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Synthesis of High-Density Nickel Cobalt Aluminum Hydroxide by Continuous Coprecipitation Method

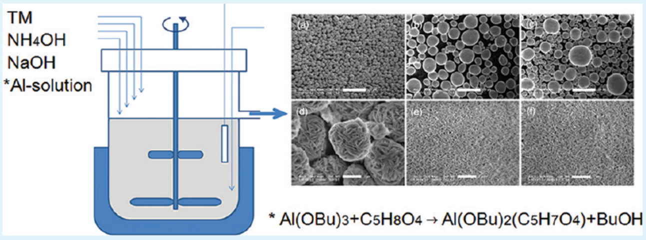
Yongseon Kim*[†,‡] and Doyu Kim[†]

[†]SAMSUNG SDI CO., LTD, Yongin-si, Gyeonggi-do, 446-577, Korea

[‡]Department of Materials Science and Engineering, Seoul National University, Seoul, 151-742, Korea

Supporting Information

ABSTRACT: Spherical nickel cobalt aluminum hydroxide ($Ni_{0.80}Co_{0.15}Al_{0.05}$-hydroxide, NCA) was prepared by a continuous coprecipitation method. A new design of the Al solution and the feeding method was applied, which enabled to prevent rapid precipitation of $Al(OH)_3$ and to obtain spherical NCA with large enough particle size and high density. The active material ($LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ or LNCA) prepared from it showed higher tap-density than that made from NCA prepared by general processes, and homogeneity of Al-distribution was also improved. It is expected that the electrode density of lithium ion batteries adopting LNCA could be improved with the new process proposed in this study.



KEYWORDS: *coprecipitation, hydroxide, doping, cathode, lithium ion battery*

INTRODUCTION

Lithium nickel oxide ($LiNiO_2$, LNO) is a promising alternative to $LiCoO_2$ (LCO) which is widely used in lithium ion batteries.[1−5] LNO is isostructural with LCO, whose crystal structure consists of layers of transition metal cations separated from Li layers by oxygen, and belongs to the space group $R\bar{3}m$.[6−10] This material has advantages over conventional LCO in that it has a higher specific energy, is less toxic, and its raw materials are less expensive. However, there are still safety, cyclability, and thermal stability concerns existent.[11−15] Structurally ordered LNO compounds are known to be difficult to synthesize because nonstoichiometric $Li_{1-\delta}Ni_{1+\delta}O_2$ phases usually form. It is reported that excess of Ni ions with an oxidation number of +2 occupy the Li layer by replacing Li ions.[16,17] Mixing Co with Ni is a good way to stabilize LNO. It is reported that $Li(Ni_{1-x}Co_x)O_2$ (LNCO) exhibits less disorder in the sequence of Ni and Li than LNO.[12,18,19] Doping Al has been found very effective to improve durability of battery cells because it stabilizes the charge-transfer impedance on the cathode.[20,21] Thus, Al-doped LNCO, which is generally called LNCA in brief, is expected as a new high performance cathode material with structural and thermal stability.

To make a homogeneous mixture of transition metals, many studies adopted coprecipitation methods.[22−24] The method also enables to get spherical particles, which provides high electrode density because they can be packed due to good fluidity. Commercial $Li(Ni_{1-x-y}Co_xMn_y)O_2$ (LNCM) is a well-known example produced by the process.[25] LNCA is also synthesized using the coprecipitation method, but generally Al is not introduced during the coprecipitation process but mixed when Li-raw material is mixed with the coprecipitated $(Ni_{1-x}Co_x)(OH)_2$ (NC) before high-temperature heating process. This is because coprecipitation of metals containing Al is very difficult to get a large enough size and high enough density of the particles, which is essential for high volumetric capacity of the cathode.[26−28]

In this study, we synthesized nickel cobalt aluminum hydroxide (NCA) precursors by a continuous coprecipitation method. A new design of the aluminum solution and its feeding method was applied in order to control the nucleation rate. Large enough particle size and high density of NCA particles could be obtained. The property of the NCA coprecipitates and the LNCA cathode materials made from them were investigated in comparison with those from conventional methods.

