Impact of the Synthesis Conditions on the Performance of LiNi\textsubscript{x}Co\textsubscript{y}Al\textsubscript{z}O\textsubscript{2} with High Ni and Low Co Content

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One way to lower the cost of lithium ion batteries using LiNi\textsubscript{x}Mn\textsubscript{y}Co\textsubscript{z}O\textsubscript{2} (NMC) or LiNi\textsubscript{0.80}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} is to lower the Co content in the positive electrode materials. This work systematically studied the impact of the synthesis conditions on the performance of LiNi\textsubscript{x}Co\textsubscript{y}Al\textsubscript{z}O\textsubscript{2} (x > 0.8, y < 0.05 and x + y + z = 1) (NCA) with high Ni and low Co content. The impacts of oxygen flow rate, sintering temperature, initial Li/TM ratio and sintering time on the structural and electrochemical properties of NCA were systematically studied. The conditions when impurity phases such as Li2CO3 and Li3AlO2 appear were carefully examined. The impact of residual lithium compounds on the electrochemical performance was also discussed. It was found that the synthesis conditions, which affect the a-axis, c-axis and NiLi content of the NCA samples, have strong impacts on the lithium diffusion at low and high states of charge based on differential capacity vs. voltage (dQ/dV vs. V) measurements at various rates and temperatures. Additionally, the reversible capacity and cycling stability correlated strongly with the intensity of the dQ/dV vs V peak at 3.5 V (discharge) measured with a C/20 rate at 30°C.

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Lithium ion batteries (LIBs) with higher energy density, lower cost and longer lifetime are desired for electric vehicle and energy storage applications. LiNi\textsubscript{0.80}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} and related materials with varied values of x, y and z in LiNi\textsubscript{x}Co\textsubscript{y}Al\textsubscript{z}O\textsubscript{2} are used in applications that require high energy density such as electric vehicles due to their high specific capacity in a relatively narrow voltage range between 3.3 and 4.3 V (vs Li/Li\textsuperscript{+}). This material was developed from LiNiO\textsubscript{2} by substituting with Al and Co. Substituting Al for Ni was shown to improve the thermal stability and safety, however, decrease the specific capacity. The presence of Co was believed to lower the nickel content in the lithium layer (Ni\textsubscript{Li}) on based studies in LiNi\textsubscript{x}Mn\textsubscript{y}Co\textsubscript{z}O\textsubscript{2} (NMC). However, the impacts of Ni and Co content on the structural, electrochemical and thermal stability of LiNi\textsubscript{x}Co\textsubscript{y}Al\textsubscript{z}O\textsubscript{2} (x > 0.8, y < 0.05 and x + y + z = 1) (NCA) have not been systematically studied in the literature. Additionally, the Co price peaked at 43.32 USD/lb in 2017–2018 whereas the price of Ni and Al were only 1/7 and 1/44 respectively, as reported on InfoMine (http://www.infomine.com/investment/metal-prices). It is thus important to significantly decrease the Co content and increase the Ni content to lower the cost of NCA. Increasing the Ni content and decreasing the Al content would also increase the specific capacity of the material, which would further decrease the cost of lithium ion cells in terms of $/KWh.

Ni-rich NMC materials with a Ni content of up to 85% have been studied in the literature. It was reported that oxygen or dry-air environment as well as relatively low sintering temperatures (700–850°C) are required to lower the Ni\textsubscript{Li} content in Ni-rich NMC materials. However, the impacts of synthesis conditions on NCA with high Ni content (80% - 100%) have not been systematically explored in the literature. In Ni-rich NMC materials, the presence of Mn\textsuperscript{4+} promotes the existence of Ni\textsuperscript{3+}, to maintain charge neutrality, which can migrate to the Li layer. In high-Ni NCA materials, all the transition metals stay at 3+, thus the content of Ni on the Li layer could be low. The impact of Al on the synthesis requirements also need to be explored. This work studies the impact of the key synthesis steps, including the oxygen flow rate, heating temperature, initial Li to transition metal (Li/TM) ratio and heating time on the physical, structural and electrochemical properties of NCA with Ni content above 80%.

J. Li et al. recently reported the observation of kinetic hindrance of lithium diffusion in NCA. They showed that the differential capacity vs voltage (dQ/dV vs V) peak of Li/NCA half cells at ~3.5 V is strongly dependent on temperature and testing current. It was discussed that charge-discharge capacity retention can be improved when the dQ/dV vs V peaks in NCA at ~3.5 and 4.17 V (vs Li/Li\textsuperscript{+}), that show kinetic hindrance due to poor lithium diffusion, were partially or completely avoided during charge discharge cycling. This work will further discuss the impact of synthesis conditions on the peaks in dQ/dV vs V of Li/NCA cells at 3.5 V and 4.17 V and on the cycling stability of the material.

Experimental

Reagents used for the synthesis of NCA included nickel cobalt aluminum hydroxide precursors with Ni: Co: Al ratios of 88: 09: 03, 90: 05: 05 and 92: 05: 03 provided by Hunan Zoomwe Zhengyuan Advanced Material Trade Co., Ltd and LiOH·H2O (purity >99.8%, FMC Corporation).

Reagents used for coin cells included 1:2 v/v ethylene carbonate-diethyl carbonate (EC:DEC, BASF, purity 99.99%) and lithium hexafluorophosphate (LiPF\textsubscript{6}, BASF, purity 99.9%, water content 14 ppm).

Synthesis procedures.—The NCA precursors were mixed with a stoichiometric equivalent of LiOH·H2O by hand grinding using a mortar and pestle until a homogenous consistency was achieved (about 10–15 minutes). Samples with Li/TM molar ratios of 1.0, 1.02 and/or 1.05 were prepared. The powder mixtures were sintered at 480°C for 3 h and then cooled to room temperature. The heated powder mixtures were ground again and sintered at 480°C for another 2 h before sintering at designated temperatures for 12 h or 24 h. The heating was done in a tube furnace under the flow of oxygen. A Thermo-Scientific tube furnace (Lindberg Blue M with UP150 controller) was used for the heating process. The dimensions of the tube were 4.4 cm in diameter and 1.22 m in length. Flat alumina crucibles with dimensions of 0.5 cm in depth, 2.7 cm in width and 3.8 cm in length were used to hold the samples. 2 g of precursors were used for the synthesis of each sample, which together with LiOH·H2O...
filled up ~95%, by volume, of the crucible. Three samples were heated at the same time under the same conditions. The crucibles were arranged in series near the center of the furnace tube. Unless specified otherwise, the heating and cooling rate was 10 °C/min. The final product is referred to by composition – initial Li/TM ratio – temperature - heating time. For example, the sample with 90% Ni, 5% Co and 5% Al made with an initial Li/TM ratio of 1.05 at 700 °C for 12 h is called NCA900505-1.05-700. Some elements in the naming scheme may be eliminated for convenience, which will be clear in the context. The synthesized samples were stored in sealed containers in an argon-filled glove box to minimize air exposure.

