Investigating the Removal of Layered Double Hydroxides in [\(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05+x}\text{O}_2\) (\(x = 0, 0.05\)] Prepared by Coprecipitation

Aaron Liu,1,2* Ning Zhang,2,3 Jing Li,2 Jhoynner Martinez,4 Andreas Korinek,4 Gianluigi Botton,4 and J. R. Dahn1,3,∗∗

1Department of Chemistry, Dalhousie University, Halifax B3H 4R2, Canada
2School of Metallurgy, Northeastern University, Shenyang 110819, People’s Republic of China
3Department of Physics and Atmospheric Science, Dalhousie University, Halifax B3H 4R2, Canada
4Canadian Centre for Electron Microscopy, McMaster University, Hamilton L8S 4L7, Canada

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As lithium ion battery technology expands into more demanding applications such as electric vehicles, attention has shifted toward nickel-rich materials such as \(\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2\) (NCA). Precursor syntheses have therefore attempted different coprecipitation is a common method to synthesize mixed metal hydroxides (M(OH)\(_2\)) M = divalent transition metals) as the precursor materials to the lihated metal oxides. While the syntheses of NMC precursor materials are well understood due to the divalent transition metals, the introduction of Al\(^{3+}\) for NCA precursor materials complicates the synthesis and affects the products significantly. Ammonia is a chelating agent commonly used in NMC precursor synthesis but it does not complex well with Al to produce large spherical particles. NCA precursor syntheses have therefore attempted different routes, using either a different chelating agent,6–11 coprecipitating as carbonates,12 or adding the Al as a separate [Al(OH)\(_x\)] (x > 4) solution.13–16 Another issue is that an extra anion needs to be incorporated into the layered structure in order to balance the charge of the trivalent Al\(^{3+}\) cation, resulting in the formation of a new layered double hydroxide (LDH) phase.27–29 Increases in the Al content of the precursor result in a larger proportion of LDH phase in the material as more anions are incorporated into the material. One serious concern is that the Al and Ni atoms are likely all in the LDH phase, since the presence of Al requires a counterbalancing anion. Thus, the Al may not be uniformly distributed as a solid solution in the material.

LDH phases have been reported in supercapacitor research, even in NCA hydroxides.19,20 LDH in supercapacitor research originated from work on hydroxides, such as nickel hydroxide. There is a large body of work on the 2 known phases of Ni(OH)\(_2\), denoted as α-Ni(OH)\(_2\) and β-Ni(OH)\(_2\).21–27 α-Ni(OH)\(_2\) is isostructural to the LDH phase, with water molecules intercalated between brucite-type layers of Ni(OH)\(_2\). β-Ni(OH)\(_2\) does not have any intercalated molecules. It is known that α-Ni(OH)\(_2\) is readily converted into β-Ni(OH)\(_2\) by a process called chemical ageing.22–26,28,29 Although ageing can occur in pure water or at room temperature, the process accelerates at higher temperatures and/or more alkaline conditions. Incorporated anions, such as nitrates and sulfates, are removed faster than water molecules.22–26 There are two proposed mechanisms for the ageing process. The first is via a dissolution-recrystallization mechanism, where the α-Ni(OH)\(_2\) phase slowly dissolves at high pH29 and precipitates back out as β-Ni(OH)\(_2\).22,24 Another proposed mechanism is that ageing occurs analogously to a zipper, with hydroxide acting as the zipper interlocking when intercalated molecules are expelled, with the differences in interlayer spacing creating compressional forces that squeeze out other intercalated molecules.26 While both proposed mechanisms have some supporting evidence, neither can fully resolve the range of conditions under which ageing is observed. The low solubility of Ni(OH)\(_2\) in neutral or slightly basic conditions makes dissolution-recrystallization unlikely, while the zipper analogy fails to explain why increasingly alkaline conditions speed up the ageing process. It is possible that the two proposed processes do not occur exclusively, but in combination. Unfortunately, there has been little to no work reported on the conversion of LDH phases with trivalent cations to phases with no intercalated molecules, which will be referred to as the removal of LDH hereafter. While it is expected that factors that influence ageing in Ni(OH)\(_2\) will also influence removal of the LDH phase, the inclusion of the trivalent cation and counterbalancing anion adds a new and uncertain aspect to this process.

The literature on NCA materials synthesis often omits reporting precursor characterization5,16,20–23 or commercially supplied precursors are used more or less without comment.34–37 Where precursor characterization was reported, there was a lack of discussion as to the presence, formation, or removal of the LDH phase.9,11,13–15 Even when a group reported precursors with no LDH14 and with LDH15 using the same synthesis method, there was only a brief mention about LDH presence.