RESULTS AND DISCUSSION

The reactor for coprecipitation is composed of three feeding lines in general (Figure 1): for transition metal (TM) aqueous solution, ammonia solution which forms a TM-NH_3 complex, and NaOH solution which reacts with the complex and makes final product of coprecipitates. The coprecipitate of TM-hydroxide is known to be synthesized following the reaction below.[25] If the TM solution reacts directly with the NaOH solution, only small particles with poor density are obtained because of too fast reaction speed. Therefore, ammonia solution should be added to make TM-NH_3 complex, which slows down the reaction. This prevents formation of too many nuclei and promotes growth of existing particles, resulting in synthesis of large-sized particles with high density. The particles

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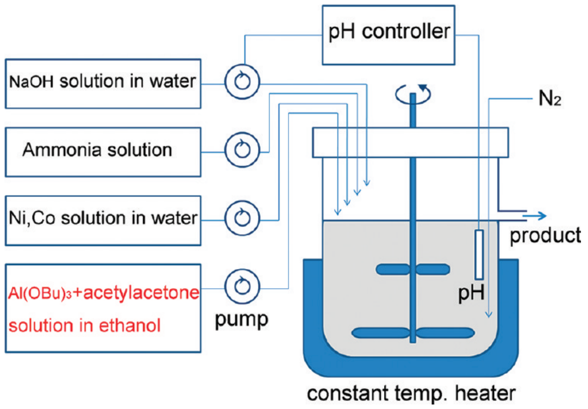

Figure 1. Schematic presentation of the reactor for continuous coprecipitation of NCA_cpN precursor.

obtained from the coprecipitation were composed of needle-shaped primary particles and showed spherical outlines under high speed stirring of the solution.

$$TM^{2+} + nNH_4OH \rightarrow TM(NH_3)_n{}^{2+} + nH_2O$$

$$TM(NH_3)_n{}^{2+} + 2OH^- + nH_2O \rightarrow TM(OH)_2 + nNH_4OH \qquad (1)$$

It would be the simplest way to get coprecipitates containing Al that Al is dissolved with TM in the same batch of water and the mixed solution is injected into the reactor. However, the coprecipitate got from this method (named as NCA_cp) showed small average particle size (under 5 μm) and coarse surface (Figure 2a, d). We tried injecting Al solution separately, but the particle shape did not improve. Change of other conditions such as pH, temperature of the reactor, TM/NH_4OH ratio, feeding speed, and the residence time of the particles in the reactor (this is related to the feeding speed) were not effective either.

It seems that size and density of the particles decrease with introduction of Al because Al makes precipitate of $Al(OH)_3$ when reacted with NH_4OH while the TM solution is stabilized by NH_4OH by making TM-NH_3 complex which is still soluble in water. This implies $Al(OH)_3$ is formed far faster than hydroxide of other transition metals the moment that the metal solution(s) is put into the reactor and diffuses. Rapid precipitation of Al-hydroxide would generate a lot of nuclei, thus continuous nucleation and formation of small particles prevails over growth of existing particles to a larger size. This makes it difficult to get large and dense powder which is essential for high density cathode of lithium ion batteries.

Thus, reactivity of Al should be controlled to get high density of Al-doped coprecipitates. For this purpose we used acetylacetone which is one of the effective chelating agents. A chelated aluminum alkoxide solution was prepared reacting aluminum trisec. butoxide with acetylacetone in ethanol. Acetylacetone suppresses hydrolysis and condensation by substituting highly reactive alkoxy ligands (eq 2),[29] which enables to control the precipitation rate of Al. This solution kept separately and fed by an independent line (Figure 1) because mixing of it with TM solution made precipitates as time goes by.

$$Al(OBu)_3 + C_5H_8O_4 \rightarrow Al(OBu)_2(C_5H_7O_4) + BuOH \qquad (2)$$

Using this new design of solutions and the feeding method, we prepared NCA coprecipitate (named as NCA_cpN) which contains 5 at % Al. The SEM images of them are shown images b and e in in Figure 2, which show that both average particle size and the density are greatly improved comparing with the NCA_cp powder (Figure 2a, d). NC coprecipitate was also prepared for a comparison and the images are presented (Figure 2c, f), which indicates that the morphological quality of NCA_cpN is comparable to that of NC whose production conditions have been fully optimized commercially. From the EDS-mapping, we could confirm that Al is homogeneously distributed in NCA-cpN particles (Figure 3). The results show that the coprecipitation method proposed in this study is suitable for the production of high density LNCA cathode materials because the morphological character of LNCA is largely dependent on that of the NCA precursors. It may be another merit of the process that doping amount of Al can be easily controlled just by changing the feeding speed of the Al solution. We set the feeding speed of the solutions so that the