**Scanning electron microscopy imaging (SEM).**—A NanoScience Phenom Pro G2 Desktop Scanning Electron Microscope (SEM) with a backscattered electron detector was used to study the morphology of the samples synthesized at Dalhousie University. Samples were prepared by mounting the powder on adhesive carbon tape prior to imaging. The images of samples were collected with an accelerating voltage of 5 kV and current of 10 μA.

**Powder X-ray diffraction (XRD).**—Powder X-ray diffraction (XRD) was carried out using a Siemens D5000 diffractometer equipped with a Cu target X-ray tube and a diffracted beam monochromator. Diffraction patterns were collected in the scattering angle (2θ) range of 15–70° at 0.02° intervals with a dwell time of 3 s. A 1° divergence slit, 1° anti-scattering slit and 0.2 mm receiving slit were used for the measurements.

**Titration for measuring residual LiOH and Li$_2$CO$_3$ content.**—The 0.1 M NaOH solution was first calibrated with potassium hydroxide (Sigma-Aldrich, purity ≥ 99.95%), which was then used to calibrate the 0.05 M HCl solution. 0.1 g of the synthesized materials were first submerged and stirred in 30 mL deaerated deionized water (18 MΩ) for 20 mins. The solution and powder mixture were titrated with 0.05 M HCl solution using a G20S Compact Titrator (METTLER TOLEDO) at room temperature. The contents of LiOH or Li$_2$CO$_3$ in the liathed samples were calculated from the ratio of the weight of LiOH or Li$_2$CO$_3$ calculated from the titration results and the weight of the original NCA sample.

**Coin cells.**—Electrodes were made following the procedures set out in the paper by Marks et al.37 A slurry with a mixture of 94 wt% active material, 3 wt% Super-S carbon black and 3 wt% PVDF with NMP as the solvent was first prepared. Electrodes were made by coating the slurry on an Al foil with a 150 μm thickness by spreading followed by drying at 120 °C for 3 hours in air. The electrodes were then calendared at a pressure of about 2000 atm. Single side coated electrodes were punched (1.2 cm diameter) for coin cells. The active material loading was ~ 15 mg/cm². The electrodes were dried overnight at 120 °C in a vacuum oven before use. The electrolyte used was 1.0 M LiPF$_6$ in EC:DEC (1:2). The separators used were one Celgard 2320 (Celgard) next to the lithium electrode and one polypropylene blown-microfiber separator (3M) adjacent to the positive electrode. Galvanostatic charge/discharge cycling using standard 2325 coin cells with lithium metal as the negative electrode was done using an E-One Moli Energy Canada battery testing system. All the cells were tested with a current density of 10 mAg (~C/20) for 5 cycles between 3.0 and 4.3 V (vs. Li/Li$^+$), respectively, at 30 C.

**Results and Discussion**

**Impact of oxygen flow rate and sintering temperature.**—Figures 1a–1c show the XRD patterns of NCA920503 made at 730 °C with oxygen flow rates of 60, 30 and 15 sccm, respectively. The XRD patterns of NCA920503 made at 820 °C with oxygen flow rates of 60 (d), 30 (e) and 15 (f) sccm, respectively. The initial Li/TM was 1.05. The panels on the right show expanded views of the (104) and (018, 110) reflections. The black dots show the original data points, the solid red lines show the calculated pattern from Rietveld refinement while the green lines show the differences between the measured and calculated patterns. Figure S1 in the supporting information shows the corresponding results for NCA900505. Rietveld refinements were performed on the data assuming a hexagonal layered phase in the R-3 m space group (α-NaFeO$_2$-type structure) to extract lattice information.37 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 compositions, which assume the Li occupation is 1.0 and the sum of Ni, Co, Al occupations are 1.0. Preferred orientation parameters were also fit. Figure 1 shows that the calculated results match the measured data very well. Figures 1a–1c and Figures 1d–1e show that samples made with higher oxygen flow rate show narrower peak width when the sintering temperature was the same. Additionally, Figure 1 shows a clearer separation of the K$_{\alpha}$ and K$_{\alpha}^\prime$ peaks in samples made at higher temperature when the oxygen flow rate was fixed, indicating narrower peaks. Therefore, Figure 1 indicates that samples made at higher temperature showed narrower peaks indicating larger grain size when sintered at higher temperature. Figure S1 shows the same trends for NCA900505.

Figure 2 shows the impurity region between 18–35° in the XRD patterns shown in Figure 1 for NCA920503. Figures 2a–2c show the results for samples made at 730 °C with oxygen flow rates of 60, 30 and 15 sccm, whereas Figures 2a–2c show the corresponding results for samples made at 820 °C. Figure S2 in the supporting information shows the corresponding results for NCA900505. Figures 2d and 2E show the reference XRD patterns of Li$_2$CO$_3$ (JCPDS #00-083-1454) in red and Li$_3$AlO$_3$ (JCPDS 800-027-1209) in blue. Figures 2a–2d show that the main impurity phase was Li$_2$CO$_3$ when the samples...
were made at 730 °C, and that the intensities of the peaks from the impurity phase decreased with increasing oxygen flow rate. Figure 2a shows that very little Li2CO3 phase was observed when the oxygen flow rate was 60 sccm. The Li2CO3 phase was likely from the small amount of Li2CO3 in the LiOH·H2O starting material that did not react completely. For samples made at 820 °C, Figures 2c and 2d show that only the Li2CO3 impurity phase was observed when the oxygen flow rate was 15 sccm, while the peak intensity was stronger than that of samples made at 730 °C under the same conditions. When the oxygen flow rate increased to 30 and 60 sccm, the Li2CO3 impurity phase was not observed, instead, a Li5AlO4 phase that has reflections at 19.7, 23.7, 23.8, 24.1 and 34.5° appeared. Figure S2 in the supporting information shows similar results for NCA900505.

To confirm the observation of the Li5AlO4 phase, commercial NCA801505 (Ecopro, Korea) was re-heated to 950 °C. Figures S3a and S3b in the supporting information show the XRD patterns of NCA801505 with and without addition of 5% excess LiOH·H2O, respectively, after heating at 950 °C for 2 h with an oxygen flow rate of 60 sccm, whereas Figure S3c show the patterns for the pristine NCA801505. Figures S3a–S3b in the supporting information show the impurity region in XRD patterns of the corresponding samples. Figures S3c and S3d show the XRD patterns of the pristine Eco-pro material which has no impurity phases as received. Figures S3a and S3b show that the Li5AlO4 phase was observed in NCA801505 after heating at 950 °C for 2 h, while the intensities of peaks from the Li5AlO4 phase were stronger when 5% excess LiOH was added. Figure S3 therefore indicates that commercial NCA decomposes to create Li5AlO4 if heated to sufficiently high temperatures and that excess LiOH·H2O promotes more Li5AlO4.

