cycling. This leads to a capacity loss due to the change in relative position between the positive and negative curves, which is a-b. Additionally, loss of positive electrode active mass causes the positive curve to “shrink” and also causes capacity loss of the full cell. Arrow d shows the change in the charge end point capacity of the positive electrode before and after cycling. The capacity loss due to active mass loss of the positive active material is then d-c. It is extremely important to realize that only the shift loss, a-b and the positive active material loss d-c can be directly measured, not the individual quantities a, b, c and d.

In this work, the differential capacity versus voltage (dQ/dV vs. V) of Li/NCA half cells as a function of temperature and testing current (C-rate) was studied. A kinetic hindrance of lithium diffusion at both low and high state of charge of NCA was observed. In-situ X-ray diffraction (XRD) measurements were applied to measure the volume changes of NCA as a function of lithium content and voltage. Additionally, NCA/graphite pouch cells containing 2% VC in 1.2 M LiPF6 in EC:EMC 30:70 electrolyte were charged and discharged in various voltage ranges at 40°C to explore the impacts of DOD ranges and the kinetic hindrance regions on the failure of NCA/graphite cells. The tested voltage ranges included: 3.0–4.2 V, 3.4–4.2 V, 3.6–4.2 V (fixed upper cutoff of 4.2 V), 3.4–4.0 V (narrow potential range), as well as 3.0–4.0 V, 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V (fixed lower potential). dV/dQ analysis, full cell impedance and symmetric cell analysis as well as half cells made from recovered electrodes were performed after 0, ~400 and 800 cycles. The contributions of positive electrode active mass loss and shift loss to the capacity loss of NCA/graphite cells tested under these conditions were determined. The correlation between positive electrode active mass loss, charge transfer resistance (Rct) growth, lattice volume changes, and upper and lower cutoff limits were explored. The impact of the kinetic hindrance regions in NCA is discussed in detail. The work presented here shows how the kinetic hindrance associated with lithium-ion diffusion at low and high states of charge of NCA materials can be related to the cause of particle cracking in NCA.

**Experimental**

Reagents used in this investigation included 3:7 v/v ethylene carbonate:ethyl methyl carbonate (EC:EMC) (BASF), lithium hexafluorophosphate (LiPF6) (BASF, 99.9%), N-methyl-pyrrolidone (NMP, 99.5%, Sigma-Aldrich), poly(vinylidene) fluoride (PVDF, Kynar
The electrolyte additive used in this work was 2% VC. Once cells were placed in a heated vacuum oven at 80 °C overnight (approximately 14 hours) to remove any residual water. After drying, the cells were then transferred back to an argon-filled glove box and cut open under the previous seal to release any gas that was produced. The cells were then vacuum sealed again as previously described, clamped in boats and were ready for electrochemical impedance spectroscopy (EIS) measurements.

**In-situ X-ray diffraction.**—In-situ X-ray diffraction was carried out using a Siemens D5000 diffractometer equipped with a Cu target X-ray tube and a diffracted beam monochromator. A slurry with a mixture of 92 wt% NCA active material, 4 wt% Super-S carbon black and 4 wt% PVDF as the solvent were first prepared. The aforementioned slurry, which was purposely made thicker with less NMP, was cast using a 660 μm notch bar directly onto a 2 cm diameter beryllium window. The electrode was dried overnight at 120 °C in a vacuum oven before use. The beryllium window was attached using Roscobond pressure sensitive adhesive to the positive electrode side of the cell case that had a pre-cut 1.5 cm diameter hole. The in-situ cell was then assembled in the same way as a coin cell. The cell was cycled at a rate of C/100 between 3.0–4.4 V for two cycles using an E-one Moli charger system, while diffraction patterns were collected at 0.05° intervals with a dwell time of 15 s. Each scan was approximately 3 h.

**40 °C Long term cycling.**—The pouch cells were tested for long term cycling with a C/2 rate. A cycle at a C/20 rate was included every 50 cycles. The cells were held at the top of charge until the current reached C/20 during each cycle. The tests were made at 40 ± 0.1 °C in temperature-controlled boxes. Neware (Shenzhen, China) chargers were used for these tests.

**Electrochemical impedance spectroscopy (EIS).**—All EIS spectra were measured at a temperature of 10 ± 0.1 °C using a Biologic VMP3 electrochemical test station. Data were collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10 mV. The experimental setup did not allow for reproducible solution resistance measurements due to cable and connector impedance. Therefore, all impedance spectra were manually shifted to zero on the real axis at the highest frequency measured. The area specific charge transfer resistance reported here is extracted from a Nyquist plot as the total “diameter” of the “semicircle” which is the sum of charge (both ion and electron) transfer resistance (Rct) (both electrodes) from the full cell. The total electrode area of the cells was ~68 cm².

**Symmetric cells.**—Pouch cells after formation and after cycling were discharged to 3.8 V and held at 3.8 V for 1 h before disassembling in an argon filled glove box. Small electrodes with an area of 1.51 cm² were punched from the recovered positive electrodes, which were then assembled in a coin cell. The symmetric cells were filled with control electrolyte. The AC impedance spectra were collected at 10 °C with the same settings as it was for the pouch cells.

**Differential capacity analysis (dV/dQ vs. Q).**—The voltage vs capacity (V-Q) curves of pouch cells before and after cycling were measured with the UHPC charger with a C/20 or C/100 rate at 40 °C. The NCA/Li and graphite/Li reference curves were measured from electrodes punched from pouch cells and assembled in coin cells. The dV/dQ analysis were performed using a software developed at Dalhousie University.

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301F, Arkema) and Super-S carbon black (Timcal). Vinylene carbonate (VC) (BASF, 99.97%) was used as an electrolyte additive.

Coin cells.—Small electrodes with an area of 1.51 cm² were punched from the single side-coated regions of positive electrodes taken from pouch cells before and after cycling, which were then assembled in coin cells. The electrolyte used was 1.0 M LiPF6 in 3:7 v:v ethylene carbonate:ethyl methyl carbonate (EC:EMC) (BASF, max < 20 ppm water). The electrolyte additive used in this work was 2% VC. Once cells were filled with electrolyte, they were sealed with a compact vacuum sealer (MSK-115 V, MTI Corp.) to 94% of full vacuum (~95.2 kPa gauge pressure or 6.1 kPa absolute pressure) with a 4 second sealing time at 165 °C.