In this work, \([\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05+x}\text{O}_2\) (\(x = 0, 0.05\)] precursor materials were prepared by the coprecipitation method. The materials with Al contained appreciable amounts of LDH phase. The precursor materials were then washed in a solution of NaOH to remove the LDH phase. Temperature, NaOH concentration, and stirring time were varied systematically to study their impact on LDH removal. Unwashed and washed samples were characterized by
X-ray diffraction (XRD), inductively coupled plasma optical emission spectrometry (ICP-OES), and thermogravimetric analysis/mass spectrometry (TGA-MS) to monitor LDH content, metal ratios and LDH anions. Scanning electron microscopy (SEM) and photographs were also used to monitor morphological and visual changes. The oxidation state balance in the washed NCA precursor materials containing Al and without corresponding anions is discussed.

**Experimental**

Reagents used in this work included Ni(SO₄)₂•6H₂O (Alfa Aesar, >98%), Co(SO₄)₂•7H₂O (Alfa Aesar, >98%), Al(NO₃)₃•9H₂O (Sigma-Aldrich, >98%), Ni(NO₃)₂•6H₂O (Sigma-Aldrich, >97%), Co(NO₃)₂•6H₂O (Sigma-Aldrich, >98%), NaOH (Fisher, 98.9%), and NH₃ (Sigma-Aldrich, 28–30%). Ni, Co, Al standards (1000 μg/mL, Ultra Scientific), HCl and HNO₃ (Reagent grade, Sigma Aldrich) were used to prepare solutions for ICP-OES measurements.

**Synthesis**—[Ni₀.₈₀Co₀.₁₅]₀.₉₅₋ₓAl₀.₅₀ₓ(OH)₂ (x = 0, 0.05; denoted as 5% Al and 10% Al) materials were synthesized by the coprecipitation method in a continuously stirred tank reactor. Aqueous solutions of Ni:Co:Al molar ratios. The nickel and cobalt reagents were combined into one solution (300 mL, 2 M) while the aluminum reagent was dissolved into a separate solution (150 mL, 0.21 M for 5% Al and 0.44 M for 10% Al) along with NaOH at an Al:OH molar ratio of 5. The solutions were then simultaneously added dropwise, using peristaltic pumps, to a stirred reaction vessel containing NH₃ solution (1 L, 0.5 M). A NaOH solution (10 M) and an NH₃ solution (5 M) were added to maintain a set pH and NH₃ concentration (pH 11.0 and 0.5 M NH₃). The solutions were added over the course of 20 hours, with the reaction vessel kept at 60 °C, stirring at 500 rpm, and under N₂ atmosphere. The vessel was then cooled to room temperature and the precipitate filtered and rinsed four times with water before drying overnight at 80 °C in air.

A batch of 5% Al was synthesized as specified above but prepared with deionized water and nitrate-containing reagents (Ni(NO₃)₂, Co(NO₃)₂, and Al(NO₃)₃). Deionized water, deaerated by boiling, was used to prepare all the solutions for synthesis as well as for rinsing the precipitate after filtration.

**Washing treatment.**—Synthesized materials were subjected to a washing treatment to study the removal of the LDH phase. 1 g of material was added into a beaker containing 40 mL of NaOH solution and stirred on a hot plate. The solutions were stirred at various temperatures (room temperature (20 °C)-80 °C), in various concentrations of NaOH (0 M-15 M), and for various amounts of time (5 min-240 min). The solutions were then filtered, rinsed four times, and dried overnight.

**Characterization.**—XRD patterns of samples were collected with a Siemens D5000 diffractometer equipped with a Cu target X-ray tube and a diffracted beam monochromator. Samples were measured in the scattering angle (2θ) range of 6–76° for 3 s at intervals of 0.05°.

ICP-OES measurements were carried out using a Perkin Elmer Optima 8000 ICP-OES Spectrometer to determine the elemental composition (as metal standards). Standard solutions of 0.5 and 1 μg/mL for Al and 0.1 and 2 μg/mL for Ni and Co were prepared by diluting the standards in 2% HNO₃, 8–10 mg of sample was dissolved in 2 mL of aqua regia (1:3 HNO₃:HCl) before dilution in 2% HNO₃.