Figure 3 shows the impurity regions in the XRD patterns of NCA900505 made with 60 sccm oxygen flow rate and 20 h sintering time, to summarize the impurity phases observed under different synthesis conditions. Figure 3a shows that the main impurity phase was Li2CO3 when the sample was made with a Li/TM ratio of 1.10 at 730 °C. Figure 3b shows that the main impurity phase was Li5AlO4 when the sample was made with a Li/TM of 1.05 at 820 °C, whereas Figure 3c shows that the no impurity phase was observed when the sample was made with a Li/TM of 0.9 at 820 °C. Figure 3 shows that the Li2CO3 impurity phase appears at relatively low sintering temperatures and when the Li/TM ratio is high, whereas the Li5AlO4 phase appears at the relatively high sintering temperature and relatively high initial Li/TM ratio. A minor Li5AlO4 phase in NCA900505 can be observed at ~750 °C. The critical temperature and Li/TM ratio when the Li5AlO4 phase appears depend on the NCA composition (Ni and Al content) and the excess Li amount used in the heating. The observation of the Li5AlO4 phase indicates that Al segregates at high sintering temperature, which could also happen at low sintering temperature but with much slower kinetics. This may be the first time that the appearance of the Li5AlO4 phase was reported and studied in a systematic way, to our knowledge, in the literature.

Figures 4a and 4b show a summary of the c-axis and NiLi content, respectively, for NCA900505 made at various temperatures as a function of oxygen flow rate, whereas Figures 4c and 4d show the corresponding results for NCA920503. The samples were made with an initial Li/TM ratio of 1.05. The red and black diamonds show the results for samples made at 820 and 730 °C, respectively, with a sintering time of 20 h and varied oxygen flow rates. The blue diamond...
shows the results for samples made at 730 °C with an oxygen flow rate of 60 sccm and a sintering time of 12 h. Figures 4a and 4c show that the c-axis decreased with increasing oxygen flow rate in general when the sintering temperature was the same. NCA900505 made at 730 °C with 20 h heating time and 60 sccm oxygen flow rate showed slightly larger c-axis than the sample made with 30 sccm oxygen flow rate while other conditions were the same. However, when the sample was made with 60 sccm oxygen flow rate and 12 h heating time, the c-axis decreased significantly. This indicates that there may be an increased amount of lithium loss for NCA900505 made at 730 °C with 60 sccm oxygen flow rate when heated for 20 h compared to 12 h. Figures 4b and 4d show that the NiLi content decreased with increasing oxygen flow rate when the sintering temperature was the same. Additionally, samples made at 820 °C showed slightly larger c-axis and NiLi content than samples made at 730 °C under the same conditions. This is likely due to faster lithium loss rates at higher temperature. However, samples made at 820 °C with flow rates of 30 and 60 sccm showed Li3AlO4 impurities, as a result, these samples will not be the focus of discussions in the following sections of the paper. The results regarding the c-axis and NiLi content showed in Figure 4 indicated that the liithiation reaction was more complete at higher oxygen flow rate. This is likely due to more efficient removal of water vapor as a product of the reaction. The presence of water vapor limits the formation rate of the following reactions at a low oxygen flow rate:

\[
\text{Li}_2\text{O} + \delta/2\text{H}_2\text{O} \rightarrow 2\text{LiOH}, \quad \delta\geq 1
\]

where \(\text{Li}_2(\text{Ni},\text{Co},\text{Al})\text{O}_2\delta\) can also be written as \(\text{Li}_2(\text{Ni},\text{Co},\text{Al})_2\text{O}_3\). This reaction is the main reaction. Another reaction to consider is:

\[
\text{Li}_2\text{CO}_3 + \delta/2\text{O}_2 \rightarrow 2\text{Li}_2\text{CO}_3, \quad \delta\geq 2
\]

which is a minor reaction as the Li2CO3 content in LiOH · H2O is very low.

Reactions 1 and 2 can help explain the results shown in Figure 2. For example the intensity of Li2CO3 impurity phase decreased with increasing oxygen flow rate according to Reaction 2. Additionally, water vapor causes Reaction 1 to move to the left, which increases the NiLi content. Condensed water at the end of the furnace tube after cooling was observed when the 15 sccm flow rate was used, but not when 60 sccm flow rate was used. The first sintering step of the LiOH · H2O and precursor (hydroxides) mixture at 480 °C helped remove water vapor generated from the decomposition of the precursor.

In the following discussions, all the materials were made using the 60 sccm oxygen flow rate.

**Impact of initial Li/TM ratio.**—Figure S4 in the supporting information shows the XRD patterns of NCA900505 made at 730 °C for 12 h with Li/TM ratios of 0.9 to 1.10. The expanded view of the c-axis decreased slightly as the sample made with 30 sccm oxygen flow rate while other conditions were the same. However, when the sample was made with 60 sccm oxygen flow rate and 12 h heating time, the c-axis decreased significantly. This indicates that there may be an increased amount of lithium loss for NCA900505 made at 730 °C with 60 sccm oxygen flow rate when heated for 20 h compared to 12 h. Figures 4b and 4d show that the NiLi content decreased with increasing oxygen flow rate when the sintering temperature was the same. Additionally, samples made at 820 °C showed slightly larger c-axis and NiLi content than samples made at 730 °C under the same conditions. This is likely due to faster lithium loss rates at higher temperature. However, samples made at 820 °C with flow rates of 30 and 60 sccm showed Li3AlO4 impurities, as a result, these samples will not be the focus of discussions in the following sections of the paper. The results regarding the c-axis and NiLi content showed in Figure 4 indicated that the liithiation reaction was more complete at higher oxygen flow rate. This is likely due to more efficient removal of water vapor as a product of the reaction. The presence of water vapor limits the formation rate of the following reactions at a low oxygen flow rate:

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where \(\text{Li}_2(\text{Ni},\text{Co},\text{Al})\text{O}_2\delta\) can also be written as \(\text{Li}_2(\text{Ni},\text{Co},\text{Al})_2\text{O}_3\). This reaction is the main reaction. Another reaction to consider is:

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In the following discussions, all the materials were made using the 60 sccm oxygen flow rate.

**Impact of initial Li/TM ratio.**—Figure S4 in the supporting information shows the XRD patterns of NCA900505 made at 730 °C for 12 h with Li/TM ratios of 0.9 to 1.10. The expanded view of the (104) and (018, 110) reflections and the impurity regions are also shown in the same row. Rietveld refinement was performed on the data and the results are shown in the same scheme as in Figure 1. Figures 5a and 5b show the c-axis and NiLi content from Rietveld refinements as a function of the initial Li/TM ratio, respectively. Table I shows the detailed refinement results as well as the associated impurity (LiOH and Li2CO3) contents obtained from acid titration. Figure 5a shows that the c-axis decreased significantly with increasing initial Li/TM ratio between 0.9 and 1.0, then dropped slightly more as the Li/TM ratio increased from 1.0 to 1.05. The c-axis did not change significantly with further increase of the Li/TM ratio. Table II also shows that the residual LiOH and Li2CO3 contents increased from 0.25(2)% to 1.6(1)% to 2.8(2)% and 2.3(1)% respectively, when the initial Li/TM ratio increased from 1.0 to 1.05.