All cells were placed in a temperature-controlled box at 40 ± 0.1 °C and held at 1.5 V for 24 hours to ensure complete wetting. Then cells were clamped with rubber blocks in cell holding “boats” while they were charged at C/20 using a Maccor series 4000 automated test system (Maccor Inc.), where C/20 is the current required to complete a full charge or discharge in 20 hours. The cells were charged to the upper cutoff voltage and discharged to 3.8 V at 40 °C. The cells were then transferred back to an argon-filled glove box and cut open under the previous seal to release any gas that was produced. The cells were then vacuum sealed again as previously described, clamped in boats and were ready for electrochemical impedance spectroscopy (EIS) measurements.

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Figure 1. Voltage-capacity (V-Q) curves of the positive electrode and negative electrode against lithium in blue and red, respectively. Solid lines show the scenario of a full cell before cycling while dashed lines show the cell after cycling.

**Pouch cells.**—402035-size NCA/graphite pouch cells (170 mAh) were obtained dry (no electrolyte) and sealed from Umicore (Ko-
Results and Discussion

Figure 2a shows the differential capacity as a function of voltage (dQ/dV vs V) for NCA/Li coin cells measured at various temperatures between 3–4.3 V with C/20 rate. The black, red, blue and green lines show results measured at 20, 30, 40 and 55°C, respectively. These results were measured for the second charge and discharge of separate cells. Figure 2a shows that the peak height at about 3.5 V during discharge decreased significantly with decreasing temperature from 55 to 20°C, indicating a kinetic hindrance to lithium diffusion. Additionally, a significant shift of the peak at ∼3.5 V during charge to higher voltages can also be observed when the temperature decreased. The dQ/dV peaks in other regions (3.6–4.3 V) were not impacted by temperature significantly. Figure 2b shows dQ/dV vs V for cells measured at various C-rate between 3–4.3 V at 40°C. The red, blue, green and black lines show results measured at C/40, C/20, C/10 and C/5 rate, respectively. Figure 2b shows that the peak height at about 3.5 V during discharge decreased significantly with increasing C-rate from C/40 to C/5, again indicating a kinetic hindrance to solid state lithium diffusion. These results were measured sequentially on the same cell. Additionally, a significant shift of the peak at ∼3.5 V during charge to higher voltage can also be observed when C-rate increased. A large voltage drop at the beginning of discharge can be observed in the high voltage peak around ∼4.17 V. The peaks in other regions (3.6–4.1 V) are not affected significantly by changing the C-rate in the range explored.

Figures 2a and 2b show that the dQ/dV peaks of NCA/Li cells at about 3.5 and 4.17 V are strongly and mildly dependent on temperature and C-rate, respectively. This suggests that lithium diffusion is quite slow at low states of charge and somewhat slow at a high state of charge. These phenomena will be referred to as kinetic hindrance regions in NCA in the rest of this paper. At low state of charge, Van der Ven et al. argue that lithium diffusion is limited by the limited number of divacancies available.30 Large electrostatic repulsion and a high migration energy barrier are expected when Li ions migrate through a tetrahedral site to an octahedral site. At high states of charge, the interlayer spacing decreases significantly and the average valence state of transition metal ions increases from 3+ to near 4+, which could also lead to an increase in Li+ migration barriers.30 Observation of these kinetic hindrances in NCA through studies of dQ/dV vs. V have not been reported in the literature to our knowledge. Kinetic hindrance of lithium diffusion could also lead to cracking of the secondary particles during high rate cycling due to the formation of large concentration gradients, and associated strain gradients, within particles.

Figure 3 shows diffraction patterns from the in-situ XRD experiment. The left panel shows cell voltage as a function of time, which is aligned with the diffraction patterns. For clarity, only every other pattern was shown here while the intensity was sequentially offset. The cells were charged and discharged between 3.0–4.3 V at a rate of C/100 for 1.5 cycles. Each XRD scan was about 3 h. As the diameter of active material coated on beryllium (Be) window was smaller than beam width at lower angles (18–20°), the intensity of the detected (003) peak was much lower than normally observed. The impurity peaks from Li and Be are labeled in the graph. Figure 3 shows that the (003) and (104) reflections at ∼19 and 45°, respectively, shifted to the left and then shifted the right during charge. The trend was reversible in the following discharge and charge processes. This indicates that the c-axis increased and then decreased during charge. There were no two-phase regions observed in this voltage range.

Rietveld refinements were performed on the data assuming a hexagonal layered phase in the R-3m space group (α-NaFeO2-type structure) to extract lattice information. It was assumed that Li was on the 3a sites (lithium layer), transition metals were on the 3b sites (transition metal layer), and oxygen was on the 6c sites. The exchange of Ni and Li atoms between 3a and 3b sites was allowed with constraints such that the stoichiometry of the phase was fixed to the values assumed from composition derived from the cell capacity. Preferred orientation parameters were fit in order to compensate for the low intensity of the (003) peak, which does not impact the extraction of the peak positions and lattice constant.

Figures 4a, 4b and 4c show the a-axis, c-axis and volume of the NCA unit cell as a function of specific capacity, respectively, whereas Figures 4A, 4B, 4C and 4D show the corresponding results as a function of cell voltage. Figures 4d and 4D show the cell voltage as a function of specific capacity and the differential capacity as a function of cell voltage, respectively. The red, blue and green symbols show the results for first charge, first discharge and second charge. Figure 4a shows that the c-axis increased from ∼14.20 to ∼14.47 Å when the capacity reached about 190 mAh/g during the first charge, corresponding to ∼68% delithiation assuming a theoretical capacity of 279 mAh/g. The c-axis then decreased to ∼14.01 Å with further charging to 250 mAh/g, corresponding to ∼90% delithiation. Figure 4b shows that the a-axis continuously decreased from ∼2.87 to 2.81 Å during the first charge. Figure 4c shows that the unit cell volume gradually decreased from 101.1 to 99.36 Å³ when the capacity reached about 190 mAh/g during the first charge, corresponding to ∼68% delithiation assuming a theoretical capacity of 279 mAh/g. The c-axis then decreased to ∼14.01 Å with further charging to 250 mAh/g, corresponding to ∼90% delithiation. Figure 4d shows that the a-axis continuously decreased from ∼2.87 to 2.81 Å during the first charge. Figure 4c shows that the changes in the c-axis, the a-axis and the unit cell volume were reversible during the following cycles. Additionally, Figures 4A shows that the c-axis and unit cell volume, respectively, started to drop dramatically when the voltage was above ∼4.05 V (vs Li) then started to decrease with further charging. Figures 4A and 4C show that the c-axis and unit cell volume, respectively, started to drop dramatically when the voltage was above ∼4.05 V (vs Li). This result agrees well with the observation of lattice changes in Ref. 6 after the first cycle.