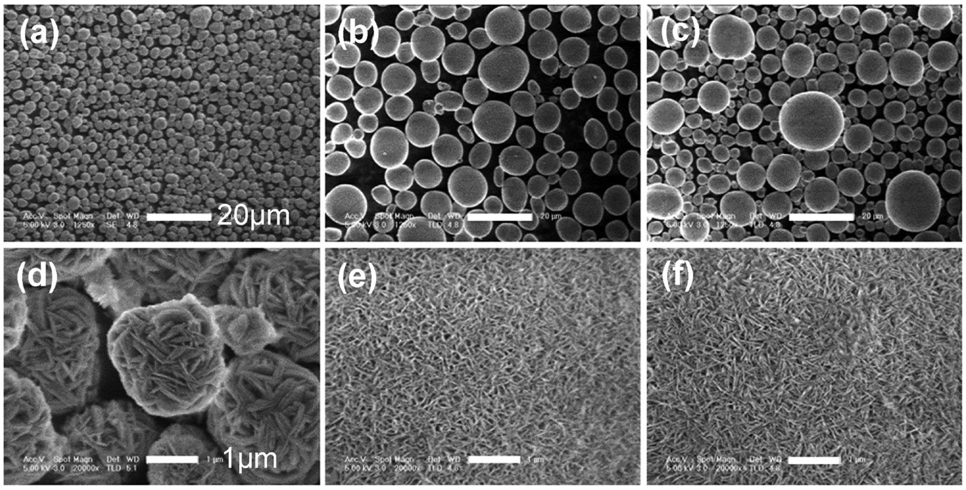

Figure 2. SEM images of (a, d) NCA_cp, (b, e) NCA_cpN, and (c, f) NC coprecipitates. The white scale bars indicates 20 μm of length in a−c, and 1 μm in d−f.

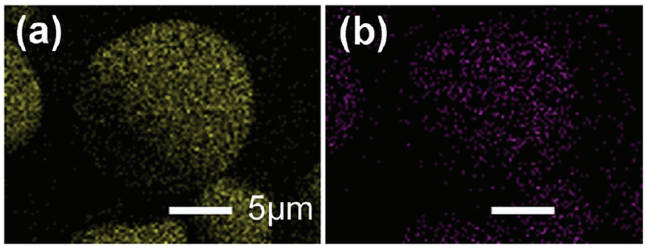

Figure 3. Distribution of (a) Ni and (b) Al in NCA_cpN obtained from EDS mapping. The white scale bars indicate 5 μm of length.

input ratio of Al/(Al+TM) to be 0.05 in this study. The ratio for NCA_cpN analyzed by ICP-OES was 0.055, which well-corresponded with the input ratio.

XRD patterns of NC and NCA_cpN presented in Figure 4 show that all the peaks of NC coincide with those of $Ni(OH)_2$ reported. The pattern of NCA_cpN (Figure 4b) was same with that of NC, except the appearance of a small broad peak at $2\theta \approx 11°$. This peak is reported to be generated by so-called layered double hydroxide (LDH).[30] Addition of Al^{3+} into the $TM(OH)_2$ structure breaks charge neutrality, and this is compensated by incorporation of anions such as NO_3^-, SO_4^{2-}, or some water between the $TM(OH)_2$ slabs, leading to formation of the LDH, a structure of misalignment or stacking fault of layers.[30,31] The LDH peak of NCA_cpN shows that Al^{3+} is homogeneously incorporated over the particle of TM-hydroxide: although the LDH phase itself is a kind of secondary phase, appearance of it indicates that Al does not form a separate $Al(OH)_3$ phase, but makes a complex with transition metals on atomic level. The data of NCA_cp are omitted in Figure 4 because they were similar to that of NCA_cpN, but the LDH peak was not as sharp as that of NCA_cpN.