TGA-MS measurements were carried out using a TA Instruments SDT Q600 coupled with a Discovery MS. Experiments went from room temperature up to 950 °C at a heating rate of 5 °C/min under an air flow.

SEM imaging was carried out using a NanoScience Phenom G2 Pro Desktop SEM to image samples. Powder samples were prepared by sputtering on adhesive carbon tape.

EDS mapping of the commercial Ni₀.₉₀Co₀.₀₅Al₀.₀₅(OH)₂ sample was carried out at the Canadian Centre for Electron Microscopy. The powder sample was prepared by embedding in carbon paste into a graphite block and then cross-sectioned with a JEOL CP polisher at 6 kV for 4 hours. SEM imaging was performed using a FEI Magellan 400 microscope, equipped with two Oxford XMAX 80 EDS detectors. SEM images were acquired at 2 kV and EDS maps were acquired at 5 kV.

**Results and Discussion**

Figure 1a shows the XRD patterns of the two synthesized materials (5% Al, bottom; 10% Al, middle) compared with a commercial Ni₀.₉₀Co₀.₀₅Al₀.₀₅(OH)₂ material (Guizhou Zoomwe Zhengyuan Advanced Material Co., Ltd., top), along with the reflections for 2 Ni(OH)₂ phases (β-Ni(OH)₂ (blue), JCPDS #00-014-0117; α-Ni(OH)₂•0.75H₂O (red), JCPDS #00-038-0715). The structures for the two phases, β-Ni(OH)₂ and α-Ni(OH)₂•0.67H₂O, are shown in Figs. 1b and 1c, respectively. While the 5% Al and 10% Al samples are not actually composed of β-Ni(OH)₂ and α-Ni(OH)₂ phases, it is believed that the β-Ni(OH)₂ phase is isostructural to an NCA(OH)₂ phase with no LDH and the α-Ni(OH)₂ phase is isostructural to a NCA(OH)₂ phase with LDH. The expected structures of the NCA(OH)₂ phases with and without LDH (referred to hereafter as the LDH phase and the no LDH phase, respectively) are shown later. The most surprising feature in Fig. 1 is that the commercial sample of Ni₀.₉₀Co₀.₀₅Al₀.₀₅(OH)₂ does not contain any sign of the LDH phase, yet it contains 5% Al. This can be seen in some literature samples but, it was uncertain how the charges balanced. This observation was one reason that this study was performed.

As Al content increased from 5% to 10%, the amount of LDH phase present in the XRD patterns of the samples made in-house increased (Fig. 1a). This increase in the LDH phase is expected due to an increase in trivalent Al³⁺, which requires the inclusion of additional anions to balance excess charges. There are 4 possible LDH anions in the material: OH⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻ as well as the possibility for inter-layer H₂O molecules. The source of sulfate and nitrate ions are the metal reagents, and the carbonate can come from dissolved carbon dioxide in water or from impurities in the NaOH. The presence of an LDH phase is concerning, as the Al is likely to be concentrated in the LDH phase and may not be uniformly distributed within the precursor material.

Figure 2 shows results from preliminary tests to remove the LDH phase from the sample with 5% Al. Fig. 2a shows XRD patterns of a
A series of samples washed in 12 M NaOH at various initial temperatures while stirring at room temperature, along with an expanded view of the (001) reflection of the LDH phase at about 11.5° and an arbitrary scale to judge the degree of LDH removal. The scale was used to summarize all the preliminary tests in Fig. 2b and other 5% Al washing treatments. Fig. 2b shows a summary of how various conditions impacted LDH removal from the sample with 5% Al.

Fig. 2b shows that the parameters probed (initial NaOH temperature, NaOH concentration and time spent stirring at room temperature) all influenced LDH removal. As each of these parameters increased, more LDH was removed during the washing treatment. Fig. 2b shows a summary of how LDH removal was influenced by each parameter. The least aggressive conditions which fully removed the LDH phase from the 5% Al sample was washing at 60°C in 12 M NaOH for 15 minutes, depending on whether a lower temperature or lower NaOH concentration is preferable.

The preliminary washing treatments to remove the LDH phase from the 5% Al sample were useful in identifying conditions that affected LDH removal, but stirring at room temperature and varying initial NaOH temperature does not allow for a thorough understanding of the impact of temperature and time. As such, a matrix of washing treatments at 3 temperatures, 3 NaOH concentrations and 4 stirring times was carried out. The solutions were stirred at the set temperature instead of room temperature. The goal of this matrix was to gain a better understanding of each individual parameter, as well as to find the least aggressive conditions needed to completely remove the LDH phase.