Figure 2 showed that NCA has kinetic hindrance issues, which could lead to large concentration gradients from the surface to bulk in a secondary particle during high rate cycling. This could cause lattice mismatch within a particle and as a result generate micro-cracks. Figure 4 shows that the c-axis and unit cell volume change dramatically at high state of charge, which could also lead to generation of micro-cracks during long term cycling due to mechanical stress.31 To further study the impact of kinetic hindrance and volume change in NCA on its cycling stability, NCA/graphite cells were tested with various voltage ranges. The voltage ranges were selected so that the dQ/dV peaks at ∼3.5 and 4.17 V (vs Li) (Figure 2) were included or omitted. Figure S2 shows the dV/dQ vs Q fitting results of received NCA/graphite pouch cells, through which the alignment of positive and negative V-Q curves can be determined. Figure S3 shows that voltages of 3.0, 3.4, 3.6, 4.0, 4.1, 4.2 and 4.3 V in NCA/graphite
pouch cells correspond to voltages of 3.54, 3.6, 3.72, 4.1, 4.2, 4.29 and 4.38 V (vs Li), respectively, such that the NCA is at the same state of charge in NCA/Li cells. The voltages would shift slightly to lower values (~10 mV from C/40 to C/5) at higher C-rates (Figure 2b) during discharge, however, the 3.5 V peak would still be eliminated when the lower cutoff voltage is 3.4 V in full cells.

Figure 5 shows the long term cycling results of NCA/graphite cells with 2% VC electrolyte. The cells were tested at 40 °C with C/2 rate and with a constant voltage hold when the current decayed to C/20 at the top of charge. One C/20 cycle was performed in every 50 cycles. One of the two pair cells were stopped after about 400 cycles while the other one was kept on for about 800 cycles. Figures 5a1, 5b1, 5c1 and 5d1 show capacity, normalized capacity, absolute capacity loss and voltage hysteresis (ΔV), respectively, as a function of cycle number for cells tested with 3.0–4.2 V, 3.4–4.2 V or 3.6–4.2 V. ΔV was calculated from the differences between the average charge and average discharge voltages. Figures 5a2, 5b2, 5c2 and 5d2 show the corresponding results for cells tested between 3.0–4.0 V or 3.4–4.0 V while Figures 5a3, 5b3, 5c3 and 5d3 show the corresponding results for cells tested between 3.0–4.1, 3.0–4.2 V or 3.0–4.3 V. The legends in the graphs show how the various symbols correspond to the various voltage ranges. Figure S1 shows the same results plotted against cumulative discharge capacity (throughput).

Figures 5a1–5d1 (left panel) show the results for cells tested with a fixed upper cutoff voltage of 4.2 V and various lower cutoff voltages. Figures 5c1 and 5d1 show that cells with larger lower cutoff voltages presented less absolute capacity loss and ΔV growth, respectively, during cycling. Figure 5c1 shows that cells tested between 3.0–4.2 V,
3.4–4.2 V and 3.6–4.2 V exhibited absolute capacity losses of 26.7, 19.2 and 12.5 mAh in ∼800 cycles, respectively, while Figure 5d1 shows that the cells had ΔV increases of 14, 5.5 and 3.9 mV correspondingly. Cells with larger lower cutoff voltages showed smaller initial ΔV, which is likely because the dQ/dV peaks at ∼3.5 V (vs Li), that showed kinetic hindrance, were omitted. The cells with lower cutoff voltages of 3.0, 3.4 and 3.6 V showed an initial ΔV of 70, 58 and 44 mV at C/2 rate.

Figures 5a2–5d2 (middle panel) show the results for cells tested with intermediate voltage ranges. Figure 5c2 shows that cells with smaller lower cutoff voltage exhibited larger capacity loss and ΔV growth. Figure 5c2 shows that cells tested between 3.4–4.0 V, 3.0–4.2 V and 3.0–4.3 V after ∼900 and 900 cycles or ∼151, 120 and 92 Ah throughput were ∼167, 191 and 189 Ω cm², respectively, corresponding to Rct growth rates of ∼2.5, 1.2 and 1.6 Ω cm²/Ah throughput. If Rct growth is mainly due to parasitic reactions between the electrolyte and the positive electrode, then one would expect cells with same upper cutoff voltage to have similar impedance growth. Additionally, since cells cycled between 3.6–4.2 V spent more time in the middle and high voltage range, one would also expectcells tested in this range to have larger impedance growth. This is true when comparing cells tested between 3.4–4.2 V and 3.6–4.2 V. However, this is not the case when comparing to cells tested between 3.0–4.2 V, which indicates that impedance growth is associated with other mechanisms such as micro-crack generation. Figure 6b shows the results for cells tested between 3.0–4.0 V and 3.4–4.0 V in black and red, respectively. Figure 6b shows similar trends as Figure 6a that cells with larger lower cutoff voltage had smaller Rct after cycling for ∼800 cycles. The Rct for cells with lower cutoff voltages of 3.0, 3.4 and 3.6 V after ∼900, 800 and 900 cycles or ∼151, 120 and 92 Ah throughput were ∼418, 191 and 189 Ω cm², respectively, corresponding to Rct growth rates of ∼2.5, 1.2 and 1.6 Ω cm²/Ah throughput. If Rct growth is mainly due to parasitic reactions between the electrolyte and the positive electrode, then one would expect cells with same upper cutoff voltage to have similar impedance growth. Additionally, since cells cycled between 3.6–4.2 V spent more time in the middle and high voltage range, one would also expect cells tested in this range to have larger impedance growth. This is true when comparing cells tested between 3.4–4.2 V and 3.6–4.2 V. However, this is not the case when comparing to cells tested between 3.0–4.2 V, which indicates that impedance growth is associated with other mechanisms such as micro-crack generation. Figure 6b shows the results for cells tested between 3.0–4.0 V and 3.4–4.0 V in black and red, respectively. Figure 6b shows similar trends as Figure 6a that cells with larger lower cutoff voltage had smaller Rct after cycling for ∼800 cycles. The Rct for cells tested between 3.0–4.0 V and 3.4–4.0 V after ∼800 and 900 cycles or ∼115 and 110 Ah throughput are ∼167
and 113 Ω cm$^2$, respectively, corresponding to $R_{ct}$ growth rates of ∼1.1 and 0.6 Ω cm$^2$/Ah throughput. Figure 6c shows the results for cells tested between 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V in red, blue and green, respectively. Figure 6c shows that cells with larger upper cutoff voltages had larger $R_{ct}$ after cycling for ∼800 cycles. $R_{ct}$ for cells with upper cutoff voltages of 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V after ∼800, 900 and 800 cycles or ∼128, 152 and 138 Ah throughput were ∼223, 418 and 495 Ω cm$^2$, respectively, corresponding to $R_{ct}$ growth rates of ∼1.4, 2.5 and 3.3 Ω cm$^2$/Ah throughput.