Figure 6 shows the voltage versus specific capacity of Li/NCA900505 coin cells. The NCA900505 was made at 730 °C for 12 h with varied Li/TM ratios. The cells were tested between 3.0–4.3 V with 10 mA/g current at 30 C. Figures 6a, 6b and 6c show the results for NCA900505 with initial Li/TM ratios of 1.0, 1.02 and 1.05, respectively, whereas Figures 6a, 6b and 6c show the corresponding differential capacity vs. voltage (dQ/dV vs V) plots. The black solid lines and the red dashed lines show results from repeated cells. Table II shows a summary of the reversible and irreversible capacities (IRC) for the corresponding samples. Table II shows that reversible capacity of NCA900505 increased from 210.6 (2) to 2202 (2) mA/hg when the initial Li/TM ratio increased from 1.0 to 1.02, which did not change significantly with a further increase of the Li/TM ratio. Table II also shows that the IRC decreased first and then stabilized with increasing Li/TM ratio. Figures 6a, 6b and 6c show that the major differences in the dQ/dV vs V curves of the samples are in the 3–3.6 V region. The peak during charge indicated by the blue arrows became sharper and the peak during discharge indicated by the red arrows became more pronounced when the initial Li/TM ratio increased from 1.0 to 1.05. The indicated peaks at ~ 3.5 V have been associated with a kinetic hindrance of lithium diffusion as discussed by J. Li et al. 35

Figure 7a shows the capacity as a function of cycle number for NCA900505 made with initial Li/TM ratios of 1.0, 1.02 and 1.05 from the same cells discussed in Figure 6. The cells wereycled with 10 mA/g current (~C/20) for 3 cycles and then cycled with 40 mA/g current (~C/5) for 21 cycles at 30 C between 3.0–4.3 V. The red diamonds, blue triangles and black circles show the results for NCA900505 made with initial Li/TM ratios of 1.0, 1.02 and 1.05, respectively. The results from two pair cells are shown for each sample. Figure 7a shows that the three samples had similar capacities of ~200 mA/hg at a C/5 rate. Table II shows that the sample with an initial Li/TM ratio of 1.0 had the best C/5 specific capacity even though it had the smallest capacity at a C/20 rate. Figure 7a also shows that the sample with an initial Li/TM ratio of 1.0 had the best capacity retention, while the samples with initial Li/TM ratios of 1.02 and 1.05 lost ~20 mA/hg capacity in 20 cycles.
Table I. Detailed refinement results for NCA900505 made at 730°C with a 12 h sintering time with Li/TM ratios of 0.9 to 1.10 as well as the associated impurity (LiOH and Li₂CO₃) contents obtained from acid titration. “n/a” means that titration was not performed.

| Li/TM  | a (±0.0004 Å) | c (±0.001 Å) | Ni/Li (±0.5%) | Bragg-f | LiOH (±0.02%) | Li₂CO₃ (±0.1%) |
|-------|---------------|--------------|--------------|---------|---------------|---------------|
| 0.9   | 2.8735        | 14.210       | 4.9          | 1.76    | n/a           | n/a           |
| 0.95  | 2.8714        | 14.206       | 4.0          | 1.75    | n/a           | n/a           |
| 1     | 2.8692        | 14.198       | 1.0          | 1.41    | 0.25          | 1.6           |
| 1.02  | 2.8694        | 14.194       | 0.9          | 1.56    | 0.30          | 1.4           |
| 1.05  | 2.869        | 14.192       | 0.8          | 1.82    | 0.28          | 2.3           |
| 1.1   | 2.8703        | 14.193       | 1.5          | 1.95    | n/a           | n/a           |

Table II. The summary of the reversible and irreversible specific capacity for NCA900505 made at 730°C for 12 h with varied Li/TM ratios.

| Li/TM  | 1st CC (mAh/g) | 1st DC (mAh/g) | 1st IRC (mAh/g) | 1st IRC% | C/5 capacity (mAh/g) | C/5 Rate capability |
|-------|----------------|----------------|-----------------|----------|----------------------|---------------------|
| 1.00  | 239(1)         | 210.6(2)       | 29(1)           | 12.0(5)  | 200.1(2)             | 95.2                |
| 1.02  | 243(1)         | 220.2(2)       | 22.4(4)         | 9.2(2)   | 202(1)               | 91(1)               |
| 1.05  | 242.2(8)       | 218.5(7)       | 23.6(0)         | 9.8(0)   | 200.5(7)             | 91.2 (5)            |

Figures 7b, 7c and 7d show dQ/dV vs. V, before (cycle 5) and after (cycle 24) the C/5 cycling test in black and red lines, respectively, for samples with initial Li/TM ratios of 1.0, 1.02 and 1.05, respectively. Figure 7b shows that there was little change in dQ/dV vs. V during cycling for the sample with an initial Li/TM ratio of 1.0. Figures 7c and 7d show that dQ/dV vs. V for the samples with initial Li/TM ratios of 1.02 and 1.05 changed significantly during cycling, mostly in the peaks at ~3.5 V (discharge) and ~4.17 V (charge). The shifts of the peaks in dQ/dV vs. V at the beginning of charge and the beginning of discharge indicates significant impedance growth during cycling. Table I showed that the impurity content of LiOH and Li₂CO₃ was similar between samples with Li/TM ratios of 1.0 and 1.02, while the sample with an initial Li/TM ratio of 1.05 had much larger impurity content. As a result, the differences in cycling stability.
are not simply due to residual lithium compounds at the surface. Further discussions regarding the cycling performance will be discussed later.

Based on these results, it is important to optimize the initial Li/TM ratio for a given NCA composition in order to achieve the highest reversible capacity and a minimal content of residual lithium compounds on the surface, when other conditions are fixed such as oxygen flow rate, sintering temperature and heating time. However, it appears to be a special case for NCA that the dQ/dV vs. V peaks that are associated with kinetic hindrance of lithium diffusion at \( \sim 3.5 \) and 4.17 V are very sensitive to the synthesis conditions such as the initial Li/TM ratio, which affects the crystallite structure including the c-axis and the NiLi content. The correlation between the dQ/dV vs. V peak at \( \sim 3.5 \) V with cycling stability will be discussed later.