Figure 2a shows the XRD results summary of the matrix of studies on the 5% Al sample, with Figs. 2b–2d showing a selected sample series generally based on temperature, NaOH concentration, and stirring time, respectively. Fig. 2 clearly illustrates that as each parameter increased, the prevalence and rate of this color change increased as can be seen in Fig. S2a. The color change sometimes changed color, with the solution going from light green to various shades of brownish green if the solution changed color. As conditions become more aggressive, the prevalence and rate of this color change increased as can be seen in Fig. S2a. The color change
seemed to be independent of LDH removal, as there were samples with LDH completely removed that changed color and samples that did not change color. XRD patterns showed no significant differences in the structure (Fig. S2b), and it is believed that the color change stemmed from the oxidation of Ni or Co, with corresponding removal of hydrogen from a neighboring oxygen but maintaining the layered structure.38–40 This would be similar to what is occurring to the Al as the LDH gets removed, except that Al lost a charge balancing anion and did not undergo oxidation.

Figure 4 shows the ICP-OES results for the matrix of studies on the 5% Al sample. Metal atomic ratios were normalized to 1 to denote the stoichiometric ratios of the metals. The amount of Al lost is reported as the difference of the Al stoichiometric ratio of a washed sample when compared to the “original” unwashed sample. Fig. 4a shows a summary, while Fig. 4b shows the Ni:Co ratio and the (Ni + Co):Al ratio as a function of Al loss. Figs. 4c–4e show results for selected sample series where temperature, NaOH concentration and stirring time were generally varied, respectively.

Fig. 4a indicates that the parameters that improve LDH removal, namely an increase in temperature, NaOH concentration or stirring time, will also increase the amount of Al leached away from the material. Fig. 4b confirms that only Al is leached away, as the Ni:Co ratios remain consistent and the (Ni + Co):Al ratios increased as Al loss increased. This is reasonable, as only Al is noticeably soluble at high pH.13,14,28 This highlights the importance of finding the mildest conditions to fully remove the LDH phase, as those conditions will minimize Al loss of the material. Similar to Fig. 3b, Fig. 4c showed an increase in the loss of Al when the temperature increased from 50 C to 60 C. The maximum Al loss tested in this matrix was a difference of 0.0140 ± 0.0009 in the Al stoichiometric ratio when the sample was washed at 70 C in 12 M NaOH for 15 minutes, so the material has around 3.6% Al remaining after the washing treatment.

Figure 5 shows TGA-MS results for four 5% Al samples: (a) unwashed, (b) washed in deionized water at 70 C, (c) washed in 12 M NaOH at room temperature, and (d) washed in 12 M NaOH at 60 C. Only the sample characterized in Fig. 5d showed complete LDH removal. The top panels of Figs. 5a–5d show the relative mass and rate of mass loss as a function of temperature, while the bottom four panels show the ion currents of 4 m/z ratios as a function of temperature. These m/z ratios correspond to 3 possible LDH anions in the material: OH−, NO3−, and CO32−. The m/z ratio of 18, corresponding to water was also monitored. Since some of the reagents also contained sulfates, m/z ratios corresponding to SO42− were also monitored, but no signals were observed. The difference in backgrounds for m/z ratios of 17, 18 and 44 between Fig. 5a and subsequent samples is attributed to the presence of adsorbed water in the vacuum chamber of the MS.

All the samples tested showed similar trends in mass loss as seen in the top panels of Figs. 5a–5d. Mass loss from the start to around 200 C is attributed to the removal of surface and intercalated water.17,18 The large mass loss between 200 C to 300 C is due to the decomposition of the hydroxide into oxides. LDH anions appeared to evolve from the material during or after the decomposition. The decomposition of the material evolves water, and it is hard to differentiate between water from the LDH phase and water from decomposition. Therefore, more attention will be focused on the lower 2 panels (corresponding to NO3− (mass 30 for NO) and CO32− (mass 44 for CO32−) when looking for LDH anion signals.