Figure 7a shows the correlation between $\Delta V$ increase and $R_{ct}$ growth for cells after ∼800 cycles for cells testing in the various voltage ranges, while Figure 7b shows the correlation between $\Delta V$ increase rate and $R_{ct}$ growth rate based on per Ah throughput. The $R_{ct}$ increase was interpolated to the 800th cycle as some of the cells were observed between cells tested at 3–4.0 V and 3.0–4.2 V. The blue crosses show the results for cells cycled between 3.0–4.0 V, 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V (c). The EIS was measured at 10°C with a cell voltage of 3.8 V.

Figure 7b shows similar trends as observed in Figure 7a.

Figure 7a shows the correlation between $\Delta V$ increase and $R_{ct}$ growth (a) and correlation between $\Delta V$ increase rate and $R_{ct}$ growth rate based on Ah throughput (b) for cells after 800 cycles at various voltage ranges. The results for cells cycled between 3.0–4.0 V, 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V are shown in red crosses, where the red dashed line is a linear fit to the data, the blue crosses are for cells cycled between 3.0–4.2 V (this particular point has a red cross because it is part of the previous experimental series, but it has blue label), 3.4–4.2 V and 3.6–4.2 V, where the blue dashed line is a linear fit to the data. The green cross is for cells cycled between 3.4–4.0 V. The data point for cells tested between 3.0–4.0 V is shown as a red cross as it is part of the first experimental series, but it has a green label because it is also part of the series of experiments with a 4.0 V upper cutoff.

8b and 8c show the EIS spectra of positive/negative, positive/positive and negative/negative symmetric cells made from cells tested between 3.0–4.0 V, respectively. The inset in Figure 8c shows an expanded view of the negative/negative spectra. Figures 8a, 8b and 8c show the corresponding results for cells tested between 3.0–4.2 V. The impedance of the positive/positive and negative/negative symmetric cells were divided by two from the measured value. The black and red lines show the results for cells after ∼400 and 800 cycles, respectively. The solid and dashed lines show the results for repeated cells. Figures 8b and 8B show that the positive electrode charge transfer impedance increased significantly with cycling, and that the positive electrode charge transfer impedance was larger for cells tested between 3.0–4.2 V for cells run between 3.0–4.0 V after ∼800 cycles. Additionally, Figures 8c and 8C show that the negative electrode impedance increased little with cycling while no significant differences of negative impedance were observed between cells tested at 3.4–4.0 V and 3.0–4.2 V. Figure 8 shows that the impedance growth of NCA/graphite full cells originated mostly from the positive electrode during cycling.

The NCA/graphite pouch cells after ∼400 and 800 cycles were stopped and moved to UHPC chargers to measure high quality V-Q curves for dV/dQ analysis. The cells were tested with a C/20 or C/100 rate at 40°C. Despite the fact that the cells were tested between 3.4–4.2 V, 3.6–4.2 V and 3.0–4.1 V during cycling, all the cells were tested between 3.0–4.2 V when tested on the UHPC charger to collect data for dV/dQ analysis. The measured dV/dQ vs. Q of NCA/graphite pouch cells can be fitted using the positive/Li and negative/Li reference curves as described by H. Dahn et al. Figure S5 shows example
Fitting results for cells tested between 3.0–4.3 V after 0, ∼400 and 800 cycles. Figures S5a1, S5b1 and S5c1 show the dV/dQ vs Q, V-Q and dQ/dV vs V for cells before cycling, respectively. Figures S5a2–S5c2 and Figures S5a3–S5c3 show the corresponding results for cells after ∼400 and 800 cycles, respectively. The black solid line and red dashed line show the measured and calculated results, respectively, while the red and blue solid lines show the positive and negative reference data. Figure S5 shows that the measured data can be fitted very well for cells before cycling. The positive peak at ∼4.1 V in the full cell dQ/dV vs V curves labelled as Peak 2 in the figure cannot be fitted well after cycling, however, the positive peak at ∼3.9 V in full cell dQ/dV labelled as Peak 1 in the figure can be fitted very nicely. Peak 1 and Peak 2 in full cells correspond to the dQ/dV vs V peaks of NCA/Li cells at ∼3.98 and 4.18 V (vs Li) during charge shown in Figure 2. dV/dQ vs. Q fitting for the cycled cells was performed by ignoring the positive peak at high state of charge (Peak 2).

Figures 9a and 9A show the dQ/dV vs V curves of NCA/graphite pouch cells tested between 3.6–4.2 V and 3.0–4.3 V, respectively. The solid lines show the measured data and the symbols show the calculated results based on the dV/dQ vs Q fits shown in Figure S5. The black, blue and red colors show the results for cells after 0, ∼400 and 800 cycles, respectively. Figures 9a and 9A show that the measured data from cells before cycling can be fitted nicely. Conversely, Peak 2 from NCA at high states of charge cannot be fitted any more for cells after cycling, while good fits to Peak 1 from NCA can still be achieved. Additionally, Figures 9a and 9A show that the area of Peak 2 decreased with increasing cycle number, while the expected intensity, based on the calculated curves changed little with cycling.