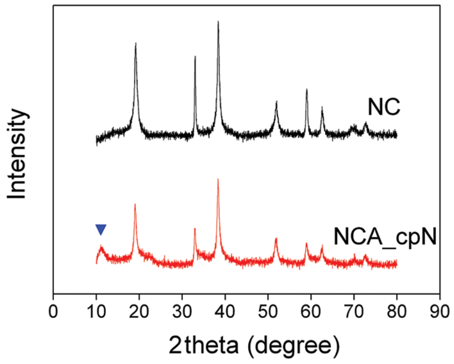

Figure 4. XRD patterns of NC and NCA_cpN coprecipitates. The LDH peak of NCA_cpN is marked with an inverse triangle.

SEM images of LNCA cathode materials synthesized from NCA_cpN and NC coprecipitates are shown in Figure 5 (a, LNCA_cpN) and (b, L(NC+A)). The particle size and shape of LNCAs were similar to those of the coprecipitate precursors, and there were little morphological difference between LNCA_cpN and L(NC+A). Relative composition of metals of LNCAs was nearly same with that of the precursors. The amount of Li was a little smaller than the stoichiometric composition for all the samples, probably because Ni tends to occupy Li sites when Ni contents is high.[17] Average particle size, tapping density, and exact composition analyzed by ICP-OES of the coprecipitates and cathode materials synthesized from them are presented in Table 1.

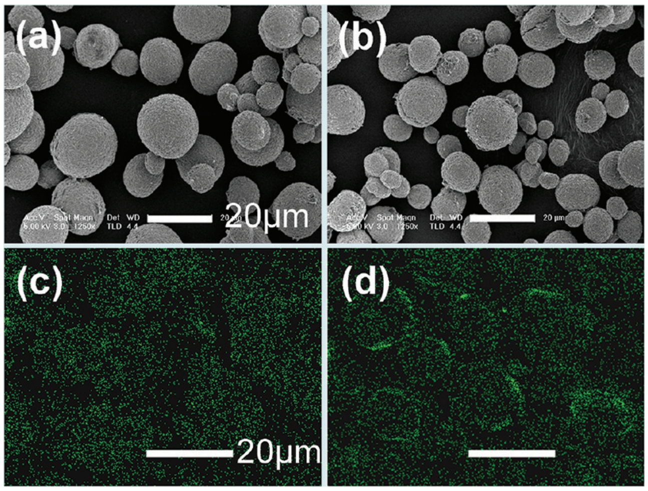

Figure 5. SEM images of LNCA and mapping of Al-distribution on the cross sections: LNCA_cpN ((a), (c)) and L(NC+A) ((b), (d)). The white bars indicate 20 μm of length.

Table 1. Average Particle Size, Tap Density, And Exact Metal Composition of the Samples

	average size (μm)	tap density (g/cm^3)	composition
NCA_cp	4.2	1.24	$Ni_{0.801}Co_{0.146}Al_{0.053}$
NCA_cpN	12.7	1.88	$Ni_{0.795}Co_{0.149}Al_{0.055}$
NC	12.5	1.95	$Ni_{0.845}Co_{0.155}$
LNCA_cp	3.8	1.98	$Li_{0.982}Ni_{0.801}Co_{0.148}Al_{0.051}$
LNCA_cpN	12.0	2.66	$Li_{0.990}Ni_{0.794}Co_{0.152}Al_{0.054}$
L(NC+A)	12.2	2.64	$Li_{0.987}Ni_{0.803}Co_{0.148}Al_{0.049}$

The tap density of LNCA_cpN was higher than LNCA_cp owing to highly dense NCA_cpN precursor. Thus, it is expected that electrode density of lithium ion batteries adopting LNCA as a cathode material could be greatly increased with the coprecipitation process proposed in this study. Actually, high volumetric energy density is one of the most important properties of lithium ion batteries. Figure 5c, d shows EDS mapping of Al-distribution on the cross sections of LNCA_cpN and L(NC+A) particles. Al was homogeneously distributed all over the particles of LNCA_cpN (Figure 5c), whereas accumulation of Al is found near the surface of L(NC+A) (Figure 5d). Comparison of the figures clearly shows that addition of Al during the coprecipitation process is more favorable for homogeneous doping than the conventional method, which completely depends on thermal diffusion during the firing.