In the unwashed sample (Fig. 5a), the MS data indicates that both monovalent NO3− and divalent CO32− are present as LDH anionic species. However, after any sort of washing treatment (Figs. 5b–5d), the nitrate signal disappeared. Since the LDH phase was still present after washing the 5% Al sample with deionized water (degree of LDH removal shown in Fig. 2b and TGA/MS in Fig. 5b) or at room temperature with 12 M NaOH (XRD pattern shown in Fig. 3b and TGA/MS in Fig. 5c), it is believed that anion exchange occurred, and the nitrate anions were exchanged for either hydroxides or carbonates. When the washing treatment completely removed the LDH phase (degree of LDH removal and XRD pattern in Fig. 3 and TGA/MS in Fig. 5d), both the nitrate and carbonate anion signals disappeared as expected. The mass loss of the sample without LDH phase was also
Figure 4. Metal atomic ratios were determined by ICP-OES and normalized to 1, with Al lost (reported as a difference of the Al stoichiometric ratios) being determined by comparison with the unwashed sample. A summary of ICP-OES results (a) and metal ratios as functions of Al loss (b) for the washing of $[\text{Ni}_{0.80}\text{Co}_{0.15}]_{0.95}\text{Al}_{0.05}(\text{OH})_2$ samples are shown. Al stoichiometric ratios of sample series based on temperature (c), NaOH concentration (d), and stirring time (e) are shown along with amount of Al lost.

slightly less than samples with LDH, with the no LDH sample losing around 24% of its original mass and samples with LDH losing around 26%. However, this mass loss difference was not used as a conclusive indication of LDH phase presence in samples due to the unknown amount of surface and intercalated water in the samples.

Washing treatments of the 10% Al sample.—A 10% Al sample was synthesized to see how LDH removal is affected when a material has more LDH phase. Additionally, more LDH should increase the MS signals of the LDH anions, as the nitrate and carbonate signals in Fig. 5 were not very strong.

Figure 5. TGA-MS data (heated to 950°C in air) for the washing of $[\text{Ni}_{0.80}\text{Co}_{0.15}]_{0.95}\text{Al}_{0.05}(\text{OH})_2$ samples ((a) unwashed, (b) deionized water at 70°C, (c) 12 M NaOH at room temperature, and (d) 12 M NaOH at 60°C). The top panels show relative mass and rate of mass loss as a function of temperature, while the bottom 4 panels show the ion currents of m/z 17 (OH), 18 ($\text{H}_2\text{O}$), 30 (NO), and 44 (CO$_2$).
Figure 6a shows XRD patterns of a series of 10% Al samples washed in 12 M NaOH at 70°C for various amounts of time, along with an expanded view of the (001) reflection of the LDH phase and an arbitrary scale to judge the degree of LDH removal. The scale for the 10% Al samples is different than the scale for the 5% Al samples (Fig. 2a), with an enlarged “partial LDH removal” portion to account for the increased amount of LDH in the material.

Figure 6b shows a summary of the XRD results of the washed 10% Al samples. Once again, the summary clearly illustrates that more of the LDH phase is removed as conditions became more aggressive. Fig. 6a shows that LDH removal occurred quickly in the beginning, but required a much longer stir time before LDH was completely removed from the material. Compared to the 5% Al sample, the complete removal of the LDH phase required more aggressive conditions. Washing the 10% Al sample in 15 M NaOH at 80°C completely removed the LDH phase, as well as washing at 70°C in 12 M NaOH for 240 minutes.

Color changes while washing the 10% Al sample were more frequent, due to conditions being more aggressive (Fig. S3a). Again, the color change seemed to be independent of the amount of LDH removal, this time with samples undergoing color change showing both complete LDH removal and incomplete LDH removal (Fig. S3b).

Figure 7 shows the ICP-OES results for the washed and unwashed 10% Al samples. Metal atomic ratios were normalized to 1, and the amount of Al lost reported as a difference of the Al stoichiometric ratios of the washed samples when compared to the unwashed sample. Fig. 7a shows a summary, while Fig. 7b shows the Ni:Co ratio and the (Ni + Co):Al ratio as a function of Al loss. Figs. 7c–7e show samples where temperature, NaOH concentration and stirring time were generally varied, respectively.
Figure 7. Metal atomic ratios were determined by ICP-OES and normalized to 1, with Al lost (reported as a difference of the Al stoichiometric ratios) being determined by comparison with the unwashed sample. A summary of ICP-OES results (a) and metal ratios as functions of Al loss (b) for the washing of [Ni$_{0.80}$Co$_{0.15}$]$_{0.90}$Al$_{0.10}$(OH)$_2$ samples. Al stoichiometric ratios of sample series based on temperature (b), NaOH concentration (c), and stirring time (d) are shown along with amount of Al lost.