Figure 9b shows the dQ/dV vs. V curves of cells tested between 3.0–4.2 V, 3.4–4.2 V and 3.6–4.2 V after ∼800 cycles in blue, red and green colors, respectively. The solid lines show the measured data while the symbols show the calculated results based on the dV/dQ vs Q fitting shown in Figure S5. Figure 9B shows the corresponding results for cells tested between 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V. Figures 9b and 9B show that the measured intensity of Peak 2 from cells after cycling was much smaller than expected. Figure 9b shows that the area of Peak 2 increased with increasing lower cutoff voltage when the upper cutoff voltage was fixed at 4.2 V, while Figure 9B shows that the area of Peak 2 decreased with increasing upper cutoff voltage when the lower cutoff voltage was fixed at 3.0 V. Figures 9c and 9C show dQ/dV vs V of cells tested between 3.6–4.2 V and 3.0–4.2 V after ∼800 cycles, respectively. The dQ/dV vs V curves of the same cells were measured with C/20 and C/100 rates using the UHPC charger, which are shown in black and red colors, respectively. Figures 9c and 9C show that the measured intensity of Peak 2 recovered when the current decreased from C/20 to C/100, while the intensity of Peak 1 changed very little. This indicates that the suppression of Peak 2 after cycling is related to a kinetic hindrance of lithium diffusion at high state of charge in NCA, which does not apparently affect diffusion at intermediate states of charge! This is rather amazing since the kinetic hindrance of this peak (see Figure 2) was not so dramatic when the NCA was fresh. The good fits to the Peak 1 region using reference data

Figure 8. EIS spectra of positive/negative (a), positive/positive (b) and negative/negative (c) symmetric cells made from cells tested between 3.0–4.0 V for 400 and 800 cycles, respectively. The inset shows an expanded view of the negative/negative spectra. EIS spectra of positive/negative (A), positive/positive (B) and negative/negative (C) symmetric cells made from cells tested between 3.0–4.2 V for 400 and 800 cycles, respectively. The inset shows an expanded view of the negative/negative spectra.
Figure 9. dQ/dV vs V of NCA/graphite pouch cells tested between 3.6–4.2 V (a) and 3.0–4.3 V (A), respectively. dQ/dV vs V of cells tested between 3.0–4.2 V, 3.4–4.2 V and 3.6–4.2 V after ~800 cycles (b) and the corresponding results for cells tested between 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V (B). dQ/dV vs. V of cells tested between 3.6–4.2 V (c) and 3.0–4.2 V (C) after ~800 cycles, which were measured using C/20 and C/100 rates with the UHPC charger.

measured from fresh NCA electrodes suggests that the bulk structure of NCA has not deteriorated significantly during cycling. It is possible that the poor kinetics of peak 2 after cycling could be due to the lattice contraction at high states of charge (associated with peak 2) which could cause electrical disconnect of micro-cracked regions. Electrical connections might be re-established during expansion upon lithiation. Such a scenario might explain the behaviors of peaks 1 and 2 in Figure 9 but this is speculation by the authors.

To further confirm what has been observed from dV/dQ vs Q fitting results in NCA/graphite pouch cells in Figure 9, half cell coin cells were constructed from recovered electrodes of cycled cells. The differences in active material mass of punched electrode disks from the machine made pouch cells are negligible. The cells were measured at 40°C between 3.0–4.2 V with a current of 10 mAh/g using UHPC chargers, which was about a C/20 rate. Figures 10a and 10A show V-Q curves of reconstructed coin cells from positive electrodes from pouch cells tested between 3.0–4.0 V and 3.0–4.2 V, respectively. Even though some pouch cells were tested between 3.0–4.0 V, all the reconstructed coin cells were tested between 3.0–4.2 V to probe the peak at high state of charge. The black, blue and red lines show the results for positive electrodes from pouch cells tested after 0, ~400 and 800 cycles, respectively. Figures 10b and 10B show the corresponding normalized dQ/dV vs V which were calculated by dividing by the measured coin cell capacity. Figure 10a shows capacities of 2.37, 2.32 and 2.26 mAh for cells tested between 3.0–4.0 V after 0, ~400 and 800 cycles, respectively. Figure 10a shows that pouch cells after 800 cycles between 3.0–4.0 V had about ~4.6% capacity loss on the positive side. Figure 10a also shows that the polarization of the NCA electrode increased with increasing cycle number of the pouch cells. Figure 10A shows that coin cells made from electrodes from pouch cells tested between 3.0–4.2 V after 0, ~400 and 800 cycles had capacities of ~2.37, 2.27 and 2.08 mAh, respectively. Figure 10A shows that the positive electrode from pouch cells tested between 3.0–4.2 V after ~800 cycles had ~12% capacity loss. Additionally, Figure 10B shows that the polarization of the NCA electrode increased significantly in the regions of the peaks near 3.5 and 4.17 V with increasing cycle number for the pouch cells tested between 3.0–4.2 V.

Figure 10b shows that the changes in dQ/dV vs V of NCA electrodes from pouch cells cycled between 3.0–4.0 V were minimal except that the total area under the dQ/dV curve decreased slightly. The features from the discharge peaks at ~3.5 and 4.17 V (vs Li) were maintained. Figure 10B shows that the area under the dQ/dV vs V curve of NCA electrodes decreased significantly after 800 cycles between 3.0–4.2 V, while the features at ~3.5 and 4.17 V (vs Li) also changed significantly.