Besides the initial Li/TM ratio, oxygen flow rate and sintering temperature, sintering time can also affect the properties of the materials. Longer sintering time could lead to closer completion of Reactions 1 and 2 in the forward direction. However, longer sintering time could also lead to the gradual decomposition of the lithiated product in an oxygen environment as shown by Reaction 3 below:\[^{38-40}\]

\[
\text{Li} (\text{Ni}_{x} \text{Co}_{y} \text{Al}_{z}) \text{O}_2 = \text{Li}_{1-x} (\text{Ni}_{x} \text{Co}_{y} \text{Al}_{z}) \text{O}_{2-x} + \delta/2 \text{Li}_2\text{O}_{2x/2}, \quad [3]
\]

where \( \text{Li}_{1-x} (\text{Ni}_{x} \text{Co}_{y} \text{Al}_{z}) \text{O}_{2-x} \) can also be written as \( \text{Li}_x (\text{Ni}_{x} \text{Co}_{y} \text{Al}_{z})_2 \text{O}_2 \) (\( \alpha = (2-2\delta)/2, \delta \leq 1 \)) and \( x + y + z = 1 \) (\( 0.8 \leq x \leq 1, 0 \leq y \leq 0.2, 0 \leq z \leq 0.2 \)). This would lead to lithium loss in the lithiated materials. In general, lithium loss occurs rapidly at the beginning of heat-treatment of LiMO\(_2\) (M = Ni, Co and Al) due to rapid lithium loss at the grain boundaries, which is followed by a slower process due to slower lithium diffusion from the bulk to the lithium-poor surface.\[^{36-40}\] It was shown by Antolini et al.\[^{39}\] that the lithium loss rate is proportional to \( t^{0.5} \) at a given temperature for a diffusion-controlled process. The impact of sintering time on the synthesis of various NCA compositions will, thus, be discussed in detail.

**Impact of sintering time.**—Figure 8 shows an expanded view of certain regions in the XRD patterns of samples made at 730 \( ^\circ \)C with an initial Li/TM ratio of 1.02, but with different sintering times. Figures 8a–8c show an expanded view of the (104) reflections from NCA920503, NCA900505 and NCA880903, respectively, made with a 12 h sintering time, while Figures 8d–8f show the corresponding results for samples made with a 24 h sintering time. Figures 8a–8f show an expanded view of the (018) and (110) reflections from the corresponding samples. The calculated results from Rietveld refinement are shown in the same way as in Figure 1. Table III shows the XRD fitting results and the impurity contents of LiOH and Li\(_2\)CO\(_3\) measured from acid titration. Figure 8 shows that the XRD peaks became sharper for NCA880903 when the heating time increased from 12 to 24 h, which suggests larger grain size after longer heating time. Table III shows that the c-axis and NiLi content decreased slightly with increasing heating time for NCA920503 and NCA900505, suggesting slight lithium loss after long sintering time. Figure 8 shows that the XRD peaks became broader for NCA920503 and NCA900505 when the heating time.
increased from 12 to 24 h. This is possibly caused by inhomogeneous strain in the material caused by lithium loss during long-time heating. Figure 8 and Table III suggest that the impact of heating time on the structural properties depends on NCA composition when other conditions are the same. Additionally, Table III shows that the amount of residual lithium compounds decreased significantly with increasing heating time from 12 to 24 h for all samples studied.

Figures 9a and 9c show the SEM images of NCA900505 made with heating times of 12 and 24 h, respectively, whereas Figures 9b and 9d show the corresponding results at a larger magnification. Figure 9a shows that black dots on the surface of the sample made with 12 h heating time can be observed which are likely residual lithium compounds, as the images were taken in backscattered electron (BSE) mode that is sensitive to atomic number contrast (Z-contrast). Figure 9c shows that very few black spots can be observed on the surface of samples made with 24 h heating time, which agrees with the titration results shown in Table III that the amount of residual lithium compounds decreased with increasing heating time. Additionally, Figures 9b and 9d show that the particle size increased with increasing heating time, which is consistent with the XRD results that show increasing grain size in Figures 8c and 8f.

Figure 10 shows the electrochemical results for samples made with different heating times. The cells were tested between 3–4.3 V with C/20 current (10 mA/g) for three cycles followed by cycling with C/5 current (40 mAh/g) for 21 cycles at 30°C. Figures 10a–10c show the voltage as a function of capacity for NCA880903, NCA900505 and NCA920503 made with 12 h sintering time, respectively, whereas Figures 10d–10e show the corresponding results for samples made with 24 h sintering time. Figures 10A–10F show dQ/dV vs. V for the corresponding samples. The black solid lines and red dashed lines show results for repeated cells at a C/20 rate, while the green lines show the results for the C/5 cycle. The second cycles of the C/20 test and C/5 test were selected for the dQ/dV vs. V plot. Table IV shows a summary of capacities of the corresponding samples. Figures 10a–10f and Table IV show that NCA880903 made with a 12 h heating time has a reversible capacity of 214.9(1) mAh/g and an IRC of 10.1(8)%, whereas NCA880903 made with 24 h heating time showed slightly higher reversible capacity and lower IRC of 218(1) mAh/g and 8(1)%, respectively. These results are consistent with the XRD studies in Figure 8 and Table III that NCA880903 made with a 24 h heating time showed a smaller c-axis and a smaller NiLi content due to more completed reactions. Moreover, Table IV shows that NCA880903 made with a 12 h heating time presented slightly better C/5 rate capability than the sample made with 24 h heating time. Figures 10a–10f and Table IV also shows that NCA900505 and NCA920503 made with 12 h heating time had reversible capacities of 220(2) and 228.2(5) mAh/g, respectively, while the IRC was less than 10%. When the heating time increased to 24 h, the reversible capacities decreased slightly to

### Table III. Detailed refinement results for NCA920503, NCA900505 and NCA880903 made with 12 and 24 h sintering time at 730°C with an initial Li/TM ratio of 1.02, as well as the associated impurity (LiOH and Li₂CO₃) contents obtained from acid titration.

| Composition | Time (h) | \(a\) (±0.0004 Å) | \(c\) (±0.001 Å) | NiₓLi (±0.5%) | Bragg-R | LiOH (±0.02%) | Li₂CO₃ (±0.1%) |
|-------------|---------|-----------------|----------------|-----------------|---------|----------------|----------------|
| 880903      | 12      | 2.8668          | 14.194         | 0.6             | 1.86    | 0.25           | 0.8            |
| 880903      | 24      | 2.8684          | 14.189         | 0.5             | 2.35    | 0.17           | 0.5            |
| 900505      | 12      | 2.8694          | 14.194         | 0.9             | 1.79    | 0.30           | 1.4            |
| 900505      | 24      | 2.8698          | 14.201         | 1.4             | 2.23    | 0.04           | 0.9            |
| 920503      | 12      | 2.8731          | 14.198         | 1.6             | 1.72    | 0.11           | 0.7            |
| 920503      | 24      | 2.8709          | 14.199         | 1.6             | 1.72    | 0.11           | 0.7            |
Figure 9. The SEM images of NCA900505 made with 12 h (a, b) and 24 h (c, d) heating time, respectively.