Similar to the 5% Al samples (Fig. 4), Fig. 7 shows that the factors that improve LDH removal also increase the amount of Al leached away from the 10% Al samples (Fig. 7a) and that only Al is leached away (Fig. 7b). Fig. 7d shows the effect of NaOH concentration on Al leaching better than Fig. 4d since Fig. 4d only had two data points. The maximum Al loss measured for the 10% Al sample was a difference of 0.043 ± 0.002 in the Al stoichiometric ratios when washed at 70°C in 12 M NaOH for 240 minutes, so the material has around 5.7% Al remaining after the washing treatment.

Figure 8 shows SEM images of the unwashed 10% Al sample (Figs. 8a–8b), after washing at 70°C in 12 M NaOH for 240 minutes (Figs. 8c–8d), and after washing at 80°C in 15 M NaOH for 15 minutes (Figs. 8e–8f). The samples appear to be morphologically similar, with similar particle sizes even after aggressive washing conditions that completely removed the LDH phase. The images in Fig. 8 do not support a dissolution-recrystallization mechanism as the main driver of LDH removal, as the LDH phase was completely removed while particle morphology remained similar. It may be possible that the particle surfaces dissolved slightly and allowed the removal of intercalated molecules, triggering the start of the zipper mechanism.

Figure 9 shows TGA-MS results for four 10% Al samples: (a) unwashed, (b) washed in deionized water at 70°C, (c) washed in 12 M NaOH at room temperature, and (d) washed in 15 M NaOH at 80°C. Only the sample in Fig. 9d showed complete LDH removal as indicated in Fig. 6b. The top panels of Figs. 9a–9d show the relative mass and rate of mass loss as a function of temperature, while the bottom four panels show the ion currents of 4 m/z ratios (corresponding to OH$^-$, H$_2$O, NO$_3^-$ (mass 30 corresponds to NO), and CO$_3^{2-}$ (mass 44 corresponds to CO$_2$) as a function of temperature. Once more, m/z ratios corresponding to SO$_4^{2-}$ were monitored, but no signals were observed.

The signals for both monovalent NO$_3^-$ (NO as mass 30) and divalent CO$_3^{2-}$ (CO$_2$ as mass 44) in the unwashed sample (Fig. 9a), were stronger than in Fig. 5a, indicating more intercalated ions in the 10% Al sample than the 5% Al sample, as expected from a material with more LDH. Unlike the 5% Al sample, the nitrate signal did not disappear, from anion exchange or LDH removal, upon washing in deionized water at 70°C (Fig. 9b), but it did disappear when washing in 12 M NaOH at room temperature (Fig. 9c). This may indicate that the 10% Al sample bonds the LDH anions tighter than the 5% Al sample, perhaps due to the higher density of Al$^{3+}$. When the washing treatment completely removed the LDH phase (Fig. 9d), both the nitrate and carbonate anion signals disappeared. The mass loss of the sample without LDH phase was also slightly less than samples with LDH, with the no LDH sample losing around 23% of its original mass and samples with LDH losing around 26–28%. Once again, this mass loss difference was not used as a conclusive indication of LDH phase presence in samples due to the unknown amounts of water in the samples, but it was noted that this difference was also observed in the 5% Al sample.

Washing treatments of 5% Al prepared with deaerated water and nitrate reagents (DN).—From the TGA-MS data for both the 5% Al sample (Fig. 5) and the 10% Al sample (Fig. 9), the nitrate signal
may disappear even when the LDH phase was not removed, while the carbonate signal only disappeared in the samples that had no LDH by XRD. It may be possible that the carbonate anions remained due to the presence of dissolved CO$_2$ and associated carbonic acid species in the water. Another plausible scenario is that carbonates are held more tightly since they are divalent anions. If this is the case, perhaps less aggressive conditions are needed to remove the LDH phase from materials with no divalent anions. Since it is believed that the main source of carbonates came from CO$_2$ dissolved in water, a new 5% Al sample was synthesized using only deaerated water for all solutions and for rinsing. Additionally, although sulfate signals were not observed in TGA-MS experiments, nitrate-containing reagents were used to avoid divalent SO$_4^{2-}$ anions potentially being incorporated. This batch will be denoted as DN, and showed similar amounts of the LDH phase to the original 5% Al sample by XRD (seen later in Figs. 12a/12b). Washing treatments of DN were conducted with regular deionized water, not deaerated water.