To identify if these changes were due to active positive electrode mass loss or some other phenomena, capacity normalized dQ/dV vs V curves were plotted. Figure 10c shows that there were almost no changes in the normalized dQ/dV vs V curves of the NCA electrode before and after cycling between 3.0–4.0 V. This indicates that the capacity loss of the recovered NCA electrode was mainly due to active mass loss. Figure 10C shows that there were almost no changes...
in the normalized dQ/dV vs V features between 3.6–4.1 V for the NCA electrode before and after cycling between 3.0–4.2 V. This indicates that the bulk structure of the material did not deteriorate, otherwise one would expect changes in this region. However, the discharge peaks at ∼3.5 and 4.17 V (vs Li) showed significant changes in that the peak intensity decreased dramatically with increasing cycle number. These peaks displayed kinetic hindrance of lithium diffusion as indicated in previous discussions (Figure 2 and Figure 9). The deterioration of the features at ∼3.5 and 4.17 V (vs Li) when pouch cells were cycled above 4.0 (vs Li) also contributes to capacity loss. Figures 10B and 10C show that the capacity loss of the NCA electrode after cycling between 3.0–4.2 V was mostly due to loss of active mass in addition to suppression of the dQ/dV peaks at both low and high state of charge which display kinetic hindrance. Since the dQ/dV features between 3.8–4.1 V (vs Li) did not change significantly during cycling, the area of these peaks or the capacity within this range can be used to estimate the active material loss. The estimated active positive electrode mass loss from cells cycled between 3.0–4.0 V and 3.0–4.2 V (pouch cell) are ∼5(1)% and ∼9(1) %. However, these results are slightly over estimated due to large polarization of the electrodes after 800 cycles.

Table I shows the fitting parameters obtained from dV/dQ vs Q fitting for cells after 0, ∼400 and 800 cycles. The exact same cells were used for comparing the changes before and after ∼400 or 800 cycles. Figure 11 shows dV/dQ vs Q fitting results. Figures 11a and 11b show the shift loss in mAh and the positive electrode active mass loss in percentage for cells cycled between 3.0–4.2 V, 3.4–4.2 V and 3.6–4.2 V, respectively. The red and black colors show the results of cells after ∼400 and 800 cycles, respectively. Figures 11A and 11B show the corresponding results for cells tested between 3.0–4.0 V, 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V. Figure 11a shows that the shift loss for cells tested between 3.0–4.2 V, 3.4–4.2 V and 3.6–4.2 V were ∼3.8(8), 6.6(8) and 8.3(8) mAh after ∼400 cycles, respectively, and ∼6.8(8), 8.5(8) and 11.1(8) mAh after ∼800 cycles, respectively. Figure 11a shows that the shift loss increased with increasing lower cutoff voltage when the upper cutoff voltage was fixed at 4.2 V. With reference to Figure 1, if the positive electrode mass loss (d–c) in Figure 1 decreases with increasing lower potential (as in Figure 11b), then the shift loss (a–b in Figure 1) will increase with increasing lower potential (as in Figure 11a). Figure 11A shows that the shift loss for cells tested between 3.0–4.0 V, 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V were ∼6.1(8), 3.4(8), 3.8(8) and 7.1(8) mAh after ∼400 cycles, respectively, and ∼7.4(8), 6.2(8), 6.7(8) and 8.4(8) mAh after ∼800 cycles, respectively. The shift loss decreased, in general, as the upper cutoff increased, again, because the mass loss (Figure 11B) increased as the upper cutoff decreased. For cells tested between 3.0 and 4.3 V both the shift loss and the mass loss were large which suggests a positive-negative electrode interaction that onsets above 4.2 V that increases the shift loss. Figure 11b shows the positive electrode interaction.
Table I. Fitting parameters from dV/dQ calculation. The same cell was measured at cycle 0 and 400 and another cell was measured at cycle 0 and 800. Active electrode masses (NM and PM) are in grams. Capacity shifts (n_i or n_f and p_i or p_f) are in mAh.

| Cycle_0 | Cycle_400 | Cycle_800 |
|---------|-----------|-----------|
| Range (V) | Cell_ID | NS (n_i) | PS (p_i) | NM | PM | Cell_ID | NS (n_f) | PS (p_f) | NM | PM | Cell_ID | NS (n_f) | PS (p_f) | NM | PM |
| 3.4–4.2 | 908 | –6.2 | –20.5 | 0.86 | 1.05 | 907 | –5.6 | –26.2 | 0.87 | 1.04 | 908 | –4.6 | –26.3 | 0.86 | 1.00 |
| 3.4–4.2 | 907 | –6.4 | –21.0 | 0.87 | 1.07 | 910 | –5.6 | –22.5 | 0.88 | 1.03 | 909 | –5.8 | –26.9 | 0.87 | 1.01 |
| 3.4–4.2 | 909 | –6.8 | –21.7 | 0.87 | 1.07 | 911 | –7.2 | –24.3 | 0.88 | 1.01 | 910 | –8.0 | –29.2 | 0.89 | 0.97 |
| 3.4–4.2 | 912 | –7.3 | –20.7 | 0.89 | 1.05 | 911 | –7.9 | –27.8 | 0.88 | 1.01 | 912 | –9.2 | –31.1 | 0.89 | 0.96 |
| 3.4–4.2 | 903 | –7.1 | –20.4 | 0.88 | 1.06 | 904 | –7.1 | –26.2 | 0.89 | 1.02 | 903 | –7.6 | –29.4 | 0.88 | 1.01 |
| 3.4–4.2 | 904 | –7.2 | –19.8 | 0.89 | 1.04 | 905 | –7.2 | –24.3 | 0.88 | 1.01 | 905 | –5.8 | –29.4 | 0.87 | 1.01 |
| 3.4–4.0 | 914 | –6.2 | –22.4 | 0.87 | 1.08 | 913 | –6.7 | –28.1 | 0.88 | 1.04 | 914 | –6.3 | –30.1 | 0.87 | 1.03 |
| 3.4–4.0 | 913 | –6.2 | –21.1 | 0.86 | 1.07 | 913 | –5.2 | –26.9 | 0.86 | 1.04 | 914 | –6.3 | –30.1 | 0.87 | 1.03 |

NS: negative shift (mAh), error: +/−0.4 mAh. (This corresponds to “n_i or n_f” in Figure 1 as indicated).
PS: positive shift (mAh), error: +/−0.8 mAh. (This corresponds to “p_i or p_f” in Figure 1, as indicated).
NM: negative mass (g), error: +/−0.02 g.
PM: positive mass (g), error: +/−0.02 g.