In summary, we synthesized NCA($Ni_{0.80}Co_{0.15}Al_{0.05}$-hydroxide) coprecipitate by an advanced method of continuous coprecipitation proposed in this study. The reactivity of Al was successfully controlled using acetylacetone as a chelating agent. This made growth of particles prevail over nucleation and enabled increase in average particle size and high density. High density LNCA cathode material with large enough particle size could be obtained from the coprecipitate of this study, which is expected to improve electrode density of lithium ion batteries, resulting in higher volumetric energy capacity. Compared with the conventional process, which dopes Al by thermal diffusion during the firing, higher homogeneity of Al-distribution could be obtained by the new coprecipitation method.

EXPERIMENTAL SECTION

Aqueous solutions of transition metals, ammonia, and NaOH were added to a 5 L reactor. The metal solution was prepared by dissolving $NiSO_4·6H_2O$ (EP grade, Incheon Chemicals Ltd., Korea) and $CoSO_4·7H_2O$ (EP, Nihon Kagaku Ltd., Japan) in deionized water. Concentration of the solution was 1.5 M and the injection rate was 0.1−0.5 mol/h. Commercial ammonia solution (28 wt %, Dongwoo Finechem Ltd., Korea) was added to the reactor while maintaining a constant TM/NH_4OH molar ratio ($\approx$ 1.0). The feed pump of NaOH (99%, OCI Ltd.) solution was connected to a pH sensor/controller and its pumping rate was automatically controlled to maintain a constant pH of 12.3 ± 0.1. Solution in the reactor was stirred with 600 rpm of speed and the temperature was controlled in 30−70 °C range. The product slurry overflowed through an outlet and it was washed and dried.

The coprecipitate containing Al was synthesized in two kinds of method. One is the general method in which Al salt ($Al(NO_3)_3$-$9H_2O$, EP grade, SAMCHUN Chemicals Ltd., Korea) is dissolved with transition metals in the same batch (the sample is named as NCA_cp). Another method proposed in this study prepared separate Al solution and injected it through a separate line (NCA_cpN). The Al solution was prepared by reacting aluminum trisec. butoxide (>98%, Acros) with acetylacetone (>99%, Sigma-Aldrich) in 1:1 molar ratio. The concentration was 0.8 M in ethanol. All the NCA samples were designed in the composition of $Ni_{0.80}Co_{0.15}Al_{0.05}$-hydroxide. A schematic diagram of the coprecipitation method and the reactor for NCA_cpN is shown in Figure 1.

The metal hydroxide coprecipitates were mixed with LiOH-H_2O (>99%, Samchun Chemicals Ltd., Korea) and fired at 750−850 °C for 15 h to make LNCA cathode materials. The Li/(TM+Al) molar ratio of mixing was fixed at 1.03 considering a little evaporation loss of Li. For a comparison with the conventional synthesis method of LNCA, we prepared coprecipitates of nickel cobalt hydroxide (NC, designed in the composition of $Ni_{0.842}Co_{0.158}$-hydroxide, which becomes the same composition as the NCA ($Ni_{0.80}Co_{0.15}Al_{0.05}$) with addition of 5 at % Al). Al_2O_3 nanopowder (99.9%, Baikalox) was added to the NC when LiOH-H_2O is mixed before the firing process to get LNCA, which is named as L(NC+A).

Thus, we prepared three kinds of coprecipitates (NCA_cp, NCA_cpN, and NC) and cathode materials (LNCA_cp, LNCA_cpN, and L(NC+A)) using them as precursors. Particle shapes of the samples were observed with a field-emission scanning electron microscope (FE-SEM, JEOL 6360F) image, and size distribution of powders was measured by a laser diffraction particle size analyzer (LS 13320, Beckman). The homogeneity of Al-distribution was examined by EDS mapping on the surface and the cross section. Exact composition of the materials was measured by inductively coupled plasma-mass spectroscopy (ICP-OES, 5300DV, Perkin-Elmer). The crystal structure of the samples was analyzed by powder X-ray diffraction (XRD; Rigaku, D-max 2500, Japan). Tap density of powder was measured using a mass cylinder attached to an electric vibrator.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Size distribution of particles, SEM images of powders obtained with various pH, and reproducibility of the method. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel.: 82-2-880-8333. Fax: 82-2-884-1578 E-mail: yskim01@snu.ac.kr.

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