Figure 10 shows the TGA-MS results for three DN samples: (a) unwashed, (b) washed in 12 M NaOH at room temperature, and (c) washed in 12 M NaOH at 50°C. Only the sample in Fig. 10c showed complete LDH removal (Fig. 12a and S4b). The top panels of Figs. 10a–10c show the relative mass and rate of mass loss as a function of temperature, while bottom four panels show the ion currents of 4 m/z ratios (corresponding to OH$^-$, H$_2$O, NO$_3^-$ (mass 30 corresponding to NO), and CO$_3^{2-}$ (mass 44 corresponding to CO$_2$) as a function of temperature.

The unwashed sample (Fig. 10a) contained only a trace of divalent CO$_3^{2-}$ (CO$_2$ as mass 44), indicating the synthesis procedure dramatically reduced the amount of carbonate anions, but did not eliminate their presence altogether. The nitrate signal seems to be stronger when compared to the unwashed 5% Al sample (Fig. 5a), likely due to the fact that the DN sample was made from nitrates instead of sulfates and due to the scarcity of carbonates in balancing the excess charges. The trend of the mass loss of a sample without LDH phase (Fig. 10c) being slightly less than samples with LDH (Figs. 10a–10b) continued, with the no LDH sample losing around 23% of its original mass and samples with LDH losing around 24%.

Figure 11 shows a summary of the XRD results (Fig. 11a) and ICP-OES results (Fig. 11b) for the DN samples. As seen before for 5% and 10% Al samples made with regular DI water, increasingly aggressive conditions removed more of the LDH phase, but leached more Al. Complete removal of the LDH phase from the DN sample was accomplished by washing in 12 M NaOH at 60°C for 15 minutes or at 50°C for 30 minutes. None of the conditions used to wash DN

Figure 8. SEM images of [Ni$_{0.80}$Co$_{0.15}$]$_{0.90}$Al$_{0.10}$(OH)$_2$ samples ((a,b) unwashed, (c,d) 12 M NaOH at 70°C for 240 minutes and (e,f) 15 M NaOH at 80°C for 15 minutes). (a), (c) and (e) show images at low magnification while (b), (d) and (f) show images at higher magnification.

Figure 9. TGA-MS data (heated to 950°C in air) for the washing of [Ni$_{0.80}$Co$_{0.15}$]$_{0.90}$Al$_{0.10}$(OH)$_2$ samples ((a) unwashed, (b) deionized water at 70°C, (c) 12 M NaOH at room temperature, and (d) 15 M NaOH at 80°C). The top panels show relative mass and rate of mass loss as a function of temperature, while the bottom 4 panels show the ion currents of m/z 17 (OH), 18 (H$_2$O), 30 (NO), and 44 (CO$_2$).
samples resulted in a color change (Fig. S4). The maximum Al loss tested for DN was a difference of $0.014 \pm 0.002$ in the Al stoichiometric ratios when washed at 60°C in 12 M NaOH for 15 minutes, so the material has around 3.6% Al remaining after the washing treatment. Compared to the 5% Al samples made in regular DI water, milder conditions were required to completely remove the LDH phase from DN samples, but the material leached similar amounts of Al.

Figure 12 shows a more thorough comparison between the 5% Al sample made using regular DI water and DN. XRD pattern comparisons for washing at 50°C in 12 M NaOH (Fig. 12a) and at 60°C in 9 M NaOH (Fig. 12b) are shown. For each comparison, the XRD pattern of a 5% Al sample washed under the same conditions but at 10°C higher was included as well. ICP-OES comparisons for samples washed with varying temperatures, NaOH concentrations and stirring times are shown in Figs. 12c–12e. The temperature series (Fig. 12c) were washed in 12 M NaOH for 15 minutes, except the room temperature sample (30 minutes). The NaOH concentration series (Fig. 12d) were washed at 60°C for 15 (12 M NaOH) or 30 minutes (6 M and 9 M). The stirring time series (Fig. 12e) were washed at 50°C in 12 M NaOH.

XRD comparisons of the washed 5% Al samples and washed DN samples (Figs. 12a–12b) indicate that more of the LDH phase was
removed from DN than 5% Al under the same conditions. In fact, the degree of LDH removal for DN samples was similar to washing the 5% Al samples at 10°C higher. This seems to indicate that the presence of carbonate anions in the LDH phase made LDH removal more difficult. It is possible that any presence of divalent anions will hinder LDH removal, but this was not tested in this study. The amount of Al leached seems to be perhaps slightly increased for DN samples under the same conditions. While the differences in Al lost between 5% Al and DN samples were not very large (the uncertainties overlapped in some cases), the consistent trend of DN samples leaching more Al than 5% Al under the same conditions provide weak support for this conclusion.