active mass loss for cells tested between 3.0–4.2 V, 3.4–4.2 V and 3.6–4.2 V were ~4.2(5), 2.5(5) and 2.5(5) percent after ~400 cycles, respectively, and 7.2(5), 4.9(5) and 4.3(5) percent after ~800 cycles, respectively. Figure 11b shows that the positive electrode active mass loss decreased with increasing lower cutoff voltage when the upper cutoff voltage was fixed at 4.2 V. Figure 11B shows the positive mass loss of cells tested between 3.0–4.0 V, 3.0–4.1 V, 3.0–4.2 V and 3.0–4.3 V are ~3.1(5), 3.9(5), 4.4(5) and 4.3(5) percent after ~400 cycles, respectively, and 4.8(5), 6.0(5), 7.2(5) and 10.1(5) percent after ~800 cycles, respectively. This result agrees very well with the reconstructed coin cell data in Figure 10, which suggested that the mass losses of the NCA electrode cycled between 3.0–4.0 and 3.0–4.2 V were about 5(1) and 9(1) percent, respectively, after 800 cycles. Figure 11B shows that the positive mass loss increased with increasing upper cutoff voltage when the lower cutoff voltage was fixed at 3.0 V.

To further explore the cause of Rct growth as observed in Figures 6 and 8, Figure 12a shows the correlation between cathode mass loss...
Correlation between positive electrode active mass loss and lattice volume change.

Figure 12b shows that the positive electrode active mass loss increased dramatically from ~4% for 3.6–4.2 V cells to ~10% for 3.0–4.3 V cells while the volume change only increased from 4.7 to 5.3 Å³, corresponding to ~0.5% volume change compared to the initial lattice volume. Additionally, the positive electrode active mass losses for the 3.4–4.0 V range and the 3.6–4.2 V ranges were almost the same but the volume changes were very different, ~1.6 and 4.7 Å³, respectively, corresponding to a ~3% volume change difference compared to the initial lattice volume. Moreover, the volume change for the 3.0–4.1 V range was less than that of the 3.6–4.2 V range, however, the positive electrode active mass loss for cells cycled in the 3.0–4.1 V range was larger than for those tested in the 3.6–4.2 V range. Figure 12b suggests that there is no strong correlation between positive electrode active mass loss and lattice volume change. Figures S6a and S6b show the correlation between the positive electrode active mass loss and the c-axis and a-axis changes, respectively, and the mass loss but this is highly non-linear. Figures S6c and S6d show the correlation between the positive electrode active mass loss and the lattice volume change. Figures S6c and S6d show a good correlation between the positive electrode active mass loss and the c-axis change of the lattice. Figure S6b shows that there may be a correlation between the a-axis change and the positive electrode active mass loss and the capacity and the DOD ranges, respectively. The a and c-axis changes were calculated from the differences between the maximum and minimum values along the path. Figure S6 shows that even though the c-axis change was the same for cells tested between 3.0–4.2 V, 3.4–4.2 V and 3.6–4.2 V, the active mass loss was significantly different. Additionally, the mass loss increased dramatically from 3.0–4.2 to 3.0–4.3 V when the c-axis change increased little. Figure S6a shows that there is no strong correlation between cathode mass loss and c-axis change of the lattice. Figure S6b shows that there may be a correlation between the a-axis change and the mass loss but this is highly non-linear. Figures S6c and S6d show a good correlation between the positive electrode active mass loss and the cycled capacity or DOD range, but we believe this is fortuitous. The reasons for this are explained below.

Figure 12c shows dQ/dV vs V of a Li/NCA half cell as a function of cell voltage (vs Li/Li⁺). The regions marked by red lines at voltages below 3.6 V (vs Li) and above 4.1 V (vs Li) marked by areas 1 and 2, respectively, correspond to a full cell voltage of 3.4 and 4.0 V, respectively. This regions display kinetic hindrance to lithium diffusion. The area marked by blue lines labeled as area 3 shows the region that does not deteriorate during cycling as displayed in Figure 10C and does not show kinetic hindrance to lithium diffusion.

and Rct increase in ~800 cycles. S. Watanabe et al. claimed that the generation of micro-cracks (presumably correlated to positive electrode active mass loss in this paper) of NCA is highly dependent on the width of the cycling range, not on the upper or lower cutoff voltage. Watanabe et al. suggested that the volume change of NCA was responsible for the generation of micro-cracks. To verify this assumption, Figure 12b shows the correlation between the mass loss (after ~800 cycles) and lattice volume change. The lattice volume change was calculated from the in-situ XRD results. Red symbols show the results for voltage ranges 3.0–4.0 V, 3.0–4.1, 3.0–4.2 V and 3.0–4.3 V, the blue symbols show the results for voltage ranges 3.4–4.2 V and 3.6–4.2 V while the green symbol shows the results for the voltage range 3.4–4.0 V. Figure 12a shows that Rct increased almost linearly as the positive electrode active mass loss increased. Recall that Figure 8 showed that the impedance growth was mostly from the positive electrode side in full cells during cycling. This suggests that the Rct increase is directly related to the positive electrode active mass loss or generation of micro-cracks. Provided that internal cracks develop that do not allow electrolyte access (For example see Schemes 1d, 1e and 1f), then it is possible for Rct to increase even though more surface area is created. Scheme 1 is modelled after Figure 1 in McGrogan et al. who showed with acoustic emission spectroscopy and EIS, that Rct (the diameter of the impedance “semicircle”) increases in LiMn2O4 when microcracking events occur. In later work, Tsai et al. show clearly in Figure 3 of reference 33 that Rct (Rct is proportional to 1/Jo reported in Ref. 33) increases as internal cracks in NCA are created. Therefore, it is believed that the increases in Rct that are associated with mass loss are primarily due to internal cracks that are not penetrated by electrolyte.

Figure 12b shows that the positive electrode active mass loss increased from ~4% for 3.6–4.2 V cells to ~10% for 3.0–4.3 V cells while the volume change only increased from 4.7 to 5.3 Å³, corresponding to ~0.5% volume change compared to the initial lattice volume. Additionally, the positive electrode active mass losses for the 3.4–4.0 V range and the 3.6–4.2 V ranges were almost the same but the volume changes were very different, ~1.6 and 4.7 Å³, respectively, corresponding to a ~3% volume change difference compared to the initial lattice volume. Moreover, the volume change for the 3.0–4.1 V range was less than that of the 3.6–4.2 V range, however, the positive electrode active mass loss for cells cycled in the 3.0–4.1 V range was larger than for those tested in the 3.6–4.2 V range. Figure 12b suggests that there is no strong correlation between positive electrode active mass loss and lattice volume change. Figures S6a and S6b show the correlation between the positive electrode active mass loss and the c-axis and a-axis changes, respectively, and the mass loss but this is highly non-linear. Figures S6c and S6d show the correlation between the positive electrode active mass loss and the lattice volume change. Figures S6c and S6d show a good correlation between the positive electrode active mass loss and the cycled capacity or DOD range, but we believe this is fortuitous. The reasons for this are explained below.