Figure 10. Voltage as a function of specific capacity for NCA880903 (a), NCA900505 (b) and NCA920503 (c) made with 12 h sintering time, respectively. Voltage as a function of specific capacity for NCA880903 (d), NCA900505 (e) and NCA920503 (f) made with 24 h sintering time, respectively. dQ/dV vs. V for NCA880903 (A), NCA900505 (B) and NCA920503 (C) made with 12 h sintering time, respectively. dQ/dV vs. V for NCA880903 (D), NCA900505 (E) and NCA920503 (F) made with 24 h sintering time, respectively. The second cycles of the C/20 test and C/5 test were selected for the dQ/dV vs V plot. The cells were tested between 3–4.3 V with C/20 current (10 mA/g) for three cycles followed by cycling with C/5 current (40 mAh/g) for 21 cycles at 30 °C.
due to differences in the crystallite lattice such as the NiLi content, the XRD observation in Figure 8. It shows that the impact of sintering time trends for NCA880903 and for the other samples are opposite. This is capability than the same samples made with 24 h heating time. The NCA900503 made with 12 h heating time showed worse C/5 rate capacity loss from C/20 to C/5 was mostly from the 3–3.6 V region. Moreover, Figures 10A and 10B show that the 3.6 V peaks during both charge and discharge were less pronounced in NCA880903 made with 12 h than with 24 h heating time. This explains why the NCA880903 sample made with 24 h heating time showed better rate capability than NCA880903 made with a 12 h heating time, as capacity loss from C/20 to C/5 was mostly from the 3–3.6 V region. Figures 10B and 10E show that NCA900503 made with 12 h heating time had more pronounced peaks at ~3.5 V than that of the sample made with 24 h heating time, while Figures 10C and 10F show the same trends for NCA920503. This explains why NCA900505 and NCA920503 made with 12 h heating time showed worse C/5 rate capability than the same samples made with 24 h heating time. The trends for NCA880903 and for the other samples are opposite. This is because that the reactions were more complete for NCA880903 with longer heating time whereas lithium loss occurred in NCA900505 and NCA920503 during the 24 h heating. These results agree with the XRD observation in Figure 8. It shows that the impact of sintering time can depend on the NCA composition. Additionally, the differences in the 3.6–4.1 V regions of dQ/dV vs. V of NCA samples made with 12 and 24 h heating time are minimal. Figure 10 shows that dQ/dV vs. V peaks in NCA that are related to kinetic hindrance of lithium diffusion at ~3.5 V are very sensitive to the sintering time, and these peaks are related to the reversible capacity, IRC and rate capability. This can be due to differences in the crystallite lattice such as the NiLi content, the level of lithiation or residual lithium compounds on the surface. Figures 11a–11c show the capacity as a function of cycle number for NCA880903, NCA900505 and NCA920503, respectively. The blue crosses and the red diamonds show the results for samples made with 12 and 24 h heating time, respectively. Figures 11a–11c show dQ/dV vs. V for NCA880903, NCA900505 and NCA920503 made with 12 h heating time during the C/5 cycles, whereas Figures 11d–11f show the results for the corresponding samples made with 24 h heating time. The black and the red lines show dQ/dV vs. V of the fifth and the 24th cycle, respectively, corresponding to the cycling data displayed in Figures 11A–11C. Figures 11A shows that NCA880903 made with 12 h heating time showed slightly better capacity retention than the material made with 24 h heating time. Figures 11a and 11b show that the changes during cycling in dQ/dV vs. V of NCA880903 made with a 12 h heating time were less than those of the material made with 24 h heating time, which agrees well with the cycling results in Figure 11A. Recall that NCA880903 made with a 12 h heating time had a larger c-axis, larger NiLi content and smaller 3.6 V peaks in dQ/dV vs. V than those of the sample made with 24 h heating time. Additionally, Table III showed that NCA880903 made with 24 h heating time had lower amounts of residual lithium compounds than the corresponding sample made with 12 h heating time. As a result, residual lithium compounds may not be the cause of the poor cycling stability of NCA880903 made with 24 h heating time. The trends for NCA880903 and for the other samples are opposite, which were explained in the discussion of Figure 10. This shows that the impact of sintering time on cycling stability can depend on the NCA composition.

Figures 11B and 11C show that the NCA900505 and NCA920503 samples, respectively, made with a 12 h heating time showed much worse capacity retention than the samples made with 24 h heating time. Figures 11b and 11c show that the changes in dQ/dV vs. V during cycling were mostly at the 3.6 V (charge) and 4.17 V peaks. The voltages at the beginning of charge shifted to higher values while the voltages at the beginning of discharge shifted to lower values, which indicate impedance growth in the cell. The areas of the peak at 4.17 V during charge decreased from cycle 5 to cycle 24, which could be related to impedance growth so that the cells reached the upper cutoff voltage faster so that the capacity in this region could not be fully delivered. Additionally, little changes in dQ/dV vs. V in the middle range between 3.6–4.1 V during cycling were observed. Figures 11c and 11f show that dQ/dV vs. V was much more stable for NCA900505 and NCA920503, respectively, made with 24 h heating time than the corresponding samples made with 12 h heating time. Figure 11 shows that when the same NCA composition was made with different heating time, the samples that had larger 3.6 V peaks in dQ/dV vs. V measured at a C/20 rate presented higher reversible capacity, worse C/5 rate capability as well as worse cycling stability. The same samples also had smaller c-axes and lower NiLi content.

### Table IV. A summary of the reversible and irreversible specific capacity results for NCA920503, NCA900505 and NCA880903 made with 12 and 24 h sintering time at 730°C with an initial Li/TM ratio of 1.02.

| Sample     | 1st CC (mAh/g) | 1st DC (mAh/g) | 1st IRC (mAh/g) | 1st IRC% | C/5 capacity (mAh/g) | C/5 Rate capability (%) |
|------------|----------------|----------------|-----------------|----------|----------------------|-------------------------|
| 880903_12h | 239(2)         | 214.9(1)       | 24(2)           | 10.1(8)  | 207.4(8)             | 94.2(2)                 |
| 880903_24h | 236(2)         | 218(1)         | 18(2)           | 8(1)     | 206.6(9)             | 93.9(1)                 |
| 900505_12h | 243(1)         | 220(2)         | 22(4)           | 9(2)     | 202(2)               | 91.2(3)                 |
| 900505_24h | 236.4(2)       | 214(1)         | 22(1)           | 9(1)     | 200(1)               | 93.2(8)                 |
| 920503_12h | 244.5(7)       | 228.2(5)       | 16.3(2)         | 6.6(0)   | 203(1)               | 89.7(1)                 |
| 920503_24h | 242.5(5)       | 225(1)         | 17.5(2)         | 7.2(2)   | 208(1)               | 92.5(1)                 |

214(1) and 225(1) mAh/g for NCA900505 and NCA920503, respectively, while the IRC increased slightly. These results are consistent with the XRD studies in Figure 8 and Table III that the c-axis and NiLi content increased with longer heating time for these samples due to slight lithium loss. Additionally, Table IV also shows that the C/5 rate capability of NCA900505 and NCA920503 made with 12 h heating time was worse than that of the samples made with 24 h heating time.