Discussion on the mechanism of LDH removal.—As discussed earlier, chemical ageing of α-Ni(OH)_2 to β-Ni(OH)_2 may occur via two proposed mechanisms, but there is little to no work reported on the removal of LDH, which is the conversion of the LDH phase to the no LDH phase. While not the purpose of these studies, there may be some contributions to the discussion of the LDH removal process that can be made based on the results found here.

LDH removal in this work occurred more prominently when conditions became increasingly alkaline, and this supports the dissolution-recrystallization mechanism due to the increasing solubility of the metals above pH 12. However, ICP-OES results (Figs. 4b and 7b) showed that the Ni:Co ratio remained consistent while the (Ni + Co):Al ratio increased, indicating that only Al was dissolving and not fully precipitating back into the material. Due to the slightly different solubility of Ni and Co, a slight shift should occur in the Ni:Co ratio if the two metals really were dissolving in enough quantities to remove the LDH. It is also uncertain how the intercalated anion would affect LDH removal in the dissolution-recrystallization mechanism, but this effect was demonstrated by comparing 5% Al with DN, where the material with minimal divalent carbonate anions completely removed the LDH phase at milder conditions. Most importantly, SEM images (Fig. 8) do not show significant morphological change despite complete LDH removal, indicating that dissolution-recrystallization cannot be the main driver of LDH removal.

With the proposed zipper mechanism, significant morphological changes and metal dissolution (and loss) would not be expected. It is also conceivable that a divalent anion, such as carbonate, would be more difficult to expel from the material due to its attractive forces to the two nearby Al atoms, which would hinder LDH removal as corroborated with DN requiring less aggressive conditions for removal. On the other hand, the zipper mechanism cannot explain why the conversion process accelerates as the conditions become more alkaline, and the effect of NaOH concentration on LDH removal was clearly demonstrated in this work (Figs. 2, 3, 6 and 11).

Another potential driving force for the removal of LDH in this work is the removal of hydrogen as the LDH phase converts to the no LDH phase (Fig. 2c). As the wash becomes increasingly alkaline, it may be more favorable to remove hydrogen atoms. Viewed in this way, the reaction is almost like an acid-base reaction that makes water. Consider the overall reaction below which is consistent with the observations in this paper:

\[
M_{1-x}Al_{x}(OH)_2 + xNaOH (aq) \\
\rightarrow M_{1-x}Al_x(O_2H_{2-x}) + xNaA (aq) + xH_2O
\]

where M represents the transition metals Ni and Co, and A represents a monovalent charge compensating anion. Perhaps the drive to remove hydrogen from the material is so strong that even the hydrogen atoms far from an Al may get removed, resulting in the oxidation of Ni or Co. This could explain why color changes were observed (Figs. S2-S3) in increasingly aggressive conditions.

Conclusions

The coprecipitation method was used to synthesize three batches of [Ni_{0.80}Co_{0.15}]_{0.95-x}Al_{0.05}x(OH)_2 (x = 0, 0.05, with 1 batch of
x = 0 prepared from deaerated water and nitrate reagents) materials. All synthesized materials had appreciable amounts of the LDH phase. Washing the material in hot concentrated NaOH was shown to remove the LDH phase, and a study of the conditions indicated that increasing temperature, NaOH concentration, and/or stirring time will increase LDH removal, Al leaching and color change. Increasing the Al content, as seen when going from 5% Al to 10% Al, increased the LDH content and also increased the difficulty of LDH removal. Complete removal of the LDH phase in 5% Al samples could be achieved by a washing treatment of either 60°C/15 min/12 M NaOH or 70°C/30 min/9 M NaOH. In the case of the 10% Al sample, washing at 70°C/240 min/12 M NaOH or 80°C/15 min/15 M NaOH could completely remove the LDH phase. Washing samples in aggressive conditions, such as the aforementioned washes of the 10% Al sample, do not alter particle morphology significantly. TGA-MS results seemed to indicate that divalent carbonate anions were harder to remove from the material than monovalent nitrate anions, so a batch of 5% Al was synthesized using deaerated water and nitrate-containing reagents. This sample, with trace presence of carbonate anions, had the LDH phase completely removed at milder conditions compared to the sample with both types of anions. Studies of how LDH affects the electrochemical performance of these materials are under way.

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ORCID

Aaron Liu  https://orcid.org/0000-0001-8797-9570
Jing Li  https://orcid.org/0000-0003-3698-7102
J. R. Dahn  https://orcid.org/0000-0002-6997-2436

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