Figure 12c shows dQ/dV vs V of a Li/NCA half cell as a function of cell voltage (vs Li/Li⁺). The regions marked by red lines at voltages below 3.6 V (vs Li) and above 4.1 V (vs Li) marked by areas 1 and 2, respectively, correspond to a full cell voltage of 3.4 and 4.0 V, respectively. The region marked by blue lines labeled as area 3 shows the region that does not change shape during cycling as discussed in Figure 10C. Figure 12b shows that the volume changes were ~5.12, 4.97 and 4.67 Å³, corresponding to ~5%, 4.9% and 4.6% of the initial volume, while the positive electrodes mass loss after 800 cycles was ~7.3(5), 5.0(5) and 4.7(5) percent for voltage ranges of 3.0–4.2 V, 3.4–4.2 V and 3.6–4.2 V, respectively. Figure 12b shows that the mass loss decreased significantly, and the volume change was similar for the three cases when the lower cutoff voltage increased and the upper cutoff voltage was fixed at 4.2 V. Figure 12b suggests that eliminating area 1 in the dQ/dV vs V curve of NCA, by increasing the lower cutoff voltage can help minimize positive electrode active mass loss during cycling. Figure 12b shows that the positive electrode active mass loss increased incredibly rapidly with the volume change when the upper cutoff voltage increased from 4.1 to 4.3 V and the lower cutoff voltage was fixed at 3.0 V. The volume change increased only from ~5.12 to 5.28 Å³, corresponding to a ~0.1% volume difference comparing to the initial lattice volume, while the active mass loss increased from 7.3(5) to 10.0(5) percent. This suggests that volume change alone is not the cause of the increased mass loss when cells are tested between 3.0 and 4.3 V compared to 3.0 to 4.1 V. Instead it appears that eliminating area 2 in the dQ/dV vs V curve of NCA...
Figure 13. Contour plots of positive electrode active mass loss in percentage (a), capacity loss due to positive electrode active mass loss in mAh (b), $\Delta V$ increase (c), capacity loss due to shift loss (d), measured absolute capacity loss (e) and calculated absolute capacity loss (f). The x-axes and y-axes are upper cutoff voltage and lower cutoff voltage, respectively. The red dots show the original data points.

(see Figure 12c) helps minimize the positive electrode active mass loss during cycling. Figures 12b and 12c show that positive electrode active mass loss can be minimized when areas 1 and 2 are partially or completely avoided. As discussed in Figures 2, 9 and 10, areas 1 and 2 are the regions that display kinetic hindrance associated with lithium diffusion in NCA. This suggests that besides the volume change in the lattice, kinetic hindrance issues in NCA also play a significant role to induce positive electrode mass loss during cycling. When lithium diffusion is slow, then larger lithium concentration gradients will form in particles and since the lattice constants depend on the lithium content, the internal stresses will become large. Therefore it is important to avoid the regions of slow Li-ion diffusion if particle fracturing is to be avoided as is indicated by the blue colored region in Figure 12c.

To summarize the dV/dQ vs Q fitting results and the long term cycling results (after 800 cycles), Figures 13a–13f show contour plots of positive electrode active mass loss in percentage, absolute capacity loss due to positive electrode active mass loss in mAh, $\Delta V$ increase, absolute capacity loss due to shift loss (in mAh), measured absolute capacity loss (in mAh) and calculated absolute capacity loss which is the sum of the shift loss and capacity loss due to positive electrode mass loss based on the dV/dQ vs. Q analysis results, respectively. The x-axis and y-axis are the upper cutoff voltage and lower cutoff voltage, respectively. The red dots show the original data points. Some local
minima in the contour plots are certainly due to the limited number of data points. The capacity loss due to positive electrode active mass loss was calculated by multiplying the percent mass loss by the initial capacity in the voltage range. Figures 13a and 13b show that the capacity loss due to positive electrode active mass loss was the largest near 3.0–4.3 V, while it is the smallest when the lower cutoff voltage was above 3.4 V and the upper cutoff voltage was 4.0 V when the dQ/dV peaks at ~3.5 V and 4.17 V were avoided. Figure 13c shows that the ΔV growth was the largest near 3.0–4.3 V and the smallest near 3.4–4.0 V. Figure 13d shows that the shift loss was the largest near 3.6–4.2 V as discussed previously. Figures 13b and 13d show that when the positive electrode active mass loss was small, shift loss was the major contributor to the total capacity loss and vice versa. It is therefore true that electrolyte reactions do contribute to capacity loss.15 Figures 13c, 13e and 13f show the trends of ΔV growth, measured capacity loss, and calculated capacity loss match very well. Capacity loss and impedance growth decrease with increasing upper cutoff voltage and increasing lower cutoff voltage. The calculated capacity losses from positive electrode active mass loss and shift loss were smaller than the measured capacity loss under the same conditions, indicating a loss of lithium inventory from parasitic electrolyte regeneration of micro-cracks within the electrode particles, and shift loss, active material mass loss, which is assumed to be related to the generation of micro-cracks within the secondary particles. There was no linear relationship between positive electrode active mass loss and cumulative lattice volume change. Most importantly, the positive electrode active mass loss can be minimized when the dQ/dV vs V peaks in NCA at ~3.5 and 4.17 V (vs Li), that show kinetic hindrance due to poor lithium diffusion, were partially or completely avoided during charge-discharge cycling. When lithium diffusion is slow, then larger lithium concentration gradients will form in particles and since the lattice constants depend on the lithium content, the internal strains and stresses will become large. Therefore it is important to avoid the regions of slow Li-ion diffusion if particle fracturing is to be avoided. Figures 12 and 13 summarize the crux of this work.

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