The impact of synthesis conditions on dQ/dV vs. V and cycling stability.—To further examine the changes in the dQ/dV vs. V before and after cycling, the cells were tested for two cycles with a C/20 rate and two cycles with a C/40 rate after the C/5 cycling at 30°C. Figures 12a and 12b show the specific capacity as a function of cycle number for NCA900505 and NCA920503, respectively, made with 12 h heating time at 730°C with an initial Li/TM ratio of 1.02. The red, green, black and blue triangles show the capacity of the first C/20 cycles, the C/5 cycles, the recovered C/20 and C/40 cycles, respectively. Figures 12c and 12d show the corresponding dQ/dV vs. V of the C/20 cycle before the C/5 cycling, the C/20 cycle after the C/5 cycling and the C/40 cycle after the C/5 cycling in red, black and blue lines respectively. Figure 12a shows that the capacities of NCA900505 and NCA920503 made with 12 and 24 h heating time at 30°C with an initial Li/TM ratio of 1.02.
Figure 11. The specific capacity as a function of cycle number for NCA880903 (A), NCA900505 (B) and NCA920503 (C) cells, respectively. The blue crosses and the red diamonds show results for samples made with 12 and 24 h heating time, respectively. The dQ/dV vs. V for NCA880903 (a), NCA900505 (b) and NCA920503 (c) made with 12 h heating time during the C/5 cycles. The dQ/dV vs. V for NCA880903 (d), NCA900505 (e) and NCA920503 (f) made with 24 h heating time during the C/5 cycles.

made with 12 h heating time during the C/20 cycles before the C/5 cycling and the C/20 and C/40 cycles after the C/5 cycling were 221, 211 and 216 mAh/g, respectively. Figures 12a and 12b show the capacity can be partially recovered when the cells were tested with a slower rate for NCA900505 and NCA920503 made with 12 h heating time. Figures 12c and 12d show that the dQ/dV vs. V peaks at ~3.5 V during discharge were suppressed significantly, when measured with a C/20 rate after cycling, for NCA900505 and NCA920503 made with a 12 h heating time, whereas the corresponding peaks during charge shifted to higher voltages. Additionally, the regions between ~3.6 and 4.1 V in dQ/dV vs. V were not affected during cycling. Figures 12c and 12d also show that the dQ/dV vs V peaks at ~3.5 V can be mostly recovered when measured at C/40 rate after cycling. Figure 12c shows that the dQ/dV vs. V peak at 4.17 V for NCA900505 made with a 12 h heating time during charge can be almost completely recovered when measured at C/20 or C/40 rate. These results indicate that the cell failure is mostly due to polarization growth in the cell, which can be caused by impedance growth and/or increased kinetic hindrance at low and high state of charge in NCA.

To study the impact of residual lithium compounds, 1 wt% Li₂CO₃ was purposely mixed with NCA920503 made with 24 h heating time. This sample is referred to as NCA_24h + 1% Li₂CO₃. The mixture was tested in coin cells and compared to NCA920503 made with 12 and 24 h heating times. Figures 13a and 13b show the voltage vs capacity and dQ/dV vs. V results measured with C/20 rate at 30 °C, respectively. Figures 13c and 13d show the dQ/dV vs. V measured with C/5 rate and the corresponding capacity vs cycle number, respectively. The blue and red lines show the results for NCA920503 made with 12 h and 24 h heating time, respectively, which are referred to as NCA_12h and NCA_24h, respectively. The green and black lines show the results for NCA_24h + 1% Li₂CO₃, which are from repeated cells. Figure 13a shows that voltage at the beginning of charge in the first cycle for NCA_24h + 1% Li₂CO₃ was much higher than that for NCA_12h and NCA_24h, which could be related to the added Li₂CO₃.41,42 Additionally, Figure 13a shows that NCA_24 + 1% Li₂CO₃ has smaller first charge capacity and larger irreversible capacity than NCA_12h and NCA_24h. Figure 13b shows that the dQ/dV vs. V peak at 3.5 V for NCA_24h + 1% Li₂CO₃ was smaller than that of NCA_24h during discharge, whereas, the peak during charge shifted to higher voltage slightly. Additionally, Figure 13b shows that the dQ/dV vs. V peaks at ~3.5 V for NCA_12h were larger than those of NCA_24h during both charge and discharge. Figure 13c shows that the dQ/dV vs. V peak at ~4.2 V during charge was almost the same for NCA_24h + 1% Li₂CO₃ and NCA_24h while the peak shrank significantly for NCA_12h when measured with C/5 rate. Figure 13d shows that NCA_12h had the worst capacity retention, while the capacity retention for NCA_24 + 1% Li₂CO₃ and NCA_24h were similar. However, NCA_24h + 1% Li₂CO₃ had lower capacities than NCA_12h and NCA_24h, likely due to larger impedance when Li₂CO₃ was added. Figure 13c shows that the dQ/dV vs. V peak for NCA_24h + 1% Li₂CO₃ shifted slightly to higher voltages during charge and lower voltages during discharging compared to NCA_24h.
Figure 12. Specific capacity as a function of cycle number for NCA900505 (a) and NCA920503 (b) made with 12 h heating time at 730°C and an initial Li/TM ratio of 1.02. dQ/dV vs. V for NCA900505 (c) and NCA920503 (d) made with a 12 h heating time at 730°C and an initial Li/TM ratio of 1.02 before and after cycling. The cells were tested for two cycles with a C/20 rate and two cycles with a C/40 rate after the C/5 cycling at 30°C.

Recall that the content of residual lithium compounds in NCA_12h was much larger than NCA_24h. Figure 13 suggests that the differences in the dQ/dV vs. V and cycling stability of NCA samples made with different heating times were not caused by the differences in the content of residual lithium compounds, but by the differences in the crystallite lattice such as NiL1.

Figure 14 shows the dQ/dV vs. V for NCA900505 made using four different conditions including samples made with Li/TM ratios of 1.0, 1.02 and 1.05 using a 12 h heating time and a Li/TM ratio of 1.02 using a 24 h heating time. These samples are labelled 1.0–12h, 1.02–12h, 1.05–12h and 1.02–24h, respectively. Figures 14a–14c show dQ/dV vs. V for these samples measured using a C/40 rate at 40°C, a C/20 rate at 30°C and a C/5 rate at 30°C, respectively. The black, red, blue and...
Figure 14. dQ/dV vs. V for NCA900505 made from four different conditions including samples made with Li/TM ratios of 1.0, 1.02 and 1.05 using 12 h heating time and a sample with a Li/TM ratio of 1.02 using a 24 h heating time. These are labelled as 1.0–12h, 1.02–12h, 1.05–12h and 1.02–24h, respectively. dQ/dV vs. V for the corresponding samples measured with a C/40 rate at 40°C (a), C/20 rate at 30°C (b) and C/5 rate at 30°C (c), respectively. dQ/dV vs. V for 1.0–12h (d), 1.02–12h (e) and 1.05–12h (f) measured at various conditions. The blue, red and black lines show the results measured with a C/40 rate at 40°C, a C/20 rate at 30°C and a C/5 rate at 30°C, respectively.

green lines show the results for samples 1.0–12h, 1.02–12h, 1.05–12h and 1.02–24h, respectively. Figure 14a shows that dQ/dV vs. V for the four samples were almost identical and that the charge and discharge peaks were almost symmetrical when measured with a C/40 rate at 40°C. There was no large hysteresis in the 3.6 V peak between charge and discharge. Figure 14b shows dQ/dV vs. V for the four samples were identical in the regions above 3.6 V, and that differences appear in the 3–3.6 V region when cells are tested with a C/20 rate at 30°C. The dQ/dV peak area in the 3–3.6 V region increased in the order of 1.0–12h, 1.02–24h, 1.02–12h, and 1.05–12h. Additionally, large hysteresis was observed between charge and discharge in this region. Figure 14c shows that dQ/dV vs. V for the four samples were almost identical during discharge when cells were tested with a C/5 rate at 30°C, and that differences observed during charge were mostly in the 3–3.6 V region. Figure 14c shows that the discharge peaks in the 3–3.6 V region were supressed significantly when cells were tested at C/5.

Figures 14d–14f show the same results in a different layout. Now dQ/dV vs. V data for the same sample measured at various conditions are plotted in the same panel. The blue, red and black lines show the results measured with a C/40 rate at 40°C, a C/20 rate at 30°C and a C/5 rate at 30°C, respectively. Figures 14d–14f show that when the C-rate increased from C/40 to C/5, the changes in dQ/dV vs. V were mostly in the 3–3.6 V region and in the 4.1–4.3 V regions. During charge, the 3.5 V peak shifted to higher voltage and the voltage at the beginning of charge increased dramatically, whereas the area of the 4.17 V peak decreased slightly. During discharge, the area of the 3.5 V peak decreased significantly while the voltages at the beginning of discharge decreased significantly. Figure 14 shows that the dQ/dV peaks of Li/NCA cells at about 3.5 and 4.17 V are strongly and mildly dependent on temperature and C-rate, respectively, as discussed by J. Li et al. This suggests that lithium diffusion is quite slow at low states of charge and somewhat slow at a high state of charge. Figure 14 also shows that the synthesis conditions, which affects the c-axis and NiLi content of the NCA samples, also impact the lithium diffusion at low and high states of charge.

Figure 15a shows dQ/dV vs. V of NCA900505 samples made using various conditions. This data were measured with a C/20 rate at 30°C (the same graph as Figure 14b). The red arrow indicates the discharge peak between 3.0–3.6 V, which is labelled as Peak 1. Figures 15b and 15c show the correlation of the reversible discharge capacity and capacity retention, respectively, with the maximum of Peak 1.
in dQ/dV vs. V for NCA900505 samples including 1.0–12h, 1.02–12h, 1.05–12h and 1.02–24h, respectively. Figure 15b shows that the reversible capacity increased as the maximum of Peak 1 in dQ/dV vs. V increased. Conversely, Figure 15c shows that the capacity retention decreased as the maximum of Peak 1 in dQ/dV vs. V increased. The same trends can be seen in the data for NCA880903 and NCA920503 made with 12 and 24 h as shown in Figures 10 and 11. The reasons why Peak 1 is strongly correlated with the cycling stability of the NCA materials made at various conditions are not clear, and requires further studies.

Conclusions

One way to lower the cost of lithium ion batteries using NMC or NCA is to lower the Co content in the positive electrode materials. This work systematically studied the impact of the synthesis conditions on the performance of LiNi0.5Co0.2Al0.3O2 (x ≤ 0.8, z ≥ 0.05 and x + y + z = 1) (NCA) with high Ni and low Co content, which has not been fully explored in the literature. The impacts of oxygen flow rate, sintering temperature, initial Li/TM ratio and sintering time were studied.

Adequate oxygen flow rate was critical for the efficient removal of water vapor, as a product of the reactions, to ensure minimal NiLi content. At low temperatures, Li2CO3 was the main impurity phase when the initial Li/TM ratio was high. At relatively high temperatures, Li2Al2O4 was the main impurity phase, which was not observed at low initial Li/TM ratios. The temperature and the initial Li/TM ratio when the Li2Al2O4 phase appeared depend on the NCA composition, in particular, the Li, Ni and Al contents.

At fixed sintering temperature and oxygen flow rate, the c-axis and NiLi decreased with increasing initial Li/TM ratios up to 1.05, while the content of residual lithium compounds increased. Additionally, electrochemical studies showed that the highest reversible capacity was achieved when NiLi was minimum. The dQ/dV vs. V peaks that are associated with kinetic hindrance of lithium diffusion at ∼3.5 and ∼4.17 V were very sensitive to the initial Li/TM ratio.

The impact of sintering time depends on the NCA compositions. Longer sintering time results in a more completed reaction that leads to a decreased c-axis and NiLi content, which was the case for NCA880903. However, longer heating time could also lead to the gradual decomposition of the lithiated product that results in an increased c-axis and NiLi content, which was the case for both NCA900505 and NCA920503. However, the content of residual lithium compounds decreased with increasing heating time. Electrochemical studies showed that the major differences in dQ/dV vs. V of samples made with 12 and 24 h heating time was in the 3–3.6 V region. The reversible capacity, C/5 rate capability and cycling stability were significantly affected by the sintering time. dQ/dV vs. V peaks in NCA that are related to kinetic hindrance of lithium diffusion were very sensitive to the sintering time. By purposely mixing 1 wt% Li2CO3 with NCA920503 made with a 24 h heating time, it was shown that the differences in dQ/dV vs. V and cycling stability of NCA samples made with different heating times were not caused by the differences in the content of residual lithium compounds, but by the differences in the crystallite lattice such as NiLi.

Moreover, dQ/dV vs. V for samples with the same composition but made with varied conditions were almost identical when measured with a C/40 rate at 40 °C, while significant differences could be observed in the 3–3.6 V and 4.1–4.3 V regions when measured with a C/20 rate at 30 °C. The synthesis conditions, which affect the a-axis, c-axis and NiLi content of the NCA samples, apparently have strong impacts on the lithium diffusion at low and high states of charge due to kinetic hindrance of lithium diffusion. Additionally, it was shown that the reversible capacity and cycling stability correlated strongly with the intensity of the dQ/dV vs. V peak at 3.5 V (discharge) (Peak 1) measured with a C/20 rate at 30 °C. The reversible capacity increased while the capacity retention decreased as the maximum of Peak 1 in dQ/dV vs. V increased. Further studies are required to understand the dependence of the dQ/dV vs. V peaks at ∼3.5 and ∼4.17 V on the synthesis conditions as well as the correlation between the intensity of Peak 1 with the cycling stability of the synthesized materials. This study will be of strong interest to both industrial and academic researchers working on the development and understanding of NCA materials.

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